Gels Horizons: From Science to Smart Materials

Sandhya P. K.
Sreekala M. S.
Sabu Thomas *Editors*

Phenolic Based Foams

Preparation, Characterization, and Applications

Springer

Gels Horizons: From Science to Smart Materials

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Preface

Phenolic foams are considered as the most efficient insulation material that are commonly available and are inexpensive. Compared with other types of foams phenolic foams possess good fire resistance, less smoke during burning, low heat conduction coefficient, and good balance between cost and mechanical properties. Phenolic foams are considered as a leading candidate in various fields such as construction industry, petrochemicals, aerospace, and fire protection. However, the extreme friability and brittleness of phenolic foams limits their applications. So it is very important to improve the toughness of the phenolic foams by reinforcing with other materials.

Numerous efforts have been made to improve the toughness of phenolic foams over the past decades. Thus, it is essential to acquire knowledge about the preparation, properties, and applications of phenolic foams by research scholars and students. Most of the research works were done to improve the properties of phenolic foams according to its targeted applications. The toughness of phenolic foams can be enhanced by adding various toughening agents like flexible polymers, natural fillers, and nanofillers. All the efforts were to improve the physical properties of phenolic foams by maintaining their inherent thermal, insulation, and evolution of less toxic substances during burning. The effort of researchers to prepare bio-based phenolic foams is also appreciable since it is easily available, cost-effective, and reduces the environmental pollution.

This book is divided into 25 units. The first unit focuses on the general introduction about phenolic foams. The succeeding two units deal with the introduction of foam manufacture and the chemistry behind it. Next three units discuss the effect of hybrid fillers and toughening agents on the properties of phenolic foams. The following chapter describes the properties of phenolic syntactic foams. The next two units are about the morphology and shape memory effects of PF foams. The following few chapters discuss the mechanical, thermal, electrical, and flame retardant properties of PF foams. This book also covers PF foams with nanofillers such as clay, CNT, graphene, and nanosilica as reinforcements. The last eight chapters include discussion of bio-based PF foams and applications of PF foams.

We hope all the scientific community and students will be benefitted by this book and we look forward to have suggestions and feedback to improve upon it.

Kottayam, India Sandhya P. K.
Kalady, India Sreekala M. S.
Kottayam, India Sabu Thomas

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Prof. Sabu Thomas is currently Vice Chancellor of Mahatma Gandhi University, Kerala, India. He is an outstanding leader with sustained international acclaim for his work in nanoscience, polymer science and engineering and green materials. He has received more than 30 national and international awards. He has published over 1200 peer-reviewed research papers, reviews, and book chapters. He has co-edited 150 books and is an inventor of 15 patents. The H index of him is 114 and has more than 62,000 citations. He has delivered over 350 plenary/inaugural and invited lectures in national/international meetings over 40 countries. He has supervised 115

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Abbreviations

AC	Activated carbon
APTES	3-aminopropyltriethoxysilane
BA	Boric acid
BF-a	Bisphenol F benzoxazine
BP	Boiling point
BPF	Bio-based phenol formaldehyde
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAGR	Compound annual growth rate
CAP	Cellulose acetate propionate
CF	Carbon foams
CF	Cellulose fiber
CFC	Chlorofluorocarbon
CGO	Carboxyl graphene oxide
CHP	Cumenehydroperoxide
CLTPFs	Cork powder-reinforced larch tannin-based rigid phenolic foams
CNF	Carbon nanofibers
CNT	Carbon nanotube
CP	Cork powder
CTE	Coefficient of thermal expansion
DABCO	1,4-diazabicyclo[2.2.2]octane
DBTDL	Dibutyltindilaurate
DGMWF	DOPO-g-GPTS-modified wood fiber
DGMWFCPF	DGMWF composite phenolic foam
DHL	Depolymerized hydrolysis lignin
DOPO	10-(2,5-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DOPU	Novel phosphorus-containing polyurethane
EMAS	Engineering material arresting system
EMI	Electromagnetic interference
EMW	Electromagnetic waves

EPRA	European phenolic resins association
ESCO	Engineering arresting systems corporation
FAA	Federal aviation administration
FEM	Finite element method
FPF	Fiber-reinforced phenolic foam
FR	Flame retardant
FST	Fire, smoke, and toxicity
FT-IR	Fourier transform infrared spectroscopy
GA	Glutaraldehyde
GNPs	Graphene nanoparticles
GO	Graphene oxide
GPTS	γ-glycidoxy propyl trimethoxy silane
HCFCs	Hydrochlorofluorocarbons
HCM	Hollow ceramic microspheres
HCMs	Hollow carbon microspheres
HDI	Hexamethylenediisocyanate
HGB	Hollow glass beads
HGM	Hollow glass microspheres
HL	Hydrolysis lignin
HPMs	Hollow polymer microspheres
HTAB	Hexadecyl trimethyl ammonium bromide
ICAO	International civil aviation organization
ICs	Integrated circuits
IPDI	Isophoronediisocyanate
ISO	Isocyanate
LDPE	Low-density polyethylene
LNG	Liquefied natural gas
LOI	Limiting oxygen index
LRPFs	Lignin particle-phenolic foams
LTPFs	Larch tannin-based rigid phenolic foams
LTPRs	Larch tannin-based phenolic resins
MB	Microballoon
MCC	Modified microcrystalline cellulose
MCMB	Mesocarbon microbeads
MDF	Medium density fiberboard
MDI	Diphenylmethanediisocyanate
mHRR	Mean heat release rate
MMC	Micron melamine cyanurate
MMT	Nano-montmorillonite
MWCNTs	Multiwalled carbon nanotubes
NBRP	Nitrile butadiene rubber powder
NMC	Nanometer melamine cyanurate
OI	Oxygen index
OSB	Oriented strand board
PAPI	Polyaryl polymethylene isocyanate

PBA	Poly (n-butyl acrylate)
PC	Polycarbonate
PCC	Phosphorus-containing cardanol
PCF	Phenolic carbon foams
PCL	Polycaprolactone
PDCP	Phenyl dichlorophosphate
PDMS	Polydimethoxy silane
PE	Polyethylene
PEG	Polyethylene glycol
PEG-BAE	Polyethylene glycol borate
PEGPs	Polyethylene glycol phosphates
PEPA	Pentaerythritol phosphate
PF	Phenolic foams/Phenol formaldehyde
PFTNs	PF/TiN nanocomposites
PHRR	Peak heat release rate
PLA	Polylactic acid
PMMA	Poly-methyl methacrylate
PN	Propargyl ether novolac
PO	Polyol
PP	Polypropylene
PPS	Permeable pavement systems
PPUP	Phosphorus-containing polyurethane prepolymer
PS	Phenolic syntactic foams
PS	Polystyrene
PU	Polyurethane
PUF	Phenol-urea-formaldehyde
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
RF	Resorcinol formaldehyde
RF-Cas	Resorcinol-formaldehyde-based carbon aerogels
RFI	Radio frequency interference
rGO	Reduced graphene oxide
RIPH	Resin-impregnated paper honeycomb
RSA	Runway safety areas
SAECD	Novel cardanol-based siloxane
SE	Shielding effectiveness
SEM	Scanning electron microscopy
SFE	Surface free energy
SGO	Silica nanospheres/graphene oxide
SiCNWs	Silicon carbide nanowires
SIP	Structural insulating panel
SMF	Shape memory foam
SMPF	Shape memory phenolic foam
SuDS	Sustainable drainage system
SWCNT	Single-walled carbon nanotube

TAPC	P–N tung oil-based reactive flame retardant
TDI	Toluene diisocyanate
TEA	Triethylamine
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
THR	Total heat release
TiN	Titanium nitride
TMA	Thermomechanical analysis
TPSs	Thermal protection systems
TPU	Thermoplastic polyurethane
UF	Urea-formaldehyde
VNA	Vector network analyzer
VOC	Volatile organic compound
WBPs	Wood-based panels
WCs	Wood composites
WF	Wood fiber
WPC	Wood plastic composite
WPC	Wood polymer composites
WRPFs	Wood flour-reinforced phenolic foams
ZGO	α-zirconium phosphate/graphene oxide

Chapter 1
Phenolic-Based Foams: State of the Art, New Challenges, and Opportunities

P. K. Sandhya, M. S. Sreekala, and Sabu Thomas

1 Introduction

Polymeric foams usually contain two or more phases in which one phase must be gaseous and dispersed in a solid polymer matrix like thermosets, elastomers, rubbers, or thermoplastics. Based on the backbone rigidity of the polymer, foams exist as semi-rigid or rigid material, semi-flexible, or flexible. The degree of cross-linking, crystallinity, and the chemical composition of the polymer matrix also depends on the nature of foams. Phenolic foam (PF) is closed-cell rigid polymeric foam prepared from phenolic resin by adding foaming agent, surfactant, and curing agent. The excellent fire-resistant properties, thermal insulation, and mechanical properties of phenolic foam make them a leading candidate as an insulation material in the construction industry. In recent years, polymeric foam is widely studied and continues to grow at a fast pace. Among the different polymeric foams, phenolic foam is very important. PFs were first introduced in the early 1940s in German industry as a substitute for balsa material. It is an environment-friendly fireproof polymer foam material with high thermal insulating and excellent high-temperature properties. It also exhibits no-flame, smoke, and toxic gases during burning. The excellent properties of phenolic foams are due to its fine pore structure and chemical structure. It is found that most of traditional PF exhibits closed-cell structure with thermal and electrical insulating properties that restricts its application scope. Therefore, it is necessary to develop PF with new cell structure and functions in order to broaden its applications. PF is known as a third-generation emerging thermal insulation composite with great development potential.

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The various methods such as mechanical, physical, and chemical are used for the preparation of phenolic foams. The enlargement of blowing agent and curing of the phenolic resin together manages the formation of the foam. Hence, two important parameters in the production of foam are the reactivity and viscosity of the phenolic resin [1]. The amount of monomer, pH, and water content of the resin can also affect the properties of the prepared foam. Emulsifiers can regulate the quality and properties of the foam by developing a homogeneous and stable oil-in-water emulsion that exists between phenolic resin and blowing agent. The non-ionic surfactant polyethylene glycol sorbitan monooleate (Tween 80) and silicon oil (alternative to Tween 80) are the most commonly used surfactants. The foaming of the phenolic resin either through physical or chemical processes can be induced with the help of blowing agents and carbon dioxide is an example of blowing agent formed by in situ. The curing reaction of the resin can be increased by help of catalysts. It can be achieved by decreasing the gelation time and participate in the foaming process. Phenol sulfonic acid and p-toluene sulfonic acid are some of organic acids that are used as catalysts in the foaming process. Based on the targeted application various additives like flame retardants, plasticizers, thickeners, or fillers are added at the time of preparation. Physical blowing method is used for the preparation of most of phenolic foams in which phenolic resoles, physical blowing agents, catalysts, and surfactants are mixed and transferred into an oven. Heat causes the gasification and expansion of the blowing agents, and curing of the phenolic resoles occurs and resulted in the formation of solid phenolic foams [2].

Foams made from polyurethane, polyvinyl chloride, or polystyrene are characterized by less brittleness and friability, which made the PF foams less popular. But these foams other than PF possess weak fire resistance and produce toxic gases during combustion. Due to these reasons, the fire-retardant phenolic foams regained an interest in industrial segments. However, PFs have certain mechanical weaknesses because of their rigidity, which also makes them brittle and highly friable. Because of this, several studies have focused on the improvement of mechanical properties of phenolic foams. In the past few years, to decrease environmental pollution and to overcome the deficiencies of traditional PFs, researchers have explored the use of natural fillers and reinforcements such as pulp fiber, lignin, wood flour, and flax. Moreover, PFs also have shortcomings in its petroleum-based raw materials such as phenol, which restrict their large-scale applications. Pure phenolic foams consist of large number of methylene bridges and it makes the foam very brittle and limits the construction applications. To overcome these problems, researchers modify the molecular structure and multiple complexes of PF using biomass.

The performance of PFs can be improved by increasing its toughness using renewable biomass resources as toughening agents. Recently, the biomass resources that are rich and inexpensive have been used to toughen PFs. The resultant PF shows low thermal conductivity, good thermostability, and increased mechanical properties. The high temperature resistance properties of PFs are due to the presence of large number of hindered phenolic sites, flame retardants, char-forming agents, and synergistic agents [3]. The toughening agents such as polyvinyl alcohol (PVA), polyethylene glycol (PEG), and epoxy resin can be used for improving the toughness of phenolic foams [4]. Cardanol, a phenolic material of bio-origin from cashew nut shell liquid, can be effectively used to improve its toughness. Phenolic foam possesses many advantages such as low smoke density, smoke toxicity, and no dripping of molten plastic during combustion. Phenolic resins and their foams are low cost. PFs are thermally stable over a broad temperature range from −196 to 200 °C. PFs found a wide range of applications due to its low thermal conductivity. In addition to that, PFs are highly resistant to chemicals and solvents. During the foaming and curing process, it is difficult to control the cell morphology of the pores because phenolic resins contain various solvents [5]. The cell density and cell uniformity of PFs determine the physical performance of different polymer foams. The factors that affect the cell density of the foam are the type of reinforcing particle, degree of cure and the viscosity before the foaming, and the weight fraction of the particles.

The compression strength, air tightness, flame retardancy, and other related properties of phenolic foams are mainly depending on the physical and chemical properties of the phenolic resin. The factors such as reaction time, reaction temperature, pH, initial formaldehyde/phenol molar ratio (F/P), and catalyst type and loading determine the properties of phenolic resins [6]. Phenolic foams with closed-cell possess outstanding thermal insulating properties as well as fire resistance. These types of PFs can be used as heat and fire barriers in buildings.

The mechanical beating of air into a liquid mixture of phenolic resole, surfactant, and acid catalyst for 10 min resulted in the formation of liquid phenolic froths and can be molded into desired shapes after curing [2]. This method is called as froth templating and used to produce open porous phenolic foam panels (Fig. 1).

The pyrolysis of phenolic foams produces large carbon foam panels that reproduce the shape of initial foam precursors (Fig. 2a) which has wide range of applications [2]. After pyrolysis, the carbon yield is 48% and the volume of carbon foam is reduced by 50% than the precursor phenolic foam. The electrical conductivity of the produced carbon foam was found to be 17 S/m while that of precursor phenolic foam is 3·10−8 S/m. The synthesized carbon foams can be used as porous electrodes.

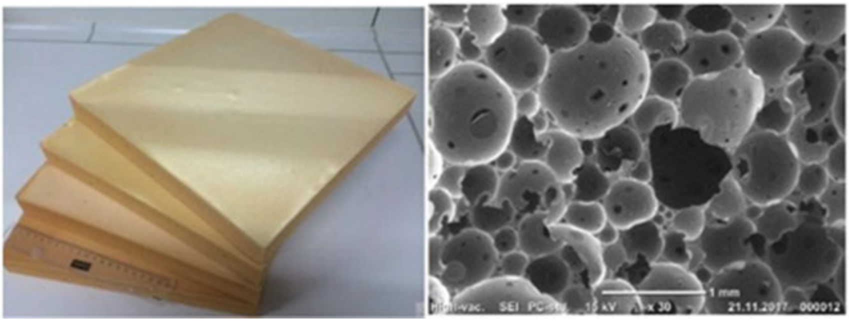

Fig. 1 **a** Phenolic foam panels (300 mm × 300 mm × 40 mm) **b** SEM image of phenolic foams possessed interconnected macroporous structure [2]

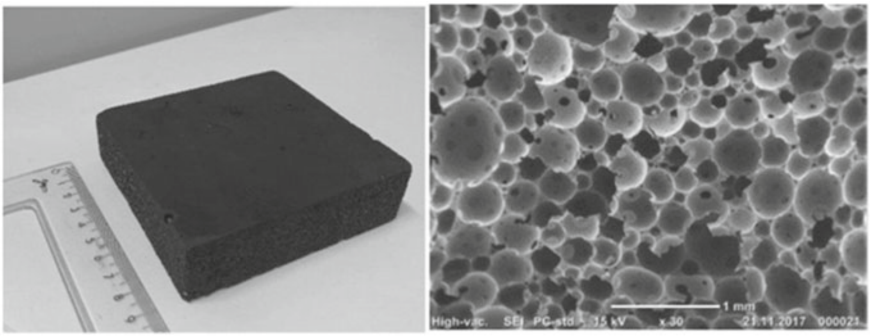

Fig. 2 **a** Monolithic carbon foam produced by pyrolysis of phenolic foams **b** Macroporous structure of carbon foam [2]

From literature review, it is found that great number of research works have been done in the field of improving the properties of phenolic foams according to the targeted applications until now. It is also evident from the previous papers that the researchers put efforts in improving the toughness of phenolic foams since 1970s. On considering the applications of phenolic foams in the field of industry, most of the works were concentrated to solve the problems associated with that field. The primary efforts of the researchers were concentrated to the identification and introduction of chemical modifiers suitable for enhancing the flexibility and toughness to phenolic foam. But the efforts were only marginally successful and negotiate with required toxicity, smoke density, and flammability. The next approach of the researchers is to increase the toughness of the phenolic foams by the addition of inert fillers. The efforts were resulted in the formation of phenolic foams with homogeneity and good texture, but have high foam density. The next modifiers were the nanofillers and research works in this field with modified nanofillers to tune the desired properties are still going on. With the intention to minimize the use of fossil fuels, the research works with phenolic resin that are obtained from a variety of biomass resources, which are rich in quantity and inexpensive drawing the attention of researchers.

2 Toughening Agents in Phenolic Foams

The addition of fillers can improve the mechanical properties of the phenolic foam as well as lower the material cost. Brittleness and friability are the major drawbacks of PF foams and it can be overcome by the toughening of PF foams. The toughening of PF foams can be achieved by either physical or chemical toughening. Physical toughening is achieved by the addition of rubber or fibers [7]. Currently, great numbers of studies have concentrated on chemical toughening and it can be attained by active groups of polymers like polyethylene glycol [8, 9], polyurethane prepolymer [10], polyether [11], cardanol [12], dicarboxylic acid [13], etc. In chemical toughening, with the help of chemical reaction, the flexible polymer chains are introduced in between the rigid backbone of the phenolic matrix. The complications exist in the case of uniform dispersion and compatibility can be minimized by chemical toughening. But the toughening agents are highly flammable, which in turn decrease the flame retardancy of phenolic foams [7]. Researches were carried out in this field and it was found that by the introduction of flame-retardant elements like boron, silicon, phosphorus etc. into toughening agents improves toughness and maintains flame retardancy of phenolic foams [14–16].

2.1 Nanofillers

The introduction of nanoparticles into phenolic foams provides high cell uniformity and cell density, which ultimately improves the mechanical strength of the carbon foam. The nanofillers such as graphene and multi-walled carbon nanotubes (MWCNT) [17] have received great attention as toughening agents in PF foam [18, 19]. Graphene is two-dimensional carbon-based nanomaterial consisting of sp^2 carbon atoms which possess excellent thermal, electrical, and mechanical properties [20–23]. The hybrids of graphene oxide (GO) such as zirconium phosphate/graphene oxide (ZrP/GO) and silica nanospheres/graphene oxide (SiO_2/GO) increased the flame retardancy and toughening efficiency of graphene oxide and these nanofillers improved the flame-retardant and mechanical properties of PF foams. Liu et al. [24] functionalized GO with magnesium aminotris-(methylenephosphonate) (Mg-AMP) which acts as an effective flame retardant when introduced into PF foam. Various studies based on phenolic resin reinforced with modified graphene also exist [25, 26]. The reinforcement of reduced graphene (from graphene oxide using potato starch as the reducing agent) into PF resin and its properties are discussed in one of our works [27]. Figure 3 shows the SEM images of the PF foams with different weight percentages of RGO. Figure 3a shows the SEM images of neat PF and the cell walls are broken. Figure 3b–d represents foams with varying wt% of RGO. It can be observed in Fig. 3c that all the cells are of equal shape, size, and distributed uniformly and are due to presence of RGO sheets. But in Fig. 3d the agglomeration of the RGO sheets increases and cells get ruptured.

Figure 4 shows optical microscopy images of the pure phenolic foam and the toughened foams with PEGPs (polyethylene glycol phosphate). Majority of the cells in PF and toughened PF foam are closed and average size is about 130 nm. The cells are regular, denser, uniform, and hexagon shaped for toughened foams PEGP200 (Fig. 4b) and PEGP400 (Fig. 4c) whereas cells of PEGP600 (Fig. 4d) and the pure PF (Fig. 4a) are ellipsoid-like. Structural homogeneity is observed only for PEGP200 and PEGP400 [14].

Carbon nanotubes (CNT) can act as a promising toughening agent and conductive filler for various polymer matrixes due to its excellent electrical, mechanical, and high aspect ratio [28]. Patle and colleagues [29] introduced MWCNTs into the resin-based matrix and observed an increase in the mechanical, thermal, electrical, and

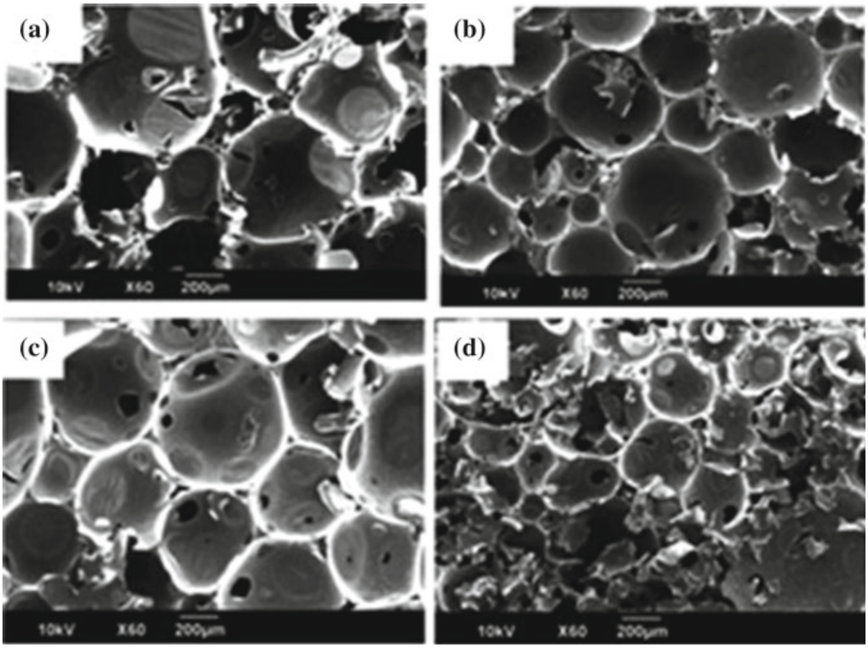

Fig. 3 SEM images of neat PF foam **a**, 0.08 wt% RGO **b**, 0.12 wt% RGO **c**, and 0.15 wt% RGO **d** [27]

EMI shielding properties of carbon foams. Song et al. [30] used multi-walled carbon nanotubes in polyimide to improve the dispersion of nanoparticles in PF foam and improved the mechanical and thermal properties of PF foam. Phenolic resins reinforced with CNT exhibits improvement in mechanical and thermal properties of PF foam [31, 32].

Nano-montmorillonite (MMT) is widely used to increase the flame resistance and thermal stability of polymer composites. MMT is a natural resource and possesses excellent thermal barrier properties hindering the thermal degradation [33]. MMT can improve the flame resistance of phenolic resin and its foam. Xu et al. [33] improved the flame resistance of PF foam by the incorporation of MMT and increased the toughness of PF using bio-oil.

Silica solution is an environmental-friendly, nontoxic, and odorless nanomaterial. Nanosilica is characterized by high surface area and possesses hydroxyl groups on its surface. The low viscosity of silica nanoparticles makes them readily diffuse into the system. PF/silica nanocomposite foams were prepared by Li et al. [31] with increased thermal and mechanical properties than PF foam. Guo and co-workers [34] prepared PF foam reinforced with nano-SiO_2 and an increase in mechanical properties of PF foam is observed.

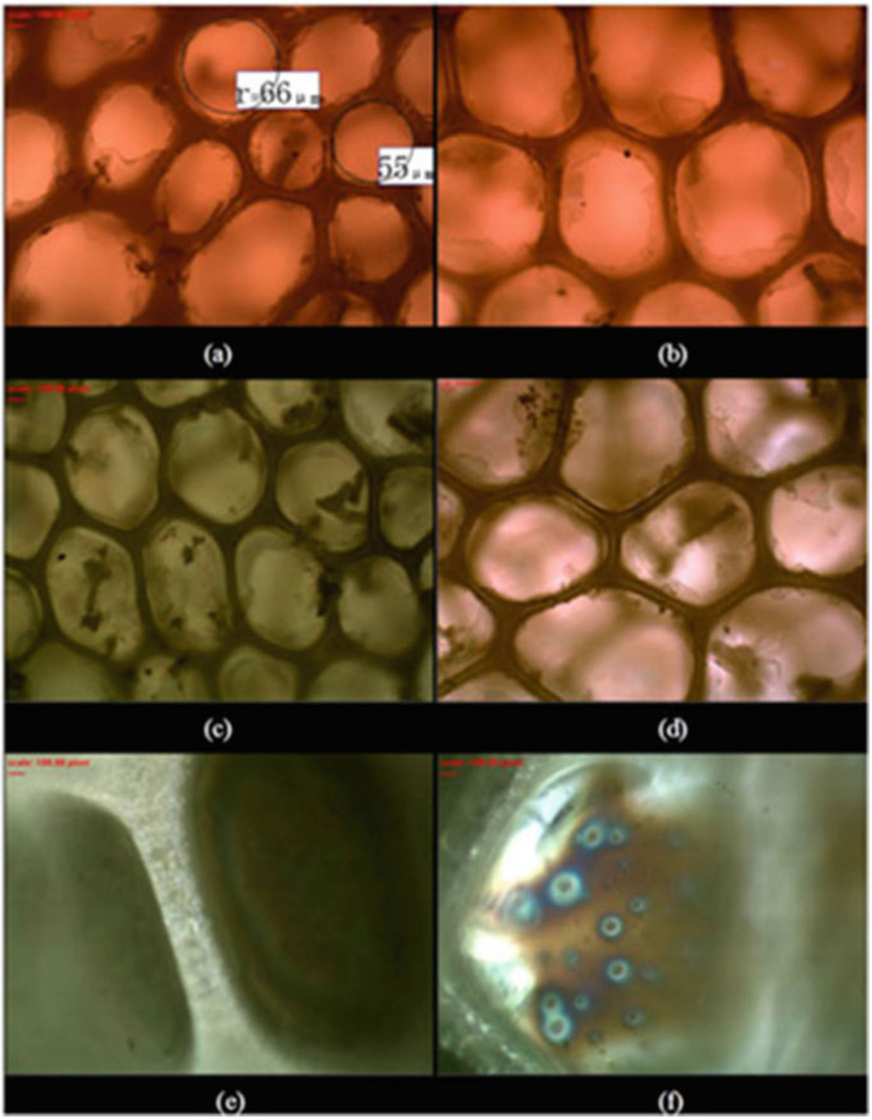

Fig. 4 Optical microscopic images of pure phenolic foams (**a** ×100 transmission; **e** ×400 reflection), PEGP200 (**b** ×100 transmission), PFPEGP400 (**c** ×100 transmission; **f** ×400 reflection), and PFPEGP600 (**d** ×100 transmission) [14]

2.2 Natural Fillers

The advantages of natural fillers such as biodegradability, high specific properties, recyclability, low cost, good thermal and acoustic insulating properties, etc. draw the attention of researchers toward natural fillers. Lignin is a natural polymer and acts as a bio-based phenolic source instead of petroleum-derived phenol for the preparation of phenolic resin. Lignin has similar networking structure as phenolic resin. On comparing the reactivity of lignin with phenol, lignin is less reactive due to less reactive sites that are available for the hydroxymethylation reaction with formaldehyde. Gao and colleagues [35] prepared lignin-modified phenolic resin and the prepared phenolic foam exhibits good mechanical and thermal insulation properties. Lignin- and silicon whiskers-modified PF foams were successfully prepared by Zhang et al. [36] and showed improved mechanical properties. Wang and co-workers [37] synthesized lignin-modified phenol and the prepared foam exhibits better compression strength and thermal insulation properties.

Wood flour is well known for its low density and high mechanical properties. It is considered as one of the most extensively used natural filler and is made up of lignin and extractives, cellulose, and hemicelluloses [38]. Several research works have demonstrated the improvement in the properties of PF foams when wood flour is introduced into PF resin [38, 39]. Eco-friendly reinforced phenolic foam is obtained by the addition of a biodegradable and renewable resource, which decreased the amount of blowing agent required in foam preparation. Domı´nguez et al. [40] successfully prepared wood flour-based phenolic foams and studied the thermal degradation properties of phenolic foams.

Cellulose is an environmental-friendly, renewable, and most abundant natural resource and considered as one of the best polymer reinforcing material. High specific strength, non-toxicity, degradability, low price, and density are some of the characteristic properties of cellulose [41]. Supramolecular structure and insolubility of cellulose in organic solvents and water limits the modification of cellulose. Ethyl cellulose, a derivative of cellulose, is well known for its high mechanical strength, non-toxicity, and biocompatibility. However, it has poor flame retardancy, modification of ethyl cellulose is essential [41]. Ma et al. [42] modified microcrystalline cellulose (MCC) with itaconic acid and attached it to an excellent flame-retardant 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). This modified cellulose can increase the mechanical and flame retardancy of PF foams. Saz-Orozco and colleagues [43] observed 21% increase in compressive modulus and 18% increase in compressive strength when 2 wt% cellulose fiber is incorporated into PF foam.

2.3 Polymers

The introduction of flexible polymers into PF is a chemical toughening process to improve the toughness of PF foam. Polyurethane oligomers can serve as a good modifier to enhance the toughness and strength of phenolic foam. It is considered as an effective modification because it reduces the thermal conductivity and density of phenolic foam [44]. Apart from that, the flame retardancy of phenolic foam could be maintained by introducing phosphorus-containing polyurethane modifier with low environmental pollution. Studies on polyurethane reinforced phenolic foams are reported elsewhere [45, 46]. The esterification of phosphorus pentoxide (P_2O_5) with polyethylene gives polyethylene glycol phosphates (PEGPs) and it could be used as toughening agent in PF foams [14]. Epoxy resin-modified phenolic resins offer high fracture toughness and excellent flame resistance to PF foam [47]. The addition of appropriate amount of cardanol-based siloxane into the resin improved the flexural strength, flame-retardant properties, and reduced the pulverization ratio of PF foams [12].

3 PF Foam Production Methods

The different processes used for the production of PF foam are batch, continuous, semi-continuous, and microwave foaming process. Industrially, batch process is the least expensive and easiest process even though it involves high operating cost. This process involves the mixing of resin, emulsifiers, and other additives using a paddle-type stirrer, followed by the addition of blowing agent and the acid catalyst. Then the foaming mixture is transferred into a mold and is heated in between 50 and 80 °C [48]. After completing the curing process, the foam samples are removed from the mold and additional drying and post-curing are performed based on the required application. The continuous foaming process requires less operations and produces high-quality foam, but it is more costly to implement industrially. Mixing head and its characteristics are important; low-pressure dynamic and high-pressure static mixing heads are used in this process. Low-pressure mixing head produces constant quality foam mixtures within a period of short time. High-pressure mixing heads produce more homogeneous mixture and finer cell structure foam. Semi-continuous process is a combination of batch and continuous process, requires less investment, and produces good quality foams. Microwave foaming technology is a recently developed simple and cost-effective process. In this process, the mixing of the components occurs at high speeds for a few minutes, then subjected to aging at room temperature and the foaming process occurs inside a microwave device [1].

4 Current Problems and Solutions

The wide range applications of phenolic foams are limited due to its high hardness, low elongation, brittleness, poor toughness, etc. [49]. The main raw material used in the synthesis of phenolic foam is phenolic resin and contains 50–90% of phenolic foam [50]. Brittleness of PF foam is one of the main drawbacks of PF foam and it is determined by molecular structure of the phenolic resin. This is because there are three active sites on the benzene ring of phenol located at two ortho- and one para-position of the phenolic hydroxyl group. Formaldehyde reacts with these sites during the polycondensation process, degree of cross-link density increases, and toughness of the phenolic foam decreases. The toughness of the phenolic foam can be enhanced by decreasing the active point on the benzene ring [51]. 3-pentadecyl-phenol obtained from nut shell oil can be used as a modifier to prepare a foamable phenolic resin. Best value of toughness is obtained when the modifier is 15% of the total amount of phenol. Poor fracture resistance is another drawback of phenolic foams. Generally, most rigid polymer foams undergo brittle and fracture during manufacture and application. These problems can be reduced by the introduction of toughening agents [52, 53]. Addition-type (elastomers, inorganic nanoparticles) and reaction-type (polyethylene glycol, epoxy resin, polyvinyl alcohol) toughening agents are used for this purpose [32]. But the use of these flammable polymers lowers the fire resistance property of phenolic foams. So, it is necessary to improve the toughness of PF foam and maintain the flame retardancy at the same time. This issue can be rectified by the use of phosphorus-containing polymeric modifiers. For instance, phosphorus-containing PUs15, phosphorus-containing polyethers10, etc. are capable of improving the toughness and flame resistance of PF foam [32]. While the addition of polyurethane [54], polyisocyanate [55], and polyacrylamide [56] worsen the flame retardancy with increase in mechanical properties of PF foam. On the other hand, the addition of inert fillers such as talc, glass, mica, etc. gives homogeneity and good texture to foam but it adversely affects the viscosity of foam. These fillers increase the viscosity of foam and resulted in the formation of heavier foams. The reinforcement of aramid fibers like Nomex and Kevlar [57] natural fibers like bamboo and cellulose fiber, glass fiber could produce enhancement in mechanical properties of PF foam, but it affects the mixing and foaming process. As a result, the foams based on these fillers suffer from high density and poor surface quality.

After the discovery of nanofillers, the reinforcement of fillers has become another fruitful way to enhance the toughness and strength of PF foam. The nanofillers such as MWCNT [58], graphene phenolic foam [19], clay nanoparticles [59], etc. could improve the properties of PF foam. The presence of clay nanoparticles produces increase in strength and glass transition temperature of PF foam by raising the cell density and cross-linking of the foam. Functionalized MWCNTs could boost the thermal property and compressive strength, by keeping good flame retardancy along with EMI property. The introduction of functionalized graphene could improve the flame retardancy, mechanical strengths, and thermal properties of PF foam.

5 Applications of PF Foam

Mechanical properties and compressive strength of phenolic foam determine its applications in various fields. Phenolic foams found applications as insulation for buildings, aerospace applications, petrochemicals, and other industrial applications.

The excellent properties of PF such as flame and creep resistance, non-drip property, etc. widen the application of PF in the field of in the fabrication, construction, and transportation industries. Phenolic foam possesses great flame, smoke, and toxicity (FST) properties, which is considered as the important properties of insulators. Phenolic foam is found to be a very useful material for insulation of buildings and transport vehicles due to its high ignition temperature (595 °C). Phenolic foams produced by microwave foaming method are used for building insulation and for LNG (liquefied natural gas) ships [60]. Moreover, PF foam produces little smoke and toxic gases during combustion [61]. While considering the applications of PF foams, it is very important to conduct research on the field of toughening agents with flame retardancy [7]. Supercapacitors are new type of advanced energy storage device and the study on this field is mainly concentrated on electrode materials with a large specific surface. In recent times, hierarchical porous carbon is used as an electrode material for supercapacitors. The hierarchical porous carbon obtained from carboxyl graphene oxide/phenolic foam is suitable for the production of real energy storage in supercapacitors [62]. The increased use of electronic devices such as communication equipment and wireless networks leads to serious electromagnetic interference (EMI) pollutions. In such situations, the high-performance EMI shielding materials are used for protecting the environment and human beings from harmful electromagnetic radiations [17]. MWCNTs and nano-Fe_3O_4-reinforced PF foam by in situ polymerization exhibit high electrical conductivity and high-performance EMI shielding [17]. Building industry requires new technologies of preserving energy and conserving the environment from exterior wall becomes the topic of interest due to the energy crisis existing in the world. As stated above, the excellent heat-insulating and flame-retardant properties of phenolic foams make it as a good exterior wall material [63]. In recent years, studies based on flexible strain sensors are developed and these are important components in wearable electronics [64]. Flexible and multipurpose strain sensor based on phenol formaldehyde foam as the raw material is constructed and it is used for monitoring human motion [64]. The heavy metals present in wastewater can be removed by carbonaceous adsorbents. These adsorbents could be prepared from low-cost phenolic resin-based carbon foam and it is successfully used for the removal of lead and copper ions from water [65].

6 Conclusion

The characteristic properties of phenolic foams over other polymeric foams extend its applications in various fields such as construction, petrochemical industry, thermal insulation, aerospace applications, etc. However, its high brittleness and friability limit the applications of PF foams. Therefore, it is essential to enhance its properties without affecting its inherent properties. Many research works were done in the field of PF foams for improving its mechanical properties by reinforcing nanofillers, natural fillers, and polymers as toughening agents into the PF resin. Researchers have studied the properties of phenolic foams by different approaches and concentrated on the impact of each modification on the final characteristic of the PF foam. Moreover, this modification affects the viscosity and reactivity of the foaming mixture and therefore controlling of foaming and curing kinetics is essential. Research works using biomass-based resin will be explored in future since it reduces the environmental pollution and the use of phenol obtained from petrochemicals. The new innovations and the property-enhancing research works will definitely extend the application of phenolic foams to new areas.

References

1. Mougel C et al (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer 164:86–117
2. Jalalian M, et al (2019) Mechanically whipped phenolic froths as versatile templates for manufacturing phenolic and carbon foams. Mater Des 168:107658
3. Zhang L, Liang S, Chen Z (2018) Influence of particle size and addition of recycling phenolic foam on mechanical and flame retardant properties of wood-phenolic composites. Constr Build Mater 168:1–10
4. Hu X et al (2016) Flame retardant, thermal, and mechanical properties of glass fiber/nanoclay reinforced phenol–urea–formaldehyde foam. Polym Compos 37(8):2323–2332
5. Song SA, Chung YS, Kim SS (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93
6. Hu X-M, Zhao Y-Y, Cheng W-M (2015) Effect of formaldehyde/phenol ratio (F/P) on the properties of phenolic resins and foams synthesized at room temperature. Polym Compos 36(8):1531–1540
7. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54(7):1962–1970
8. Hu XM et al (2014) Effect of polyethylene glycol on the mechanical property, microstructure, thermal stability, and flame resistance of phenol–urea–formaldehyde foams. J Mater Sci 49(4):1556–1565
9. Wang FY, Ma CCM, Wu WJ (2001) Kinetic parameters of thermal degradation of polyethylene glycol-toughened novolac-type phenolic resin. J Appl Polym Sci 80(2):188–196
10. Yang H et al (2013) A novel polyurethane prepolymer as toughening agent: preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 128(5):2720–2728
11. Yang H et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 19(3):1–10
12. Bo C et al (2019) Enhancement of flame-retardant and mechanical performance of phenolic foam with the incorporation of cardanol-based siloxane. Polym Compos 40(6):2539–2547
13. Choi MH, Byun HY, Chung IJ (2002) The effect of chain length of flexible diacid on morphology and mechanical property of modified phenolic resin. Polymer 43(16):4437–4444
14. Sui X, Wang Z (2013) Flame-retardant and mechanical properties of phenolic foams toughened with polyethylene glycol phosphates. Polym Adv Technol 24(6):593–599
15. Martin C et al (2006) Synthesis of novel boron-containing epoxy–novolac resins and properties of cured products. J Polym Sci A Polym Chem 44(21):6332–6344
16. Benin V, Durganala S, Morgan AB (2012) Synthesis and flame retardant testing of new boronated and phosphonated aromatic compounds. J Mater Chem 22(3):1180–1190
17. Li Q et al (2016) Open-cell phenolic carbon foam and electromagnetic interference shielding properties. Carbon 104:90–105
18. Li X, Wang Z, Wu L (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. RSC Adv 5(121):99907–99913

19. Li X et al (2016) One-step in situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6(78):74903–74912
20. Lin X-M et al (2018) Spectroscopic investigations on the origin of the improved performance of composites of nanoparticles/graphene sheets as anodes for lithium ion batteries. Carbon 127:47–56
21. Huang Q et al (2015) A facile and green method for synthesis of reduced graphene oxide/Ag hybrids as efficient surface enhanced Raman scattering platforms. J Hazard Mater 283:123–130
22. Iqbal MZ, et al (2016) Processable conductive graphene/polyethylene nanocomposites: effects of graphene dispersion and polyethylene blending with oxidized polyethylene on rheology and microstructure. Polymer 98:143–155
23. Jia Y, et al (2017) Magnetically separable sulfur-doped SnFe2O4/graphene nanohybrids for effective photocatalytic purification of wastewater under visible light. J Hazard Mater 338:447–457
24. Liu L, Wang Z (2018) Facile synthesis of a novel magnesium amino-tris-(methylenephosphonate)-reduced graphene oxide hybrid and its high performance in mechanical strength, thermal stability, smoke suppression and flame retardancy in phenolic foam. J Hazard Mater 357:89–99
25. Yu K et al (2018) Preparation and characterization of phenolic foam reinforced with expandable graphite and expanded graphite. J Cell Plast 54(3):545–559
26. Luo X, Yu K, Qian K (2018) Morphologies and compression performance of graphene oxide/SiO_2 modified phenolic foam. High Perform Polym 30(7):803–811
27. Sandhya PK et al (2020) Thermal and electrical properties of phenol formaldehyde foams reinforcing with reduced graphene oxide. Polym Compos 41(10):4329–4339
28. Li Q et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Compos Part A Appl Sci Manuf 82:214–225
29. Patle VK, et al (2020) Three dimension phenolic resin derived carbon-CNTs hybrid foam for fire retardant and effective electromagnetic interference shielding. Compos Part C: Open Access 2:100020
30. Song SA et al (2017) Mechanical and thermal properties of carbon foam derived from phenolic foam reinforced with composite particles. Compos Struct 173:1–8
31. Li P et al (2016) Enhancement of the interfacial interaction between poly (vinyl chloride) and zinc oxide modified reduced graphene oxide. RSC Adv 6(7):5784–5791
32. Yang Z et al (2013) Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes. J Appl Polym Sci 130(3):1479–1488
33. Xu P et al (2019) Preparation and characterization of bio-oil phenolic foam reinforced with montmorillonite. Polymers 11(9):1471
34. Guo Y, et al (2018) Mechanical property of lignin-modified phenolic foam enhanced by nano-SiO_2 via a novel method. Chem Pap 72(3):763–767
35. Gao C, et al (2021) One-pot depolymerization, demethylation and phenolation of lignin catalyzed by HBr under microwave irradiation for phenolic foam preparation. Compos B Eng 205:108530
36. Zhang N, et al (2020) Mechanical property of lignin-modified phenolic foam enhanced by whisker silicon. J Disper Sci Technol 41(3):348–354
37. Wang G et al (2018) One-pot lignin depolymerization and activation by solid acid catalytic phenolation for lightweight phenolic foam preparation. Ind Crops 124:216–225
38. Del Saz-Orozco B, et al (2014) Effects of formulation variables on density, compressive mechanical properties and morphology of wood flour-reinforced phenolic foams. Compos B Eng 56:546–552
39. Del Saz-Orozco B, et al (2015) Lignin particle-and wood flour-reinforced phenolic foams: Friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos B Eng 80:154–161

40. Domínguez JC et al (2017) Thermal properties and thermal degradation kinetics of phenolic and wood flour-reinforced phenolic foams. J Compos Mater 51(1):125–138
41. Ma Y et al (2018) Preparation and characterization of DOPO-ITA modified ethyl cellulose and its application in phenolic foams. Polymers 10(10):1049
42. Ma Y, Gong X, Jia P (2020) The effects of DOPO-g-ITA modified microcrystalline cellulose on the properites of composite phenolic foams. J Renew Mater 8(1):45
43. Del Saz-Orozco B, et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Compos B Eng 75:367–372
44. Yuan H et al (2013) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 62(2):273–279
45. Yang C, Zhuang Z-H, Yang Z-G (2014) Pulverized polyurethane foam particles reinforced rigid polyurethane foam and phenolic foam. J Appl Polym Sci 131:1
46. Yang Y, He J (2015) Mechanical characterization of phenolic foams modified by short glass fibers and polyurethane prepolymer. Polym Compos 36(9):1584–1589
47. Auad ML et al (2007) Flammability properties and mechanical performance of epoxy modified phenolic foams. J Appl Polym Sci 104(3):1399–1407
48. Pilato L (ed) (2010) Phenolic resins: a century of progress., vol 11. Springer, New York
49. Shao-tang LI, et al (2004) Study of phenolic foam toughening modification. Fiber Reinforced Plastics/Composite 4
50. Xiao W, Huang Z, Ding J (2017) The mechanical and thermal characteristics of phenolic foam reinforced with kaolin powder and glass fiber fabric. IOP Conf Ser Mater Sci Eng 274:1
51. Cui Y et al (2017) Synthesis and characterization of bio-oil phenol formaldehyde resin used to fabricate phenolic based materials. Materials 10(6):668
52. Aliha MRM et al (2018) Experimental and theoretical fracture toughness investigation of PUR foams under mixed mode I+ III loading. Polym Test 67:75–83
53. Linul E, et al (2020) Static and dynamic mode I fracture toughness of rigid PUR foams under room and cryogenic temperatures. Eng Fract Mech 225:106274
54. Shen H, Lavoie AJ, Nutt SR (2003) Enhanced peel resistance of fiber reinforced phenolic foams. Compos Part A Appl Sci Manuf 34(10):941–948
55. Smith SB (1983) Thermocell Development Ltd. US Patent 4,390,641
56. Kako Y, Kiguga T, Sanuki T (1978) Sumitomo Durez Company, Ltd. US Patent 4,131,582
57. Kim M, Choe J (2016) Development of the fire-retardant sandwich structure using an aramid/glass hybrid composite and a phenolic foam-filled honeycomb. Compos Struct 158:227–234
58. Basbagill JP (2008) Fiber reinforced phenolic foam: climatic effects on mechanical properties and building applications in northern Thailand. University of Southern California
59. Desai A et al (2008) Mechanical behavior of hybrid composite phenolic foam. J Cell Plast 44(1):15–36
60. Gi KB (2008) Development of microwave foaming method for phenolic insulation foams. J Mater Process Technol 201(1–3):716–719
61. Kim J, Lee J-H, Song T-H (2012) Vacuum insulation properties of phenolic foam. Int J Heat Mass Transfer 55(19–20):5343–5349
62. Li X et al (2017) Facile synthesis of hierarchical porous carbon derived from carboxyl graphene oxide/phenolic foam for high performance supercapacitors. RSC Adv 7(69):43965–43977
63. Yu Z, Liang DX (2016) Study on preparation of insulation and flame retardant building materials with inorganic compound phenolic foam. Chem Eng Trans 55:325–330
64. Wang Y et al (2019) Preparation of super-hydrophilic polyphenylsulfone nanofiber membranes for water treatment. RSC Adv 9(1):278–286
65. Lee C-G et al (2015) Lead and copper removal from aqueous solutions using carbon foam derived from phenol resin. Chemosphere 130:59–65

Chapter 2
Introduction on Foam Manufacture

Shahram Mehdipour-Ataei and Maryam Mohammadi

1 Introduction

1.1 Mechanism of Foaming

Foaming is generally defined as putting of bubbles into a matrix. Depending on the nature of the bubble, matrix, and the type of putting the bubble into the matrix, a wide range of foams can be prepared. The traditional method of preparing foams is based on using a mechanical stirrer or whipping of the surfactant solution. However, this method is not suitable for industrial production or quantitative laboratory studies because it is difficult to precisely control the amount of bubbles that must enter the liquid. The industrial production involves passing a stream of gas through an orifice (sparging) and then growing bubbles in solution. Several factors including interfacial tension, surface cleanliness, and gas flow rate affect the nucleation, growth, and separation of bubbles from the orifice. The size of the bubble determines the speed of the rise. According to Dickinson [1], the size of the bubble produced by an orifice can be estimated via balancing the buoyancy force and the surface tension acting on the bubble. As the bubble rises and reaches the interface, a thin layer forms on the surface of the column. The lifespan of this thin layer and the possibility of forming a foam layer depend on several factors including surfactant concentration, drainage rate, surface tension gradient, diffusion, and external disturbance factors. The nucleating of gas bubbles is an alternative method of foam production. The supersaturating of a liquid with gas or in situ production of gas, for example, by a chemical reaction is the basis of this method. In this process, by reducing the pressure, the gas is released

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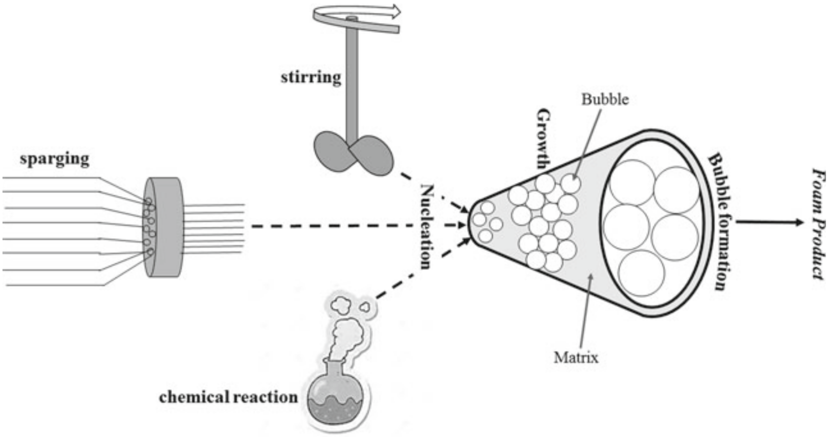


Fig. 1 Illustration of foaming mechanisms

from the solution and size of the bubble is affected by the dynamic surface properties. Cavity model and Fick's law can be used to describe bubble nucleation and growth, respectively [1–8]. The described mechanisms of foaming are illustrated in Fig. 1.

1.1.1 Water Foam

The most common method of water foaming is the severe shaking of a closed vessel containing a little amount of surfactant solution. The aerosol method is also usual in the production of shaving cream, hair styling mousse, and whipped cream. Another popular method is to bubble the gas directly into the surfactant solution. Pure liquids cannot generate foam because when the bubble enters below the surface of the pure liquid, the gas bubble bursts immediately after draining. On the other hand, in the presence of a surfactant solution, the liquid–air interface increases, and a restoring force restores the equilibrium. Two governing mechanisms of this phenomenon are Gibbs and Marangoni effect. These are inline with each other and usually both of them are considered. Polymers, particles, cations, and special anions that are adsorbed on mineral salts are surfactants that make foaming in the aqueous medium. These materials are often able to form a foam at very low concentrations of about 10^{-9} M. The cleanliness of the system has an important effect on the foam formation. The purity of the water must also be assured. A simple way is to shake the water vigorously and check how long the bubble stays in it. The durability of even one second indicates the presence of active surface impurities [2, 9, 10].

1.1.2 Glass Foam

In these foams, the solid phase is glass, which is filled with a gas phase. Powder method is usually used for conversion of glass to foam, which involves sintering a mixture of glass powder and special additives that facilitate the formation of a gas phase during heating. These additives are pore-forming or gas-forming agents that are used in small amounts. As the temperature of the mixture increases and the softening temperature passes, the glass particles begin to sinter and surround pore-forming agents. After a certain temperature, the gas is released and thus cavities appear in all parts of the sintered body. Recently, cold technology has been developed to produce foam glass. In this method, the heat treatment step is deleted and the whole process is done at room temperature. The method is based on the chemical reactions of water glass and fine powder of aluminum. One of the products of this reaction is gaseous hydrogen, which causes a gas bubble to form. The advantage of this method is the possibility of applying to the established unit. The problem with this method is the presence of explosive hydrogen and the difficulty of preparing a homogeneous foam. The reaction in the interfaces of water glass and aluminum does not allow uniform distribution. The proposed solution to this problem is to delay the foaming reaction using additives [11].

1.2 Role of Mixing in Foaming

Mixing is a challenging process in the foaming of materials. The more stirring, the better the mixing, but the more foam is created and the more bubble is introduced. This will create many problems including non-controlled structural features and reduced product quality. To solve this problem, chemical defoamers are used to prevent foaming. These materials are expensive and in some cases cause contamination in the final product. Thus, some modifications which are proposed to control mixing include (1) placing the mixer blade from the center to reduce the vortex, which reduces the amount of air and foaming; (2) using a vacuum during mixing and then entering the air in a controlled way after mixing; and (3) replacing a top-entering agitator with an inline mixer that has been piped for recirculation. The return line should be extended below the liquid level to prevent foaming. For cases where the amount of solid is high, an inline rotor/stator mixer is proposed to disperse the powder at high speed. Also in the bubbling method for preparing liquid foams, due to the slow process and initial non-uniformity, the liquid solution drains significantly during the production process and the produced foams possess a wet surface and dry bottom. A system is developed based on firefighting technology for this problem, in which a jet of a high-speed solution is mixed with the gas flow. This strategy allows us to prepare a large amount of uniform foam at high speed and a variable amount of liquid. In brief, uniform massive foam is made by an apparatus providing turbulent mixing of gas with a narrow jet of surfactant solution [9, 12].

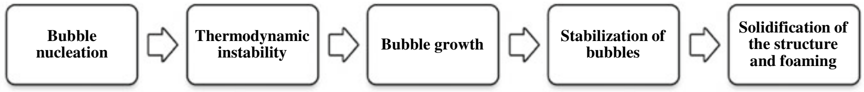
2 Foaming of Polymers

In general, polymer foaming consists of three steps: (1) the formation of a polymer/gas solution: the complete dissolution of a large amount (solubility threshold) of the blowing agent into the polymer under high pressure through temperature-dependent diffusion (stretching of a gas bubble in the shear field during the foaming process helps to improve diffusion); (2) cell nucleation and growth induced by a sudden thermodynamic instability via changing the temperature, pressure, and amount of gas in the prepared homogeneous supersaturated solution; and (3) cell stabilization by controlling the growth of bubbles and preventing coagulation and collapse. Then, the foam structure is obtained by removing the blowing agent from the mixture and the foam product is attained by stabilizing the cell via returning temperature and pressure to ambient conditions. Cells are frozen bubbles of various shapes and sizes after solidification of the plastic [5–7, 13, 14].

The first polymer foams were developed during 1930 decade. Polymeric foams are prepared by mixing a gas phase in the form of air bubbles or air tunnels into the solid phase. This mixing is very fast until the system reaches a uniform state like coffee foam. The solid phase is a polymer matrix and the gas is a blowing agent. In conventional foam processing, the most common blowing agents are fluorocarbons, chlorofluorocarbons, n-pentane, and n-butane. These materials are highly soluble in the polymer matrix. The blowing agent can be chemical or physical. Chemical agents are chemicals that take part in a chemical reaction and produce gases such as nitrogen or carbon dioxide. Physical agents are inert gases or liquids with a low boiling point that do not interact during the foaming process and are inert to the polymer matrix. Compared to chemical blowing agents, the physical type can be processed below critical temperatures with no limitation of degradation temperature. They also have a lower price and create a better foam morphology than chemical ones. However, special equipment and high skill are required to handle these blowing agents. Physical agents can be a supercritical phase. For example, supercritical carbon dioxide is used in the batch foaming method. In this way, carbon dioxide dissolves in the polymer matrix, increasing the free volume between the molecular chains and the mobility of the chains. After saturation, carbon dioxide is rapidly depressurized to induce foam in the polymer matrix. During this process, micro-foams are usually prepared. Using this method and applying nano-clay in a PLA matrix, nano-foam production has also been reported in another attempt [5–7, 15–17].

2.1 *Nucleation, Growth, Stabilization, and Solidification*

To initiate bubble nuclei, it is necessary to create sites with low potential energy. The most common method is to use nucleating agents, which cause supersaturated gases to escape from these sites and form bubble nuclei. The bubble nuclei are also formed by the physical mixing of foaming agents with a polymer liquid. The



Scheme 1 The mechanism of foaming

blowing gases are also obtained directly from foaming agents and there is no need to dissolve the foaming agent in the melt. These three mentioned nucleation methods are related to a certain category. The first one is widely used for polymers with high free volume, the second is appropriate for melt due to low potential energy, and the third is mainly used for thermoset plastics and reactive molded ones [8]. The use of shear field or any agent that causes the orientation of molecular chains and treatment by low-energy infrared radiation are the other methods. The bubble growth is affected by several factors including the amount and nature of foam constituents, molding process, equipment, melt viscosity, gas permeability, foaming agents, temperature, and pressure. As the bubble grows, its surface area increases and becomes unstable. One method of stabilization is using of surfactants to reduce surface tension and form fine bubbles with reducing gas penetration. Another way is to increase the melt viscosity to prevent the bubble wall form thinning. In practice, cooling or crosslinking helps to this. The next step is solidification. In thermoplastics, solidification is a completely physical process and is influenced by three factors: (1) cooling the melt with water, air, or any other media: this is related to the fact that the bubble does not conduct heat properly, the bubble wall solidifies, and inside remains at a high temperature. Almost long time is needed for cooling the bubble core, and the cooling rate should not be too high, as it will break the bubble due to wall shrinkage. (2) Gas release in the melt: dissolving the gas in the melt increases the plasticity of the melt. Then, this gas enters the bubble and increases the viscosity of the wall, which results in accelerated solidification. (3) Degradation and degassing of foaming agents: the rate of solidification is affected by heat absorption during degassing of physical foaming agents, heat absorption or degradation of chemical foaming agents, and heat release during crystallization of crystalline plastics. In thermosets, polymerization and molding occur simultaneously. Increasing the temperature and addition of a catalyst increase the solidification rate [18]. The overall concept of foaming process is illustrated in Scheme 1.

3 Classification of Polymer Foam Processing Techniques

All techniques of foam manufacturing include the three stages of cell initiation, nucleation, and stabilization. The classification of techniques is usually based on growth and stabilization. Accordingly, the most common methods of producing plastic foams include physical, chemical, and mechanical foam formation.

3.1 Physical Foaming

A liquid or gas foaming agent is added to the plastic and is released during the melting process. In some cases, such as fluoropolymers, a solid nucleating agent, which is stable at the process temperature, is used. In physical foaming, inert gases are dissolved in molten polymers or paste materials under pressure, and then, as the temperature increases or the pressure decreases, the dissolved gases are removed and foam is formed. In the process of foam beads, a liquid with a low boiling point is mixed with a polymer or filtered on polymer particles under pressure and then heated to turn the liquid into a foam. Aliphatic hydrocarbons, arenes, alcohols, ethers, ketones, aldehydes, low boiling point liquids, and hollow spheres are examples of these agents [19].

3.2 Chemical Foaming

Chemical reactions control the foaming process, i.e., the rate of polymerization. In addition, the rate of activation of the blowing agent is controlled through a decrease of solubility in monomer solution as the reaction progresses or thermal degradation occurs. This method cannot be used for non-crosslinkable polymers or those like fluoropolymers. In chemical method, foaming agents are added to the resin, then heated, and pressed to release gas—usually nitrogen—into the foam.

3.3 Mechanical Foaming

This method has limited applications. It is similar to whipping cream in which air is mixed with a melt. Mixing simply enter air into the melt, thus acting as a blowing gas. In other words, the air is drawn into the resin by mechanical agitation. The resin must be in a liquid state or have a low viscosity.

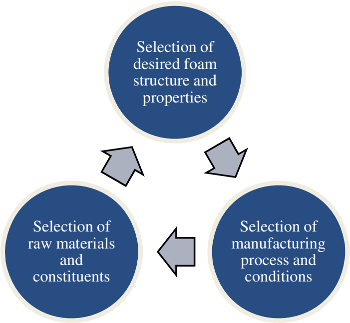
Another classification of foaming processes is based on creating a pressure difference between inside and outside the cell. If the external pressure is reduced, the process is decompression, and if the internal pressure is increased, it is expansion. Both decompression and expansion methods can be stabilized using both chemical and physical methods. Other methods are sintering resin particles in the presence of a gas or dispersion of a gas or solid in a melt polymer [18, 20, 21].

4 Polymer Foam Processing Techniques

Compared to ceramics and porous metals, the processing of plastic foams is relatively simple. It involves two main stages of mixing including the introduction and dispersion of gas and molding including cooling or curing. Cavities in these materials are formed during the molding process. In addition to the matrix, which is a high molecular weight polymer in liquid or bead form with foaming agents, fillers, additives, catalysts, and surfactants, are also used. Additives include lubricants, stabilizers, fire retardants, crosslinking agents, colorants, and nucleating agents. Fillers are usually glass, calcium carbonate, carbon black, barium sulfate, silicate, wood powder, and metal powder.

Foam products, especially polymeric type cover a wide range of applications. Hence, special properties are required in a specific application. Controlling the foam structure means that the size of the cells and the composition of the foam should be adjusted for gaining the desired properties. The determining factor of foam structure is the manufacturing process and the condition. Therefore, designing the foam structure and using the appropriate processing make it possible to provide products with the desired properties and high quality [3, 4, 6, 7, 18, 20–22]. Depending on the type of polymer, the size and shape of the foam cells, and the final application of the foam product, diverse manufacturing methods can be applied to prepare the foam (Scheme 2). The suitable selection of equipment and process conditions also results in low cost and reliability.

The manufacturing of plastic foams is comparable to that of common processing plastics. The common methods and equipment of plastic production such as extrusion are also usable to prepare foams. From film and sheet to molded products can be prepared in this way. Extrusion, injection molding, and bead foaming are the most preferred processes due to higher productivity than other methods. Continuous foam production processes such as extrusion and injection molding are limited to melt-processable polymers. Discontinuous processes are developed for non-melting and thermally degradable polymers. Laboratory-scale methods have also been developed. However, there is a need to develop new methods such as three-dimensional printing in the manufacturing of foams. This method has been specifically reported



Scheme 2 The relation of structure, properties, and manufacturing of foams

for the production of polyurethane foam. Improved properties, providing products in desired dimensions, shapes, or complex objects, and the possibility of using various materials such as polymers, composites, metals, and ceramics are the advantages of this technique [3, 4, 6, 7, 13, 15, 23, 24].

In the following sections, the manufacturing methods of polymer foams are reviewed.

4.1 Slab-Stock/Slab-Stock by Pouring

In this method, a mixture of materials is continuously poured on a moving conveyor. The conveyor has a wall and foam is formed on the wall using a mixer. The final product is a shapeless large slab, which is cut into slabs with suitable dimensions [14, 24].

4.2 Molding

The process consists of two steps: mixing and molding. Mixing is done by a paddle-type high-speed mixer. Molding includes a hydro-press, a digester, and an aluminum mold with a suitable design for gas outlet. Virgin or pre-expanded beads are poured into the mold and subjected to heating and pressing. Liquids cannot be used in this case. The molded product is then demolded after setting or curing. This method can be applied as a single step including direct placement of plastics with foaming agents in a mold and then pressing and molding or two steps including pre-forming of plastics with foaming agents and then mold pressing. Productivity, high quality, and simplicity are the advantages of this method. The molding method for obtaining products with complex shapes saves about 15% compared to slab-stock, which requires secondary operations. Molding of rigid foams is also possible but it has a limited application [18].

4.2.1 Low-Pressure Molding

In this method, the pre-heated liquid mixture is poured into the mold. The mold is preheated and covered with a release agent. Demolding is done after curing and cooling. Depending on the mold design, the amount of waste in this method is varied from zero to 5% by weight. The best results are obtained when the release agent is sprayed on a clean and hot mold just before each pouring. The release agent solvent must be completely removed before pouring the foam materials into the mold. Compared to slab-stock, which requires minor curing and infrared heaters located on top of the conveyor, the molding process needs excess heating by an external heater. Using of microwave reduces curing time from 20 to 4 min. Additionally, improved properties are gained by microwave curing compared to conventional heating. Dielectric heating is also accepted for curing [25].

4.3 Batch Foaming

This method is used on a laboratory scale to investigate the effect of blowing materials and foam constituents on foaming behavior. In this method, the polymer sample is placed in a high-pressure chamber that saturated with an inert gas such as carbon dioxide or nitrogen. Then, the solubility of the gas in the polymer is decreased by heating the sample and removing the pressure. A major drawback of this method is a very long time required to saturate the polymer with gas, which is due to the low gas permeability of the polymer at room temperature [13, 26].

4.4 Extrusion

This method allows the production of low-density foams with simple two-dimensional geometry. The main steps of the process are mixing, extrusion, and cold molding. Expandable beads containing blowing agents are usable, but the most widely used system is the direct gas extrusion. In this process, the plastic and foaming agent are subjected to the processes of softening, mixing, and degradation (chemical foaming)/degassing (physical foaming)/injection of pressure with inert gas (mechanical) of the foaming agents. In this way, the polymer is fed to the extrusion first, and then the blowing agent is injected into the extruder barrel to dissolve the gas in the melt polymer under high pressure. The dissolved gas softens the melt polymer and a uniform mixture of polymer and gas flows along the extruder. The mixture then exits from the die and foaming occurs due to pressure drop. The extruder head provides enough pressure to prevent foaming near the outlet. After being extruded into the mold, the materials are foamed and the final product is obtained after the cold molding process. In the next step, the foam is stabilized according to the viscoelastic behavior and strain hardening. The effective parameters in this process include extrusion pressure, temperature, and residence time. Single-screw and double-screw extruders can be used. The advantages of the double-screw extruder are less energy consumption and higher efficiency of melting process compared to the single-screw type. The limiting factor is the internal high pressure, which requires special designs. The problem with both types is that the three processes of melting, mixing, and cooling must be performed at a short L/D of approximately 30 to 1. The tandem system is proposed to overcome this problem. In this way, melting and mixing of blowing agents is done in a basic extruder and then a gradual cooling profile is applied along the second extruder (tandem line), which improves the quality of the foam. Although this system is more expensive than conventional types, it is more common due to the overall cost-effectiveness and versatility. Extrusion foaming is continuous (despite the batch method), cheap, and easy but it is still difficult to smooth the foam and create large amounts of closed cells in cases such as starch biodegradable foams. The use of thermoplastic polymers as an additive is suggested but it decreases biodegradability [13, 14, 18, 25].

4.5 Extrusion Molding

In this method, a mixture of reagents is injected into the mold, and demolding is done after curing. This method produces high-density foams with complex two- and three-dimensional geometries despite extrusion. The low cost of materials, high-dimensional stability, low energy consumption, short cycle time, and improved mechanical properties are the advantages of this method. Supercritical nitrogen is usually used as a blowing agent of this process to produce high-density foams with high cell density. Moreover, the softening effect of nitrogen in the polymer/nitrogen mixture decreases the process temperature resulting in reduction of energy and cost [13, 24].

4.6 Injection Molding

This process bears high productivity and quality. It is an applicable economical method for the production of large plastic foams with complex three-dimensional shapes and special dimensions. The method is more complex and expensive than the slab-stock method; however, it is known as the main method of producing structural foams. Depending on the mold temperature, this method is classified into the cold and hot molding. An injection molding machine that includes a plasticizing injector, mold clamping, and a driving system is the main equipment of this process. The process includes feeding of raw materials, heating, plasticizing, mold closing, injection, foaming, cooling, demolding, and post-treatment. In this way, the polymer and additives are mixed and injected into the feed cylinder to heat and soften. The physical foaming agents are injected directly at the end of the plasticization, mixed evenly, and injected into the mold at high pressure and speed. The chemical blowing agents can be injected directly from the barrel of a modified injection machine or through an accumulator. As the pressure drops sharply, the melt plastic produces a large amount of saturated gas that forms bubbles. The mixture fills a part of the mold (shot) and the gas bubbles at high pressures immediately expand and fill the cavity, completely. As the cells are collapsed against the mold surface, a thin layer of melt forms on the rigid core of the foam. The thickness of the shell can be controlled by the amount of injected melt, mold temperature, type and amount of blowing agent, temperature, pressure of the melt, and the parameters of the injection machine, especially the injection speed. Finally, after bubble expansion, cooling, molding, and demolding, a foam product is obtained. Injection pressure, temperature, and speed are the determining factors in this method [14, 18, 25].

4.6.1 Gas Pressure Injection Molding

There are various methods of gas injection systems. In this process, when the plastic enters the mold (after injection shot), the gas pressure is removed and the remaining melt is foamed. A seal mold under pressure with inert gas is used. This pressure is to prevent the plastic mixture from foaming when entering the mold.

4.6.2 High-Pressure Molding

A mixture of heated melt with blowing agent is injected into a mold. A pressure much higher than the gas pressure of the blowing agent is created in the mold. After solidification of the shell with the desired thickness, the second step is performed by opening the mold. Thus, the pressure is reduced which causes the remaining melt to foam. Foam density, wall thickness, and surface finishing depend on the constituents and the amount of foam mixture.

4.6.3 Low-Pressure Method with Co-Injection

This process includes separate injection of two compatible plastic components. In this way, solid plastic is injected from a plasticator to form a solid and smooth shell. At the same time, another plastic containing blowing agent is injected, separately to form a foamed core.

4.6.4 Low-Pressure Method with Surface Finishing in Low-Pressure Molding

This method includes no co-injection or injection-compression molding. The volume of the mold cavity is always larger than the volume of the plastic in the unfoamed state. Low pressure allows bubbles to nucleate and grow. Foam expansion occurs during filling. Defects may occur due to bubble growth on the surface of the mold. These defects and surface roughness are visible. Therefore, secondary operations including sanding, filling, and painting are needed. Moreover, controlling of process variables including the temperature of melt and mold, injection speed, blowing agent, cyclical heating/cooling of the mold surface, and direct injection of blowing agent into the melt may improve surface properties during the manufacturing [25].

4.6.5 Reaction Injection Molding

This method is a combination of chemical processes and injection. In this process, highly reactive liquid plastics are mixed under high pressure, then injected into a mold to react, polymerize, and foam. Heating the foam mixture, mechanical mixing (high pressure), pre-injection molding, solidification and heating, extrusion, post-treatment, and heating are the steps of the process. In this method, the reaction between the raw materials causes the release of an inert gas such as nitrogen or carbon dioxide into the plastic to form foam. This method is relatively new and is used to prepare structural foams. The short production cycle of 0.5–6.0 min, low price, easy insertion, and low energy consumption are the advantages of this method. Moreover, shorter cycles with no solvent washing, improved surface finishing, and fast injection into the mold are the advantages of this method over low-pressure mechanical mixing systems. Liquid injection molding, which is a type of reaction injection molding, involves continuous mixing and injection. In this method, the whole shot is mixed in a chamber before being injected into the mold [18, 25].

4.7 Heat/Microwave Sintering

Heat sintering involves mixing the powder of foam mixture, placing the mixture in a metal mold, and finally sintering for several hours. This method is time-consuming, expensive, and requires a large number of molds. Using microwave as a heat source instead of the usual methods, the sintering time can be reduced to a few minutes. In this way, the uniformity of the sintered body is also improved. Some materials and polymers, such as polyethylene, do not absorb microwaves. Thus, a modifying coating layer such as carbon black is required. In this case, a transparent mold such as glass should be used. Thus, the mold must be selected such that it has a low microwave reflection and provides observation of the foaming process. Some holes in the mold wall are also considered as the outlet of solvent gases. The microwave foaming method has been widely used for phenolic foams. It takes a long time to produce large-sized phenolic foams by conventional systems and there are environmental restrictions on the use of blowing agents like $CFCl_3$. Therefore, a resole foaming method has been developed using microwave and air. The process consists of three steps: (1) mixing the resole and hardener with air bubbles (resole can be cured at 250 °C without hardener, but it takes a long time to completely cure, so the viscosity decreases before solidification, and air bubbles can escape), (2) injection of the mixture into the mold, and (3) microwave foaming. The temperature inside the resole should increase to 150–250 °C, rapidly to make the air bubbles 5–10 times large. Additionally, in the production of phenolic foams, it is necessary to remove the produced water during the curing reaction. In conventional foaming methods, the temperature is usually less than 100 °C, which reduces the possibility of water evaporation. The microwave generates heat by vibrating polar molecules such as water or resole despite hot plate, which induces slow and non-uniform conduction heat into the material [18, 27–29].

4.8 Bead Foaming

This method is used to produce low-density foam products with complex three-dimensional geometries. These foams are prepared using the sintering process of the beads. These beads are unfoamed when sold, and a pre-expansion step must be performed by a pre-expander system. Then pre-expand beads must be stabilized. After stabilization, the beads are ready to enter the mold. Polystyrene bead foams are one of the most common types.

Expandable plastic foams are plastic concentrates containing blowing agents. These materials are formed into precise solid spheres. The two main stages of this process include pre-expansion of virgin beads by heat (hot steam is the most common due to economical aspect). This step brings the density of beads to the desired value within the molded product. In the next step, these beads are transferred into a two-cavity mold by air through a tube. If the beads do not fill the mold properly, the vibration of the mold is exerted to properly arrange the beads. The final expansion is done in the mold by steam or live steam, which enters through the pores of the mold. During expansion, beads melt, adhere to each other, form a relatively smooth shell, and fill the mold. Multi-cavity molds with small sections can also be used. After the heating cycle, the cooling cycle is performed. Due to the insulation of the beads, it takes a long time to cool before demolding. If the heat is not completely removed, the product will be distorted. Water is sprayed on the mold to cool it. The release agent is also used to facilitate cooling, especially for molds with complex shapes. In these processes, the molds have two walls. The inner wall is the actual shape of the product and has some pores for penetration of steam into the foam. Moreover, the produced hot gases leave the product through these pores. The outer wall is a steam cover. Before demolding, stabilization is done by vacuum and water spraying on the inner wall of the mold. The production pressure in this type of molding is low. Thus, cheap molds such as aluminum are usable. Long manufacturing cycles are required if large amounts of blowing agents (such as the production of expanded styrene-acrylonitrile) are used. Post-mold curing is not required in this process [13, 25].

4.9 Spraying

This method is used for filling molds where large surfaces such as panels are desired. This method can be used without a mold. The equipment has suitable price and is portable. In this method, the mixing of components and materials is done by atomization of materials when leaving the nozzle of the spray. Heat can also be used to reduce the viscosity of the polymer. In airless spraying, the spray gun moves approximately 30 inches from the surface and the final properties are obtained 24 h after spraying. The spraying rate of 1.8–3.6 kg/min is usually applied. The surface must be completely clean. Adhesion of the foam to the spray surface is another problem. In cases where the spray surface and the foam material are not compatible, modifications should be made to the surface [24, 25].

4.10 Pour Foaming

In this method, the polymerization and molding of the foam occur simultaneously. The materials are completely mixed before pouring and converting to a fluid. The materials and molds are under little pressure or with no pressure. Therefore, there is no need for high-strength equipment and molds. Due to the low pressure of the process, this method can be used to produce large-scale products and pouring operations can be done in the established unit. The process is unable to apply for structural foams. It is mainly used for preparing thermosets with high foam-ability. High-strength products with low-dimensional accuracy are obtained in this method [18].

4.11 Rotation Foaming

The equipment in this method requires little capital but a lot of production time. The raw materials are pre-formed, then they are placed in a mold and the mold is tightly closed. The mold is then rotated in a furnace to melt the plastic and make it flow through the mold. Heating is continued until the foaming agents are degraded. The final shape is created after expansion, and finally the product is demolded, cooled, and solidified. In this method, (1) the materials are in the form of powder, small particles, or liquid that are easily melted and form a smooth surface; (2) raw materials must be melted, poured into molds, and then flowed to fill cavities instead of melting and then injecting into molds; and (3) the mold should rotate in one or two directions with low pressure. The mold is usually made of aluminum and is heated by steam from a jacket or hot air circulation system. The rotation speed of 1–5 rpm is usually applied.

4.12 Hollow Blowing

This process is performed using a two-headed mold. The method is similar to the processing of conventional plastics and includes (1) preforming of material by extrusion or injection, (2) heating the preform in the mold and foaming, (3) introducing compressed air for blowing and molding, and (4) cooling and demolding [18].

4.13 Thermal Degradation/Treatment

This method can be done in two ways: (1) thermal degradation of block or graft copolymer that has thermally stable and thermally labile blocks, (2) heat treatment of polymers with high T_g which are blended with organic materials or thermally labile polymers. The additives in this method must be completely degraded, otherwise it will contaminate the polymer matrix. In this way, we have reported the preparation of nano-foams with designed structures. Nanofoams are made through thermolysis or heat treatment of thermally labile blocks as a disperse phase in the thermally stable continuous phase. In brief, the foam is obtained via introducing thermally labile blocks into the polymer building, casting the polymer solution, then removing labile blocks and the produced gas [15, 30–34].

4.14 Frothing

This urethane process is introduced by DuPont. This method is a two-stage system based on the introduction of an excess volatile liquid into the formulation. In this method, a pre-expanded foam stream is poured into the mold, where the expansion continues until the desired density is reached. In the foaming stage, the stream is completely liquid and flows easily. This method is suitable for filling cavities and producing panels. The advantages of this method include low mold pressure during foaming, the possibility of achieving low and uniform density, and laying down of expanding foam without causing collapse or density change.

4.15 Casting

This method is a simple non-mechanical pouring method, reaction injection molding, or liquid injection molding. Plastic components and additives are dissolved in a suitable solvent and poured into molds. Polymerization and foaming take place inside the mold. Molds are usually heated or cured in the oven, or both of them. This method applies to materials with suitable solubility [25].

4.16 Phase Separation

This method involves mixing two or more polymers with additives in suitable solvents. The matrix material is then separated from the solvent by a chemically controlled method or thermal cooling so that the solvent accumulated in the polymer matrix forms two completely separated phases. The removal of the solvent gives the final foam structure. This method is specific to non-cross-linkable polymers because the polymer must be soluble in a solvent. Today, one of the main methods of preparing porous materials is phase separation.

4.17 Leaching

This method involves dissolving the polymer matrix in a highly volatile solvent, casting the solution onto a mold, and selective leaching of water-soluble mineral salts or organic compounds, which were previously mixed with the polymer matrix. The problem with this method is the presence of unwanted contaminants such as solvents or salts in the porous polymer structure. To overcome this problem, the melt molding/particulate leaching method has been proposed instead of the solution molding/particulate leaching. In this way, the polymer matrix is pre-mixed with solid leachable additives and then pressed together. Similar to the solvent cast method, this product enters the same solid leaching stage.

4.18 Etching

This method includes using high-energy radiation to create chain scission in the polymer and remove degraded molecules. The polymer film is then etched with an acidic solution or base to remove the loose polymer. Polycarbonate and polyester films made in this way are commercially available.

4.19 Stretching

The process involves controlled stretching of semi-crystalline polymers in dry, molten, or solution state. In this method, after several times of stretching, the amorphous areas between the crystalline are degraded and the cavities are prepared in the range of a few nanometers.

4.20 Sintering

The sintering process includes mechanical compression of polymer particles at high temperatures. This method can be used for both thermoplastic and thermoset polymers [18].

4.21 Foam Preparation Methods Based on Foam Structure

In this section, some foam structures comprised of the manufacturing process and condition are described.

Foamed film and sheet: These foams are prepared by feeding plastics and additives containing specially treated expandable pellets or injection into the barrel using a tubular film extruder. In both methods, the extruded material passes from the inside to the annular tubing die and expands on an internal sizing mandrel by blowing air into the tube or drawing a tube. The die design is very important because in foam extrusion, the viscosity of the melt is very high and thus the defects are easily transferred to the product. To solve this problem, the die is designed in such a way that the flow is restricted and a uniform flow enters the die [25].

Structural foamed body: Injection molding processes with low or high pressure are used for this purpose. The conventional extruders can be used. The blowing agent can be mixed with the plastic as it enters the hopper, or entered into the melt of screw plasticator, or mixed with the melt by a stirrer. If the surface and inner materials are not the same, the surface materials do not contain foaming agents and softening is done separately. Then, the surface and core are combined during the molding. If the same material is used for the surface and the inside, different molding processes are used to form the unfoamed and foamed surfaces. Two processes of creating an unfoamed surface include: (1) increasing the temperature of the melt and the viscosity to prevent the surface from foaming, and (2) increasing the surface pressure and preventing the separation of gases from the melt. In comparison with these foams, freely foamed body structures are the foams in which foaming occurs throughout the volume of the material [18, 25].

Crosslinking foamed body: The temperature range of bubble expansion is very narrow and difficult to control. By using crosslinking agents, the viscoelasticity of the melt is increased and the temperature range of the bubble expansion is widened.

Combined foamed body: If the foaming occurs in matrix resin mostly combined plastic foam is obtained [18].

Structural web molding: This low-pressure process is the gap between structural foam molding and injection molding. It does not have the usual surface properties of structural foam or defects like the swirl pattern. It is applicable to prepare large light smooth surfaces.

Foam reservoir molding or elastic reservoir molding: This process is used to make plastic sandwiches. In this way, the plastic composite is placed in the heated mold and compressed [25].

5 Conclusion

In general, in all methods of foam production, matrix material, blowing agent, filler, composition, conditions and type of process determine the properties and characteristics of the foam product. Also, the process type and conditions determine the selection of raw materials and composition, and vice versa. Therefore, despite focusing on extrusion and injection molding as the most common methods, the appropriate manufacturing process is selected according to the desired properties of the foam product. Thus, a set of factors including the type of raw materials, structure, final properties of the foam, cost, and applicability of the process must be considered. Due to the extensive properties of foam structures, it is important to address the methods of production and develop improved new methods.

References

1. Dickinson E (1992) An Introduction to food colloids. Oxford University Press, New York
2. Pugh RJ (1996) Foaming, foam films, antifoaming and defoaming. Adv Colloid Interface Sci 64:67–142
3. Landrock AH (1995) Handbook of plastic foams: types, properties, manufacture and applications. Elsevier
4. Okoroafor MO, Frisch KC (1995) Introduction to foams and foam formation. Handbook of plastic foams: types, properties, manufacture and applications. William Andrew Publishing/Noyes, New Jersey
5. Lee ST, Ramesh NS (2004) Polymeric foams: mechanisms and materials. CRC Press
6. Lee ST, Park CB, Ramesh NS (2006) Polymeric foams: science and technology. CRC Press
7. Klempner D, Frisch KC (1991) Handbook of polymeric foams and foam technology. Hanser, New York
8. Yang J, Jiang T, Liu B, Zhang C, Zeng X, He L, Gong W (2021) Experimental and numerical analysis of bubble nucleation in foaming polymer. Mater Des 109577
9. Saint-Jalmes A, Vera MU, Durian DJ (1999) Uniform foam production by turbulent mixing: new results on free drainage vs. liquid content. Eur Phys J B 12(1):67–73
10. Xu C, Wang H, Wang D, Zhu X, Zhu Y, Bai X, Yang Q (2020) Improvement of foaming ability of surfactant solutions by water-soluble polymers: experiment and molecular dynamics simulation. Polymers 12(3):571
11. Spiridonov YA, Orlova LA (2003) Problems of foam glass production. Glass Ceram 60(9–10):313–314
12. Charles Ross & Son Company (1842). http://www.mixers.com
13. Nofar M, Park CB (2017) Polylactide foams: fundamentals, manufacturing, and applications. William Andrew, Elsevier BV
14. Sivertsen K (2007) Polymer foams. Polymer physics. Spring, Massachusetts Institute of Technology, USA
15. Aram E, Mehdipour-Ataei S (2016) A review on the micro-and nanoporous polymeric foams: Preparation and properties. Int J Polym Mater 65(7):358–375
16. Fujimoto Y, Ray SS, Okamoto M, Ogami A, Yamada K, Ueda K (2003) Well-controlled biodegradable nanocomposite foams: from microcellular to nanocellular. Macromol Rapid Commun 24(7):457–461
17. Lu H, Wang J (2020) Current research and patents of polymer foaming. Recent Pat Mech Eng 13(3):280–290

18. Liu PS, Chen GF (2014) Porous materials. Butterworth-Heinemann, Elsevier
19. Ajorloo M, Fasihi M, Taki K (2020) One-step regulating the microstructure in physical foaming process of polypropylene. Mater Manuf Process 35(8):935–939
20. Lee ST, Park CB (eds) (2014) Foam extrusion: principles and practice. CRC Press
21. Ebnesajjad S (2015) Fluoroplastics: melt processible fluoropolymers - the definitive user's guide and data book. Elsevier, William Andrew
22. Rosato DV, Rosato DV, Rosato M (2004) Plastic product material and process selection handbook. Elsevier
23. Ebnesajjad S (2013) Introduction to fluoropolymers: materials, technology and applications. William Andrew, Elsevier
24. Ge C, Priyadarshini L, Cormier D, Pan L, Tuber J (2018) A preliminary study of cushion properties of a 3D printed thermoplastic polyurethane Kelvin foam. Packag Technol Sci 31(5):361–368
25. Gama NV, Ferreira A, Barros-Timmons A (2018) Polyurethane foams: past, present, and future. Materials 11(10):1841
26. Liu J, Qin S, Wang G, Zhang H, Zhou H, Gao Y (2021) Batch foaming of ultra-high molecular weight polyethylene with supercritical carbon dioxide: influence of temperature and pressure. Polym Test 93:106974
27. Zubair M, Ferrari R, Alagha O, Mu'azu ND, Blaisi NI, Ateeq IS, Manzar MS (2020) Microwave foaming of materials: an emerging field. Polymers 12(11):2477
28. Aghvami-Panah M, Jamalpour S, Ghaffarian SR (2021) Microwave-assisted foaming of polystyrene filled with carbon black; effect of filler content on foamability. SPE Polymers
29. Kim BG (2008) Development of microwave foaming method for phenolic insulation foams. J Mater Process Technol 201(1–3):716–719
30. Mehdipour-Ataei S, Saidi S (2007) Preparation and characterization of sulfone-based polyimide nanofoams grafted with poly (propylene glycol). e-Polymers 7(1)
31. Nofar MR, Park CB (2018) Introduction to plastic foams and their foaming. Elsevier
32. Mehdipour-Ataei S, Aram E (2014) New polyimide and nanoporous structures with low dielectric constant. Adv Polym Technol 33(3)
33. Aram E, Mehdipour-Ataei S (2013) Preparation of thermally stable, low dielectric constant, pyridine-based polyimide and related nanofoams. J Appl Polym Sci 128(6):4387–4394
34. Mehdipour-Ataei S, Saidi S (2008) Structure–property relationships of low dielectric constant, nanoporous, thermally stable polyimides via grafting of poly (propylene glycol) oligomers. Polym Adv Technol 19(7):889–894

Chapter 3
Materials and Chemistry of Phenolic Foams

Felipe M. de Souza, Anil M. Palve, and Ram K. Gupta

1 Introduction

The term polymer is derived from the Greek word "*poly*" meaning "*many*", and "*mer*" means "*units* or *parts*". A polymer is a large molecule made of repeating structural units called monomers. Generally, these repeating units contain carbon, hydrogen, and other elements such as O, N, S, F, Cl, P, Si, etc. Polymeric materials have become essential and playing a ubiquitous role in human life. They have a very important role in the modernization of our life and are found almost everywhere in daily use such as in clothes, shoes, bikes, cars, toys, electronic devices, bedding, couches, cars, constructions to name a few. There are two major types of polymeric materials namely thermoplastic and thermoset (Fig. 1). Thermoplastics are the polymers that become soft when exposed to heat and return to their original conditions after cooling. Monomers in thermoplastic are held together by relatively weak intermolecular forces. A broad class of thermoplastics like polyethylene, polypropylene, polystyrene, polycarbonate, polyvinyl chloride, and polylactic acid has been used in foam-making processes. The word "*foam*" originates from the medieval German word "*veim*" meaning "*froth*". A thermosetting plastic remains solid after heating and cannot be reshaped by cooling and because of this property, they are hard to reuse or recycle using conventional methods. Thermoset polymers are mechanically stronger than thermoplastic and can be used for high-temperature applications due to their three-dimensional network and a high degree of cross-linking. Due to high strength, durability, and resistance to heat, they find their wide applications in automobiles, construction, varnishes, glues, etc.

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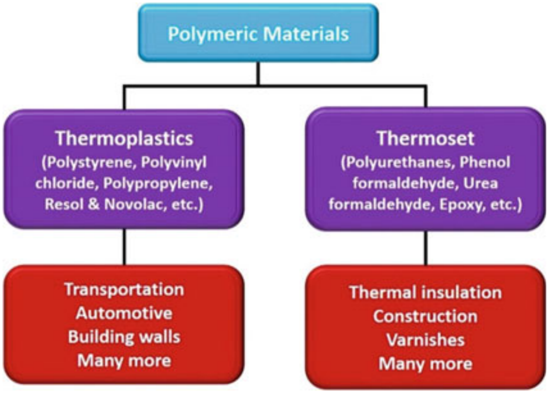

Fig. 1 Major classification of polymeric materials based on heat effect and principal applications

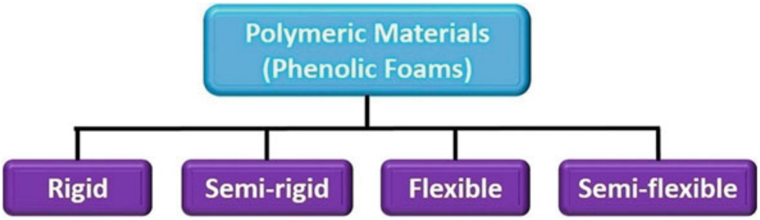

Fig. 2 Classification of polymeric phenolic foam material based on their composition

The polymeric foams are additionally classified as rigid, semi-rigid, semi-flexible, or flexible depending upon their compositions, cellular morphology, physical, and thermal distinctiveness (Fig. 2). The above mention classification of polymeric materials is due to the rigidity of polymeric backbone, chemical composition, degree of cross-linking, degree of crystallinity, etc. Foamed polyvinyl chloride was perhaps the foremost thermoplastic material that was made available in the market during World War II. After the importance of polyvinyl chloride in the market, polyurethane and polystyrene foams were synthesized and made available in the market. In 1862 Alexander Parkes synthesized cellulose nitrate (celluloid). The primary cellular polymer to be positioned in the market was sponged rubber, which was developed in 1914. It was synthesized using natural rubber latex with the addition of gas-producing substances like sodium and ammonium carbonate or sodium polysulfide [1].

In 1872, German Scientist Adolph Von Baeyer first discovered the phenol–formaldehyde resin. Later in 1907, the father of phenolic resin L. H. Baekeland synthesized phenolic resins (Bakelite) [2]. After the development of phenolic resins, it was commercialized in the early 1940s by the German industry as a balsa material substitute [3]. After the commercialization of Bakelite and its uses, much later bisphenol-A (polycarbonate and epoxide resin) mainly became an important part of the development of phenolic resin materials. Over the past couple of decades, phenolic polymers have been attracted to manufacturers because of their uses in insulating products and flame-resistant materials. Before 1968, resols and novolacs were the major products obtained from the reaction between phenols and formaldehyde. D'Alessandro synthesized improved phenolic resin foam using polyhalogenated saturated fluorocarbons. The polymeric foams are available in different shapes such as boards, sheets, slabs, blocks, molded shapes, 3D shapes, etc. Due to their several advanced and tunable properties, polymeric materials have emerged as potential materials for commercial applications.

Due to social and economic impact, the global market of the polymer industries has increased tremendously. The leading producers and consumer countries of polymeric foam are North America, Europe, and Japan. In recent years, Latin American and other Asian countries (such as Argentina, Mexico, Brazil, India, South Korea, etc.) have also been started producing polymeric foams. The applications of polymers phenolic foams are now not only limited to household goods but also has been used in a variety of industries such as aviation, aerospace, medical devices, etc. [4]. Phenolic foams have unique properties such as low inflammability, high-quality thermal insulation, outstanding flame resistance, less smoke density, and non-toxicity [3]. Phenolic foams are versatile polymers used in a variety of applications such as structural strength, thermal-fire-moisture resistance, etc. Applications of polymeric foams are dependent upon their classification. Generally, flexible foams are used in packaging, footwear, cushioning, automotive interiors, carpet, textiles, and fibers, etc. while rigid foams are used in insulating windows, doors, appliances (e.g. refrigerator), sealants, plumbing pipes, etc.

The general composition and method for preparing phenolic foams involve mixing a liquid phenolic resole, a blowing agent, a catalyst, a surfactant, and optical additives as well as an acid curing agent into a considerably uniform composition [3, 5, 6]. The physical and mechanical properties of foams considerably vary from those of solid matter. Due to the different range of properties, foams have a larger scope of applications as compared with solid materials. In all commercial foams, phenolic foams are well known as rigid thermoset foams. Phenolic foams own high thermal stability with good thermal insulation, admirable fire resistance, and low toxic gases during combustion [5]. The properties of foams are also dependent upon the cell geometry (i.e. open/closed cells). Open cells are useful for sound insulation and closed cells are more appropriate for thermal insulation. But, phenolic foam production by several industries has faced many issues ranging from waste discard, recyclability, and the depletion of the ozone layer by the chlorofluorocarbons which are used as blowing agents [1]. Different attempts are also made to convert phenolic foams into useful monolithic nitrogen-containing activated carbon foams [7]. Lightweight carbon with red mud hybrid foam was synthesized using phenolic resin as a carbon source and red mud as filler from industrial wastes [4]. The pioneering approach in the synthesis has been attempted such as bark-derived phenol–formaldehyde resins [8]. There are emerging areas in the synthesis of lignin-derived bio-based polymers for flame retardants and mechanical strengths [9]. The use of renewable sources for the production of phenolic foams has great importance in the present situation. The efforts in the synthesis of phenolic foams using a renewable source such as cardanol (a byproduct of the cashew industry) [10], glycerides of coconut oil [6] were reported in the literature. Though the polymeric foams have an environmental impact, it is necessary to modify the process and overcome the issues with renewable sources. In the forthcoming years, novel approaches such as halogen-free, phosphorus, nitrogen-based, and bio-based polymeric foams may get placed on the conventional type of production of the phenolic foams.

2 Materials and Chemistry of Phenolic Foams

The phenolic foams were officially introduced in the market around 1940 as a replacement for wooden-based materials such as balsa [3]. Phenolic foams present several advantages such as high thermal and environmental stability, low thermal conductivity, and improved flame retardancy. In phenolic foams, carbonization takes place around 500 °C leading to a formation of a protective char layer that prevents the spread of fire. This phenomenon explains why phenolic foams present flame resistance properties [11]. Also, they present high thermal stability allowing them to remain functional under low temperatures as −200 or as high as 200 °C [12, 13]. Their low thermal conductivity also plays a role in their properties by slowing down the heat transfer, which ends up improving thermal stability [14]. Despite that, phenolic foams lost some space for wide applications compared with other polymers such as polystyrene, polyvinyl chloride, polyurethanes because of the lack of mechanical properties, usually presenting a lower compressive strength and friability in comparison to other polymers [3]. However, after the Montreal and Kyoto protocols, both industry and scientific community focused their efforts on finding eco-friendly materials [15]. Fortunately, phenolic foams have a low heat and smoke release when burned along with the low toxicity of the smoke, which is mostly composed of carbon dioxide. Because of that many new materials are being employed along with different synthetic approaches, which are discussed through this session.

Phenol is a white translucent solid with a melting temperature of 43 °C and a boiling point of 182 °C. Phenol chemistry is based on the resonance of the aromatic ring with the hydroxyl group at the ε (*epsilon*) position, which can be activated under an alkaline environment to donate electrons to the ring at *o* (*ortho*) and *p* (*para*) positions turning these regions in reactive nucleophilic centers. The resonance structure of phenol is described in Fig. 3 [16, 17]. These active sites can react with formaldehyde and yield mono, di, or tri-substituted compounds with higher functionality of hydroxyl groups (Fig. 4). The attachment of methylol functions increases the reactivity of the ring due to the electron donor effect. These activating groups increase the reactivity of the aromatic ring allowing it to react promptly as nucleophilic species [18]. The increase of functionality allows these types of structures to be used as starting materials to synthesize either branched or cross-linked polymeric foams. The hydroxy-methylphenol derivatives can react with phenols to form phenolic polymers (Fig. 4) [19].

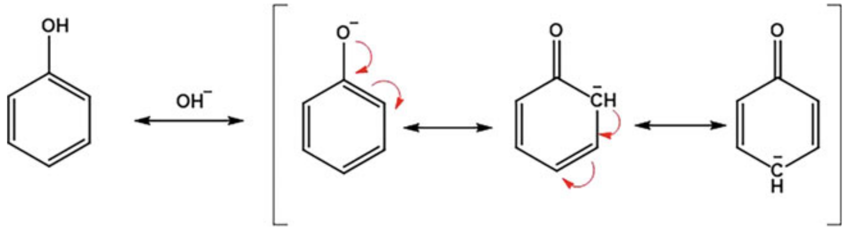

Fig. 3 Resonance structure of phenol under alkaline condition

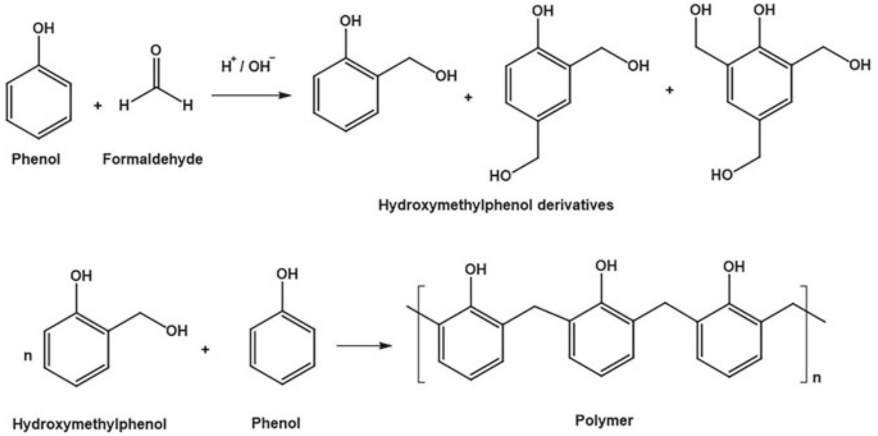

Fig. 4 Phenol and formaldehyde reactions to yield derivatives of hydroxymethylphenol and polymer

The different types of functionalization that can be performed on a phenol molecule can provide phenolic foams with a range of properties [19]. Commercially, the components of the phenolic foams are sold as an aqueous solution with stabilizers such as methanol in different ratios of formaldehyde and phenol (F/P) [20]. The F/P ratio is an important parameter that determines the type of phenolic resin. For example, novolacs resins are formed when a higher concentration of phenol and low pH is used, while resol type of phenolic resins are prepared using a higher concentration of formaldehyde catalyzed under higher pH (Fig. 5) [21]. Resol types of phenolic materials are not as stable as novolacs types due to the formation of a cross-linked structure at a higher temperature. Cross-linking is promoted by the presence of methylol groups in the structure [16, 22]. The phenol compound itself presents vast chemistry that can be employed in many ways as discussed. However, many other phenolic compounds are also used in both industry and research. The chemical structure of some common phenols is given in Fig. 6.

In general, phenolic foams are prepared by reacting phenols with isocyanates. The reactivity of phenols toward isocyanates mostly depends on the solvents and

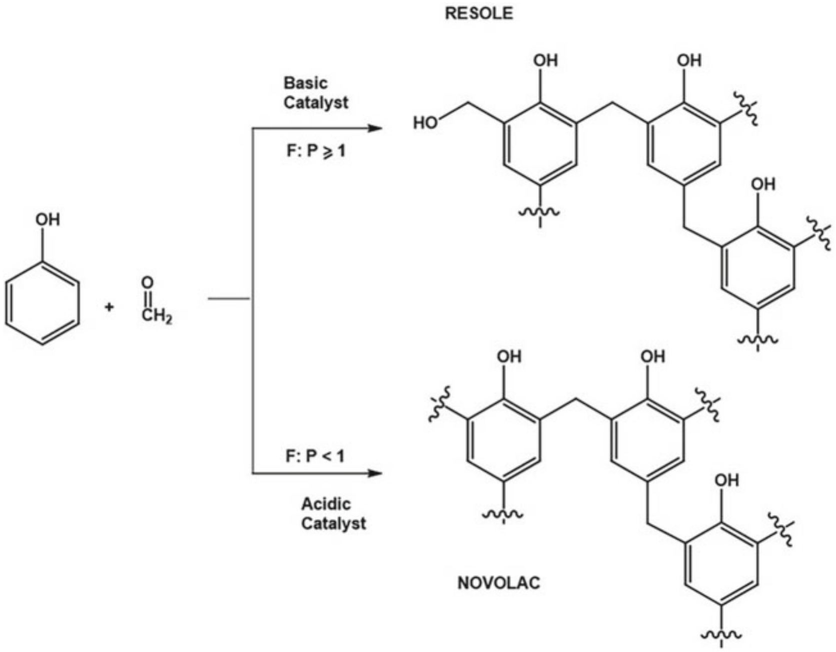

Fig. 5 Synthesis of resol and novolac phenolic resins and respective conditions. “Adapted with permission [21]. Copyright (2015) American Chemical Society.”

substituents groups on the phenolic compound. A study concluded that the use of aprotic and polar organic solvents such as cyclohexanone demonstrated the highest reaction rate followed by 1,4-dioxane, while the lowest reaction rate was observed for xylene. For the substituent groups, it was observed that electron-withdrawing groups in the phenolic compounds prompted the reaction between the hydroxyl and isocyanate. It was believed that due to the withdrawing effect of electrons on the O–H bond, the oxygen could pull the electron from the hydrogen turning it into a partial positively charged. In that condition, the electron-rich nitrogen from the isocyanate group (-NCO) is prompt to attack the hydrogen and yield the urethane linkage [23]. Besides the understanding of the proper chemical structure that yields the highest reaction rate, there are some other external factors such as reaction temperature [24], time [25], concentration and type of catalyst [25, 26], pH [26], and formaldehyde/phenol ratio [27–29], which can affect the output of the reaction. Other factors such as low reactivity and steric hindrance of phenolic compounds could also affect the properties of phenolic foams. For example, lignin, a low-cost bio-derived material with many phenolic groups, can be used to obtain phenolic foams, however, its low reactivity due to steric hindrance and poor dispersibility in most solvents prohibit its industrial applications. It has been demonstrated that low molecular weight lignin

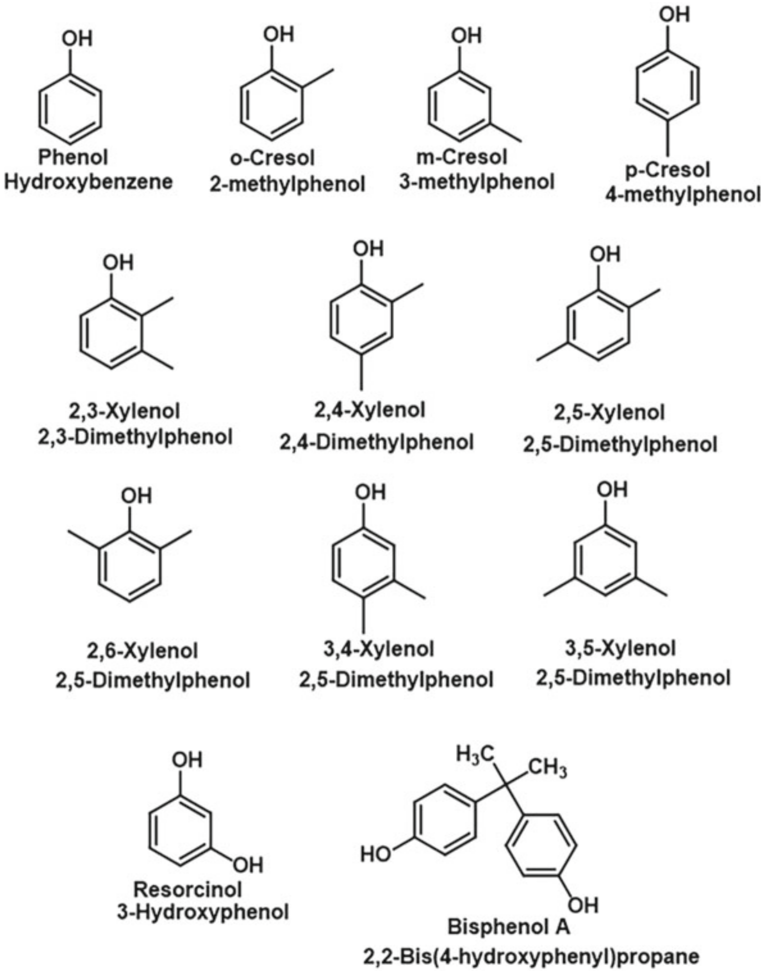

Fig. 6 Chemical structure of the most used phenolic compounds

presents more reactive sites to allow the methylol reaction, which is the main requirement to obtain phenolic foams [30, 31]. A previous report proposed the depolymerization process to obtain a lower molecular weight lignin macromolecule for phenolic foams [32]. The procedure consisted of depolymerization of the lignin catalyzed by sulfuric and solid acid (HZSM-5), followed by phenolation and hydroxymethylation. After the lower molecular weight, lignin functionalized with phenolic and methylol was obtained, it was cross-linked by using a resol resin. The schematics are described in Fig. 7 [32].

One of the main sources for the extraction of phenol is coal tar, which started at the end of the nineteenth century and is still considered as a primary source for obtaining phenol with a combination of other approaches [33–35]. Coal tar is a mixture of

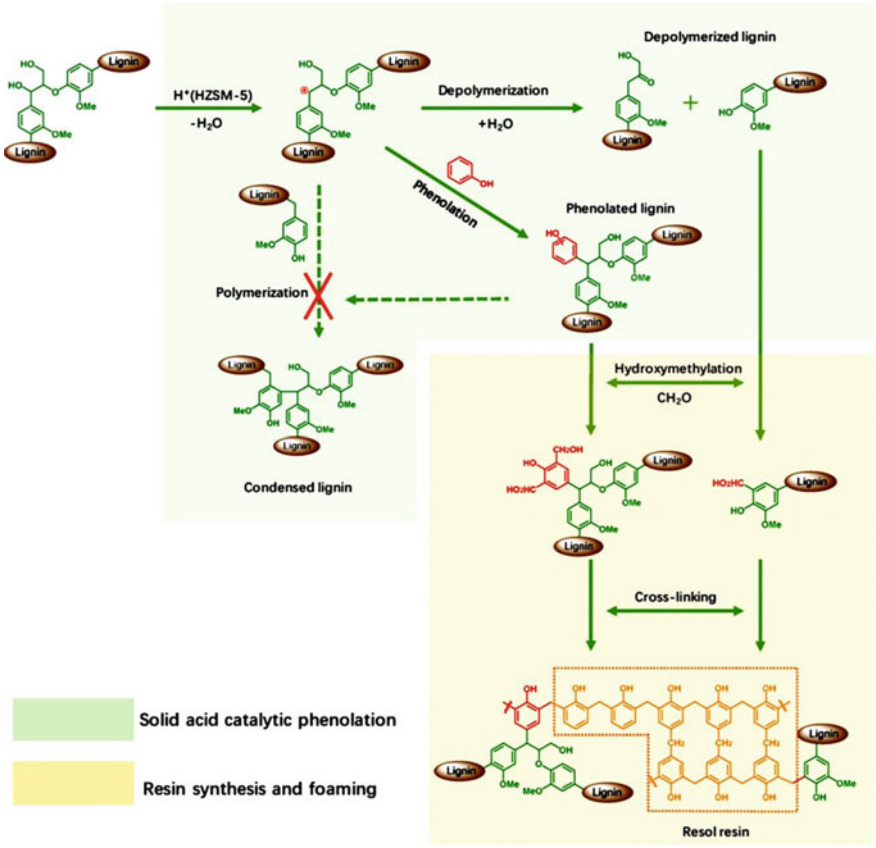

Fig. 7 Schematics for the depolymerization of lignin through acid catalysis followed by phenolation and hydroxymethylation. Concluded with cross-link reaction with Resol resin to obtain the phenolic foam. “Adapted with permission [32]. Copyright (2018) Elsevier.”

condensed organic compounds as leftovers from coal carbonization. Phenol can be separated with a sodium hydroxide treatment to precipitate it as sodium phenolate. After extraction, it can return to the phenol form through bubbling of carbon dioxide [22]. Phenols are also produced through liquid effluents from the gasification processes of gas-making plants [36, 37]. A report even demonstrated a 93% efficiency of phenol removal from wastewater by using methyl isobutyl ketone [38]. In earlier days, phenol got huge attention due to its first important applications in the synthesis of Aspirin (acetylsalicylic acid) back in 1898 and Bakelite in 1910 [2]. Following that trend, Bisphenol A was also scaling up in the productions, which demanded new approaches to synthesize these phenolic compounds for various applications [22]. The predominant synthetic route to obtain phenol nowadays is named Hock process or cumene process, which yields phenol and acetone as a byproduct [39]. This process is used to produce most of the phenol worldwide (~97%). The starting

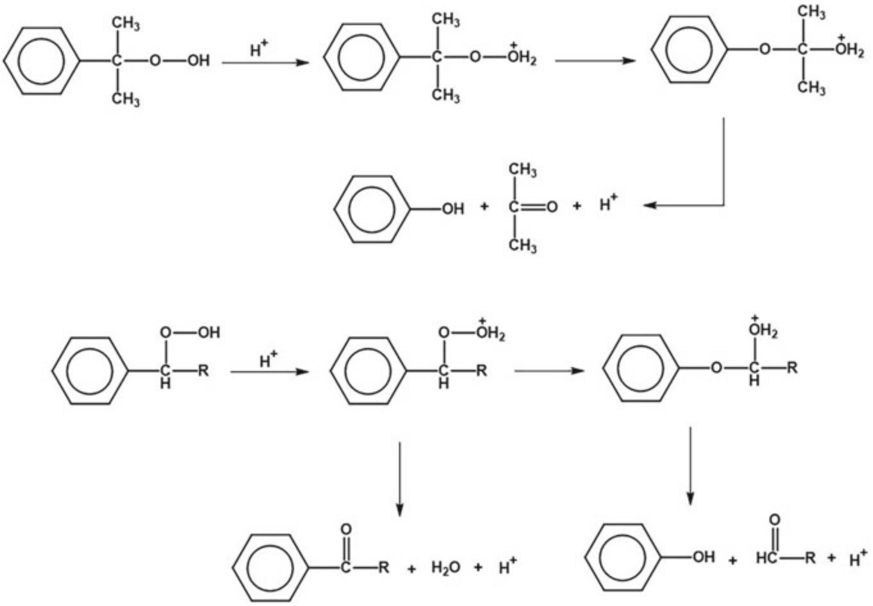

Fig. 8 Synthetic route for phenol and acetone through cumene named Hock process or acetone process [39]

material for this process is synthesized by reacting benzene and propylene, which is then oxidized in air yielding cumene hydroperoxide (CHP). A strong inorganic acid is then used as a catalyst to decompose cumene hydroperoxide into phenol and acetone. The mechanism of this process is shown in Fig. 8 [39].

Several different approaches were developed along the time. During the 1960s, Dow and California Research Corp simultaneously developed a commercial process to synthesize phenol from toluene [22]. In another approach, benzene was used as a starting material for the synthesis of phenol [22, 40]. In this process, benzene was oxidized and catalyzed by N_2O and zeolite (ZSM-5), respectively, at high temperatures (300–450 °C) to produce a large quantity of phenol [22, 40]. This process was developed by the Boreskov Institute of Catalysis and later commercialized by Solutia Industries [22, 40]. Another method uses chlorobenzene as the starting material that goes through hydrolysis to synthesis phenol. In another approach, ammonia was used to convert benzene into phenol, however, due to relatively low conversion efficiency, these methods have not been applied to the industry [40].

Although the production of phenol using petrochemical sources is a well-established process, the fluctuating price of petrochemicals and thus phenolic compounds and growing concerns for the environment encourage scientists and researchers to find alternative sources for commercial production of phenol. There are some materials from bio-sources such as lignin, oil from cashew nutshell, etc., which can be used as alternative sources for phenol compounds. Lignin, a natural phenolic compound widely found in most plants in large amounts, is mostly used for

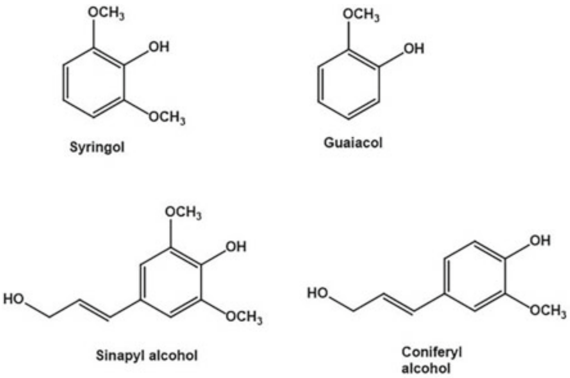

Fig. 9 Phenolic derivatives from lignin sources. “Adapted with permission [50]. Copyright (2008) Elsevier.”

the production of phenols. The main feedstocks for lignin are woods [41, 42], forest [43], agricultural [44, 45], and pulp industry residues [46–49]. The most relevant points that reinforce the use of lignin for industrial applications are the abundance and competitive price. However, the quality of some bio-renewable phenolic foams and resins still has some disparity in properties compared with the foams derived using petrochemicals along with the difficult separation process to obtain pure phenol [41]. Hence, they can be used to complement the formulation of final products to reduce cost and keep satisfactory properties [50]. As mentioned, lignin is a polymeric structure mostly considered as a macromolecule, thus to obtain phenol and oligomeric derivatives from lignin, a depolymerization process is required. The fast pyrolysis process to obtain phenol-based compounds from lignin is the mostly used method that takes place through pyrolysis of lignin between 400 and 600 °C at a fast heating rate along with quick condensation of the liquids that are formed. This process yields around 75 wt.% of phenolic compounds that can be used for the synthesis of phenolic foams and resins [51, 52]. The extraction of phenol through lignin also generates other substances such as syringol, guaiacol, sinapyl, and coniferyl alcohol as shown in Fig. 9 [50]. Their chemistry is highly related to their substituent groups in a way that oxygen atoms adjacent to the hydroxyl groups may increase the polarization by increasing the reactivity [53].

Since the use of phenol as a starting monomer for phenolic-formaldehyde resins and plastics, it has made a huge impact in the industries. In addition to its applications in phenolic-formaldehyde resins and plastics industries, it got quick attention to polyurethane industries. Phenol-based polyols for polyurethane industries provide many possible variations yielding end products with superior mechanical and flame retardant properties. The popularity of phenol-based compounds as polyols for polyurethanes is due to the high reactivity of phenolic -OH groups toward isocyanate. Other materials such as catalysts, surfactants, and blowing agents are also very important for the foaming industries [54]. The phase separation between the less dense and polar polyols and the denser and non-polar isocyanate is believed to slow down the reaction rate, therefore, it becomes necessary to implement catalysts and surfactants [54, 55]. The most used catalysts are usually tertiary amines such as

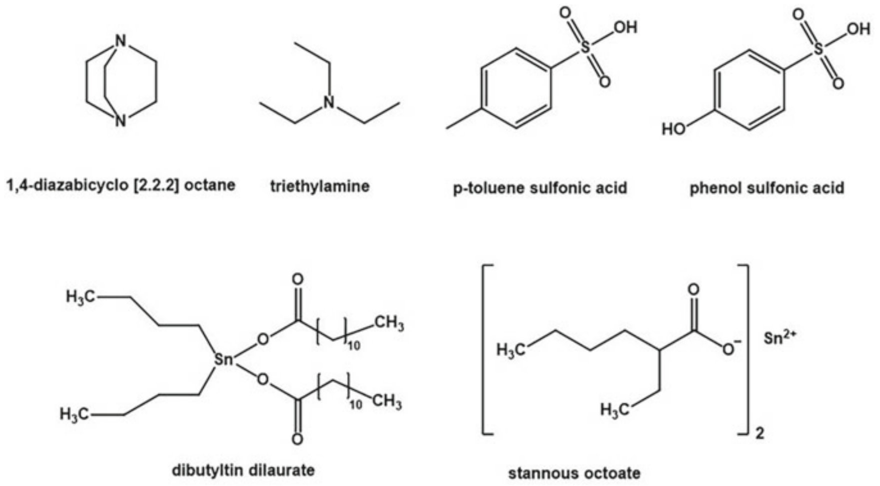

Fig. 10 Chemical structure of some common catalysts for phenolic foams

1,4-diazabicyclo[2.2.2] octane (DABCO) and triethylamine (TEA) [56]. Another type of catalyst often used is organometallic compounds such as dibutyltindilaurate (DBTDL) and stannous octoate. Organic acids like p-toluene sulfonic acid and phenol sulfonic acid are used along with inorganic acids in the phenolic foams. The chemical structure of some common catalysts is shown in Fig. 10. The role of these catalysts is to polarize the bonds from both isocyanate and phenol/polyols creating an intermediate that rearranges to form the urethane linkage [57–59]. The catalyst enhances their reactivity allowing the reaction to occur faster and at room temperature. Their mechanism is described in Fig. 11 [57, 60–62].

The polarization effect of tin-based catalysts is more pronounced in aromatic isocyanates such as diphenylmethanediisocyanate (MDI) or toluene diisocyanate (TDI) compared with aliphatic ones such as hexamethylenediisocyanate (HDI) or isophoronediisocyanate (IPDI). However, for the zirconium-based catalyst, the observed reactivity was the same regardless of the type of isocyanate used [55]. A novel type of catalyst that has been employed in the formulation of polyurethanes is the $CuCo_2O_4$/graphitic carbon nitride, which diminishes the production of CO and imparts flame-retardant properties, which can add a synergy effect for phenolic foams that inherently present this property [63].

Other important components for foam formulation are the surfactants that are responsible for improving the superficial area between the reactants allowing them to mix properly, working in pairs with the catalyst. Along with that they also grant stable formation of the foam by controlling the pore size to obtain a regular cellular morphology. This factor highly influences the mechanical properties of the foams and their interactions with fillers [55]. Surfactants are mostly silicon-based compounds such as silicone oils, nonylphenolethoxylates, polydimethylsiloxane-polyoxyalkylene along with some organic compounds. The non-ionic surfactants are

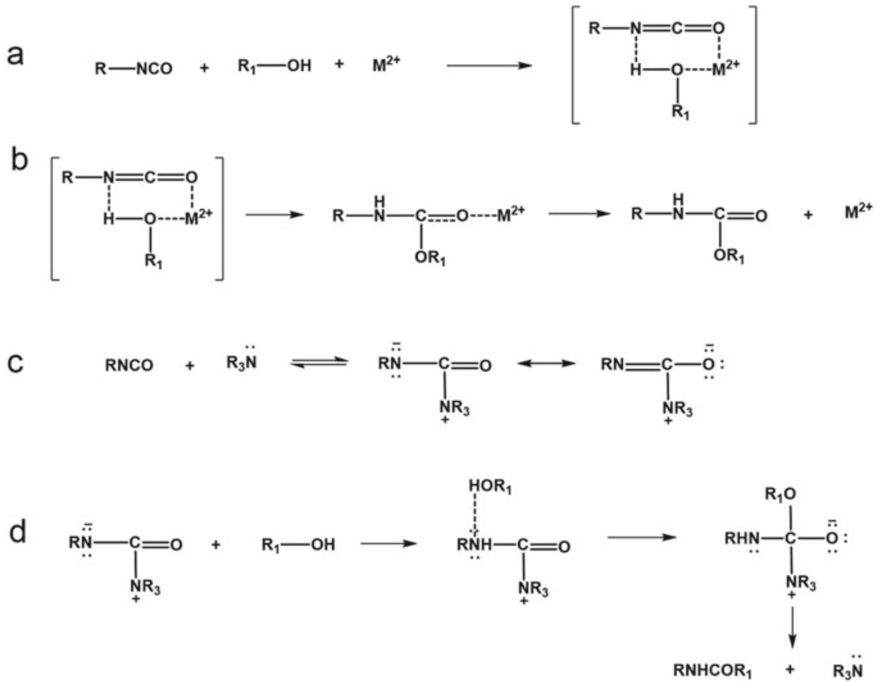

Fig. 11 Mechanism of bond polarization through the use of **a** and **b** organo-metallic and **c** and **d** tertiary amine catalysts. "Adapted with permission [60]. Copyright (2007) Elsevier"

known to improve the superficial area and are easier to include in the formulation due to their fixed value of critical micelle concentration [64]. In general, a low concentration (0.5–5 wt%) of surfactants is required in phenolic foams. An appropriate amount of surfactants is required to maintain the cellular structure of the foams. Low concentration may destabilize the structure while a higher concentration of the surfactants may increase the chance of collapsing the cellular structure along with an increase in the cost of production. A study developed an approach that does not require the use of surfactant because in some cases, they present low molecular weight, an increase in delamination, and corrosion can be observed [65, 66].

Blowing agents like surfactants also play an important role in controlling the morphology and cell structure of the foam. They can react with the isocyanate forming a urea function and liberating carbon dioxide that gets entrapped within the structure of the cell while increasing the overall volume of the foam. Carbon dioxide acts as in-situ blowing agents, especially for resol-based phenolic foams. Before the international regulations, many types of chlorofluorocarbons (CFCs) were used as blowing agents; however, the depletion of the ozone layer due to their exaggerated use forced the international regulation to restrict their distribution. After that, H_2O appeared as a suitable and environmentally friendly chemical blowing agent for

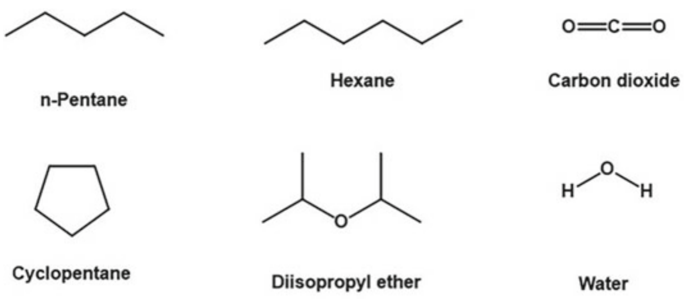

Fig. 12 Common blowing agents used in phenolic foams

the foaming process. Hydrocarbon-based blowing agents such as cyclopentane, *n*-pentane, *iso*-pentane, *iso*-butane, hexane, etc. can also be employed in phenolic foams due to their low boiling points [67]. Figure 12 shows the structure of some common blowing agents used in phenolic foams. The structure of a phenolic foam largely depends on the type of blowing agent used during the foaming process. For example, highly volatile blowing agents will produce open-celled foams. Curing agents are also used during the curing process of the foam to provide cross-linking in the structure. Organic acids such as toluene sulfonic acid, benzene sulfonic acid, xylene sulfonic acid, phenol sulfonic acid, and inorganic acids such as hydrochloric acid, sulfuric acid, phosphoric acid are commonly used as a curing agent in phenolic foams.

Other components such as plasticizers can be also added into a polyurethane formulation that reduces the hardness of the materials. The decrease of brittleness in foam can be acquired by implementing a bulky and flexible group in the chain in one of the reagents, usually the polyol or through the physical blend. The large and flexible group may allow the polymeric chains to decrease the brittleness of the polymer [68, 69], along with pigments for implementing color and aesthetics [70], fillers to reduce cost and improve the desired properties [71], flame retardants, and smoke suppressants [72, 73]. As discussed earlier, phenols are aromatic rings with a hydroxyl group that presents versatile chemistry. Mannich's reaction is one of the most studied procedures in phenol chemistry. In basic terms, it consists of a phenol dissolved in a solution of formaldehyde and water along with the addition of an amine-based compound such as diethanolamine that chemically attaches to the aromatic ring through the formation of a methylene bridge. The scientific community still exploits the parameters that influence this reaction such as the amount of formaldehyde/amine ratio, pH, temperature, and kinetics [74–76]. Cardanol oil has been reported in many studies as a renewable and viable option for epoxy and phenol–formaldehyde resins as well as phenolic polyurethanes [77]. Cardanol is obtained from cashew nut shell liquid and the main constituents of cashew nut shell liquid are cardanol, cardol, and 2-methylcardol as shown in Fig. 13 [78]. Cardanol is composed of several aromatic oils that present a phenol group with variations of aliphatic chains in the *m* position with degrees of unsaturation [79].

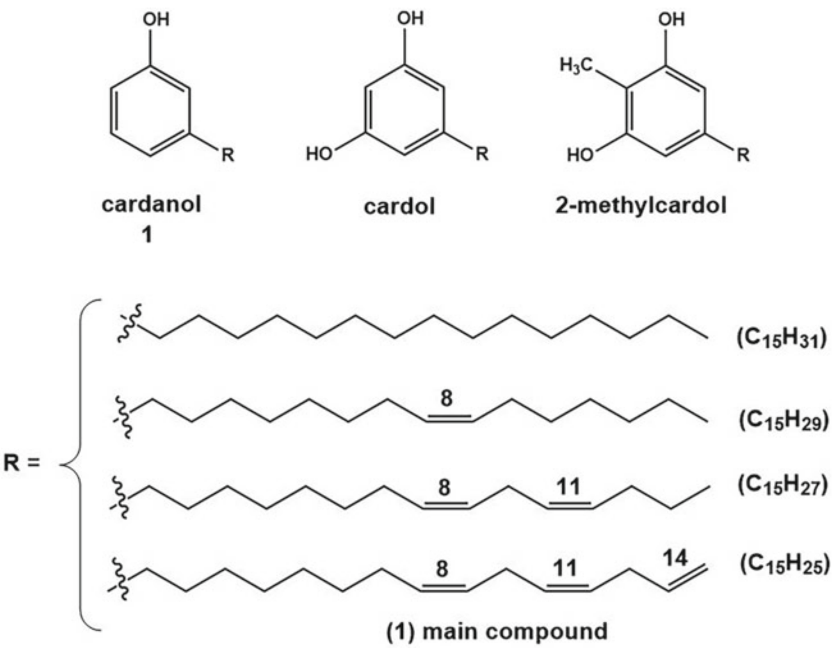

Fig. 13 The main component of cashew nutshell liquid [78]

Mannich's reaction was performed to convert cardanol oil into a polyol for making polymeric foams. The procedure consisted of three synthetic steps. First, the reaction between para-formaldehyde and diethanolamine was carried out to synthesize *N*-(2-hydroxyethyl)-1,3-oxazolidine, also mentioned as intermediate of Mannich's reaction. The second step was the reaction of this intermediate compound with the aromatic ring in the cardanol oil, performing an electrophilic substitution at *ortho* and *para* positions. In the third step, the cardanol-based polyol was further functionalized with propylene oxide to increase the functionality of the polyol from 3 to 5. The synthetic route is described in Fig. 14 [79]. This approach presents some advantages such as increase the functionality of the polyol without an excessive increase of viscosity. This is due to the formation of the intermediate, *N*-(2-hydroxyethyl)-1,3-oxazolidine, that prevents the condensation reaction between formaldehyde and phenol, while still acting as a Mannich base due to the presence of an iminium cation and alternating state between cyclic and open structure, hence, facilitating the processing to obtain the foams (Fig. 15) [75, 77, 79]. The foams obtained through this method provide biodegradability, flame retardancy, and satisfactory mechanical properties compared with petrochemical-based foams.

Another interesting approach utilized cardanol oil modified with a phosphorus-based compound, named 10-(2,5-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), to improve the inherent flame-retardant properties of the phenolic foams [80]. Also, a silicon-based segment originated

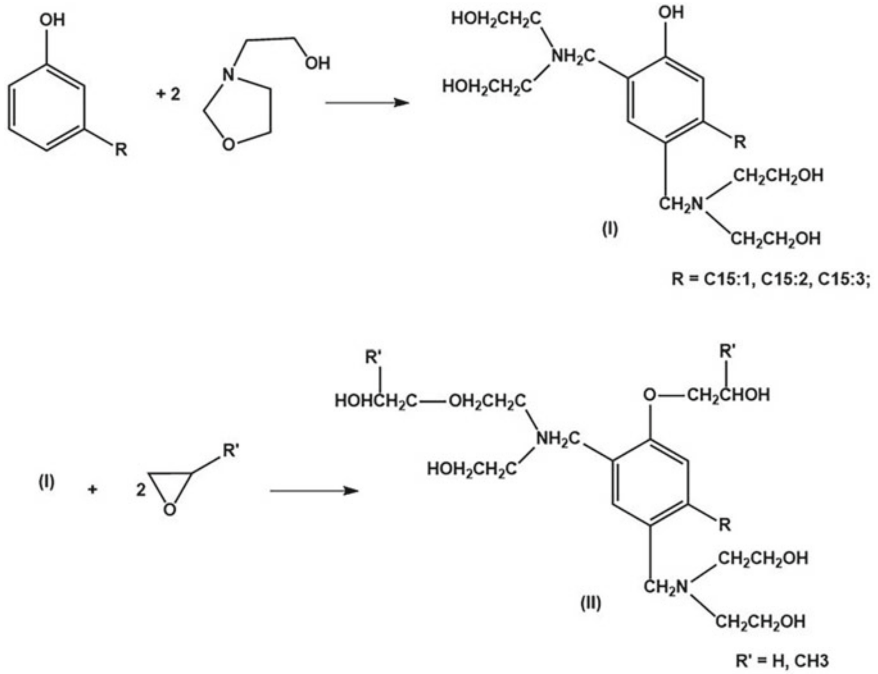

Fig. 14 Synthetic route for cardanol-based polyol. "Adapted with permission [79]. Copyright (2012) Springer"

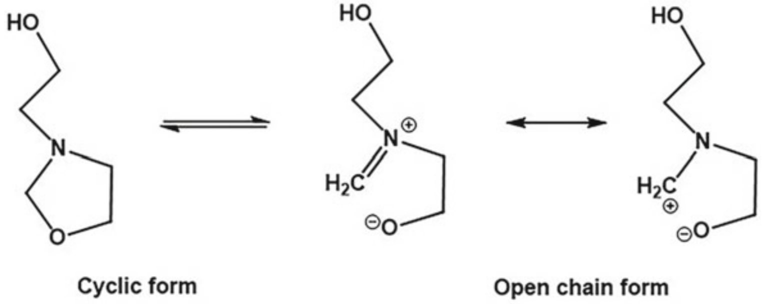

Fig. 15 Alternating structures of *N*-(2-hydroxyethyl)-1,3-oxazolidine for open and cyclic form. "Adapted with permission [79]. Copyright (2012) Springer."

from polydimethylsiloxane was attached to improve the mechanical properties by reducing the brittleness that usually accompanies the phenolic foams. A relevant factor that cardanol-based foams impart is the plasticizer effect on mechanical properties that reduces brittleness. This phenomenon occurs due to the presence of the 15 carbon aliphatic unsaturated chain attached to the aromatic ring. It allows the polymeric chains to slip pass each other while increasing the free volume of the foams [81]. The procedure to obtain the cardanol polyol functionalized with DOPO consisted of an epoxidation of the unsaturation of the aliphatic chain of cardanol oil followed by ring-opening with DOPO. Along with that, the phenolic hydroxyl reacted with epichlorohydrin followed by hydrolysis, hence, making the polyol inherent flame-retardant [82]. As previously discussed, the viscosity is an important parameter that has to be controlled to allow a proper mixing between the components of the foams. In this case, the isocyanate, hexamethylenediisocyanate (HDI) was added in excess to react with polyethylene glycol. This approach increased the linearity and flexibility of the chains, which is reflected as ease processing and more flexibility for the phenolic foam, by reducing the natural brittleness and pulverization.

The general trend for research nowadays is leaning toward a greener and environmentally friendly approach. In that line, many researchers are finding a middle ground by partially replacing petrochemical compounds with environmentally friendly fillers into industrial phenolic foams to improve their property. As an example, a facile procedure to improve the mechanical properties of phenolic resol resin by blending it with around 2 wt.% of cellulose fibers was reported [83]. It demonstrated an effective increase in the modulus and compressive strength of the foam even surpassing other well-known mechanical reinforce composites of aramids and glass fibers [13, 84]. The previous procedure is often described as physical toughening, which is the blending of the filler with the foaming components without chemical reaction as a means to enhance the mechanical properties. Compounds such as fibers and rubbers can be employed for this end [84–86]. It has some advantages such as ease processing, facile procedures, and usually lower cost. However, the distribution of the filler is usually not regular throughout the foam, which may cause inner defects. Besides, the effects of the toughening may decrease over time since the filler tends to migrate, which creates irregularities that may deteriorate other properties. A different approach that can be used to counter this situation is the chemical toughening. In this case, the toughening agent is chemically bonded to the structure of the foam. It brings the positive points of longer term efficiency and proper dispersion through the foam, avoiding irregularities [87]. A novel phosphorus-based phenolic polyol was synthesized by using phenyl dichlorophosphate (PDCP) as the toughening agent. The PDCP reacted with trimethylamine at 0 °C to form a good leaving group for the further reaction with polyethylene glycol to obtain the polyol that was mixed with industrial phenol resin. The synthesis can be described in Fig. 16 [88].

A concern that usually comes with both physical and chemical fillers is the deterioration of other properties that were not targeted. For example, some toughening agents may cause an increase in the flammability of the foam. As a way to avoid this scenario, this approach yielded a polyol that increased both mechanical as well as the flame retardant properties of the foam [88]. A follow-up procedure implemented silicon at the polymeric chain of the polyol, as a means to improve compressive strength, friability, and thermal stability [89]. Following the same trend, another seldom approach includes the use of boron as a toughening and flame retardant agent.

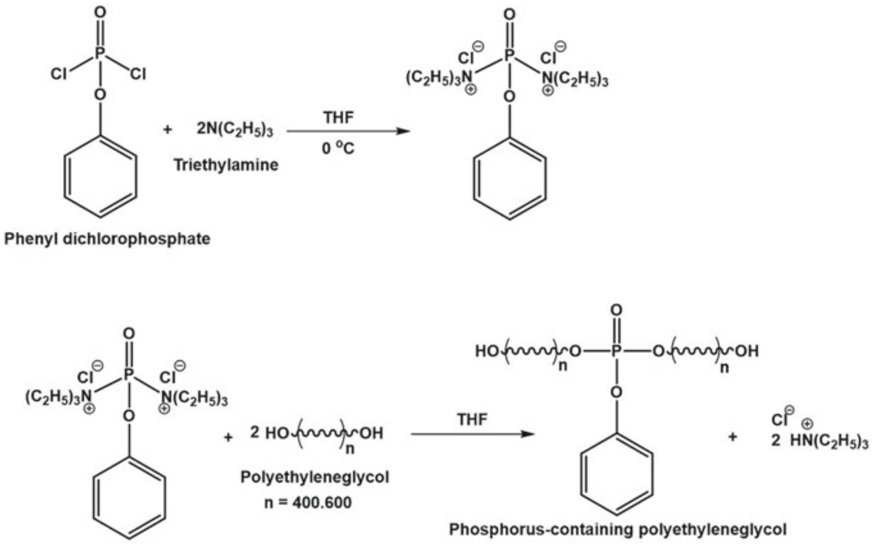

Fig. 16 Synthesis of phosphorus-based polyol for the enhancement of mechanical and flame retardant properties. "Adapted with permission [88]. Copyright (2012) Springer"

A report described a procedure that used boric acid (BA) to react with polyethylene glycol (PEG) at 110–150 °C dissolved in xylene to form a branched polyol (PEG-BA). This material was then cured with a phenolic resin to obtain an inherent flame-retardant and toughened foam after the reaction with isocyanate. The reaction is described in Fig. 17 [87]. Finally, it is notable that the synthesis of phenolic foams allows many possibilities, including the source of starting materials that can be petrochemicals, mostly resol and novolacs resins, or renewable, mostly cardanol oil and lignin. The factors like low cost, abundance, inherent flame-retardant properties, and ease modification of synthetic procedures prompt its use as a viable polymeric material for large-scale applications.

1,3-dihydroxybenzene know as resorcinol is a derivative of phenol that has a huge commercial application in phenolic foams. Its condensate form with formaldehyde is used to improve the adhesion on rubber and tires and allows curing at room temperature [90]. The main synthetic route to obtain resorcinol consists of the sulfonation process of benzene with sulfur trioxide at 150 °C in the presence of sulfuric acid as a catalyst [90]. The obtained product is *epsilon* and *meta* substituted aromatic ring with sulfonate groups more precisely, benzene-1,3-disulfonate. This compound is then placed to react with sodium hydroxide at 350 °C. The product obtained at the end of this reaction is extracted for the organic phase with diisopropylether. Finally, it is distilled to obtain the purified resorcinol. The points that limit the use of resorcinol are related to the cost of production and safety concerns. Despite that, previous studies have obtained a copolymer based on lignin–resorcinol–glyoxal. The synthesis

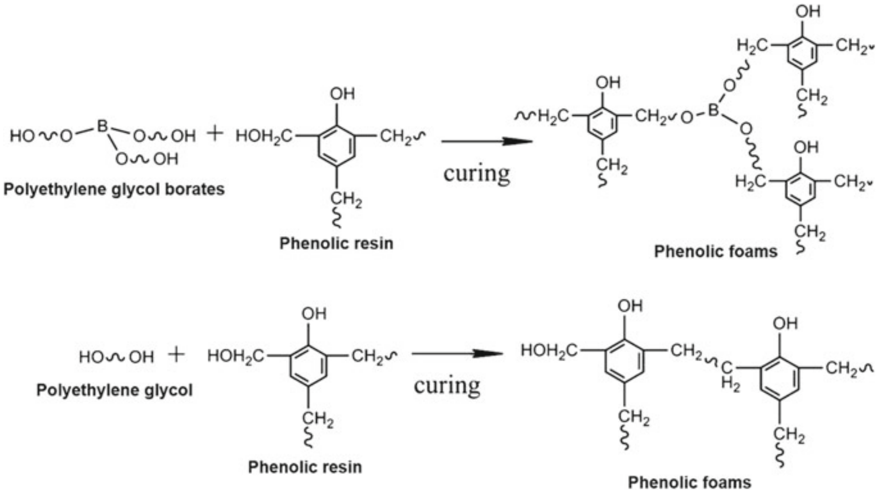

Fig. 17 Synthesis of a boron-based branched polyol with further curing process with phenolic resin. “Adapted with permission [87]. Copyright (2015) American Chemical Society”

was performed under mild alkali media with stirring of the three monomers (Fig. 18) [91].

As previously described, the Mannich’s reaction is an extremely valuable tool when it comes to the synthesis of phenolic resins. The chemical attachment of amino alcohol through the methylene bridge, usually in the *ortho* position of the phenol, increases the functionality of the polyol making it suitable for foaming reactions [77]. A general procedure of this reaction can be performed with the mixture of the phenol and the amine-functionalized reagent such as alcohol. Then a formaldehyde or paraformaldehyde solution can be added with a concentration of around 25–37%. The temperature should be maintained around 50–70 °C and digesting for around 2 h. After the completion of the reaction, both water as a byproduct of the reaction as well as formaldehyde is removed through vacuum distillation around 90–120 °C. It is important to mention that the lower temperature range reduces the tendency of condensation to form oligomers. This condensate is nothing but an oligomer of two or three phenolic groups; however, it causes an increase in the viscosity, which may harden the processing. Previous studies on this reaction established that it occurs in a two-step process, in which an ammonium cation is formed between the formaldehyde and the amine reaction (primary or secondary). The ammonium cation then reacts with the phenolate anions at *ortho* and/or *para* positions following a mechanism based on SN_1 [92, 93]. Another type of mechanism that follows the SN_2 is also possible. In this scenario, there is a coupling of formaldehyde with two molecules of the alkylamine compound, leading to a neutral molecule. Then, the phenolate anion attacks the methylene group, which is under an electron-withdrawing effect of the two amine groups. SN_1 is prompt to happen when the reaction mixture is under acidic media, hence forming amine salts. Oppositely, SN_2 can occur under basic or neutral media.

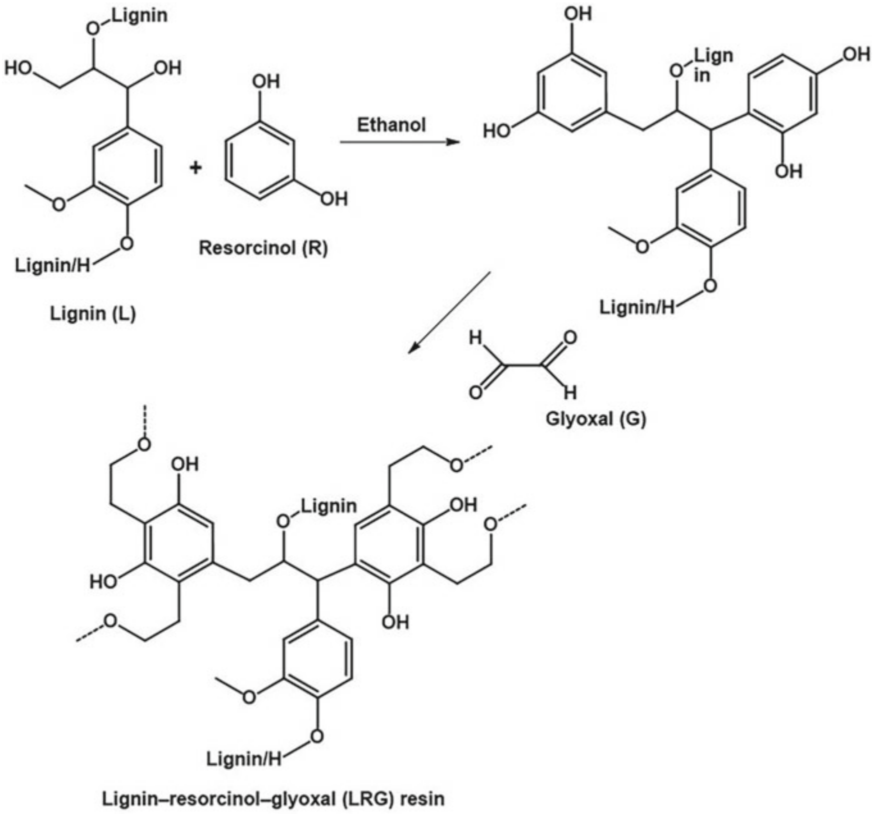

Fig. 18 Facile synthesis for lignin–resorcinol–glyoxal copolymer resin for further implementation in the polymeric matrix. "Adapted with permission [91]. Copyright (2020) Elsevier"

The functionalization of phenol through Mannich's reaction is a valid strategy because it allows the introduction of primary hydroxyl groups as the R groups, which are known to be more reactive toward isocyanate. This not only improves the reaction rate for the formation of the foam but also increases the functionality of the starting material. Hence, a variety of different structures can be obtained. On top of that, the addition of a tertiary amine to the structure acts as a self-catalyst by increasing the foaming process [77, 94]. As an example of this approach, a previous study reported the synthesis of a novel Mannich polyol in three steps. In the first step, a Friedel–Crafts alkylation was performed between phenol and limonene (Fig. 19). Oxazolidines were synthesized by the reaction of formaldehyde and alkanolamines in the second step of this process (Fig. 20). The third and final step consisted of the synthesis of Mannich polyol through the reaction with propylene oxide to increase the functionality of the Mannich polyol [94]. The obtained polyols were suitable to make rigid foams with satisfying mechanical, thermal, and physical properties.

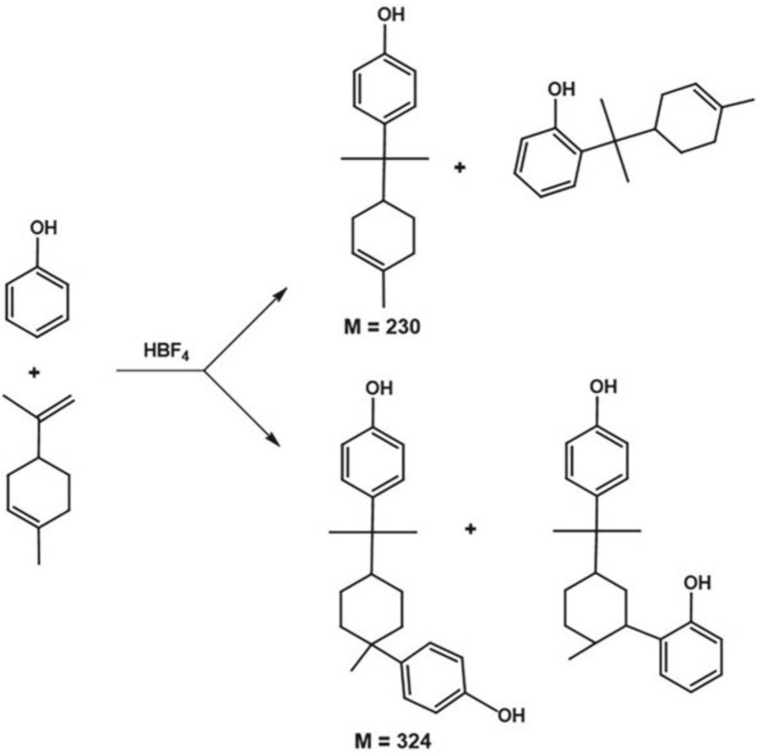

Fig. 19 Friedel–Crafts reaction between phenol and limonene. "Adapted with permission [94]. Copyright (2015) Springer"

Finally, it is notable that the synthesis of phenolic foams allows many possibilities, including the source of starting materials that can be petrochemicals, mostly resol and novolacs resins, or renewable, mostly cardanol oil and lignin. The factors like low cost, abundance, inherent flame-retardant properties, and ease modification of synthetic procedures prompt their use as viable polymeric materials for large-scale applications.

3 Chemistry-Based Applications of Phenolic Foams

The properties of phenolic foams such as inherent flame retardancy, rigidity, low thermal conductivity, high thermal stability, and low emission of toxic smoke allow their use as thermal insulators and fire protection materials for buildings and constructions. On top of that, it can also be applied as adhesives, sealants, coatings, elastomers, binders, and foams [23, 95]. The property–structure relation is crucial to understand how these materials fit for certain applications along with the versatility of phenolic

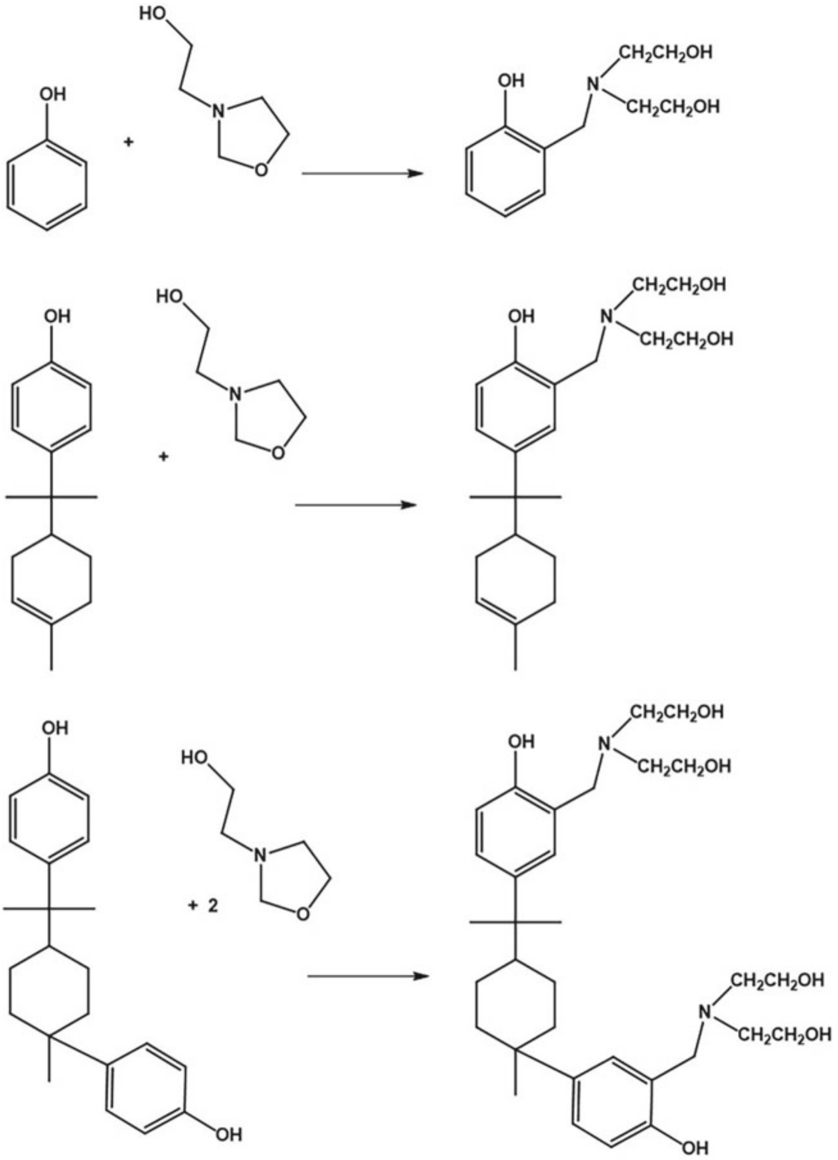

Fig. 20 Variations of Mannich bases. "Adapted with permission [94]. Copyright (2015) Springer"

foam's chemistry that broadens the range of experiments that can be designed. Thus, the following session discusses the main parameters to obtain the desired properties based on the chemical structure of the starting materials, more specifically into how the functionalization of phenolic groups influences their properties.

The functionalization of the phenolic polyol highly influences the properties of the foams. Accompanied to that, most of the phenolic starting materials are functionalized resins such as resoles and novolacs as previously discussed. Thus, it is important to understand what are the parameters that influence their properties, when it comes to design a procedure. One of the starting points is the formaldehyde/phenol ratio (F/P). A study found that under excess of formaldehyde catalyzed by alkaline media, less base was required to carry out the reaction [26]. It was also observed that for an F/P ratio of around 2.5, the polymerization happened to a lower degree [26]. For this scenario, the extra amount of formaldehyde was volatilized, which increased the porosity and shrinkage of the phenolic foam. Hence, it may hurt the mechanical properties and increase friability. Therefore, the proper control of F/P plays an important role in the properties of the phenolic foams [96]. Accompanied to that study, it was found that catalysts also might prompt a type of chemical structure. The influence of triethanolamine as a catalyst in the reaction between formaldehyde and phenol to obtain phenolic resins was studied [26]. It was observed that besides the obvious influence at the rate of reaction and condensation time, the catalyst had a slight influence in the structure. The higher population of transition state intermediates seemed to be prompted the aromatic ring substitution to occur more at *ortho* position rather than *para*. This difference in structure may impart changes on the mechanical properties, since *ortho-ortho* substitution may increase the size of dandling groups if compared with *ortho-para* substitution due to lesser bulky groups hanging on the polymeric structure [77].

The chemistry of phenolic materials is highly related to its reactive sites. In an ideal condition, a phenol compound may present functionality of three, those being the phenolic hydroxyl, *ortho* and *para* positions for nucleophilic substitution. This condition allows cross-linking to take place. This is often desired to enhance the mechanical and thermal properties of materials, which can turn them into thermosets if the crosslinking degree is high enough. The rigidity and thermal stability of phenolic foams are in part due to their inherent cross-linking capability. Previous studies have demonstrated that in a real scenario, the functionality of a phenol would be around 2.38–2.7 [27, 97, 98]. Thus, from an experimental perspective, an increase of the F/P ratio of at least 1.3 is required to prompt the cross-linking reaction. A previous study reported that cross-linking reactions occur mostly at *para-para* positions [27].

Even though the cross-link of phenolic foams is one of their signature features for a rigid structure with high compressive strength, it is also what makes it brittle and friable. To solve that issue, the synthesis of composites of phenolic foams is a viable option to obtain materials that can absorb mechanical stress without breaking. For that, multi-walled carbon nanotubes have been employed. Their large structure and many reactive sites lead to covalent bonds that diminish the stress during compression [99]. Also, the high friability is an undesirable property that comes with phenolic foams. One approach that can prevent this phenomenon is the addition of aramid compounds [99]. Another recent approach involves self-healing foams, smart devices, and recyclable composites, which are based on the concept of covalent adaptable networks or also named dynamic cross-linked chains. Polymer can be synthesized to present the reversibility of bonds. This feature shifts the properties of the material making it able to be reprocessed and acquire self-healing properties, which are not possible for highly cross-linked materials with permanent covalent bonds [100]. The reversible break and formation of these bonds can happen through Diels–Alder [101–104], transesterification [105–107], phenol-urethanes [108, 109], and in many otherways [108, 110–113]. To design an experiment with these properties, some well-known monomers are employed, such as bisphenols. They consist of two phenolic rings linked by a chemical group between them such as isopropylene, hexafluoroisopropylene, and sulfone. From the first to latter, higher is the electron-withdrawing effect. The higher this effect, the easier to disrupt and change the chemical bonds of the structure, also lower the temperature for that phenomenon to take place [114].

Another possible option that has been highlighted around the scientific community is the chemical functionalization with the attachment of a flexible segment into the structure of the phenolic resin. The reactivity of the phenolic ring allows many chemical modifications, which are greatly responsible for imparting the desired properties into the phenolic foams. The presence of an aliphatic chain could decrease the rigidity of the molecular structure. Hence, allowing the final polymer to become tougher instead of brittle. Fortunately, cardanol oil, as previously demonstrated, is a starting material that already presents an unsaturated alkyl chain at the *meta* position [115]. This feature promotes two aspects of the material. First, it decreases the brittleness improving the mechanical properties. Second, it provides an extra reactive site, which is the double bonds at the aliphatic chain, allowing further chemical modifications [115]. The low rigidity is an important factor for applications that require mechanical energy absorption. Another important feature of chemical functionalization is the increase of reactivity that fastens both the foaming and curing process. It highly affects the application of the phenolic polyurethanes since it adds a profitable aspect for large-scale applications such as thermal insulation for buildings and constructions. As previously discussed, the Mannich's reaction in phenolic compounds implements a methylene bridge along with a secondary or tertiary alkyl amine segment. The presence of these amine groups creates a self-catalyzed process for the resins, hence, notably increases the foaming reaction between hydroxyl and isocyanates groups [94]. This quick reaction allows it to be used in a "spray" foaming process. However, along with a fast reaction rate, proper control of viscosity is also important. Because, in one hand, low viscosity allows easy flow and a mixture of components, hence, a more homogenous structure of foaming. On the other hand, higher viscosity provides better control of cellular structure and may avoid coalescence during the foaming process [22, 116, 117].

External components that do not directly participate in the foaming reaction also have a strong impact on the properties of foams. The formulation of the components to manufacture foam is one of the key factors that allow the same material to acquire different properties. For the case of phenolic foams, the implementation of blowing agents and/or volatile solvents can influence the size of the pores, which bears great importance for applications such as decontamination of radioisotopes and water contaminated with heavy metals [118, 119]. The blowing agents also have a direct effect on the density of the foam, which enables them to obtain materials that are light as well as rigid [3]. The final cell structure is also relevant for the range of applications of the foam. For example, open cells are used for the soundproof environment while closed ones tend to have higher thermal insulation and better flame retardancy [120]. Finally, this session presented the main factors that influence the properties of phenolic foams regarding their chemical structure and the possible approaches to tune the features of the final material according to the experimental goal.

4 Conclusion and Future Lookout

Throughout this chapter, the importance of phenolic foams and derivate materials in terms of their chemistry and properties were discussed. Phenolic foams are known for their high compressive strength, thermal stability, and flame retardancy properties accompanied by low emission of toxic smoke. The starting materials for phenolic resins can be obtained from petrochemical sources such as phenol, bisphenols, *m*-cresols, and other variations. However, renewable sources such as cardanol, castor oil, and lignin that are promising materials with satisfactory products and tunable properties. Their greatest concern goes around their brittleness and friability, which demanded efforts from the scientific community to develop new synthetic approaches and alternative materials to nullify these drawbacks. Some of these techniques include chemical modification with flexible segments, blending with other materials to create composites, and changes in formulation for proper control of properties. This is all possible due to the chemical versatility of phenolic compounds. Still, there are many undiscovered possibilities for phenolic materials, since the chemistry of phenolic ring allows many possibilities. However, phenolic foams are already responsible for a good part of the market related to thermal insulation for household applications due to their easy source and high reactivity. As research progresses new applications for phenolic foams were found, for example, the capture of radioisotopes and removal of heavy metals from water, which will bear great importance for future scenarios.

References

1. Khemani KC (1997) Polymeric foams: an overview. ACS Symp Ser 669:1–7
2. Baekeland LH (1909) Original papers: the synthesis, constitution, and uses of bakelite. Ind Eng Chem 1:149–161
3. Mougel C, Garnier T, Cassagnau P, Sintes-Zydowicz N (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer (Guildf) 164:86–117
4. Kumar R, Sharma A, Pandey A, Chaudhary A, Dwivedi N, Shafeeq MM, Mondal DP, Srivastava AK (2020) Lightweight carbon-red mud hybrid foam toward fire-resistant and efficient shield against electromagnetic interference. Sci Rep 10:1–12

5. Li X, Wang Z, Wu L, Tsai T (2016) One-step: In situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6:74903–74912
6. Paruzel A, Michałowski S, Hodan J, Horák P, Prociak A, Beneš H (2017) Rigid polyurethane foam fabrication using medium chain glycerides of coconut oil and plastics from end-of-life vehicles. ACS Sustain Chem Eng 5:6237–6246
7. Zhao W, Gao H, Fan M (2015) Synthesis of novel monolithic activated carbons from phenol-urea-formaldehyde resin. RSC Adv 5:104936–104942
8. Li B, Feng SH, Niasar HS, Zhang YS, Yuan ZS, Schmidt J, Xu C (2016) Preparation and characterization of bark-derived phenol formaldehyde foams. RSC Adv 6:40975–40981
9. Yang H, Yu B, Xu X, Bourbigot S, Wang H, Song P (2020) Lignin-derived bio-based flame retardants toward high-performance sustainable polymeric materials. Green Chem 22:2129–2161
10. Suresh KI (2013) Rigid polyurethane foams from cardanol: synthesis, structural characterization, and evaluation of polyol and foam properties. ACS Sustain Chem Eng 1:232–242
11. Mouritz AP, Mathys Z (1999) Post-fire mechanical properties of marine polymer composites. Compos Struct 47:643–653
12. Kim D-K, Lee S-B (2006) Properties and thermal characteristics of phenol foam for heat insulating materials. Appl Chem Eng 17:357–360
13. Desai A, Nutt SR, Alonso MV (2008) Modeling of fiber-reinforced phenolic foam. J Cell Plast 44:391–413
14. Kim M, Choe J, Lee DG (2016) Development of the fire-retardant sandwich structure using an aramid/glass hybrid composite and a phenolic foam-filled honeycomb. Compos Struct 158:227–234
15. Madhava Sarma K, Bankobeza GM (2000) Montreal protocol on substances that deplete the ozone layer. Nairobi Kenya
16. Hu X-M, Zhao Y-Y, Cheng W-M (2015) Effect of formaldehyde/phenol ratio (F/P) on the properties of phenolic resins and foams synthesized at room temperature. Polym Compos 36:1531–1540
17. Pizzi A, Mittal KL (2003) Handbook of adhesive technology, revised and expanded. CRC Press
18. Haupt RA, Sellers TJ (1994) Characterizations of phenol-formaldehyde resol resins. Ind Eng Chem Res 33:693–697
19. Fontanille M, Gnanou Y (2014) Chimie et physico-chimie des polymères. DUNOD
20. Chevalier M (2006) Phénoplastes ou phénols-formols PF. Tech l'ingénieur, Fasc A3435 A 3436
21. Bessire BK, Lahankar SA, Minton TK (2015) Pyrolysis of phenolic impregnated carbon ablator (PICA). ACS Appl Mater Interfaces 7:1383–1395
22. Pilato L (2010) Phenolic resins: a century of progress. Springer
23. Yang P, Han Y, Li T (2010) Effect of substituents and solvents on phenol-isocyanate urethane reaction. Adv Mater Res 150–151:23–26
24. Astarloa Aierbe G, Echeverría JM, Riccardi CC, Mondragon I (2002) Influence of the temperature on the formation of a phenolic resol resin catalyzed with amine. Polymer (Guildf) 43:2239–2243
25. Grenier-Loustalot M-F, Larroque S, Grande D, Grenier P, Bedel D (1996) Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics. Polymer (Guildf) 37:1363–1369
26. Astarloa-Aierbe G, Echeverría JM, Vázquez A, Mondragon I (2000) Influence of the amount of catalyst and initial pH on the phenolic resol resin formation. Polymer (Guildf) 41:3311–3315
27. Manfredi LB, de la Osa O, Galego Fernández N, Vázquez A (1999) Structure–properties relationship for resols with different formaldehyde/phenol molar ratio. Polymer (Guildf) 40:3867–3875

28. Astarloa Aierbe G, Echeverría JM, Martin MD, Etxeberria AM, Mondragon I (2000) Influence of the initial formaldehyde to phenol molar ratio (F/P) on the formation of a phenolic resol resin catalyzed with amine. Polymer (Guildf) 41:6797–6802
29. Grenier-Loustalot M-F, Larroque S, Grenier P (1996) Phenolic resins: 5. Solid-state physicochemical study of resoles with variable FP ratios. Polymer (Guildf) 37:639–650
30. Tejado A, Peña C, Labidi J, Echeverria JM, Mondragon I (2007) Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis. Bioresour Technol 98:1655–1663
31. Wang G, Chen H (2014) Carbohydrate elimination of alkaline-extracted lignin liquor by steam explosion and its methylolation for substitution of phenolic adhesive. Ind Crops Prod 53:93–101
32. Wang G, Liu X, Zhang J, Sui W, Jang J, Si C (2018) One-pot lignin depolymerization and activation by solid acid catalytic phenolation for lightweight phenolic foam preparation. Ind Crops Prod 124:216–225
33. Zhao Y, Mao X, Li W, Gu X, Wang G (2017) Study on extraction phenol from coal tar with high flux centrifugal extractor. Int J Coal Sci Technol 4:333–341
34. Jiao T, Zhuang X, He H, Li C, Chen H, Zhang S (2015) Separation of phenolic compounds from coal tar via liquid-liquid extraction using amide compounds. Ind Eng Chem Res 54:2573–2579
35. Meng H, Ge C-T, Ren N-N, Ma W-Y, Lu Y-Z, Li C-X (2014) Complex extraction of phenol and cresol from model coal tar with polyols, ethanol amines, and ionic liquids thereof. Ind Eng Chem Res 53:355–362
36. Li Z, Wu M, Jiao Z, Bao B, Lu S (2004) Extraction of phenol from wastewater by N-octanoylpyrrolidine. J Hazard Mater 114:111–114
37. Medir M, Arriola A, Mackay D, Giralt F (1985) Phenol recovery from water effluents with mixed solvents. J Chem Eng Data 30:157–159
38. Yang C, Qian Y, Zhang L, Feng J (2006) Solvent extraction process development and on-site trial-plant for phenol removal from industrial coal-gasification wastewater. Chem Eng J 117:179–185
39. Rao TSS, Awasthi S (2007) Oxidation of alkylaromatics. E J Chem 4:185364
40. Weber M, Weber M (2010) Phenols. In: Phenolic resins: a century of progress. Springer, pp 9–23
41. Amen-Chen C, Pakdel H, Roy C (2001) Production of monomeric phenols by thermochemical conversion of biomass: a review. Bioresour Technol 79:277–299
42. Chum H, Diebold J, Scahill J, Johnson D, Black S, Schroeder H, Kreibich RE (1989) Biomass pyrolysis oil feedstocks for phenolic adhesives. In: Adhesives from renewable resources. American Chemical Society, pp 11–135
43. Russell JA, Riemath WF, Pasco both of W (1984) Method for making adhesive from biomass. United States Patents
44. Lee SH, Ohkita T (2003) Rapid wood liquefaction by supercritical phenol. Wood Sci Technol 37:29–38
45. Khan MA, Ashraf SM, Malhotra VP (2004) Development and characterization of a wood adhesive using bagasse lignin. Int J Adhes Adhes 24:485–493
46. Çetin NS, Özmen N (2002) Use of organosolv lignin in phenol–formaldehyde resins for particleboard production: I. Organosolv lignin modified resins. Int J Adhes Adhes 22:477–480
47. Çetin NS, Özmen N (2002) Use of organosolv lignin in phenol-formaldehyde resins for particleboard production: II. Particleboard production and properties. Int J Adhes Adhes 22:481–486
48. Alonso MV, Oliet M, Rodríguez F, García J, Gilarranz MA, Rodríguez JJ (2005) Modification of ammonium lignosulfonate by phenolation for use in phenolic resins. Bioresour Technol 96:1013–1018
49. Ono H-K, Sudo K (1989) Wood adhesives from phenolysis lignin. In: Lignin. American Chemical Society, pp 25–334
50. Effendi A, Gerhauser H, Bridgwater AV (2008) Production of renewable phenolic resins by thermochemical conversion of biomass: a review. Renew Sustain Energy Rev 12:2092–2116

51. Chum HL, Black SK, Diebold JP, Kreibich RE (1993) Phenolic compounds containing/neutral fractions extract and products derived therefrom from fractionated fast-pyrolysis oils
52. Chum H, Kreibich R (1992) Process for preparing phenolic formaldehyde resole resin products derived from fractionated fast-pyrolysis oils
53. Kresta JE, Garcia A, Frisch KC, Linden G (1981) Model studies of phenolic-urethane polymers. In: Urethane chemistry and applications. American Chemical Society, pp 27–403
54. Sonnenschein MF (2014) Polyurethanes: science, technology, markets, and trends. John Wiley & Sons
55. Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuvaraj AR (2016) Polyurethane types, synthesis and applications-a review. RSC Adv 6:114453–114482
56. Burdeniuc J, Kamzelski A (2009) Blowing catalyst compositions containing hydroxyl and surface active groups for the production of polyurethane foams. US Patent 7,495,131 1:1–40
57. Britain JW, Gemeinhardt PG (1960) Catalysis of the isocyanate-hydroxyl reaction. J Appl Polym Sci 4:207–211
58. Lai Y-C, Dvornić PR, Lenz RW (1982) Exactly alternating silarylene-siloxane polymers. 4. Step-growth polymerization reactions with dichlorosilane monomers. J Polym Sci Polym Chem Ed 20:2277–2288
59. Sasaki N, Yokoyama T, Tanaka T (1973) Properties of isocyanurate-type crosslinked polyurethanes. J Polym Sci Polym Chem Ed 11:1765–1779
60. Chattopadhyay DK, Raju K (2007) Structural engineering of polyurethane coatings for high performance applications. Progr Polym Sci 32:352–418
61. Chattopadhyay DK, Sreedhar B, Raju KVSN (2005) Effect of chain extender on phase mixing and coating properties of polyurethane ureas. Ind Eng Chem Res 44:1772–1779
62. Hepburn C (2012) Polyurethane elastomers. Springer, Netherlands
63. Shi Y, Yu B, Zhou K, Yuen RKK, Gui Z, Hu Y, Jiang S (2015) Novel $CuCo_2O_4$/graphitic carbon nitride nanohybrids: Highly effective catalysts for reducing CO generation and fire hazards of thermoplastic polyurethane nanocomposites. J Hazard Mater 293:87–96
64. Zheng J, Luo J, Zhou D, Shen T, Li H, Liang L, Lu M (2010) Preparation and properties of non-ionic polyurethane surfactants. Colloids Surf A Physicochem Eng Asp 363:16–21
65. Jin L, Liu Z, Xu Q, Li Y (2006) Preparation of soap-free cationic emulsion using polymerizable surfactant. J Appl Polym Sci 99:1111–1116
66. Lu Y, Xia Y, Larock RC (2011) Surfactant-free core–shell hybrid latexes from soybean oil-based waterborne polyurethanes and poly(styrene-butyl acrylate). Prog Org Coatings 71:336–342
67. Singh SN (2001) Blowing agents for polyurethane foams. Rapra Technology
68. Petrović ZS, Cvetković I, Hong D, Wan X, Zhang W (2008) Polyester polyols and polyurethanes from ricinoleic acid. J Appl Polym Sci 108:1184–1190
69. Nieschlag HJ, Wolff IA (1971) Industrial uses of high erucic oils. J Am Oil Chem Soc 48:723–727
70. Liu Z, Bai G, Huang Y, Ma Y, Du F, Li F, Guo T, Chen Y (2007) Reflection and absorption contributions to the electromagnetic interference shielding of single-walled carbon nanotube/polyurethane composites. Carbon N Y 45:821–827
71. Taheri N, Sayyahi S (2016) Effect of clay loading on the structural and mechanical properties of organoclay/HDI-based thermoplastic polyurethane nanocomposites. e-Polymers 16:65–73
72. Patel RH, Shah MD, Patel HB (2011) Synthesis and characterization of structurally modified polyurethanes based on castor oil and phosphorus-containing polyol for flame-retardant coatings. Int J Polym Anal Charact 16:107–117
73. Zhang M, Luo Z, Zhang J, Chen S, Zhou Y (2015) Effects of a novel phosphorus–nitrogen flame retardant on rosin-based rigid polyurethane foams. Polym Degrad Stab 120:427–434
74. Nobles WL, Potti ND (1968) Studies on the mechanism of the mannich reaction. J Pharm Sci 57:1097–1103
75. Tramontini M, Angiolini L (1994) Mannich bases-chemistry and uses. CRC Press
76. Short EL, Tychopoulos V, Tyman JHP (1992) Long chain phenols—part 30: a rate study of the mannich reaction of phenols (with particular reference to 3-pentadecylphenol). J Chem Technol Biotechnol 53:389–396

77. Ionescu M (2006) Mihail Ionescu: chemistry and technology of polyols for polyurethanes. Polimeri 26:218–218
78. Vasapollo G, Mele G, Del Sole R (2011) Cardanol-based materials as natural precursors for olefin metathesis. Molecules 16:6871–6882
79. Ionescu M, Wan X, Bilić N, Petrovic ZS (2012) Polyols and rigid polyurethane foams from cashew nut shell liquid. J Polym Environ 20:647
80. Bo C, Wei S, Hu L, Jia P, Liang B, Zhou J, Zhou Y (2016) Synthesis of a cardanol-based phosphorus-containing polyurethane prepolymer and its application in phenolic foams. RSC Adv 6:62999–63005
81. Rekha N, Asha SK (2008) Synthesis and FTIR spectroscopic investigation of the UV curing kinetics of telechelic urethane methacrylate crosslinkers based on the renewable resource—cardanol. J Appl Polym Sci 109:2781–2790
82. Bo C, Hu L, Jia P, Liang B, Zhou J, Zhou Y (2015) Structure and thermal properties of phosphorus-containing polyol synthesized from cardanol. RSC Adv 5:106651–106660
83. Del Saz-Orozco B, Alonso MV, Oliet M, Domínguez JC, Rodriguez F (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Compos Part B Eng 75:367–372
84. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Compos Part A Appl Sci Manuf 34:899–906
85. Huang Y-J, Wang C-H, Huang Y-L, Guo G, Nutt SR (2010) Enhancing specific strength and stiffness of phenolic microsphere syntactic foams through carbon fiber reinforcement. Polym Compos 31:256–262
86. Kaynak C, Cagatay O (2006) Rubber toughening of phenolic resin by using nitrile rubber and amino silane. Polym Test 25:296–305
87. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54:1962–1970
88. Yang H, Wang X, Yuan H, Song L, Hu Y, Yuen RKK (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 19:9831
89. Yang H, Wang X, Yu B, Yuan H, Song L, Hu Y, Yuen RKK, Yeoh GH (2013) A novel polyurethane prepolymer as toughening agent: preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 128:2720–2728
90. Gardziella A, Pilato LA, Knop A (2013) Phenolic resins: chemistry, applications, standardization, safety and ecology. Springer Berlin Heidelberg
91. Rao G-S, Nabipour H, Zhang P, Wang X, Xing W, Song L, Hu Y (2020) Lightweight, hydrophobic and recyclable carbon foam derived from lignin–resorcinol–glyoxal resin for oil and solvent spill capture. J Mater Res Technol 9:4655–4664
92. Kleinman EF, Volkmann RA (2015) comprehensive organic synthesis II. Choice Rev Online 52:52-4219-52–4219
93. Leonard NJ, Paukstelis JV (1963) Direct synthesis of ternary iminium salts by combination of aldehydes or ketones with secondary amine salts 1,2. J Org Chem 28:3021–3024
94. Gupta RK, Ionescu M, Wan X, Radojcic D, Petrović ZS (2015) Synthesis of a novel limonene based Mannich polyol for rigid polyurethane foams. J Polym Environ 23:261–268
95. Hu X, Cheng W, Wang D (2014) Properties and applications of novel composite foam for blocking air leakage in coal mine. Russ J Appl Chem 87:1099–1108
96. Knop A, Böhmer V, Pilato LA (2013) Phenolic resins: chemistry, applications and performance. Springer Berlin Heidelberg
97. Lenghaus K, Qiao GG, Solomon DH (2001) The effect of formaldehyde to phenol ratio on the curing and carbonisation behaviour of resole resins. Polymer (Guildf) 42:3355–3362
98. Vazquez A, Adabbo HE, Williams RJJ (1984) Statistics of resols. Ind Eng Chem Prod Res Dev 23:375–379
99. Yuan J, Zhang Y, Wang Z (2015) Phenolic foams toughened with crosslinked poly (n-butyl acrylate)/silica core-shell nanocomposite particles. J Appl Polym Sci 132

100. Shi J, Zheng T, Zhang Y, Guo B, Xu J (2020) Reprocessable cross-linked polyurethane with dynamic and tunable phenol-carbamate network. ACS Sustain Chem Eng 8:1207–1218
101. Zhang G, Zhao Q, Yang L, Zou W, Xi X, Xie T (2016) Exploring dynamic equilibrium of diels-alder reaction for solid state plasticity in remoldable shape memory polymer network. ACS Macro Lett 5:805–808
102. Zhang Y, Dai Z, Han J, Li T, Xu J, Guo B (2017) Interplay between crystallization and the Diels-Alder reaction in biobased multiblock copolyesters possessing dynamic covalent bonds. Polym Chem 8:4280–4289
103. Zeng C, Seino H, Ren J, Hatanaka K, Yoshie N (2013) Bio-based furan polymers with self-healing ability. Macromolecules 46:1794–1802
104. Liu Y-L, Chuo T-W (2013) Self-healing polymers based on thermally reversible Diels-Alder chemistry. Polym Chem 4:2194–2205
105. Montarnal D, Capelot M, Tournilhac F, Leibler L (2011) Silica-like malleable materials from permanent organic networks. Science (80-) 334:965–968
106. Capelot M, Unterlass MM, Tournilhac F, Leibler L (2012) Catalytic control of the vitrimer glass transition. ACS Macro Lett 1:789–792
107. Han J, Liu T, Hao C, Zhang S, Guo B, Zhang J (2018) A Catalyst-free epoxy vitrimer system based on multifunctional hyperbranched polymer. Macromolecules 51:6789–6799
108. Shi J, Zheng T, Guo B, Xu J (2019) Solvent-free thermo-reversible and self-healable crosslinked polyurethane with dynamic covalent networks based on phenol-carbamate bonds. Polymer (Guildf) 181:121788
109. Cao S, Li S, Li M, Xu L, Ding H, Xia J, Zhang M, Huang K (2017) A thermal self-healing polyurethane thermoset based on phenolic urethane. Polym J 49:775–781
110. Fang Z, Zheng N, Zhao Q, Xie T (2017) Healable, reconfigurable, reprocessable thermoset shape memory polymer with highly tunable topological rearrangement kinetics. ACS Appl Mater Interfaces 9:22077–22082
111. Zhang L, Rowan SJ (2017) Effect of sterics and degree of cross-linking on the mechanical properties of dynamic poly(alkylurea–urethane) networks. Macromolecules 50:5051–5060
112. Chen J-H, Hu D-D, Li Y-D, Meng F, Zhu J, Zeng J-B (2018) Castor oil derived poly(urethane urea) networks with reprocessibility and enhanced mechanical properties. Polymer (Guildf) 143:79–86
113. Chen J-H, Hu D-D, Li Y-D, Zhu J, Du A-K, Zeng J-B (2018) Castor oil-based high performance and reprocessable poly(urethane urea) network. Polym Test 70:174–179
114. Wicks DA, Wicks ZW (1999) Blocked isocyanates III: Part A. Mechanisms and chemistry. Prog Org Coatings 36:148–172
115. Voirin C, Caillol S, Sadavarte NV, Tawade BV, Boutevin B, Wadgaonkar PP (2014) Functionalization of cardanol: towards biobased polymers and additives. Polym Chem 5:3142–3162
116. Yang C, Zhuang ZH, Yang ZG (2014) Pulverized polyurethane foam particles reinforced rigid polyurethane foam and phenolic foam. J Appl Polym Sci 131:39734
117. Jing S, Li T, Li X, Xu Q, Hu J, Li R (2014) Phenolic foams modified by cardanol through bisphenol modification. J Appl Polym Sci 131:39942
118. Gao L, Li C, Wang C, Cui J, Zhou L, Fang S (2019) Structure and luminescent property of polyurethane bonded with Eu3+-complex. J Lumin 212:328–333
119. Lei S, Guo Q, Zhang D, Shi J, Liu L, Wei X (2010) Preparation and properties of the phenolic foams with controllable nanometer pore structure. J Appl Polym Sci 117:3545–3550
120. Eaves D (2004) Handbook of polymer foams. Choice Rev Online 42:42-0962-42–0962

Chapter 4
Hybrid Composite Foam: Effect of Hybrid Fillers on the Mechanical Properties of Phenolic Foams

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1 Introduction

Recently, matrix reinforcement by incorporating two or more hybrid fillers has led to the development of hybrid composites with a wide variety of material properties. Hybrid reinforcement is achieved by using more than one type of material (organic, inorganic, synthetic, and natural), shape (flakes, powder, fibers), size (aspect ratio), and orientation of fillers [1]. In recent years, hybrid composites have been developed using several fibers to modify the final properties of the composites with synergistic properties.

Hybrid polymer composites also offer a broad range of properties that could not be obtained with a single type of reinforcement. Furthermore, hybrid reinforcement with decent fiber selection enables to generate excellent properties with low density and meets the design criteria for the desired applications. Another benefit of hybridization is that high-priced reinforcement can be easily substituted or combined with cheaper materials.

Hybrid foam composites have gained their popularity nowadays due to the superior foam properties contributed by the combination of two types of filler reinforcements in the matrix. Therefore, the hybrid composite phenolic foam has been used as potential material in various applications, such as civil construction, chemical industry, marine, and aerospace [1–4]. In recent years, many researchers have conducted numerous studies on the reinforcement of phenolic foam composites to extend their applications [5]. Phenolic foam (PF) itself has excellent properties such as fire resistance, non-drip low combustibility, low toxicity, high thermal stability, and

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good chemical resistance [6, 7]. However, PF is limited in brittleness and therefore restricts their performance in various applications that require special strength.

There are two methods which had been utilized in the past few decades to overcome this issue which include chemical modification and inter-filler [8]. For chemical modification, the easiest way is to blend phenolic resin with polymeric toughening agent such as rubber [9, 10], epoxy resin [11], polyethylene glycol [12], and polyvinyl alcohol [13]. However, blending with a polymeric toughening agent will deteriorate the excellent fire retardancy of phenolic foams as these materials are flammable [11]. Therefore, it is desirable to improve their toughness properties while maintaining their excellent flame retardancy properties by selecting suitable materials and methods. Yang and his group [14] prepared phosphorus-containing polymeric modifiers, for example, phosphorus-containing polyethers. They found that the modifier could enhance both the toughness and flame resistance of PF foam. The idea to produce composite foams using inter-filler, such as graphene oxide [15], multiwalled carbon nanotubes [16], and clay [17], has resulted in uniform cell structure distribution, while increasing the viscosity of the resin before foaming and making PF foams denser. However, some researchers have chosen to use chopped fiber as reinforcers, such as glass fiber, aramid fiber [18], and natural fiber [19] to make PF foam stronger and tougher. Although this fiber reinforcement is distinctly effective in enhancing the mechanical properties of PF foam, it affects the mixing and foaming process, resulting in increased density and poor surface quality [16]. Hence, the hybrid composite foam has recently been introduced by combining two types of fillers (particulates) or fibers, or a combination that could boost both mechanical strength and flame-retardant properties. This is in agreement with Li et al. [6] who stated that silica nanospheres/graphene oxide hybrids have also improved the mechanical strength and flame-retardant properties of phenolic foam composites. In another study, Li et al. [20] reported that α-zirconium phosphate/graphene oxide hybrid synthesized had improved both flammability and mechanical strength. Desai and co-workers reported that hybrid composite phenolic foams reinforced with glass and aramid fibers have a much lower flammability and the compressive stiffness of hybrid foams can be maintained even after aging [3]. The hybrid fillers studied have displayed substantial potential for improvement in mechanical performance as well as maintaining their fire-retardant properties. With more exploration in this area, hybrid composite foam will exhibit greater potential for use in advanced applications.

2 Fillers in Hybrid Composite Foam

Phenolic foam (PF) was first introduced in the early 1940s, yet the material has not been entirely commercialized due to its brittleness and friability. Later in the early twentieth century, with the emergence of industrial revolution, rigid thermosetting foam has gained its attention due to the growing demand for cheap foam thermal insulation materials. Closed-cell PF is suitable for thermal insulation applications, while the open-cell foam was common for sound insulation applications. Since then, an effort has been made by researchers to tailor PF cell size, shape, and distribution for various purposes. To reconstruct pure PF according to the desired properties, numerous approaches have been conducted, namely, chemical modification on phenolic resin, physical blending between phenolic and other polymer resins, altering formulation and ingredients, and addition of filler in the open- and closed-cell PF system [7, 21].

Fillers are well known to comprehensively alter the mechanical strength and physical properties of polymer composites. In the past decade, many have described the use of a single type filler loading in PF. It has been proven that single component fiber system has enabled a significant improvement in the strength and thermal properties of PF. Regardless of the improvement, sometimes the use of a single filler could not overcome the limitation of producing PF with preferred properties. By recognizing the challenges of producing PF with multiple functions, the use of more than one type of filler or the fabrication of a chemically bonded hybrid particle is necessary to meet the needs. In the past decade, there have been a number of articles related to hybrid filler system in PF. To properly view the subject, we categorize hybrid fillers in PF into hybrid fiber system and hybrid particulate filler system [7, 22].

2.1 Hybrid Fiber

To date, polymer foam has been used as a core material for advanced engineering applications, such as in marine, building, automotive, and aerospace industries. Sandwich composites with the configuration of polymeric foam core have become an ideal material due to their superior strength, high specific bending stiffness, and ultra-lightweight criteria for large panels. Based on previous successful reports on sandwich structure made of polyurethane, epoxy and polystyrene foam as core materials, Kim et al. [23] proposed a new method to produce a sandwich panel using PF-filled honeycomb as core material and with aramid/glass hybrid mat as a face material. The use of hybrid mat and fiber arrangement was developed according to the criteria needed for a sandwich panel. In an effort to replace the conventional metallic honeycomb sandwich structure, the core material was filled with glass fiber/phenolic composites with PF to achieve the requirement for strength and thermal insulation properties. The fabric mat was treated with silane coupling agent to enhance the bonding strength between the matrix and the fiber, and then the face was bonded to the PF-filled honeycomb. Both aramid glass fiber mat and glass fiber mat were staked and coated with carbonized phenolic resin on the honeycomb surface to function as a protective layer targeted to improve the post-fire properties. The addition of PF has lowered the thermal conductivity for the entire core layer to 0.042 W/m.K indicating the ability of PF to block fire from further propagation [24].

In the fire exposure experiments, the thermal conductivity of the hybrid composite appeared to be 0.26 W/m.K through the 38 mm core thickness direction. In terms of strength, the hybrid honeycomb post-fire flexural strength decreased by 16% from 20.5 to 3.4 MPa and the stiffness decreased by 49% from 226 to 110 Pa.m^4 after 1 h of exposure to fire. This was also indicated by the hybrid composite PF flexural strength as it decreased by 54% of the original strength caused by core shear failure. Interestingly, the PF hybrid composite core sandwich structure produced with carbonized phenolic aramid/glass hybrid composite face was able to retain about 50% of the original strength after post-fire exposure which concluded that the hybrid composite mat sandwich with PF has the ability to replace epoxy, vinyl ester, or polyester resin. The failure mode for the entire honeycomb hybrid system was derived from delamination and cracking between the composite face and core on the fire-exposed side.

In addition, the idea of combining chopped fiber in PF has been driven by the superior properties of the resulting composite foams. The amplified properties are obtained through a synergistic effect accomplished using two types of fillers. This can also replace expensive filler reinforcement with cheaper materials to reduce cost or weight for the entire hybrid fiber composite foam system. Typically, these types of fibers can be categorized into man-made inorganic, organic fiber, and natural fiber made of mainly cellulose, and each of these fillers behave differently in PF. Previously, single-filled short stiff glass fiber reinforcement was employed to increase the strength and dimensional stability of the phenolic foams [18]. The same method was also used on PU foam where it produced high compression strength with the addition of glass fiber mat [23]. The glass fiber is capable of blocking further crack propagation and then diverted the cracks along the fiber length and finally dissipates energy in the process. Thus, fiber reinforcement allows the alteration of crack growth mode and results in high fracture toughness. Previous studies have also demonstrated that at 5% glass fiber loading in a closed-cell foam system, a few open cells were observed due to the cell wall fracture caused by frictions between the bubbles and the glass fiber. Another type of flexible short fiber is aramid fiber. Although aramid-reinforced foam produces strength and modulus similar to unreinforced PF, it consumes almost twice as much energy during fracture.

To summarize the effect between these two fillers, Shen et al. [25] compared the use of both glass and aramid fiber in the peeling test. They found a significant improvement in the peel strength and toughness to reinforce phenolic foam with aramid fibers. The addition of a small amount of 3 wt% short aramid fibers produced a sixfold of the unreinforced foam while adding 5% by weight resulting in a sevenfold increase compared to short glass fiber and unreinforced PF [25]. Careful inspection revealed that the aramid-reinforced foam had a rougher fracture surface than the glass-reinforced foam. This could be due to the formation of tiny fibrils of micro-peeling (peel of aramid stem) from the microscope due to good bonding strength before failure with phenolic resin. The study also revealed that the viscosity of the fiber/phenolic resin mixture increased significantly when fiber was added in the resin even in a small amount. Therefore, a limit of 5 wt% of 6.4 mm aramid fiber was selected to maintain the desirable foam quality. The anisotropy indicated that the glass fibers tend to align in the foaming direction. In contrast, the aramid-reinforced foam did not show significant anisotropy effect [25, 26].

By taking advantage on the inherited properties of glass fiber and aramid fiber, an experiment was conducted to determine the hybrid short fiber mechanical properties with different fiber potion in the PF open-cell system. The properties of the hybrid composite foams were assessed to determine its effects. As a result, the compressive strength increased by 275% after adding 5 wt% of glass fiber and by 36% after adding the same amount of aramid fiber. Indeed, stiff glass fibers were highly orientated along the foaming direction inducing a significant enhancement in mechanical properties in the foaming direction, whereas almost no evolution was observed in the perpendicular direction [22]. In comparison, aramid fibers were distributed randomly, and thus favored the isotropic characteristics of the foam. The hybrid exhibited marked increases in shear modulus and shear strength but portion-dependent. The contribution of both types of fibers is critical for the shear performance of phenolic foams. Moreover, the success of hybrid is contributed by fiber compatibility and strong bonding between the matrix. The failure of the PF hybrid composites is originated from the fiber pull out at the interface. Aramid indicates unusually strong cohesive strength that forces a combination of interface and matrix failure [3, 22].

Furthermore, research involving natural fibers in PF has been actively progressed aiming to produce foams with environmentally sustainable properties [21]. Natural fibers have a lot of potential to be reinforcing fillers as they are able to move along anisotropic alignment toward foaming direction during the foaming process. Apart from being economical and easily available, natural fibers exhibit a number of attractive features such as low density, good insulation, thermal properties, high specific strength, and minimum energy consumption during mixing. Recently, Tang et al. [27] have utilized bamboo fiber to improve the compression strength of PF. They stated that the addition of 2.5 wt% bamboo fiber promote the highest compression strength and improved the foam friability. The strength was achieved by the bamboo fiber in the foaming direction [27]. Currently, natural fibers (such as sisal fiber, jute fiber, ramie fiber, and straw fiber, among others) have been shown to enhance the mechanical properties of rigid polyurethane foam [23]. In a polymer matrix system, the use of a hybrid natural fiber system has induced better polymer composite performance. Although research related to the use of hybrid natural fibers in PF has not been carried out, looking at current trends, we see that future work on PF will head in the direction mentioned above [27, 28].

2.2 Hybrid Particulates

The tailor-made properties of particulate hybrid composite foams allow the production of foams with distinct properties. The rule for developing uniform and regular cells in PF is by homogeneously dispersing particulate fillers in phenolic resin. The inclusion of filler in the PF formulation may stabilize the emulsion by Pickering. These fillers also act as nucleating agents in creating more bubble nuclei when exceeding the free critical nucleating energy. In comparison to the filled fiber, the addition of particle filler can severely increase the viscosity of the filled phenolic resin. However, it is insignificant to compare with fiber systems due to its isotropic properties. Higher viscosity results in better cell uniformity and generates smaller cell size during foam expansion but on the downside it constructs a higher foam density. If the viscosity is too high, the foam will be completely inhibited from further expansion. There are a number of single filler systems from microns to nano-sized particles added in PF, such as clay, glass beads, and gypsum. These fillers come in various sizes, shapes, surface chemistry, and specific surface areas which may impart an outstanding performance on foam stiffness, compressive strength, flexural strength, and fire properties. To achieve more than one of these properties, hybrid particulate fillers have proven to be a promising solution [21].

Mineral fillers have been proven to alter the physical and mechanical strength of PF composites and function as non-flammable particles. With respect to the hybrid filler filled foam approach, the use of mineral filler components is to cater specific well-defined functions allowing for better control in inducing better cell formations. Colombo et al. [29] reported uniaxial compression behavior at low strain rate using PF with various amounts of hybrid inert minerals (gypsum, graphite, carbon) on open-cell system foam with a control cell size. Although the discussion has focused on the testing and design experiments rather than materials, this indicates that the mineral-phenolic foam examined is almost strain rate independent in the range of strain rate considered [29].

Zhou et al. [30] demonstrated thermomechanical analysis of phenolic foam reinforced with 10% glass fiber mat (100 g/m^2, average diameter of 10 μm) prepared by impregnation process and then made comparison on samples with and without the inclusion of 1% $CaCO_3$ powder. The results showed that the tensile strength, compression strength, and impact toughness were remarkably enhanced when both glass fiber mat and $CaCO_3$ powder were combined. The most significant amplification value was obtained by the tensile strength of the PF composites which increased to 112.5% when using only glass fiber mat and then increased by 215.6% when using both glass fiber mat and nucleating agents with respect to pure PF. Moreover, the hybrid composites imposed a lower thermal coefficient expansion at a temperature less than 170 °C and increased the DMA storage modulus from 212 to 332 MPa in contrast to the unfilled PF. Further examination of cell structure, PF with nucleating agent had smaller bubble size than the unfilled phenolic foams. The bubbles were initiated by heterogeneous nucleation as a result of lower free energy barrier when $CaCO_3$ was added to the resin [30].

At the nano-scale level, Hu and colleagues studied a hybrid system for montmorillonite nanoclay together with glass fiber loading in phenol–urea–formaldehyde (PUF) foam. Nanoclay has many advantages, such as toughening, flame-retardant properties, enhanced dimensional stability, excellent charring effect, low smoke, difficult to ignite, migration resistance, and low density. A similar trend in improving the compressive strength was observed when nanoclay was added where it increased the foam density and reduced the pulverization rate. The foam exhibited an increase in impact strength, oxygen index, and thermal stability, lowering the heat release rate and reducing the total smoke rate. Agglomerates can easily occur when nanoclay is added beyond the critical limit and these agglomerate nanoparticles hinder the crosslinking reactions of the macromolecular chains in phenolic resin, thus further weakening the mechanical properties of the foam. In short, the addition of optimum nanoclay loading helps to boost mechanical properties and increase the flame resistance of the foam [31].

To ensure that the filler functions as a reinforcer, the compatibility between the fillers and phenolic resin is crucial. Guo and co-workers [32] have prepared homogeneous nano-SiO_2 particles which were later inserted into the lignin-modified phenolic foam. Nanofillers were prepared by hydrolyzing tetraethyl orthosilicate (TEOS) and reacting with formaldehyde. The chemically modified surface nano-SiO_2 in phenol is more reactive than in pure phenol [32]. In response to the successful chemical assembly, the compressive strength of PF-modified lignin increased dramatically by 153% by adding only 0.1 wt% of nano-SiO_2. Interactions between particles and phenolic resins are associated with the effect of cell size on friability. The inclusion of silica causes a reduction in the friability of PF due to the formation of crosslinking structure from the reaction between silanols on silica surface and methyloxy groups in phenolic resins [20]. Similar experiments were carried out by other researchers for the hybridization of poly(n-butyl-acrylate) with silica core–shell nanocomposite particles where it was weakly crosslinked via aqueous emulsion polymerization. As a result, the shell of nanosilica particles equipped with hydroxyl groups is able to react with the hydroxyl groups of phenolic resins and provide good compatibility with phenolic resins [33].

Recently, the incorporation of carbon-based fillers in PF composites has received a noteworthy attention. Due to the filled carbon unique shape, structure, and ability to conduct electricity, graphene nano-platelet, graphite, and CNT have become the next target fillers for hybridization to further expand its applications in various fields [16, 34]. Studies have shown the use of multiwall carbon nanotubes (MWCNT) in chemically modified PF reduced the cell size. Other work has compared the effect of MWCNT and graphene. The addition of 0.5 wt% MWCNT has reduced the foam cell size by 56%, while the results were more pronounced with a decrease in cell size by 73% with the addition of 1 wt% of graphene [35]. In the carbon-filled hybrid system, the Li group [10] emphasized that graphene oxide with α-zirconium phosphate (ZGO) hybridized on its surface could enhance the friability of the foam up to 17% at 4 phr loading. Their group also conducted similar research on silica nanospheres/graphene oxide hybrid (SGO) prepared using the same method and found that the friability improved by 23% for silica nanospheres/graphene oxide hybrid with 0.5 phr loading. Meanwhile, heat flux test related to flame-retardant properties indicated that both nanoparticles produced a dense charred layer during combustion which concluded that the nanoparticles could protect the foam from thermal decomposition at higher temperatures. Both studies revealed that the peak heat release rate (pHRR) decreased with increasing amount of graphene oxide which summarized the effectiveness of graphene oxide in enhancing the fire-retardant behavior of the foam. Similar results are shown by Liu et al. [5] and Wang et al. [8] in their work for modified graphene oxide hybrid particles.

Inspired by previous work on hybrid carbon-based fillers for application in heat, electricity, and magnetism, Zeng et al. [36] extended their research using the three-dimensional structure of graphene oxide/SiO_2 (GO/SiO_2) hybrid nanomaterials in PF to cater the EMI shielding performance. The configuration of the effectiveness of the foam electromagnetic shield was connected to the foam cellular structure. The presence of 1 wt% GO/SiO_2 nanomaterials clearly enhanced the cell structure, narrowed the range of cell distribution, and reduced the density of the foam which in turn assisted an efficient conductive network. The build-up porous structure of the carbon foam was identified to create a number of interfaces which simultaneously enhanced multiple reflections and absorptions of electromagnetic waves. The penetrating electromagnetic waves were then reflected in the matrix and propagated over a greater distance in random direction electromagnetic waves. They also discovered that the EMI SE of the carbon foam increased higher than $\sim$40 dB when a small amount of GO/SiO_2 was added. The value increased up to $\sim$50 dB as the concentration of GO/SiO_2 was added up to 1.5 wt% [36].

The other class of filler is natural filler and the subject has gained a lot of research interest aimed at renewable, low-density, and cost-effective foam. The use of natural filler, such as lignin, wood floor particles, and cellulose, has been recognized to improve the fire-resistant properties, reduce friability with slight drawback in thermal stability and moisture absorptivity. Saz-Orozco et al. [37] explored and compared the mechanical properties and morphology of lignin particle-phenolic foams (LRPFs) and wood flour-reinforced phenolic foams (WRPFs) filled individually in PF and its effect on friability, thermal stability, and hygrothermal aging. The dispersion of filler and agglomeration at high filler loading is still the main issue that need to be resolved. It was concluded that at 8.5 wt.% LRPF and 1.5 wt.% WRPF indicating notable features in terms of friability, thermal stability and compressive strength to be compared with existing commercial PF [37]. Although the work did not relate to the use of hybrid filler components, the study provided significant insights in identifying the function and capabilities of each natural filler used in PF. Similar to natural fiber system, we believe that the topic of natural hybrid fillers could be the next research topic.

3 Mechanical Properties of Hybrid Composite Phenolic Foam

Recently, various industries have focused on phenolic foam (PF) due to its excellent fire resistance, low density, low water absorption, and good thermal insulation [2]. Nevertheless, the drawbacks of PF foam are its high brittleness and low mechanical strength which limit its applications in some areas which require high mechanical properties. Generally, PF exhibits lower mechanical strength and brittleness compared to other commodity plastic foams [21]. Therefore, increased mechanical strength and reduced friability are crucial to highlight its potential in various applications. The mechanical strength of PF depends on the interaction of filler with the matrix, type of filler, shape of filler, and size of filler. Moreover, by using hybrid fillers, the compatibility between the fillers, mixed ratio, or weight fraction and filler dispersion could have a significant effect on the final properties of the composite foam. For example, Luo et al. [4] reported that the compressive strength of graphene oxide/SiO_2 (GO/SiO_2)-modified phenolic foam was better for SiO_2 with a diameter of 80 nm compared to 170 nm and 250 nm. Small particles with higher surface area could provide heterogeneous nucleation sites, thus producing PF with a uniform cell structure. In the same study, the compressive strength of PF increased from 0.3 wt% up to 1 wt% GO/SiO_2 and decreased by 1.5 wt%. Desai et al. [3] also reported that the PF reinforced with glass and aramid fiber at a ratio of 3:1 has higher compressive strength than 1:3 ratio.

In addition, Hu et al. [2] reported that the toughness and compressive strength of PF could be increased through hybridization of glass fiber and nanoclay in the foam by setting the glass fiber content (5%) and varying the nanoclay content (2, 3, 4%). The results showed that the compressive strength of the PF increased compared to glass fiber in the same quantity but without nanoclay (G4). The combination of glass fiber and nanoclay has shown synergistic enhancement in the compressive strength of the PF. Furthermore, the ratio of 5%:3% (G-N-2) indicated maximum compressive strength of 0.22 MPa which was slightly higher than that of PF with a ratio of 5%:4% (G-N-3). The addition of nanoclay in hybrid composite foam also serves as nucleating agent to construct homogenous fine cellular structures with high-density foam. In addition, clay could act as a good constraining force against the expansion of foaming resin [38]. This results in smaller cell structure of foam that could withstand high compressive strength. In the same study, it was found that the impact strength of the PF increased with increasing nanoclay content up to 4%. This has shown that both reinforcements have good synergistic effects on hybrid composite PF. In another study, Desai et al. [1] used the combination of two fibers as reinforcement, namely, chopped glass and aramid fibers. In their study, the shear and compressive properties of hybrid composite foams with different fiber proportions were compared with the properties of foams reinforced with only aramid and glass fibers. Hybrid phenolic composite foam with a ratio of 1:1 exhibited high resistance to breakage and was stronger than glass fiber-reinforced phenolic foams and aramid fiber-reinforced phenolic foam. They also found that the mechanical strength of the hybrid phenolic composite foam produced was comparable to the commercial polyurethane foam at equivalent densities. The application of this foam can be extended by combining two or more reinforcements. As previously reported, aramid fibers are flammable, and it is challenging to increase the mechanical strength by reducing their proportion. Therefore, Desai and group [3] in other study have investigated glass fiber treated with silane coupling agent. They found that the hybrid foam containing high volume fraction of glass fiber (glass/aramid, 3:1) had high compressive strength. Increased glass fiber loading in the hybrid foam increased the crosslinking between inorganic glass fiber and organic PF could severely improve the mechanical properties. Shen and Nutt [18] revealed that PF reinforced with aramid fiber has improved friability properties, resistance to cracking, and more isotropic behavior. Meanwhile, PF reinforced with glass fiber showed remarkable stiffening and strengthening effects, especially in the direction of foam rising. Therefore, with the hybridization of these fibers, the friability problem could be solved, and the mechanical strength of the PF could be increased.

Graphene has been widely used in various polymer composites over the last few years due to its outstanding properties. Although graphene exhibits excellent mechanical strength, good thermal properties, and flame resistance, it has low flame-retardant performance and is easily burned at high temperatures. Zhou et al. [15] reported that graphene oxide is capable of preventing the separation of small particles from the phenolic foam matrix compared to graphene. Hydroxyl –OH and carbonyl –COOH groups in graphene oxide also have higher probability of reacting with the attached functional groups in PF [39]. Furthermore, the percentage of weight loss for PF reinforced with graphene was reported to be higher than that of PF reinforced with graphene oxide [14]. This indicates that graphene oxide has better thermal stability compared to graphene. Therefore, studies on PF reinforced with graphene oxide have been increasing. Luo et al. [4] investigated the morphological and compressive strength of PF reinforced with graphene oxide/SiO_2. It was found that the compressive strength of the hybrid foam decreased with increasing diameter size of SiO_2 from 80 to 250 nm. By increasing the particle size, the specific surface area of the hybrid materials decreased, thus fewer nucleation sites were provided. In addition, a lesser number of cells in the same per unit area were produced (i.e., fine large cells and low density) compared to small particle size that generated more number of cells (i.e., small cell and high density). Large cells with thinner cell walls are usually not resistant to high compressive strength and are easily deformed at low compressive strength. In addition, the effect of the percentage weight of GO/SiO_2 particles (0.3 wt%, 1.0 wt%, and 1.5 wt%) on the compressive strength performance of PF was also investigated in the same study. It was found that the PF with 1.0 wt% GO/SiO_2 particles showed the highest compressive strength of 0.18 MPa and compressive modulus was 3.22 MPa. In contrast, PF with 1.5 wt% GO/SiO_2 particles showed the lowest compressive strength due to the agglomeration of a large number of particles resulted in a non-uniform cell size distribution. The agglomeration exerts several negative effects on the structure by introducing cavities and cell deformations in the composite foam.

Many functionalized graphene has also been synthesized to enhance their flame-retardant activity in polymeric materials. Wang and co-worker [8] synthesized CoAl-layered double hydroxide/graphene oxide (CoAl-LDH/GO) nanohybrid and incorporated it into the PF. They found that the mechanical strength of PF had improved, while their brittleness and friability reduced. By increasing the CoAl-LDH/GO nanohybrid content (0.3–1.5 phr) into PF, it increased the compressive and flexural strength. The study concluded that the heterogeneous nucleation with immobilization of inorganic CoAl-LDH on the GO surface should increase cell density and produce small cells which could resist the cell deformation. In addition, the movement of molecular chain segment in PF has been restricted due to the hardened cell walls provided by CoAl-LDH/GO nanohybrid content. Moreover, good interaction between CoAl-LDH/GO nanohybrid and phenolic foams through the reaction of the carbonyl groups of CoAl-LDH/GO with the hydroxyl groups of the resin has improved the mechanical properties [14].

Li et al. [20] synthesized nanofillers using silica (SiO_2) nanospheres and graphene oxide (GO) sheet to produce silica nanospheres/graphene oxide (SGO) hybrid in PF.

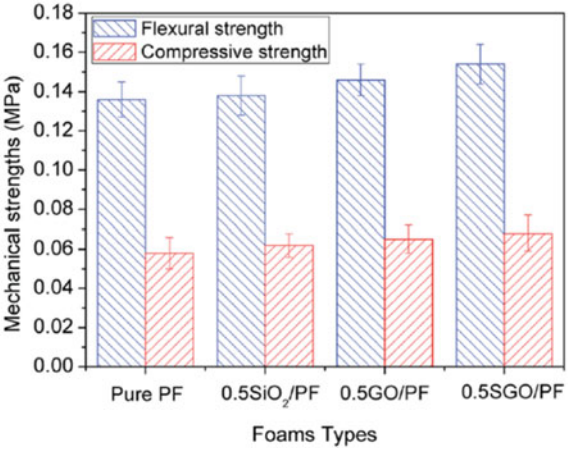

Fig. 1 Flexural and compressive strength of pure and reinforced phenolic foam [20]

The flexural and compressive strengths of the composite foam became better with the addition of SGO compared to unfilled PF foam. It can be seen from Fig. 1 that hybrid phenolic composite foam showed higher flexural strength and compressive strength compared to unfilled and single filler reinforced PF [20]. This could be due to the distribution of nanofillers at the cell walls of the foam which improved the strength of the cell walls. The added nanofillers also acted as nucleating agent, thus producing foams with more small cells with uniform size and better cell density.

Moreover, it was reported that good dispersion and interaction between SGO and PF matrix through the formation of linkages between the residual carbonyl groups (–COOH) on graphene oxide in SGO and hydroxyl (–OH) groups on resole in PF resins hindered segmental mobility of the PF chain. In addition, the hydrophobic modification of SiO_2 on the surface of GO sheet has resulted in heterogeneous nucleation of SGO nanofillers which produced more small cells withstanding external force and improving the mechanical properties [20]. In a similar study, flexural and compressive strengths increased up to 1.5 phr loading of SGO and started to decrease at higher filler loading (2 phr SGO). At higher filler loading of SGO nanofillers, the possibility of fillers to agglomerates is higher. As a result, non-uniform cell size will be produced due to poor dispersion of SGO in the PF resin and eventually it could not withstand the external force.

In another study, Li et al. [6] stated that the flexural and compressive strength of hybrid phenolic composite foam using α-zirconium phosphate/graphene oxide (ZGO) hybrid were improved compared to phenolic composite foam graphene oxide alone. It can be seen from Fig. 2 that both flexural and compressive strengths of 4ZGO/PF were higher than 4GO/PF and 4Zrp/PF. This may be due to the ZGO sheet-like structure being able to react as a reinforcing filler in the foam and thus constrained the segmental mobility of the PF chain [40]. Zhou et al. [15] reported that this could also be contributed by good dispersion and interaction between ZGO and PF matrix through the formation of linkages between residual carbonyl groups (–COOH) on graphene oxide in ZGO and hydroxyl groups (–OH) on resole in PF

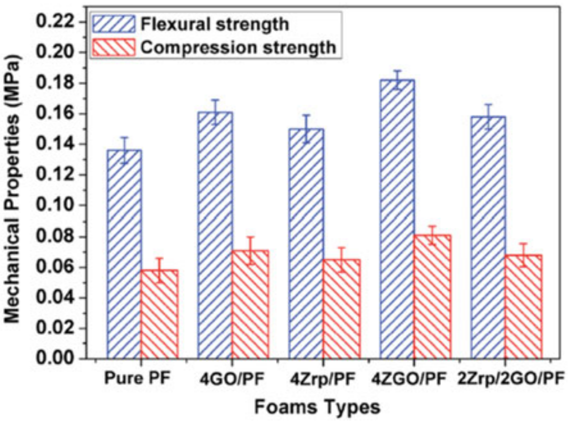

Fig. 2 Flexural and compressive strength of pure and reinforced phenolic foam [8]

resins. Nevertheless, Zrp showed poor dispersion in the PF by producing non-uniform cell structures, thus damaging the mechanical strength of 4ZrP/PF and 2ZrP/2GO/PF as shown in Fig. 2.

Furthermore, it was observed in the same study that both flexural and compressive strengths increased and reached a maximum content of 4 phr ZGO. This may be due to smaller cell size with uniform structure and sheet-like ZGO-toughened thick cell wall produced at 4 phr ZGO can withstand high external loading. The higher the ZGO phr, the tendency of the ZGO particles to agglomerate is also higher, so that both mechanical strengths became 5 phr ZGO.

Yu et al. [40] fabricated graphene oxide/Fe_3O_4 (rGO/Fe_3O_4) hybrid-modified phenolic foams for better EMI shielding and good mechanical strength. From the results, the compressive strength and compressive modulus of PF were reported to be improved with the addition of GO or rGO/Fe_3O_4. However, the compressive strength of PF containing rGO/Fe_3O_4 hybrid was higher than that of GO-reinforced PF. This was due to the hybrid filler itself in the three-dimensional structure, which helped to improve rigidity and improved mechanical strength compared to two-dimensional structure GO. They also reported that the phenolic composite foam had smaller and more uniform cell sizes by adding rGO/Fe_3O_4 hybrid filler in the PF. This consequently contributed to its higher compressive strength where the small cell size could withstand high external loading. At the same per unit area, foam with smaller cell size contains more volume fraction of solid phase than gas phase compared to foam with larger cell size. These larger cells with more gas-phase volume fraction could not withstand high external force applied, resulting in low compressive strength. In the same work, the hybrid filler weight fractions were varied in the range of 0.5 wt%, 1 wt%, and 1.5 wt% to further investigate their effect on the properties of the PF. The results demonstrated that the compressive strength of PF decreased with increasing weight fraction of hybrid fillers. This may be due to the agglomeration of high-concentration nano-sized rGO/Fe_3O_4 hybrid as discussed in other research work. In summary, the mechanical properties of the hybrid phenolic composite foam can be improved and tailored to specific requirements of particular applications by varying the filler parameters such as size, specific surface area, shape, type, and weight fraction.

4 Conclusion

Hybrid composite foam has been developed to satisfy the growing needs of various applications today. By utilizing hybrid fillers, the properties of PF can be modified for various end-use applications with excellent fire resistance and improvement in brittleness and mechanical strength. Hybrid composite foam provides multiple advantages with superior properties over composite foam materials with conventional reinforcements. In this chapter, an overview of hybrid composite foams using chemical modification and inter-fillers is discussed in general with detailed examples from scientific journals. Hybrid phenolic composite foam with advantages, such as excellent flame resistance, high mechanical strength, lightweight, less toxicity, good thermal stability, and low combustibility, can be successfully produced. However, there are several reinforcement parameters that could be modified to suit the desired final properties of PF, such as type, size, and shape of the reinforcement as discussed in this chapter. In addition, the compatibility between filler and filler matrix, weight fraction, and filler distribution are other important parameters that could promise the outstanding final properties of hybrid composite foam. Due to its excellent properties, the hybrid composite foam is capable of advanced and wide-ranging applications. Nevertheless, there is also a need for future studies to extend filler hybridization to further improve the mechanical strength, flammability, and toughness of PF, which may replace the available polymeric foam in future, such as polyurethane and polystyrene.

References

1. Desai A, Auad ML, Shen H, et al (2008) Mechanical behavior of hybrid composite phenolic foam. J CellPlast 44(1):15–36
2. Hu X, Cheng W, Nie W et al (2016) Flame retardant, thermal, and mechanical properties of glass fiber/nanoclay reinforced phenol–urea–formaldehyde foam. Polym Compos 37(8):2323–2332
3. Desai AA, Basbagill J, Nutt SR et al (2010) Diffusivity and climatic simulation of hybrid foams. J Cell Plast 46(5):461–478
4. Luo X, Yu K, Qian K (2018) Morphologies and compression performance of graphene oxide/SiO_2 modified phenolic foam. High Perform Polym 30(7):803–811
5. Liu J, Wang L, Zhang W et al (2020) Phenolic resin foam composites reinforced by acetylated poplar fiber with high mechanical properties, low pulverization ratio, and good thermal insulation and flame retardant performance. Mater 13(1):148
6. Li X, Wang Z, Wu L et al (2016) One-step in situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6(78):74903–74912

7. Landrock AH (1995) Handbook of plastic foams: types, properties, manufacture and applications. Park Ridge, New Jersey
8. Wang Z, Li X (2018) Synthesis of CoAl-layered double hydroxide/graphene oxide nanohybrid and its reinforcing effect in phenolic foams. High Perform Polym 30(6):688–698
9. Gao M, Chai ZH, Wang YH et al (2016) Phenolic foam modified with butadiene acrylonitrile rubber as a toughening agent. MatSci Eng–Chen (Ed.):155–158
10. Li L, Xu YZ, Wang CP et al (2012) Preparation and characterization of phenolic foam modified by nitrile butadiene rubber powder. Appl Mech Mater 204:4137–4142
11. Auad ML, Zhao L, Shen H et al (2007) Flammability properties and mechanical performance of epoxy modified phenolic foams. J Appl Polym Sci 104(3):1399–1407
12. GaoM YYL, Xu ZQ (2013) Mechanical and flame retardant properties of phenolic foam modified with polyethyleneglycol as toughening agent. Adv Mat Res 803:21–25
13. HorikawaT OK, Mizuno K et al (2003) Preparation and characterization of the carbonized material of phenol–formaldehyde resin with addition of various organic substances. Carbon 41(3):465–472
14. Yang H, Wang X, Yuan H et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 19(3):9831
15. Zhou J, Yao Z, Chen Y et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym Compos 35(3):581–586
16. Yang Z, Yuan L, Gu Y et al (2013) Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes. J Appl Polym Sci 130(3):1479–1488
17. Rangari VK, Hassan TA, Zhou Y et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 103(1):308–314
18. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Compos Part A-Appl S 34(9):899–906
19. Ma Y, Wang C, Chu F (2017) Effects of fiber surface treatments on the properties of wood fiber-phenolic foam composites. BioResources 12(3):4722–4736
20. Li X, Wang Z, Wu L (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. Rsc Adv 5(121):99907–99913
21. Mougel C, Garnier T, Cassagnau P et al (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer 164:86–117
22. Desai A (2008) Fiber reinforced hybrid phenolic foam. Dissertation, University of Southern California
23. Kim M, Kwon SH, Park H et al (2017) Glass fiber and silica reinforced rigid polyurethane foams. Exp Polym Lett 1:374–382
24. Kim M, Choe J, Lee DG (2016) Development of the fire-retardant sandwich structure using an aramid/glass hybrid composite and a phenolic foam-filled honeycomb. Compos Struct 158:227–234
25. Shen H, Lavoie AJ, Nutt SR (2003) Enhanced peel resistance of fiber reinforced phenolic foams. Compos Part A-Appl S34(10):941–948
26. Shen H, Nutt S, Hull D (2004) Direct observation and measurement of fiber architecture in short fiber-polymer composite foam through micro-CT imaging. Compos Sci Technol 64(13–14):2113–2120
27. Tang Q, Fang L, Guo W (2019) Effect of bamboo fibre length and loading on mechanical, thermal and pulverization of phenolic foam composites. J Bioresour Bioproduct 4(1):51–59
28. Saz-Orozco BD, Alons MV, Oliet M et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforcedphenolic foams. Compos Part B-Eng 75:367–372
29. Colombo M, Martinelli P, Zedda R et al (2015) Dynamic response and energy absorption of mineral–phenolic foam subjected to shock loading. Mater Des 78:63–73
30. Zhou J, Yao Z, Chen Y et al (2013) Thermomechanical analyses of phenolic foam reinforced with glass fiber mat. Mater Des 51:131–135

31. Guo Y, Hu L, Bo C et al (2018) Mechanical property of lignin-modified phenolic foam enhanced by nano-SiO_2 via a novel method. Chem Pap 72(3):763–767
32. Yuan H, Xin W, Yang H et al (2013) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 62(2):237–279
33. Song SA, Chung YS, Kim S (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93
34. Yu K, Luo X, Wang M et al (2018) Preparation and characterization of phenolic foam reinforced with expandable graphite and expanded graphite. J Cell Plast 54(3):545–559
35. Zeng Y, Luo X, Yu K et al (2019) EMI shielding performance of phenolic-based carbon foam modified with GO/SiO_2 hybrid nanomaterials. Phys Lett 715:166–172
36. Saz-Orozco BD, Alonso MV, Oliet M et al (2015) Lignin particle- and wood flour-reinforced phenolic foams: friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos Part B-Eng 80:154–161
37. Taki K, Yanagimoto T, Funami E et al (2004) Visual observation of CO_2 foaming of polypropylene-clay nanocomposites. Polym Eng Sci 44(6):1004–1011
38. Zhou J, Yao Z, Chen Y et al (2013) Mechanical and thermal properties of graphene oxide/phenolic resin composite. Polym Compos 34(8):1245–1249
39. Yan D, Xu L, Chen C et al (2012) Enhanced mechanical and thermal properties of rigid polyurethane foam composites containing graphene nanosheets and carbon nanotubes. Polym Int 61(7):1107–1114
40. Yu K, Zeng Y, Wang G et al (2019) rGO/Fe_3O_4 hybrid induced ultra-efficient EMI shielding performance of phenolic-based carbon foam. RSC Adv 9(36):20643–20651

Chapter 5
Toughened Phenolic Foams

Tiejun Ge, Kaihong Tang, and Ailing Zhang

1 Introduction

Phenolic foam is a new generation of flame retardant and thermal insulation materials, with high dimensional stability and low thermal conductivity [1]. British Petrochemical (BP) Company had already started to develop phenolic foam materials in the 1980s under the trade name "Cellobond" [2]. However, traditional phenolic foam materials generally have shortcomings such as high brittleness and easy pulverization, which limit the application of phenolic foams. The density of the rigid group (benzene ring) of phenolic resin to be large, the packing is tight, and the crosslinking density is high resulting in low elongation and high brittleness of the phenolic foam. Therefore, to more fully exploit the desirable properties of phenolic foam, the toughness must be improved.

In materials science, toughness is defined as the ability to resist fracture by absorbing energy, and it is usually expressed as the work done to form a fracture surface per unit area. Enabling a larger number of materials to participate in energy absorption is a basic challenge for toughening rigid polymers. Phenolic foam cannot give satisfactory fracture resistance no matter under standard test conditions or daily application. Over the past few decades, different approaches have been developed by researchers to toughen phenolic foams [3].

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The physical performance of polymer foams was determined by their cell density and cell uniformity. The toughness of phenolic foam materials was also mainly determined by the apparent density and cell structure of the foam. The viscosity and viscoelasticity of the foamable matrix, the foaming process, the type and weight fraction of the reinforcing particles all have a certain influence on the cell structure of the final phenolic foam. This chapter summarizes the factors affecting the toughness of phenolic foam, meanwhile classifies and discusses the methods of toughening phenolic foam.

2 Foam Molding

Phenolic foam molding generally needs to go through three stages: cell nucleation, cell growth, and foam stabilization. Each stage has its own control requirements due to the different functions. The ideal cell formation process is shown in Fig. 1. Figure 1a is a polymer-gas saturated solution mixed with resin matrix and foaming agent.

Figure 1b shows the cell nucleation, which is the foaming process. When the resin added with the foaming agent becomes a supersaturated solution of gas due to changes in temperature, pressure, and gas content, the gas can escape from the solution to form original microbubbles and then growth. The cell nucleus refers to the original microbubble, which is the place where gas molecules initially gather in the foamable matrix. The microstructure of the foam affects the toughness of the foam, and one of the key factors affecting the microstructure is cell nucleation [4]. The formation stage of cell nucleus plays a decisive role in the cell density and distribution. The number of cell nucleation determines cell density and can also affect cell diameter. The increase in the number of cell nucleation can lead to a gradual decrease in cell diameter. The cell nucleation rate is closely related to the concentration of foaming gas dissolved in the phenolic resin.

The open and closed cell, cell diameter, cell shape, and distribution of phenolic foam are mainly determined by the cell growth stage, as shown in Fig. 1c. When the external pressure of the foamable matrix decreases, the cells expand and the internal pressure decreases. Due to the effect of inertia, the cell still has a tendency to

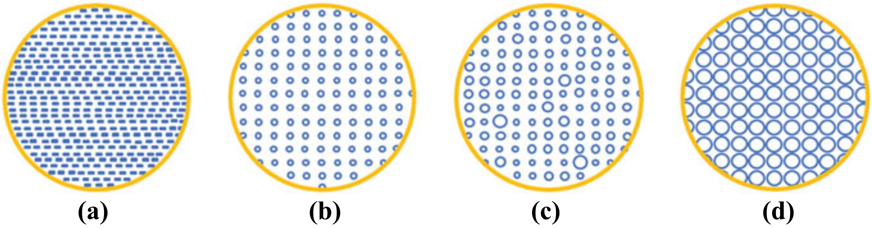


Fig. 1 Schematic diagram of the ideal cell formation process

expand after the internal pressure and the surrounding fluid reach a force balance, and the surrounding fluid is continuously pushed to flow radially outward until the cell reaches the maximum diameter. At this time, the internal pressure is lower than the fluid pressure, causing the surrounding fluid to begin to compress the cell toward the center of the cell. Then the internal pressure gradually increases, the internal pressure is higher than the fluid pressure again and the next expansion–compression vibration cycle begins. This cycle goes back and forth until the energy of the cell vibration system is exhausted and then stops the vibration. Some researchers have studied the cell vibration mechanism in the cell growth stage during the foam molding process. The results show that the vibration field is beneficial to improve the uniformity of cell, and the physical and mechanical properties of the foam. The factors that affect cell vibration and generation are the thermodynamic properties of the gas in the cell, the viscoelasticity of the resin, the gas–liquid interface tension, the external pressure, and initial conditions of the system.

During the curing process of phenolic resin to form foam, the liquid phase viscoelasticity gradually increases until it loses fluidity and cures, which proceeds simultaneously with the polycondensation reaction. The polycondensation reaction causes the molecular chain to grow and gradually become networked, the viscoelasticity of the resin is correspondingly improved, and the foam is stable after the reaction is completed. In the stage of foam stabilization, inhibiting the merging of cells to ensure cell density and preventing excessive loss of gas are two main issues. Only by effectively preventing the escape of gas can the cells be prevented from collapsing, and then a foam material with a better appearance can be obtained. Figure 1d shows the idealized cell structure. The more uniform the cell distribution and diameter, the better properties the phenolic foam gets. During the foam stabilization stage, a reasonable cooling rate also has an important impact on the density and properties of the final product. The faster the cooling rate, the greater the shrinkage rate of the cell wall. The gas in the cell has no time to cool and diffuse to the cell wall, which may cause the cell wall to rupture.

3 Toughness of Phenolic Foam

The toughness of phenolic foam is reflected in two aspects.

One aspect is that when the phenolic foam is under stress, the gas in the cells is compressed to produce gas trapping, and the cells and the resin matrix around the cells are deformed to absorb energy. Compression, rebound, and gas trapping phenomena can consume the energy of impact loads. In addition, the foam can also gradually terminate the impact load with a small negative acceleration, thus showing excellent shock absorption and buffering capacity. The foam has uneven cross-sections under force. This deformation process needs to absorb a lot of deformation work. Therefore, the higher the strength of the cell wall, the lower the possibility of cell rupture, the higher the energy consumed during the rebound process of the cell, and the better the toughness of the foam.

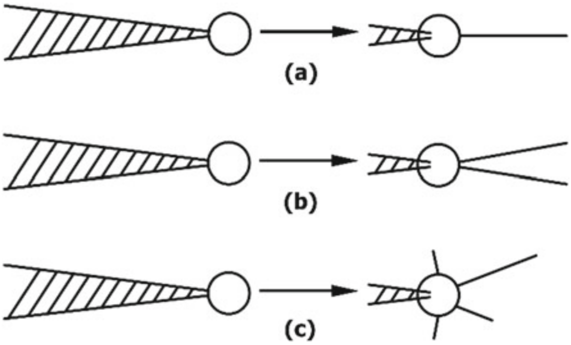


Fig. 2 Schematic diagram of crack extension

Another aspect is that the existence of cells can blunt the stress concentration at the crack tip, induce secondary cracks, and change the direction and path of crack extension. Macroscopically, it is manifested as an increase in crack extension resistance. As shown in Fig. 2, when the foam is under stress, there are three transformations in which the crack encounters the cell during the extension process: The main crack directly penetrates the cell and continues to extend forward, the secondary crack changes its original expansion direction and continues to extend forward, and the tertiary cracks turn into tiny cracks and do not continue to extend forward. Therefore, the rapid extension of cracks can consume more energy during the process of cell rupture. The better the toughness of the foam, the greater the crack extension resistance in the tough state, and the crack can be stopped after a certain distance of crack extension.

The cell geometry mainly depends on the process conditions in the cell growth stage. The faster the cell expands or the greater the shrinkage of the material, the greater the possibility of an open-cell structure. If there is external stress (tensile or shear) during the expansion of the cell, the cell may extend in the direction of the external force and obtain an anisotropic structure. To improve the toughness of phenolic foam, it is necessary to make the foam cell distribution and cell diameter as uniform as possible, so that the foam is evenly stressed. At the same time, in order to improve the deformation capability of the cells, it is also necessary to enhance the strength of the cell walls and the viscoelasticity of the resin matrix.

After the traditional phenolic foam material fractures, the crack source generated on the cross-section is relatively flat, and the crack spreads radially from the fracture source area to the surrounding, and the radiation is basically straight. It shows that the crack does not produce high elastic deformation during the extension process. When the foam is impacted, there is almost no resistance to the crack tip, which mainly reflects the characteristics of brittle fracture. Thus, in order to toughen the phenolic foam, it is necessary to increase the crack extension resistance of the foam material under stress. The phenolic foam can also be toughened by rapidly changing the crack extension direction to consume more stress load energy.

4 Cell Nucleus and Phenolic Foam Toughness

Phenolic foam generally chooses the physical foaming method. The foaming agent (inert gas or low boiling point liquid) and the phenolic resin matrix are directly mixed, and a large number of uniform and dense cell nucleus can be formed by dissolving and compressing the gas in polymer or by decomposition of the foaming agent. Then the cell nucleus expands into a phenolic foam with foam structure requirements. The cell nucleation stage is the main factor affecting the density and distribution of phenolic foam cells. Classical nucleation theory believes that there are three modes of cell nucleation: homogeneous nucleation, heterogeneous nucleation, and mixed mode. The formation of the cell nucleus is carried out in a metastable state. Homogeneous nucleation involves the nucleation of cells in the continuous phase (the gas or solvent dispersed phase) of the polymer matrix. Heterogeneous nucleation involves the nucleation of cells at the interface of two phases.

The cell structure of phenolic foam is shown in Fig. 3. The cell struts and walls determine the mechanical strength of the foam. Generally, microporous cell foam has higher strength than macroporous cell foam, because microporous cell foam has more struts and walls, which can beat more load, especially when the cell shape is uniform [5]. During the foaming process of phenolic foam, the resin with foaming gas moves along the molding wall, and the phenolic foam exhibits an anisotropic structure. The free energy required for heterogeneous nucleation is much lower than homogeneous nucleation, adding an appropriate amount of nucleating agent to the resin matrix can greatly promote the generation of cell nucleus.

When the system contains insoluble solid particles, cell nucleation will preferentially occur on the surface of these particles. Therefore, when using particles to reinforce phenolic foam, it is very important to determine the optimal foaming point to obtain excellent tough foams. Compared with pure phenolic foam, particle-reinforced phenolic foam has a completely round cell structure, smaller cell size and higher cell density [6]. The density and porosity of the particle-reinforced phenolic foams were lower than those of the pure phenolic foam due to the high cell density. The nucleating agent has an important influence on the cell density, size, and distribution of phenolic foam. Therefore, many researchers have chosen to toughen phenolic foam by adding nucleating agents in the preparation process.

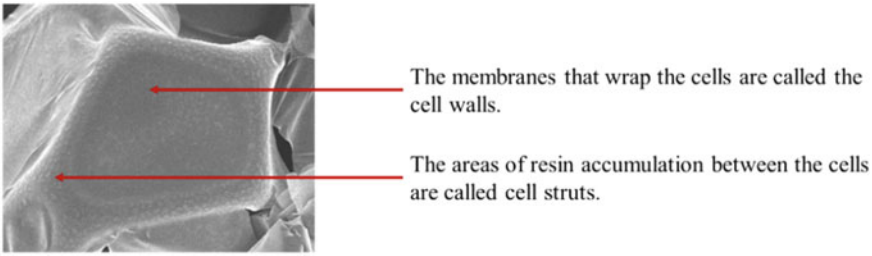


Fig. 3 Phenolic foam cell structure

4.1 Nucleating Agent

The common nucleating agents for toughening phenolic foam include hollow glass microspheres and nanoparticles.

The phenolic foam added with hollow glass microspheres is also called composite foam, and its cell formation method is different from traditional foaming. Hollow glass microspheres with a diameter of 20–250 μm and a wall thickness of 2 to 3 μm are added to a foamable phenolic resin matrix containing a curing agent, mixed uniformly, and pressurized and heated to cure into a phenolic foam. The addition of hollow glass microspheres can form voids in the resin matrix, similar to the micropores of traditional foam materials. The cell nuclei are hollow microspheres instead of gas, and then the resin matrix is foamed to obtain a combined foam, which is a filled-in composite. When there is an external force, the rigid hollow glass microspheres do not show elastic deformation but can change the crack direction. The main crack branches so that the cell structure will not develop into destructive cracks. Note that the amount of hollow glass beads added should not be too large. When the added amount exceeds the critical value of 67% (volume), the fluidity of the resin becomes poor, and cavitation is likely to occur between the hollow balls, which affects the cell structure.

Nanoparticle toughened phenolic foam is mainly achieved by affecting the two processes of cell nucleation and cell growth. The blending of nanoparticles and phenolic resin matrix expands the range of foaming temperature, which reduces the difficulty of processing to a certain extent. The reason is that a new interface is created after blending, and the nucleation energy barrier at the new interface is low, which is conducive to cell nucleation and can promote the formation of microporous structure. In addition to providing a large number of interfaces in the system, nanoparticles also have a certain barrier effect on gas, which can effectively prevent gas from escaping. In this way, the cell growth process is affected, and a phenolic foam with high cell density and small cell diameter is prepared.

Nanoparticles used to toughen phenolic foam are generally inorganic particles, such as nano-$CaCO_3$, nano-SiO_2, and nano-montmorillonite (nano-MMT), and also include multi-walled carbon nanotubes and graphene oxide, which are currently hot researched. These several common nanoadditives can affect the cell structure of phenolic foam materials, and the smaller the size, the better the formation of excellent cell structure. However, this also brings about the problem of nanoparticle dispersion, and uneven dispersion has a negative impact on the cell structure. Seung et al. found that the nanoparticles that have a high aspect ratio easily form entangled networks of bundles or ropes due to strong van der Waals interactions [7]. These networks can cause the higher viscosity of the resin and a poor dispersion state of the particles. In the foaming process, extremely high viscosity and poor dispersion of the particles lead to a high foam density and poor mechanical properties of the foam. Therefore, the focus of research involves solving the problem of dispersion of nanoparticles in the resin matrix. The higher the uniformity of the resin matrix network, the better the bending performance of the composite material. The addition of nanoparticles can enhance the thickness of the cell wall from the morphology, so the foam strength and toughness are improved. In addition to the above-mentioned common nanoparticles, Liu J et al. chose to grind red mud into fine particles to toughen phenolic foam, and the impact strength of modified foam increased by 82.3% [8].

4.2 Nucleation Density

The number and density of cell nucleation should be controlled within a reasonable range. When the amount of cells in the foam increases, the proportion of cells per unit volume increases, and the actual effective bearing area of the material against external loads after foaming will gradually decrease. The load that phenolic foam can bear is closely related to the effective bearing area of the foam. When the contribution of the cells to the strength of the foam can compensate for the strength loss caused by the reduction of the effective bearing area, the toughness of the phenolic foam material will be improved. When the cells cannot compensate for this part of the loss, the toughness of the phenolic foam material will decrease. Some researchers believe that fiber-toughened phenolic foam is achieved through the bridging effect of fibers [9]. The addition of fiber can increase the effective bearing surface area of the foam and help to toughen the phenolic foam [10].

Chopped glass fiber is an inorganic material and is easy to mix with phenolic resin evenly. The glass fiber treated with coupling agent is blended with phenolic resin and then foamed to prepare phenolic foam. The researchers tested and discussed the toughness of phenolic foam materials under different fiber reinforcement effects and found that as the content of chopped glass fiber increases, the bulk density increases and the brittleness decreases of the phenolic foam. The toughness of the chopped glass fiber toughened phenolic foam prepared by J. Zhou et al. increased by 48.1%, and the toughness of the phenolic foam modified by glass fiber and nucleating agent was increased by 85.2% [11]. Note that as the amount of chopped glass fiber increases, the viscosity of the blend increases, and the foaming process is difficult to control, so the amount of chopped glass fiber is generally controlled below 10%.

In order to save costs and prepare environmentally friendly materials, some researchers have begun to use natural fibers to toughen phenolic foam. Natural fiber toughened phenolic foam has low health hazard during processing, but polar fiber usually has poor compatibility with non-polar polymer matrix. In the process of preparing foam, natural fibers are usually modified to improve the fiber's water resistance and interface compatibility with polymers. For example, alkaline solution can change the chemical composition of the fiber and make the surface of the fiber rough, thereby improving the interface adhesion between the fiber and the resin. Natural fibers that are commonly used include wood fiber and acetylated fiber. The cells of natural fiber toughened phenolic foam are uniform and dense, and the toughness can be increased by at least 30% [12, 13].

There is a velocity gradient inside the foamable matrix in the shear flow field, which leads to the molecular orientation of the polymer. This orientation changes the distribution of voids in the foamable matrix, which in turn affects the cell nucleation process. Some researchers have found that the foamable matrix can form a large number of uniformly distributed nucleation points through the effect of the shear flow field on the molecular orientation. The greater the degree of polymer orientation, the higher the cell density. If the blowing agent is dispersed into the resin simply by high-speed stirring, the dispersion system is extremely unstable and easily damaged. Surfactants can reduce the interfacial tension and make the dispersion system thermodynamically stable. The surfactant acts as an emulsifier or foam stabilizer in it. Therefore, some researchers choose to toughen phenolic foam by adding different types of surfactants. In addition, as the number of cells increases, the number of macroporous cells increases, which increases the probability of cell merging and collapse. After the cell structure is destroyed, the phenolic foam is prone to stress concentration, causing the foam's toughness to decrease with the increase of the cell number. Therefore, the cell number and diameter of the foam should be maintained within a reasonable range when toughening the phenolic foam.

5 Cell Wall and Phenolic Foam Toughness

Phenolic foam is a porous plastic product with a phenolic resin matrix and a large number of cells inside. Since foam is composed of a large number of cells filled with gas, according to the cell structure, it can be divided into open-cell and closed-cell. When the gas diffuses and gathers near the cell nucleus, the cell gradually expands and becomes larger. When the cells grow to a certain extent, the ligament structure between the cells and the thickness of the cell wall mainly depend on the cell density.

There are two types of defects in the cell wall of phenolic foam with low closed-cell ratio. One is the pinhole-like opening as shown in Fig. 4a, which is caused by the rapid volatilization of the water droplets attached to the wall of the cell due to the heat released during the foaming process. The other is the crack-like opening as shown in Fig. 4b, which is due to the low strength of the cell wall during the foaming process, which cannot withstand the wall stretching caused by the increase in gas pressure in the cell. As shown in Fig. 4c, the foam with high closed-cell ratio has

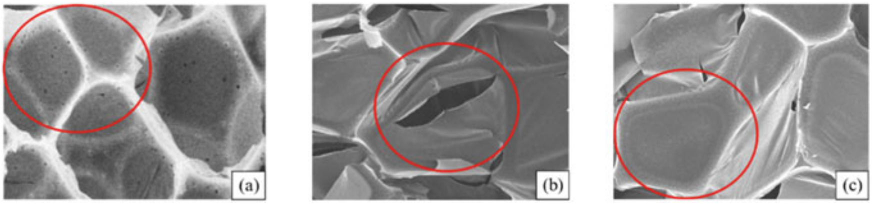


Fig. 4 Different phenolic foam cell wall structures: **a** pinhole-like opening, **b** crack-like opening, **c** closed-cell

a complete cell structure with no pinholes, cracks, or only a few cracks on the cell wall.

The higher the closed-cell ratio of phenolic foam, the more cells that can be used to bear the load, and the better the foam toughness. The cell wall and the strut of the closed-cell phenolic foam can bear the load together, and the rupture of the cell wall will not cause damage to the strut between cells. Therefore, the load that the closed-cell phenolic foam can bear is higher than that of the open-cell phenolic foam under the same conditions. The rupture of the cell wall of the open-cell foam will accelerate the destruction of the strut between cells. In order to prevent the rupture of the cell, it is necessary to limit the process of cell growth. Otherwise, the foam will become unstable, which may cause the cell wall to crack and the cell density to decrease sharply. Increasing the closed-cell ratio of the foam can start from two aspects: improving the expansion resistance of the foamable matrix and controlling the expansion speed of cell (which needs to match the time required for the stress relaxation of the cell wall).

5.1 Expansion Resistance of Foamable Matrix

Increasing the expansion resistance of the foamable matrix is to increase the strength and elasticity of the cell walls so that the cells are not easy to break during the growth stage. The expansion resistance of cell comes from the viscoelastic effect and surface tension of the phenolic resin matrix. Higher viscoelasticity and surface tension will over-resist the expansion of the cell, and too low will cause the gas to break through the cell wall and even cause the cell to collapse. When the cell grows, the surface area of the cell increases and the cell wall becomes thinner, and the foam becomes unstable. There are three methods to stabilize the foam:

1. Using a surfactant to reduce the surface tension of the resin matrix so that cells can grow uniformly, while reducing gas diffusion to stabilize the foam;
2. Controlling the viscosity and water content of the phenolic resin matrix to prevent further thinning of the cell wall to stabilize the foam; and
3. Improving the original rigid structure of the phenolic resin matrix, such as introducing flexible chains or elastomers into the resin matrix to increase the elastic load that the cell wall can bear during the expansion process.

5.1.1 Surfactant

The phenolic resin is mixed with the foaming agent and the curing agent under high-speed stirring, undergoes condensation reaction and then cured to obtain phenolic foam. The large amount of reaction heat released by the resin during the reaction vaporizes the foaming agent droplets, and the foaming matrix rapidly increases in volume while thickening. The foam in this state is unstable, and the cells may continue to expand or merge, collapse or burst. When the surfactant is added to the matrix, there is a balance between surface molecules, dissolved molecules, and molecules in the resin [14]. Surfactant molecular film obstructs and slows down fluid flow, thereby stabilizing the foam.

Denslow K R et al. studied the effect of the type and amount of surfactant on the properties of phenolic foam [15]. Experimental results show that surfactants can significantly reduce the surface tension of the phenolic resin matrix and can effectively control the foaming speed stability. The prepared phenolic foam has uniform cell diameter and distribution, which makes the foam stable.

Due to the poor compatibility between the components of the foamable matrix, the emulsifying performance of surfactants should be considered. The better the emulsification performance, the more uniform the mixing of the components, which is conducive to the formation of a uniform and microporous cell structure. It can speed up the reaction process and shorten the curing time. In addition, the surfactant must remain stable in the face of the strong acidity of the curing agent. Although there are many types of surfactants that can be used in phenolic foam, non-ionic surfactants are the best. Surfactants that are commonly used include fatty alcohol polyoxyethylene, polyoxypropylene ethers, alkylphenol polyoxyethylene ethers, and block copolymers of polysiloxane, polyoxyethylene, and polyoxypropylene. These surfactants not only have good foam stability but also have a strong emulsification.

5.1.2 Viscosity

The viscosity of phenolic resin is one of the most important performance indicators, the level of viscosity affects foaming conditions and foam properties. The high viscosity of the phenolic resin matrix will cause difficulties in uniform mixing of components, poor fluidity, and difficulty in filling the mold. Too high viscosity may also cause a lower initial speed of cell expansion and a smaller cell diameter. The low viscosity of the phenolic resin matrix may make it difficult for the resin to cure and foam at the same time, the blowing agent is easy to escape and macroporous cells appear, which is not conducive to the formation of a uniform and microporous cell structure. Therefore, the rheological properties of phenolic resin are a key factor affecting the nucleation and growth of cells, and it is an important basis for specifying foam molding processes and formulations. The main influencing factor in the late stage of cell growth is the diffusion rate, at which time the effect of the resin matrix viscosity is weakened. Material cooling or curing and cross-linking can help to increase the viscosity of the resin. The higher the degree of cross-linking, the higher the viscosity of the resin.

During the foaming and curing process, the cells may rupture due to the evaporation of water, and higher water content can increase the open-cell rate. Although lower water content can increase the viscosity of the resin and improve the cell structure; however, it may cause difficulty in the foaming process. And even if the water content is low, the open-cell structure may still appear when the temperature of the foam is too high due to the exotherm of the reaction. At high temperatures, the remaining water will generate a lot of steam. The cell ruptures when the total vapor

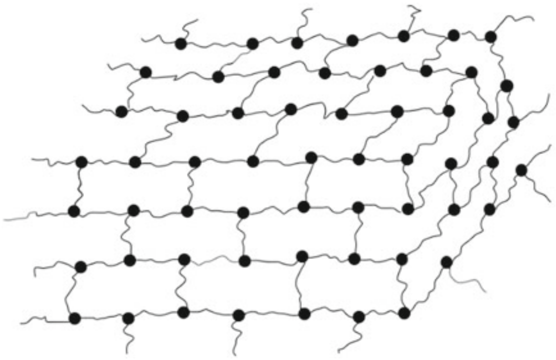


Fig. 5 Schematic diagram of phenolic resin cross-linked structure

pressure of water and blowing agent exceeds the cracking strength of the cell wall. In traditional foam preparation, the presence of water in the resin matrix acts as a heat sink to prevent the release of high heat. Rickle G K et al. studied the effect of water content on the closed-cell ratio and thermal conductivity of phenolic foam [16]. The research results show that when the water content is less than 7%, the phenolic foam has a higher closed-cell ratio, moderate apparent density, high compressive strength, and low thermal conductivity.

5.1.3 Toughened Resin Matrix

The physical interaction force between the macromolecular chains in the polymer comes from van der Waals force (also known as "intermolecular force") and hydrogen bonds. The magnitude of the force is related to the molecular structure of the polymer. This force imparts a certain strength to the polymer and also affects its processing properties. The foamable phenolic resin structure contains a large number of benzene rings connected only by methylene groups, and the resin forms a uniform and relatively stable three-dimensional network structure as shown in Fig. 5.5. This structure causes the density of the rigid group (benzene ring) to be large. The packing is tight and the degree of freedom of link rotation is small, resulting in high brittleness of the traditional phenolic foam. The cross-linking reaction of linear or branched polymer molecules into network structure or physical configuration can change the physical and mechanical properties of the polymer and the rheological properties of the polymer. The toughened resin matrix can bear more elastic load when the cells are expanded, and a phenolic foam with high closed-cell ratio, cell diameter and uniform distribution can be prepared.

When preparing phenolic resins, the common toughening method involves replacing phenol with alkylphenols with flexible chain, and reacting with formaldehyde to prepare phenolic resin. The most common alkylphenols are nonylphenol, pentadecylphenol (cardanol), tert-butylphenol, and bisphenol A. Alkylphenols that can completely replace phenol include nonylphenol and tert-butylphenol. Cardanol

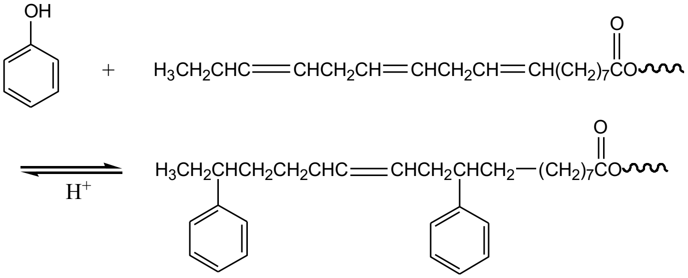


Fig. 6 Reaction process of tung oil-modified phenol

is widely used to replace phenol and react with formaldehyde to prepare resin with an excellent toughness due to its renewable and biodegradable properties [17]. They play the role of phenol in the synthesis process, and the resin can be prepared directly by basic synthesis process of phenolic resin. When alkylphenols replace phenol, it is necessary to avoid agglomeration of the resin during the preparation process.

Etherified-phenolic resin is a modified resin prepared by the etherification reaction between the modifier and the phenolic hydroxyl group. In addition to directly replacing phenol, some researchers choose to modify phenol first. They introduce flexible long chain on the phenol ring and the modified phenol reacted with formaldehyde to prepare flexible phenolic resin. The flexible alkyl chain links the brittle phenolic molecular chains, which effectively improves the brittleness of the phenolic foam. The most representative modifier is vegetable oil, as shown in Fig. 6 [18]. The conjugated bond of the long carbon chain undergoes a cationic alkylation reaction with phenol under acid catalysis, and the probability of the residual double bond participating in the reaction due to steric hindrance is small. The reaction product further reacts with formaldehyde under alkali catalysis to prepare resoles phenolic resin. According to this method of introducing long carbon chains into the resin structure, researchers have also introduced long chains of unsaturated fatty acids [19] and long chains of polyether [20] into the resin structure. The electrophilic substitution reaction is used to prepare flexible phenol, which is then polycondensed with formaldehyde to synthesize modified phenolic resin. The cell structure of the modified phenolic foam is obviously more uniform and dense than the traditional phenolic foam, and the foam has better toughness.

As a flexible group, ether bonds are often introduced into the molecular structure of phenolic resins to toughen phenolic foam. Polyurethane formed by polymerization of isocyanate compounds and polyether polyols contains very reactive—NCO groups. Some researchers introduced this group into the molecular structure of phenolic resin to improve the toughness of phenolic foam [21]. No matter what method is used to prepare polyurethane-modified phenolic foam, the reaction mechanism is the same. There are two main reactions: The hydroxyl group in the phenolic resin structure and the isocyanate group undergo a cross-linking or chain extension reaction, and the methylol group in the resole resin and the isocyanate group undergo a cross-linking reaction [22]. The introduction of flexible segments into the molecular structure of phenolic resin fundamentally changes the rigid structure of phenolic resin, thereby improving the toughness of foam products. At the same time, the characteristics of polyurethane are introduced into phenolic foam, such as high closed-cell ratio and low water absorption, which also speeds up the curing reaction and improves the strength of the product.

Some researchers choose small molecule ethylene glycol to toughen phenolic foam. According to the difference of infrared spectra of unmodified phenolic foam and ethylene glycol-modified phenolic foam (ethylene glycol content is 15% phenol), it is speculated that ethylene glycol may partially or completely generate glycerol derivatives under acid catalysis and participate in the main reaction to toughen phenolic foam. Lignin, urea, dicyandiamide, and tannin are also gradually introduced into the molecular structure of phenolic resin to toughen phenolic foam [23].

In addition to directly modifying the molecular structure of the phenolic resin to toughen the foamable matrix, adding a toughening agent or elastomer to the resin matrix to enhance the elasticity of the cell wall is also an effective method to toughen the phenolic foam. As a typical toughening material, elastomer can significantly improve the toughness of phenolic foam. The elastic body can deform when subjected to stress and absorb a large amount of load energy.

Elastomer toughened phenolic resin involves a blending process of toughened polymer and phenolic resin. In order to ensure the compatibility and uniformity of the mixture, the phenolic resin needs to be fully mechanically blended with the toughened polymer at a certain temperature to generate thermal and mechanochemical reaction [24]. Therefore, the phenolic resin is required to have no or little curing and cross-linking reaction during the blending process. The resin and toughening system must have a certain degree of miscibility in order to improve toughness and compressive properties. The miscibility between organic compounds can be predicted based on solubility parameters. Generally speaking, when the solubility parameters of two polymers differ by 0.5, they will not be miscible in any ratio. However, when preparing polymer blends with excellent properties, it is not desirable to have complete miscibility between the polymers but a certain degree of miscibility. In many cases, thermodynamic miscibility is the main driving force for uniform mixing between polymers. With the better miscibility of the two polymers, they are more likely diffuse each other to achieve a uniform mixing. The wider the transition zone, the more blurred the phase interface, the smaller the phase domain, and the greater the binding force between the two phases.

The commonly used toughening elastomer is rubber, which has good compatibility with phenolic resin. Mix the phenolic resin with an appropriate amount of liquid rubber to make the rubber phase uniformly dispersed in the phenolic resin by tiny particles. There are chemical bonds between the plastic phase and the rubber phase in the “sea-island” structure formed by the curing of rubber and resin. Rubber toughened phenolic foam is a physical blending modification, but the elastomer usually has active end groups (such as carboxyl, hydroxyl) and double bonds, they can undergo different degrees of grafting or block copolymerization with the methylol groups in the resole resin. Therefore, the toughening effect of rubber-toughened phenolic foam is better, and the heat resistance is also improved. Rubbers used to toughen phenolic foam, which commonly include nitrile rubber, styrene-butadiene rubber, natural rubber, and other rubbers containing reactive groups. The toughening effect is also related to the blending ratio. Too low rubber content cannot achieve the toughening effect, and high rubber content can affect the compatibility between the resin and the rubber. The amount of rubber added should generally be controlled between 5 and 20% [25].

Thermoplastic resins can also act as elastomers to toughen phenolic foams, such as epoxy resins and polyethylene glycols.

Polyethylene glycol (polyoxyethylene ether) main chain contains a large number of flexible ether bonds, and the chain ends are hydroxyl groups. The hydroxyl group of polyethylene glycol has affinity with the methylol group in the phenolic resin structure, which is beneficial to the compatibility of the two. Ge D et al. used polyethylene glycols of different molecular weights to toughen foams and found that polyethylene glycol-modified foams with molecular weights of 1000 and 800 have the best toughness [26]. When the molecular weight is 1000, the polyether flexible chain introduced into the foamable matrix is longer, which is beneficial to increase the tensile strength and elongation at break of cell walls. Since the added polyethylene glycol is quantitative, when the molecular weight is greater than 1000, the proportion of the hydroxyl groups at both ends of the molecular chain decreases and the probability of the hydroxyl group reacting with the methylol group of the phenolic resin structure is reduced. The introduction of polyethylene glycol can also be used to replicate the heat dissipation characteristics of water and reduce pinholes in the cell walls caused by water evaporation. When polyethylene glycol reacts with the terminal hydroxyl groups of a diisocyanate compound (such as toluene diisocyanate), the polyethylene glycol is changed to isocyanate-terminated polyoxyethylene ether. The terminal-NCO of its structure can react with the methylol of the molecular structure of the phenolic resin to chemically combine polyethylene glycol into the network structure of the phenolic resin, and the toughening effect will be better.

Usually, bisphenol-A epoxy resin is used to toughen phenolic foam, and the toughened foam also has excellent heat resistance. When epoxy resins are blended with phenolic resins, a ring cleavage etherification reaction between the epoxy groups and the phenolic hydroxyl groups or methylol groups in the molecular structure of the phenolic resins to form a highly cross-linked foamable matrix. The greater the cross-linking density, the higher the strength of the foamable matrix, the higher the load that the cell wall can bear, and the less possibility to break. Therefore, the toughness and strength of phenolic foam increase. In order to ensure that the epoxy group can react completely, it must be fully contacted with the phenolic resin matrix and mixed as evenly as possible.

5.2 Control the Rate of Cell Growth

In addition to the above methods of toughening phenolic foam, it is also necessary to control the expansion speed of cell and match the time required for the stress relaxation of the cell wall to obtain a phenolic foam with a higher closed-cell ratio. In order to stabilize the foam structure that has reached the expansion multiple, the appropriate curing timing and higher curing speed are also very important.

Shutovt FA found that phenolic foam usually has a bimodal cell structure [27, 28]. Observation of the foam material by scanning electron microscope shows that these foams contain macroporous cells with a cell diameter of 100–1000 μm and a wide distribution, as well as a large number of small cells with a cell diameter of less than 1 μm and a very narrow distribution. There are two peaks on the cell diameter distribution curve. The research results show that the strength of the bimodal cell structure foam can reach twice that of the unimodal cell structure foam of the same type and density. However, in the process of cell growth, the greater the difference in diameter between adjacent cells, the higher the possibility of cell merger. The expansion degree of the merged cells is likely to exceed the load-bearing capacity of the cell walls, causing the cells to rupture and collapse. The greater the difference in cell size, the greater the internal pressure difference of the cells, and the more unstable the cells. Reducing the surface tension of the cells can reduce the internal pressure difference, thereby slowing down the merging speed between the large and small cells. Attention should also be paid to the heating and cooling rate in the process of curing the phenolic foam. Fast heating and cooling rates may cause the cells to rupture due to the pressure difference between the inside and outside.

The rate of cell expansion is also related to the temperature during foaming. During the foaming process, a slower heating rate may cause the cell walls to gradually become thinner with the increase in the amount of pyrolysis gas generated. When the viscoelasticity of the cell wall matrix is not sufficient to suppress the expansion of the cells, the cells rupture to form a crack-like open-cell structure. Too fast a heating rate leads to rapid accumulation of pyrolysis gas, which may directly cause the foam to have an open-cell structure. Singh D et al. explored the synthesis process of phenolic resin and found that the control of the foaming temperature helped to form a uniform and microporous foam with excellent strength [29].

Some researchers have found that the cell structure of phenolic foam prepared by the microwave foaming method is more uniform [30]. Since the phenolic resin is a polar molecule, microwaves are applicable for its heating. The electromagnetic microwaves can increase the temperature of the resin uniformly and quickly, making it possible for a uniform foam structure to be obtained. The preparation process is shown in Fig. 7. Put the resin matrix mixed with the blowing agent and curing agent into the microwave device, and phenolic foam can be obtained after about 3–20 s. During the curing process, the escape of gas through the cell walls reduces the amount of gas that makes the cells grow. Therefore, if the cells do not solidify in time, the cells may tend to collapse or a large number of shrink, which may result in the prepared foam with macroporous cell structure instead of microporouscell structure. The microwave foaming process can cure the foam in time and reduce the appearance of macroporous cells.

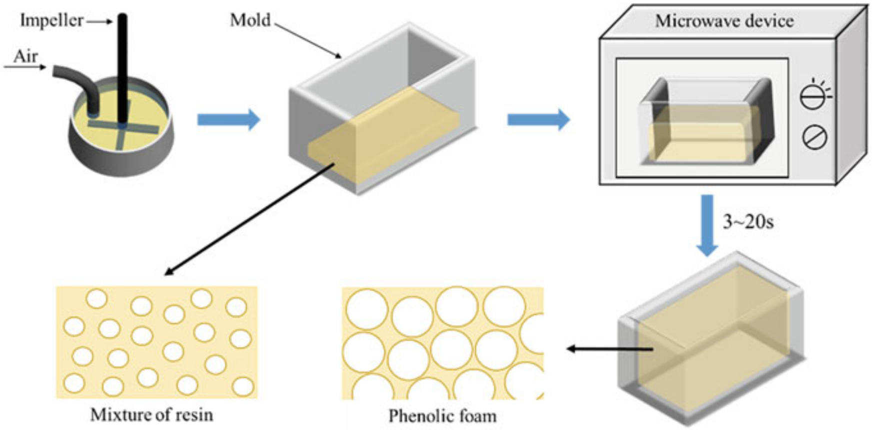


Fig. 7 Microwave foaming process

6 Testing and Characterization of Phenolic Foam Toughness

Brittle fracture is the fracture that occurs before yielding, and ductile fracture is the fracture that occurs after yielding. The elongation at brittle fracture is very low, while the elongation at ductile fracture is higher. Both brittle and ductile failure can be distinguished from the two aspects of failure energy and failure surface. Brittle fracture has lower failure energy, smoother fracture surface, and no plastic deformation. The ductile fracture has higher damage energy, rougher fracture surface, and plastic deformation of the material below the surface. The toughening of phenolic foam is to change the fracture mode of the foam from brittle fracture to ductile fracture, so that the foam has a higher elongation at break when it is stretched or impacted. The toughened foam is not easy to break when it is impacted, and it can also absorb more fracture energy once it is broken.

Therefore, mechanical performance testing (especially impact strength and bending strength) can be used as a measure of the toughness of phenolic foam. The higher the strength of the foam, the better the toughness, and vice versa. Through the mechanical performance test, the stress–strain curve of the material under various load conditions can be obtained. Compared with the strength data, the stress–strain curve can more accurately reflect the characteristics of the mechanical behavior of phenolic foam, and it is an important method to research the toughness of phenolic foam.

As shown in Fig. 8, the slope of the linear portion of the curve is Young's modulus, which corresponds to the elastic bending of the cell strut. When the stress exceeds the critical stress value of the material, the defect rapidly expands with long and branched cracks, and then obvious brittle fracture causes the stress to drop rapidly. The breaking point corresponds to the strain and strength of the stress fracture, respectively. When

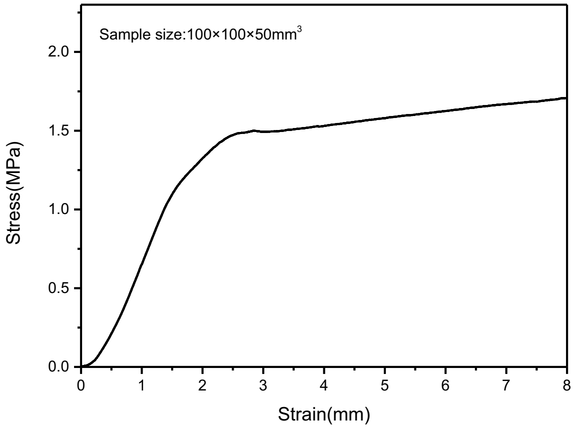


Fig. 8 Stress–strain curve of phenolic foam

the foam has one or two brittle fractures, a large number of cracks appear, which makes the foam enter the plastic yield platform. The platform area corresponds to the yield of the cell strut or the bending of the cell wall, and the stress of the platform area is also called elastic collapse stress. The foam is quite brittle in the mechanical performance test, and macroscopic yielding rarely occurs before fracture.

In the bending strength test of phenolic foam, bending deflection (bending displacement) can also be used as a measure of foam toughness [31]. Bending deflection refers to the distance of the specimen that deviates from the original position of the top or bottom surface of the span center during the bending test. As shown in Fig. 9, the displacement in the normal plane of the axis at the stress point on the foam axis is used to measure the bending deflection of the foam toughness. The greater the bending deflection, the greater the deformation that the foam bears, which means that it can bear higher strength, the better the toughness of the foam, and vice versa.

The fracture toughness of the foam can be measured at room temperature based on the ASTM (American Society of Testing Materials) standards [32]. The shape of

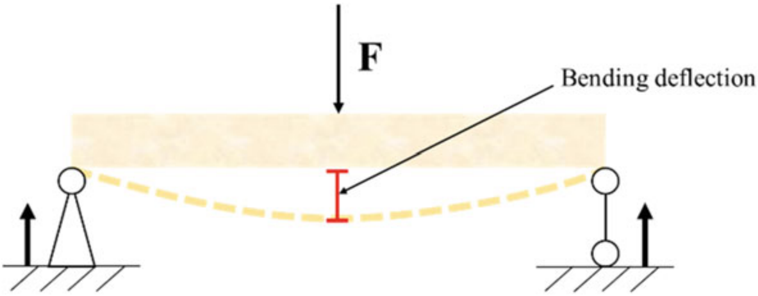
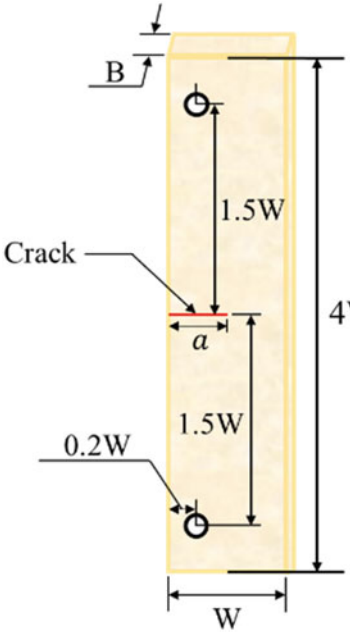


Fig. 9 Schematic diagram of bending deflection

Fig. 10 Schematic diagram of phenolic foam fracture toughness testing



the test sample is shown in Fig. 10. The tensile load was eccentrically applied to the single-edge-notch (SEN) sample. The length of the pre-crack ***a*** was 12 mm, which was generated by the tapping method using a razor blade [33]. The critical stress intensity factor (K_{IC}) was calculated as follows:

$$K_{IC} = \frac{P_Q}{B\sqrt{W}} f(a/W) \tag{5.1}$$

$$f(a/W) = \frac{\sqrt{a/W}(1.4 + a/W)}{(1 - a/W)^3}\left[3.97 - 10.88(a/W) + 26.25(a/W)^2\right] \\ -38.9(a/W)^3 + 30.15(a/W)^4 - 9.27(a/W)^5 \tag{5.2}$$

where P_Q is the critical fracture load, ***a*** is the length of the pre-crack, ***B*** is the thickness, ***W*** is the width of the sample, and *f(a/W)* is the geometric factor. The resulting fracture toughness (K_{IC}) unit is Kpa·$\mathrm{m}^{1/2}$. The higher the K_{IC} value, the better the toughness of the foam. This test result can be compared and analyzed with the tensile strength test result, and the conclusions obtained are more convincing.

The toughness of phenolic foam has a great relationship with the cell structure. The more uniform the cell distribution, the smaller the cell diameter, and the higher the closed-cell ratio, the better the foam's toughness [34]. Therefore, observing the microstructure of phenolic foam is also one of the effective methods to characterize foam toughness. The scanning electron microscope (SEM) objective lens magnification can be 10 times more than 300,000 times, which can be used to observe very small cell structures, such as structural defects that damage the sample foam, compare the cell microstructure of the toughened phenolic foam with that of the untoughened phenolic foam, and use the image analysis software to calculate the cell distribution and cell diameter range. The smaller and more uniform the cell diameter, the higher the stress load that the phenolic foam can bear. In addition, the cell walls and struts of the closed-cell phenolic foam can bear the load together to improve foam toughness.

The failure surface of the foam after the impact strength test can also be a lateral characterization of foam toughness. The cracks of the cell wall on the failure surface of the foam reflect whether the cell wall can quickly change the direction of crack extension to consume more load energy when the foam is impacted. If there are a large number of cracks and changes in the extension path, as well as the deformation of the cells and surrounding matrix resin, it may be that the foam consumes a lot of energy when subjected to impact, so the toughness of the foam is improved.

7 Conclusion

This chapter summarizes and analyzes the factors that affect the toughness of phenolic foam and discusses the influence of foam cell structure and cell wall strength on foam toughness. The energy consumed during the rebound process of the cell and the resistance of crack extension are the two main factors affecting the toughness of the phenolic foam. The toughness of phenolic foam can be increased by improving the uniformity of cell distribution and cell diameter and enhancing the deformation capability of the cells (which is the strength of the cell walls and the viscoelasticity of the resin matrix). Adding a nucleating agent during the foaming process, increasing the effective bearing area of the foam and controlling the shear rate help to improve the uniformity of cell distribution and cell diameter. Adding a nucleating agent during the foaming process, increasing the effective bearing area of the foam and controlling the shear flow field help to improve the uniformity of cell distribution and cell diameter. Improving the deformation ability of the foam cells can start from two aspects: improving the expansion resistance of the foamable matrix and controlling the expansion speed of cell (which needs to match the time required for the stress relaxation of the cell wall). As new techniques and methods emerge for toughening phenolic foams, we anticipate that researchers will develop phenolic foams with excellent toughness to be applied in a wider range of new fields.

References

1. Tondi G, Zhao W, Pizzi A et al (2009) Tannin-based rigid foams: A survey of chemical and physical properties. Bioresour Technol 100:5162–5169
2. IB, (1983) British firm develops phenolic foam process. Chem Eng News 61:10
3. Hu X, Cheng W, Wang DM (2014) Properties and applications of novel composite foam for blocking air leakage in coal mine. Russ J Appl Chem 87:1099–1108
4. Jin F, Zhao M, Park M et al (2019) Recent trends of foaming in polymer processing: A review. Polymers 11:953
5. Zhang Y, Wang Q, Li R et al (2020) A novel phenolic foam-derived magnetic carbon foam treated as adsorbent for rhodamine B: characterization and adsorption kinetics. Curr Comput-Aided Drug Des 10:159
6. Kuncir EJ, Wirta RW, Golbranson FL (1990) Load-bearing characteristics of polyethylene foam: an examination of structural and compression properties. J Rehabil Res Dev 27:229
7. Song SA, Chung YS, Kim SS (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93
8. Liu J, Li X, Zhou C (2018) Mechanical and thermal properties of modified red mud-reinforced phenolic foams. Polym Int 67:528–534
9. Cheng H, Hong C, Zhang X et al (2016) Super flame-retardant lightweight rime-like carbon-phenolic nanofoam. Sci Rep 6:33480
10. Desai A, Nutt SR, Alonso MV (2008) Modeling of fiber-reinforced phenolic foam. J Cell Plast 44:391–413
11. Zhou J, Yao Z, Chen Y et al (2013) Thermomechanical analyses of phenolic foam reinforced with glass fiber mat. Mater Des 51:131–135
12. Ma Y, Wang C, Chu F (2017) Effects of fiber surface treatments on the properties of wood fiber–phenolic foam composites. BioResources 12:4722–4736
13. Liu J, Wang L, Zhang W et al (2019) Phenolic resin foam composites reinforced by acetylated poplar fiber with high mechanical properties, low pulverization ratio, and good thermal insulation and flame retardant performance. Materials 13:148
14. Ziarati HB, Fasihi M, Omranpour H (2020) The effect of resin formulation on the cellular morphology and mechanical properties of phenolic foams. J Appl Polym Sci 137:48331
15. Denslow KR, Rickle GK (1989) Surfactant effects in phenolic foam resins. J Cell Plast 25:31–42
16. Rickle GK, Denslow KR (1988) The effect of water on phenolic foam cell structure. J Cell Plast 24:70–78
17. Bo C, Yang X, Hu L et al (2019) Enhancement of flame-retardant and mechanical performance of phenolic foam with the incorporation of cardanol-based siloxane. Polym Compos 40:2539–2547
18. Chen M, Yuan X, Wang J et al (2008) Experimentation on linseed oil modified phenolic resin as friction material. Chin J MechEng 44:190–194
19. Strocchi A, Lercker G (1979) Cardanol in germ and seed oils extracted from cashew nuts obtained by the oltremare process. J Am Oil Chem Soc 56:616–619
20. Ge T, Tang K, Tang X (2019) Preparation and properties of acetoacetic ester-terminated polyether pre-synthesis modified phenolic foam. Materials 12:334
21. Yang H, Wang X, Yu B et al (2013) A novel polyurethane prepolymer as toughening agent: Preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 128:2720–2728
22. Xu W, Chen R, Xu J et al (2019) Preparation and mechanism of polyurethane prepolymer and boric acid co-modified phenolic foam composite: Mechanical properties, thermal stability, and flame retardant properties. Polym Adv Technol 30:1738–1750
23. Londoño ZC, Du J, Chang H et al (2018) Lignin Modifications and perspectives towards applications of phenolic foams: A Review. Bioresources 13:9158–9179
24. Xu P, Yu Y, Chang M et al (2019) Preparation and characterization of bio-oil phenolic foam reinforced with montmorillonite. Polymers 11:1471

25. Megiatto JD, Ramires EC, Frollini E (2010) Phenolic matrices and sisal fibers modified with hydroxy terminated polybutadiene rubber: Impact strength, water absorption, and morphological aspects of thermosets and composites. Ind Crops Prod 31:178–184
26. Ge D, Wang S, Hu F (2003) Study of phenolic resin and foam modified by PEG and active polyethers. Fiber ReinfPlast/Compos 6:22–27
27. Fyodor FA (1986) Morphology of integral (structural) polymer foams. Makromolekulare-Chemie. MacromolSymp 2:113–123
28. Shutov FA (1983) Foamed polymers cellular structure and properties. Industrial Developments. Springer, Berlin, pp 155–218
29. Singh D, Ohri S (2010) Effect of reactant ratio and temperature on the characteristics of phenol-formaldehyde foams. J Appl Polym Sci 27:1191–1196
30. Kim BG, Lee DG (2008) Development of microwave foaming method for phenolic insulation foams. J Mater Process Technol 201:716–719
31. Kumar SA, Ahmed KS (2014) Flexural behavior of stiffened syntactic foam core sandwich composites. J Sandw Struct Mater 16:195–209
32. ASTM (2015) Standard test method for translaminar fracture toughness of laminated and pultruded polymer matrix composite materials. ASTM Int E1922–04
33. Choe J, Kim M, Kim J et al (2016) A microwave foaming method for fabricating glass fiber reinforced phenolic foam. Compos Struct 152:239–246
34. Dang A, Zhao Z, Tang C et al (2019) Effect of phenolic resin on micropores development in carbon foam with high performance. Materials 12:1213

Chapter 6
Shape Memory Phenolic Foams

Umesh R. Mahajan and S. T. Mhaske

1 Introduction

The modernization of the world seeks attention to develop smart polymeric material with tailor-made properties with high-end applications. In consonance with this shape memory foam (SMF) gains a special place in the territory of new material development and technology related to it. Shape memory foam is a unique material that can be responding to external stimuli, such as heat, light, magnetic field, solvent, water, etc., and regains its shape when the external stimuli are removed. Foam composition and morphology together with polymer processing are the main causes of the shape memory effect. As far as the polymeric foam is concerned, transition temperature plays an important role in the shape memory effect along with polymeric configurations. Below a glass transition temperature (Tg) polymer exhibits a glassy state which can be considered as an elastic state. Above Tg, polymers show a rubbery state which is deformable. The shape recovery process happens in order, fabrication consists of material of choice for shape memory effect, heating the material above Tg to deform the material into a new configuration, cooling the material below Tg to maintain the constrain, and finally removal of it.

Phenolic resins are used worldwide. Resol is the most abundant phenol–formaldehyde resin used for foam formation. The unequivocal properties of phenolic foam demand exploitation in some highly special applications like the manufacturing of space shuttles. Despite the way that both phenolic resin and the phenolic foam itself have long accounts, more up-to-date applications have gone through a moderate turn of events. They are known for their high thermal stability, thermal insulation, fire resistance with no dripping behavior, and less toxic gas production while combustion. But they show pulverization tendency and are physically brittle. These obstacles can be hurdled by either changing the base components for foam formulation or by

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reinforcing the polymeric foam with the material for tailor-made properties. Other than constantly improving the exhibition of the current materials, the advancement of new materials should suit the necessities of genuine applications to accomplish maintainability over the long haul. Stimuli-responsive foams materials have a high potential for applications in an insignificantly obtrusive medical procedure. Degradable inserts could be embedded into the human body in a compacted shape through a little cut where they acquire their shape important for the particular application in the wake of warming up to internal heat level. After a characterized timeframe the foam is degraded. In this case ensuing medical procedures to eliminate the foam isn't important. For applications in biomedicine, it is important to have customized shape memory polymers whose warm, mechanical, or debasement properties can be changed over a wide go. These are groups of polymers in which naturally visible properties can be constrained by a specific variety of sub-atomic boundaries.

2 Need and Purpose of Shape Memory Phenolic Foam

Shape memory phenolic foam shows a concatenation of switch properties. These kinds of systems improved the performance of foam material along with various property enhancements. These SMFs allow the integration of the properties of foam with stimuli responses. They have potentially changed their shape according to the way of stimuli implemented and thus impart multiple properties in the primary structure of the foam. They have the potential to impart any features such as magnetic, thermal, mechanical stress, and response to that material. The development of such switchable material enables us to prepare utterly new SMF materials that have better properties than that of conventional SMF materials.

3 Properties of Shape Memory Phenolic Foam (SMPF) and Approaches to Enhance Shape Memory Effect

The SMPF material governs shape change properties against a stimuli response. Generally, this behavior can be measured by proving heat as a stimulus, then the material is subjected to compression to form a mechanically compact shape. Again the material is heated to gain its original form followed by cooling. The SMPF material exhibits a combination of explained properties with lower flexural and compressive strength which makes this material more friable than others. The mechanical-based properties included the observance of high strength values in diverse temperature and environmental conditions. Also, it is well-known for its excellent fire-retardant properties. Their unique chemical structure offers excellent fire-retardant behavior. Once exposed to a flame, these resins release very low amounts of smoke and toxic fumes and are well-known for their natural tendency to form a porous carbonaceous substance that provides a barrier effect. Another category of properties defines the inherent strength properties of the material with its excellent thermal stability. This class comprises those materials which have excellent thermal stability and low thermal conductivity. Low densities make it possible to manufacture light structures with rigid components. Low thermal conductivity ensures reliable and economical insulations. Low rigidity makes foams attractive for energy-absorbing applications.

3.1 Mechanical Properties

SMPF shows low values for compression and flexural modulus which increases the breakdown tendency of material under a smaller value of the load. As a consequence, many researchers have reported their work based on the improvement of these properties with an increase in compression value and flexural modulus which ultimately decreases the friability of material [1]. The two approaches that are widely used in the polymeric sectors worldwide to improve the performance of polymeric material in the specific application are as follows:

- Chemical modification in phenol–formaldehyde resin;
- Addition of filler (fibers, a particle with specific geometry as a reinforcement).

As a rigid foam SMPF is anxious by the variation in compressive stress vs strain according to the density of the material. It is worth perceiving the fact that the compressive strength and Young's modulus increase with an increase in the density of the material. Regarding chemical modification, the foams are generally cured at 80 °C. There are exemptions for those that are cured at 70 °C and utilized an acid for curing. It is impossible to establish the stoichiometric relation between the OH functions of the phenolic resin and the reactive functions of the modifier because the amount of OH function is not quantified. Nevertheless, the modifier content is usually between 0 and 10 wt.%. Moreover, the filler parameters such as size, shape, geometry, surface energy, and loading percentage could change the final properties of SMPF.

3.2 Influence of Cell Size

The microstructure is often a reason for the better mechanical properties of foam material. The origin of this dependence may come from the cell density, a different distribution of the cell size, the solid fraction content, or heterogeneity across the structure. One approach for mechanical improvement includes keeping all parameters constant and produce smaller cell size foam. Moreover, various studies report the mechanical properties as a function of cell size. By changing the thickness of the polycaprolactam-based foam, the diverse size of the cell has been accomplished in the scope of 80–170 μm. An increase in the cell wall thickness and cell wall density increases the compressive modulus of the foam [2]. A 0.5–4.2 mm thick open cell with constant density crosslinked glassy carbon foam showed the independency of cell size on Young's modulus, but it is inversely proportional to flexural and compressive strength. This happens due to the decrease in the strut strength which increases the cell size [3]. The impact of cell size on the semi-static pressure mechanical conduct and the deformation behavior of plastic shut cell aluminum foams have been inspected. The result on the compressive property is surprising. Young's modulus increases with cell size. However, the cell wall thickness increases with cell size [4]. The brittle Mg alloy foam of fixed density and uniform structure has been subjected to compression property evaluation. This foam shows better deformation stability when being tested. Also, the load has been shared with the neighboring cell structure as the cell size decreased. Strain densification remains as it is [5]. A closed-cell styrene-acrylonitrile foam of density 0.15 lb/ft^3 showed the affection of cell size enhancement, which ultimately reduces the compressive strength and Young's modulus. It has occurred that there is no relation between moduli and relative density [6]. A linear and nonlinear compression behavior of polystyrene foam with different cell sizes has been investigated. Above 18% solid fraction, the compressive strength and Young's modulus increase with cell size.

Fillers as a reinforcement play a major role in the structural designing of cells in phenolic foams. The solubility of fillers determines the properties of the final foam product. As long as the system is homogenous, numerous and regular size cells are produced. They followed three mechanisms.

- Fillers act as a nucleating agent during foam formation.
- They increase the system viscosity that limits the growth and coalescence of cells.
- They act as a stabilizer during the mixing step and before the foaming stage.

All the above mechanisms combinedly promote the formation of a small size uniform cell structure. Reinforcement can be added in the form of fiber, particle, nanoparticle, hollow glass beads, and core–shell particles.

Concerning particles, mean cell diameter decreases with an increase in particle size due to a reduction in the surface area which ultimately results in higher compressive strength. A multiwalled carbon nanotube and graphene-reinforced phenolic foam have been investigated for their controlled morphology. It was found that the curing reaction happens at low temperature as early as reinforcement act as a catalyst. The density and porosity of reinforced foam were lower than standard phenolic foam due to high cell density. Compressive strength has increased from 71 to 157% [7].

Graphene-oxide-reinforced phenolic foam shows an increase in impact toughness with an increase in graphene oxide content. It showed a drastic increase in impact toughness after 0.5% addition of reinforcement [8]. Titanium nitride (TiN) nanoparticle-reinforced phenolic foams have shown an enhancement in compressive strength and tensile strength. At the point when the dose of TiN nanoparticle was 1%, compressive and tensile strength showed a 10% increment as compared to virgin phenolic foam [9]. Glass-bead-reinforced phenolic foam composite was evaluated for its mechanical properties. Results showed that a 10% addition of reinforcement gives higher compressive strength over nonreinforced phenolic foam [9].

Cellulose fiber-reinforced phenolic foam was fabricated and tested for its compressive strength. Results showed that there was a 13% decrease in cell size when a 2% addition of reinforcement is done. Also, reinforced phenolic foam showed the increment in compression modulus and strength by 21% and 18% at 2 wt.% loadings of cellulose fiber [10].

The activated carbon-reinforced microcellular phenolic foam was established and tested for its mechanical properties. It was found that the cell size and thickness decrease with an increase in activated charcoal content. The average compressive strength was found to be increased by 9% with only 1% addition [11]. Cloisite clay nanoparticle-infused phenolic foam was developed. The mean cell size was decreased to 50 μm when 2% of Cloisite clay was added. The reinforcement showed a 160% increase in compressive strength and 182% in compression modulus [12]. Lignin particle and wood floor-reinforced phenolic foam have been produced. At 8.5% expansion, the mean cell size was diminished by around 31%. Then again, a 1.5% expansion of the wood floor diminished the cell size less significantly just by 9% to 81 μm [13].

Another approach to enhance mechanical properties is the chemical modification of phenolic resin. Many polymeric species were found to be incorporated in phenolic resin to modify its compression and flexural strength with a decrease in friability. Most often, polyurethanes and polyethylene glycols (PEGs) have been utilized. The fusion of 3–7% castor-based polyurethane prepolymer in phenolic resin brought about an expansion in cell size by 18–59% [14]. PEG modified with boric acid to form a PEG borate was used as a toughening agent in phenolic foam. The mean cell size was decreased by 56%, 17%, and 17% on the addition of 4.5% of boron-modified PEG 200, 400, and 600 [15].

Regarding SMPF many approaches could be compared to enhance its mechanical properties. Various techniques that improve mechanical execution by modifying cell size are as per the following:

1. Surface stabilization of phenolic resin during mixing step through the surfactants adsorbs at phenolic–droplet resin interface and reduce coalescence of droplets.
2. Filler with surface modification may act as a stabilizer in emulsion by the Pickering phenomenon.
3. Utilization of a high boiling point foaming agent increases the cell diameter.
4. Process parameters such as time and speed of mixing influence the size and number of cells.

3.3 Compressive Strength

Compressive strength is the limit of a material or structure to withstand loads tending to decrease the size, rather than which withstands loads tending to extend. Ultimately, compressive quality restricts a material from being pushed together. It is one of the prominent properties in the application of shock absorption. The compressive strength of foam relies on the foam density as well as the toughness of the cell wall. There are three main categories to improve the compressive strength of phenolic foam by modifying the density.

1. Fiber reinforcement;
2. Addition of inert particle;
3. Chemical modification of the phenolic resin.

The first challenge to improve the compressive strength is the uniform dispersion of reinforcement in the phenolic resin matrix during foam production. The addition of reinforcement increases the density of the foam. As the external phase is included, it expands the thickness of the phenolic pitch and brings about issues during the foaming process. The enhancement in compressive strength by fiber reinforcement is based on the properties of fiber, such as stiffness, loading percentage, orientation in foam, and compatibility with phenolic resin. Fiber stiffness plays an important role in foam reinforcement. The compressive strength of phenolic foam was increased by 275% after adding 5% of glass fiber and by 36% after the addition of the same amount of aramid fiber [16]. Fiber orientation in the direction of foaming significantly enhances the compressive strength due to the isotropic nature of the foam.

Another significant factor of support liable for compressive property upgrades is the similarity between the phenolic resin and fortified strands. Alkali-treated aramid fiber increases the polar function of the surface and interacts more vigorously with phenolic resin. This improved the interfacial adhesion between the fiber and phenolic resin matrix. After the addition of 6 wt.% in phenolic resin, the compressive strength was increased by 67% as compared with unmodified fibers [17]. Besides this, an appropriate amount of fiber reinforcement into the phenolic resin needs to be promised for better mechanical properties. The addition of 2 wt.% of cellulose fibers in phenolic foam increases the compressive strength by 18%, while at 8 wt.% the loading is reduced by 19%. Bamboo strands of various lengths (<1 mm, 1–3 mm) have been fused into the phenolic foam to improve their mechanical properties. The strands with 1–3 mm length at 2.5 wt.% upgrade the compressive quality from 0.103 MPa to 0.130 MPa by 26.21% [18]. Among fibers, glass fibers are the best material to enhance the compressive property of foam due to inherent stiffness [10].

Numerous types of nano/micro/macroparticles are also used as reinforcement to improve the mechanical properties of phenolic foams. Particle reinforcement is based on the same mechanism as for fibers, i.e., their stiffness, loading percentage, and orientation in foam. While foam formation particle also acts as a nucleating agent by providing a heterogenous surface for growth which increases foam density, clay as reinforcement has gained so much attention related to the enhancement in mechanical properties. A 17% increase in compressive strength after the addition of attapulgite modified with hexadecyl trimethyl ammonium bromide (HTAB-ATP) has been reported [19]. Fortification of 0.8 wt.% of expandable graphene oxide with silica nanosphere has indicated the improvement in compressive quality by 70–80%[20]. Another fruitful endeavor has been made by the utilization of zirconium phosphate-graphene oxide hybrid to improve compressive quality. Results indicated

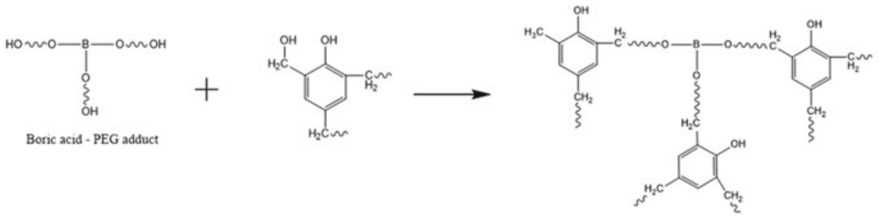

Fig. 1 The reaction of PEG–boric acid while curing of phenolic foam [15]

that compressive strength has been increased by 38% when the blended hybrid was used [21].

Chemical modification has been gaining attention since long back. It is typically based on the introduction of a flexible chain segment in the rigid phenolic backbone which decreases the crosslinking density of the phenolic foam and yield high strength. Mostly polyurethane, PEG urethane ether, dicyanamide, and epoxy long-chain components are used to modify phenolic resin.

A reaction of modified boric acid and PEG was performed to obtain a moiety with three functionalities which later crosslinked with methylol groups of phenolic resin, as shown in Fig. 1. Virgin PEG and boric acid-modified PEG were added in phenolic resin at a measure of 4 wt.%. Compared to pure PF foam, the compression strength of PEG400-toughened PF foam increases by 30.0%, whereas the compression strength of boric acid-modified PEG toughened foam increases by 80%, respectively. In both cases, compressive strength was found to increase, whereas in PEG-modified boric acid efficiency of improvement is higher. The reason for this is an increase in flexible chain length to a certain extent decreases crosslinking density, and the material can achieve high strength [15].

A new approach to introduce phosphorus and nitrogen-containing polyurethane backbone in phenolic resin has been studied as shown in Fig. 2. A 3% addition of polyurethane block improves the compression strength by 19%, whereas the advantage of polyurethane in phenolic resin lies in the chain length of the polyurethane segment [22].

A novel phosphorous and silicon base polyurethane prepolymer was used in phenolic resin to enhance compressive strength, as shown in Fig. 3. At 3% loading, the compressive strength was increased by 136%. It was also noticed that the density of the prepolymer-modified phenolic foam is higher than the unmodified phenolic foam [23].

Another endeavor has been to use dicyanamide to adjust the phenolic foam properties. The adjustment improves the compressive quality by 180% with the expansion of 8% dicyanamide to the phenolic resin [24].

An epoxy-modified phenol–formaldehyde resin is shown in Fig. 4. An improvement in the compressive strength of phenol–formaldehyde resin from 0.57 MPa to 108.20 MPa corresponds to the increase in the foam density. It is surprising that the increase in compressive strength is around 19,000%. Hence the results seem to be incongruous [25].

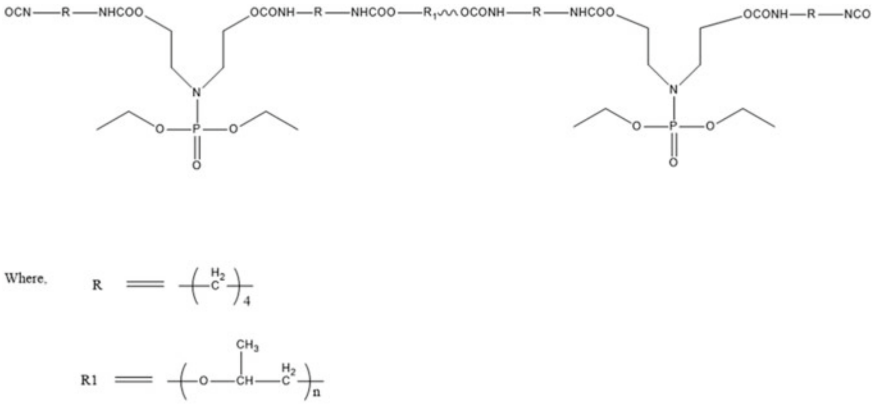

Fig. 2 Phosphorous and nitrogen-containing polyurethane segment [22]

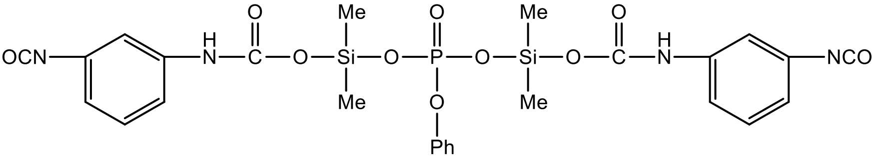

Fig. 3 Phosphorous and silicon-based polyurethane prepolymer [23]

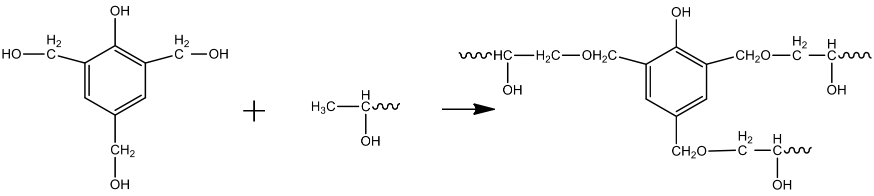

Fig. 4 Epoxy-modified resol resin synthesis process [25]

A phosphorus-containing tung oil-based siloxane-hardened phenolic foam has been set up to improve its mechanical properties. It was discovered that the compressive quality of the bio-based phenolic foam has expanded from 0.20 MPa to 0.31 MPa by 79.6% where the density of the material is unaffected [26]. As of late, another detailing has been created by utilizing kraft lignin as a greener feedstock for bio-based phenol–formaldehyde sap for foam creation. At 20% phenol replacement proportion, the compressive quality was discovered to be 1.012 MPa [27]. A novel solid acid catalytic phenolation measure has been embraced for hydrolysis of lignin, and thus the modified lignin has been utilized in lightweight phenolic foam fabrication. The compressive strength was found to decrease from 0.37 MPa to 0.27 MPa at 50% phenol substitution [28].

Among the entirety of the above which drew closer examination, fiber fortification gives the best improvement in compressive quality because of the characteristic properties like fiber solidness and direction propensity toward foaming. Also, it hampers the isotopic nature of the foam. Enhancement can be increased further by modifying the fiber surface to get better fiber–resin compatibility. Like fiber, particle–resin interaction also can play an important role in the enhancement of compressive strength. A bonding between the particle and the resin allows decreasing the density of the foam and also allows the dissipation of stress-generated dusting compression of foam. The chemical modification allows covalent bonding between added species and the phenolic resin. The chain length and flexibility of the chain contribute to increase in the ability of the foam to be compact.

3.4 Flexural Strength

The resistance to flexion or bending is called the flexural strength of the material. It represents the stress-bearing capacity of the material before yields in the flexion test. Flexural strength is mainly improved by using particles. It is based on the stiffness of the filler, their aspect ratio (Area/thickness), covalent bonding with a phenolic resin matrix, and the uniformity in structure. Flexural strength can be improved by using poly (butyl acrylate)-silica core–shell particle incorporation in phenolic resin, as shown in Fig. 5. It was found that 35% of flexural strength was increased due to the covalent bond formation between the hydroxymethyl group of phenolic resin and the silanol group of particles [29]. Likewise, the function of delicate particles is more mind-boggling brought by altering the foam lattice structure and improves cell size consistently.

The use of clay instead of pentane as a blowing agent was found to increase flexural strength. A 6 phr of clay into foam was found to increase the flexural strength by 61%.

The pathways for improvement in flexural strength are similar to those which are explained in compressive strength. Moreover, the interaction between the particle and phenolic resin interaction is the defining factor to improve flexural strength.

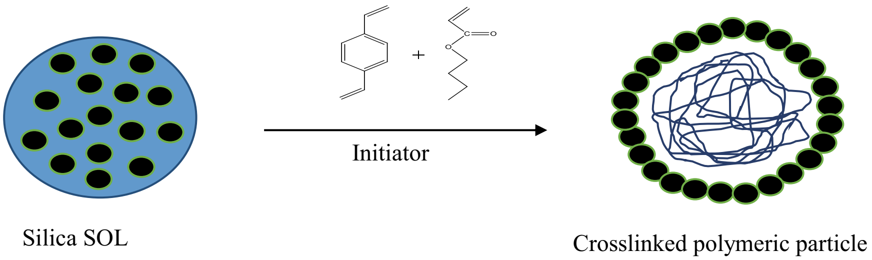

Fig. 5 Synthesis of poly (butyl acrylate)-silica core–shell particle by emulsion polymerization [29]

4 Fire-Resistant (FR) Properties

Phenolic foams are well known for their FR properties, such as low smoke density, low flammability, and lesser generation of toxic gases during the burning process. They are considered an excellent nondripping material. These properties of phenolic foams are governed by a structural component such as a benzene ring. It is well known that the molecular structure containing benzene ring and halogen atom shows superior fire resistance behavior over the others. The foam density plays a major role in flame resistance. Increasing the density may increase the number of closed cells which modify the surface in contact with flame. This results in a decrease in oxygen ratio for combustion and ultimately reduces the flammability of phenolic foam. Fire behavior can be described by three parameters, ignition source, a contributor to flame spread, and heat release. Two main tests are used to evaluate the flame-retardant behavior of foam material.

1. Limiting oxygen index (LOI);
2. Cone calorimeter test.

Limiting oxygen index is defined as the minimum concentration of oxygen in the mixture of oxygen and nitrogen that supports the ignition of the material. Hence a higher value of LOI denotes higher flame retardancy. Phenolic foam shows excellent flame retardancy with LOI ranging from 27 to 58%. It is very challenging to improve the initial value without hampering the mechanical properties of the foam. Flame retardancy in the phenolic foam is imparted by three routes:

- Introduction of nonflammable particles;
- Making the system fire retardant;
- Chemical modification in structure by introducing phosphorous, boron, or nitrogen.

Improvement in FR properties of phenolic foam depends on the reduction in oxygen permeability after the addition of filler and reduction in barrier properties due to the formation of a compact charred layer on the surface. Modified montmorillonite clay is used in the fabrication of phenolic foam. This clay exfoliates and disperses well in the phenolic matrix due to the hydrogen bonding which prevents oxygen permeability and improves the fire resistance [30]. A synergistic effect of zinc oxide, pentaerythritol, and ammonium polyphosphate to impart FR properties in phenolic foam was evaluated. Results were unbelievable on the addition of 1 wt.% of zinc oxide, which improves the LOI value by 80%. But its flexural and compressive strength was found to decrease by 27% [31]. Another attempt has been made by the use of silica-graphene oxide and alpha zirconium-graphene oxide hybrid system to improve FR properties. A slight increase in LOI of phenolic foam from 1 to 5% with an increase in graphene oxide content was observed. The LOI value further increased by increasing the amount of hybrid content [20].

The most common class of flame retardant is compounds containing phosphorous. When heat is applied, they act by generating phosphorous acid which captures

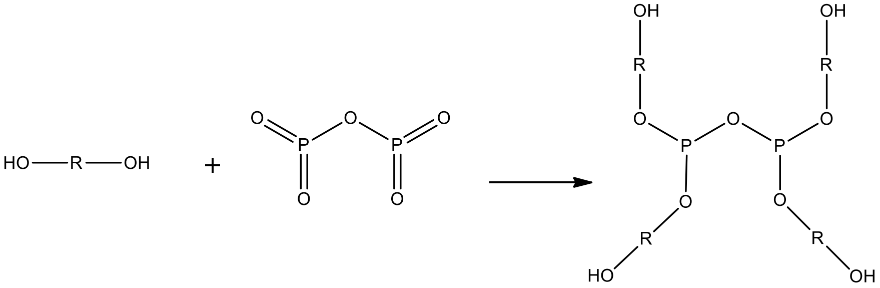

Fig. 6 Scheme for phosphorous containing PEG synthesis [32]

radicles while burning and accelerates the charring process. Along with phosphorous, Si and N are need to be added to compensate for the mechanical properties of phenolic foams. Most commonly, they are added by the reaction of modified PEG or polyurethane with phenolic resin. PEG is a flammable material due to long-chain molecules. Two different phosphorous-containing PEGs were synthesized. It was found that the LOI was reduced to 21% and 12% by adding 10 wt.% of synthesized compounds [22]. The introduction of phosphate-modified PEG (200, 400, and 600) led to an increase in the LOI by 36%, 28%, and 14%, respectively. The chain length of PEG 200 is smaller as well because the amount of phosphorous bearing is higher in PEG 200, which is the main cause of LOI increment [32]. The reaction scheme for the synthesis of modified PEG is shown in Fig. 6.

A novel phosphorous-based compound methyl-DOPO(9,10-dihydro-9-oxa-methylphosphaphenthrene-10-oxide) was synthesized to enhance the FR properties of phenolic foam. The resultant product acts as a scavenger by diluting the burnable gas in the vapor phase. When burned it forms PO, PO_2, and CH_3PO, which act as a radical scavenger [33]. A phosphorous and nitrogen-containing polyurethane framework was created. A noteworthiness improvement in LOI by 21% has been seen when 10 wt.% of the polyurethane system is added to the phenolic resin. This synergistic enhancement is attributed to the nature of nitrogen that acts as a gas source and produces nonflammable gas. These gases dilute the concentration of flammable gases and retard the decomposition of phenolic foam [34]. Recently, a magnesium amino tris-reduced graphene oxide half breed material has been arranged and used in phenolic foams for fire-resistant conduct. The LOI of the foam was expanded to 41.5% at 4 phr when contrasted with the unmodified one. It likewise diminished all-out-smoke discharge by 52.5% [35].

Besides their enhancement in mechanical properties, polyurethane and PEG system are not suitable to enhance the FR properties of phenolic foams. Phosphorous-based compounds are the most efficient way to enhance the FR properties of phenolic foams, especially in combination with nitrogen.

5 Shape Memory Properties

The shape memory behavior of foam has been broadly explored in the last decade. The core of their research relied on the fabrication, characterization, and possible application of shape memory foam. The shape memory behavior of phenolic foam can be augmented due to the higher compression even if the stiffness and strength values are reduced. Additional advantages of foam materials are lighter in weight and high recovery force.

The fundamental mechanism of shape memory behavior lies in the dual segment of the polymer. One segment serves as the elastic domain and the other is the transitional domain. At room temperature or even at low temperature both the domains are hard and the polymeric material is stiff. Upon heating, the polymer above Tg makes the transitional domain soft and deformable. The versatile area likewise goes through distortion by retaining the vitality and put away it as flexible vitality. As we chill off, the material progress area goes through the freezing of chain development and solidified the momentary space. If the deformed shape is held during cooling (a compressed form of the foam), it will stay in the same shape even after the removal of compressive force. This happens because the transition domain gets harden below Tg which prevents the recovery of the elastic domain. After heating above Tg, the transitional domain loses its ability to hold the elastic domain due to the absorption of energy in chain movement and the polymer regains its original form due to the release of elastic energy.

Two factors are the basis for the shape memory effect in SMPF. Glass modulus of foam material is responsible for shape fixity and the rubbery modulus for shape recovery. These factors decide the shape memory properties of phenolic foams. The glass transition temperature of phenolic resin plays an important role in the shape memory effect. Phenolic foam has a high crosslinking density; their Tg would be on the higher side. As far as the mechanical properties are concerned, higher thickness material has higher rigidity. As the molecular weight increases with an increase in crosslinking density, glass modulus would be shifted to the higher side, which ultimately increases the Tg. The shape memory effect in phenolic foams can be implemented by the use of

- long-chain phenol substitute;
- polyurethane pre-polymer in phenolic foam fabrication;
- long-chain epoxy polymeric backbone for phenolic foam formation.

A 20% relative density epoxy shape memory foam was synthesized and evaluated for their shape memory behavior. These foams were subjected to different conditions of stress, strain, and temperature to measure the change in properties. Tensile strain to a material failure is generally associated with the maximum recovery limit of the foam. These foams were compressed to 80% of their original volume, and multiple recovery cycles were performed. It was found that the packing temperature doesn’t affect the overall recovery strain level. Also, the temperature and maximum strain levels have a significant effect on the reversibility of foam shape [36]. The effect of long storage shape-holding capacity was investigated in polyurethane foam. The foam was strained at 80–90% strained above their glass transition temperature and then cooled to room temperature. After two months, it is reheated to gain its original length under different constant loads. It was found that the maximum stress wields at a fixed length depending on the amount of pre-strain. An expansion rate from 380 to 1273% has been accomplished from the hibernating size of grains against 1 N load [37]. This is a very important characteristic of a material used in space applications.

A magnetic susceptor filler particle was incorporated in the thermoset foam matrix to thermally activate the shape memory behavior. Results demonstrated that as the number of filler particles increased to 10 wt.%, the heating performance of foam increased without any deterioration of thermomechanical properties [39]. A net set of thermosetting foams were produced by solid-state foaming. This technique involves the direct overheating of a solid tablet of uncured resin. Composite foam can be produced from compression of fillers with uncured resin powder. Montmorillonite clay incorporated epoxy foam showed improvement in shape memory behavior. At 5 wt.% of filler content, the shape recovery property of foam is optimum without any damage. It was worth noting that the height of recovery of these foams was never lower than 97% [38].

A new ortho grid structure-based shape memory syntactic foam was designed and tested for healing impact damage repeatedly. The results implicated that the healing efficiency was 100% for all impact healing cycles. However, three-dimensional geometry recovery is confined to higher residual strength than two-dimensional recovery, and as the impact energy increases, healing efficiency slightly goes down [39]. An integral model based on the thermodynamics of foam formation has been investigated for its thermomechanical behavior. This study involves the insertion of a glass micro balloon into the shape memory polymeric matrix while fabrication of foam. Owing to the high-volume fraction of the glass balloon and the stiffness, it provides strength to the foam and increases the recovery stress. Also, it dictates that as the external confinement stress increases, the external recovered strain is reduced but the internal deformation increases. This led to better self-healing and shape recovery of the material [42].

Recent studies have focused on the applications of shape memory foams in biomedical devices. In particular, they are used to treat intracranial aneurysms. This condition is also known as a brain aneurysm. It involves weakness in the blood vessels, which results in balloon formation. To treat this condition shape memory foam may be a better material to fill that balloon with less stress generation in blood vessels. An attempt has been made by using hexamethylene diisocyanate-based polyurethane shape memory foam to treat an aneurysm. It has been predicted that 1.5 times oversized foam can be deployed bearing the capacity of 65 kPa circumferential stress, which is lesser than the minimum blood vessel wall breaking stress (700 kPa) [40]. The radio-opacity of a network polyurethane shape memory foam is enhanced by adding a small amount of tungsten. At 4 wt.% loading opacity has been found to increase without affecting its mechanical properties [41]. A novel sterilization method was implemented to determine the effect of sterilization on both thermochemical and shape recovery behavior. Both morphology and chemical structure have been affected by sterilization methods which will have an impact on shape memory behavior. The shape recovery test showed that 98% of the shape has been regained after the sterilization [42]. A polyurethane hydroxyapatite-based shape memory foam had been engineered to use as a scaffold to expedite tissue regeneration. Results were satisfying as the self-fitting performance in rabbits passes all the in vitro studies. Shape memory foam could expand in 60 s and fill the bone defect by the heat-triggered mechanism [43].

Various SMP foam from organic to inorganic material comprising inorganic poly dimethoxy silane (PDMS) and polycaprolactone (PCL) had been investigated for their shape memory effect. PCL block serves as a switching segment in foam whereas the compressive properties are based on the PDMS segment. Shape recovery was found to be decreased as the PDMS chain length increases. PDMS segment has low Tg which is caused by a decrease in compression modulus accompanied by a decrease in PCL crystalline domain [44].

6 New Trends in Shape Memory Phenolic Foam

Nowadays, increasing cost, the anticipated future need for petrochemical, and viable developmental concerns brace for an eco-friendly and renewable bio-based material. The probable replacement of petroleum-based phenol and formaldehyde is reported in regards to their application. The lignocellulosic biomasses such as bark and wood are being considered as capable alternatives. Lignin is the most richly found material on the earth and stands second in the rundown of biopolymers. Lignin contains some phenolic functionality that could be used as reinstatement for phenol in the synthesis of SMPF. Another promising way is to modify resol resin by oxidative degradation of lignosulfonate. However, phenolated lignosulfonate-based resin bids a better perspective than oxidative degraded lignosulfonate-based resin. Among the chemical and thermal techniques established in the past few decades, liquefication of biomass use of water or organic solvents like alcohol or supercritical extraction has been advised for high biomass conversion into a phenolic resin. Many attempts have been made to modify the phenolic resin with bio-based materials such as bamboo and walnut shell. It is easier to liquify walnut shells than wood at low temperatures. Cardanol, a versatile and renewable source of meta substituted phenol, would be a partial substitute for phenol. The development of bio-based phenol PF requires the investigation of green routes and techniques while keeping global environment protection of prime importance. The exploration concerning shape memory foam proceeds with its quick development, with present endeavors, separated between empowering innovations (materials, cycles, and methods) and application and prototyping. On the empowering front, there is an expanding number of reports finding novel recuperation trigger mechanisms other than outside warming, which includes photoresponsive, magnetic responsive, and humidity responsive foams. Aside from alternative triggering mechanisms, there is also an emerging interest in shape memory polymers capable of memorizing two or more temporary shapes. At different temperature stages, this kind of polymers can recover in a tandem manner from one shape to another and finally to its original shape. The interest for flower foam is expanding step by step in the floristry business, dinners, wreaths, in containers, and tabletop courses of action. The shape memory effect in those foams can preserve the space in the field of use. Additionally, a shape memory cushion that we can convey in our pocket expands into a pillow after warming which will be a superior alternative to moving explorers or in public transport.

7 Conclusion

This chapter is essentially devoted to a review of the improvement of shape memory properties, mechanical properties, and the fire-resistant properties of phenolic foams. The mechanical properties are frequently identified with the cell morphology. In reality, strands and particles have been demonstrated to lessen the cell size, to expand the cell thickness, and lastly to improve the cell homogeneity. The MWCNT and graphene oxide hybrid particles appear to be acceptable possibilities to accomplish this support for compressive quality and modulus properties. Concerning support, the presentation of adaptable chains into the inflexible spine of the phenolic pitch that is covalently connected is by all accounts extremely encouraging if the crosslinking thickness decrease isn't critical. Polyurethane and polyethylene glycol family is the most utilized item, yet dicyandiamide is by all accounts the most productive.

The shape memory properties depend on the dual segment of the polymer. The Tg of polymer assumes a significant function that fits as a shape memory impact. A long-chain polyurethane section appears to be encouraging to bestow shape memory impact in phenolic foam. Likewise, PDMS fills in as another substitute for polyurethane for development fit as a shape memory impact in phenolic foams. All things considered, little work has been completed in the territory of shape memory properties of phenolic foams.

Concerning flame retardancy properties, phenolic foams have much preferable fire properties over all other polymer foams. The improvement was credited to the homogeneous scattering of the particles that assist in diminishing the oxygen penetrability and offer a superior division of phenolic framework from the air and the warmth. Concoction adjustment containing explicit components is the most mainstream course for improving fire-retardant conduct. To begin with, components, for example, nitrogen go about as noncombustible gases sources that decline the combustible gas fixation, subsequently hindering the deterioration of the basic material. Second, phosphorous mixes, while decaying, produce phosphorous acids that quicken the singing cycle of the foams, permitting lower warmth and mass exchanges. The acquired scorch assumes the function of a defensive hindrance. Specialists attempt to substitute, at any rate mostly, the phenol with sustainable biomass assets. Biomass-based resol gums from pecan shells, wood, or bamboo powder showed the chance of substitution of traditional phenolic resol tars by creating foams with fulfilling or comparable mechanical properties. Lignin is by and large profoundly examined and gives the most intriguing outcomes. Phenolated lignin exhibited a high potential as it expanded the compressive quality and diminished the friability. Subsequently, biomass-based phenolic resol saps appear to offer intriguing viewpoints for the advancement of phenolic tar with higher mechanical properties. By and by, the durability of these bio-based materials must be considered.

References

1. Li J, Zhang A, Zhang S et al (2019) Larch tannin-based rigid phenolic foam with high compressive strength, low friability, and low thermal conductivity reinforced by cork powder. Compos B Eng 156(1):368–377
2. Liu H, Han C, Dong L (2008) Study on the cell structure and compressive behaviourof biodegradable poly(e-caprolactone) foam. Polym Eng Sci 48(12):2432–2438
3. Brenzy R, Greenthe D (1990) Effect of cell size on the mechanical behaviour of cellular material. Acta metall mater 38(12):2517–2526
4. Haijun Y, Guo Z, Li B et al (2007) Research into the effect of cell diameter of aluminium foamon its compressive and energy absorption properties. Mater Sci Eng 454(25):542–546
5. Xu Z, Fu J, Luo T, el, (2012) YangEffects of cell size on quasi-static compressive properties of Mg alloy foams. Mater Des 34:40–44
6. Chen Y, Das R, Battley M (2015) Effects of cell size and cell wall thickness variations on the stiffness of closedcellfoamsInt J Solids Struct 52(1):150–164
7. Song S, Chung Y, Kim S (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticlesComposSciTechnol 103:85–93
8. Zhou J, Yao Z, Chen Y et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym. Compos.35:3:581–586
9. Li Q, Chen L, Li X (2016) Effect of nano-titanium nitride on thermal insulating and flame-retardant performances of phenolic foam. J Appl Polym Sci 133(32):1–12
10. Zuo Y, Yao Z, Zhou J (2014) Mechanical and thermal properties of phenolic foams reinforced byhollow glass beads. Adv Mater Res 988:13–22
11. Saz-Orozco B, Alonso M, Oliet M et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foam. Compos Part B 75:367–372
12. Song S, Oh H, Kim B et al (2013) Novel foaming methods to fabricate activated carbon reinforced microcellularphenolic foams. ComposSciTechnol76:45–51
13. Rangari V, Hassan T, Zhou Y et al (2007) Cloisite Clay-Infused Phenolic Foam Nanocomposites. J Appl Polym Sci 103:308–314
14. Saz-Orozco B, Alonso M, Oliet M et al (2015) Lignin particle- and wood flour-reinforced phenolic foams: Friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos Part B 80:154–161
15. Bo C, Hu L, Zhou J et al (2015) Preparation and characterization of phenolic foams modified by castor oil-based polyurethane prepolymer Chemistry and Industry of Forest Products. J. chem. Indus. Prod. 4:8–14
16. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and theirapplication in phenolic foams. Ind Eng Chem Res 54(7):1962–1970
17. Desai A, Auad M, Shen H et al (2008) Mechanical behaviour of hybrid composite phenolic foam. J Cell Plast 44(1):15–36
18. Yu H, Wang L, Gai B (2012) Performance of modified aramid fiber reinforced phenolic foam. J. Adv. Mater. Res. 557(559):258–261
19. Tang Q, Fang L, Guo W (2019) Effects of bamboo fiber length and loading on mechanical, thermal and pulverization properties of phenolic foam composites.J. Biprod. Biores. 4:1:51–59

20. Z. H. Zhuang Z, He B, Yang Z (2010)Preparation and characterisation of phenolic foam/HTAB-ATP nanocomposites.Plast Rubber Compos39:10:460–464
21. Li X, Wang Z, Wuc L (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. RSC Adv 5:99907–99913
22. Lei L, Wang Z (2018) Facile synthesis of a novel magnesium amino-tris- (methylene phosphonate)-reduced graphene oxide hybrid and its high performance in mechanical strength, thermal stability, smoke suppression and flame retardancy inphenolic foam.J. Hazard. Mater.357:5:89–99
23. Li X, Wang Z, Wuc L et al (2016) One-step in situ synthesis of a novel a-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6:74903–74912
24. Yang H, Wang X, Yu B, et al (2012) A Novel polyurethane prepolymer as toughening agent: preparation, characterization, and its influence on mechanical and flame Retardant properties of phenolic foam.J. Appl. Polym. Sci. 128:5:2720–2728
25. Ming Gao M, Wu W, Wang Y et al (2016) Phenolic foam modified with dicyandiamide as toughening agent. J Therm Anal Calorim 124:189–195
26. Xu Q, Gong R, Cui M et al (2015) Preparation of high-strengthmicroporous phenolic open-cellfoams with physical foaming method.High Perform. Polym.27:7:852–867
27. Song F, Li Z, Jia P et al (2020) Phosphorus-containing tung oil-based siloxane toughened phenolic foam with good mechanical properties, fire performance and lowthermal conductivity. Mater Des 192(108668):1–11
28. Lia B, Yuan Z, Schmidt J et al (2019) New foaming formulations for production of bio-phenol formaldehyde foams using raw kraft lignin. Eur Polym J 111:1–10
29. Wang G, Liu X,Zhanga J et al(2018)One-pot lignin depolymerization and activation by solid acid catalytic phenolation for lightweight phenolic foam preparation.Ind Crops Prod 124:216–225
30. Yuan J, Zhang Y, Wang Y (2015) Phenolic foams toughened with crosslinked poly (n-butyl acrylate)/silica core-shell nanocomposite particles. J Appl Polym Sci 132(40):1–8
31. Niu M, Wang G (2013) Study on the nanocomposite foam of cardanol phenolic resin andorgano-modified montmorillonite. J. Adv. Mater. Res 712(715):147–155
32. Ma Y, Wang J, Xu Y et al (2015) Effect of zinc oxide on properties of phenolic foams/halogen-free flame-retardant system. J Appl Polym Sci 132(44):1–8
33. Yang H, Wang X, Yuan H et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyether. J Polym Res 19(9831):1–10
34. Suia X, Wanga Z (2013) Flame-retardant and mechanical properties of phenolic foams toughened with polyethyleneglycol phosphates. Polym Adv Technol 24(6):593–599
35. Konig A, Krokeb E (2011) Methyl-DOPO—a new flame retardant for flexible polyurethane foam. Polym Adv Technol 22(1):5–13
36. Ding H, Wang J, Liu J et al (2015) Preparation and properties of a novel flame-retardant polyurethane quasi-prepolymer for toughening phenolic foam. J Appl Polym Sci 132(35):1–8
37. Di Prima M, Lesniewski M, Gall K et al (2007) Thermo-mechanical behaviour of epoxy shape memory polymer foams.Smart Mater. Struct. 16:6: 2330–2340
38. Tey S, Huang W, Sokolowski W(2001) Influence of long-term storage in cold hibernation on strain recovery and recovery stress of polyurethane shape memory polymer foam.Smart Mater. Struct. 10:2:321–325
39. Vialle G, Di Prima M, Hocking E et al (2009) Remote activation of nano magnetite reinforced shape memory polymer foam. Smart Mater. Struct. 18:11:1–10
40. Quadrini F, Santo L, Anna E (2012) Solid-state foaming of nano–clay-filled thermoset foams with shape memory properties. Polym Plast Technol 51(6):560–567
41. Manu John M, Li G (2010) Self-healing of sandwich structures with a grid stiffened shape memory polymer syntactic foam core. Smart Mater Struct 19(7):1–12
42. Manu John M, Li G (2010) Constitutive modelling of shape memory polymer based self-healing syntactic foam. Int J Solids Struct 47(19):1306–1316

43. Hwang W, Volk B, Akberali F et al (2012) Estimation of aneurysm wall stresses created by treatmentwith a shape memory polymer foam device. Biomech Model Mechanobiol 11(5):715–729
44. Rodriguez J, Yu Y, Miller M et al (2012) Opacification of shape memory polymer foam designed for treatmentof intracranial aneurysms. Ann Biomed Eng 40(4):883–897
45. Nardo L, Moscatelli M, Silvi F et al (2010) Chemico-physical modifications induced by plasma and ozonesterilizations on shape memory polyurethane foamsJ Mater Sci: Mater Med 21(4):2067–2078
46. Xiea R, Hu J, Hoffmannc O et al (1862) (2018) Self-fitting shape memory polymer foam inducing bone regeneration: A rabbit femoral defect study. BBA Bioenergetic 4:936–945
47. Zhang D, Petersen K, GrunlanM, (2013) Inorganic−organic shape memory polymer (SMP) foams with highlytunable properties. ACS Appl Mater Inter 5(1):186–191

Chapter 7
Mechanical Properties of Phenolic Foams

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1 Introduction

With the development of technology and the requirement of industries, lightweight structures are in high demand, especially in the field of sound and thermal insulation [1], transportation, energy absorption, packaging, vibration isolation, filter assembly, structure, and many other applications [2]. Due to this, different foam structures have great potential as compared to their dense materials by the reduction of their weight. Foams are classified according to their morphology, matrix material, and applications. Mainly it is categorized into open cell, closed cell, and partially open and closed cell foam [3]. So to fulfill the requirements, researchers have developed different materials of porous structures, like metallic foam [4], polymer foam [5], ceramic foam [6], and many others. Out of which phenolic foam has attracted more attention from industries and researchers, due to its lightweight and high-temperature sustainability properties. Phenolic resin is a combination of phenol and formaldehyde, which was discovered by German chemist Sir Adolph von Baeyer in 1872. Later in 1907, it is introduced into the commercial market by L. H. Baekeland as a phenolic resin, which is also called a Bakelite. L. H. Baekeland is also known as the father of phenolic resin [7]; later in 1940, the phenolic foam was introduced into the German market which is mainly used as a wood substitute material. With the introduction of new polymer foam materials like polystyrene, polyurethane, and polyvinyl chloride which are more flexible and less brittle [8, 9], this phenolic foam gets suppressed. Phenolic foams are more brittle and less flexible as compared to other polymeric materials. Polymeric foams introduced later are not able to sustain at higher temperatures, whereas phenolic foam has very good fire retardation property.

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Since the last decade, the market demand for phenolic resin has increased, in terms of volume. The market demand for phenolic resin is approximately 4.7 million tons, which cost nearly about 10 billion USD in 2014. It is assumed that it is going to increase to about 14 billion USD in 2020 [10]. Phenolic resin has a unique chemical structure. Due to this, its fire retardation property gets enhanced. And when this resin is heated, it releases a very low amount of smoke and toxic gases as compared to another polymer foam [11, 12]. According to the application phenolic resins are available in different forms, like in powder foam to produce electrical equipment and in liquid form for different laminated and binder applications. PF has very high specific properties in terms of strength, fire sustainability, electromagnetic shielding, and others as compared to solid materials. PF has low density, low thermal conductivity, porous structure with desire porosity, and low rigidity which make it enable to make lightweight structures, low-cost thermal insulators, filtration, and energy-absorbing components. Due to this, it is specifically used for some applications like decontamination of polluted water, in space shuttle for thermal insulation, and vibration damping. Owing to less specific weight and thermal insulation property, it is very demanding in the current market, especially in the space and transportation sector. PF mainly consists of two phases; one is the gaseous phase which is trapped in the case of closed-cell foam and untrapped in the case of open-cell foam. The morphological properties (like open cell, closed cell, size of the cell, and shape) affect the properties of PF. PFs are generally rigid thermosetting foam, which is highly stable in terms of their rigidity and thermal stability [13, 14].

As PF has high rigidity, it is very brittle and also shows pulverization properties which limit the use of PF. Due to this, the mechanical properties of the PF get degraded and not able to stand at the desired load condition. Therefore, increasing the mechanical strength of PF without compromising the fire retardation property is a very difficult task. Nowadays, researchers are mainly focusing on increasing the mechanical properties of PF using chemical modification in their structure during formation or by using different reinforcement. This chapter mainly comprises how the mechanical property of PF gets increased. It includes a complete review of enhancing the mechanical properties of PF through different techniques. In the last decade, researchers are rigorously exploring this field of PF and enhancing its properties. The data obtained from the web of science while searching "phenolic foam" are shown in Fig. 1.

From Fig. 1, it has been found that, in the last 10 years, a huge amount of research work has been carried out in the area of phenolic foams.

2 Synthesis of PF

Different methods were used to manufacture phenolic foams, which mainly involve mechanical, chemical, and physical methods. These methods are then subcategorized into different techniques that are used to produce PF. Some of the methods are [2]:

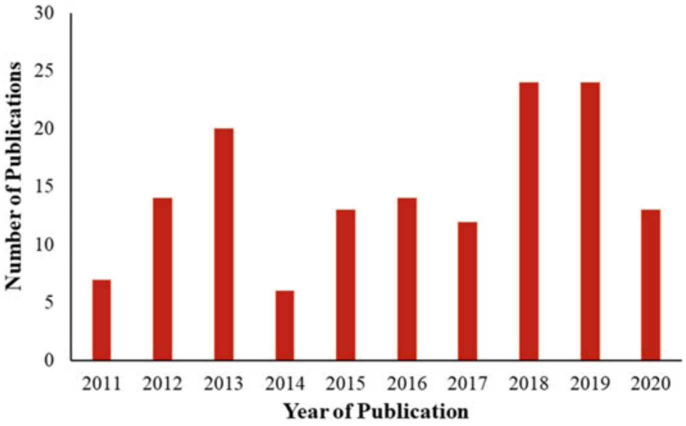

Fig. 1 The research article published on phenolic foam and its application

(a) **Mechanical agitation**—in which gaseous product is entrapped in the phenolic matrix, and the bubble trapped inside the matrix make a porous structure;

(b) **Thermal decomposition**—in this process the blowing agent is mixed with the phenolic matrix and when the heat is applied to the system gases evolve and give porous structure foam;

(c) **Volatilization of low boiling solvent**—low boiling solvent was mixed with the matrix and gets heated;

(d) **Expansion of dissolve gases**—in this process, mainly the gases present inside the matrix get expanded reducing the external pressure;

(e) **Hollow microsphere**—in this process, hollow micro balls were incorporated inside the matrix which create porosity.

(f) **Template method**—polyurethane foams are used as a template and dip into the slurry of phenolic resin and then heated for obtaining the carbon foam by removal of PU foam.

Figure 2 shows the SEM image of PF having different filler constituents at a different percentage. Along with the phenolic resin and different volatilization and gas generation source components, some other elements are also used for the manufacturing of PF. Emulsifiers, catalysts, and some other additives are also used during the preparation of PF. During foam formation, two mechanisms work simultaneously; that is, expansion of the blowing agent and curing of the resin. These two mechanisms are mainly dependent on two process parameters, which are viscosity and reactivity of phenolic resin. The viscosity of the resin controls the pore type, pore shape, and size of the foam [15, 16], whereas reactivity controls the curing and foaming time [17]. Emulsifiers are added to control the property and quality of the PF.

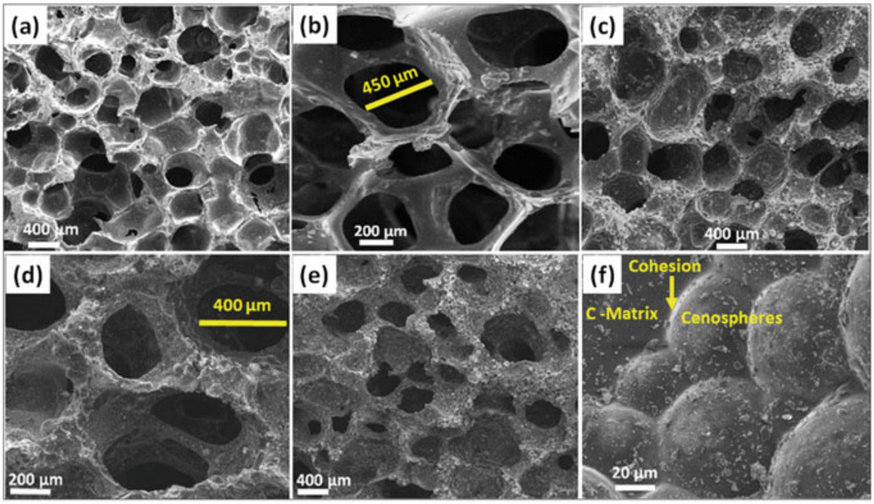

Fig. 2 SEM image of PF having different constituents in each case of analysis. Reproduced with permission from [1]

3 Why is the Need for Improving the Mechanical Properties of PF?

From the previous study, it was found that PF has high rigidity and stability as compared to other polymer foams. Because of this, they are very brittle in nature and pure PF also has less mechanical properties like low compressive and flexural strengths [9, 18, 19]. Due to this, the PF application gets limited, though it is not able to sustain at higher mechanical loading conditions. For using PF in transportation and space shuttle, it should have good mechanical strength so that it can sustain at the given conditions. Different methods were used to increase the mechanical properties of PF and are discussed in the later section.

4 How Mechanical Properties of PF Can Be Enhanced?

For increasing the mechanical strength of PF, researchers have used different methods and techniques. Mainly two approaches are adapted for increasing the mechanical strength, that is, chemical modification and the addition of filler in the phenolic matrix during manufacturing. While discussing the mechanical properties of PF, the density of the foam frequently comes into the picture. Because the mechanical properties of PF also depend on the density of the foam, Ashby et al. [20] already mentioned different models for the compression and flexural behavior of foam under different loading conditions. Through different models, the importance of foam density on

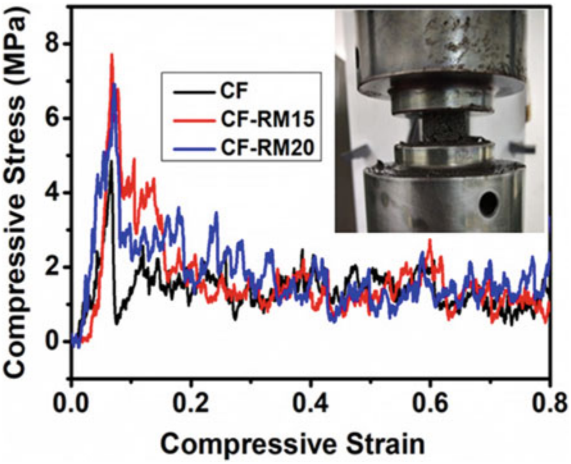

Fig. 3 The compressive stress–strain curve of lightweight carbon foam made from a phenolic resin having different constituents. Reproduced with permission from [21]

its mechanical properties was mentioned. The compressive deformation behavior of PF foam was mainly categorized into three different sections: (1) elastic region, (2) plastic region, and (3) densification. From Fig. 3, it is analyzed that during compression of foam initially elastic zone appears, then long plateau region, and after plateau region densification takes place. With the increase in density or with the addition of different filler material into foam, the compressive deformation behavior of PF varies.

5 Effect of Cell Size on the Mechanical Properties of PF

From previous work, it was found that cell size and orientation also affect the mechanical properties of the foam [13, 22]. Small pore size and uniform pore distribution throughout the component increase the mechanical properties of the foam. Though different models given by Ashby and Gibson [20] do not confirm the dependency of Young's modulus and compressive strength on the cell size of the foam, many of the researchers have reported the study in which they show the relationship between cell size and the mechanical strength of the foam. A study on foam showing the dependency of mechanical properties on cell size is mentioned in this section. Yu et al. [23] examined the compressive deformation behavior of closed-cell aluminum foam under quasi-static conditions, in which they analyzed the effect of different cell sizes, that is, 2.6, 3.2, and 3.8 mm diameter having constant relative density. From these results, it is concluded that with the increase in cell size of the foam, the maximum stress and Young's modulus of foam get increased which are mainly due to an increase in cell wall thickness. The cell wall thickness of foam gets increased with an increase in cell size. Liu et al. [24] prepared poly(e-caprolactone) foam through a chemical foaming method, and they used a scanning electron microscope to study the cell morphology.

They studied the effect of change in cell morphology and density of the compressive deformation behavior of foam. From the results, it is concluded that with an increase in cell wall thickness and cell density, the compressive strength and Young's modulus of the foam get increased. But with the change in cell wall thickness and cell size the density of the foam also varies, so no exact conclusion has been drawn on the effect of cell size on the mechanical properties of the foam. Chen et al. [25] analyzed the effect of change in cell wall thickness and the size of closed-cell styrene-acrylonitrile on the mechanical properties of the foam. Through experiment it has been found that with the change in cell wall thickness and cell size, Young's modulus and compressive strength of the foam also vary. However, the moduli of the foam do not depend on the density of the foam. Finally, it is concluded that there is no evidence that shows the dependency of mechanical properties on the cell morphology of the foam. Basically, two types of communities are there in researchers: those who are working on the foams. Some are believing that cell morphology affects the mechanical properties of the foam, while others believe in not. Basically in polymer foam, cell morphology can be varied using different methods. Some previous research shows that cell size and shape can be modified with the addition of filler or through chemical modification [26–28]. Different methods that are generally used for the modification of cell wall and cell size are:

- The addition of fillers during the formulation of PF can help in the stabilization of emulsion and also modifies the viscosity of the solution which helps in enhancing the nucleation growth of the cells.
- With the use of a foaming agent, the cell morphology of the foam can also be varied. However, foaming agents having a higher boiling point give a small cell size [28].
- By changing the speed and mixing time, the cell size and shape can be varied.
- Using surfactants for the stabilization of emulsion during foam formulation also helps in modifications of cell morphology [29].

5.1 Effect of Fibers and Particles on Cell Morphology of PF

Although the addition of different fillers and particles modifies the mechanical properties of the foam, it may also affect the cell geometry of the foam. With the addition of external agents, the viscosity of the phenolic resin mixture gets changed which affects the cell formulation. In some cases, externally added filler or particles act as a nucleating site for foam formation, and the uniform distribution of external agents confirms the uniformity of cell formation and geometry. When an external constituent is added into the phenolic resin solution and gets uniformly dispersed, three different mechanisms ensure the formation of small and regular cells inside the foam. First, the external agent acts as a nucleating site and reduces the nucleating free energy which helps in increasing the number of nucleation sites. Second, with the addition of an external agent, the viscosity of the phenolic mixture gets increased. This helps in limiting the growth of the nucleation, and a large number of small bubbles get a form which also helps in increasing the mechanical characteristic of foam. And the third one is the addition of an agent that also helps in stabilizing the emulsion through the Pickering process during mixing. Overall with these mechanisms which are mainly due to external agent addition, small and uniform size cells get formed inside the PF which helps in increasing the mechanical characteristic. Saz-orozco et al. [30] used cellulose fibers as a reinforcement in PF. They showed the effect of adding fibers on cell size, mechanical properties, and thermal stability of the foam. With the incorporation of cellulose fibers at different weight percentages, the cell size and the cell wall thickness of the foam get changed. With a 2% addition of fibers, the compressive modulus and strength of the foam get increased up to 21% and 18%, whereas the thermal stability of the foam gets decreased with the increase in the percentage of filler. From these results, it is found that with the addition of cellulose fiber at different percentages, the cell wall thickness and cell density of foam get increased. Li et al. [31] have developed PF with high thermal insulation and fire retardation application, and they used titanium nitride (TiN) nanoparticles as reinforced material. With the addition of TiN nanoparticles, they make nanoparticle composite PF known as nanocomposite PFTNs. Results show that with the addition of nanoparticles the cell distribution inside the foam gets uniform as compared to base PF. Thermal stability and the fire retardation property of the PFTNs get also increased as compared to base PF. Song et al. [12] used multi-wall carbon nanotubes (MWCNTs) and graphene as a reinforcement to control the cell morphology during the foaming of PF. They also optimized the proper foaming point for each reinforced particle to enhance the mechanical and thermal properties of PF. The particle-reinforced PFs have a lower cell size as compared to base PF, which is due to an increase in cell density inside the foam. With 0.5% of MWCNT and 1% of graphene addition, the compressive strength of PF gets increased to 71.8% and 157.3%. Li et al. [32] prepared a composite PF using multi-wall carbon nanotube (MWCNT) through an in situ polymerization process. With the help of TEM analysis, it is found that the dispersion of MWCNTs inside the PF is uniform. Through SEM it is found that due to the addition of MWCNT in PF the cell size gets decreased, cell wall thickness gets increased, and cell density also gets enhanced. All these characteristics result in an increase in the compressive strength of the foam. Yang et al. [33] prepared the composite phenolic foam using pristine and functionalized MWCNTs for fire resistance material. From the result, it is concluded that with the addition of MWCNTs the nucleation sites during foaming get increased which helps in increasing the cell density. An increase in cell density shows the decrement of cell size, due to which the mechanical properties of the foam get increased. In addition to this, the thermal stability of the foam also gets increased with the addition of MWCNTs. Yuan et al. [34] used nanocomposite particles of poly(n-butyl acrylate) (PBA)/silica as a reinforcement material in PF to improve the mechanical properties of PF. Through SEM, it is found that with the addition of nanocomposite particles the structural homogeneity of the PF gets enhanced. Through experiment results, it is found that the compressive strength, flexural strength, and elastic modulus of the PF get significantly enhanced with the addition of nanocomposite particles.

5.2 *Effect of Chemical Modification on Cell Morphology*

The cell morphology of PF can also be modified through chemical modification during the formulation of foam. With the modification of cell size and cell wall thickness through chemical modification, the compressive and flexural strengths of the foam can get increased. Very few researchers have reported the modification of foam morphology through chemical modification. Liu et al. [35] used polyethylene glycol borate (PEG-BAE) as a toughening agent in PF. With the addition of this toughening agent, the compressive and flexural strengths of the PF get increased and the pulverization ratio gets reduced as compared to pure PEG. The result shows that with the addition of 4.5 wt% of modified boron PEG200, 400, and 600, the cell size of the foam gets increased by 66, 17, and 17%, respectively. With the PEG200 and 400 modifications, it shows that the cell size of the PF is more uniform and has hexagonal shapes that help in strengthening. Whereas, in the case of PEG600 the viscosity of the solution is too high which makes the blowing agent difficult to disperse uniformly. Due to this no uniformity of the cell inside the foam.

6 Effect of Fiber Reinforcement on Mechanical Properties of PF

For increasing the mechanical strength of foams, fiber reinforcement is the most promising reinforcement. When the load is applied to the foam, the fiber reinforced in foam acts as a barrier that restricts the motion and increases the mechanical strength. During compression, the most effective parameter of fiber reinforcement is the stiffness of fiber and its concentration inside the foam. With high stiffness fiber reinforcement, the compressive strength of foam gets enhanced. However, during shearing of foam, the fiber restricts the motion of the shear plane which strengthens the material and increases the flexural strength of the foam. Also because of the high aspect ratio, fiber reinforcement restricts the motion of shear planes which increases the bending stiffness of foam. Due to fiber reinforcement, the enhancement in compressive and flexural strength of PF is discussed in the following section.

6.1 *Compressive Strength*

It is defined as the strength of the material or resistance of the material toward the compressive load acting on foam. Foams that are specifically used for energy absorption, compressive strength is the main parameter. According to the ASTM D1621-standard of rigid plastic cellular for compression, the compressive strength of the material is defined as the maximum stress that occurred before 10% strain. From previous work, it is observed that the compressive strength of the foam depends on the toughness of the cell wall and the density of the foam [36]. Different methods were adopted to improve the compressive strength of PF, in which fiber reinforcement is one of the promising reinforcements. Fiber-reinforced PF provides high stiffness as compared to base until the addition of fiber starts agglomerating. If the addition of fiber percentage increases up to a certain level at which it starts agglomerating, then the stiffness of the foam starts decreasing. Therefore, during the formulation of PF reinforced with fiber, uniform distribution of fiber inside the foam is the first challenge. While adding fibers into the phenolic resin, the viscosity of the mixture gets increased. This may create problems during the mixing and expansion of gas inside the PF [9]. Desai et al. [37] used glass and aramid fibers as a reinforcement in PF at different proportions. In this work, they reinforced the PF with glass fiber and aramid fiber separately, and then they made a hybrid composite. From the results, it is found that the hybrid-reinforced composite has higher stiffness and strength as compared to PF, which has only glass and aramid fibers. Shen et al. [38] with the addition of aramid and glass fiber as a reinforcement, the mechanical properties of the PF get increased. With the addition of aramid fibers, the brittleness of the PF gets decreased, whereas the crack resistance and isotropic behavior property of PF get enhanced. In the case of glass fibers reinforcement, the stiffness and strength of the foam also get enhanced, which concludes that with the addition of fibers the mechanical properties of the PF get enhanced.

During the addition of fibers into the PF, the compatibility between reinforced fiber and the phenolic matrix is also very important. If the interfacial bonding or wettability between the reinforced fiber and matrix is not proper, then despite increasing the strength of the foam it starts decreasing. Yu et al. [39] modified the surface of aramid fiber through chemical modification and used it as a reinforcement in PF. They used sodium hydride and methyl-sulfoxide for chemical treatment. They compared the characteristics of modified and unmodified aramid fiber reinforcement. Through the experiment, it has been found that the PF reinforced with modified reinforced fiber shows high compressive strength and modulus, with lower brittleness as compared to unmodified aramid fiber reinforcement. In the case of thermal conductivity, the presence of oxygen contained in modified aramid fiber decreases the conductivity of PF. Ma et al. [40] prepared DOPO-g-KH550 treated wood fibers which are known as DKTWF. With the use of DKTWF reinforcement, they developed DKTWF composite PF. The synthesis of DOPO-g-KH550 was first characterized by SEM, FT-IR, and H-NMR. Compared with the wood fibers, the treated wood fibers show high crystallinity and thermal stability as compared to the untreated ones. From the results, it was found that the compressive strength of the DKTWF-composite PF is less as compared to PF. But with the increase in the percentage of addition of reinforcement, it starts increasing. With the addition of DKTWF, the thermal stability of the PF also gets reduced. Yuan et al. [41] used phosphorus-containing polyurethane prepolymer (DOPU) as reinforcement in PF. They first synthesize the DOPU and then it is characterized through NMR and FT-IR. They used DOPU and glass fiber as a reinforcement in PF, and with the use of this reinforcement compressive and bending strength, apparent density, and water absorption of the PF get enhanced. Through results, it is analyzed that with the addition of DOPU in glass-fiber-reinforced PF, the compressive strength and apparent density of the PF increase irregularly at a different percentage. With 3% DOPU and 0.5% glass fiber, the thermal stability of PF gets enhanced, whereas the char yielding also gets increased.

6.2 Flexural Strength

The flexural strength of the material defines the strength of the material when the transverse load is acting on it. Due to fiber reinforcement, the flexural strength of the PF gets enhanced significantly, which is mainly due to the high stiffness and aspect ratio of fibers. Reinforced fiber has covalent bonding with the phenolic matrix, which helps in stabilizing the microstructure of PF during formulation, which gives uniform microstructure and enhanced the flexural property. Li et al. [42] used nitrile butadiene rubber powder (NBRP) as a filler in PF. They analyzed the effect of the addition of NBRP on the mechanical and microscopic properties of PF. With the addition of NBRP, the mechanical properties of PF get varied. With 1–3% addition of NBRP the properties varied marginally. But with 5% addition, the compressive strength of foam starts decreasing but at the same time, the bending stiffness of the PF gets enhanced as compared to base PF. Yuan et al. [41] synthesized phosphorous-containing polyurethane prepolymer (DOPU) and used it as a reinforcement in PF. The modified foam having 53.4 kg/m^3 shows the greatest specific bending stiffness.

7 Effect of Particle Reinforcement on the Mechanical Properties of PF

Microscale or nanoscale particles are used as a reinforcement in PF. The measurement of reinforcement particles can be done with the use of SEM and TEM. The previous work had shown that particle reinforcement also shows the same mechanism of strengthening as found in fiber reinforcement in PU foam. The strength of the particle reinforcement also depends on the stiffness of particles, the concentration of particles in phenolic resin mixture, and wettability in between particle and phenolic resin. Particles have a low aspect ratio as compared to fibers and because of this, it makes PF less anisotropic behavior. Same as fiber reinforcement, particles also act as nucleating sites during foaming and increases the cell density inside the foam. Uniform and finer cells are obtained through particle reinforcement. Particle reinforcement also affects the viscosity of the foam, but in comparison to fibers, particle addition does not create problems during foam as it has a low aspect ratio. With the addition of particles, the density of the foam gets increased [43].

7.1 Compressive Strength

Like fiber reinforcement, particle reinforcement also strengthens the compressive strength of PF. Rangari et al. [43] used a sonochemical technique for the incorporation of cloister-clay nanoparticles inside the PF. First, the clay particles were added into the phenolic resin, and then through ultra-sonication, they get dispersed throughout the mixture. Through microstructural analysis, it has been found that the cell shape and size are uniform throughout the foam. Result also shows the enhancement of compressive strength and modulus with the addition of nanoparticles as compared to neat PF. Zuo et al. [44] prepared phenolic composite foam using hollow glass beads (HGB) as a reinforcement. They investigate the effect of the addition of this reinforcement on the thermal and mechanical properties of composite PF. Through morphological analysis of composite foam, it is found that the average cell size of composite PF gets reduced with the addition of HGB. However, the compressive strength of the composite foam also gets significantly improved. The addition of HGB also improves the thermal stability of the composite foam. In PF thermal conductivity is less due to porosity. With the addition of nanoparticles the porosity gets reduced which helps in increasing the thermal conductivity of foam. Li et al. [45] synthesized silica nanosphere/graphene oxide (SGO) hybrid particles and used them as reinforcement in PF. For the synthesis of hybrid SGO particles, immobilization of silica particles on the graphene oxide sheet was done and then it is characterized through FESEM and TEM. Through the results, it has been shown that with the addition of SGO the compressive strength of PF gets increased up to 36.2% as compared to base PF. However, the addition of SGO also increases the thermal stability of the PF. Due to SGO, there is a reduction in heat release rate and total heat release during the formulation of PF. Luo et al. [46] in their work prepared SiO_2/graphene oxide nanoparticles of different sizes and used them as reinforcement in PF. They varied the size and volume fraction of SiO_2/GO inside the PF and analyzed the morphological and mechanical properties of PF. It is found that with SiO_2/GO-80 nanoparticles, the compressive strength and cell structure compatibility are more as compared to other sizes of reinforcement. With SiO_2/GO-80, the mean cell size of the PF is nearly about 117 μm and with 1% of this size reinforcement, the compressive strength and modulus get increased to 80 and 61%, respectively, than the pure PF. This hybrid composite nanoparticle PF can be formulated according to the application requirement by changing the size and proportion of components.

7.2 Flexural Strength

With the addition of particles, the flexural strength of the PF also gets varied. The interaction between the particles and the phenolic matrix plays an important role during the enhancement of the flexural strength of the PF. Particles with good wettability show enhancement in a flexural property, whereas improper bonding degrades the property. Yuan et al. [34] used poly(n-butyl acrylate)/silica core–shell nanoparticles which enhanced the mechanical properties of PF. With 180 nm side-particle reinforcement, the flexural strength of the PF gets increased up to 35%. This is mainly due to the formation of a covalent bond between the hydroxymethyl group and phenolic resin. But if the addition of nanoparticles is extended beyond a certain percentage then the viscosity of phenolic resin becomes too high which can create problems during the formulation of foam and may create some cracks inside the PF that reduces the flexural strength of the foam. The particles which get easily deformed and used as reinforcement in PF are more complex to study. Because the addition of soft particles increases the uniformity of cell shape and size, at the same time they decrease the rigidity of the PF. Li et al. [42] show that with the addition of 3 wt% of nitrile butadiene rubber powder, the compressive strength of the PF gets enhanced and the cell shape and size are more uniform. But the flexural strength of the foam gets decreased. For the improvement of the flexural strength of PF, some researchers have reported chemical modification during the formation of PF. With the use of polyethylene glycol or polyurethane components in a phenolic resin, they introduced a flexible chain that acts as a backbone to the phenolic resin. Owing to this backbone, the crosslinking density of the PF gets reduced, due to which the flexural strength of the foam gets enhanced. Sui et al. [47] used phosphate PEG at different molar masses to modify the structure of phenolic resin. The modification of the chemical structure of phenolic resin was carried out in the presence of phosphorous pentoxide. The addition of PEG shows that the modification in structure increases the toughness of foam which enhances the mechanical properties. With the addition of 6 wt% of PEG200, 400, and 600, the flexural strength of the foam gets enhanced to 12, 15, and 7%, respectively.

8 Conclusion

Phenolic foam has wide applications in different areas, but due to low mechanical properties, its application gets limited. So increasing the mechanical strength of PF itself is a very vast area of research. The mechanical strength of PF mainly relates to cell morphology and reinforcement like fibers or particles. The cell morphology can be controlled through different methods like chemical modification, types of filler used and their proportion, type of particles used, their size, proportion, and their wettability with the phenolic matrix. The cell size and shape also depend on the number of nucleating size that is generated during the formulation of PF. Fiber reinforcement improves the mechanical properties of PF in terms of compression and flexural strength. The strengthening of PF due to the addition of fibers depends on the stiffness of fiber, aspect ratio, and wettability with the phenolic resin matrix. Due to the high aspect ratio, fiber addition makes PF anisotropic, which makes the foam higher in strength in one direction and a little weaker in another direction. Fiber addition also affects the formulation of foam as it increases the viscosity of the mixture. In comparison to fiber addition, particle addition does not provide anisotropy inside the foam as it has a low aspect ratio. With particle addition, the mechanical properties enhancement follows the same kind of mechanism as considered during fiber reinforcement. The strength of the PF reinforced with particles depends on the size of the particle, the percentage of the addition of particles, and the wettability of the particles. The mechanical properties of PF can also be enhanced through the modification of the chemical structure. The mechanical properties of PF can be enhanced, by making the cell more flexible without the breakage of cell during loading. Through chemical modification during formulation, there is an introduction of a flexible chain in the rigid structure of PF.

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References

1. Kumar R, Mondal D, Chaudhary A et al (2018) Excellent EMI shielding performance and thermal insulating properties in lightweight, multifunctional carbon-cenosphere composite foams. Compos A Appl Sci Manuf 112:475–484
2. Landrock AH, Handbook of plastic foams: types, properties, manufacture and applications (1995) Elsevier
3. Pandey A, Birla S, Mondal D et al (2018) Compressive deformation behavior and strain rate sensitivity of Al-cenosphere hybrid foam with mono-modal, bi-modal and tri-modal cenosphere size distribution. Mater Charact 144:563–574
4. Pandey A, Muchhala D, Kumar R, et al (2020) Flexural deformation behavior of carbon fiber reinforced aluminium hybrid foam sandwich structure. Composites Part B: Engineering 183:107729
5. Hadlock T, Sundback C, Hunter D et al (2000) A polymer foam conduit seeded with Schwann cells promotes guided peripheral nerve regeneration. Tissue Eng 6:119–127
6. Twigg MV, Richardson JT (2007) Fundamentals and applications of structured ceramic foam catalysts. Ind Eng Chem Res 46:4166–4177
7. Baekeland LH (1909) The synthesis, constitution, and uses of Bakelite. Ind Eng Chem 1:149–161
8. Nutt SR, Shen B, Vaikhanski L (2003) Composite foams for sandwich structures. J Korean Ceram Soc 40:625
9. Auad ML, Zhao L, Shen H et al (2007) Flammability properties and mechanical performance of epoxy modified phenolic foams. J Appl Polym Sci 104:1399–1407
10. Mougel C, Garnier T, Cassagnau P et al (2019) Phenolic foams: A review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer 164:86–117
11. Pilato L, Phenolic resins: a century of progress (2010) Springer
12. Song SA, Chung YS, Kim SS (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93
13. Li X, Wang Z, Wu L et al (2016) One-step in situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6:74903–74912

14. Li Q, Chen L, Zhang J et al (2015) Enhanced mechanical properties, thermal stability of phenolic-formaldehyde foam/silica nanocomposites via in situ polymerization. Polym Eng Sci 55:2783–2793
15. Jing S, Li T, Li X, et al (2014) Phenolic foams modified by cardanol through bisphenol modification. Journal of Applied Polymer Science 131
16. Yang C, Zhuang ZH, Yang ZG (2014) Pulverized polyurethane foam particles reinforced rigid polyurethane foam and phenolic foam. Journal of Applied Polymer Science 131
17. Gardziella A, Pilato LA, Knop A, Phenolic resins: chemistry, applications, standardization, safety and ecology (2013) Springer Science & Business Media
18. Brezny R, Green DJ (1990) The effect of cell size on the mechanical behavior of cellular materials. Acta Metall Mater 38:2517–2526
19. Choe J, Kim M, Kim J (2016) A microwave foaming method for fabricating glass fiber reinforced phenolic foam. Compos Struct 152:239–246
20. Gibson LJ, Ashby MF, Cellular solids: structure and properties (1999) Cambridge university press
21. Kumar R, Sharma A, Pandey A et al (2020) Lightweight carbon-red mud hybrid foam toward fire-resistant and efficient shield against electromagnetic interference. Sci Rep 10:1–12
22. Sebastian MT, Wang H, Jantunen H (2016) Low temperature co-fired ceramics with ultra-low sintering temperature: a review. Curr Opin Solid State Mater Sci 20:151–170
23. Yu H, Guo Z, Li B et al (2007) Research into the effect of cell diameter of aluminum foam on its compressive and energy absorption properties. Mater Sci Eng, A 454:542–546
24. Liu H, Han C, Dong L (2008) Study on the cell structure and compressive behavior of biodegradable poly (ε-caprolactone) foam. Polym Eng Sci 48:2432–2438
25. Chen Y, Das R, Battley M (2015) Effects of cell size and cell wall thickness variations on the stiffness of closed-cell foams. Int J Solids Struct 52:150–164
26. Ranka M, Katepalli H, Blankschtein D et al (2017) Schizophrenic diblock-copolymer-functionalized nanoparticles as temperature-responsive Pickering emulsifiers. Langmuir 33:13326–13331
27. Aveyard R, Binks BP, Clint JH (2003) Emulsions stabilised solely by colloidal particles. Adv Coll Interface Sci 100:503–546
28. Zhou J, Yao Z, Chen Y et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym Compos 35:581–586
29. Forgiarini A, Esquena J, Gonzalez C et al (2001) Formation of nano-emulsions by low-energy emulsification methods at constant temperature. Langmuir 17:2076–2083
30. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Compos B Eng 75:367–372
31. Li Q, Chen L, Li X, et al (2016) Effect of nano-titanium nitride on thermal insulating and flame-retardant performances of phenolic foam. Journal of Applied Polymer Science 133
32. Li Q, Chen L, Li X et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Compos A Appl Sci Manuf 82:214–225
33. Yang Z, Yuan L, Gu Y et al (2013) Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes. J Appl Polym Sci 130:1479–1488
34. Yuan J, Zhang Y, Wang Z (2015) Phenolic foams toughened with crosslinked poly (n-butyl acrylate)/silica core-shell nanocomposite particles. Journal of Applied Polymer Science 132
35. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54:1962–1970
36. Secretariat O (2000) The Montreal protocol on substances that deplete the ozone layer. United Nations Environment Programme, Nairobi, Kenya
37. Desai A, Auad ML, Shen H et al (2008) Mechanical behavior of hybrid composite phenolic foam. J Cell Plast 44:15–36
38. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Compos A Appl Sci Manuf 34:899–906

39. Yu HY, Wang LY, Gai GQ Performance of modified aramid fiber reinforced phenolic foamAdvanced Materials Research, Trans Tech Publ, 2012;258–261.
40. Ma Y, Geng X, Zhang X et al (2018) A novel DOPO-g-KH550 modification wood fibers and its effects on the properties of composite phenolic foams. Pol J Chem Technol 20:47–53
41. Yuan H, Xing W, Yang H et al (2013) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 62:273–279
42. Li L, Xu YZ, Wang CP, et al Preparation and characterization of phenolic foam modified by nitrile butadiene rubber powderApplied Mechanics and Materials, Trans Tech Publ, 2012;4137–4142.
43. Rangari VK, Hassan TA, Zhou Y et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 103:308–314
44. Zuo YX, Yao ZJ, Zhou JT Mechanical and thermal properties of phenolic foams reinforced by hollow glass beadsAdvanced Materials Research, Trans Tech Publ, 2014;13–22.
45. Li X, Wang Z, Wu L (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. RSC Adv 5:99907–99913
46. Luo X, Yu K, Qian K (2018) Morphologies and compression performance of graphene oxide/SiO2 modified phenolic foam. High Perform Polym 30:803–811
47. Sui X, Wang Z (2013) Flame-retardant and mechanical properties of phenolic foams toughened with polyethylene glycol phosphates. Polym Adv Technol 24:593–599

Chapter 8
Thermal Stability of Phenolic Foams

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1 Introduction

The manufacturing of polymeric foams is widely arousing in the world today and continues to grow exponentially. Being lightweight, excellent insulating capabilities, energy-absorbing behavior, and comfortable for handling are some of the major reasons for this rapid pace. They have found applications in transporting, goods packaging, automobiles, insulation, decorative moldings, and also as flame retardants. Phenolic foams are widely used because they are fairly cheap and the most effective insulation materials. These foams have excellent fire properties and remarkably have less emission of smoke, and when exposed to heat these do not spill molten plastic. Phenolic foams are extremely chemical and solvent resistant.

The use of phenolic foams has expanded for insulation applications. In comparison with other polymeric foams, PF foams have some meritorious features. The use of foaming agents such as chlorofluorocarbon (CFCs) and hydrochlorofluorocarbon (HCFCs) has been limited because they can induce loss of ozone and global warming [1]. During combustion commercial polymer foams produce poisonous gases, resulting in the search for alternative materials and preparation methods [2, 3]. Previously, several researchers reported the fabrication of PF foams by using various foaming methods, and homogeneous mixing of phenolic resins with additives [3–7].

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Because PF exhibits poor thermal conductivity [8–12] and good resistance toward fire [1, 13–15], it can slow the rate of burning [16–18], minimize smoke formation [19], reduce the evolution of toxic gases, and retard molten droplets from forming [20].

Compared to expanded polyurethane and polystyrene foams, these characteristics make PF more suitable for fabricating thermal insulating materials [21–23]. Under compression, it exhibits good mechanical properties so that PF is also used as packaging and cushioning materials [21]. PF also draws much attention in many areas where fire resistance is needed, such as architectural materials, military, and civilian aircraft [13]. It is the less expensive polymer foam compared to all other foams. The low mechanical property of PF has limited its broader applications [24, 25]. Researchers' quest for new sustainable raw material resources has become an urgent issue because worldwide industries need more petroleum feedstock [26]. Thermal insulation research has therefore gained high attention by strengthening and enhancing PF's mechanical strength. Structural applications of phenolic foam have, however, been significantly restricted due to the excessive fragility and friability that creates significant problems while using structural sandwich panels [19]. Several attempts have been made in the past few decades to manufacture tougher phenolic foams by reinforcing with inert fillers such as carbon black, mica, asbestos, oak, and cork [27] and, in general, by enhancing the strength and homogeneity of foam materials, but none of the reinforcements has been able to enhance the hardness without improving the density [13]. Thermal insulation has wide uses in electronics. In order to minimize heat loss between a system and its surroundings, the thermal insulation material plays a crucial role in energy conservation or maintaining the temperature of the system at a constant value. We may divide thermal insulations into different types, such as sheet insulation, fibrous insulation, foam insulation, and vacuum panels.

In general, foam insulation is evolved from plastics or resins. It is divided into open-cell foams and closed-cell foams. While powder and fibrous insulations do have good efficiency in insulation but are expensive to produce. Moreover, due to the absorption of moisture, powders and fibers can agglomerate into larger particles and therefore reduce the efficiency of the insulation. Because of easiness to manufacture and maintain foam insulation is gaining more attention in engineering applications. Due to low thermal conductivity and excellent mechanical performance, polyurethane (PU) foams are the most popular foam for insulation applications [13]. Moreover, PU foams are chemical resistant too.

Polyethylene (PE) and polystyrene (PS) foams are other famous insulation foams, where PE foams are good insulators and moisture-resistant. All commercial foams (PU, PE, and PS) have excellent thermal insulating properties, but these are more susceptible to burning and are not suitable to be used in hazardous situations. In contrast, phenolic resins are not easy to burn. They don't spill except though they do. These are therefore suitable for use as insulation for household and industrial applications. In relative to other resins, phenolic foam has superior fire-resistant properties, less smoke while combustion, and a low coefficient of heat conduction

[28]. It is also thermally stable over a wide temperature range, from 19 to 200 °C but it is highly fragile and has less mechanical performance [11, 16, 23, 29].

2 Phenolic Foams

Recently, due to their fabulous potential applications, polymeric foams found to be used in the fields such as thermal and sound insulation, packaging materials, structural, and domestic components [30, 31]. The highly specialized applications, such as decontamination of nuclear and polluted water or space shuttle manufacturing are the areas where phenolic foam found its application because of its specific properties. The global phenolic foam market is playing with billions of euros due to their substantial profit-making (Fig. 1) [32]. Usually the polymeric foam comprised two or more phases. One is a gaseous phase dispersed as rubbers, elastomers, thermoplastics, or thermosets in a solid polymer matrix. According to the rigidity of the backbone of polymers, the foams can be again classified as flexible, semi-flexible, semi-rigid, or rigid. Depending on the degree of crystallinity and crosslinking, the characteristics and chemical composition of the polymer matrix change. Compared to other dense materials, the physical and mechanical properties of foams differ greatly. Foams can actually allow a wider range of applications compared to dense solids [33]. The major features associated with foams are given in the following:

- The fabrication of light structures is possible by combining with rigid components due to their low densities.
- Authentic, cost-effective insulation due to its low thermal conductivity.
- Because of low rigidity these foams found their applications as energy absorption materials.

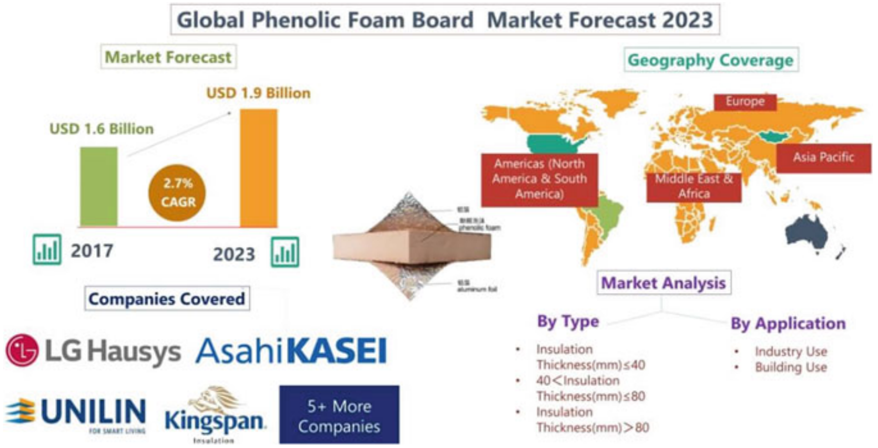

Fig. 1 Global market of phenolic foam in 2023 [32]

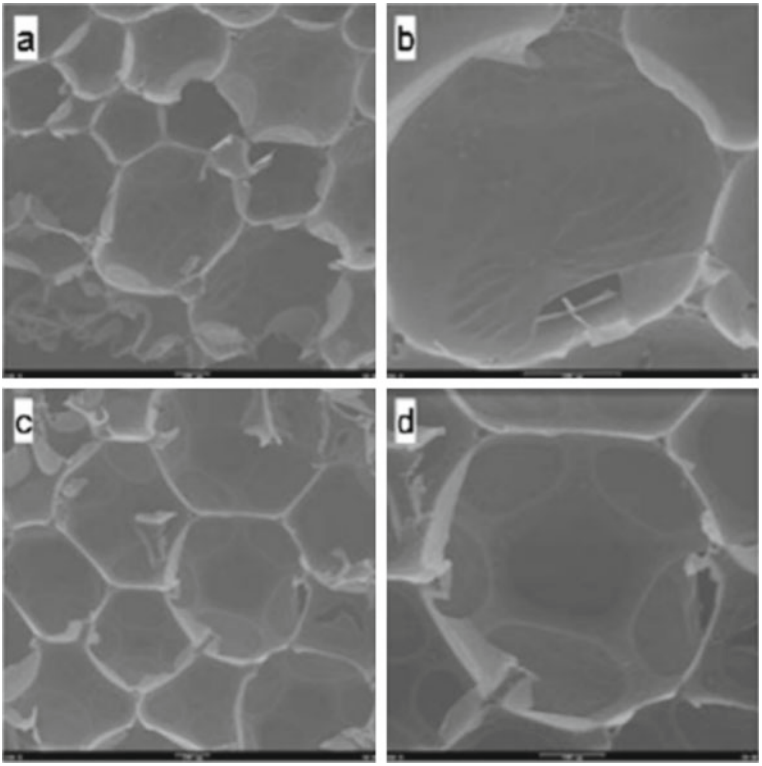

Fig. 2 SEM image of phenolic foams [34]

The final properties of the foam are determined by the structure of the cells (open or closed, diameter, and shape) (Fig. 2) [34]. For instance, cells that are closed are used for thermal insulation, and cells with open structures are used for making sound insulation materials [33]. Because of the excellent thermal stability, superior thermal insulation, magnificent fire retardance, no dripping behavior, and less emission of toxic gases during combustion, PF is considered as viable rigid thermosetting foams than any other commercial foams [35]. The major drawback severely limiting their applications is the chance of brittleness and pulverization [4]. So researchers are concentrating on enhancing the gross mechanical properties along with preserving their outstanding fire-retardant behavior.

The mechanical properties of the foam can be changed via two methods. The former depends on the composition of the foam. The type and quantity of each part in the formulation can be modified to maximize the final properties of the foam for a given phase [3, 36–38]. Moreover, the properties of the foam can be modified by the addition of other constituents to the reaction mixture. Fibers are used, for example, to boost the compressive and flexural strengths [39]. C. Mougel et al. [30] found that polyethylene glycol increases the deformation of cell walls and provides a nucleating agent or small particles to improve the density of the cell wall [15, 40–43]. In comparison, the property of fire resistance increased with the inclusion of flame-retardant materials [44]. The second path goes by the manufacturing method used for the production of foams. An open mold would prefer a high nonhomogeneous open cell content, while the use of a closed mold can result in a more homogeneous density with probably a high closed cell content [3].

3 Thermal Stability of Phenolic Foam Composites

Liu et al. [45] used a simple method for simultaneous reduction and functionalizing of GO without any external reduction agent. In relative to unreinforced foam there was a substantial improvement in mechanical properties by the inclusion of 4 phr Mg-rGO in PF foam. The reinforced PF foam exhibited a reduction in the pulverization ratio. Mg-rGO-reinforced PF foam exhibited higher thermal stability. The functionalization of GO with Mg improved the tortuous path which effectively hindered heat and mass transfer. The method outlined here offers a potential solution for the production of Mg-rGO as an efficient and promising flame-retardant.

The chemical composition, morphological analysis, mechanical properties, friability, thermal stability, and flame retardancy of the rigid phenolic foams (LTPFs) based on larch tannin and cork powder reinforcements to fabricate LTPFs (CLTPFs) were analyzed [46]. The findings revealed that relative to neat PF, the LTPFs displayed lesser morphology of the cells, compressive strength and thermal stability, high friability, and high flame retardancy. The limiting oxygen index (LOI) of LTPF10 was 47.8%. CLTPFs 10 exhibited superior cell morphology, high compressive and thermal properties, weak thermal conductivity, and low friability, relative to the unreinforced LTPFs 10. The compressive strength and module of CLTPFs 12 improved by 14.84% and 16.18%, respectively, at a cork powder concentration of 1 wt.%; the pulverization ratio and thermal conductivity of CLTPFs decreased by 18.4% and 32.29%, respectively. Furthermore, the cork powder reinforcement enhanced the thermal properties of LTPFs. The LOI values of CLTPFs were significantly smaller than the LTPF values. With 1 wt% minimum cork powder reinforced, LTPF demonstrated better features.

MWCNT-PF composite foams were fabricated by using ultrasonic cavitation with three different types of MWCNTs, including pristine, carboxyl, and amino MWCNT [41]. It was observed that there was a good increase in thermal stability and flame-retardant properties of the prepared PF composite foam with the loading of different MWCNT. At high temperatures, this resulted in high thermal stability and better stabilizing action of MWCNTs on phenolic foam. A closed-cell structure was observed from SEM results and increased cell diameter due to the higher content of MWCNTs, while the diameter of the cell decreased as a result of homogeneous dispersion of MWCNT.

By minimizing susceptibility to cause a fracture, decreasing the rate of crack propagation, and preventing the systemic breakdown of cell walls, the addition of

MWCNTs greatly influenced the strengthening of phenolic foam's compressive properties, including 0.05 wt% MWCNT-COOH enhanced the actual foam strength by 31%. Two types of carbon nanoparticles, a multi-wall carbon nanotube and graphene, were used to reinforce the phenolic foams to increase the mechanical and thermal efficiency by means of a short-period microwave foaming process [1]. Compared with the neat phenolic foam the particle-reinforced phenolic foams show higher thermal stability at 40–390 °C (Fig. 3). Thanks to the high cell density, particle-reinforced phenolic foams exhibited low thermal conductivity compared with the neat phenolic foam. Until the particle-reinforced phenolic foams begin pyrolyzing, they showed better thermal stability than the unreinforced phenolic foam. Both specimens displayed a significant weight loss of around 450 °C. This was often associated with the temperature of the phenolic materials on self-ignition (480 °C).

In order to improve the thermal and mechanical properties of phenolic foams, Li et al. [4] added the nanosilica particles to PF foam via in situ polymerization. Compared to neat PF foam, reinforced PF foam exhibits higher thermal stability. The rate of pyrolysis was lower and the residues of the char were higher than the neat PF. Sample thermal insulation was measured and it was associated with nanoreinforcement effects and subsequent cell structure. Because the mean size of the cell (MPF0.5) was smaller and the narrower cell size distribution than that of pure PF, the thermal conductivity of MPF0.5 decreased by 8.86% primarily. Furthermore,

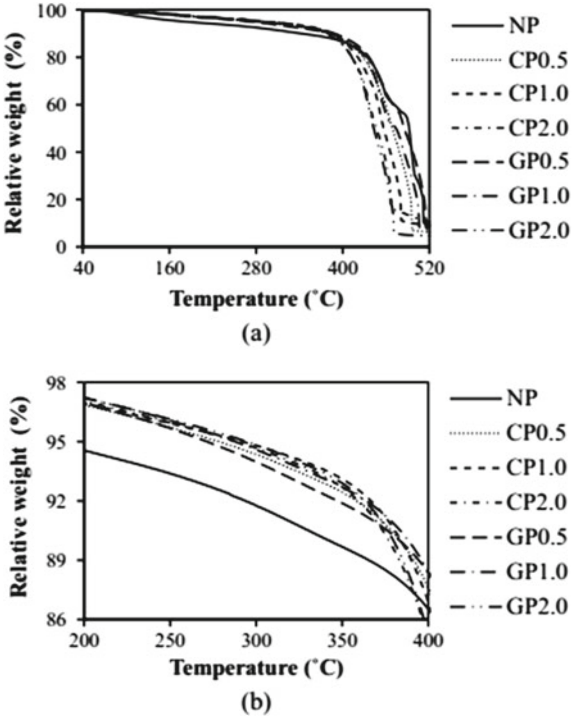

Fig. 3 TGA analysis of the phenolic foams: **a** Relative weight from 40 °C to 52 °C and **b** relative weight from 200 °C to 400 °C [41]

compared to pure PF foam, the cell distribution of MPF2s is more homogeneous. Based on the theory of thermal transfer, lower loading of silica sol in MPF0.5 cannot accelerate vibration of the molecular segment, which disrupts heat transmission. The results of the friability showed that the pulverization ratio pure PF is higher than that of MPFs and a significant decline of 58.29% was observed for the sample MPF2 [the lowest pulverization ratio (1.258%)], compared to pure PF.

By using high-intensity ultrasound technique, the PF nanocomposite foams were designed by incorporating organically functionalized attapulgite (ATP) (hexadecyl trimethyl ammonium cations absorbed on ATP) in nanometer scale into PF matrix to enhance thermal and mechanical properties of the prepared foam [9]. The thermal stability of PF was enhanced by HTAB-ATP incorporation. There has been an increment in the initial weight loss temperature of PF/HTAB-ATP nanocomposites at 30 °C, specifically. The introduction of HTAB-ATP drastically increased the viscosity of phenolic foam, but with increasing temperature, the gap between phenolic resin and HTAB-ATP-incorporated phenolic resin decreased. A good compatibility was observed for HTAB-ATP-modified phenolic resin compared to pure phenolic resin, and it also exhibited a higher curing degree than neat. Because of the narrow uniform cells and high cure rate, the compressive properties of PF/HTAB-ATP nanocomposites increased by 20%; moreover, the friability was also enhanced.

The phenolic (PF) and lignin particle-reinforced phenolic (LRPF) foam and lignin used as reinforcement (LR) thermal degradation kinetics have been observed [47]. Using a discrete distributed energy activation model (discrete DAEM) and a model-free kinetic (MFK) approach from Vyazovkin, the activation energies from the degradation processes were derived. The discrete DAEM has been checked by comparing the expected values to the data obtained at 8 °C/min. The kinetic parameters were calculated using heating ramps of 6 and 12 °C/min using the model. By comparing with the findings obtained for the PF, the reinforcement effect on the LRPF kinetics was observed. The activation energies of the PF ranged from 79.9 to 177.6 kJ/mol for reactions of non-zero mass fractions, and the activation energy for the LRPF ranged from 91 to 187 kJ/mol. The values for the activation energy for the LR are lower than for the foams (150–187 kJ/mol). Due to the use of LR, the LRPF's degradation mechanism was modified; therefore the average range of LRPF activation energy was between the levels for the PF and LR. Using the Vyazovkin method even the activation energy dependency on conversion was measured and compared with the findings of DAEM, so there was no compensation effect kinetic parameter observed.

PF has been applied to kaolin powder and glass fiber cloth to boost its thermal stability and mechanical properties [48]. The addition of kaolin powder resulted in the formation of uniform small cells of PF with thicker ribs to the wall, which resulted in superior mechanical properties. Improvement in thermal stability and mechanical properties with the addition of the kaolin powder was observed as it was deposited in PF backbones. However, if a significant proportion of the powder was incorporated into PF, particles continued to accumulate which produced large cells within the foam which was counterproductive to the mechanical and thermal characteristics of foam. On the other side, tension was added to both backbones and fabric by applying all fabric and powder to PF, resulting in the foam's innocuous mechanical properties.

The thermal stability was greatly enhanced since glass fiber fabric prevented the gas from coming out from PF foam. The IR results showed neither fabric nor kaolin powder interacts with the matrix.

Zhang et al. [25] successfully formulated phenolic foams reinforced with silicon whiskers and lignin (LWSPF). They have achieved a homogeneous dispersion of silicon whiskers and lignin was achieved within the host matrix. The efficiency of the composite materials was considerably enhanced by the implementation of silicon whiskers and lignin. This is because the foam cells are more homogeneous with reduced dimensions. From the TGA results, it was clear that the incorporation of silicon whisker and lignin material (0.6% and 10%, respectively) increased the PF's char yield by 55.6%. The thermal stability and mechanical properties of the composite were greatly improved due to the development of strong chemical bonds (Si–O) and the uniform dispersion of silicon whisker. The bending and compression strengths of the fabricated LWSPF got improved by 80.5% and 81.1%, respectively, relative to those of the neat PF foam.

In order to enhance the thermal and mechanical properties bamboo fiber was used as reinforcement for PF by combining phenolic resin and bamboo fiber with the help of foaming additives [49]. The thermal behavior of the reinforced foam was investigated from TG results and it showed that the deterioration of composite foams was high at initial temperatures and then essentially preserved throughout the same decomposition phase. Moreover, the thermal conductivity of both the pure PF and the reinforced foams were studied with both forms of fiber and the calculated value was 0.045 W/(m.K). The findings showed that a good addition of bamboo fibers to the resin matrix significantly increased the compressive and flexural properties and decreased its ratio of pulverization. An even homogeneous morphology of cells for unreinforced PF foams and the reinforced foam exhibiting large wide cells was observed from SEM analysis. All reinforced foams had higher LOI values (<40%).

Flax fiber mats modified by polyaryl polymethylene isocyanate (PAPI) were used as a reinforcing material for the preparation of phenolic foam-based composites [50]. The PAPI isocyanate groups interacted well with the phenolic hydroxyl groups of the phenolic resin, which was proved from findings of the FTIR spectral analysis. Initial decomposition of the prepared composite was observed from TGA results, suggesting that urethane groups and excess PR appear to induce degradation at lower decomposition temperatures. But a higher char residue was found at 700 °C due to the presence of a large number of benzene rings in PAPI and PR. Compared to the conventional composites the LOI values were superior for reinforced foams with higher PAPI loading. From the mechanical performance, they observed that there was similarity in the internal bonding, flexural strength, and impact strength. FF-PAPI/PR13 demonstrated the least mechanical performance, with the increasing content of PAPI mechanical properties improved steadily. At low PAPI content, the foam exhibited a large number of holes and voids. As long as with growing PAPI materials, the composites were becoming increasingly thick.

Yuan et al. [7] successfully fabricated a group of PF foams by using toughening agents. A small rise in heat resistance was observed from the TGA result showing that nanocomposite particles are efficient for improving thermal stability. The superior flame retardant efficiency of phenolic foam was remained intact after toughening which was proved from the LOI results. When the filler loading was less than 0.09 phr a homogeneous cell structure was observed from SEM findings. They analyzed the ideal filler loading was 0.03 phr. With the rise in the loading of nanoparticles, the flexural and compression strength demonstrate the first improvement and then depletion. Flexural strength, compressive strength, and elastic module were increased by 36.0%, 42.9%, and 32.3% relative to neat phenolic foam.

4 Thermal Stability of Toughened Phenolic Foams

Hu et al. [51] designed a new method for the addition of lignosulfonate into resole foam. A consistent cellular fine structure was observed from the SEM images. At 897.2 °C a residual carbon of approximately 48.56% was observed from the TGA analysis which showed the modified phenolic foam had a satisfactorily strong thermal stability. Two PF foams were fabricated by successful incorporation of toughening agents containing phosphorus—PPEG400 and PPEG600 [34]. They have researched the flammability and mechanical properties of phenolic foams modified by PPEG400 and PPEG600. Due to the early degradation of PPEG and the catalysis of carbonized phenolic foam, modified PF composites exhibited lower initial degradation temperatures and increased char residues than pure PF.

Improvement in the expansion ratio of the cells was observed by the addition of 5 wt% PPEG600 and it also facilitated uniform cell forming. When the toughening agents (PPEG) were loaded at 10 wt%, the LOI value of the modified phenolic foam found decreased and it remained at 40%. Both the modified PF foams showed high flame retardancy, which was revealed from the UL-94 results. There was a decrease in the peak heat release rate (PHRR) and the overall heat release (THR) of the sample modified with 10 wt% of PPEG600 material by 42% and 35%, respectively. The addition of 5 wt% PPEG600 and PPEG400 increased the toughness of the PPEG/PF systems.

Jing et al. [14] prepared phenolic foams modified with cardanol at different loadings. From TGA results it was clear that the thermal stability of the foam got improved by the addition of 5 wt% cardanol (Fig. 4). In relative to the neat PF foam, thermal stability got reduced when the cardanol loading exceeded 5 wt%. When cardanol dosage was more than 5 wt%, it improved prepolymer viscosity. The apparent density tests showed that the modified foams (5 wt% cardanol loading) produced the lowest apparent density. From the morphological analysis, they found that the diameter of some cells got increased with increasing cardanol loading which suggested that the cure cycle increased via a combination of cells. About the mechanical properties, the mechanical efficiency was marginally increased for phenolic foams with 5 wt% cardanol loading. Phenolic cardanol-modified foams improved by 22% in flexural strength and 28% in bending modules relative to unmodified phenolic foams, suggesting that cardanol integration increases the durability of phenolic foams. The mechanical efficiency of modified foams decreased when the cardanol loading was 15 wt% maximum.

Yuan et al. [52] synthesized a unique additive [phosphorus-containing prepolymer polyurethane (DOPU)] and then toughened PF foam were manufactured using DOPU and glass fiber. The FT-IR spectral findings revealed that DOPU isocyanate groups interacted fully with the phenolic resin hydroxyl groups. TGA suggested that putting together 3 wt% DOPU and 0.5 wt% glass fiber improved thermal efficiency along with increased char residue. Additionally, LOI values marginally decreased with higher prepolymer polyurethane content but were still higher than standard foam values.

Combining with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), a unique phosphorous-containing cardanol (PCC) derived from cardanol, which is a safe meta-substituted phenol and toxic by-product of the cashew industry, was exploited for manufacturing bio-based phenolic foams (PF) [53]. PCC showed higher thermal resistance. During combustion PO-free radicals are generated and

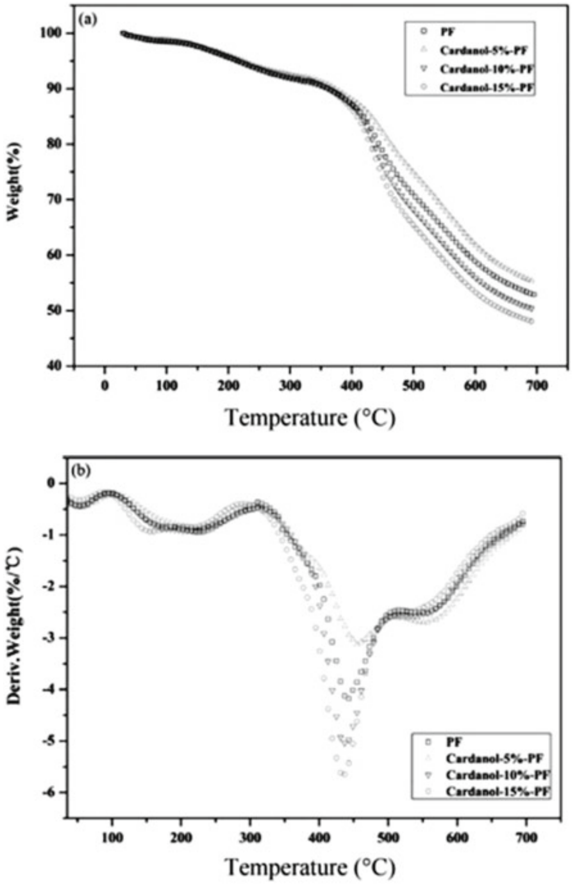

Fig. 4 **a** TGA and **b** DTG curves of phenolic foams with different contents of cardanol at nitrogen atmosphere [14]

these trapped free radicals in the gas phase resulted in improved flame retardancy. However, the phosphaphenanthrene group generated a char residue that hinders further polymer combustion. Furthermore, these modified PF foam demonstrated superior mechanical properties than neat PF. With 4% PCC, the compressive and flexural strength of PF got improved by 79.59% and 20.98%, respectively. As long as the PCC loading increases the pulverization ratio of bio-based PFs was declined. The results in this study suggest that PCC could be used as a phenol replacement to resolve the disadvantages of inherent brittleness and high friability. Based on cardanol a unique environmentally benign, halogen-free flame retardant (PSNCFR), containing P, Si, and N on the backbone chain, has been designed and integrated into PF [54]. The smoke production of PF foam was effectively stopped, improved flame retardancy, and helped to create a composite char defense against flames.

The thermal stability of integration of PSNCFR was increased by the integration of P, N, and Si in the system (Fig. 5). Compared to cardanol PSNCFR exhibited high char residue. PSNCFR implementation increased the flexural properties nearly by 155% of that of neat PF. A high LOI rating (41.9%) was observed for PSNCFR-modified PFs. Cone calorimetry measurements found that the PSNCFR-modified PFs showed higher flame retardancy. In fact, the PSNCFR-modified PFs TSP showed a reduction of 64.55%, indicating strong inhibition of smoke. By modifying the route of degradation PSNCFR operated in both the vapor phase and the condensed phase

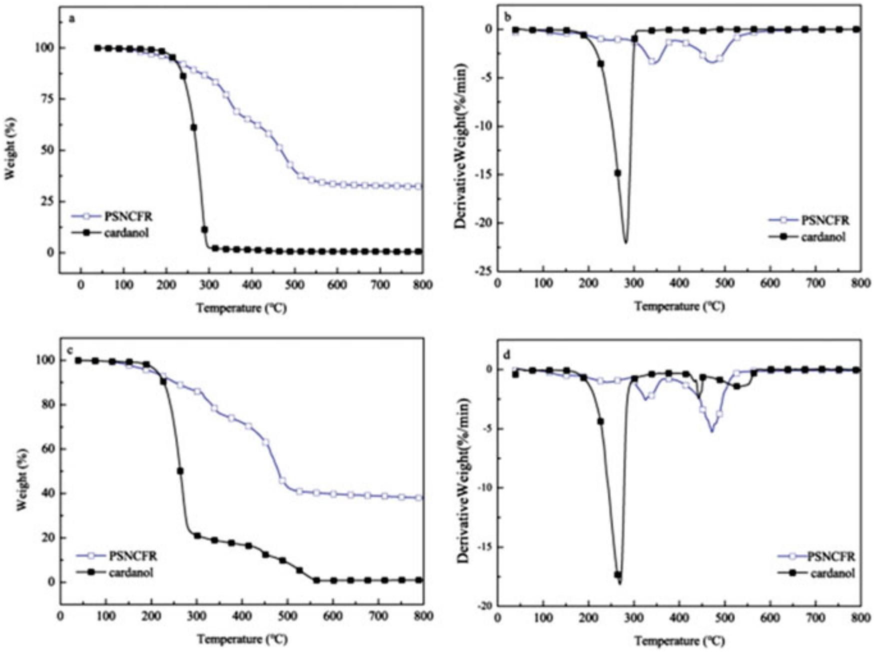

Fig. 5 **a** TGA and **b** DTG curves of cardanol and PSNCFR under N2, **c** TGA and **d** DTG curves of cardanol and PSNCFR under air [54]

to reduce exothermic reactions and combustion, thus maximizing the production of chars with the less evolution of volatiles. Thus, PSNCFR can be used in PF planning to deal with inherent fragility and high flammability disadvantages.

In order to fabricate biomass-based PF foam (TDKPFs), a unique reactive tung oil-based toughener with P and Si was prepared and inserted into PF's rigid molecular structure [55]. The fabricated TDKPF exhibited excellent thermal insulating property due to their low thermal conductivity. These long, bendy chains efficaciously advanced the compressive and bending strengths, which have been nearly 180% and 198% than that of pristine PF, respectively. The introduction of alkyl radical long chains decreased the flame retardancy of these TDKPFs with an improved limiting element index of 41.7%. The higher heat-release rate of the TDKPFs was reduced by 15.6% which was observed from cone measurement tests. Above all, a superior smoke suppression was shown by TDKPFs (7.29 m^2/m^2), thereby indicating a discount of 75.8% over pure PF (30.2 m^2/m^2). TDKPFs found great potential as insulation materials since the mechanism analysis discovered that throughout combustion the compact hybrid barrier inhibited the transfer of warmth, O_2, and mass.

In order to prepare toughened closed cell phenolic foams, lignin was isolated from sugarcane bagasse and used as a partial phenol replacement [56]. Using thermogravimetric (TG) and differential scanning calorimetry (DSC) techniques, the thermal stability of phenolic and ligno-phenolic foam has been studied under air and nitrogen atmosphere. From the thermal analysis data, it was clear that the thermal stability of the modified foam was not affected by partial replacement of phenol with lignin, rather than compromising its application. Zhou et al. [11] designed phenolic foam reinforced with fiberglass and glass fiber mats functionalized with nucleating agents. The properties of phenolic foam reinforced with fiberglass mat were analyzed using thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) where the unreinforced phenolic foam was taken as a control sample. Compared to non-reinforced foam, reinforced phenolic foam with fiberglass mats exhibited the least coefficient of thermal expansion.

After reinforcement, the glass transition temperature of the phenolic foam matrix remained unchanged. Analyzing DMA, the reinforced phenolic foam showed better storage modulus than that of unreinforced foam, and the loss modulus of the reinforced PF foam was lesser than that of the latter. Throughout the reinforcement, the glass transition temperature of the phenolic foam matrix remained the same observed from TMA and DMA. The abundance of substances, including the number of phenols and long-chain alkanes, makes it more likely to replace the whole bio-oil with hard resin phenols [57]. A large number of flexible functional groups are introduced into the structure of PF by using bio-oil to partially replace the phenol. Compared to PF the toughened PF foam showed the least spray ratio, higher compressive strength, and flexural strength.

The addition of bio-oil also made the cell sizes of the foams smaller and more uniform. This showed that bio-oil has had a beneficial effect on foam durability. Similar to other toughening agents, the addition of bio-oil resulted in the degradation of flame retardancy of the toughened BPF foams due to the decrease in LOI, char residue at 600 °C (Fig. 6), and the mild rise in thermal conductivity. The bio-oil may

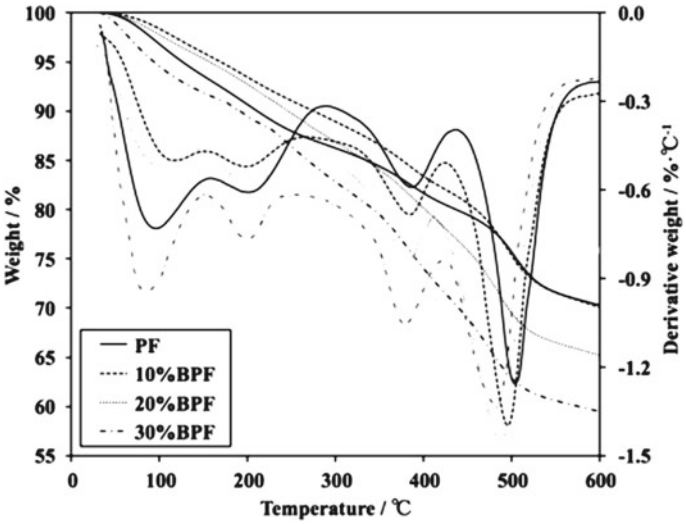

Fig. 6 Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of PF and BPFs [57]

Table 1 Degradation data of PF and BPFs by TG analysis [57]

Foams	$T_{-5\%}$ (°C)	T_{mas} (°C)	Residue at 600 °C (%)
PF	126	505	70.27
10%BPF	169	495	70.10
20%BPF	156	489	65.22
30%BPF	103	482	59.79

also be used as a green toughening agent since the disadvantages of bio-oil were mild and the BPFs retained strong flame-retardant properties, thermal insulation, and thermal stability (Table 1).

Hu et al. [43] fabricated phenolic foams reinforced with glass fiber and nanoclay for improving their mechanical properties, thermal properties, cell structure, and flame retardancy. Reduction of fire hazards was observed with the incorporation of nanoclay by increasing the composite foam's thermal stability, reducing the maximum heat release rate, total heat release, and total smoke release of the prepared foam. Because of the excellent synergistic effects of glass fiber and nanoclay, it remarkably improved foam's compression strength, thermal stability, and flame retardance. The average cell aperture was reduced by the addition of nanoclay and glass fiber. A significant reduction in pulverization rate was observed from the results by adding glass fibers and nanoclay. With increasing loading of glass fiber and nanoclay, the compression strength of the composite foam first improved and then falls while the impact strength of the composite foam increased. From the morphological analysis, it was clear that the number of open cells increases by excessive addition of glass fiber but the cell size can be controlled by an appropriate amount of nanoclay. The higher loading of clay enhanced the cell wall thickness and number of open cells.

5 Conclusions

This chapter focuses on the analysis of the enhancement of thermal properties of phenolic foams either by reinforcements or by toughening. The thermal properties depend on the morphology of the cell. In truth, the addition of reinforcements and toughening agents has been shown to minimize the diameter of the cell, enhance the density of the cell, and eventually boost the homogeneity of the cell. The new cell formation is promoted by the fillers which can act as nucleating agents. In addition, reinforcements and toughening agents improve the viscosity which inhibits cell growth and coalescence. In addition, fillers can also play the role of surfactant, and the particles embedded in the cell wall can enhance the thickness of cell walls, decreasing cell collapse and merging. Therefore, the parameters of the formulation and procedure need to be optimized for better performance. Finally, thanks to today's fantastic sustainability growth, one section of this analysis was devoted to PF generated from biomass-based resole resin. Researchers have aimed to replace the phenol with green biomass energy, at least partly. Environmentally benign solvent resins like cardanol, lignin, walnut shells, wood, or bamboo powder are efficient for replacing traditional phenolic resins with superior or equivalent thermal properties by manufacturing foams.

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References

1. Song SA, Chung YS, Kim SS (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93. https://doi.org/10.1016/j.compscitech.2014.08.013
2. Lee LJ, Zeng C, Cao X et al (2005) Polymer nanocomposite foams. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2005.06.016
3. Pilato L (2010) Phenolic resins: A century of progress
4. Li Q, Chen L, Zhang J, Zheng K, Zhang X, Fei Fang XT (2015) Enhanced Mechanical Properties, Thermal Stability of Phenolic-Formaldehyde Foam/Silica Nanocomposites via In Situ Polymerization. POLYM ENG SCI 55:2783–2793. https://doi.org/10.1002/pen.24169
5. Zhao YK, Chen TY, Su SW, Wu CF (2010) Heat insulation performance for application of phenolic resin foam material as construction material. In: IET Conference Publications
6. Cardona F, Kin-Tak AL, Fedrigo J (2012) Novel phenolic resins with improved mechanical and toughness properties. J Appl Polym Sci. https://doi.org/10.1002/app.34719

7. Yuan J, Zhang Y, Wang Z (2015) Phenolic foams toughened with crosslinked poly (n-butyl acrylate)/silica core-shell nanocomposite particles. J Appl Polym Sci 132:1–8. https://doi.org/10.1002/app.42590
8. Yang H, Wang X, Yu B et al (2013) A novel polyurethane prepolymer as toughening agent: Preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci. https://doi.org/10.1002/app.38399
9. Zhuang ZH, He B, Yang ZG (2010) Preparation and characterisation of phenolic foam/HTAB-ATP nanocomposites. Plast Rubber Compos 39:460–464. https://doi.org/10.1179/174328910X12691245470239
10. Tseng C, jen, Kuo K te, (2002) Thermal radiative properties of phenolic foam insulation. J Quant Spectrosc Radiat Transf. https://doi.org/10.1016/S0022-4073(01)00129-7
11. Zhou J, Yao Z, Chen Y et al (2013) Thermomechanical analyses of phenolic foam reinforced with glass fiber mat. Mater Des 51:131–135. https://doi.org/10.1016/j.matdes.2013.04.030
12. Kim J, Lee JH, Song TH (2012) Vacuum insulation properties of phenolic foam. Int J Heat Mass Transf. https://doi.org/10.1016/j.ijheatmasstransfer.2012.05.051
13. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Compos Part A Appl Sci Manuf. https://doi.org/10.1016/S1359-835X(03)00136-2
14. Jing S, Li T, Li X et al (2014) Phenolic foams modified by cardanol through bisphenol modification. J Appl Polym Sci. https://doi.org/10.1002/app.39942
15. Sui X, Wang Z (2013) Flame-retardant and mechanical properties of phenolic foams toughened with polyethylene glycol phosphates. Polym Adv Technol 24:593–599. https://doi.org/10.1002/pat.3121
16. Deng DQ, Xu L (2003) Measurements of thermal expansion coefficient of phenolic foam at low temperatures. Cryogenics (Guildf). https://doi.org/10.1016/S0011-2275(03)00122-X
17. Yun MS, Il LW (2008) Analysis of bubble nucleation and growth in the pultrusion process of phenolic foam composites. Compos Sci Technol. https://doi.org/10.1016/j.compscitech.2007.05.010
18. Periadurai T, Vijayakumar CT, Balasubramanian M (2010) Thermal decomposition and flame retardant behaviour of SiO 2-phenolic nanocomposite. J Anal Appl Pyrolysis 89:244–249. https://doi.org/10.1016/j.jaap.2010.08.010
19. Rangari VK, Hassan TA, Zhou Y et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 103:308–314. https://doi.org/10.1002/app.25287
20. Ma Y, Wang J, Xu Y et al (2013) Preparation and characterization of phenolic foams with eco-friendly halogen-free flame retardant. J Therm Anal Calorim. https://doi.org/10.1007/s10973-013-3180-6
21. Gontier C, Bouchou A, Vinot C (2001) A mechanical model for the computation of phenolic foams in compression. Int J Mech Sci. https://doi.org/10.1016/S0020-7403(01)00019-4
22. Pizzi A, Celzard A, Fierro V, Tondi G (2012) Chemistry, morphology, microtomography and activation of natural and carbonized tannin foams for different applications. In: Macromolecular Symposia
23. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Compos Part B Eng 75:367–372. https://doi.org/10.1016/j.compositesb.2015.01.049
24. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Lignin particle- and wood flour-reinforced phenolic foams: Friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos Part B Eng. https://doi.org/10.1016/j.compositesb.2015.05.043
25. Zhang N, Hu L, Guo Y et al (2020) Mechanical property of lignin-modified phenolic foam enhanced by whisker silicon. J Dispers Sci Technol 41:348–354. https://doi.org/10.1080/01932691.2019.1578662
26. Shukla SK, Maithani A, Srivastava D (2014) Studies on the effect of concentration of formaldehyde on the synthesis of resole-type epoxidized phenolic resin from renewable resource material. Des Monomers Polym 17:69–77. https://doi.org/10.1080/15685551.2013.840469

27. Knop A, Scheib W (1979) Chemistry and Applications of Phenolic Resins. Springer, New York, USA
28. Wang G, Liu X, Zhang J et al (2018) One-pot lignin depolymerization and activation by solid acid catalytic phenolation for lightweight phenolic foam preparation. Ind Crops Prod. https://doi.org/10.1016/j.indcrop.2018.07.080
29. Mutlu I, Oner C, Findik F (2007) Boric acid effect in phenolic composites on tribological properties in brake linings. Mater Des. https://doi.org/10.1016/j.matdes.2005.09.002
30. Mougel C, Garnier T, Cassagnau P, Sintes-Zydowicz N (2019) Phenolic foams: A review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer (Guildf) 164:86–117. https://doi.org/10.1016/j.polymer.2018.12.050
31. Landrock AH (1995) Handbook of Plastic Foams: Types, Properties. Elsevier Science, Manufacture and Applications
32. Forecast of Global Phenolic Foam Board Market 2023. In: MRRPB10618002. www.marketresearchreports.com
33. Eaves D (2004). Handbook of polymer foams. polimeri
34. Yang H, Wang X, Yuan H, et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 19:. https://doi.org/10.1007/s10965-012-9831-7
35. Li X, Wang Z, Wu L, Tsai T (2016) One-step: In situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6:74903–74912. https://doi.org/10.1039/c6ra12208f
36. Gardziella A, Pilato LA, Knop A (2000) Phenolic Resins. Springer-Verlag, Berlin Heidelberg
37. Xiang-Ming Hu, Yan-Yun Zhao W-MC (2015) Effect of Formaldehyde/Phenol Ratio (F/P) on the Properties of Phenolic Resins and Foams Synthesized at Room Temperature. Polym Compos 36:1531–1540. https://doi.org/10.1002/pc.23060
38. Zhou J, Yao Z, Chen Y, et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym Compos. https://doi.org/10.1002/pc.22698
39. Desai A, Auad ML, Hongbin Shen, Nutt SR (2008) Mechanical behavior of hybrid composite phenolic foam. J Cell Plast. https://doi.org/10.1177/0021955X07078021
40. Gao M, Yang YL, Xu ZQ (2013) Mechanical and flame retardant properties of phenolic foam modified with polyethyleneglycol as toughening agent. In: Advanced Materials Research
41. Yang Z, Yuan L, Gu Y, et al (2013) Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes. J Appl Polym Sci. https://doi.org/10.1002/app.39326
42. Li Q, Chen L, Li X, et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Compos Part A Appl Sci Manuf. https://doi.org/10.1016/j.compositesa.2015.11.014
43. Wang XHWCWND (2015) Flame Retardant, Thermal, and Mechanical Properties of Glass Fiber/Nanoclay Reinforced Phenol–Urea–Formaldehyde Foam. Polym Polym Compos 37:2323–2332. https://doi.org/10.1002/pc.23411
44. Ma Y, Wang J, Xu Y et al (2015) Effect of zinc oxide on properties of phenolic foams/halogen-free flame retardant system. J Appl Polym Sci 132:1–8. https://doi.org/10.1002/app.42730
45. Liu L, Wang Z (2018) Facile synthesis of a novel magnesium amino-tris-(methylenephosphonate)-reduced graphene oxide hybrid and its high performance in mechanical strength, thermal stability, smoke suppression and flame retardancy in phenolic foam. J Hazard Mater 357:89–99. https://doi.org/10.1016/j.jhazmat.2018.05.052
46. Li J, Zhang A, Zhang S et al (2019) Larch tannin-based rigid phenolic foam with high compressive strength, low friability, and low thermal conductivity reinforced by cork powder. Compos Part B Eng 156:368–377. https://doi.org/10.1016/j.compositesb.2018.09.005
47. Carlos Domínguez J, Del S-O, Oliet M et al (2020) Thermal degradation kinetics of a lignin particle-reinforced phenolic foam. J Cell Plast. https://doi.org/10.1177/0021955X20932889
48. Xiao W, Huang Z, Ding J (2017) The mechanical and thermal characteristics of phenolic foam reinforced with kaolin powder and glass fiber fabric. IOP Conf Ser Mater Sci Eng 274. https://doi.org/10.1088/1757-899X/274/1/012013

49. Tang Q, Fang L, Guo W (2019) Effects of Bamboo Fiber Length and Loading on Mechanical, Thermal and Pulverization Properties of Phenolic Foam Composites. J Bioresour Bioprod 4:51–59. https://doi.org/10.21967/jbb.v4i1.184
50. Gao L, Tang Q, Chen Y et al (2018) Investigation of novel lightweight phenolic foam-based composites reinforced with flax fiber mats. Polym Compos. https://doi.org/10.1002/pc.24130
51. Hu L, Zhou Y, Liu R et al (2013) Synthesis of foaming resol resin modified with oxidatively degraded lignosulfonate. Ind Crops Prod 44:364–366. https://doi.org/10.1016/j.indcrop.2012.11.034
52. Yuan H, Xing W, Yang H et al (2013) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 62:273–279. https://doi.org/10.1002/pi.4296
53. Bo C, Hu L, Chen Y et al (2018) Synthesis of a novel cardanol-based compound and environmentally sustainable production of phenolic foam. J Mater Sci 53:10784–10797. https://doi.org/10.1007/s10853-018-2362-9
54. Bo C, Shi Z, Hu L et al (2020) Cardanol derived P, Si and N based precursors to develop flame retardant phenolic foam. Sci Rep 10:1–12. https://doi.org/10.1038/s41598-020-68910-6
55. Song F, Li Z, Jia P et al (2020) Phosphorus-containing tung oil-based siloxane toughened phenolic foam with good mechanical properties, fire performance and low thermal conductivity. Mater Des. https://doi.org/10.1016/j.matdes.2020.108668
56. De Carvalho G, Frollini E (2002) Lignin in phenolic closed cell foams: Thermal stability and apparent density. J Macromol Sci - Pure Appl Chem 39 A:643–656. https://doi.org/10.1081/MA-120004509
57. Yu Y, Wang Y, Xu P, Chang J (2018) Preparation and characterization of phenolic foam modified with bio-oil. Materials (Basel) 11:12–14. https://doi.org/10.3390/ma11112228

Chapter 9
Thermal Conductivity of Phenolic Foams

Zhonglei Ma

1 Introduction

Cellular materials composed of numerous micro- or nanoscale bubbles have attracted significant commercial and industrial interests in thermal insulation materials [1–4]. Compared with the solid polymers, the cellular materials exhibit superior comprehensive properties such as reduced mass density, increased specific mechanical properties (mechanical property to density ratio) [5, 6]. Especially, the introduction of gaseous phase with a low conductivity significantly decreases the thermal conductivity of cellular materials and endows them with excellent thermal insulating capacities [7, 8]. Due to these advantageous superiorities, cellular materials have been widely applied to many space-related applications for thermal protection systems (TPS) to effectively protect the aerodynamic surfaces, propulsion systems, and ground equipment against rigorous heating environments [9]. They also have been used as inner wall and core material of the sandwich structures for thermal insulation in building to effectively reduce heat loss and save energy [10]. Therefore, the cellular materials have wide applications in aerospace, nuclear engineering and building for conservation of energy, and control of heat transfer [11, 12].

Polymeric foams such as polystyrene (PS) [13, 14], polyurethane (PU) [15, 16], polyethylene (PE) [17], and polyvinyl chloride (PVC) [18] foams have been commercialized as thermal and acoustic insulating cellular materials for decades. The low relative density (dr) endows the polymeric foams with sufficiently low thermal conductivity for thermal insulation (Fig. 1). However, the commercial polymer foams are usually highly flammable and release pungent smoke and toxic gases during the

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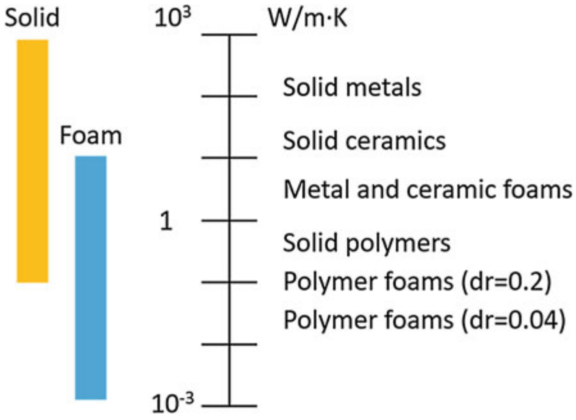
Fig. 1 Range of thermal conductivities of the foams and solids [25]



combustion, which will seriously threaten the survival of human beings [19]. Moreover, the foaming agents such as chlorofluorocarbon (CFCs) and hydrochlorofluorocarbons (HCFCs) used for the fabrication of these polymeric foams have been restricted by many countries and organizations due to ozone depletion and global warming concerns [20]. Some environmentally friendly strategies such as supercritical fluid foaming, microwave foaming, and mechanically whipping techniques have been developed for the fabrication of polymeric foams [21–23]. In addition, mechanical properties, thermal stability, and chemical reagent resistance also should be taken into consideration for high-tech applications in areas such as aerospace and nuclear engineering [24]. The PU foams often exhibit relatively poor acid and alkaline resistance, which greatly limits their practical applications in some special areas.

Therefore, more efficient insulation materials with reduced environmental impacts, improved performances, and advanced techniques for thermal insulation have become important issues.

Phenolic foams (PFs) are known as rigid thermosetting polymeric foams with low thermal conductivity, outstanding chemical resistance, outstanding thermal and acoustic insulation performances, especially excellent flame resistance and low smoke production [25–27]. In the early 1940s, PFs were first introduced in German industry as aircraft thermal insulation materials. Furthermore, PFs exhibit high thermal stability over the broad temperature range from –196 to 200 °C and a high self-ignition temperature of 480 °C [28]. These specific features facilitate the phenolic foams to be used in some highly specialized applications, particularly as thermal insulation materials in aerospace, building, shipbuilding, petroleum, and chemical industry [29–31]. The cell geometry (open/closed, cell size, and density) has great effects on the final performances of the foams [32]. Foams with closed cells are preferred for thermal insulation while those with open cells are more suitable for sound insulation applications [33, 34]. The closed-cell foams containing high molecular weight gases possess the lowest thermal conductivity except those filled with vacuums. In the aviation and aerospace industry, phenolic foams also have been widely used as the key technology of spacecraft thermal protection system (TPS) to protect the aerospace vehicles by minimizing the heat transfer into the interior structures [9]. They occupy a large economic weight for insulation and have a substantial global market in the billions of euros. However, PFs present relatively higher thermal conductivity than the other polymeric foams owing to the high thermal conductivity (0.4 W/m·K) of the solid phenolic polymer [28]. Therefore, reducing the thermal conductivity of PF for high insulation capacity by various strategies such as optimizing preparation processes, adding low thermal-conductivity fillers, regulating foam density and cellular morphologies are of great interests in both academia and industry.

2 Theories of Thermal Conduction Mechanisms

2.1 Thermal Conductivity in Polymeric Foams

Thermal conductivity k and thermal diffusivity a are two important physical parameters for evaluating the thermal insulating performances. Thermal conductivity refers to the capacity of a material to conduct heat perpendicular to the heat flow direction through a unit surface per unit of length and temperature [35]. According to the Fourier's law, the thermal conductivity is defined as:

$$k = -q/\nabla T \tag{1}$$

where q is the heat flux (the amount of heat flowing across a unit area per unit time), $\bigtriangledown T$ is the temperature gradient. The units of k are W/m·K. Equation 1 is suitable for the problems of steady conduction, for which the temperature profile does not change with time. For the non-steady conduction, the difference in heat entering and leaving a small element should be taken into consideration. The difference remains within the element causing its temperature to change with time τ:

$$\rho C_P \frac{\partial T}{\partial \tau} = \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right) \tag{2}$$

where ρ represents the density, the specific heat C_p represents the thermal capacity per unit volume of the material (the heat required to increase the temperature of a unit volume by one degree K). Given the ρ, C_p, and k constant values, the non-steady conduction equation can be expressed as:

$$\frac{\partial T}{\partial \tau} = a \frac{\partial^2 T}{\partial x^2} \tag{3}$$

where a, the thermal diffusivity of the material is defined as:

$$a = k/\rho C_p \tag{4}$$

The units of a are the same as those for any diffusion coefficient: m^2/s.

For polymeric foams, heat transfer takes place by four distinct mechanisms including conduction via the solid cell walls and struts (k_s), conduction via the gas in the cells (k_g), thermal radiation through the cell walls and across the cells (k_r) and thermal convection within the cells (k_c). Therefore, the total thermal conductivity (k_t) of polymeric foams can be expressed as [36]:

$$k_t = k_g + k_s + k_r + k_c \tag{5}$$

The conduction of heat represents an autonomous thermal transfer from a high-temperature region to a low-temperature region without the bulk movements. The molecules transmit part of their kinetic energy to the adjacent atoms through collision. The thermal convection can be ignored when the cell diameter is smaller than 3 mm [36]. Considering that most of the polymeric foams have smaller cell diameters less than 500 μm, the total thermal conductivity of polymeric foams can be adjusted into [37]:

$$k_t = k_g + k_s + k_r \tag{6}$$

In general, the k_s mainly depends on the foam density. k_g shows inverse relationship with the porosity and cell density, while k_r mainly depends on the foam density and cell diameter [38, 39]. Typically, heat transfer via the gas comprises 40%–50% of the total heat transfer. The thermal insulation properties of the polymeric foams are derived from the intrinsic thermal conductivities and thermal diffusivities of the materials and cell gases, as well as the cellular morphologies such as porosity, cell size, cell wall and strut content, etc. [40].

2.1.1 Conductivity Via Solid Phase

Various theoretical models have been established to estimate the solid conductivity k_s of the cellular materials. Placido et al. [41] developed a dodecahedral cell model to calculate k_s by introducing the geometric factors of strut diameter, cell diameter, and cell wall thicknesses. It is noted that this model is more suitable for cellular materials with uniform cell size but not recommended for polymeric foams with non-uniform structures. An alternative unit cubic cell model related to the porosity is developed to estimate k_s [42]. If the unit cubic cell consists of struts as shown in Fig. 2a, k_s of the polymeric foams can be expressed as:

$$k_s = k_{st}x^2 + k_f\left(1 - x^2\right) + \frac{2x(1 - x)k_{st}k_f}{k_{st}(1 - x) + k_f x} \tag{7}$$

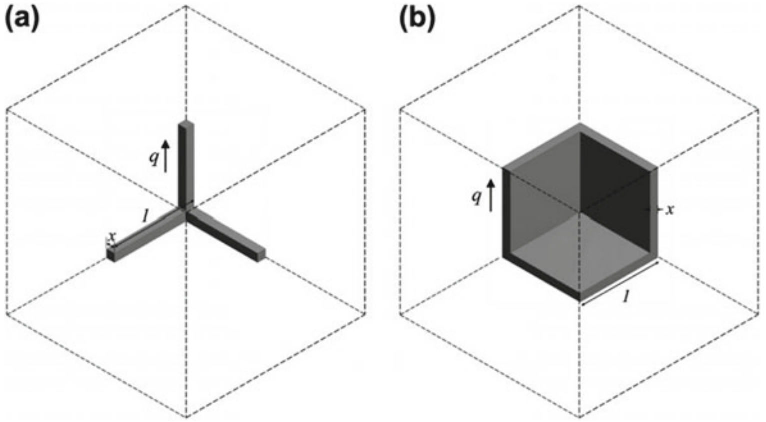


Fig. 2 Unit cubic cells consist of struts (**a**) and walls (**b**) [42]

where k_{st} and k_{f} refer to thermal conductivities of the strut and the fluid in the cells, respectively. χ refers to the relative thickness of the strut as a function of the porosity ε:

$$x = \frac{1}{2} + \cos\left(\frac{1}{3}\cos^{-1}(2\varepsilon - 1) + \frac{4}{3}\pi\right) \tag{8}$$

If the unit cubic cell consists of walls as shown in Fig. 2b, k_{s} of the polymeric foams can be expressed as:

$$k_s = \frac{k_f\varepsilon^{\frac{2}{3}} + k_w\left(1 - \varepsilon^{\frac{2}{3}}\right)}{k_f\left(\varepsilon^{\frac{2}{3}} - \varepsilon\right) + k_w\left(1 - \varepsilon^{\frac{2}{3}} + \varepsilon\right)}k_w \tag{9}$$

where k_{w} refers to the thermal conductivity of the wall. Kim et al. [42] reported that the k_{s} values calculated by Eqs. 7 and 9 corresponding to the struct-cubic and wall-cubic cell models are 1.26 and 2.42 mW/m·K, respectively.

2.1.2 Conductivity Via Gas Phase

The conductivity via gas k_{g} in a continuum range can be estimated by:

$$k_g = \frac{1}{3}\rho c_{\upsilon} l a \tag{10}$$

where ρ refers to the foam density, c_υ refers to the specific heat at constant volume, l represents the mean free-path of gaseous molecules, and a is the speed of sound. However, the gas conduction mechanism is changed when the gas pressure is very low so that the distance of conduction is same or smaller than the mean free path of gaseous molecules. Based on the gas conduction theory for rarefied gas region, Kwon et al. [43] developed an equation of k_g at room temperature as follow:

$$k_g = \frac{k_{g0}}{1 + \frac{0.032}{P\Phi}} \tag{11}$$

where $k_{\text{g}0}$ represents the thermal conductivity of gas at a continuum range. P and Φ refer to the gas pressure (Pa) and cell size of the polymeric foams (m).

2.1.3 Conductivity Via Radiation

Radiative heat transfer contributes significantly to the total thermal conductivity when the environment temperature of the polymeric foams is very high. The conductivity via radiation k_r can be estimated by:

$$k_r = \frac{16\sigma T^3}{3E_R} \tag{12}$$

where σ and E_R refer to the Stefan–Boltzmann constant and Rosseland extinction coefficient, respectively, and T represents the average temperature. The Rosseland extinction coefficient is expressed as

$$\frac{1}{E_R} = \frac{C_1 C_2}{4\sigma T^5} \int\limits_0^\infty \frac{1}{E_\lambda} \cdot \frac{1}{\lambda^6} \left[\exp\left(\frac{C_2}{\lambda T}\right) - 1\right]^{-1} d\lambda \tag{13}$$

where, $C_1 = 2\pi hc^2$ and $C_2 = hc/k_\text{B}$, where h represents the Planck constant, c represents the light speed in vacuum and k_B is the Boltzmann constant, and λ is the wavelength. The spectral extinction coefficient E_λ can be expressed by:

$$E_\lambda = -\frac{\ln(\tau_\lambda)}{L} \tag{14}$$

where L is the thickness of the material. Therefore, the conductivity via radiation k_r can be estimated by measuring τ_λ. Kim et al. [42] reported that the average k_r of phenolic foams at 298 K is calculated to be 2.44 mW/m·K, and the $k_\text{s} + k_\text{r}$ is measured as 5 ± 0.25 mW/m·K. Accordingly, the k_s value of phenolic foams is obtained to be 2.56 ± 0.25 mW/m·K, which agrees well with the theoretical result

(2.42 mW/m·K) of Eq. 9, indicating that the conductivity via solid is much closer to the wall-cubic cell model than the strut-cubic cell model.

2.1.4 Thermal Conductivity in Syntactic Foams

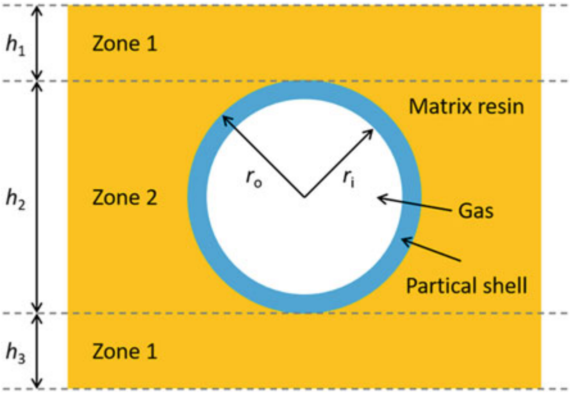
Phenolic syntactic foams filled with hollow particles have also attracted great interests in weight-sensitive applications such as aerospace and marine structures. To establish theoretical models for the thermal conductivity, syntactic foams are equivalent to three-phase microstructures consisting of the matrix polymer, hollow particle shell, and gas within the hollow particles. Theoretical models such as Liang model, Felske model, Porfiri model, and Park model have been established to predict the thermal conductivity of syntactic foams [44]. The effective thermal conductivity of syntactic foams can be estimated by considering the material parameters such as hollow particle volume fraction and wall thickness. For the Liang model [45], a unit cell-based model (Fig. 3) containing a single hollow particle embedded in the matrix polymer is proposed to estimate the thermal conductivity of syntactic foams. The average thermal conductivity of two polymer regions (Zone 1) is expressed as:

$$\overline{k_1} = k_p \tag{15}$$

where k_p refers to the thermal conductivity of the matrix polymer. The average thermal conductivity of Zone 2, where matrix polymer, particle shell, and gas are coexisted, is expressed as:

$$\overline{k_2} = \frac{1}{h_2 S}\left(k_p V_p + k_h V_h + k_{gas} V_{gas}\right) \tag{16}$$

Fig. 3 Unit cell-based model with single hollow particle [44]



where V_p, V_h, and V_gas refer to the volumes of the polymer matrix, hollow particle shell, and gas cell, respectively. S represents the surface area of the entire cross-section. k_p, k_h, and k_gas refer to the thermal conductivities of the polymer matrix, hollow particle shell material, and gas phase, respectively. Based on the rule of mixtures, the effective thermal conductivity k_eff of syntactic foams can be obtained using the thermal conductivities for Zones 1 and 2:

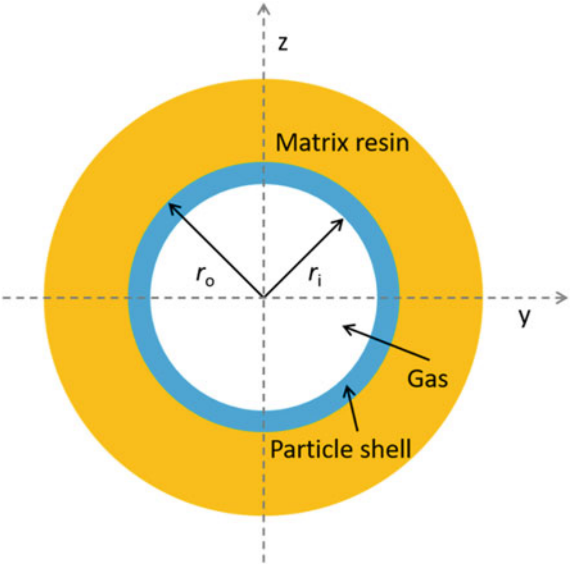
$$k_\mathrm{eff} = \left[\frac{1}{k_p}\left(1 - \left(\frac{6\Phi}{\pi}\right)^{\frac{1}{3}}\right) + 2\left(k_p\left(\frac{4\pi}{3\Phi}\right)^{\frac{1}{3}} + \pi\left(\frac{2\Phi}{9\pi}\right)^{\frac{1}{3}}\left(k_h\left(\frac{\rho_s - \rho_{gas}}{\rho_h - \rho_{gas}}\right) + k_{gas}\left(\frac{\rho_h - \rho_s}{\rho_h - \rho_{gas}}\right) - k_p\right)\right)^{-1}\right]^{-1} \tag{17}$$

where ρ_h, ρ_gas, and ρ_s refer to the effective densities of the hollow particle shell, gas phase, and hollow particle, respectively. The unit cell-based model with single hollow particle is suitable for polymeric syntactic foams with the particle volume fraction lower than 0.52.

For the Felske model [46], it is assumed that two concentric particles including the hollow particle shell and gas cell are embedded in the matrix polymer (Fig. 4). The effective thermal conductivity k_eff of the syntactic foams can be defined as the ratio of the average flux to the average temperature gradient in the unit cell and is expressed as:

$$k_{eff} = \left(\frac{1 + 2\Omega\Phi}{1 - \Omega\Phi}\right)k_p \tag{18}$$

Fig. 4 Three-phase microstructures of the polymeric syntactic foams [44]



where k_p refers to the thermal conductivity of the matrix polymer. Parameter Ω is defined as $\Omega = (\gamma - 1)/(\gamma + 2)$, and γ is defined as:

$$\gamma = 2\left(\frac{k_h}{k_p}\right)\left(\frac{1-\eta^3}{2+\eta^3}\right) \tag{19}$$

where η refers to the radius ratio calculated by the ratio of internal (r_i) to outer (r_o) radius of the hollow particle. This model is suitable for polymeric syntactic foams with a low hollow particle volume fraction. With the increasing hollow particle volume fraction, the particle-to-particle contact occurs and a preferred path for heat conduction is created, thus leading to deviated model predictions from the experimental results.

3 Types of Thermally Insulating Phenolic Foams

Phenolic foams with tailored cellular morphologies and excellent comprehensive properties are highly desirable for thermal insulation applications. Various types of phenolic foams containing different matrix, micro- or nanofillers, and hollow particles, as well as the phenolic-based carbon foams have been developed to gain the improved thermal insulation and mechanical properties. Significant efforts have been devoted to investigate the heat conductivities of the solid polymer and gas in the cells, porosity, as well as cellular morphologies (such as foam density, cell size, cell density, and cell size distribution) on the thermal conductivity of phenolic foams.

3.1 Phenolic Foams with Tailored Morphologies and Modified Matrix

Phenolic foams have attracted great interests due to their high thermal stability over a broad temperature range, excellent flame resistance, and low generation of toxic gases during combustion. Nevertheless, the conventional phenolic foams prepared from petroleum-based products usually show large brittleness and frangibility and have inferior mechanical strength compared with other polymeric foams, which greatly limited their application areas [47]. Therefore, chemical modification, in-situ polymerization, improved foaming technology, and control of cellular morphologies are needed to ensure their low thermal conductivity and improved mechanical properties [48, 49]. Lei et al. [50] successfully prepared phenolic foams with controllable nanometer pore structures via a novel foaming method of phenol–formaldehyde novolac resin solution under pressure (Fig. 5). The nanometer pore structures can be effectively tailored by changing the resin concentration and foaming pressure and can significantly enhance the compressive strength, toughness, and

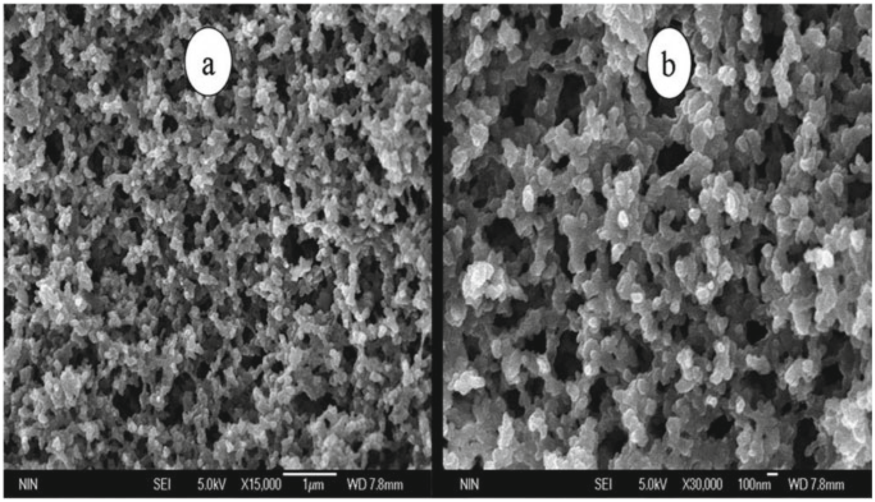


Fig. 5 SEM microphotographs of phenolic foams [50]

thermal insulation properties of the phenolic foams. With the same mass density of 120 kg/m^3, the nanoporous phenolic foams show improved compressive strength of 1.03 MPa (improved by 28.8%), specific strength of 8.58 MPa·cm^3/g (improved by 28.8%), and decreased thermal conductivity of 0.028 W/m·K (decreased by 50.9%) compared with the conventional PF (0.057 W/m·K) [36]. Lee et al. [22] also developed a microwave phenolic foaming method for the resole-type phenolic foams using microwave and air instead of blowing agents. The manufactured phenolic foams (120 kg/m^3) exhibit a low thermal conductivity 0.029 W/m·K for efficient thermal insulation (Table 1).

Natural products such as lignin, larch tannin, cardanol, and chestnut tannins have been employed in the preparation of renewable biomass-based phenolic foams [51–56]. Carvalho et al. [36] fabricated the closed-cell lignophenolic biofoams using lignin, extracted from sugarcane bagasse, as partial substitutes of phenol. They found that the presence of lignin does not show a significant effect on the thermal conductivity of the phenolic foams (0.057 W/m·K) with the foam density of 120 kg/m^3, but dramatically enhances the compression strength from 0.8 to 10 MPa. Xu et al. [57] successfully prepared the bio-based phenol formaldehyde (BPF) foams using depolymerized hydrolysis lignin with high phenol substitution ratios (30–50 wt%) by a proprietary low-temperature/low-pressure depolymerization process. The resultant 30% BPF foams with a foam density of 40 kg/m^3 exhibited satisfactory cellular structures and thermal conductivity of 0.033 W/m·K with excellent thermal stability up to 200 °C, indicating that they can be utilized as the insulation and fire-resistant materials. Wang et al. [58] also prepared the lightweight phenolic foams with high lignin substitution rate up to 50 wt%. The PFs exhibit low thermal conductivities of 0.035–0.038 W/m·K with foam densities of 30–40 kg/m^3.

Table 1 Thermal conductivities of phenolic foams

Materials	Foam density (kg/m^3)	Cell size (µm)	Cell density (cells/cm^3)	Thermal conductivity (W/m·K)	Ref.
PF	32–120			0.021–0.045	ASTM C1126 (2015)
PF	120	0.8		0.028	Lei et al. [50]
PF	120			0.029	Lee et al. [22]
Lignophenolic foams	450	4.7		0.072	Carvalho et al. [36]
PF	120			0.057	Carvalho et al. [36]
Lignin-based PF	40	435 ± 61		0.033	Xu et al. [57]
Lignin-based PF	33.52	40–70		0.035	Wang et al. [58]
LTPF/1 wt% CP	36	221.41	9.64×10^4	0.02942	Li et al. [64]
PF/1 wt% MWCNT	65.3	100.2	5.5×10^{11}	0.058	Song et al. [28]
PF/1 wt% Graphene	48.7	85.2	9.6×10^{11}	0.057	Song et al. [28]
PF/2 wt% MWCNTs	47.2	102.0	5.6×10^6	0.0264	Tian et al. [65]
PF/1 wt% TiN	40	102.1	1.7×10^6	0.0312	Tian et al. [37]
Microcellular PF/1 wt% AC	107.9	165.9		0.064	Song et al. [67]
PF/Red mud	45			0.0259	Liu et al. [26]
PF/20 vol% HCM	1175			~0.25	Huang et al. [68]
Carbon foams/HCM	220			0.11	Wang et al. [69]
PF-50 vol% HGM	720			0.14	Wang et al. [10]
Carbon foams	480			0.023	Farhan et al. [74]
Carbon foams	240	0.18		0.06	Guo et al. [75]
Carbon foams	730	0.02		0.24	Guo et al. [75]

For natural product-based phenolic foams, it still remains a challenge to obtain the commercial availability of depolymerized natural products and scale-up fabrication of the foams. The optimum depolymerization and foaming processes including the blowing agent levels, catalyst loading, curing temperature need to be further investigated [59]. The natural products also demonstrate a high potential to decrease the friability of the phenolic foams. Hence, biomass-based phenolic foams seem to offer interesting perspectives for the development of polymeric foams for thermal insulation materials with combined high mechanical properties and low thermal conductivity [25].

3.2 Phenolic Foams Containing Micro- or Nanofillers

Many works have focused on the improvement of the physical properties by introducing micro- or nanofillers such as multiwalled carbon nanotubes (MWCNTs) [28], graphene [60], nano-titanium nitride (TiN) [37], cellulose fiber (CF) [61], cloisite clay [62], silica particles [63] to realize the reinforcement and control of cellular morphologies. The incorporation of fillers exhibits a crucial effect on the thermal conductivity of phenolic foams due to the thermal conductivity of fillers and their influences on the cell morphologies such as cell size, cell density, and cell size distribution. The thermal conductivities of phenolic foams containing various fillers were determined experimentally.

Li et al. [64] successfully prepared the larch tannin-based rigid phenolic foams (LTPFs) by substituting petroleum-derived phenol with up to 30 wt% larch tannin and cork powder-reinforced LTPFs (CLTPFs). The thermal conductivity of LTPFs increased with an increase in larch tannin content due to the inferior cell morphology and decreased with the incorporation of cork powder due to the high cell density and cell uniformity of CLTPF. The CLTPF containing 1 wt% cork powder (CP) exhibited a decreased thermal conductivity of 0.02942 W/m·K, which was lower than that of other LTPFs and PFs. The combination of larch tannin and cork powder provides a green and economical way to use the natural biopolymers to fabricate phenolic foams with reinforced properties. Song et al. [28] reported that the modified PFs with 1 wt % MWCNTs and 1.0 wt % graphene, which show relatively small and uniform cells, possess higher specific compressive strength with improvements of 71.8% and 157.3%, respectively, than the pure PF. Meanwhile, the thermal conductivities of these two kinds of modified PFs are 0.058 and 0.057 W/m·K, respectively, decreased by 36.3% and 37.4% compared with that of the pure PF (0.091 W/m·K). Tian et al. [65] also investigated the effect of MWCNT on the thermal conductivity of the phenolic foam prepared by in-situ polymerization. Owing to the uniform cell morphology with the smallest cell size and highest cell density, the PF containing 2 wt% MWCNTs exhibits the lowest thermal conductivity of 0.0264 mW/m·K, which greatly decreased by 26.9% compared with that of pure PF. Therefore, the thermal conductivity of PFs can be lowered by a uniform cell morphology tailored by the

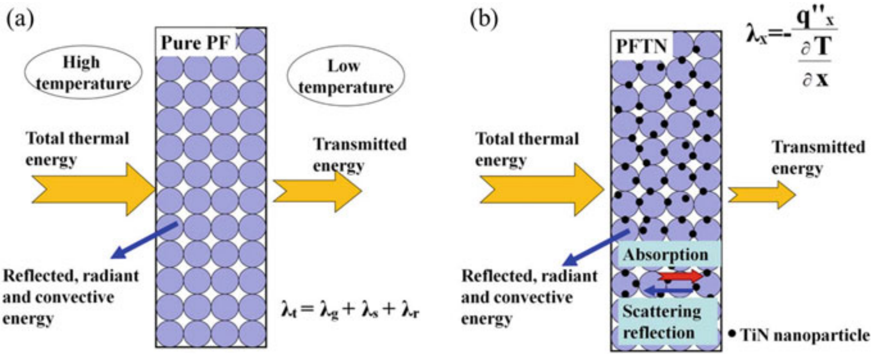


Fig. 6 The model of thermal transfer for pure PF and PF containing TiN nanoparticles [37]

MWCNT content. However, the introduction of too much MWCNTs will increase the thermal conductivity of the foams with less uniform cellular structures [66].

Furthermore, Tian et al. [37] employed titanium nitride (TiN) nanoparticles into the PF to prepare the PF/TiN nanocomposites (PFTNs) with enhanced thermal insulation and flame retardance via in situ polymerization. The incorporation of TiN significantly reduced the thermal conductivity of PF over a wide temperature range (–20 to 60 °C). In addition, the PFTNs present gradually increased thermal conductivity as the temperature increases in the range of –20 to 60 °C. The PFTNs containing 1 wt% TiN exhibit the lowest thermal conductivity of 0.0262 (at –20 °C) and 0.0312 W/m·K (at 20 °C), which reduce by 23.7 and 19.4% compared with the pure PF. The related reason is that PFTNs have higher porosity and cell density, smaller cell size, and narrower cell sizes distribution. Moreover, the encapsulated TiN nanoparticles in the phenolic matrix can act as an effective radiation blocking agent. Different from the pure PF, part of the energy is scattered, reflected, and absorbed by the TiN nanoparticles back to the high-temperature surface, thus leading to the significantly weakened heat transfer during the thermal conductivity tests (Fig. 6).

New approaches using either environment-friendly blowing agents or no blowing agents have also been used in the fabrication of phenolic foams. Song et al. [67] fabricated the activated carbon (AC)-reinforced microcellular phenolic foams using the simple and cost-effective microwave foaming technology instead of the blowing agents. The microcellular phenolic foams containing 1 wt% AC with a foam density of 107.9 kg/m^3 exhibit a low thermal conductivity of 0.064 W/m·K, which is similar to that of the commercial PU foam (0.06 W/m·K).

3.3 Phenolic Syntactic Foams Containing Hollow Microspheres

Polymer syntactic foams prepared by dispersing hollow glass, ceramic, and carbon microspheres in polymer matrix are closed-cell composite materials. The introduction of hollow microspheres with gaseous interior into the phenolic matrix to obtain decreased thermal conductivity has also attracted great attention for integrated insulation materials in marine, acoustic, and aerospace applications. Huang et al. [68] successfully prepared the insulation integrated phenolic foams by incorporating the hollow ceramic microspheres (HCM). The resultant phenolic foams with ceramic microsphere fraction of 20 vol% exhibit a decreased thermal conductivity of ~ 0.25 W/m·K, which is much lower than that without ceramic microspheres (~0.425 W/m·K). Wang et al. [69] reported that the thermal conductivity of phenolic-derived carbon foams was decreased from 0.25 to 0.11 W/m·K by introducing 2 wt% HCM.

Wang et al. [10] reported the preparation of phenolic syntactic foams using phenol–formaldehyde resin, p-toluene sulfonic acid, γ-aminopropyltriethoxysilane (APTES), and glutaraldehyde (GA) cooperative treated hollow glass microsphere (HGM) (Fig. 7). The influences of HGM volume fraction and temperature on the thermal conductivity of phenolic syntactic foams were investigated in detail. With increasing HGM content, the thermal conductivity of the syntactic foams gradually decreases due to the increasing closed cells in matrix, which effectively block the heat transfer pathway. At room temperature, the thermal conductivity reduced from 0.25 to 0.14 W/m·K with the addition of 50 vol% HGM. Besides, the thermal conductivity of syntactic foams increases rapidly at higher temperature because of the enhanced thermal conductivity of gas and radiative conductivity. Therefore, the incorporation of HGM endows the phenolic syntactic foams with enhanced thermal insulation properties especially at high temperatures and wide application prospects as core materials for sandwich structures.

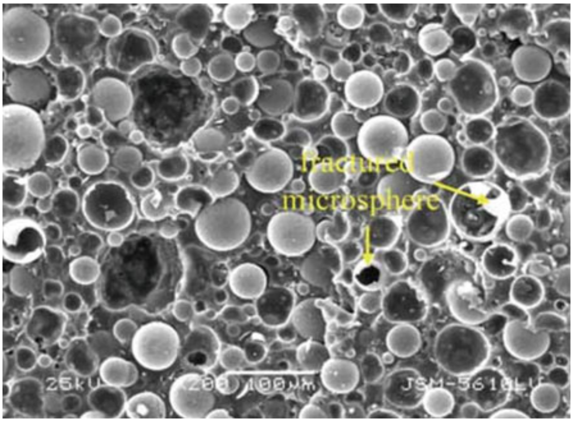


Fig. 7 SEM images of the fracture surface of phenolic syntactic foams with 50 vol% HGM treated at 800 °C [10]

3.4 Phenolic-Based Carbon Foams

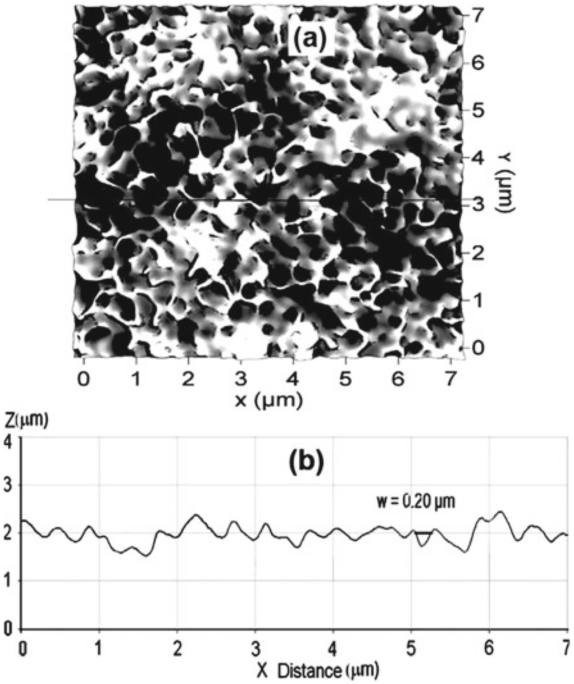
Ablative materials represent an effective approach for thermal protection systems (TPS) to protect the space aircraft from severe heating during hypersonic flight through a planet's or the earth's atmosphere [70]. Carbon foams (CFs) fabricated by carbonizing organic precursor foams from coal, pitch, or thermosetting plastics are attractive ablative materials because of their lightweight, high-temperature resistance, and tailorable thermal conductivity [71]. Phenolic foams showing excellent flame resistance and low generation of toxic gases during combustion can be used as promising precursor materials for carbon foams [72].

Song et al. [73] fabricated the carbon foams via carbonization of the phenolic precursor foams at 1000 °C in a nitrogen atmosphere. Compared with PFs, the CFs show lower thermal conductivity owing to the thinner cell walls and reduced cell size after carbonization. Farhan et al. [74] developed the CF by soft templating method with phenolic resin and coal tar pitch as matrix precursor and polyurethane (PU) foam as an organic sacrificial template. Compared with the carbon felt (foam density 150 kg/m^3) with a thermal conductivity of 0.17 W/m·K, the CFs (foam density 480 kg/m^3) show a significantly reduced thermal conductivity of 0.023 W/m·K. Guo et al. [75] developed the phenolic-based CF with controllable cellular structures by foaming of resin solution under the pressure of 4 MPa and then carbonizing. The average cell size of CF can be controlled in the range of 100–300 nm by changing the resin concentration (Fig. 8). CFs with mass density of 240 kg/m^3 and cell size of 180 nm exhibit a low thermal conductivity of 0.06 W/m·K and a high compressive strength of 13.1 MPa and can be used as high-strength thermal insulation materials. Zhang et al. [76] also reported the fabrication of syntactic CF by adding hollow carbon microspheres (derived from hollow phenolic microspheres) to phenolic resin, followed by post-curing, pre-carbonization, and carbonization. The thermal conductivity increased greatly after carbonization at temperatures higher than 400 °C attributed to the highly ordered carbon structures. Table 1 shows the tailored thermal conductivities of phenolic foams with various material systems, foam density, and cellular morphologies, indicating their great potential for thermal insulation applications.

4 Conclusion

Phenolic foams are attractive thermal insulation materials in aerospace, building, shipbuilding, petroleum, and chemical industry applications, owing to their extremely low thermal conductivity combined with other satisfactory comprehensive properties such as outstanding chemical resistance, excellent thermal stability, and flame resistance. For hypersonic aircraft enduring long-term aerodynamic heating, the lightweight phenolic foams have been used as efficient thermal insulation materials to prevent the external heat from transferring into the interior to protect the main

Fig. 8 Confocal laser scanning microscope image **a** with section of measured profile **b** of phenolic-based carbon foams with the foam density of 240 kg/m^3 [75]



structures and internal equipment. Phenolic-based carbon foams can be applied as ablative materials, which can be heated up to 3000 °C under anaerobic conditions, for space aircraft under extreme heating conditions during hypersonic flight through a planet's or the earth's atmosphere. Furthermore, the outstanding flame retardancy of phenolic foams endows them to be promising thermal insulation materials for building industry that has very high fire safety requirements. Therefore, the phenolic foams are superior to other commonly used organic insulation materials such as PS, PU, PE, and PVC foams. Compared with the traditional inorganic insulation materials such as rock wool, concrete foams, and expanded perlite, the phenolic foams exhibit improved thermal insulation properties with decreased mass weight and building wall thickness, widened usable space within the building, and reduced energy consumption for internal heating due to the high porosity with high percentage of closed cells. In addition, phenolic foams have been widely used as insulation materials for fishing vessel refrigerated tanks and liquefied natural gas (LNG) carriers in shipbuilding, as well as storage tanks, equipment, and pipelines in petroleum and chemical industry.

Further research is needed to develop novel phenolic foams with improved thermal insulation properties combined with other advantageous comprehensive properties via environmentally friendly green fabrication processes. The heat transfer models with higher prediction accuracy and the relationship between cellular morphologies and thermal conductivity considering the detailed geometric parameters are needed to provide constructive theoretical and practical guidance for controllable fabrication of thermal insulation phenolic foams.

References

1. Tseng CJ, Kuo KT (2002) Thermal radiative properties of phenolic foam insulation. J Quant Spectrosc Radiat Transfer 72(4):349–359
2. Fan W, Zhang X, Zhang Y et al (2019) Lightweight, strong, and super-thermal insulating polyimide composite aerogels under high temperature. Compos Sci Technol 173:47–52
3. Hasanzadeh R, Azdast T, Doniavi A et al (2019) Multi-objective optimization of heat transfer mechanisms of microcellular polymeric foams from thermal-insulation point of view. Therm Sci Eng Prog 9:21–29
4. Arduini Schuster M, Manara J, Vo C (2015) Experimental characterization and theoretical modeling of the infrared-optical properties and the thermal conductivity of foams. Int J Therm Sci 98:156–164
5. Ma Z, Zhang G, Yang Q et al (2018) Tailored morphologies and properties of high-performance microcellular poly(phenylene sulfide)/poly(ether ether ketone) (PPS/PEEK) blends. J Supercrit Fluids 140:116–128
6. Ma Z, Zhang G, Yang Q et al (2013) Fabrication of microcellular polycarbonate foams with unimodal or bimodal cell-size distributions using supercritical carbon dioxide as a blowing agent. J Cell Plast 50(1):55–79
7. Hu F, Wu S, Sun Y (2019) Hollow-structured materials for thermal insulation. Adv Mater 31(38):1801001
8. Gibson LJ, Ashby MF (1997) Cellular solids: structure and properties. Cambridge University Press
9. Cheng H, Xue H, Hong C et al (2017) Preparation, mechanical, thermal and ablative properties of lightweight needled carbon fibre felt/phenolic resin aerogel composite with a bird's nest structure. Compos Sci Technol 140:63–72
10. Huang C, Huang Z, Wang Q (2018) Effect of high-temperature treatment on the mechanical and thermal properties of phenolic syntactic foams. Polym Eng Sci 58(12):2200–2209
11. Notario B, Pinto J, Solorzano E et al (2015) Experimental validation of the Knudsen effect in nanocellular polymeric foams. Polymer 56:57–67
12. Baetens R, Jelle BP, Gustavsen A (2011) Aerogel insulation for building applications: a state-of-the-art review. Energy Build 43(4):761–769
13. Huang HX, Xu HF (2011) Preparation of microcellular polypropylene/polystyrene blend foams with tunable cell structure. Polym Adv Technol 22(6):822–829
14. Yen YC, Lee T, Chiu D et al (2014) Polystyrene foams with inter-connected carbon particulate network. J Cell Plast 50(5):437–448
15. Septevani AA, DaC E, Annamalai PK et al (2017) The use of cellulose nanocrystals to enhance the thermal insulation properties and sustainability of rigid polyurethane foam. Ind Crops Prod 107:114–121
16. Luo F, Wu K, Lu M et al (2015) Thermal degradation and flame retardancy of microencapsulated ammonium polyphosphate in rigid polyurethane foam. J Therm Anal Calorim 120(2):1327–1335
17. Rodríguez Pérez MA, González-Peña JI, Witten N et al (2002) The effect of cell size on the physical properties of crosslinked closed cell polyethylene foams produced by a high pressure nitrogen solution process. Cell Polym 21(3):165–194
18. Luong DD, Pinisetty D, Gupta N (2013) Compressive properties of closed-cell polyvinyl chloride foams at low and high strain rates: Experimental investigation and critical review of state of the art. Compos B 44(1):403–416

19. Ma Y, Wang J, Xu Y, et al. (2015) Effect of zinc oxide on properties of phenolic foams/halogen-free flame retardant system. J Appl Polym Sci 132(44).
20. Lee LJ, Zeng C, Cao X et al (2005) Polymer nanocomposite foams. Compos Sci Technol 65(15):2344–2363
21. Ma Z, Zhang G, Yang Q et al (2015) Mechanical and dielectric properties of microcellular polycarbonate foams with unimodal or bimodal cell-size distributions. J Cell Plast 51(3):307–327
22. Kim BG, Lee DG (2008) Development of microwave foaming method for phenolic insulation foams. J Mater Process Technol 201(1):716–719
23. Jalalian M, Jiang Q, Coulon A, et al. (2019) Mechanically whipped phenolic froths as versatile templates for manufacturing phenolic and carbon foams. Mater Des 168: 107658.
24. Delgado Sánchez C, Sarazin J, Santiago Medina FJ et al (2018) Impact of the formulation of biosourced phenolic foams on their fire properties. Polym Degrad Stab 153:1–14
25. Mougel C, Garnier T, Cassagnau P et al (2019) Phenolic foams: A review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer 164:86–117
26. Liu J, Li X, Zhou C (2018) Mechanical and thermal properties of modified red mud-reinforced phenolic foams. Polym Int 67(5):528–534
27. Li Q, Chen L, Ding J et al (2016) Open-cell phenolic carbon foam and electromagnetic interference shielding properties. Carbon 104:90–105
28. Song SA, Chung YS, Kim SS (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93
29. Yun MS, Lee WI (2008) Analysis of bubble nucleation and growth in the pultrusion process of phenolic foam composites. Compos Sci Technol 68(1):202–208
30. Del Saz OB, Oliet M, Alonso MV et al (2012) Formulation optimization of unreinforced and lignin nanoparticle-reinforced phenolic foams using an analysis of variance approach. Compos Sci Technol 72(6):667–674
31. Del Saz OB, Alonso MV, Oliet M et al (2014) Effects of formulation variables on density, compressive mechanical properties and morphology of wood flour-reinforced phenolic foams. Compos B 56:546–552
32. Xu Q, Gong R, Cui MY et al (2015) Preparation of high-strength microporous phenolic open-cell foams with physical foaming method. High Perform Polym 27(7):852–867
33. Rochefort Malcolm RL, Holland Philip, Coppock Vincent (2014) Phenolic Foam. UK Pat. Appl. GB 2, 505, 974 A, 19 Mar 2014.
34. Gong R, Xu Q, Chu Y et al (2015) A simple preparation method and characterization of epoxy reinforced microporous phenolic open-cell sound absorbent foam. RSC Adv 5(83):68003–68013
35. Forest C, Chaumont P, Cassagnau P et al (2015) Polymer nano-foams for insulating applications prepared from CO_2 foaming. Prog Polym Sci 41:122–145
36. De Carvalho G, Pimenta JA, Dos Santos WN et al (2003) Phenolic and lignophenolic closed cells foams: thermal conductivity and other properties. Polym-Plast Technol Eng 42(4):605–626
37. Li Q, Chen L, Li X, et al. (2016) Effect of nano-titanium nitride on thermal insulating and flame-retardant performances of phenolic foam. J Appl Polym Sci 133(32).
38. Braginsky L, Shklover V, Witz G, et al. (2007) Thermal conductivity of porous structures. Phys Rev B 75(9): 094301.
39. Thirumal M, Khastgir D, Singha NK et al (2008) Effect of foam density on the properties of water blown rigid polyurethane foam. J Appl Polym Sci 108(3):1810–1817
40. Ferkl P, Toulec M, Laurini E et al (2017) Multi-scale modelling of heat transfer in polyurethane foams. Chem Eng Sci 172:323–334
41. Placido E, Arduini-Schuster MC, Kuhn J (2005) Thermal properties predictive model for insulating foams. Infrared Phys Technol 46(3):219–231
42. Kim J, Lee JH, Song TH (2012) Vacuum insulation properties of phenolic foam. Int J Heat Mass Transfer 55(19):5343–5349

43. Kwon JS, Jang CH, Jung H et al (2009) Effective thermal conductivity of various filling materials for vacuum insulation panels. Int J Heat Mass Transfer 52(23):5525–5532
44. Gupta N, Pinisetty D (2013) A review of thermal conductivity of polymer matrix syntactic foams-effect of hollow particle wall thickness and volume fraction. JOM 65(2):234–245
45. Chsner A, Murch GE (2011) Heat transfer in multi-phase materials. Springer, Berlin Heidelberg
46. Felske JD (2004) Effective thermal conductivity of composite spheres in a continuous medium with contact resistance. Int J Heat Mass Transfer 47(14):3453–3461
47. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54(7):1962–1970
48. Auad ML, Zhao L, Shen H et al (2007) Flammability properties and mechanical performance of epoxy modified phenolic foams. J Appl Polym Sci 104(3):1399–1407
49. Yang H, Wang X, Yu B et al (2013) A novel polyurethane prepolymer as toughening agent: Preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 128(5):2720–2728
50. Lei S, Guo Q, Zhang D et al (2010) Preparation and properties of the phenolic foams with controllable nanometer pore structure. J Appl Polym Sci 117(6):3545–3550
51. Zhuang XW, Li SH, Ma YF et al (2011) Preparation and characterization of lignin-phenolic foam. Adv Mater Res 236–238:1014–1018
52. Niu M, Wang GJ (2013) Study on the nanocomposite foam of cardanol phenolic resin and organo-modified montmorillonite. Adv Mater Res 712–715:147–155
53. Zhou M, Shi H, Li C et al (2020) Depolymerization and activation of alkali lignin by solid acid-catalyzed phenolation for preparation of lignin-based phenolic foams. Ind Eng Chem Res 59(32):14296–14305
54. Lagel MC, Pizzi A, Giovando S et al (2014) Development and characterisation of phenolic foams with phenol-formaldehyde-chestnut tannins resin. J Renewable Mater 2(3):220–229
55. Merle J, Birot M, Deleuze H et al (2016) New biobased foams from wood byproducts. Mater Des 91:186–192
56. Li B, Feng SH, Niasar HS et al (2016) Preparation and characterization of bark-derived phenol formaldehyde foams. RSC Adv 6(47):40975–40981
57. Li B, Wang Y, Mahmood N et al (2017) Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin. Ind Crops Prod 97:409–416
58. Wang G, Liu X, Zhang J et al (2018) One-pot lignin depolymerization and activation by solid acid catalytic phenolation for lightweight phenolic foam preparation. Ind Crops Prod 124:216–225
59. Londoño Zuluaga C, Du J, Chang HM et al (2018) Lignin modifications and perspectives towards applications of phenolic foams: A review. BioResources 13:9158–9179
60. Sandhya PK, Sreekala MS, Boudenne A, et al. (2020) Thermal and electrical properties of phenol formaldehyde foams reinforcing with reduced graphene oxide. Polym Compos 1–11.
61. Del Saz OB, Alonso MV, Oliet M et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Compos B 75:367–372
62. Rangari VK, Hassan TA, Zhou Y et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 103(1):308–314
63. Yuan J, Zhang Y, Wang Z (2015) Phenolic foams toughened with crosslinked poly (n-butyl acrylate)/silica core-shell nanocomposite particles. J Appl Polym Sci 132:42590
64. Li J, Zhang A, Zhang S et al (2019) Larch tannin-based rigid phenolic foam with high compressive strength, low friability, and low thermal conductivity reinforced by cork powder. Compos B 156:368–377
65. Li Q, Chen L, Li X et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Compos A 82:214–225
66. Song F, Jia P, Bo C et al (2021) The mechanical and flame retardant characteristics of lignin-based phenolic foams reinforced with MWCNTs by in-situ polymerization. J Dispersion Sci Technol 42:1042–1051
67. Song SA, Oh HJ, Kim BG et al (2013) Novel foaming methods to fabricate activated carbon reinforced microcellular phenolic foams. Compos Sci Technol 76:45–51

68. Ge D, Shi M, Yao Y, et al. (2019) Preparation and properties of anti-insulation integrated phenolic resin composites. IOP Conf Ser: Mater Sci Eng 472: 012047.
69. Wang S, Luo R, Ni Y (2010) Preparation and characterization of resin-derived carbon foams reinforced by hollow ceramic microspheres. Mater Sci Eng A 527(15):3392–3395
70. Pulci G, Tirillò J, Marra F et al (2010) Carbon-phenolic ablative materials for re-entry space vehicles: Manufacturing and properties. Compos A 41(10):1483–1490
71. Wu X, Liu YG, Fang M et al (2011) Preparation and characterization of carbon foams derived from aluminosilicate and phenolic resin. Carbon 49(5):1782–1786
72. Chuang W, Lei P, Zhen Hai S, et al. (2019) Preparation, thermal stability and deflection of a density gradient thermally-conductive carbon foam material derived from phenolic resin. Results Phys 14: 102448.
73. Song SA, Lee Y, Kim YS et al (2017) Mechanical and thermal properties of carbon foam derived from phenolic foam reinforced with composite particles. Compos Struct 173:1–8
74. Farhan S, Wang RM, Jiang H et al (2014) Preparation and characterization of carbon foam derived from pitch and phenolic resin using a soft templating method. J Anal Appl Pyrolysis 110:229–234
75. Lei S, Guo Q, Shi J et al (2010) Preparation of phenolic-based carbon foam with controllable pore structure and high compressive strength. Carbon 48(9):2644–2646
76. Zhang L, Ma J (2009) Processing and characterization of syntactic carbon foams containing hollow carbon microspheres. Carbon 47(6):1451–1456

Chapter 10
Electromagnetic Interference Shielding in Phenolic Foam

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1 Introduction

In the modern world, electronics and telecommunication devices are growing very fast and these devices are generating more and more electromagnetic (EM) waves. These high-frequency EM waves are not only affecting the electronic system but also the surrounding environment and the lives of humans and animals [1–4]. In general, the EMI mechanism consists of three modes, i.e. reflection, absorption, and transmission of incoming EM radiations. For high reflection, the shielding materials must have high electrical conductivity whereas for achieving high absorption, the shielding materials require a magnetic permeability. Conventionally, metals such as aluminum, copper, steel, iron zinc, etc. have been used as an effective EMI shielding material due to their high electrical conductivity [5, 6]. However, high density, easy corrosion, and economical processing make them an undesirable choice for advanced EMI shielding materials. Furthermore, the high reflection in these metals limits their use in those applications where absorption dominant is required such as stealth technology or other electronic devices [7]. The main necessities for an EMI shielding material are lightweight, good electrical conductivity, and thermal stability. Recently, carbon foams have many advantages over the metal-based counterparts due to their lightweight, open porosity, high surface area, excellent electrical and thermal conductivity, resistance to corrosion, and chemical and thermal stability [8–14]. Carbon foams are lightweight high-performance materials comprising of an interconnected cell wall structure. The carbon foam can be an open cell structure or a closed-cell structure. In open-cell foam, porosity can play an important role in achieving high

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EMI shielding effectiveness (SE) especially absorption because an open porous structure provides a high chance for multiple reflections [15, 16]. In accordance with the scientific advancement, numerous methods such as foaming agent, temperature and pressure release, freeze-drying, and template methods [11, 17–21] are available to obtain different carbon foams from various sources such as resins/polymers [15, 22–24], polyurethanes [25], pitch [26, 27], biomass materials [28, 29], waste materials, chemical materials, gases, and so on [30]. Nevertheless, phenolic resin foams are being developed due to their potential applications such as sound and thermal insulation, packaging, filters, energy absorption, energy storage, and EMI SE [31, 32]. In the 1940s, the first phenolic foam was developed by the German industry. Later on, in 1964, the reticulated vitreous (glassy) carbon foam was developed by Ford et al. [33]. They reported that carbon foams were produced by carbonization of thermosetting organic polymer foams through simple heat treatment. However, due to the highly porous structure, carbon foams have low compressive strength. Also, the EMI SE properties of phenolic resin-based carbon foams depend on electrical conductivity. As we know that phenolic foams are low electrically conducting and cannot prevent EM wave. It was reported that the incorporation of conducting and magnetic fillers in the phenolic foam foams can improve the electrical conductivity, thermal stability, mechanical strength, and EMI shielding properties [34–37].

This chapter describes and covers up to date research on the phenolic resin-based foam for EMI shielding applications. We have discussed the role of conducting and magnetic fillers on the EMI shielding properties of phenolic resin-based foams. Also, the addition of dielectric and magnetic fillers in combination with carbon fillers is explored in this chapter as these are gaining interest nowadays due to the demand for EM absorbing materials.

2 A Brief Review of Electromagnetic Interference Shielding

Electromagnetic interference is the intervention or disturbance that affects an electrical circuit due to either EM induction or EM radiation generated from an external device. To achieve effective EMI shielding, a high EMI shielding capability of 99% absorption of the incoming EM waves (20 dB) is required. Therefore, EMI shielding enclosures are primarily designed to protect against EM radiations. High-speed switching in micro-circuitry may generate EMI in the form of short EM pulses. Therefore, common sources of EMI include electronic devices such as radio and calculators, cash registers, computers, video games, televisions, and communication systems. In general, EMI shielding effectiveness (SE) is defined as the logarithmic ratio of the incident power (P_I) and transmitted power (P_T) can be expressed as the following equation [38, 39];

$$SE_T = 10log_{10}\frac{P_I}{P_T} = 20log_{10}\frac{E_I}{E_T} = 20log_{10}\frac{H_I}{H_T} \quad (1)$$

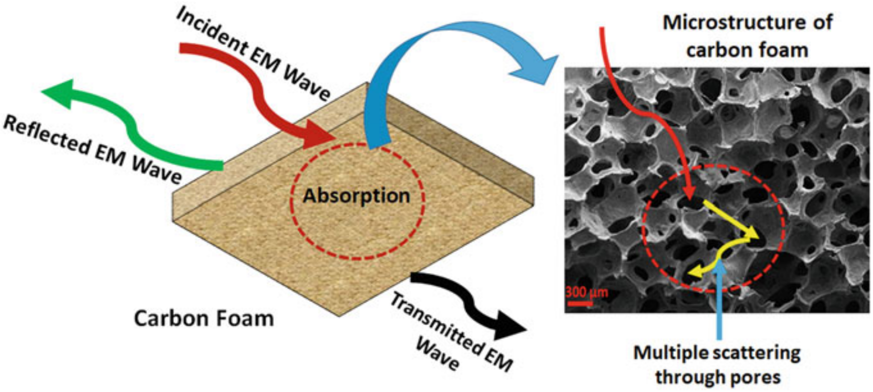

Fig. 1 Electromagnetic wave interaction with carbon foam

where, P_I (E_I or H_I) and P_T (E_T or H_T) are the intensity (electric or magnetic field) of the incident and transmitted electromagnetic waves, respectively, through a shielding material. When this EM wave falls on the surface of shield material, the total shielding efficiency (SE_T) depends on three shielding components for interrupting the transmission of EM radiation such as reflection (SE_R), absorption (SE_A), and multiple internal reflections (SE_M) as displayed in Fig. 1 and can be written as follow;

$$SE_T(dB) = SE_R + SE_A + SE_M \tag{2}$$

Here SE_R is the surface reflection from free charge carriers in the system, SE_A is several loss mechanisms related to electrical polarization and magnetization processes and SE_M is shielding effectiveness due to multiple reflections. If the SE_A is >10 dB, the SE_M can be ignored then the shielding equation can be written as [40];

$$SE_T = SE_R + SE_A \tag{3}$$

$$T = |S12|^2 = |S21|^2 \tag{4}$$

$$R = |S11|^2 = |S22|^2 \tag{5}$$

$$A = 1 - R - T \tag{6}$$

where S_{11} is a forward reflection coefficient, S_{22} is a reverse reflection coefficient, S_{12} represents a forward transmission coefficient, S_{21} is a reverse transmission coefficient.

Further, SE_T, SE_A, and SE_R can be calculated using the following equations[41].

$$\mathrm{SE}_T(\mathrm{dB}) = 10\log_{10}\left(\frac{1}{|S_{12}|^2}\right) = 10\log_{10}\left(\frac{1}{|S_{21}|^2}\right) \tag{7}$$

$$\mathrm{SE}_A(\mathrm{dB}) = 10\log_{10}\left(\frac{T}{1-R}\right) = 10\log_{10}\left(\frac{|S_{21}|^2}{1-|S_{11}|^2}\right) \tag{8}$$

$$\mathrm{SE}_R(\mathrm{dB}) = 10\log_{10}\left(\frac{1}{1-R}\right) = 10\log_{10}\left(\frac{1}{1-|S_{11}|^2}\right) \tag{9}$$

Here, $\mathrm{SE_R}$ is associated with impedance matching of two materials; however, $\mathrm{SE_A}$ is associated with dielectric and magnetic permeability of the materials.

Further, $\mathrm{SE_T}$, $\mathrm{SE_{R,}}$ and $\mathrm{SE_A}$ can also be described as [38, 42];

$$\mathrm{SE}_R(\mathrm{dB}) = 10\log_{10}\left(\frac{\sigma}{16 f \varepsilon_0 \mu_r}\right) \tag{10}$$

$$\mathrm{SEA}(\mathrm{dB}) = 20\frac{t}{\delta}\log_{10}\mathrm{e} = 8.68\left(\frac{t}{\delta}\right) = 8.68t\left(\frac{\sigma f \mu_r}{2}\right)^{1/2} \tag{11}$$

where, σ, f, ε, μ, t, and δ represent electrical conductivity, angular frequency, permittivity, permeability, thickness, and skin depth of the shielding material, respectively. The skin depth of a material is the penetration depth where the power of the EM wave gets reduced up to 37%. So, skin depth can be defined as [13];

$$\delta = \sqrt{\frac{2}{f\mu\sigma}} = -8.68\left(\frac{t}{SE_A}\right) \tag{12}$$

The relative complex permittivity (ε´ and ε˝) and relative complex permeability (μ' and μ") could be helpful for further understanding of the EMI shielding mechanism. Where ε´ is the real part of the permittivity, which reflects the storage capacity of the electromagnetic energy, while the ε˝ is the imaginary part of the permittivity, which represents the energy dissipation processes including the conduction and polarization relaxation loss. Similarly, real permeability (μ´) and imaginary permeability (μ˝) are magnetic storage and magnetic losses, respectively. These complex parameters were calculated by Nicholson–Ross and Weir's theoretical calculation using scattering parameters (S_{11} and S_{21}) [43, 44].

Several methods are reported for the measurement of shielding effectiveness. The basic principle for these methods is the same; however, the testing setup could differ from each other. All of these methods' shielding effectiveness is calculated by the measurement of the energy of EM waves that penetrate the material and the energy of the EM wave that is transmitted through the material[45]. The Vector Network Analyzer (VNA) is used for the generation and measurements of EM waves.[46] Generally, four methods, i.e. (i) open-field method, (ii) shielded box method, (iii) Shielded room method, and (iv) coaxial transmission line method are used for the

EMI shielding measurement [2]. Out of these four different methods, the coaxial transmission line is a well famous method for the EMI shielding measurement due to its repeatability and ability to use in a wide range of frequencies. The test setup contains VNA, two coaxial cables for receiving and transmitting EM waves, and a sample holder.

3 Electromagnetic Interference Shielding in Phenolic-Based Carbon Foams

Phenolic resin is a thermosetting polymer produced by condensation polymerization between phenol and formaldehyde. Phenolic resin can provide lightweight products like carbon foam and offer significant benefits over metal-based composites [36, 47]. Phenolic foams (PF) have excellent properties that make them an attractive candidate for multifunctional applications such as lightweight materials, thermal insulation, energy absorption, fire protection, EMI shielding, energy storage, and water purifications. In this chapter, we describe and cover up to date research on the phenolic resin-based carbon foam for EMI shielding applications.

The EMI shielding performance depends on electrical conductivity, dielectric and magnetic permeability, and conducting fillers. As we know that phenolic foams have low electrical conductivity and cannot prevent EM waves. It is reported that carbon fillers such as carbon nanotubes (CNT) [48, 49], graphene [50, 51], carbon nanofibers (CNF) [10, 52] have great potential due to their lightweight, small diameter, high aspects ratio, exceptional electrical and thermal conductivity, and ultrahigh mechanical strength, which make them ideal reinforcement over conventional fillers for high EMI SE properties. The incorporation of carbon fillers in the phenolic resin matrix can improve the electrical conductivity, thermal stability, and EMI shielding properties.

Furthermore, the synergistic effect of magnetic loss and dielectric loss greatly contributes to the enhancement of absorption [53, 54], it is necessary to reinforce dielectric and magnetic fillers such as MnO_2 Fe_2O_3, Fe_3O_4, ZnO, SiO_2 in phenolic foams. These dielectric and magnetic fillers help in impedance matching to balance dielectric permittivity and magnetic permeability, which is most essential for microwave absorption [55]. However, the eddy-current losses induced by the EM wave may reduce the permeability of magnetic materials. Therefore, the eddy-current phenomenon can be suppressed by using a small amount of conducting fillers, which further leads to an increase in the interaction of EM wave with the material. The EMI SE of phenolic resin-based carbon foams reinforced with various fillers in the X-band frequency range (8.2–12.4 GHz) is shown in Table 1. From this table, it is observed that the EMI SE not only depends on the fillers but also depends on the properties such as density and thickness of carbon foams.

Agrawal et al. [56] demonstrated phenolic resin-based carbon-MnO_2 composite foams for EMI shielding applications. The carbon foams reinforced with the different

Table 1 EMI SE of phenolic resin-based carbon foams reinforced with various fillers in the X-band (8.2–12.4 GHz) frequency range

Materials/Filler	Density g/cm^3	Thickness (mm)	EMI SE (dB)	References
Carbon foam	0.25	2.5	27.5	[56]
Carbon foam–MnO_2	0.30	2.5	45.0	[56]
Carbon foam–Fe_3O_4–ZnO	0.40	2.75	48.5	[57]
Carbon foam–MWCNTs	0.32	2.0	57.2	[58]
Carbon foam–MWCNTs–Fe_3O_4	0.13	2.0	62	[35]
Carbon foam–SiC nanowires	0.59	4.0	47	[59]
Graphene aerogels	0.004	4.0	35	[60]
Carbon foam–rGO decoration	0.31	2.0	50.7	[61]
Carbon foam–GO/SiO_2	–	10	50	[37]
Carbon foam–rGO/Fe_3O_4	0.016	3.0	65	[62]
Carbon foam–MCMB	0.01	1.8	54.8	[15]
Magnetic carbon foam	–	3.05	54.02	[63]
Carbon foam–cenospheres	0.32	2.0	48.6	[13]
Carbon foam–red mud	0.46	2.0	51.4	[16]

loading of MnO_2 ranging from 0 to 8 wt% were prepared from phenolic resin as a carbon matrix using the polyurethane (PU) foam template method followed by carbonization at 1000 °C in an inert atmosphere. The SEM images of carbon foam containing 2 wt. % MnO_2 are shown in Fig. 2a. From this image, it was found that $MnO_2$is uniformly dispersed in the resin-based carbon matrix. This study reported the decreasing trend of electrical conductivity with increasing MnO_2 content in the carbon foam. The electrical conductivity of the carbon foam without MnO_2 was 24.5 S/cm and it decreases to 6 S/cm at 8 wt % MnO_2. This may due to the

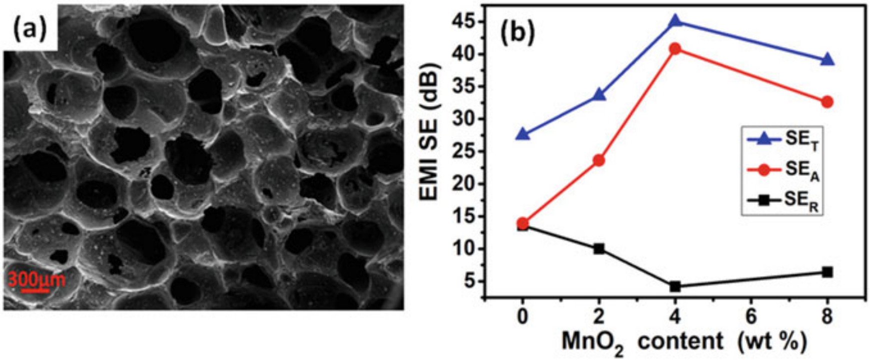

Fig. 2 **a** SEM image of carbon foam with 2 wt % MnO_2 and **b** EMI SE of carbon foam with various MnO_2 content at 8.2 GHz. Reproduced with permission from [56]

intrinsic, dielectric, and magnetic nature of MnO_2, which blocks the conducting network in composite foam. However, the magnetic nature of MnO_2 in the resin-based carbon matrix is responsible for enhancing the EMI SE in carbon-MnO_2 composite foam. The EMI SE of carbon-MnO_2 composite foams was measured in the X-band frequency range (8.2–12.4). Figure 2b represents the total (SE_T), absorption (SE_A), and reflection (SE_R) of carbon MnO_2 composite foam as a function of MnO_2 content at 10.7 GHz. It is observed that the absorption is increased with an increase in the content of MnO_2 in all the composite foams. When the MnO_2 content increases from 0 to 2 wt %, the SE_A component increases from 13.9 to 23.6 dB, and the total EMI SE increases from 27.5 to 33.6 dB, respectively. Furthermore, the total EMI SE reached a maximum value of 45.0 dB with excellent absorption of 40.8 dB when MnO_2 content increase to 4 wt %. The enhanced SE_A in carbon foam is mainly due to good dispersion of MnO_2, dipolar relaxation, polarization, and ordered porous structure of the composite foam. Furthermore, the MnO_2 nanoparticles act as a polarized center in the presence of microwave, which gives rise to excellent absorption. However, carbon foam containing 8 wt. % MnO_2 shows a decrease EMI SE_T of 39 dB with a SE_A of 32.6 dB, which is due to agglomeration of MnO_2 nanoparticles.

In another work, Kumar et al. [57] used Fe_3O_4 and Fe_3O_4–ZnO nanoparticles for improving microwave absorption properties in carbon foam. Initially, carbon foam was prepared by phenolic resin using the PU foam template method followed by carbonization. Afterward, the carbonized foam was coated with a ferrofluid (Fe_3O_4) solution using a dip coating. In other cases, carbon foam was coated with Fe_3O_4 and ZnO nanoparticles. After coating, foam samples were sintered at 650 °C for 10 min in an inert atmosphere. Initially, EMI SE_T is found to be 22.3 dB over the frequency range of 8.2−12.4 GHz for the as pristine carbon foam. The carbon foam coated with Fe_3O_4–ZnO shows a good EMI SE in a wide frequency range 8.2–12.4 GHz and the value of SE_T and SE_A are 48.5 and 41.5 dB, respectively, at 8.2 GHz. This improved microwave absorption is due to impedance matching of magnetic (Fe_3O_4) and dielectric (ZnO) particles and multiple reflections of the EM wave from an interconnected porous structure.

CNTs have captured the attention and interest of many researchers due to their lightweight, small diameter, high aspect ratio, exceptional electrical and thermal conductivity, and ultrahigh mechanical strength, which make them ideal reinforcement over conventional carbon fillers for high EMI SE properties [64, 65]. However, the biggest challenge is to use CNT loadings at lower concentrations without compromising on the overall σ and EMI SE of the nanocomposites. The filler loadings at higher concentrations may badly affect the mechanical properties of the nanocomposites and are also very costly indeed. A recent investigation reveals that a lower weight percentage of CNTs in the polymer matrix can increase the EMI SE of composite foam.

Patle et al. [58] used multi-walled carbon nanotubes (MWCNTs) for improving the electrical and EMI shielding performance of phenolic resin-derived carbon foam. In this investigation, different concentrations (0–2 wt %) of MWCNTs were mixed with phenolic resin solution and carbon hybrid foam was prepared by PU template method followed by carbonization at 1000 °C. The EMI SE of carbon hybrid was measured in

X-band frequency (8.2–12.4 GHz). The measured EMI SE was found to be increased with an increase in MWCNTs content. The EMI SE_T is measured to be 29.7 dB with SE_A and SE_R values of 15.9 dB and 13.8 dB, respectively, for the hybrid foam containing 0 wt % MWCNTs. The hybrid foam with 1 wt % MWCNTs exhibited SE_T of 57.2 dB and SEA of 50.4 dB which leading to an absorption dominating mechanism. The enhanced EMI SE is due to the high conductivity of MWCNTs, which provide a conduction path in the resin-based carbon matrix, which contributes to higher absorption in the carbon hybrid foam.

In another work, Li et al. [35] used an in-situ polymerization process to fabricate phenolic foam. In this study, they used different content of MWCNTs as a conducting filler and nano-Fe_3O_4 as a magnetic filler and prepared two types of foams, one is closed-cell phenolic foam (PF) and the second is open-cell carbon foam (C-PF). The phenolic foam and carbon foam are named as PFCxFs and C-PFCxFs, respectively, where x and s are the weight fraction of MWCNTs and nano-Fe_3O_4, respectively. The EMI shielding properties of PF and C-PF as a function of MWCNTs and Fe_3O_4 content were also discussed. It was found that pure PF having an electrical conductivity of 6.2×10^{-12}S/cm whereas the incorporation of nanoparticles leads to the improvement of electrical conductivity, and it is found to be 2×10^{-1}S/cm for PF with 2wt% MWCNTs along with 7wt % Fe_3O_4. Similarly, the electrical conductivity of pure CPF is 1.6×10^{-5}S/cm and it increased to 3.6 S/cm by only 2wt% MWCNTs and 7wt % Fe_3O_4 loading. Figure 3a, b shows the EMI SE of closed-cell phenolic foam and open-cell carbon foam at 2 wt % MWCNTs and various loading of Fe_3O_4 respectively. It is obvious that the EMI SE of both phenolic and carbon foam increases with increasing nano-Fe_3O_4. The EMI SE of 2 mm thick closed-cell phenolic foam (PFC2F7) reached up to ~34 dB in X band frequency (8–12 GHz) at only 2 wt% MWCNTs and 7 wt% Fe_3O_4 content. However, open-cell carbon foam (C-PFC2F7) with 2 mm thickness exhibited EMI SE of ~62 dB at 8–12 GHz

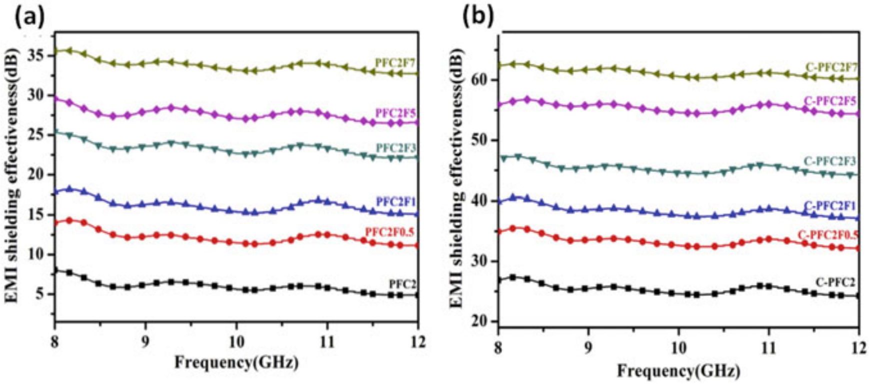

Fig. 3 **a** EMI SE of closed-cell phenolic foam with 2 wt % MWCNTs and various Fe_3O_4 loadings in the frequency range 8–12 GHz and **b** EMI SE of open-cell carbon foam with 2 wt. % MWCNTs and various Fe_3O_4 loadings in the frequency range 8–12 GHz. Reproduced with permission from [35]

at the same MWCNTs (2 wt %) and Fe_3O_4 (7 wt %) loading. The increasing EMI SE in both cases is mainly due to the high conductivity of MWCNTs and excellent microwave absorbing properties of nano-Fe_3O_4. Furthermore, the Fe_3O_4-MWCNTs constructed a conductive network in the phenolic and carbon matrix for electrons migrating and hopping due to the single-dimensional structure and high conductivity of the MWCNTs.

Farhan et al. [59] reported a novel approach for high-performance EMI shielding using the situ grown silicon carbide nanowires (SiCNWs) grown on phenolic resin-based carbon foam via powder molding method. In-situ SiCNWs were grown inside the porous structure by using different weight ratios of silicon powder ranging from 0 to 20 wt% and pyrolyzing at 1500 °C under argon atmosphere. The EMI shielding performance of carbon foams was carried out in the X band frequency range. It was observed that the EMI SE of the carbon foam increasing with the increase in SiCNWs content. Initially, EMI SE was found to be ~19 dB over the frequency range of 8−12 GHz for the carbon foam containing 0 wt% silicon powder. The maximum EMI SE obtained was ~47 dB for the carbon foam of 20 wt% silicon powder in the same frequency range. Furthermore, the absorption of carbon foam increases with the increase in SiCNWs and suggesting an absorption dominating mechanism in carbon foam [66]. The higher contents of SiCNWs have increased the polarization loss, which leads to enhance absorption. Additionally, the porous structure of carbon foam provides multiple internal reflections that contribute to excellent absorption in composite foam.

Graphene is a single layer of sp^2 bonded carbon atoms and has excellent charge career mobility, high thermal conductivity, large specific surface area, and excellent mechanical properties [67, 68]. Graphene or reduced graphene oxide (rGO) has been successfully reinforced with a different type of polymer/carbon matrix for improving the EMI shielding of carbon foams [50, 61, 69, 70]. Very few research works have been conducted on phenolic foam reinforced with graphene for EMI shielding till date. Furthermore, the highly porous structure might make the carbon foam brittle, which greatly influences the overall performance of carbon foam. To resolve this problem, Chen and his co-workers [60] prepared graphene aerogels by graphene oxide (GO) as a carbon precursor and phenolic resin as a binder by a hydrothermal method followed by annealing at three different temperatures, i.e. 500, 900, or 1300 °C for 2 h under an argon atmosphere, and the resultants were denoted as p-GA-500, p-GA-900, and p-GA-1300, respectively. To increase the mechanical strength of graphene aerogel, the epoxy resin was impregnated into the graphene aerogel and cured at 120 for 2 h in a vacuum oven, and the resultant aerogels were denoted as epoxy/p-GA-500, epoxy/p-GA-900, and epoxy/p-GA-1300. Figure 4a shows the EMI SE of graphene aerogels annealed at different temperatures. From Fig. 4a, it was found that EMI SE of graphene aerogels depends on the annealing temperature. The aerogel (epoxy/p-GA-1300) annealed at a higher temperature leads to a higher EMI SE. The obtained EMI SE of annealed aerogel (epoxy/p-GA-1300) is reached to 35 dB in the X-band frequency range. Furthermore, it was also observed that the thickness of aerogels influences the EMI SE as displayed in Fig. 4b. The

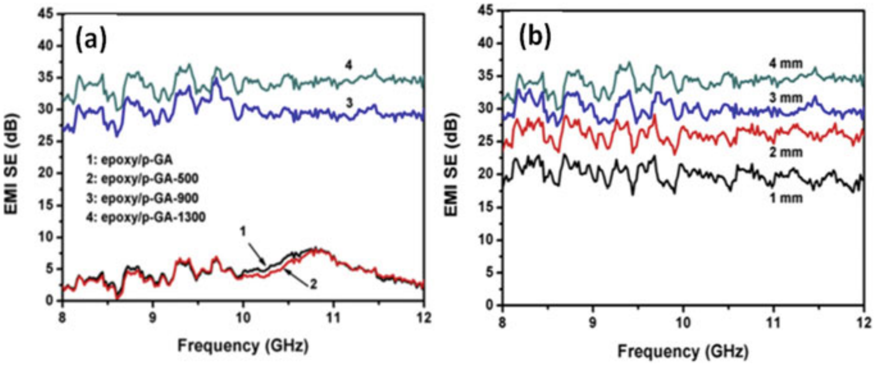

Fig. 4 EMI SE of graphene aerogels; **a** epoxy/p-GAs annealed at different temperatures and **b** epoxy/p-GA-1300 (1:10) with different sample thicknesses. Reproduced with permission from [60]

EMI SE of the aerogel (epoxy/p-GA-1300) with a 1 mm thickness increased from 21 to 35 dB for the aerogel of 4 mm thickness.

Agrawal et al. [61] prepared carbon–rGO composite foams from phenolic resin and rGO using the PU foam template method. Two different processes were adopted to prepare the carbon–rGO composite foam. In one process, 0–4 wt % of rGO was mixed in phenolic resin and foam was synthesized using the PU foam impregnation method followed by carbonization at 1000 °C as shown in Fig. 5a. In the second process, the as-received carbon foam was decorated with graphene oxide (GO) using dip coating and heat-treated at 950 °C in an inert atmosphere to obtained rGO decorated carbon foam as shown in Fig. 5b. After incorporation and decoration, the foam samples were characterized for microstructural analysis. The SEM image of as-received carbon is shown in Fig. 5c, which confirms that composite foam is highly porous. The decoration of 1 wt% rGO on carbon foam is shown in Fig. 5d. The uniform decoration of rGO on the carbon foam surface could also be seen at higher magnification (Fig. 4d). The uniform decoration of rGO helps to improve the electrical conductivity and EMI SE of carbon foams. The rGO incorporated carbon foam displayed electrical conductivity of 52.4 S/cmat only 4.0 wt% rGO loading. Whereas, the electrical conductivity of rGO decorated carbon foam exhibited 58.5 S/cm with graphene decoration of only 1 wt %. The EMI SE of carbon foams was measured in the X-band and found that with increasing the rGO content, the SE_T and SE_A increased significantly in both the process incorporation and decoration. The SE_T, $SE_{A,}$ and SE_R for pristine carbon foam are 23.2, 12.2, and 12.0 dB, respectively, at 8.2 GHz. In rGO (4 wt %) incorporated carbon foam, the value of SE_T and SE_A increased to 44.6 and 37.2 dB, respectively, at 8.2 GHz. However, in rGO (1 wt %) decorated carbon foam, the value of SE_T and SE_A is reported to be 50.7 and 44.6 dB, respectively, at 8.2 GHz. The decoration of rGO on the foam surface makes a heterojunction structure that helps to form a conducting network for faster electron transport leads to high EMI SE in rGO decorated carbon foam. The interconnected open pore

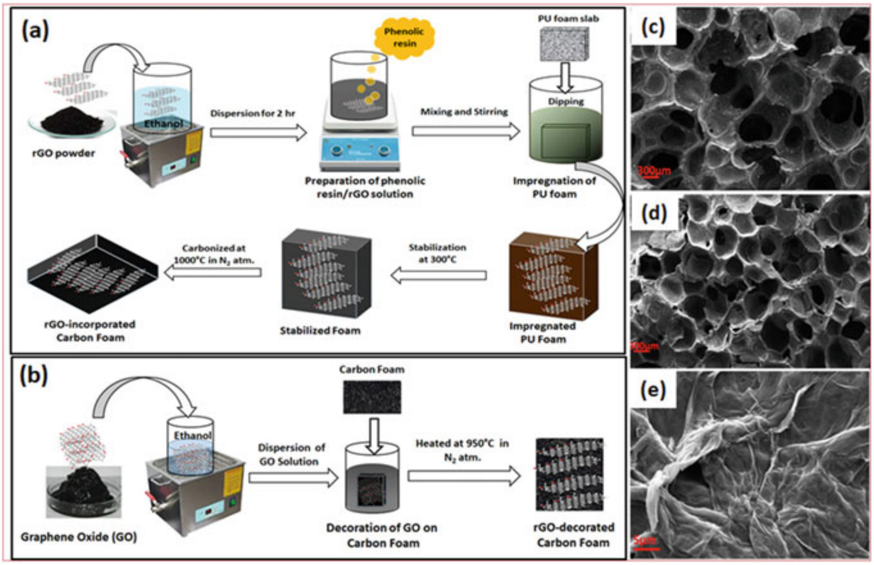

Fig. 5 Schematic illustration for the synthesis of carbon–rGO composite foam; **a** rGO incorporated, **b** rGO decorated carbon foam, SEM images of **c** as received carbon foam, **d** carbon foam with 1 wt % rGO decoration, and **e** uniform decoration of rGO at high magnification. Reproduced with permission from [61]

structure is also responsible for enhancing microwave absorption. Furthermore, the high impedance mismatch between air, carbon, and graphene sheets helps to transfer the EM energy in the form of heat leading to the enhancement in absorption [71].

In the series of work related to the improvement of EMI shielding performance, Zeng et al. [37] have developed the phenolic resin-based carbon foam by incorporating the GO/SiO_2 hybrid nanomaterials via in situ preparation method. To understanding the effect of incorporation of GO/SiO_2 in the resin matrix, the EMI shielding properties have been evaluated in the X-band frequency range. It was found that the EMI SE of plain carbon foam was nearly 18 dB but after incorporation of GO, the EMI SE reached the value of 22.8 dB. This is due to the electrical conductivity of GO, which provides a conductive network inside the resin matrix. It is interesting to note the EMI SE of carbon foam was significantly increased up to ~50 dB as the concentration of GO/SiO_2 rises to 1.5 wt %. The enhanced EMI shielding performance is because GO/SiO_2 clusters increase electrically conductive paths, which has a strong interaction with the EM wave and thus can significantly attenuate the EM wave [72].

Furthermore, the EMI shielding of phenolic-based foams has been improved by graphene and Fe_3O_4 nanoparticles. Yu et al. [62] demonstrated rGO/Fe_3O_4 hybrid-modified carbon foam for EMI shielding applications. First, they have synthesized rGO/Fe_3O_4 by co-precipitation method then rGO/Fe_3O_4 hybrid-modified carbon foam has been fabricated by mixing the phenol and different wt % (0–1.5) rGO/Fe_3O_4

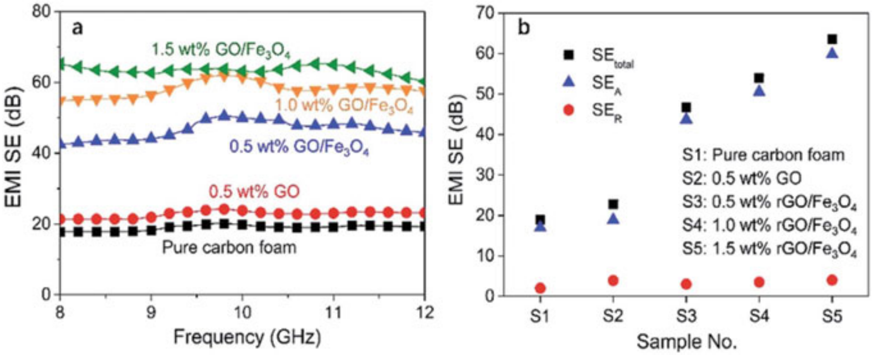

Fig. 6 **a** The EMI SE of various carbon foams in the X-band and **b** total EMI (SE_{total}), absorption (SE_A), reflection (SE_R) of carbon foam at the frequency of 10 GHz. Reproduced with permission from [62]

followed by carbonization at 800 °C. The EMI SE of pure carbon foam and foam with different loading of rGO/Fe_3O_4 content is measured in X-band and shown in Fig. 6a. It was observed that the EMI SE of carbon foam increases significantly with an increase of the rGO/Fe_3O_4 content. The SE_{total}, SE_A, and SE_R of carbon foam at 10 GHz are plotted against rGO/Fe_3O_4 content as shown in Fig. 6b. In Fig. 6b, it was found that SE_{total} and SE_A increase with an increase in the rGO/Fe_3O_4 content, whereas SE_R is negligible over all the rGO/Fe_3O_4 content. The as-received carbon foam showed EMI SE of 20 dB and its value further increased to 65 dB at only 1.5 wt % rGO/Fe_3O_4 loading. The enhanced EMI SE is mainly due to the magnetic properties such as hysteresis and dielectric loss of Fe_3O_4, which has strong interaction with EM waves. It was also observed porous structure of carbon foams contributed to the absorption domination due to multiple reflections and absorption of EM waves.

Recently, Sharma et al. [15] have used a different type of carbon filler, i.e. graphitized mesocarbon microbeads (MCMB) for improving the EMI SE of phenolic resin-based carbon foam.

The effect of MCMB on EMI shielding properties of phenolic resin-based carbon foams was discussed in this study. It was observed that with an increase in MCMB content, electrical conductivity, dielectric properties were increased. Figure 7a shows the EMI SE of carbon–MCMB composite foam in 8.2–12.4 GHz with various MCMB content. The maximum EMI SE of carbon–MCMB composite foam at 20 wt. % of MCMB addition was 62.4 dB. The results show that the increase in electrical conductivity of composite foam is responsible for the enhancement of EMI SE. Figure 7b shows the relation between SE_A, SE_R, and electrical conductivity. It was found that with an increase in the electrical conductivity, the SE_A increases continuously while the SE_R slightly decreased. The uniform distribution and strong adhesion of MCMBs with carbon matrix provide high conductivity and thus cause a strong polarization for EM wave attenuation.

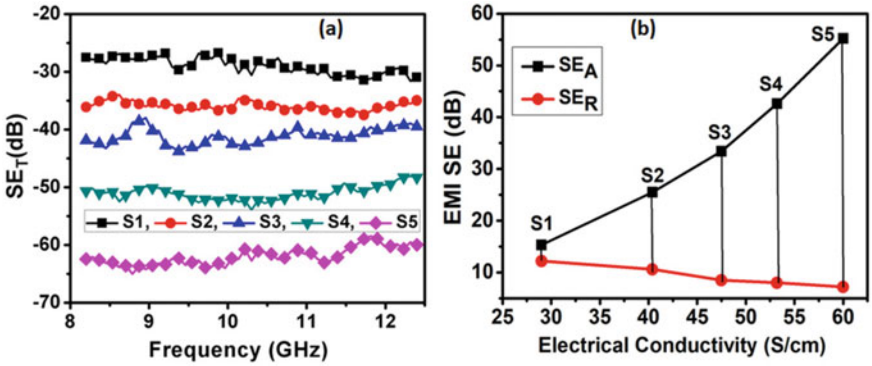

Fig. 7 **a** EMI SE of carbon–MCMB composite foams in X-band frequency range and **b** The SE$_A$, SE$_R$ of carbon–MCMB composite foams at 8.2 GHz as a function of electrical conductivity. (S1 = pristine carbon foam; S2 = carbon foam with 5 wt % MCMB; S3 = carbon foam with 10 wt % MCMB; S4 = carbon foam with 15 wt % MCMB S5 = carbon foam with 20 wt % MCMB). Reproduced with permission from [15]

In recent times, global attention toward environmental protection has accelerated the rate of recycling industrial waste and utilizing it in novel products. Industrial wastes such as fly ash [73] blast furnace slag [74], rice husk ash [75], waste glass [76], and red mud [77, 78] are a major nuisance for societies everywhere. Kumar et al. [13] used fly ash-derived cenosphere to fabricate phenolic resin-derived carbon foam for EMI shielding properties. Cenospheres are the lightweight and hollow microsphere in which silica and alumina are the major constituents. Through this experiment, it was observed that the EMI SE of carbon foam increases with the increase in cenosphere content. The maximum EMI SE was found to be 48.6 dB with SE$_A$ of 42.9 dB at 8.2 GHz for the carbon foam containing 30 wt % cenosphere. The improved absorption can be attributed to the porosity in foam as well as the cenosphere, the EM wave deeply penetrates inside carbon foam, and attenuation is achieved by the repeated reflection.

In another work, Kumar et al. [16] used red mud for the fabrication of carbon-red mud hybrid foam for EMI shielding applications. The different content (0–20 wt %) red mud was mixed with phenolic resin solution, the foams were synthesized by the PU foam template method followed by carbonization at 1100 °C in an argon atmosphere. The EMI SE of hybrid foam was measured in the X band and shown in Fig. 8a. The EMI SE of hybrid foam without red mud was found to 22.6 dB due to reflection (SE$_R$ 9.9 dB) and absorption (SE$_A$ 12.7). It was observed that EMI SE increases with the increases in red mud content. The maximum EMI was obtained 51.4 dB with excellent absorption 45.5 dB and very minute reflection 5.9 dB at 8.2 GHz for the hybrid foam containing 20 wt % red mud. Besides, the absorption of hybrid foam can further correlate with skin depth. Skin depth (δ) and absorption (SE$_A$) at 8.2 GHz for all hybrid foams are shown in Fig. 8b. It was observed that the skin depth of hybrid foam decreases with an increase in red mud content. In the

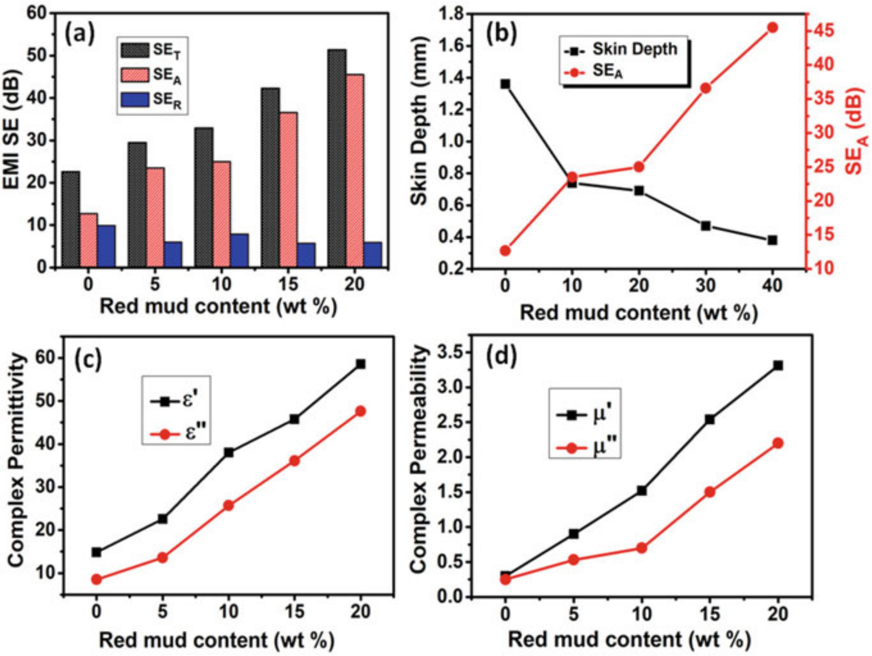

Fig. 8 **a** EMI SE, **b** Skin depth versus SE$_A$, **c** Complex permittivity, and **d** Complex permeability of hybrid foam with various red mud content at 8.2 GHz [16]

above Eq. (13), it was mentioned that that skin depth is inversely proportional to SE$_A$. Therefore, as received carbon foam exhibited high skin depth (1.3 mm) and low absorption (12.7) whereas hybrid foam containing 20 wt % red mud exhibited low skin depth (0.38 mm) and high absorption (45.5). The enhanced EMI SE due to absorption was due to the high dielectric and magnetic loss of red mud constituents such as Fe_2O_3, Al_2O_3, and SiO_2 and further correlate with complex permittivity (ε' and ε'') and permeability (μ' and μ'') of hybrid foams. The ε' and $\varepsilon''$and μ' and μ'' of hybrid foams were measured in X band frequency range and their values are presented at 8.2 GHz as shown in Fig. 8c, d. From Fig. 8c, it was seen that ε' and ε'' of hybrid foams increase with an increase in red mud content. The maximum value of ε' and ε'' is 58.6 and 47.6, respectively, for the hybrid foam containing 20 wt % red mud content. The ε' and ε'' increases with an increase in the red mud content can be ascribed to enhanced dipole orientation polarization and interfacial polarization, which significantly improve the absorption in hybrid foams. Furthermore, the μ' and μ'' of hybrid foams increase with an increase in the red mud content (Fig. 8d). In hybrid foam containing 20 wt % red mud, the maximum value of μ' and μ'' is found to be 3.3 and 2.2, respectively. The improved value of μ' and μ'' is due to the presence of Fe_2O_3 in red mud, which significantly enhanced the absorption component. Thus, such industrial wastes offer a new approach to prepare advanced products and can be used as effective EMI shielding materials.

4 Conclusions and Future Outlook

In this chapter, we reviewed the recent progress in the development of phenolic-based carbon foams for EMI shielding applications. The excellent EMI shielding performance of phenolic-based foam has opened up a new area of making lightweight microwave absorbing devices. Very limited studies are reported on the development of lightweight phenolic resin-based carbon foams for EMI shielding applications. To make efficient EMI shielding foam, the foam materials must exhibit good electrical conductivity and dielectric constant. These requirements can only be reached when phenolic resin-based foams are modified with conducting and magnetic fillers. Therefore, the phenolic foams have been modified with various conducting and magnetic fillers such as CNTs, graphene, rGO, MCMB, MnO_2, ZnO, Fe_3O_4, SiO_2, and some industrial wastes such as cenosphere and red mud. It was found that the graphene and Fe_3O_4-reinforced phenolic resin-based carbon foam have excellent EMI shielding performance. It was found that the addition of different types of fillers in phenolic resin and generation of a cellular structure through foaming enables to combine of several multifunctional characteristics with the possibility of a tailor-made control of the EMI shielding properties. It is visualized that the developed composite foam can directly be used in structural panels for EMI shielding and radar absorption. Instead of lightweight, thinner, and flexible, EMI shielding materials need to be developed and explored for next-generation flexible electronic devices. Therefore, newly developed 2D materials will be key fillers for enhancing the EMI shielding performance of the phenolic-based carbon foams. The following research direction could be explored in the future.

(i) The CNTs and graphene materials have already been synthesized, which could be further used for the development of efficient EMI shielding materials.
(ii) Recently, MXene has shown outstanding EMI shielding performance because MXene has both conducting and magnetic properties, which make it an excellent filler for future EMI shielding applications.
(iii) The industrial waste materials are continuously increasing and polluting the environment, so there is a lot of scopes to explore these wastes in phenolic-based foams for EMI shielding applications.
(iv) Till date, the reported EMI shielding value is good enough for commercial purposes but for stealth technology, there is a need for new advanced materials having excellent microwave absorbing capabilities.

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References

1. Chung D (2012) Carbon materials for structural self-sensing, electromagnetic shielding and thermal interfacing. Carbon 50:3342–3353
2. Geetha S, Satheesh Kumar KK, Rao CRK et al (2009) EMI shielding: methods and materials—A review. J Appl Polym Sci 112:2073–2086
3. Carlberg M, Koppel T, Ahonen M et al (2018) Case-control study on occupational exposure to extremely low-frequency electromagnetic fields and the association with meningioma. Biomed Res Int2018
4. Markham D (1999) Shielding: quantifying the shielding requirements for portable electronic design and providing new solutions by using a combination of materials and design. Mater Des 21:45–50
5. Chung DDL (2020) Materials for electromagnetic interference shielding. Mater Chem Phys 255:123587
6. Wenderoth K, Petermann J, Kruse KD et al (1989) Synergism on electromagnetic inductance (EMI)-shielding in metal-and ferroelectric-particle filled polymers. Polym Compos 10:52–56
7. Wang Y, Jing X (2005) Intrinsically conducting polymers for electromagnetic interference shielding. Polym Adv Technol 16:344–351
8. Vix-Guterl C, Frackowiak E, Jurewicz K et al (2005) Electrochemical energy storage in ordered porous carbon materials. Carbon 43:1293–1302
9. Dash R, Chmiola J, Yushin G et al (2006) Titanium carbide derived nanoporous carbon for energy-related applications. Carbon 44:2489–2497
10. Dhakate SR, Subhedar KM, Singh BP (2015) Polymer nanocomposite foam filled with carbon nanomaterials as an efficient electromagnetic interference shielding material. RSC Adv 5:43036–43057
11. Gallego NC, Klett JW (2003) Carbon foams for thermal management. Carbon 41:1461–1466
12. Jiang Q, Liao X, Yang J et al (2020) A two-step process for the preparation of thermoplastic polyurethane/graphene aerogel composite foams with multi-stage networks for electromagnetic shielding. Compos Commun 100416
13. Kumar R, Mondal DP, Chaudhary A et al (2018) Excellent EMI shielding performance and thermal insulating properties in lightweight, multifunctional carbon-cenosphere composite foams. Compos Part A Appl Sci Manuf 112:475–484
14. Song SA, Lee Y, Kim YS et al (2017) Mechanical and thermal properties of carbon foam derived from phenolic foam reinforced with composite particles. Compos Struct 173:1–8
15. Sharma A, Kumar R, Patle VK et al (2020) Phenol formaldehyde resin derived carbon-MCMB composite foams for electromagnetic interference shielding and thermal management applications. Compos Commun 22:100433
16. Kumar R, Sharma A, Pandey A et al (2020) Lightweight carbon-red mud hybrid foam toward fire-resistant and efficient shield against electromagnetic interference. Sci Rep 10:1–12
17. Inagaki M, Morishita T, Kuno A et al (2004) Carbon foams prepared from polyimide using urethane foam template. Carbon 42:497–502
18. Klett J, Hardy R, Romine E et al (2000) High-thermal-conductivity, mesophase-pitch-derived carbon foams: effect of precursor on structure and properties. Carbon 38:953–973
19. Yadav A, Kumar R, Bhatia G et al (2011) Development of mesophase pitch derived high thermal conductivity graphite foam using a template method. Carbon 49:3622–3630
20. Li M-Z, Jia L-C, Zhang X-P et al (2018) Robust carbon nanotube foam for efficient electromagnetic interference shielding and microwave absorption. J Colloid Interface Sci 530:113–119
21. Chen Z, Xu C, Ma C et al (2013) Lightweight and flexible graphene foam composites for high-performance electromagnetic interference shielding. Adv Mater 25:1296–1300
22. Duan H, Zhu H, Yang J et al (2019) Effect of carbon nanofiller dimension on synergistic EMI shielding network of epoxy/metal conductive foams. Compos Part A Appl Sci Manuf 118:41–48

23. Feng D, Liu P, Wang Q (2019) Exploiting the piezoresistivity and EMI shielding of polyetherimide/carbon nanotube foams by tailoring their porous morphology and segregated CNT networks. Compos Part A Appl Sci Manuf124:105463
24. Wang S, Luo R, Ni Y (2010) Preparation and characterization of resin-derived carbon foams reinforced by hollow ceramic microspheres. Mater SciEng A 527:3392–3395
25. Gavgani JN, Adelnia H, Zaarei D et al (2016) Lightweight flexible polyurethane/reduced ultralarge graphene oxide composite foams for electromagnetic interference shielding. RSC Adv 6:27517–27527
26. Prieto R, Louis E, Molina JM (2012) Fabrication of mesophase pitch-derived open-pore carbon foams by replication processing. Carbon 50:1904–1912
27. Wang Y, He Z, Zhan L et al (2016) Coal tar pitch based carbon foam for thermal insulating material. Mater Lett 169:95–98
28. Zeng Z, Zhang Y, Ma XYD et al (2018) Biomass-based honeycomb-like architectures for preparation of robust carbon foams with high electromagnetic interference shielding performance. Carbon 140:227–236
29. Yuan Y, Ding Y, Wang C et al (2016) Multifunctional Stiff Carbon Foam Derived from Bread. ACS Appl Mater Inter 8:16852–16861
30. Chen C, Kennel EB, Stiller AH et al (2006) Carbon foam derived from various precursors. Carbon 44:1535–1543
31. Landrock AH (1995) Handbook of plastic foams: types, properties, manufacture and applications. Elsevier
32. Inagaki M, Qiu J, Guo Q (2015) Carbon foam: Preparation and application. Carbon 87:128–152
33. Ford WD (1964) Method of making cellular refractory thermal insulating material, Google Patents
34. Li Q, Chen L, Li X et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Compos Part A Appl Sci Manuf 82:214–225
35. Li Q, Chen L, Ding J et al (2016) Open-cell phenolic carbon foam and electromagnetic interference shielding properties. Carbon 104:90–105
36. Song SA, Chung YS, Kim SS (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93
37. Zeng Y, Luo X, Yu K et al (2019) EMI shielding performance of phenolic-based carbon foam modified with GO/SiO2 hybrid nanomaterials. Chem Phys Lett 715:166–172
38. Saini P, Choudhary V, Singh B et al (2011) Enhanced microwave absorption behavior of polyaniline-CNT/polystyrene blend in 12.4–18.0 GHz range. Synth Met 161:1522–1526
39. Singh AP, Mishra M, Sambyal P et al (2014) Encapsulation of γ-Fe 2 O 3 decorated reduced graphene oxide in polyaniline core–shell tubes as an exceptional tracker for electromagnetic environmental pollution. J Mater Chem A 2:3581–3593
40. Kumar R, Dhakate SR, Gupta T et al (2013) Effective improvement of the properties of light weight carbon foam by decoration with multi-wall carbon nanotubes. J Mater Chem A 1:5727–5735
41. Bhattacharjee Y, Biswas S, Bose S (2020) Chapter 5-Thermoplastic polymer composites for EMI shielding applications. In: Joseph K, Wilson R, George G (eds) Materials for Potential EMI Shielding Applications, Elsevier, pp 73–99
42. Gupta TK, Singh BP, Mathur RB et al (2014) Multi-walled carbon nanotube–graphene–polyaniline multiphase nanocomposite with superior electromagnetic shielding effectiveness. Nanoscale 6:842–851
43. Nicolson A, Ross G (1970) Measurement of the intrinsic properties of materials by time-domain techniques. IEEE Trans Instrum Meas 19:377–382
44. Weir WB (1974) Automatic measurement of complex dielectric constant and permeability at microwave frequencies. Proc IEEE 62:33–36
45. Tong XC (2016) Advanced materials and design for electromagnetic interference shielding. CRC Press

46. Tseng C-H, Chu T-H (2005) An effective usage of vector network analyzer for microwave imaging. IEEE Trans Microwave Theory Tech 53:2884–2891
47. Sreekala M, George J, Kumaran M et al (2002) The mechanical performance of hybrid phenol-formaldehyde-based composites reinforced with glass and oil palm fibres. Compos Sci Technol 62:339–353
48. Yang J, Liao X, Li J et al (2019) Light-weight and flexible silicone rubber/MWCNTs/Fe3O4 nanocomposite foams for efficient electromagnetic interference shielding and microwave absorption. Compos Sci Technol 181:107670
49. Yang Y, Gupta MC, Dudley KL et al (2005) Novel carbon nanotube-polystyrene foam composites for electromagnetic interference shielding. Nano Lett 5:2131–2134
50. Wu Y, Wang Z, Liu X et al (2017) Ultralight graphene foam/conductive polymer composites for exceptional electromagnetic interference shielding. ACS Appl Mater Inter 9:9059–9069
51. Zhang H-B, Yan Q, Zheng W-G et al (2011) Tough graphene− polymer microcellular foams for electromagnetic interference shielding. ACS Appl Mater Inter 3:918–924
52. Li G, Xie T, Yang S et al (2012) Microwave absorption enhancement of porous carbon fibers compared with carbon nanofibers. J Phys Chem C 116:9196–9201
53. Ren Y-L, Wu H-Y, Lu M-M et al (2012) Quaternary nanocomposites consisting of graphene, Fe3O4@ Fe core@ shell, and ZnO nanoparticles: synthesis and excellent electromagnetic absorption properties. ACS Appl Mater Inter 4:6436–6442
54. Sun D, Zou Q, Qian G et al (2013) Controlled synthesis of porous Fe3O4-decorated graphene with extraordinary electromagnetic wave absorption properties. Acta Mater 61:5829–5834
55. Singh R, Kulkarni SG (2014) Nanocomposites based on transition metal oxides in polyvinyl alcohol for EMI shielding application. Polym Bull 71:497–513
56. Agarwal PR, Kumar R, Kumari S et al (2016) Three-dimensional and highly ordered porous carbon-MnO2 composite foam for excellent electromagnetic interference shielding efficiency. RSC Adv 6:100713–100722
57. Kumar R, Singh AP, Chand M et al (2014) Improved microwave absorption in lightweight resin-based carbon foam by decorating with magnetic and dielectric nanoparticles. RSC Adv 4:23476–23484
58. Patle VK, Kumar R, Sharma A et al (2020) Three dimension phenolic resin derived carbon-CNTs hybrid foam for fire retardant and effective electromagnetic interference shielding. Compos Part C 2:100020
59. Farhan S, Wang R, Li K (2016) Electromagnetic interference shielding effectiveness of carbon foam containing in situ grown silicon carbide nanowires. Ceram Int 42:11330–11340
60. Chen Y, Zhang H-B, Wang M et al (2017) Phenolic resin-enhanced three-dimensional graphene aerogels and their epoxy nanocomposites with high mechanical and electromagnetic interference shielding performances. Compos Sci Technol 152:254–262
61. Agrawal PR, Kumar R, Teotia S et al (2019) Lightweight, high electrical and thermal conducting carbon-rGO composites foam for superior electromagnetic interference shielding. Compos Part B Eng 160:131–139
62. Yu K, Zeng Y, Wang G et al (2019) rGO/Fe 3 O 4 hybrid induced ultra-efficient EMI shielding performance of phenolic-based carbon foam. RSC Adv 9:20643–20651
63. Lou Z, Li R, Wang P et al (2020) Phenolic foam-derived magnetic carbon foams (MCFs) with tunable electromagnetic wave absorption behavior. Chem Eng J 391:123571
64. Salvetat J-P, Bonard J-M, Thomson N et al (1999) Mechanical properties of carbon nanotubes. Appl Phys A 69:255–260
65. Zeng S, Li X, Li M et al (2019) Flexible PVDF/CNTs/Ni@ CNTs composite films possessing excellent electromagnetic interference shielding and mechanical properties under heat treatment. Carbon 155:34–43
66. Hao X, Yin X, Zhang L et al (2013) Dielectric, electromagnetic interference shielding and absorption properties of Si3N4–PyC composite ceramics. J Mater Sci Technol 29:249–254
67. Geim AK, Novoselov KS (2010) The rise of graphene. Nanoscience and technology: a collection of reviews from nature journals, World Sci 11–19

68. Neto AC, Guinea F, Peres NM et al (2009) The electronic properties of graphene. Rev Mod Phys 81:109
69. Yan D-X, Ren P-G, Pang H et al (2012) Efficient electromagnetic interference shielding of lightweight graphene/polystyrene composite. J Mater Chem 22:18772–18774
70. Eswaraiah V, Sankaranarayanan V, Ramaprabhu S (2011) Functionalized graphene–PVDF foam composites for EMI shielding. Macromol Mater Eng 296:894–898
71. Chaudhary A, Kumar R, Dhakate SR et al (2019) Scalable development of a multi-phase thermal management system with superior EMI shielding properties. Compos Part B Eng 158:206–217
72. Lu M-M, Cao M-S, Chen Y-H et al (2015) Multiscale assembly of grape-like ferroferric oxide and carbon nanotubes: a smart absorber prototype varying temperature to tune intensities. ACS Appl Mater Inter 7:19408–19415
73. Zacco A, Borgese L, Gianoncelli A et al (2014) Review of fly ash inertisation treatments and recycling. Environ Chem Lett 12:153–175
74. Ding L, Ning W, Wang Q et al (2015) Preparation and characterization of glass–ceramic foams from blast furnace slag and waste glass. Mater Lett 141:327–329
75. Pode R (2016) Potential applications of rice husk ash waste from rice husk biomass power plant. Renew Sustain Energ Rev 53:1468–1485
76. Phonphuak N, Kanyakam S, Chindaprasirt P (2016) Utilization of waste glass to enhance physical–mechanical properties of fired clay brick. J Cleaner Prod 112:3057–3062
77. Samal S, Ray AK, Bandopadhyay A (2013) Proposal for resources, utilization and processes of red mud in India—A review. Int J Miner Process 118:43–55
78. Liu W, Yang J, Xiao B (2009) Application of Bayer red mud for iron recovery and building material production from alumosilicate residues. J Hazard Mater 161:474–478

Chapter 11
Flame Retardant Modification of Phenolic Foam

Fei Song and Puyou Jia

1 Introduction

Energy resources support the high-quality survival and rapid development of human beings and are the key to sustainable economic development. Therefore, energy conservation and emission reduction have become a common concern of all countries in the world [1]. Compared with Western developed countries, China's building energy consumption is relatively high. The energy consumption per unit building area is more than 2–3 times that of developed countries. The energy consumption of building materials and buildings accounts for 47.3% of the total energy consumption, which exceeds the sum of all developed countries. According to this situation, there is an urgent need for building energy conservation [2], and one of the most important energy-saving measures is to take heat insulation measures for the building envelope to improve its thermal performance. In addition, fires can cause significant losses to human lives and property. Therefore, special attention should be paid to fire protection for building insulation materials, especially in the field of public high-rise buildings. In the case of a fire in a closed system such as a building, vehicle, ship, or aircraft, the fire should be separated and the fire should be restricted from spreading from one place to another in order to save lives and property and give people enough time to evacuate. For this reason, the thermal insulation material developed not only needs to have low thermal conductivity to ensure thermal insulation effect, but also has low flammability to prevent fire or as a fire barrier to limit the spread of fire when a fire occurs.

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At present, polystyrene foam, polyurethane foam, and polyvinyl chloride foam, which have good thermal insulation effects, occupy the leading position of building thermal insulation materials in the market. However, this type of material has low heat resistance, is very easy to burn, and releases a large amount of toxic smoke and gas, which not only causes environmental pollution, but also becomes one of the main factors causing casualties in fires [3]. Phenolic foam (PF), as a flame-retardant thermal insulation material that can achieve flame-retardant grade without external flame retardant, has low thermal conductivity, self-extinguishing, heat resistance, flame penetration resistance, chemical corrosion resistance, no dripping on fire, and low smoke, and has gradually attracted wide attention [4]. The flame-retardant characteristics of PF are determined by its high cross-linked structure and high aromatic ring content. PF hardly generates toxic gas when it is thermally decomposed and forms a carbon protective layer during the combustion process to inhibit the continuous combustion of the foam in the layer [5, 6]. At present, phenolic foam has been widely used in high-rise buildings, insulated pipes, transportation and flowers, and other fields, which is one of the fastest growing foam varieties in recent years [7, 8]. Phenolic foam has the above unique advantages and also has defects such as poor mechanical properties, high brittleness, and a high pulverization rate caused by its own molecular structure, which seriously hinders its development and application in various fields [9]. Therefore, seeking an effective method to enhance the toughness and mechanical properties of phenolic foam without sacrificing its inherent advantages is an important research direction of current phenolic foam research.

In recent years, many researchers have conducted numerous studies on the strengthening of phenolic foam composites. The most extensive way to enhance phenolic foam is to add flexible chains inside or outside the molecular network of phenolic foam to enhance its toughness. Unfortunately, the presence of flexible chains tends to adversely affect the Flame-retardant of PF, which hinders their application as a fire-resistant material [10]. For foam composites, ensuring strong flame retardancy and thermal stability can reduce the possibility of the deterioration of load carrying ability or catastrophic failure of these composite structures due to temperature changes and fire [11–13]. To improve the problem of reduced flame retardancy caused by the introduction of flexible chains, researchers have done a lot of research, mainly using three technologies: (1) Adding traditional nitrogen and phosphorus flame retardants while adding tougheners to modify its flame retardancy [14]; (2) Prepare a reactive flame-retardant toughening agent containing nitrogen, phosphorus, silicon and boron, and other flame-retardant elements, and toughen it and modify it [15]; (3) Blend nano-materials such as nano-silica, nano-montmorillonite, nano-carbon fiber, and phenolic resin to form a nano-modified phenolic foam with an interpenetrating network structure, which improves the material′s resistance while improving the mechanical properties and combustion performance of the material [16, 17].

2 Boron-Containing Flame Retardant Modified Phenolic Foam

Boric acid, borate, and organoboron compounds can all be used as flame retardants. In the combustion process, boron-containing flame retardants will be dehydrated to generate boron oxide compounds, such as boroxine and boric anhydride [18]. The B—O—C or B—O—B structure in these compounds has good thermal oxidation stability, promotes the formation of a dense carbon layer, prevents oxygen and heat from reaching the internal combustion part of the material, and protects the underlying material from further degradation [19].

Wang et al. [20] studied the effect of B_2O_3 on the compressive strength and heat resistance of phenolic foam. The B_2O_3 can condense with the hydroxyl group in the phenolic resin to form a B—O bond during the curing process. This bond has a longer bond and good flexibility. The introduction of an appropriate amount of B_2O_3 slightly enhances the compressive strength of the phenolic foam. The B—O bond (774 kJ/mol) has a bond energy much higher than the C—C bond (334 kJ/mol). The more B_2O_3 added, the better the heat resistance of the modified phenolic foam. The 7 wt% B_2O_3modified phenolic foam compared with pure phenolic foam, the decomposition temperature at 5% and 10% mass loss is increased by 94 °C and 194 °C, respectively, and the residual carbon rate at 800 °C is as high as 66.37%. Liu et al. [21] used polyethylene glycol borate (PEG-BAE) prepared by the esterification reaction between boric acid and PEG to toughen phenolic foam. It is found that the limiting oxygen index (LOI) value of pure PF is 40.5%, whereas the value of PEG400 toughened PF decreases to 33.5%. This result indicates that the introduction of PEG400 into pure PF weakens its good flame retardancy considerably. However, when PFs are toughened by PEG-BAEs, their LOI values all increase compared with the one toughened by PEG400. Among the PEG-BAEs, PEG200-BAE is the most effective flame-retardant toughening agent with a LOI value of 39.0%. The LOI values of the PF toughened by PEG400-BAE and PEG600-BAE are 38.5% and 35.5%, respectively. The reason may be that the esterification rate of PEG200-BAE is higher than that of the other two, therefore the boron content of PEG200-BAE is the highest among the three PEG-BAEs. Moreover, all the foams can pass the UL-94 V0 rating. LOI is the minimum oxygen content volume percentage to maintain material combustion in the oxygen–nitrogen mixture [20], which can be calculated by using Eq. (1) [11].

$$\mathrm{LOI} = \mathrm{C_f} + \mathrm{Kd} \tag{1}$$

where C_f is the critical or threshold value of the oxygen concentration in percentage volume, K is a factor which is obtained from the table, provided in ASTM–D–2863 and d is oxygen concentration.

3 Nitrogen-Containing Flame Retardant Modified Phenolic Foam

Nitrogen-containing flame retardants are mainly triazine organic compounds, including guanidine salts, dicyandiamide, melamine, biurea, and their derivatives [23]. Nitrogen-containing flame retardants are environmentally friendly flame retardants. Their main advantages are low toxicity, solid state, no corrosive and toxic gases, and less smoke in the event of a fire. The organic nitrogen flame retardant absorbs the heat generated by the flame combustion when it is thermally decomposed, and at the same time releases water vapor and nitrogen-containing incombustible gases (such as N_2, NO_2, and NH_3), which greatly reduces the surface temperature of the substrate under the combined action of the two; water vapor and nitrogen-containing non-combustible gases not only reduce the flammable gas and O_2 produced when the substrate is decomposed in the flame, but also the nitrogen-containing gas can react with O_2 to further consume O_2, and can also trap free radicals to stop the production the chain reaction of combustion [24].

Ge et al. [25] added melamine at the phenolic resin synthesis stage to study the effect of different amounts of melamine on the properties of phenolic foam. Because melamine has good reactivity with formaldehyde, the addition of melamine effectively reduces the free aldehyde in the phenolic resin and tends to be gentle with the increase in the amount of melamine. The melamine greatly enhances the flame-retardant properties of phenolic foam. The more the amount of melamine, the greater the LOI value. The introduction of melamine also effectively improves the toughness of the phenolic foam. The bending deflection of the 4.5 wt% melamine-modified phenolic foam is 100% stronger than that of the pure phenolic foam. Wang et al. [26] used solvothermal method to synthesize micron and nanometer melamine cyanurate (MMC and NMC) using cyanuric acid and melamine as raw materials, and used MMC and NMC with PEG to toughen phenolic foam, respectively. The flexural strength of the phenolic foam toughened with only 5 parts of PEG is 28% higher than that of the pure phenolic foam, but the LOI value is reduced by 17.1%. After the incorporation of MMC and NMC, the flexural strength of the phenolic foam can not only be further enhanced, but also the flame-retardant performance has also been improved, and the LOI value is close to that of pure phenolic foam. In comparison, the reinforcement effect of NMC is better than that of MMC. Dicyandiamide was used as a toughening agent to prepare modified phenolic foam, which has lower apparent density [10]. The incorporation of dicyandiamide into PF dramatically improved the compressive strength and impact strength. Meanwhile, the flame-retardant performance of the modified foams also improved. The phenolic foam modified by 0.5–2 g dicyandiamide content can all pass the V-0 rating, with the high LOI value of 47.2–48.1%. The char yield of phenolic foam modified with dicyandiamide is increased, and its rate of heat release, total heat release, mass loss rate of the modified PF is decreased.

4 Phosphorus-Containing Flame Retardant Modified Phenolic Foam

Phosphorus-containing flame retardants can be divided into two categories according to their properties and composition: Inorganic flame retardants, mainly red phosphorus, phosphate, polyphosphate, etc., have the advantages of low cost, simple method of use, but low water resistance and easy to migrate; organic flame retardants mainly include phosphates, phosphites, phosphines, organic phosphorus salts, etc., with the advantage of having dual functions of flame retardancy and plasticization. Phosphorus-containing flame retardant is a flame retardant that can play a flame-retardant effect in both the gas phase and the condensed phase [27]: (1) Condensed phase flame-retardant mechanism. Phosphorus-containing flame retardants are decomposed and polycondensed to produce acid sources with strong dehydration effects, such as phosphoric acid, metaphosphoric acid, polyphosphoric acid, and polymetaphosphoric acid. These acid sources can act as catalysts to promote the formation of a dense and complete carbon layer and release water vapor to take away heat. The dense carbon layer can act as a barrier to block the transfer of oxygen and heat to the substrate, delay the diffusion of pyrolysis volatiles and reduce the release of smoke, thereby inhibiting the spread of fire. (2) Gas-phase flame-retardant mechanism. During the combustion process, some acid sources further decompose to form free radical scavengers HPO·and PO·, which can capture H· and OH· in the flame, thereby inhibiting the chain reaction of combustion. The reaction is shown in Fig. 1 .

Yang et al. [28] used commercially available liquid phosphate (CR-741) and diethyl aluminum phosphinate as flame retardants, and prepared modified phenolic foam by blending with phenolic resin. The results show that the effect of diethyl aluminum phosphinate on the flame-retardant performance of phenolic foam is not obvious. CR-741 effectively enhances the flame-retardant properties of phenolic foam. The blending amount of 5 wt% has the best flame-retardant effect. Compared with pure phenolic foam, the peak heat release rate is reduced by 26.5%. The average smoke release rate does not change significantly, but the total smoke release decreases as the amount of CR-741 increases. Huang et al. [29] modified phenolic foam with pentaerythritol phosphate (PEPA). Thermogravimetric analysis shows that the content of PEPA in phenolic foam increases, and its initial decomposition temperature and residual carbon rate increase. This is because PEPA is used as a phosphorus

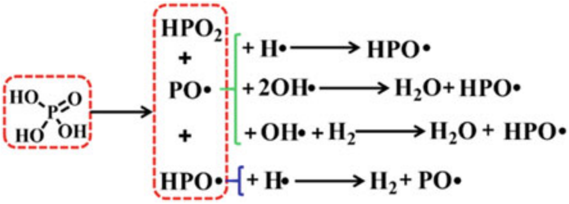

Fig. 1 Phosphorous gas flame-retardant mechanism

flame retardant to produce phosphorus-based oxyacids to catalyze the heat absorption and dehydration of hydroxyl-containing compounds during thermal decomposition of phenolic foam. Thus produces a dense carbon layer rich in polyphosphates, which reduces the heat transferred to the substrate. Therefore, the flame retardancy of phenolic foam increases with the increase of PEPA, and its maximum LOI value exceeds 60%. Yang et al. [30] prepared phosphorus-containing flame-retardant tougheners PPEG400 and PPEG600 by reacting phenyl dichlorophosphate with PEG400 and PEG600, respectively, and used them to modify phenolic foam. Though the incorporation of PPEG reduced the LOI value of phenolic foam, it still remained at 40% when the loading of toughening agents was 10 wt%. UL-94 results showed all samples can pass V0 rating, indicating the modified foams still have great flame retardance. From the microscale combustion calorimeter results, the peak heat release rate and total heat release of sample modified with 10 wt% PPEG600 content were decreased by 42% and 35%, respectively, compared to the pure PF. TGA results showed that the PF composites possessed lower initial decomposition temperature but higher char residues than pure PF, mainly owing to the degradation of PPEG in advance and the catalysis of the carbonization of phenolic foam.

In recent years, reactive phosphorus-containing flame-retardant tougheners have been increasingly used to modify phenolic foam. Bo et al. [31, 32] designed and synthesized cardanol-based phosphorus-containing polyurethane prepolymer (PPUP) and phosphorus-containing cardanol (PCC) to modify phenolic foam. The results show that both PPUP and PCC can effectively improve the flame-retardant properties of phenolic foam. When the content of PPUP is greater than or equal to 3 wt%, the LOI value of modified foam is greater than that of pure phenolic foam and increases with the increase of PPUP content. For PCC-modified phenolic foam, the blending amount is 4 wt%, and the flame-retardant effect is the best. Its total heat release, peak heat release rate, and average heat release rate are reduced by 13.55%, 33.43%, and 13.42%, respectively, compared with pure phenolic foam. Yuan et al. [33] synthesized novel phosphorus-containing polyurethane (DOPU) prepolymer and obtained a series of modified phenolic foams by blending glass fiber and DOPU in various ratios. TGA indicated that adding 3 wt% DOPU and 0.5 wt% glass fiber together, not only increased the thermal stability, but also improved the amount of char residue. In addition, LOI values decreased slightly with increasing content of polyurethane prepolymer, but were still superior to those of conventional foam.

5 Silicon-Containing Flame Retardant Modified Phenolic Foam

Silicon-containing flame retardants can be divided into inorganic silicon type and organic silicon type flame retardants according to their types. They are considered as “completely environmentally friendly” additives because their use can reduce harmful effects on the environment. Inorganic silicon flame retardants mainly include amorphous silicon such as clay, kaolin, montmorillonite, silsesquioxane, and SiO_2, which are used as a protective layer to cover the surface of the polymer during combustion. Wei et al. [34] synthesized montmorillonite modified phenolic resin by in-situ polymerization and blended with carbon fiber to prepare montmorillonite/carbon fiber/phenolic foam composite material. The layered montmorillonite undergoes orientation movement during the foaming and expansion process of the phenolic resin, and finally wraps the montmorillonite layer outside the foam cells after curing. The montmorillonite coating layer can block the contact of oxygen in the air with the foam matrix and the transfer of heat, thereby playing a flame-retardant effect. Zhang et al. [35] silanized nano-SiO_2 formed in phenol solution with tetramethyldisiloxane, and prepared modified phenolic resin and foam by one-pot method. The results show that the phenolic resin forms chemical crosslinks with nano-SiO_2 through Si—O and Si—O—Si bonds. Si–O and Si—O—Si have higher bond energy than C—C bases, so the heat resistance of the modified phenolic foam has been improved. When the content of nano-SiO_2 is 2 g, the carbon residue rate at 800 °C is 20.77% higher than that of pure phenolic foam, and its flame-retardant performance has also been effectively improved, and the LOI value is as high as 53.1%, an increase of 49.16%. Li et al. [36] successfully synthesized silica nanospheres/graphene oxide hybrid (SGO) by fixing silica nanospheres on the surface of graphene oxide and prepared SGO-modified phenolic foam by in-situ polymerization. The LOI of the SGO-toughened PF is higher than that of GO and SiO_2-toughened PFs, indicating some synergistic effect in flame retardancy between GO and SiO_2 nanospheres. The LOI of the SGO-toughened PFs increases gradually with increasing the SGO content. The increase in LOI is probably because the SiO_2 nanospheres covered on the surface of GO sheets can hinder the decomposition of GO sheets, and thus maintain the physical barrier effect of the sheets to the heat and mass transfers at high temperatures. The Cone calorimetric results indicate that the addition of SGO into PF leads to a reduction in peak heat release rate and total heat release. Moreover, the thermal stability of the PFs containing SGO is enhanced compared with the pure PF foam. As the amount of inorganic silicon flame retardant increases, the viscosity of the foaming system increases, and the particles are prone to agglomeration. This makes the foaming process difficult to control and is not conducive to the foaming operation, which often makes the resulting foam mechanical properties and processability is reduced [37].

Silicone-based flame retardants are mainly polysiloxanes, such as silicone oil, silicone resin, and silicone rubber. The Si—O bond of the main chain of polysiloxane decomposes and breaks at high temperature, and the Si—C bond is oxidized, degraded, and condensed. The reaction process is shown in Fig. 2 [38, 39]. Finally, an amorphous SiO_2 with large specific surface area, low density, and low surface energy is formed, which migrates and covers the surface of the carbon layer to form a silicon protective layer. The carbon layer covered with the silicon protective layer not only plays a role of heat insulation to inhibit the transmission of heat and oxygen to protect the unburned part, but also acts as a barrier to prevent thermal degradation products from migrating to the surface. Therefore, the silicone-based flame retardant makes the composite material have excellent flame retardancy and smoke

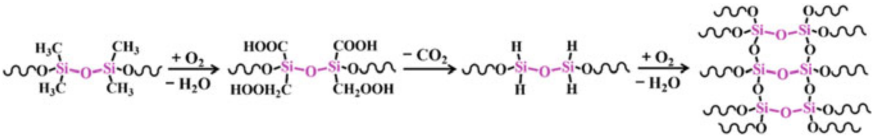

Fig. 2 Polysiloxane flame-retardant mechanism

suppression by forming a denser protective layer, thereby playing an important role in the condensation phase. Bo et al. [40] synthesized reactive cardanol-based siloxane (SAECD) and prepared phenolic foams modified with different contents of SAECD. LOI is increased progressively with the increase in SAECD. The results of the cone calorimeter test showed that the addition of 3 wt% SAECD could effectively reduce the heat release rate and total heat release of the foam by the condensed phase flame-retardant mechanism. The peak heat release rate, the average heat release rate, and the total heat release are reduced by 9.10%, 4.11%, and 7.55%, respectively, compared with pure phenolic foam, and the ignition time is delayed by 19 s.

6 Compound Flame Retardant Modified Phenolic Foam

Phosphorus-based flame retardant, as a carbonization agent, can be combined with nitrogen-containing compounds to construct intumescent flame retardation, consequently leading to outstanding flame retarding performance [27]. In our previous study, a P–N tung oil-based reactive flame retardant (TAPC) has been developed from triethyl phosphite and cyanuric chloride [41]. The addition of TAPC improved the flame-retardant properties of the foam, resulting in an LOI as high as 40.83% (an increase in 27.20% compared with that of pure PF). Additionally, TAPC enhances the thermal stability of the foam, the residual mass of the TAPC-modified foams also increased substantially, by approximately 10%. Recently, combining phosphorus and silicon has received much attention. Early investigations proved that phosphorus and silicon indeed show some synergy effect in flame retarding. The P–Si system has been proved to be of great value due to its inherent high flame-retardant efficiency, good environmental compatibility, and good thermal durability at elevated temperatures [42]. For instance, P-containing tung oil-based siloxane was embedded into the rigid molecular structure of PF, resulting in a superb mechanical, low thermal conductivity, excellent flame retardant, and smoke-suppressant, as shown in Fig. 3 [43]. With the increase of flame-retardant content, the residual char of TAPC-modified PFs gradually become complete, and the microscopic morphology of the char layer becomes denser and smoother, as shown in Fig. 4. Ma reported that they had synthesized a novel 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) grafted γ-glycidoxy propyl trimethoxy silane (GPTS) and introduced on the surface of wood fiber (WF) [44]. DOPO-g-GPTS modified wood fiber (DGMWF) was then used to prepare DGMWF composite phenolic foam (DGMWFCPF). With the increase of

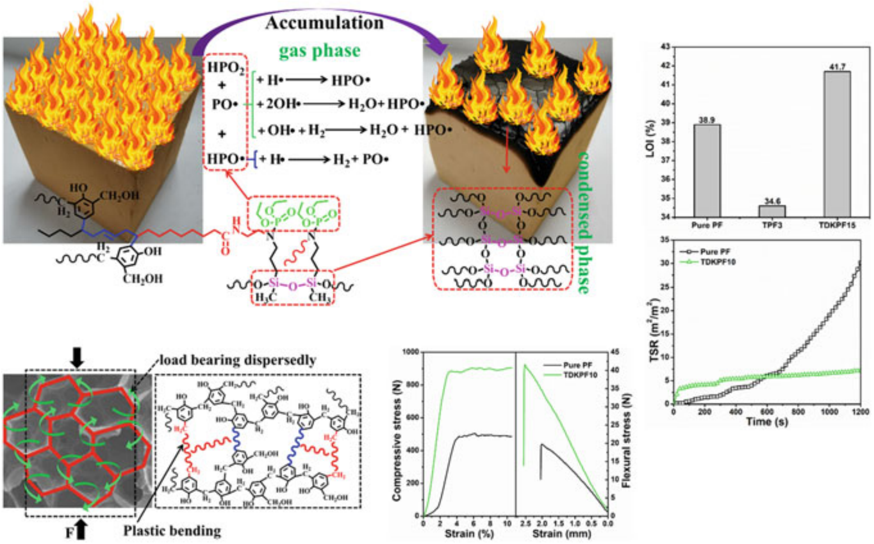

Fig. 3 Illustrative scheme of toughening and flame-retardant mechanism of TAPC-modified PFs [43]

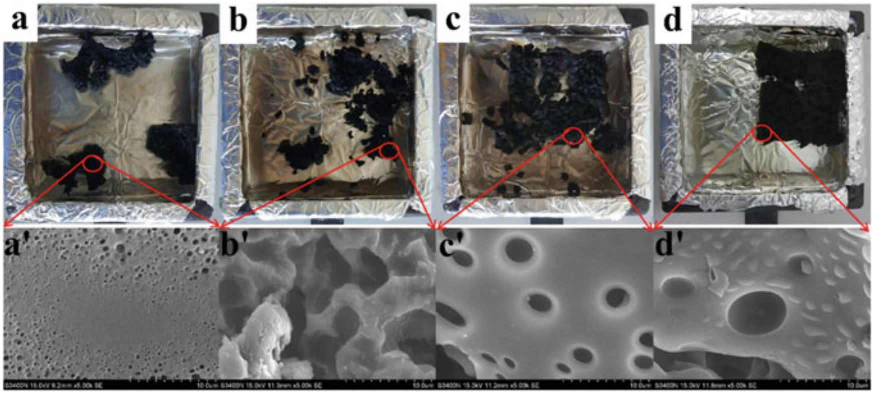

Fig. 4 Photographs and SEM (×5 k) of residue chars of pure PF (a, a'), TDKPF5 (b, b'), TDKPF10 (c, c'), and TDKPF15 (d, d') [43]

DGMWF, there were more and more flame retardants, LOIs of DGMWFCPF were gradually increased.

7 Nano-Materials Modified Phenolic Foam

Nanoparticles have a strong interaction with polymer due to their small size, large surface area, and large interfacial area in the composites. Unlike conventional rigid particles, the infusion of nanoparticles into polymers often can improve the toughness, strength, and heat resistance of the polymer material products, simultaneously. Generally, the phenolic resin nanocomposites are prepared by mixing or blending with surface modified nanoparticles. For instance, Yang reported that using MWCNTs is an effective way for improving the mechanical and thermal properties of brittle phenolic foam [45]. Compared to the neat phenolic foam counterpart, MWCNTs affect the properties of phenolic foam in three ways: providing remarkable stiffening and strengthening effects via cell walls/MWCNTs junctions to achieve macroscale compressive property enhancement, increasing cell density, and decreasing cell size by inducing heterogeneous bubble nucleation, and offering a stabilizing effect to restrain the thermal motion of phenolic chains, and to hinder the flux of volatile degradation products out of cell walls that slow thermal degradation to slightly improve the thermal stability and fire resistance. Wang et al. [46] synthesized a layered double hydroxide/GO (CoAl-LDH/GO) nanohybrid via a hydrothermal method to be added to phenolic resin to prepare phenolic foam Composite materials. The TGA results show that the immobilization of CoAl-LDH nanoparticles on GO surface greatly promotes the thermal stability of GO, thus the CoAl-LDH/GO-modified PF has better flame retardancy compared with the GO-modified foam. The addition of the CoAl-LDH/GO nanohybrid results in an increase in the limiting oxygen index and a decrease in the peak heat release of the modified PF in cone calorimeter test. Moreover, the thermal stability of the PF foam is enhanced by the addition of the nanohybrid. Yuan et al. [47] adopted a new type of cross-linked poly (n-butyl acrylate) (PBA)/silica core–shell nanocomposite particles as toughening agent to improve the mechanical properties of phenolic foams. TGA result indicates that nanocomposite particles lead to a slight increase in the heat resistance of phenolic foams. The LOI result demonstrates that the incorporation of nanocomposite particles will not damage the excellent flame-retardant performance of phenolic foam.

8 Conclusion

With the frequent occurrence of fires in high-rise buildings in recent years, building exterior wall insulation materials with non-combustible, energy-saving, and good thermal insulation are developing rapidly and become a research hotspot of new materials. In this way, flame-retardant modification of traditional organic insulation materials emerges, but it is often necessary to add a large amount of flame retardant to achieve the standard flame-retardant effect. Emerging foam materials (such as polyamide foam, graphene foam, and ceramic foam) have been actively developed, but such materials are expensive and require harsh process conditions. Phenolic foam is cheap, easy to process, and shape, and due to its excellent flame-retardant properties, only a small amount of flame retardant is needed in the subsequent flame-retardant modification. Through the flame-retardant modification of phenolic foam, it has more improvements in functional properties, thus it has excellent mechanical properties and flame-retardant properties to open up a wider range of applications.

References

1. Berardi U (2017) A cross-country comparison of the building energy consumptions and their trends. Resour Conserv Recycl 123:230–241
2. Aditya L, Mahlia TM, Rismanchi B et al (2017) A review on insulation materials for energy conservation in buildings. Renew Sust Eeneg Rev 73:1352–1365
3. Zhou W, Bo C, Jia P et al (2018) Effects of Tung oil-based polyols on the thermal stability, flame retardancy, and mechanical properties of rigid polyurethane foam. Polymers 11:45
4. Sazorozco BD, Alonso MV, Oliet M et al (2015) Lignin particle-and wood flour-reinforced phenolic foams: friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos Part B Eng 80:154–161
5. Guo Y, Hu L, Bo C et al (2018) Mechanical property of lignin-modified phenolic foam enhanced by nano-SiO2 via a novel method. Chem Pap 72:763–767
6. Auad ML, Zhao L, Shen H et al (2007) Flammability properties and mechanical performance of epoxy modified phenolic foams. J Appl Polym Sci 104:1399–1407
7. Deshmukh G, Birwal P, Datir R et al (2017) Thermal insulation materials: a tool for energy conservation. J Food Process Technol 8:670
8. Basso MC, Pizzi A, Al-Marzouki F et al (2016) Horticultural/hydroponics and floral natural foams from tannins. Ind Crop Prod 87:177–181
9. Song F, Jia P, Bo C et al (2020) Preparation and characterization of Tung oil toughened modified phenolic foams with enhanced mechanical properties and smoke suppression. J Renew Mater 8:535–547
10. Gao M, Wu W, Wang Y et al (2016) Phenolic foam modified with dicyandiamide as toughening agent. J Therm Anal Calorim 124:189–195
11. Kumar SA, Kumar S, Nagaraja BK (2020) Thermal stability and flammability characteristics of phenolic syntactic foam core sandwich composites. J Sandw Struct Mater. https://doi.org/10.1177/1099636220926661
12. Wang YZ, Li FM, Kishimoto K et al (2010) Wave localization in randomly disordered layered three-component phononic crystals with thermal effects. Arch Appl Mech 80:629–640
13. Wang YZ, Li FM, Huang WH et al (2008) The propagation and localization of Rayleigh waves in disordered piezoelectric phononic crystals. J Mech Phys Solids 56:1578–1590
14. Yuan H, Xing W, Yang H et al (2013) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 62:273–279
15. Hu L, Wang Z, Zhao Q et al (2017) Flame retardant and mechanical properties of toughened phenolic foams containing a melamine phosphate borate. Polym-Plast Technol 56:678–686
16. Li Q, Chen L, Li X et al (2016) Effect of nano-titanium nitride on thermal insulating and flame-retardant performances of phenolic foam. J Appl Polym Sci 133:43765
17. Song F, Jia P, Bo Cet al (2020) The mechanical and flame retardant characteristics of lignin-based phenolic foams reinforced with MWCNTs by in-situ polymerization. J Disper Sci Technol 1–10
18. Zhang T, Liu W, Wang M et al (2017) Synthesis of a boron/nitrogen-containing compound based on triazine and boronic acid and its flame retardant effect on epoxy resin. High Perform Polym 29:513–523

19. Chen S, Ai L, Zhang T et al (2020) Synthesis and application of a triazine derivative containing boron as flame retardant in epoxy resins. Arab J Chem 13:2982–2994
20. Wang B, Li H, Zhang Yet al (2013) Preparation and properties of Boron-modified phenolic foams composites. Materials China 641–645
21. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54:1962–1970
22. Suzanne M, Delichatsios MA, Zhang J (2014) Flame extinction properties of solids obtained from limiting oxygen index tests. Combust Flame 161:288–294
23. Lv J, Liang J, Liang B (2016) Research progress on synthesis of halogen-free phosphorus nitrogen flame retardant. New Chem Mater 44:12–14
24. Fang Y, Miao J, Yang X, Zhu Y, Wang G (2019) Fabrication of polyphosphazene covalent triazine polymer with excellent flame retardancy and smoke suppression for epoxy resin. Chem Eng J 385:123830
25. Ge T, Tan X, Liu H et al (2015) Research of phenolic resin and foam modified by Melamine. J Shenyang Inst Chem Technol 29:134–139
26. Wang Z, Xu S, Hu L et al (2014) Preparation and characterization of nano melamine cyanurate and its application in phenolic foam. Chinese J Mater Res 28:401–406
27. Huang Y, Song ML, Ma JJ et al (2013) Synthesis of a phosphorus/silicon hybrid and its synergistic effect with melamine polyphosphates on flame retardant polypropylene system. J Appl Polym Sci 129:316–323
28. Yang M, Jiang H, Zhao X et al (2018) The preparation and properties of green phenolic foam plastics. Synth Mater Aging Appl 47:11–17
29. Huang P, Wu M, Zhang P et al (2016) Properties of phenolic foam modified by pentaerythritol phosphate/urea. J Wuhan Inst Technol 38:120–124
30. Yang H, Wang X, Yuan H et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 19:9831
31. Bo C, Wei S, Hu L et al (2016) Synthesis of a cardanol-based phosphorus-containing polyurethane prepolymer and its application in phenolic foams. Rsc Adv 6:62999–63005
32. Bo C, Hu L, Chen Y et al (2018) Synthesis of a novel cardanol-based compound and environmentally sustainable production of phenolic foam. J Mater Sci 53:10784–10797
33. Yuan H, Xing W, Yang H et al (2012) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 62:273–279
34. Wei D, Li Y, Li W et al (2011) Study on phenolic resin/montmorillonite nanocomposites and its foams. New Chem Mater 39:131–134
35. Zhang N, Hu L, Guo Y et al (2019) Characterization of phenolic foam modified by silanized Nano-SiO_2. Chem Indus Prod 39:53–60
36. Li X, Wang Z, Wu L (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. RSC Adv 5:99907–99913
37. Zhang N, Hu L, Guo Yet al (2019) Mechanical property of lignin-modified phenolic foam enhanced by whisker silicon. J Disper Sci Technol: 1–7
38. Camino G, Lazzari M (2001) Polydimethylsiloxane thermal degradation part 1. Kinetic aspects. Polym: Int J Sci Technol Polym 42:2395–2402
39. Lageard M, Lomakin S M, Camino G (2002) Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms. Polym: Int J Sci Technol Polym 43:2011–2015
40. Bo C, Yang X, Hu L et al (2019) Enhancement of flame-retardant and mechanical performance of phenolic foam with the incorporation of cardanol-based siloxane. Polm Composite 40:2539–2547
41. Song F, Jia P, Xiao Y et al (2019) Study on toughening phenolic foams in phosphorus-containing Tung oil-based derivatives. J Renew Mater 7:1011–1021
42. Tang Z, Li Y, Zhang YJ et al (2012) Oligomeric siloxane containing triphenylphosphonium phosphate as a novel flame retardant for polycarbonate. Polym Degrad Stab 97:638–644
43. Song F, Li Z, Jia P, Bo C, Zhou Y (2020) Phosphorus-containing tung oil-based siloxane toughened phenolic foam with good mechanical properties, fire performance and low thermal conductivity. Mater Design 192:108668

44. Ma Y, Geng X, Zhang X et al (2019) Synthesis of DOPO-g-GPTS modified wood fiber and its effects on the properties of composite phenolic foams. J Appl Polym Sci 136:46917
45. Yang Z, Yuan L, Gu Y et al (2013) Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes. J Appl Polym Sci 130:1479–1488
46. Wang Z, Li X (2018) Synthesis of CoAl-layered double hydroxide/graphene oxide nanohybrid and its reinforcing effect in phenolic foams. High Perform Polym 30:688–698
47. Yuan J, Zhang Y, Wang Z (2015) Phenolic foams toughened with crosslinked poly(n-butyl acrylate)/silica core-shell nanocomposite particles. J Appl Polym Sci 132:42590

Chapter 12
Modification in Phenolic Foams and Properties of Clay Reinforced PF

Grace Moni and Simone A. Silva

1 Introduction

Synthetic foams were of great interest in the recent years and among them the one with polymer matrix modified foams become a known class because of its ability to produce products with tailored properties with light weight characteristics [1]. Thermoset nanocomposite foams come under the polymer matrix synthetic foams and only fewer studies were reported in the case of the same. It includes polyurethanes, polyisocyanurate, polyamides, epoxy resins, polyesters, and phenolic resins [2]. Phenolic resins are the major one among the resin systems with impressive performance till date [3].

Phenolic foams (PF) were formulated in different means by the addition of fibers, nanoparticles, clay, and even by the modifications of the chemical constituents of the polymeric structure to improve the properties without compromise [4]. This chapter reviews the properties of the PF, the modification approaches adopted so far to improve the properties of phenolic foams, and the research carried out so far in the field of clay reinforced PF to modify the properties of the foams.

2 Properties of Phenolic Foams

Phenolic foams have an extraordinary property compared to other commonly used synthetic foams. It is the excellent fire resistance property with much less environmental impacts which make it unique in the current scenario. That is the high flame

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retardancy and the less generation of toxic gases during ignition make it superior. Other properties of the foam include its low thermal conductivity and high thermal stability compared to other counterparts. But there is some drawback such as the high friability which arises due to the brittle nature and the decreased mechanical performance due to the low compressibility and flexural properties [5]. In spite of the drawbacks the PF, their outstanding fire resistance and environmentally benign nature along with the cost effectiveness make them efficient in applications which demand fire resistant property. Research is going on in the fields of PF with different additive alternatives to make it more appropriate for such applications by improving the drawbacks and make them more fruitful. The major approaches consist in chemical modification, and addition of filler, more over some works are also carried out by using clay as the reinforcing agent and are reviewed below.

3 Modifications of Phenolic Foams

3.1 Chemical Modification

Chemical modifications play in order to improve the ability to deform the cell wall without breaking it by introducing flexible chains in the rigid backbone of the phenolic resin, consequently decreasing the crosslink density and increasing strength of the phenolic foams.

The phenolic foam (PF) arrangement is carried out by competition between two mechanisms: expansion and cure may simultaneously occur. Thus, the reactivity and viscosity are significant variables for the polymerization of PF [4]. The low viscosity should allow the injected PF formation in industrial pumps avoiding problems, as obstruction by accelerated curing process in the mixing, and, the high viscosity may control the cell growth and the coalescence, causing structural characteristics such as the wall thickness, size of the cells or macro defects. Moreover, higher viscosity may restrain the foam expansion and leads to higher density than expected [6–8].

The chemical modification with the active groups such as hydroxy [9], amino, epoxy [10], isocyanate [11] in the polymerization procedure [12] may lead to major diversity of effects in the final mechanical properties of the polymer. Chemical modification of phenolic resins by polyurethane, glycols, or bio resources, as vanillin [13], vegetable oils, castor oil [14], and lignin [15] is often employed to increase the compressive and flexural strength and decrease the friability, these pendants branches may play as a surfactant or modify the resin viscosity [16].

Moreover, the type of components in the phenolic resin, another factor must be considered is the influence of the formulation variables, such as ratio between monomers, and additives (plasticizers, flame retardants, fillers), stirring speed shift on the mechanical properties and density of the final foam [4, 16].

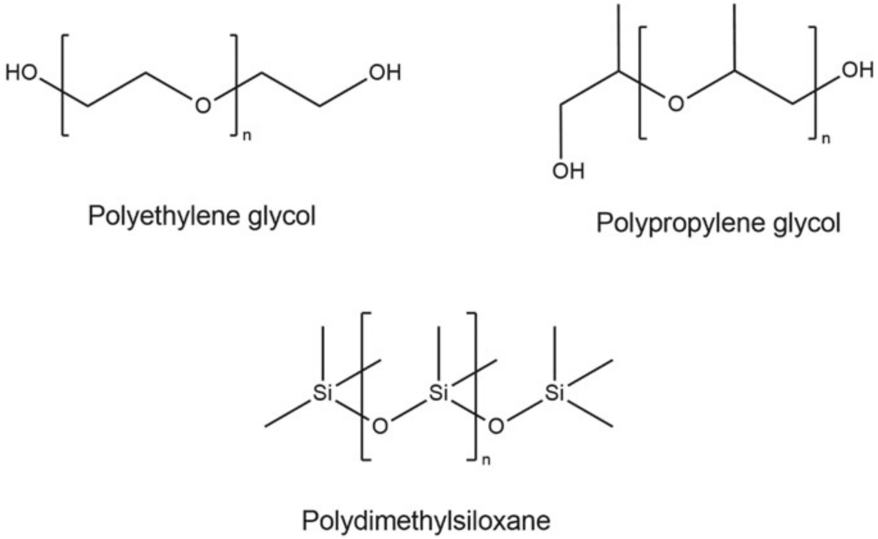

Fig. 1 Structures of the mostly used plasticizers

3.1.1 Plasticizers

Plasticizer is a material that improves the flexibility or assisting in processing of the polymer. It can be a liquid, solid, or a polymer of low molar mass, natural or synthetic source. Usually, the plasticizer must have a certain solvency degree in the host polymeric matrix to check over the plasticizer effect, where the continuous addition results in a progressive decreasing glass transition, in other words, greater flexibility and friability, being that, oligoethers, for example, polyethylene glycol, are the most employed plasticizer for phenolic foams [11, 17–20], as well as, silicones, as polydimethylsiloxane may be used (Fig. 1). Moreover single or blend plasticizer can be used for polymerization [21].

3.1.2 Flame Retardants

Although the inherent polyphenolic foams high heat resistance, some applications and environmental restrictions demand the addition of flame retardants. Flame retardants are substances employed to slow down the spread of the flame after the combustion process has started, or they are used to delay the initial moment of combustion of the material, increasing the time that pyrolysis takes to start. According to their nature, flame retardants can have chemical or physical action and act in a solid, liquid, or gaseous state, these substances are introduced, which content halogen atoms or phosphorus into formulation [22].

Table 1 Bond energies for Carbon-Halogens linkages [23]

Bond	Bond energy (KJ .mol^{-1})	Temperature (initial degradation in °C)
C_{aliph}–F	443-450	>500
C_{arom}–Cl	419	>500
C_{aliph}–Cl	339-352	370–380
$C_{benzilic}$–Br	214	150
C_{aliph}–Br	285-293	290
C_{arom}–Br	335	360
C_{aliph}–I	222-235	180
C_{aliph}–C_{aliph}	330-370	400
C_{aliph}–H	**390-436**	**>500**

Chemical Flame Retardants

Usually, commercial fire-retardant systems available are based on halogen-containing compounds, where its mechanism of action occurs by breaking of the carbon–halogen bond, the order of stability of these compounds is showed in Table 1 [23].

Comparing the thermal stability of these compounds in Table 1, it can be observed which iodine compounds have low stability required to stand polymer processing, the other hand, fluorine compounds are a lot stable to be useful, despite that some fluorine compounds can be used as a component in a synergistic mixture. Brominated compounds have been broadly used for several years due low cost, high performance against flame spread, good compatibility with miscellaneous polymeric matrices. However, these halogen flame retardants do not absorb the heat accordingly, the pyrolysis is triggered, releasing toxic gases and soot into the environment [24–27].

One alternative to replace halogens-containing flame retardants is phosphorus-based flame retardants, include red phosphorus, inorganic phosphates, organophosphorus compounds, and chlorophosphorus compounds. They can be employed alone, or in synergic combinations with others nitrogen, halogen-content retardants and/or inorganic nanofillers (carbon nanotubes, phyllosilicates). Phosphorus-based retardants exhibit high performance but produce rise quantities of smoke, soot, and low to moderate toxic vapors according to Lethal Dose-LD-values [22].

Physical Flame Retardants

Flame retardants of physical action are products based on magnesium, aluminum hydroxide (trihydrate alumina). Also, some boron and phosphorus compounds have been operating absorbed huge heat quantities of the ambient, avoiding the formation

Table 2 Cells size of modified phenolic foams [31, 32]

Reference	Density (Kg .m^{-3})	Phenolic foam type	< D_{cell} > [μm]
Bo et al. [10]	38	PF	100
		PF + 3% PU prepolymer	173
		PF + 7% PU prepolymer	129
Liu et al. [13]	25	PF	386
		PF + 4.5 wt% PEG 200	642
		PF + 4.5 wt% PEG 400	450
		PF + 4.5 wt% PEG 600	450

of toxic and inflammable gases along combustion, thus, prevent the pyrolysis process of the material [26, 27].

3.1.3 Ratio Between Components

In the chemical modification of phenolic resins by PU or PEG is often used to increase the compressive and flexural strength and decrease the friability, because one or more components can play as surfactant or modifier viscosity. Therefore, ratio among contents of a PF formulation is directly associated with the size, shape, uniformity of distribution cells in the polymeric matrix showing dependence on increase or decreasing compressive properties. According to the literature, the variation of the PU prepolymer into PF showed cell size increase up, similar results were obtained with different molar mass PEG, leads to improvement of the compressive strength, flexural strength, and friability properties, as listed in Table 2 [28–30].

Another way to modifier phenolic foams is to introduce renewable resources, in order to decrease the consumption and dependence of the petroleum products. Several researches aim the total or partial substitution of phenol by bio-oils from renewable biomass, with comparable properties to the conventional fossil raw materials [33, 34].

Lignin Materials

Lignin is one of the main components in lignocellulosic biomass can be a potential substitute to phenol, due to the amorphous polyphenol material, in which the three-dimensional structure is based on three monomeric precursors: coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol (Fig. 2) [35].

Bio-based phenol formaldehyde foams can be prepared by depolymerized hydrolysis, lignin can be obtained via depolymerization process by raw kraft lignin, organosolv lignin, total or partially replacing phenol [21, 33, 36]. Although to manipulate lignocelluloses materials, it is a challenger, because they require severe conditions, as high temperature or pressure and solvent, which limit the large-scale application.

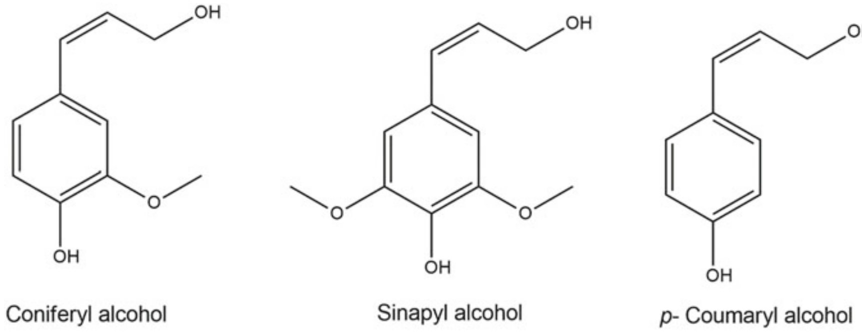

Fig. 2 Lignin precursors structure

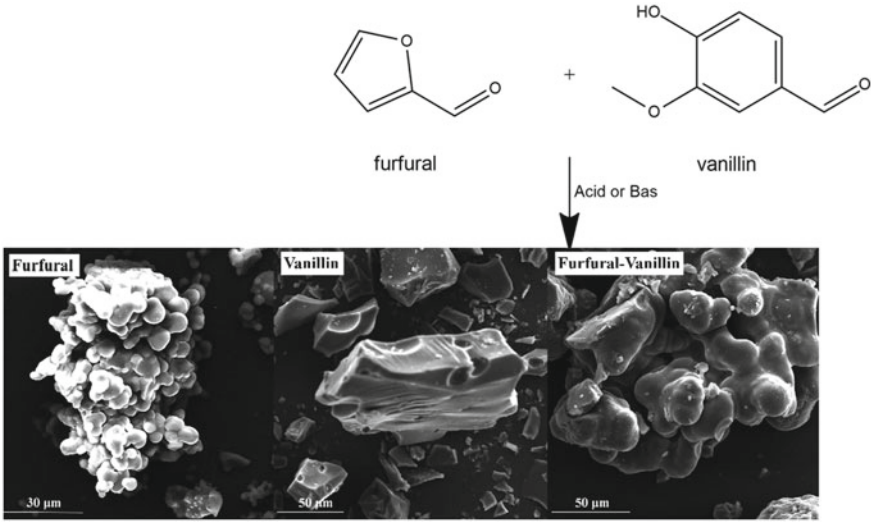

Fig. 3 Representation of the furfural-vanillin cross-polymerization [37]

Others; Biomass, Vegetable Oils

Others biomass, such as vanillin and furfural, can be employed to synthesize phenolic foams or resin by cross-polymerization carried out in acid or basic catalysis (Fig. 3) [37].

Furan ring react by electrophilic substitution reaction, while the aldehyde group reacts by aldol condensation reactions, where in the opening of the furan rings can yield some even more reactive sites into polymerization [13].

Another biomaterial, cardanol, is a byproduct of the cashew processing industry, show unique phenolic compound carrying a 15-carbon side chain in the meta-position exhibit different degrees of unsaturation (monoene, diene, and triene). Cardanol can react with formaldehyde under basic conditions to form foaming resol resin. The partial replacement of phenol by cardanol to obtain phenolic foam may help to improve the mechanical properties with the modification of the side chain such as epoxidation [38].

3.2 Addition of Fillers

The shortcomings of PF alone include less compressive resistance and decreased foam friability. Fillers are the one additive that can help to improve the mechanical properties, friability, and at the same time they help to decrease the final cost of the PF material. Many types of filler materials of natural origin such as cellulose, lignin, or wood floor particles, even though they decrease the thermal stability above 300 °C and the fire resistance characteristics. Also, fillers of organic and inorganic origin such as clay [39], glass fibers [40], aramid fibers [41], multiwall carbon nanotubes (MWCNT) [42] were reinforced with PF to obtain the desired properties with varied final cost. Natural fillers like lignin or wood floor particles [43], cellulose [44] were also used as the filler material even though they had a tendency to decrease the thermal stability above 300 °C and the fire retardancy of the resultant PF. In addition to this all the factors such as the filler nature, geometry, and amount also impact the foam expansion significantly.

3.3 Density

Another important factor to be considered is the density of the foams that reflect on the mechanical behavior, as on compressive modulus and strength of phenolic foams [45, 46].

4 Phenolic Foams with Clay Reinforcement

Clays are of different types and in the case of PF, montmorillonite, Closite, Mineral clay, Kaolin, and Nanoclay are incorporated into the matrix and they were studied in detail by considering the different aspects. Thus the effects of these different clay materials on phenolic foams were discussed in detail in different sessions below which constitute the essence of the chapter.

4.1 Montmorillonite Reinforced Phenolic Foams

Montmorillonite (MMT), one of the natural sources that are reinforced with PF is found to have improved fire resistance, thermal stability, and compressibility properties. These studies were carried out by Wei et al. [47] and Xu et al. [48] in detail to get a clear insight of the reinforcement effects.

Wei et al. [47] modified the PF with montmorillonite/carbon fibers and they studied the mechanical properties and analyzed the morphological aspects too to support the results. The thickness of the MMT was about 20–40 nm and is oriented in a particular manner in the PF matrix such that the bubbles are surrounded by MMT layers. The dispersed layers improved the compressive strength by 35–40% and antiflaming properties of the composites as a whole. With further increase in the MMT content above 7% agglomeration is resulted. By the addition of carbon fibers which have mechanical and thermal stability of its own, contributed to the flexural strength of the resultant composites and is increased by 58%. Thus the addition of MMT/Carbon fiber contributed to the improved stabilities of the PF.

Xu et al. [48] aimed to improve the toughness of PF by adding Bio-oil and to improve the flame resistance by incorporating with the MMT into the above ingredients. They have analyzed the mechanical, thermal, morphological, and flame resistance properties in order to assess its viability. In this work the incorporation of MMT into Bio-Oil/PF improved the interaction between the two by hydrogen bonding without altering its basic structure. The SEM micrograph reveals the uniform cell size and distribution of the bubbles. Foam with 2% and 4% MMT content showed better compressive strength and lower pulverization ratio. They also showed better flame resistance as revealed by LOI (Limiting Oxygen Index) analysis and improved thermal stability by TGA analysis.

Closite 10A clay nanoparticle which is the chemically modified MMT infused PF was prepared and analyzed by Rangari et al. by giving a detailed account of the morphological, mechanical, and thermal aspects [39]. The introduction of the clay nanoparticle increased the crosslinking between PF and clay particle as clear from the increase in Tg from DSC analysis and TGA studies. An increase in mechanical properties such as compressive strength and compressive modulus by 60 and 80%, respectively, was observed due to the even distribution of the clay nanoparticle in the PF matrix and uniform cell size as clear from the SEM analysis.

Thus the incorporation of MMT is meant to be a promising additive for PF to improve the flame resistance, thermal, and mechanical aspects of the resulting system as a whole.

4.2 Nanoclay, Mineral Clay, and Kaolin Reinforced Phenolic Foams

PF was also reinforced with nanoclay, kaolin powder, and mineral clay, and the different aspects with respect to flame retardancy, mechanical characteristics, and thermal stability were analyzed in detail. Hu et al. [49] studied the effect of addition of nanoclay/glass fiber combinations into the PF resins. They analyzed the flame retardancy, thermal stability, and toughness of the synthesized materials. Incorporation of glass fiber improved the impact strength and helped to decrease the brittleness and pulverization effect on the PF. On the other hand the introduction of nanoclay helped to improve the toughness and compressive strength. The compressive strength first increased and showed a maximum for 3% of nanoclay infusion and then decreased considerably with further decrease in nanoclay content. The cell size is also controlled by the nanoclay addition, a particular amount of clay helped to improve the cell size and further increase in nanoclay content increased the thickness of the cell wall and percentage of open cells as clear from the SEM analysis. The flame retardancy and thermal stability of the synthesized PF are also improved by the addition of glass fiber/nanoclay. The optimal ratio of glass fiber/nanoclay which showed the improved performance was found to be 5%:3%.

In another work kaolin powder (a type of clay) and a mixture of kaolin powder/glass fiber fabric were incorporated with the phenolic resin and PF are synthesized by Xiao et al. [50]. The synthesized PF was tested to analyze the mechanical and thermal stabilities as well. PF with kaolin alone showed evenly distributed small cells which supports the presence of thicker wall ribs that leads to the enhanced mechanical properties. If excess powder was added agglomeration seems to be prominent. With the addition of glass fiber fabrics to the kaolin powder, the thermal stability was increased prominently and the mechanical properties were also improved to a certain extent. The PF is subjected to high temperatures and even though the pore structure was not affected which endures the applicability of the resin even in harsh environments.

5 Conclusion

Phenolic foams are of great importance when we consider them in the aspect of fire retardancy and their environmental friendly nature while processing. The modifications made on the PF, such as chemical modifications, addition of fillers, and density, also helped to increase its material properties to a greater extend. Only fewer reports were available in the field of clay reinforced PF. Even though the clay reinforcement supports the enhancement of the PF material properties as a whole in terms of flame retardancy, thermal stability, mechanical characteristics, pore structure, etc.

References

1. Lee LJ, Zeng C, Cao X et al (2005) Polymer nanocomposite foams. Compos Sci Technol 65:2344–2363
2. Afolabia LO, Ariff ZM, Hashim SFS et al (2020) Syntactic foams formulations, production techniques, and industry applications: a review. J Mater Res Technol 9:10698–10718
3. Pilato L (2013) Phenolic resins: 100 Years and still going strong. React Funct Polym 73:270–277
4. Mougel C, Garnier T, Cassagnau P (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer 164:86–117
5. Mougel C, Garnier T, Sintes-Zydowicz N et al (2019) Density effect on morphological, mechanical and friability properties of phenolic foams. J Mater Sci Eng Adv Technol 19:43–78
6. Pilato L (2010) Phenolic Resins: A Century of Progress. Springer, Berlin Heidelberg, p 545
7. Jing S, Li T, Li X et al (2014) Phenolic foams modified by cardanol through bis-phenol modification. J Appl Polym Sci 131(4):39942/1–39942/7
8. C Yang ZH, Zhuang ZG, Yang (2014) Pulverized polyurethane foam particles reinforced rigid polyurethane foam and phenolic foam. J Appl Polym Sci 131(1)
9. Manuela TN, Cornelia V (2013) Influence of the nanoparticle type on the thermal decomposition of the green starch/poly(vinyl alcohol)/montmorillonite nanocomposites. J Therm Anal Calorim 111(3):1903–1919
10. Urszula S, Bogumiła K, Sławomira P, Sylwia C (2015) Preparation and characterization of carbon foams derived from cyanate esters and cyanate/epoxy copolymers. J Therm Anal Calorim 122(1):271–279
11. Yang H, Wang X, Yu B et al (2013) A novel polyurethane prepolymer as toughening agent: preparation characterization, and its influence on mechanical and flameretardant properties of phenolic foam. J Appl Polym Sci 129:2720–2728
12. Gao M, Wu W, Wang Y et al (2016) Phenolic foam modified with dicyandiamide as toughening agent. Therm Anal Calorim 124:189–195
13. Xu Q, Hu X, Zhang L et al (2020) Crosspolymerization between the model furans and phenolics in bio-oil with acid or alkaline catalysts. Green Energy & Environment (pre-proof)
14. Bo C, Hu L, Zhou J et al (2015) Preparation and characterization of phenolic foams modified by castor oil-based polyurethane prepolymer. Linchan Huaxue Yu Gongye 35(4):8–14
15. Del Saz-Orozco B, Oliet M, Alonso MV et al (2012) Formulation optimization of unreinforced and lignin nanoparticle-reinforced phenolic foams using an analysis of variance approach. Compos Sci Technol 72:667–674
16. Yang H, Wang X, Yuan H et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 19(3):9831
17. Rudin A, Choi P (2013) The elements of polymer science and engineering, 3rd edn. Elsevier Inc., New York, p 584
18. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54(7):1962–1970
19. Sui X, Wang Z (2013) Flame-retardant and mechanical properties of phenolic foams toughened with polyethylene glycol phosphates. Polym Adv Technol 24(6):593–599
20. Dvorko IM, Mokhov MV (2012) Plastic foams based on novolac phenol-formaldehyde composites modified with oligoethers. Int Polym Sci Technol 39(11):T39–T42
21. Zhang N, Li Z, Xiao Y et al (2020) Lignin-based phenolic resin modified with whisker silicon and its application. J Bioresources Bioprod 5:67–77
22. Wilkie CA, Morgan AB (2010) In fire retardancy of polymeric materials: 2nd edn. CRC Press, Boca Raton, FL, USA pp 15–42
23. Van Krevelen DW (1978) Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions, Elsevier, New York, 1997; Mita, I., Aspects of Degradation and Stabilisation of Polymers, Jellinek, H.H.G., Ed., Elsevier, New York, 1978, 247–294

24. Alaee M, Arias P, Sjodin A, Bergman A (2003) An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environ Int 29:683–689
25. Pieronia MC, Leonel J, Fillmann G (2017) Retardantes de chama bromados: Uma revisão. Quim Nova 40(3):317–326
26. Marques VD, Ribes DD, Canil VM, Gatto DA (2018) Retardantes de chama comerciais em quatro variedades de eucalipto. Revista Matéria 23(3):1–9
27. Paula MO, Moreira GR, Segundinho PGA (2014) Análise termomecânica da madeira de Corymbia citriodora submetida a gradientes térmicos. Floresta e Ambiente 21(3):358–368
28. Pickering SU (1907) CXCVI. Emulsions. J Chem Soc Trans 91(0):2001–2021
29. Aveyard R, Binks BP, Clint JH (2003) Emulsions stabilised solely by colloidal particles. Adv Colloid Interface Sci 100–102:503–546
30. Zhou JT, Yao ZJ, Chen YX et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym Compos 35(3):581–586
31. Bo C-y, Hu L-h, Zhou J, Zhou Y-h (2015) Preparation and characterization of phenolic foams modified by castor oil-based polyurethane prepolymer. Linchan Huaxue Yu Gongye 35:8–14
32. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54:1962–1970
33. Li B, Wang Y, Mahmood N et al (2017) Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin. Ind Crops Prod 97:409–416
34. Yu Y, Wang Y, Xu P, Chang J (2018) Preparation and characterization of phenolic foam modified with bio-oil. Materials 11:2228
35. Dence CW, Lin SY (1992) Methods in lignin chemistry. Springer Verlag, Berlin, p 608
36. Lia B, Yuana Z, Schmidt J, Xua C (2019) New foaming formulations for production of bio-phenol formaldehyde foams using raw kraft lignin. Eur Polymer J 111:1–10
37. Xu Q, Hu X, Zhang L et al (2020) Cross polymerization between the model furans and phenolics in bio-oil with acid or alkaline catalysts, Green Energy & Environment
38. Liang B, Li X, Hu L et al (2016) Foaming resol resin modified with polyhydroxylated cardanol and its application to phenolic foams. Ind Crops Prod 80:194–196
39. Rangari VK, Hassan TA, Zhou YH et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 103:308–314
40. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Compos A 34A(9):899–906
41. Yu H, Wang L, Gai G (2012) Performance of modified aramid fiber reinforced phenolic foam. Adv Mater Res 557–559:258–261
42. Eslami Z, Yazdani F, Mirzapour MA (2015) Thermal and mechanical properties of phenolic-based composites reinforced by carbon fibres and multiwall carbon nanotubes. Compos. Appl Sci Manuf 72:22–31
43. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Lignin particle- and wood flour-reinforced phenolic foams: friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos B Eng 80:154–161
44. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Compos B Eng 75:367–372
45. Mougel C, Garnier T, Sintes-Zydowicz N, Cassagnau P (2019) Density effect on morphological, mechanical and friability properties of phenolic foams. J Mater Sci Eng Adv Technol 19(2):43–78
46. Del Saz-Orozco B, Alonso VM, Oliet M et al (2014) Composites: Part B 56:546–552
47. Wei D, Li D, Zhang L et al (2012) Study on phenolic resin foam modified by montmorillonite and carbon fibers. Procedia Eng 27:374–383
48. Xu P, Yu Y, Chang M, Chang J (2019) Preparation and characterization of bio-oil phenolic foam reinforced with montmorillonite. Polymers 11:1471. https://doi.org/10.3390/polym11091471

49. Hu X, Cheng W, Nie W, Wang D (2016) Flame retardant, thermal, and mechanical properties of glass fiber/nanoclay reinforced phenol–urea–formaldehyde foam. Polym Compos 37(8):2323–2332
50. Xiao W, Huang Z, Ding J (2017) The mechanical and thermal characteristics of phenolic foam reinforced with kaolin powder and glass fiber fabric. IOP Conf Ser: Mater Sci Eng 274:012013. doi: https://doi.org/10.1088/1757-899X/274/1/012013

Chapter 13
Graphene Reinforced Phenolic Foams

Michał Strankowski

1 Introduction

Polymer nanocomposites are a very versatile group of materials extensively widening the scope of possible polymeric composite usage. Phenolic foams belong to a group of materials showing relatively high fire resistance, thermal stability in a wide, temperature range and are characterized by a relatively low production of toxic gases during combustion [1].

To improve the thermal and mechanical properties of the phenolic foam (which limit its potential application), the proper modification of graphene is a key to obtain nanocomposites with phenolic foam matrix and extended possible foams application field [2].

During the past 10 years, very often used for modifications of polymeric materials is not pure graphene, but its derivatives (Graphene Oxide, Reduced Graphene Oxide, Chemically Modified Graphene Oxide) were used, which enabled good interaction with the wide range of polymer matrices [3–7].

2 Graphene Derivatives in Phenolic Foam Modification

An interesting study was performed by Xia Luo et al. [8] where the authors describe graphene nanoparticles (GNPs) and graphene oxide (GO) and the effect of surface free energy (SFE) induced by the aforementioned fillers on the cellular structure and mechanical properties of phenolic nanocomposite foams.

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An introduction of graphene nanofillers (GNPs and GO) determines crucial interfacial parameters between fillers and the matrix. Optimal addition for the GO nanofiller into phenolic foam was established at 0.6 wt% graphene oxide, where good mechanical properties and cell microstructure were obtained (Fig. 1) [8]. This improvement of the mechanical properties in phenolic foams proves that graphene derivatives can be very effective as a nanofiller.

In past years, very interesting studies focused on graphene hybrid materials where, apart from graphene, additional modifiers were used, thanks to which it is.

Now possible to obtain a synergic effect of graphene derivatives in hybrid compounds. An interesting research has been investigated by Li X et al. [1], where authors have studied α-zirconium phosphate/graphene oxide hybrid (ZGO) with α-zirconium phosphate (α-ZrP) nanoparticles immobilized on the surface of graphene oxide (GO) sheets. The ZGO was incorporated into phenolic (PF) foams reducing their high brittleness and friability. The authors reported that the addition of ZGO at 4 phr improves the flexural (34%) and compressive strengths (40%) of the ZGO-toughened PF foams (Fig. 2) [1].

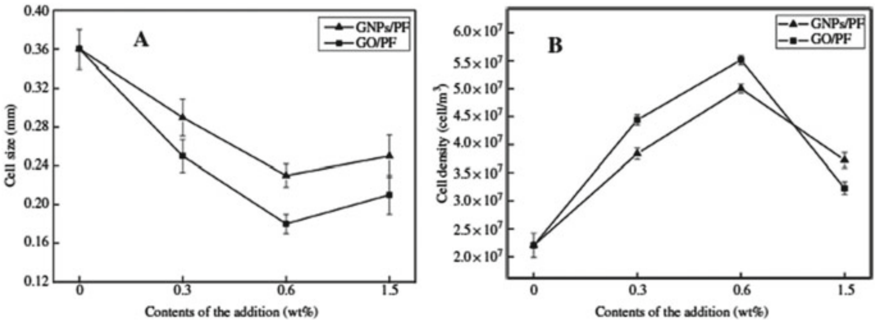
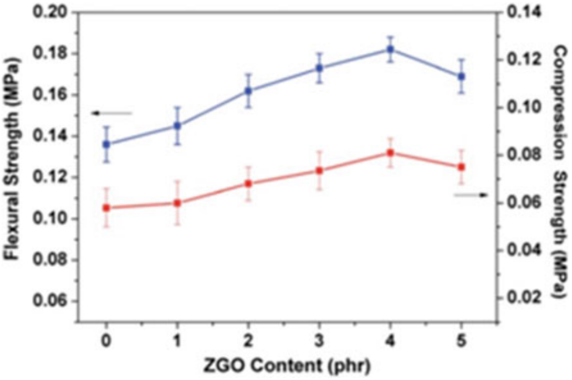


Fig. 1 Phenolic foams with addition (GNP or GO) nanofiller: **a** cell size distribution, **b** compressive strength properties [8]

Fig. 2 ZrP/GO content on flexural and compressive strengths of PF foams with ZrP/GO modifier [1]



The authors reported that the flame retardancy of the toughened PF foams increase (from 38% LOI for pure PF to 42% LOI for 4 phr ZGO addition into PF matrix) and the thermal stability of these materials is also improved (from T5%(mass loss) = 163 °C for pure PF to T5%(mass loss) = 204 °C for 4 phr ZGO nanomodifier in PF). These improved materials can be applied as, for example, thermal insulating materials [1].

Li X et al. [9] also investigated materials based on phenolic foams modified by graphene-based hybrid nanoparticles (SGO) consisting of GO sheets and SiO2 nanospheres. In their study, the incorporation of 1.5 phr SGO into PF foam leads to a 32% increase in the flexural, a 36% increase in compressive strength (Fig. 3). Moreover, it has been proven that the addition of SGO nanomodifier improves the flame retardancy of nanocomposite PF foams (from 38% LOI for pure PF to 41% LOI for 2 phr SGO addition into PF matrix) and thermal stability of the PF foams (from T5%(mass loss) = 163 °C for pure PF to T5%(mass loss) = 199 °C for 2 phr SGO nano- modifier in PF) [9].

The continuation of research related to nanocomposite phenolic foams modified with graphene oxide (GO) modified with layered double hydroxide (CoAl-LDH/GO) was presented by Li X et al. [10]. The most impact on the technical properties of the introduced nanofiller was observed for 0.9 phr in PF matrix. The compressive strength of nanohybrid material 0.9 CoAl-LDH/GO/PF (79 kPa) increases by 55% in comparison to the pure PF foam (51 kPa) (Fig. 4). Moreover, the flexural strengths of nanohybrid material 0.9 CoAl-LDH/GO/PF (173 kPa) increase by 35% in relation to the pure PF (128 kPa) (Fig. 4) [10].

The fractured surfaces of PF foams nanocomposites were described by scanning electron microscopy (SEM). In Fig. 5, the material design as 0.9 CoAl-LDH/GO/PF (Fig. 5d) possesses smaller cell size and more orderly structure in comparison to the materials 0.9 GO/PF and 0.9 CoAl-LDH/PF (Fig. 5b, c). Additionally, these modified materials (CoAl-LDH/GO modified PF foams) also have better flame retardancy compared to the non-modified foams.

Similar derivative of graphene nanofiller effect on phenolic foams cell structure was described also by Xia Luo et al. [11], where the graphene oxide/SiO2 hybrid

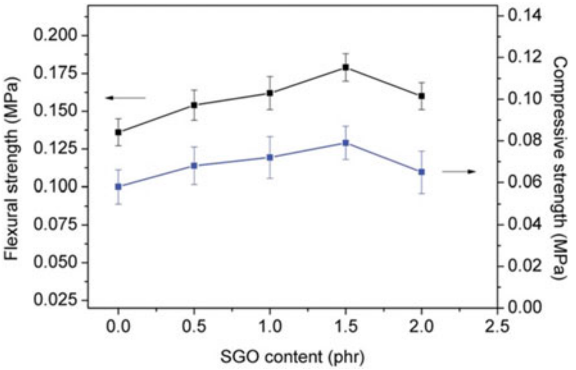


Fig. 3 SGO content on flexural and compressive strengths of PF foams [9]

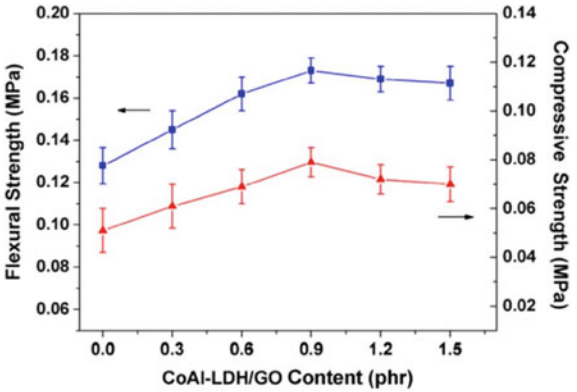


Fig. 4 CoAl-LDH/GO (GO: graphene oxide; LDH: layered double hydroxide; PF: phenolic) content on flexural and compressive strengths of PF foams [10]

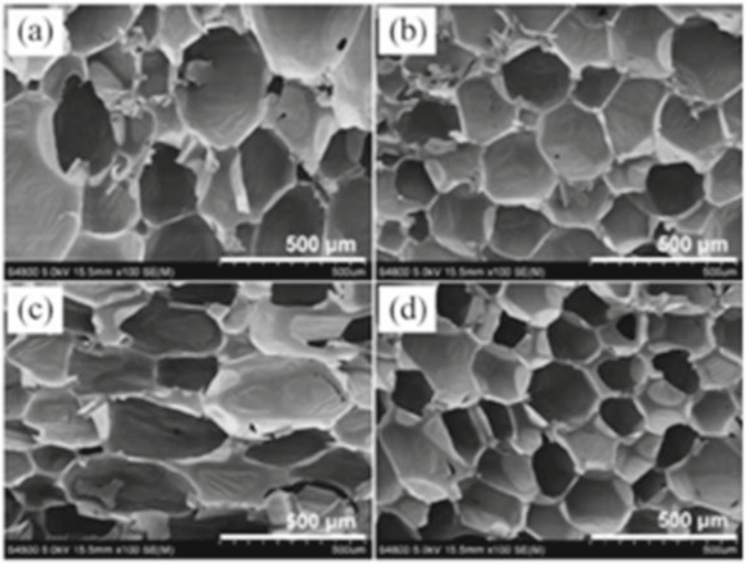


Fig. 5 SEM images of **a** neat PF foam, **b** 0.9GO/PF, **c** 0.9CoAl-LDH/PF and **d** 0.9CoAl-LDH/GO/PF [10]

materials were added into phenolic resin to prepare phenolic foam nanocomposites (Fig. 6).

It was previously explained how the cell structure was changed by using hybrid nanofiller (GO/SiO2) where the archived smaller cell diameter and higher the cell density of the reinforced phenolic foams (better cell morphology). For 1wt%GO/SiO2-80 modified phenolic foams presents a mean cell size of 117 μm

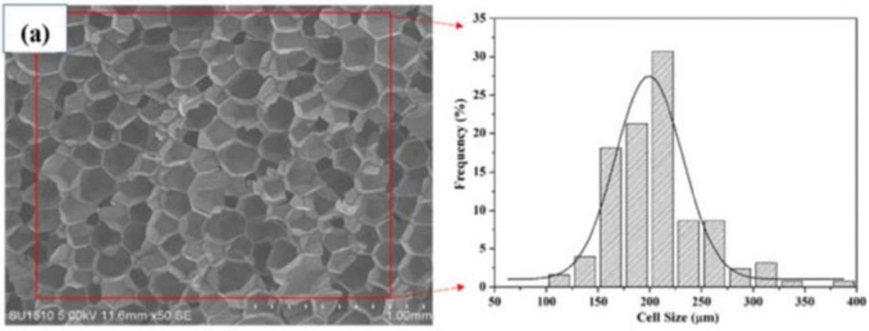
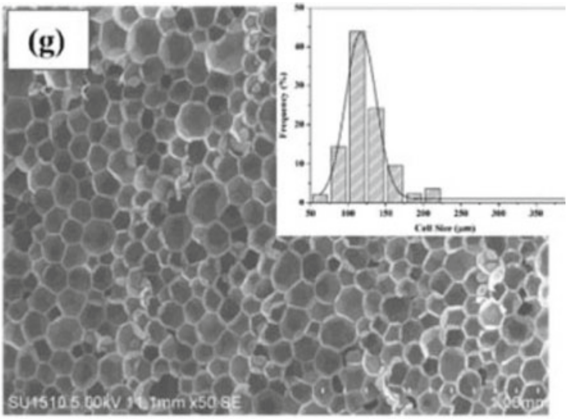


Fig. 6 SEM microphotograph of the pure PF surface and cell distribution [11]

Fig. 7 SEM microphotograph of the PF/(1.0 wt% GO/SiO2-80) material pure and cell distribution [11]



with a narrow cell distribution from 50 to 224 μm (Fig. 7), in comparison to the pure PF foam with wider cell distribution and cell size about 200 μm (Fig. 6) [11]. In this study [11] the authors emphasize also an excellent compressive strength and modulus of nanocomposite (PF/(1wt%GO/SiO2-80)), which has increased by 80% and 61%, compared to the non-modified PF form. Therefore, it can be seen that the addition of nanofillers, from the group of graphene derivatives, undoubtedly has a positive effect on the morphology of phenolic foams.

Phenolic foams modified with graphene derivatives from the GO/SiO2 group have additional properties related to an electromagnetic interference shielding performance (EMI), which was investigated by Zeng Y et al. [12]. EMI SE parameter describes the material's ability to attenuate the intensity of the electromagnetic wave. For non-modified (PCF—phenolic carbon foams) in the measure frequency rand (8–12 GHz) this material exhibits good EMI shielding capacity equal 18 dB. The addition of the modified nanofiller based on GO increases these parameters to about 23 dB which is connected with higher conductivity of this nanocomposite material (Fig. 8a). Another modification based on GO/SiO2 content highly increases EMI

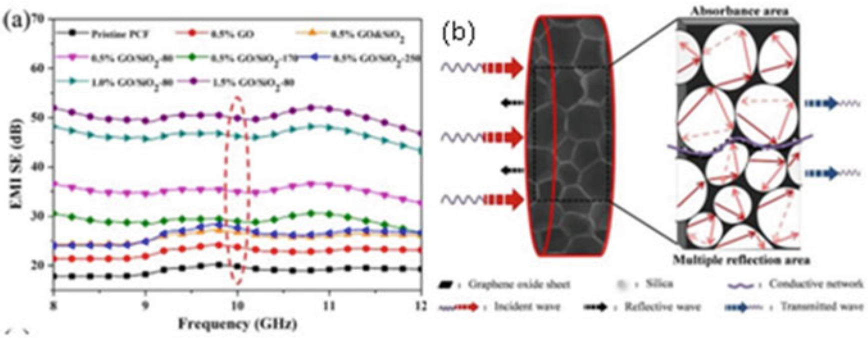


Fig. 8 **a** EMI SE as a function of frequency for PCF materials, **b** Schematic description of incident wave distribution in phenolic-based carbon foams [12]

shielding. For material containing 1.5 wt% of GO/SiO2 in PCF matrix the value of EMI SE increases to 50 dB which means that this 3D structure can shield more than 99% of electromagnetic radiation [12]. The visible enhanced EMI shielding performance is explained by the fact that GO/SiO2 clusters increase electrically conductive paths which have a strong interaction with electromagnetic waves and this behavior can significantly reduce the impact from electromagnetic field (Fig. 8b) [13].

The relationship between the cellular structure and the multipoles of the composites is shown in Fig. 8b. This porous structure creates a large number of interfaces which enhance multiple reflections and absorptions points of electromagnetic waves. The authors prove that the EMI of the GO/SiO2 hybrid nanomaterials reinforced PCF matrix was greater than other-size particles [12].

High-performance electromagnetic interference (EMI) shielding materials, based on phenolic carbon foams, have been intensively investigated by Kejing Yu et al. [14]. The authors reported the new materials based on reduced graphene oxide/Fe_3O_4 (rGO/Fe_3O_4) hybrid-modified carbon foams for EMI shielding applications. Figure 9a presents the cellular morphology of the non-modified carbon foams which possess closed-cell structure morphology and the cell size of about 200 µm. The introduction of 1.5 wt% rGO/Fe_3O_4 hybrid nanofiller into foam matrix reduced cell size to 130 µm (Fig. 9b).

Strain versus stress curves of the pure PCF foam and modified nanomaterials are showed in Fig. 10a. These results clearly prove that adding GO or rGO/Fe_3O_4 hybrid nanofillers into PCF foam improves mechanical properties. rGO/Fe_3O_4 hybrid nanofiller seems to be more effective in comparison to the GO.

Best results were obtained for the addition 1 wt% rGO/Fe_3O_4 hybrid nanofiller (Fig. 10a).

Figure 10b shows the EMI SE results for the carbon foams materials. Authors observed that the pure carbon foam performs EMI shielding capacity with an average EMI SE of about 19 dB. Introduction of the foam hybrid graphene derivative (1.5 wt% rGO/Fe_3O_4) dramatically increased this parameter up to 65 dB. Enhanced EMI shielding performance is connected with Fe_3O_4 behaving as a magnetic material

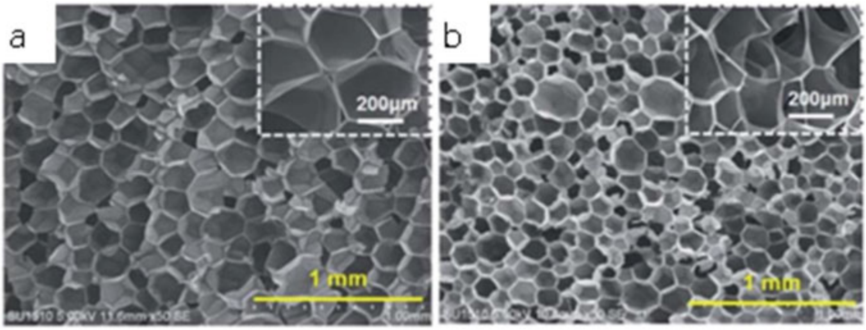


Fig. 9 SEM images of **a** pure carbon foam, **b** 1.5 wt% rGO/Fe_3O_4 hybrid-modified carbon foams [14]

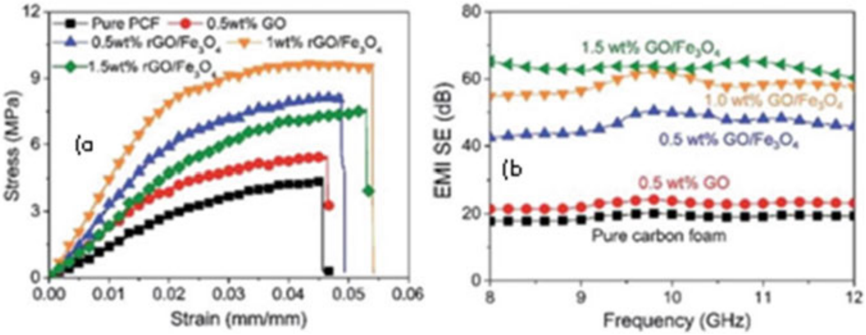


Fig. 10 Mechanical properties of the carbon foams: **a** stress–strain curves, **b** EMI SE [dB] of various carbon foams in the function of Frequency [GHz] [14]

which possess strong interaction with the magnetic component of electromagnetic wave (Fig. 9b).

Some pro-ecological applications based on Graphene nanoplatelet (GnP)/reused phenolic foam (re-PF)/wood composite boards were prepared by Jeong In Han et al. [15]. The authors add different amounts of the GnP to the PF matrix to investigate the effect on thermal and flame retardant properties of these nanocomposites.

The thermal stability of the composite increases with the addition of GnP nanofiller from PF wood matrix (re-PF/W) (thermal degradation Tonset = 212 °C) to Tonset = 243 °C registered for 20 wt% GnP modified material (20 GnP/re-PF/W) [15]. Also very important parameter LOI% (Limiting Oxygen Index) increases for these composite boards materials from 27% (re-PF/W) to 32% (20 GnP/re-PF/W) respectively [15].

An interesting comparison regarding the impact of carbon nanoparticles (multi-wall carbon nanotubes and graphene) on phenolic foams was presented by Song et al. from the Korea research group [2]. Noteworthy is the relatively simple method of

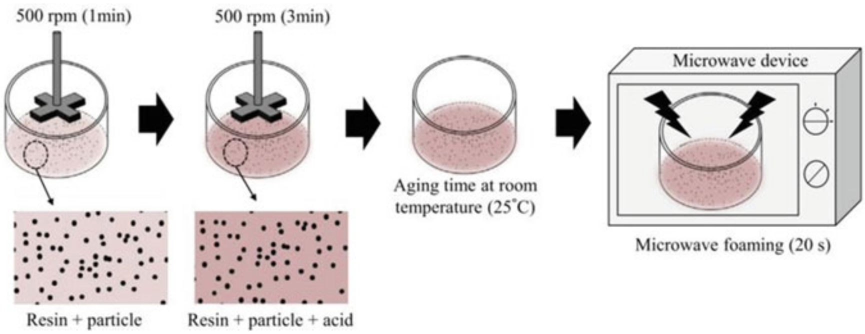


Fig. 11 Preparation of reinforced phenolic foam [2]

obtaining nanocomposites according to the diagram shown in Fig. 11. The phenolic foam which was fabricated by applying the microwaves and was monitored the degree of cure inside the phenolic resin in real time.

Based on phenolic foam's SEM images (Fig. 12) anisotropic structures can be seen. The addition of the nanofiller (MWCNT or Graphene) makes the material more uniform and smaller average cell size (75 µm at 2 wt% Graphene in PF compared with the pure PF matrix cell size 318 µm) (Fig. 13). The carbon reinforced phenolic foams (CP—MWCNT, GP—Graphene) show smaller cell size for both modified materials in comparison with the pure phenolic foams (Fig. 13). The authors also observed that higher nanofiller particles content (2 wt%) in phenolic foam matrix causes the creation of some aggregates.

Figure 13b shows the compressive strength of the phenolic foams with different types and amounts of the nanofiller. The compressive strength of the reinforced materials was improved and compared with the PF (for 1–2 wt% of graphene in PF equal 170 kPa). The authors conclude that the phenolic foam's smaller cell size possesses higher compressive strength in comparison to the large cell foams (Pure

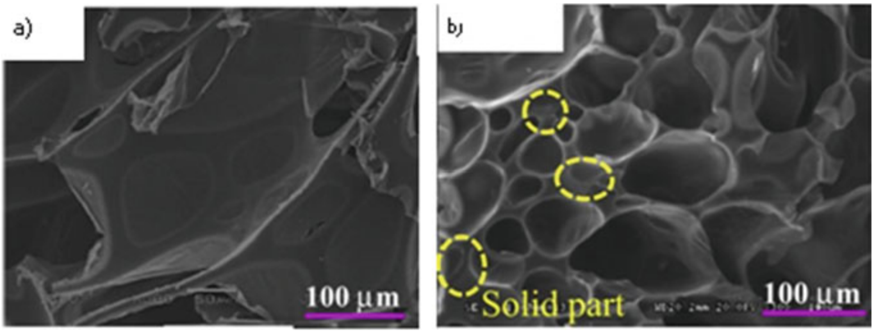


Fig. 12 SEM of the phenolic foams **a** pure phenolic resin, **b** Phenolic foam with 2.0 wt% Graphene [2]

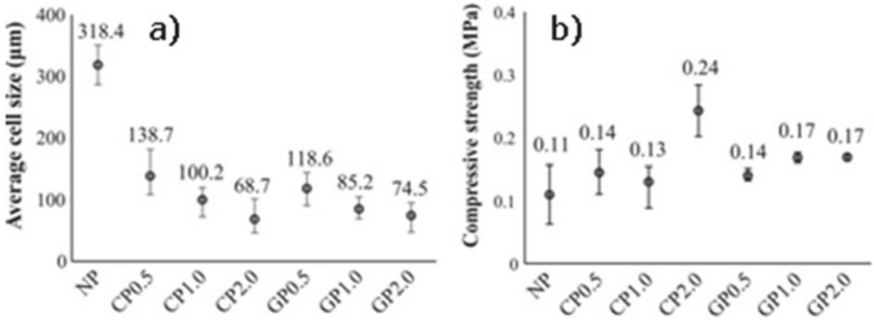


Fig. 13 Nanocomposite phenolic foams characterization: **a** average cell size **b** compressive strength [2]

PF), because these materials have more ribs and walls within foam morphological structure [2].

According to this study, the reinforcement of the phenolic foams using graphene causes good resin viscosity (for is important during production) and a good dispersion of the particles. This method is very promising in terms of improving material's thermal and mechanical properties.

Phenolic foams modified with graphene oxide (GO) in order to improve reinforced mechanical properties of these materials were presented by Zhou J et al. [16].

Mechanical parameters, for polymeric foam materials, are one of the most important factors influencing behavior application in the environment. These nanocomposite materials (containing GO nanofiller) show small changes to strength improvement (within experimental errors) (Fig. 14a) [16]. More noticeable changes are visible via impact toughness increase (up to 16% for 0.5 wt% GO in PF foam matrix) (Fig. 14a). In the case of these systems, it is worth concluding that such small addition

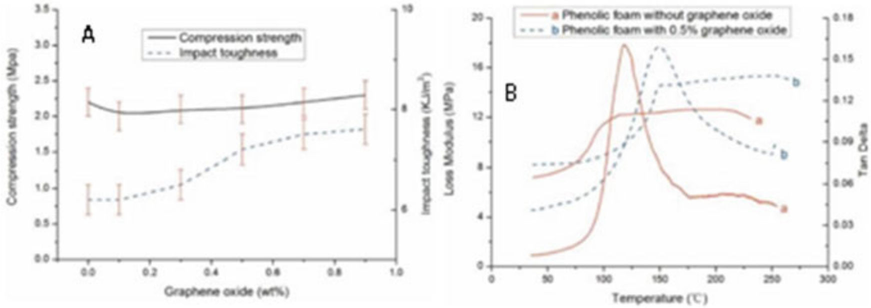


Fig. 14 **a** Compression strength and impact toughness of phenolic foam (PF) modified with graphene oxide (GO), **b** Loss modulus and tan δ vs. temperature. Phenolic foam **a** without graphene oxide, **b** with 0.5% graphene oxide [16]

of the GO nanofiller (up to 0.9 wt%) not always allows to obtain a big improvement of the nanocomposite materials.

In turn, such relatively low GO addition may result in a significant increase in the glass transition temperature (Tg) of graphene oxide reinforced phenolic foam compared with non-modified phenolic foams. Figure 14b presents Tg temperature of phenolic foam and PF with 0.5 wt% GO nanofiller increasing from Tg = 118 °C to Tg = 150 °C [16].

Similar, low content of the graphene oxide nanofiller (0.1–0.7 wt% GO) was used to modified phenolic foams by a researcher from China, Luan et al. [17]. This study presented the influence of GO modifier (the percentage of phenolic foams close area), which remains small. However, some decrease in the thermal conductivity properties of phenolic foams can be seen (up to 25 mW/ m · K) [17].

Phenolic foams modified using graphene derivatives can be also used as high-performance supercapacitors [18]. Li et al. [18] present a new type of advanced energy storage device based on these materials.

The authors successfully prepared modified materials according to the synthesis of CGO/phenolic based on three steps method, where the CGO addition was between 0.05% and 0.30% (Fig. 15). Finally, porous carbon foam (RGPF) was prepared by carbonizing CGO/PF [18]. This process can be performed as low-cost preparation method, what is important for eco-friendly based materials production. The authors achieve CGO modified hierarchical porous materials with good electrical conductivity, which could be conducive and used successfully for the electron transport. Prepared nanocomposites (especially RGPF with 0.2 wt% CGO) possess a high

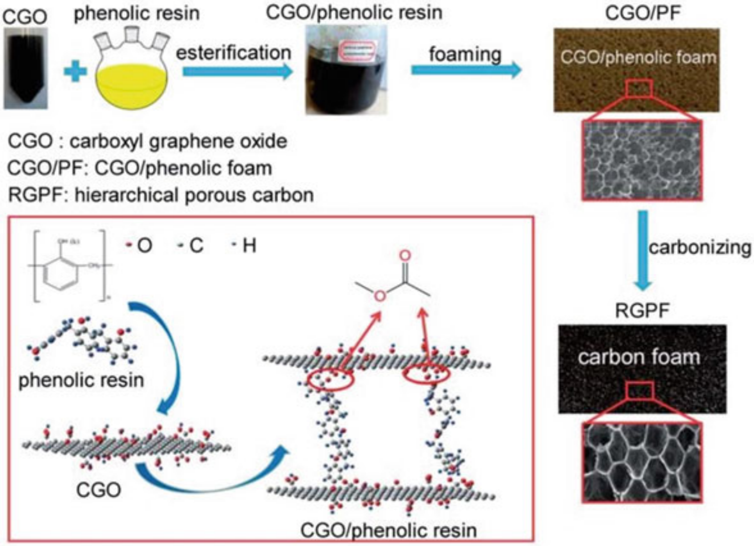


Fig. 15 Synthesis of Carboxyl Graphene Oxide (CGO)/phenolic foam and hierarchical porous carbon foam (RGPF) materials [18]

specific capacitance of 273 F/g in comparison to the non-modified PF material, where this parameter is equal to 114 F/g [18]. These electrode materials (designed as RGPF-0.20%-800) also presented a very promising life cycle with 93% specific capacitance retained after 10 000 cycles.

These hierarchical porous carbon materials seem to be very promising CGO/PF nanocomposites for energy storage supercapacitors.

Some innovative modified nanofillers, based on magnesium amino-*tris*-(methylene phosphonate) and reduced graphene oxide (rGO), which Liu L et al. [19] introduced to phenolic foam (PF), were successful in terms of increasing mechanical properties and thermal stability of PF.

This research presents one-step synthesis of a novel magnesium amino-*tris*-(methylene phosphonate) (Mg-AMP)-reduced graphene oxide (Mg-rGO) hybrid nanofiller. This modifier was able to improve the basic properties of PF like mechanical properties, flame retardant behavior, and thermal stability (based on TGA results) of the modified phenolic (PF) foam systems. High improvement was observed for the limiting oxygen index (LOI) of the foam with 4 phr Mg-rGO nanofiller, which increased up to 42% in comparison with the LOI = 38% for PF foam.

The authors conclude that Mg-rGO hybrid nanofiller (which is an interesting modification of GO since it was obtained by reducing and functionalizing GO form) enhances the thermal stability of the phenolic foam more effectively than classic graphene oxide (GO) [19].

3 Conclusion

This brief book chapter describes graphene and graphene derivatives which can be used to modify phenolic foams and improve their applications reducing eventual restriction for these materials. Phenolic foams (PF) possess very attractive and wide engineering applications such as insulation (low densities, low thermal conductivity), energy absorption (low rigidity), and fire protection (no drip protection, low toxic gases production, good LOI index). These materials exhibit excellent fire retardancy but sometimes their mechanical properties could constitute some limitations for different applications. Therefore, using different graphene derivatives (GO, rGO, etc.) causes significant improvement in mechanical, thermal, fire retardant properties and, what's more, defines well (regular) cell size in phenolic foam materials.

It was proven that the addition of the graphene-based nanofiller can successfully improve the mechanical properties of phenolic foam materials. Proper integration with polymer matrix allows to increase compressive or flexural strength and friability of these materials.

Good possibility of introducing and producing modified phenolic foams, as well as homogenizing nanoparticles, allows for trouble-free homogenization of the reacting system, which in consequence grants the manufacturer a possibility of acquiring a well-defined nanocomposite product. What's more, graphene-based nanofillers can play a pivotal role as a surfactant and well-embedded in the cell morphology can limit the thickness reduction of cell walls. Therefore, this new group of nanofillers (graphene derivatives) seems to be good candidates to achieve proper reinforcement (at relatively low addition into PF matrix). Graphene modified phenolic foams are very promising materials with wide application possibilities enabling their usage in an even more demanding environments.

References

1. Li X, Wang Z, Wu L, Tsai T (2016) One-step: In situ synthesis of a novel α- zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6:74903–74912. https://doi.org/10.1039/c6ra12208f
2. Song SA, Chung YS, Kim SS (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 103:85–93. https://doi.org/10.1016/j.compscitech.2014.08.013
3. Kim H, Abdala AA, Macosko CW (2010) Graphene/Polymer nanocomposites. Macromolecules 43:6515–6530. https://doi.org/10.1021/ma100572e
4. Bhattacharya M (2016) Polymer nanocomposites-a comparison between carbon nanotubes, graphene, and clay as nanofillers. Materials (Basel) 9:1–35. https://doi.org/10.3390/ma9040262
5. Young RJ, Kinloch IA, Gong L, Novoselov KS (2012) The mechanics of graphene nanocomposites: a review. Compos Sci Technol 72:1459–1476. https://doi.org/10.1016/j.compscitech.2012.05.005
6. Mittal V (2014) Functional polymer nanocomposites with graphene: a review. Macromol Mater Eng https://doi.org/10.1002/mame.201300394
7. Dreyer DR, Park S, Bielawski CW, Ruoff RS (2010) The chemistry of graphene oxide. Chem Soc Rev 39:228–240. https://doi.org/10.1039/b917103g
8. Luo X, Yu K, Qian K et al (2018) Effects of graphene surface energy on the structure and mechanical properties of phenolic foams. J Polym Eng 38:343–350. https://doi.org/10.1515/polyeng-2017-0132
9. Li X, Wang Z, Wu L (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. RSC Adv 5:99907–99913. https://doi.org/10.1039/c5ra19830e
10. Wang Z, Li X (2018) Synthesis of CoAl-layered double hydroxide/graphene oxide nanohybrid and its reinforcing effect in phenolic foams. High Perform Polym 30:688–698. https://doi.org/10.1177/0954008317716976
11. Luo X, Yu K, Qian K (2018) Morphologies and compression performance of graphene oxide/SiO2 modified phenolic foam. High Perform Polym 30:803–811. https://doi.org/10.1177/0954008317731136
12. Zeng Y, Luo X, Yu K, Qian K (2019) EMI shielding performance of phenolic- based carbon foam modified with GO/SiO2 hybrid nanomaterials. Chem Phys Lett 715:166–172. https://doi.org/10.1016/j.cplett.2018.11.040
13. Lu MM, Cao MS, Chen YH et al (2015) Multiscale assembly of grape-like ferroferric oxide and carbon nanotubes: a smart absorber prototype varying temperature to tune intensities. ACS Appl Mater Interfaces 7:19408–19415. https://doi.org/10.1021/acsami.5b05595
14. Yu K, Zeng Y, Wang G et al (2019) RGO/Fe_3O_4 hybrid induced ultra-efficient EMI shielding performance of phenolic-based carbon foam. RSC Adv 9:20643–20651. https://doi.org/10.1039/c9ra04244j
15. Han JI, Kim MJ, Song EJ et al (2019) Flame retardant and thermal properties of wood-based composite boards prepared by graphene nanoplatelet/reused phenolic foam. Appl Chem Eng 30:371–378. https://doi.org/10.14478/ace.2019.1022

16. Zhou J, Yao Z, Chen Y, Wei D, Xu T (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym Compos 35:581–586. https://doi.org/10.1002/pc.22698
17. Luan JP, Wei XF, Zhou XP et al (2015) Study on phenolic foams modified by graphene oxide. Adv Mater Res 1095:510–513. https://doi.org/10.4028/www.scientific.net/amr.1095.510
18. Li X, Li X, Zhou J et al (2017) Facile synthesis of hierarchical porous carbon derived from carboxyl graphene oxide/phenolic foam for high performance super-capacitors. RSC Adv 7:43965–43977. https://doi.org/10.1039/c7ra08602d
19. Liu L, Wang Z (2018) Facile synthesis of a novel magnesium amino-tris-(methylenephosphonate)-reduced graphene oxide hybrid and its high performance in mechanical strength, thermal stability, smoke suppression and flame retardancy in phenolic foam. J Hazard Mater 357:89–99. https://doi.org/10.1016/j.jhaz-mat.2018.05.052

Chapter 14
Nano Silica Reinforced Phenolic Foams

Seyyedeh Fatemeh Hosseini, Masoumeh Kiyanfar, Hoda Daneshvar, and Mir Saeed Seyed Dorraji

1 Introduction

Nanotechnology is attracted a great deal of attention because of its potential applications and it is rapidly growing in various fields such as electronics, aerospace, defense, medical, dental, nanocomposite, and so on. At the nanoscale, materials exhibit better physical, chemical, and biological properties over the individual atoms and molecules of bulk matter[1–5]. Since silicone materials commercially produce in 1940, they have considerable applications in most areas of science and engineering. Silica particles are normally a white amorphous powder or colloid suspension. Their melting point is 1600 °C [6]. One of the significant properties of them is their slow-burning rate which makes them useful in flame retardant applications [7]. Today, silica particles can be produced in different sizes. In recent years, silica nanoparticles (NPs), SiO_2, are widely used as fillers to reinforce the polymer performance. They can significantly improve the thermal, mechanical, physical, and chemical properties of polymers [8]. Silica NPs have been easily synthesized [9–11], and the size of them can be controlled during the synthesis process [12]. Moreover, they are odorless, less toxic, easily accessible, highly stable, and biocompatible particles [13, 14]. It is easy and inexpensive to make hydrophilic silica NPs on a large scale [15, 16].

Polymer nanocomposites are the most important class of composites. They have attracted researchers' attention to study them in the academic and industrial levels [17]. Polymer nanocomposites are generally organic matrix which is filled with inorganic additives. The volume fraction and size of the fillers have a remarkable effect on the mechanical, dynamic, and thermal properties of polymer nanocomposite [18]. Among the different polymer nanocomposites, silica polymer nanocomposite has been studied a lot and it has been successfully used for various applications in

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different fields because silica as a reinforcement agent has significant advantages such as the high specific surface area, high aspect ratio, high Young's modulus, and strength [19].

Recently researchers have combined nanoparticles with foaming technology and have produced polymer nanocomposite foams. The increasing demand for lightweight materials with added functionalities and also the high effect of a small number of nanoparticles on the polymeric foam materials have led to the development of these materials. The materials used in foam preparation affect the structure and characteristics as well as the final application of foam. Nanoparticles improve the cellular structure and properties of the polymeric matrix of foams [20–22]. Nanofillers as nucleating agents help in the bubble formation step and cause an improvement in cell morphology and final properties of the foams. Also, an increased expansion ratio can reduce the amount of resin needed for foam formation [23, 24].

Phenolic foams have attracted more attention compared to other commercial polymeric foams such as polystyrene (PS) and polyurethane (PU) because of their advantages like low flammability, high thermal stability, no smoke, and toxic gas production during combustion, etc. [24, 25]. These features make them useful for different applications such as insulation, decontamination, fire protection, packaging, structural and domestic elements, agriculture, horticulture, and energy absorption. But phenolic foams also have weaknesses that limit their applications (such as brittleness, pulverization, and low tensile strength) [26]. Fortunately, studies have shown that the use of fillers in micro or nanoscale such as fibers, clays, carbon nanotubes, graphene, and silica can improve the mechanical properties of phenolic foams without deteriorating their excellent fire resistance. Studies show that silica NPs can easily be dispersed in solutions and react with the resol resin. In this reaction, they can form a chemical crosslinked network which increases the stability of the polymer chains of the phenolic resin /silica nanocomposites [13].

2 Preparation of Silica Nanoparticle Reinforced Phenolic Foams

Silica NPs are generally obtained in an alkaline ethanol/H_2O solution and the commonly used silicon sources are tetraethyl orthosilicate (TEOS) and tetrapropyl orthosilicate [27–29]. Today, the biological method for the synthesis of silica NPs has attracted considerable attention because of its advantages like environmental friendliness, low-toxicity, cost-effectiveness, easy isolation, etc. [30, 31]. The homogeneous dispersion of nanoparticles in the polymeric matrix is so important factor in the composite preparation. The dispersion extent of silica NPs plays an important role in the mechanical properties of silica-reinforced phenolic foam[32].

In the preparation of silica/polymer composite, the widely used methods are the blending process, sol–gel process, and in-situ polymerization[6]. To synthesis silica NPs reinforced phenolic foam, first silica phenolic resin is prepared, and then it is converted into the foam by incorporating other components. For the synthesis silica phenolic resin, silica NPs are dispersed in the formaldehyde solution under ultrasonic mixing, and then formaldehyde consisted of silica is added dropwise to the mixture of phenol and aqueous sodium hydroxide. The reaction proceeds at 85 ˚C for 3.5 h under constant agitation [32]. Besides phenolic resin other basic components that are used in phenolic foam formation are blowing agent, surfactant, and curing agent. The blowing agent that is commonly used is n-Pentane. Also, Tween 80 as a surfactant is applied. Acids such as phosphoric acid, p-toluene-sulfonic acid, phenol sulfonic acid, and sulfocarbolic acid are used as curing agents. In some works, a mixture of different acids and distilled water were used. Silica phenolic resin, blowing agent, surfactant, and curing agent are mixed under rapid stirring for a few minutes. Then the mixture is quickly poured into a mold and is allowed to cure and foam at 75 ˚C for 90 min [32–35].

3 Microstructure of Reinforced PFs

It is well known that a full understanding of the thermal or mechanical properties of the foams strongly depends on their unique density [36]. There are various methods, which can be employed to examine the properties of microstructure and cell structure of silica nanoparticles in PFs, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In practice, the ratio of the sample mass, m, to the geometrical volume, v, is defined as the foam density, ρ, as shown below [35]:

$$\rho = \frac{m}{v} = \frac{m}{\pi r^2 h}. \tag{1}$$

The cell density of the foams is defined as the number of cells per unit volume, which is calculated by the following equation:

$$N_f = \left(\frac{nM^2}{A}\right)^{3/2} \times \frac{\rho}{\rho_f}, \tag{2}$$

where A is area obtained from the SEM photograph; M is the magnification of SEM images; n is the number of cell in area, ρ and ρ_f are the densities of curried phenolic resin and PF, respectively [34]. It is important to notice that the modifiers in foams can create a lot of interfaces, which increase the cell nucleation by reducing the energy barrier of the cell nucleation, according to heterogeneous cell nucleation theory. Therefore, the relevance between the particle size and the total number of the nucleated cells can be calculated by the following equation:

$$N_b(t) = \int_0^t J_{hom}\left(t'\right) + A_{hct}\left(t'\right) J_{het}\left(t'\right) dt'$$

$$\approx \int_0^t A_{het}\left(t^{'}\right) J_{het}\left(t^{'}\right) dt^{'}, \tag{3}$$

where J_{het} is the heterogeneous nucleation rate and A_{het} is the specific surface area of the nucleating agent. According to this equation, as A_{het} increases, the number of nucleated cells increases [35]. On the other hand, the variation in the free energy of the system for heterogeneous and homogeneous nucleation can be estimated, respectively, by the following equations:

$$W_{het} = W_{hom} F(\theta_c, \beta) \text{Heterogeneousnucleation}. \tag{4}$$

$$W_{hom} = \frac{16\pi r^3}{3(P_{bub,cr} - P_{sys})^2} \text{Homogeneousnucleation}, \tag{5}$$

where $F(\theta_c, \beta)$ is the shape factor with values equal to or less than 1, which is calculated as follows:

$$F(\theta_c, \beta) = \frac{1}{4}\left[2 - 2\sin(\theta_c - \beta) + \frac{\cos\theta_c cos^2(\theta_c - \beta)}{\sin\beta}\right], \tag{6}$$

where β is the semi-conical angle (0–90°) that displays the geometry of the nucleation locations and θ_c is the contact angle between the bubble surface and the second phase. It is worth emphasized that the Talc particles create heterogeneous nucleation locations by reducing the activation energy barrier for the bubble nucleation, and thus increasing the nucleation rates. Yuan et al. [34] synthesized the nanocomposite poly(n-butyl acrylate) /silica with core–shell structure as an improvement agent in PFs through aqueous emulsion polymerization. The microstructure properties of pure and reinforced PFs with the different dosages of the nanocomposite were examined by SEM (Fig. 1). SEM studies displayed that the apparent density of the modified foams (about 25 ± 0.5 kg/m^3) is lower than that of the pure PFs (314 kg/m^3). Besides, the addition of an appropriate dosage of the nanocomposite (from 0.015 phr to 0.09 phr) leads to improve the structural homogeneity (shape and cell distribution) of reinforced foams compared to the pure PFs.

It is well known that the viscosity of the resin increases as the dosage of the nanocomposites rises. The bubbles created during the foaming process become larger with increasing temperature until the cell wall ruptures. Despite the defect created in the structure, a homogenizing process of foam happens to create a uniform cell structure, owning to the fluidity of the resin. In addition, the proper viscosity of the resin can preserve the cell structure without rupture. If the viscosity is very low, the regular cell structure could not be obtained well. If the viscosity is very high, the homogenization process will be difficult, due to the particle agglomeration.

Luo et al. [35] examined the effect of weight fractions(0, 0.3, 1, and 1.5 wt%) and different sizes (80, 170, and 250 nm) of GO/SiO_2 hybrid materials in the PFs. The cell

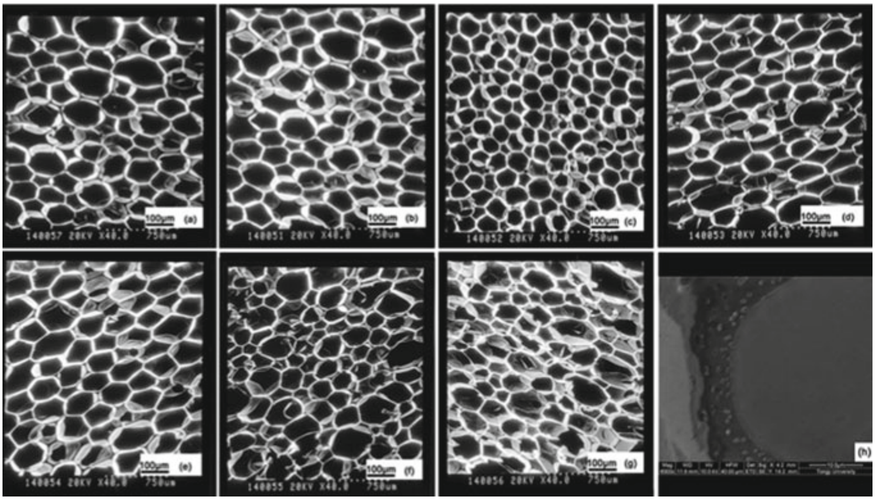

Fig. 1 SEM images of the PFs reinforced by different dosages of nanocomposites: (a) 0 phr; (b) 0.015 phr; (c) 0.03 phr; (d) 0.06 phr; (e) 0.09 phr; (f) 0.12 phr; (g) 0.15 phr. (Reproduced from[34])

structure and the cell morphology of the modified PFs were studied by SEM (Fig. 2). The SEM results revealed that the cell density significantly improved by 75.4%, compared to the pure PF. In particular, the modified PF with 1 wt% of GO/SiO_2-80 displays the narrowest cell size distribution and the most uniform cell morphology. It is speculated that the presence of graphene oxide nanoparticles as nucleating agents can reduce the free energy of nucleation and increase the likelihood of uniform cell formation. Moreover, the SiO_2nanoparticles with good hydrophilic can well disperse in phenolic resin and help to improve the cell structure. Thus, the combination of GO and SiO_2 with high quantity oxygen groups can improve the cell morphology and increase the viscosity of the phenolic resin, which can prevent the thinning of cell walls and the expansion of cells. It is noteworthy that the cell distribution is dependent on the modifier size. The cell size distribution became non-uniform and the mean cell size enhanced when the nanocomposite size was enhanced from 80 to 250 nm. The large nanoparticles can easily aggregate and the air between the particle gaps expands significantly with the increase of heat.

Li et al. [33] prepared the silica/ PF nanocomposites with the different contents of silica (0.5, 1, 2, 3, and 4 wt%) by in-situ polymerization. The formation of chemical bonding between resin and silica nanoparticles was confirmed using Fourier transform infrared spectroscopy (FT-IR), which silica nanoparticles can perform as a bridge to obtain the structure of the crosslinked network. The microstructure properties of the pure PFs and the modified PFs were studied by SEM (Fig. 3). The results displayed that the shape of all the cells in modified foams is hexagon; however, the pure PF has various shapes such as oval, pentagon, circle, and hexagon. Moreover, the cell size distributions, the cell distributions, the cell wall thickness, and the mean

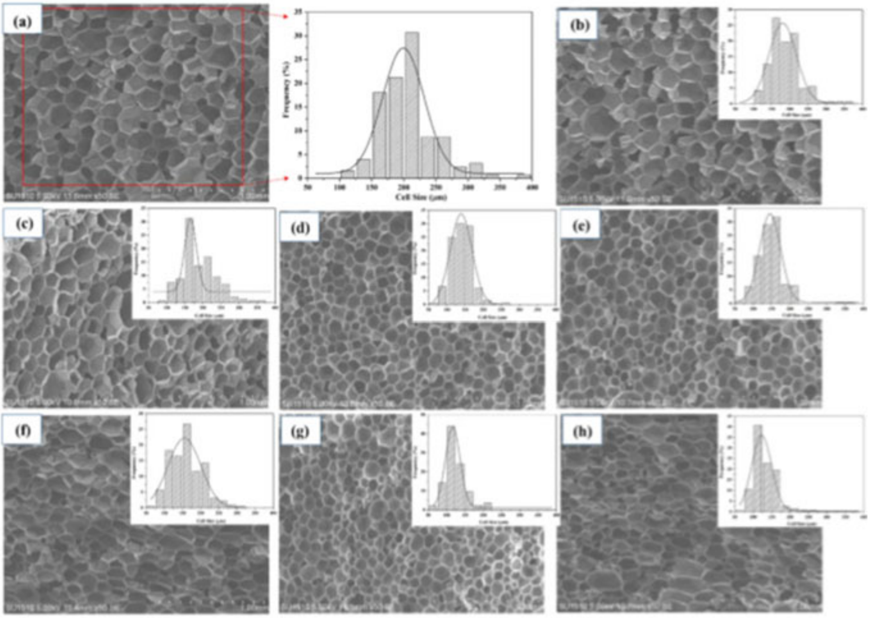

Fig. 2 SEM images and the cell size distribution of PFs with different contents of **a** 0; **b** 0.3 wt% GO; **c** 0.3 wt% GO&SiO_2; **d** 0.3 wt% GO/SiO_2-80; **e** 0.3 wt% GO/SiO_2-170; **f** 0.3 wt% GO/SiO_2-250; **g** 1.0 wt% GO/SiO_2-80; **h** 1.5 wt% GO/SiO_2-80. (Reproduced from[35])

cell size of modified PFs with 2 wt% silica sol are narrower, more uniform, thicker, and smaller than that of the pure PF and other foams, respectively.

Li et al. [37] prepared the nanocomposite of graphene oxide/ silica nanospheres (SGO) via SiO_2immobilization on the surface of GO sheets and its effect as the modifier on the microstructure properties of PFs was studied by optical microscope (Fig. 4). Based on the results obtained, the structure of the prepared foams with the different nanofillers (GO, SiO_2, and GO/SiO_2) are mainly closed cells. However, the sample of SGO (0.5 wt%)/ PF has smaller cell sizes and a more uniform cell structure than the pure PFs and other modified forms. It is probably due to the differences in the surface nature and the dispersion between the resin and the fillers during the heterogeneous nucleation process. It is important to notice that SGO is much more effective than GO in the nucleation process because of the immobilization of the GO surface by SiO_2 nanospheres and the changing from hydrophilic to hydrophobic [38]. In addition, due to the presence of graphene oxide, agglomeration does not occur between the SGO particles and thereby it is uniformly dispersed in the foam matrix. Compared to the pure PFs, as the dosage of SGO increases, the cell sizes related to SGO-reinforced PFs decrease. During the foaming process, the more cells were produced by SGO that leads to an increase in cell density and a decrease in cell size compared to pure PFs [39]. However, the cell size distribution of the sample

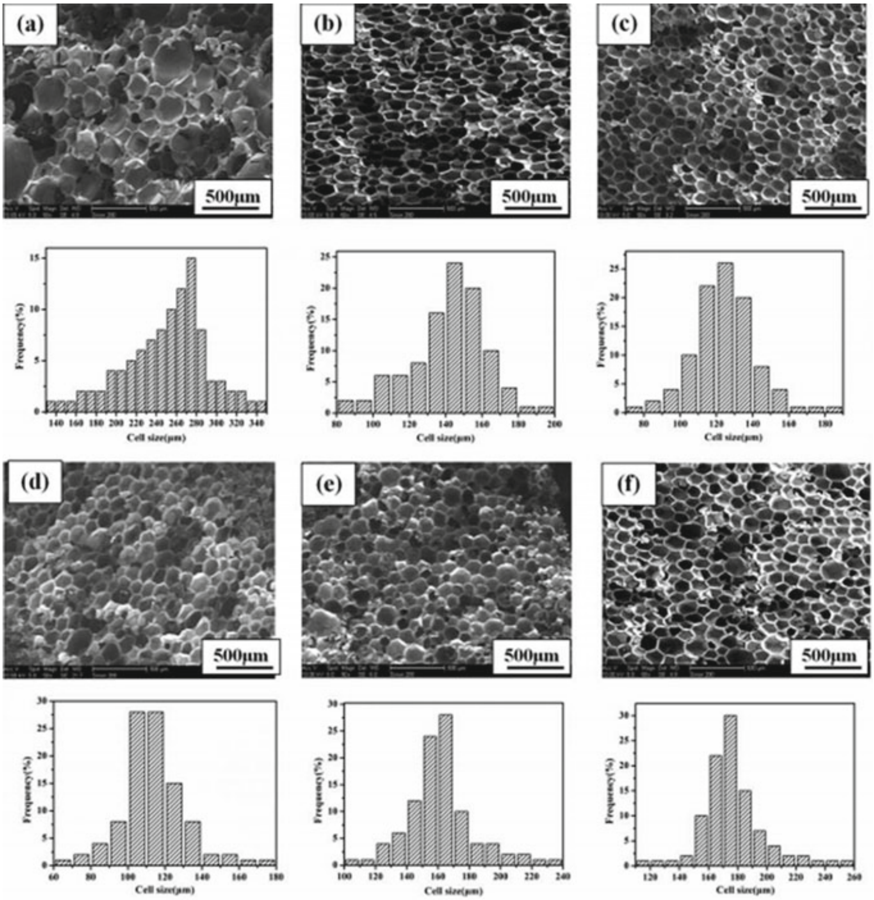

Fig. 3 SEM images and cell sizes distributions of PFs with different contents of nanoparticles: **a** 0; **b** 0.5 wt%; **c** 1 wt%; **d** 2 wt%; **e** 3 wt%; **f** 4 wt% (100 ×); **g** 0 (800 ×); **h** 2 wt% (800 ×). (Reproduced from[33])

SGO (2 wt%)/ PF is not uniform due to the agglomeration between SGO particles at higher weight fractions (2 phr) [40].

4 Physical Properties

4.1 Mechanical Properties

The most important disadvantage of PFs is that they have a low mechanical strength that prevents their widespread usage [41–44]. It is well known that the inorganic

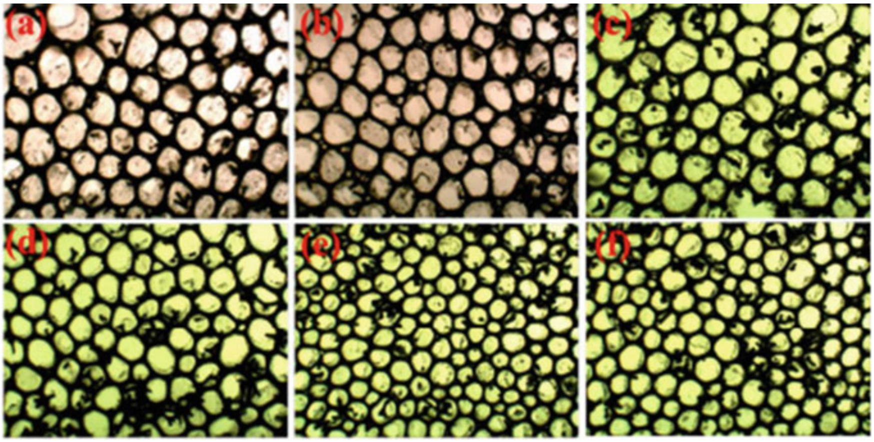

Fig. 4 Optical images of **a** pure PF and toughened PFs using **b** 0.5GO, **c** 0.5SiO$_2$, **d** 0.5SGO, **e** 1.5SGO, **f** 2.0SGO. (Reproduced from [37])

nanoparticles such as silica have unique mechanical strength. The combination of the inorganic materials with the PFs is a promising method to improve their mechanical properties, which are obtained from the synergy among the components [45–48]. This can be explained by the presence of large quantities of active hydroxyl groups on the silica surface and the formation of a strong chemical bond between silica and resol [14]. When silica nanoparticles are added into the system, during the foaming process, the crosslinked network is formed, which acts as a bridge for the connection of the resol with the resol [13]. As mentioned earlier, the mechanical properties of PFs strongly depend on their microstructure such as cell size distribution, cell wall thickness, and mean cell size. For example, the PFs with high cell density, small mean cell size, and narrow cell size distribution have a better compression property, which can be due to the existence of more walls and ribs to undergo compression [49]. Meanwhile, the worse cell morphology leads to poor compression function. The mechanical properties of the different types of nano silica/PF composites have been widely investigated by the experimental studies.

Yuan et al. [34] investigated the effect of the different dosages of the crosslinked poly (n-butyl acrylate) (PBA)/silica nanocomposites on the mechanical properties of PFs. The results showed that compared to the pure PFs, the PFs containing 0.03 phr of modifier have the highest flexural strength (0.209 MPa), the compressive strength (0.08 MPa), and the elastic modulus (2.491 MPa), which enhances by 36.0%, 42.9%, and 32.3%, respectively. On the other hand, the toughness can be estimated by using the area under the stress–strain curve, in which the better toughness is characterized by a larger area. The modified foams containing 0.015, 0.03, 0.06, and 0.09 of nanocomposite have a bigger area than that of other foams. It can be explained by the covalent bond between the hydroxyl groups (-OH) on the nanocomposite surface and hydroxymethyl groups (-CH$_2$OH) of the phenolic resol. This in turn can lead to a significant improvement in the compatibility of the phenolic matrix and the nanocomposite.

Luo et al. [35] studied the impact of the nanoparticle type, weight fraction, and diameter of GO/SiO_2 hybrid on the mechanical properties of the PFs. The compressive strength and modulus of modified foams with GO/SiO_2 hybrid are higher than the pure PFs and the other modified foams. It can be due to the greater cell density and the smaller cell size of the PFs reinforced by GO/SiO_2 hybrid, which can lead to the distribution of compression force in a larger number of cell walls and thus improve the compressive strength. Meanwhile, as the diameter of the hybrid materials increases, the compression property in the modified PFs decreases. This may be due to the reduction of cell density and the pressure-bearing cell walls with the increasing the size of GO/SiO_2hybrid material. Besides, the compressive modulus and strength were first enhanced and then reduced when the GO/SiO_2 content in the modified PF increased. The PFs modified by 1 wt% GO/SiO_2display an outstanding compressive modulus and strength of 3.22 and 0.18 MPa, which increases by 61% and 80%, respectively, compared to other foams. However, the agglomeration of the hybrid material with a larger size (1.5 wt%) leads to the formation of un-uniform cell structure and thereby the cell deformation and the poor compression property.

To better understand the impact of different contents of silica sol on the mechanical properties of PFs, Li et al. [33] prepared the nano silica-reinforced PFs by in-situ polymerization. Compared to the pure PFs, the mechanical strength of reinforced PFs is increased due to the chemical bonds between the silanols in silica and the phenolic groups in the resin. It is found that the sample reinforced with 2 wt% nano silica has the optimum performance. The compressive modulus, tensile strength, and compressive strength of the recent sample increase by 38.55%, 57.14%, and 47.37%, respectively, compared to the pure PFs. Meanwhile, this sample has a tensile modulus of 1.38, which decreases by 45.67%, compared to the pure PFs. This can be explained by the excellent elasticity and better cell morphology of this sample versus the other foams. However, the mechanical performance of the reinforced foams decreases when the silica sol content increases to more than 2 wt%. It can be due to the thinner the cell walls, the wider the cell distribution, and the larger the mean cell size, compared to 2 wt% nano silica-reinforced PFs. Moreover, the compression properties of modified foams were studied by the quasi-static compression stress–strain curves (Fig. 5). This curve has three stages: (1) the rapid growth of stress with increasing strain, which attributed to the cell wall in the foams; (2) the yielding process, which can be explained by the rapid destruction of cells; (3) the increasing the stress only with the increasing strain, which can be due to the densification of the cells. It is found that the compression properties of the PFs reinforced with 2 wt% nano silica are superior compared to other foams, due to the formation of the chemical crosslink bonding between the silica and the phenolic resin.

Li et al. [37] studied the mechanical properties of the pure and the reinforced PFs by the hybrid materials of SGO. The flexural and compressive strengths of the reinforced PFs are enhanced compared to the pure PFs. There are two reasons for this result: first, the high-strength nanofillers are introduced into the cell walls of the foams and lead to increase the strength in the cell walls; secondly, the nanofillers as

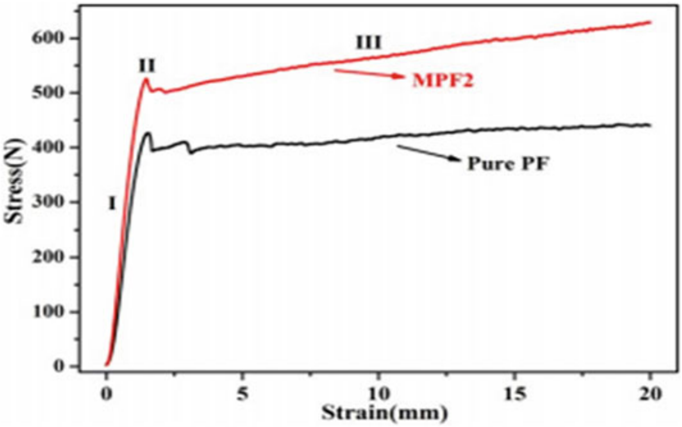

Fig. 5 .The stress–strain curves for pure PFs and reinforced PFs with 2wt% nano silica. (Reproduced from[33])

a nucleating agent can increase the cell density and the small cells, which they lead to enhance the compressive strength of the modified PFs due to the presence of more cell walls and ribs undergo pressure. Besides, the flexural and compressive strengths of the modified PFs by SGO are higher than those of other PFs modified by GO and SiO_2. This can be explained by the strong chemical reaction between SGO sheets and phenolic resin. Therefore, the ester bonds between the carbonyl groups (–COOH) on the SGO surface and the hydroxyl groups (–OH) on the PF surface are formed in the acidic medium and at high temperatures. Moreover, the changing of the SGO surface from hydrophilic to hydrophobic leads to improve the heterogeneous nucleation and producing more cells to enhance mechanical performance. In this study, the effect of SGO content on the mechanical properties of the reinforced foams was also examined. The results showed that the modified foams by 1.5 phr of SGO have an excellent flexural and compressive strength of 0.179 MPa and 0.079 MPa, which increases by 31.6% and 36.2%, respectively, compared to the pure PFs. This can be because of the smaller cell size and uniform cell structure and thereby it can undergo great external pressure. Meanwhile, the reduction in the mechanical performance with the increasing of loading (2 phr) is attributed to the particle agglomeration of SGO and their weak dispersion in the PFs. Therefore, the enhancing of the mechanical strengths in the PFs depends on enough addition of nanofillers.

Guo et al. [50] prepared the silica nanoparticle using the phenol solvent instead of other organic solvents. They investigated the mechanical properties in four types of PFs (PF): derived from phenolic resin (PF1), derived from nano silica-reinforced phenolic resin (PF2), derived from lignin/nano silica-reinforced phenolic resin (PF3), and derived from lignin-reinforced phenolic resin (PF4). The results showed that PF2 and PF3 have a compressive strength of 0.35 and 0.38 MPa, which increases by 192% and 153%, respectively, compared to PF1 (0.12 MPa) and PF4 (0.15 MPa). It is worth emphasizing that nano silica acts as a modifier and bridge between each part of the resin matrix and thus the formation of the crosslinked network structure. The only 0.1 wt% of nano silica as the optimal value in PFs was required (much lower than previous reports) due to the strong bonding among lignin, silica, and phenolic resin.

4.2 Thermal Stability and Degradation

The macromolecular foams with low thermal conductivity (κ) have potential applications in the materials of the thermal insulation for buildings [26]. It is necessary to study the thermal conductivity properties of pure and reinforced foams. According to the large volume of the gaseous phase in the PFs, conductivity through gases is a major factor in heat transfer, although, the main amount of heat is transferred through solid polymers. As a result, various factors affect the thermal conductivity of the foam, such as the cell size distribution, porosity, cell distribution, thermal conductivity of raw materials, and cell density. Moreover, an additive agent such as silica nanoparticles has a significant effect on the thermal conductivity of foams. On the other hand, the decomposition process of polymeric materials must first be known to justify the increase in their thermal stability. Thermal decomposition of all PFs is a four-step process, which is mainly originated by (1) the evaporation of water and blowing agents in the foam ($T < 100$ °C), (2) the further dehydration of cured PFs ($T \sim 160$ °C), (3) the evaporation of the surfactants such as free phenol and Tween 80 (from 250 to 400 °C), and (4) the phenolic resin degradation (from 400 to 800 °C) with the maximum decomposition temperature of 467.8 °C [37].

Using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and difference thermogravimetry (DTG), many research groups have studied the enhanced thermal stability in nano silica/PF composites compared to the pure PFs. Several mechanisms have been proposed to explain the improvement of thermal stability in nano silica/PF composites. For instance, the interfacial interaction containing the covalent chemical bonds between the organic phase (resin) and inorganic phase (silica) prevents the movement of the polymer chain and leads to an increase in temperatures [51]. Yuan et al. [34] found that the addition of poly (n-butyl acrylate) (PBA)/silica nanocomposites did not affect the thermal stability of the PFs. Meanwhile, the addition of the nanocomposite into the system has very little effect on the glass transition temperature (Tg) of the PFs. This can be due to the high crosslinking degree in the pure PFs, in which the addition of the nanocomposite into the system does not lead to a significant change in the total crosslinking degree of the reinforced foams.

Li et al. [33] investigated the thermal conductive properties in the phenolic-formaldehyde foams reinforced by silica nanoparticles with different content (0.5, 1, 2, 3, and 4 wt%). The results exhibited that the modified foams have lower thermal conductivities than pure foams. This can be attributed to the more uniform cell distribution, narrower cell size distribution, smaller mean cell size, and lower cell density of the modified foams compared to pure PFs. In particular, the modified foams by 4 wt% nano silica have the highest thermal conductivity, compared to other foams, which can be explained by the high content of silica sol. As a result, selecting the optimal amount of silica sol is essential to reduce the thermal conductivity of improved foams. The TGA and DTG results showed the thermal stability of reinforced foams by 2 wt% nano silica is higher than other foams. This can be explained by forming an insulating silica layer on the polymer surface and strong interfacial interaction between silica and foam, which lead to the protection of the foam interior.

Li et al. [37] studied the effect of SGO on the thermal stability of PFs. The TG results showed that T_{max} and the weight loss temperatures at 5 and 30% ($T_{-5\%}$ and $T_{-30\%}$) of modified foams are higher than those of pure foams. Besides, residues of reinforced foams at 750 °C are higher than the pure PFs. Thus, the thermal stability of modified foams by SGO enhances, compared to the pure PFs. This can be explained by the immobilization of SiO_2 nanospheres on the GO surface that it prevents the GO decomposition.

4.3 Flame Retardant Properties

The PFs are commonly used in the thermal insulation materials, due to outstanding flame retardant performance [52]. Therefore, it is necessary to study the flame retardant of the PFs. The tests of limiting oxygen index (LOI), UL 94 vertical burning, and cone calorimetric are used to measure the flame retardant in the pure and reinforced foams (discussed in detail in ref. [37]. Yuan et al. [34] evaluated the flammability of the pure and modified foams with crosslinked poly (n-butyl acrylate) (PBA)/silica core–shell nanocomposites by using LOI tests. The results showed that the nanoparticles have a small impact on the LOI of PFs and the unique flame retardant function of purePFs is still preserved. It is worth emphasized that the content of the modified nanocomposite is very low. Li et al. [37] investigated the effect of silica nanospheres/graphene oxide (SGO) hybrid on the flame retardant performance of the pure and modified foams. The LOI results displayed that the synergistic effect between silica nanospheres and GO leads to increase LOI in the modified foams, compared to SiO_2 and GO-reinforced PFs. Besides, as the SGO amounts in foams increase the LOI values of modified foams increases. This can be due to the SiO_2 layer formed on the GO surface, which can prevent the GO decomposition. As a result, the GO sheets act as a physical barrier against the heat and mass transfers, especially at high temperatures [52]. Another reason for the increase in LOI can be explained by the higher cell density of modified foams by SGO. The results of the cone calorimetric test showed that the mean heat-release rate (mHRR), the total heat release (THR), and peak heat-release rate (PHRR) of the modified foams are lower than those of the pure foams. Besides, the values of mHRR, THR, and PHRR decrease when the loading contents of SGO increase. For example, the THR and PHRR of modified foams by 1.5 wt% SGO decrease by 6.4% and 21.4%, respectively, compared to pure PFs, meanwhile, the time of ignition enhances 10 s. Moreover, both the pure and modified foams can pass the UL 94 V0 rating.

4.4 Pulverization Ratio

The high friability is a critical problem for the PFs, which leads to reduce their applications. Therefore, adding silica nanoparticles to PFs as an improving agent could be a promising solution to this problem. The weight loss of the specimen after friction is defined as the friability (discussed in detail in ref. [33]). Hence, the pulverization ratios (Pr) is calculated as follows:

$$Pr = \left(\frac{(m_b - m_a)}{m_b}\right) \times 100\%, \tag{7}$$

where m_b is the weight of specimen before friction; and m_a is the weight of the specimen after friction[53]. Li et al. [33] studied the relationship between pulverization ratios and the silica sol content as a modifier in the PFs. The results showed that the pulverization ratios decrease to a minimum value of 1.258% with the increasing the content of silica sol to 2wt%. This can be due to the strong chemical bond between hydroxyl groups (OH) on the SiO_2 surface and resol. Thereby, the formed crosslink structure has a high resistance to friability. Meanwhile, the pulverization ratios increase when the silica sol content is beyond 2wt%. Generally, all modified foams have the pulverization ratios lower than that of the pure PFs. This is probably due to the better cell morphologies of reinforced PFs than that of pure PFs.

Li et al. [37] investigated the effect of different dosages of SGO on the pulverization ratios of the PFs. It is found that the pulverization ratios of modified foams by nanoparticles are higher than that of the pure PFs. Moreover, the pulverization ratios reduce gradually with the increasing the SGO content in foams to 2 phr. This can be explained by the strong interaction between SGO and phenolic resin, the increasing of the heterogeneous nucleation, and the ultrahigh aspect ratio. However, when the content of SGO is 2 phr, the pulverization ratios increase slightly that it can be originated by the agglomeration of the particles of SGO at higher values and thus creating defects in cell structure.

4.5 Electromagnetic Interference (EMI) Shielding

Today, it is very important to reduce the interference of electromagnetic waves in electronic and telecommunication devices by electromagnetic interference (EMI) shielding. The incorporation of the conductive nanoparticles with foams has attracted a lot of attention in the field the shielding materials because of their outstanding chemical and physical properties. Therefore, it is essential to combine the PFs with nanostructured materials to increase its applications [54]. The phenolic-based carbon foams reinforced by GO/SiO_2 nanoparticles were fabricated by Zeng et al. [55]. The results showed that the EMI SE values of foams increases, as the content of nanoparticles increases. Thus, the EMI shielding performance of modified foams enhances compared to the pure PFs. Besides, the modified foams with 1.5% GO/SiO_2 and the particle size of 80 nm have the EMI SE values of 50 dB (equal to more than 99% shielding) in the high-frequency range at 10 mm thickness. This may be attributed to the increasing cell–matrix interface with the introduction of nanoparticles into the matrix, which leads to the enhancement of the cell density. Thus, the electromagnetic waves are more reflected and scattered by the cell–matrix interfaces in the foams with high density. Moreover, the porous structure with the lower the transmission coefficient and the tiny pore size in the synthesized foams leads to the greater attenuating of electromagnetic waves.

5 Conclusion

This review is mainly focused on an overview of the improvement of mechanical properties and the flame retardant properties of nano silica-reinforced phenolic foams. The mechanical properties of phenolic foams strongly depend on their microstructure such as cell size distribution, cell wall thickness, and mean cell size. The addition of nanoparticles usually leads to an increase in the cell density and narrowest cell size distribution. Moreover, the SiO_2 nanoparticles with good hydrophilic can well disperse in phenolic resin and help to improve the cell structure. In regards to mechanical properties, silica nanoparticles have unique mechanical strength. The combination of the inorganic materials with the PFs is a promising method to improve their mechanical properties, which are obtained from the synergy among the components. The large quantities of active hydroxyl groups on the silica nanoparticle surface and the formation of a strong chemical bond between nano particle and polymer matrix. Silica nanoparticles can act as a modifier and bridge between each part of the resin matrix and thus the formation of the crosslinked network structure which enhance the mechanical properties of reinforced foams. Moreover, the presence of additive agents such as silica nanoparticles can significantly affect the thermal conductivity of foams, as well. For instance, 2 wt% nano silica-reinforced PF has reduced the thermal conductivity which can be explained by forming an insulating silica layer on the polymer surface and strong interfacial interaction between silica and foam, which lead to the protection of the foam interior. Moreover, the flame retardant properties, pulverization ratio and electromagnetic interference (EMI) shielding of nano silica-reinforced phenolic foams have been reviewed. Generally, all modified foams have the pulverization ratios lower than that of the pure PFs. This is probably due to the better cell morphologies of reinforced PFs than that of pure PFs. The EMI shielding performance of modified foams enhances compared to the pure PFs. The increase in cell–matrix interface with the introduction of nanoparticles into the matrix can lead to the enhancement of the cell density. Thus, the electromagnetic waves are more reflected and scattered by the cell–matrix interfaces in the foams with high density.

References

1. Kickelbick G (2003) Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale. Prog Polym Sci 28:83–114
2. Sorensen CM, Klabunde KJ (2001) Nanoscale materials in Chemistry. Inc New York, NJ, pp 169–221
3. Wang Z, Pinnavaia TJ (1998) Nanolayer reinforcement of elastomeric polyurethane. Chem Mater 10:3769–3771
4. Drexled KE (1986) Engines of creation: the coming era of nanotechnology
5. Zeng QH, Wang DZ, Yu AB, Lu GQ (2002) Synthesis of polymer–montmorillonite nanocomposites by in situ intercalative polymerization. Nanotechnology 13:549
6. Oja PK, Nanosiliko A (2013) Nanosilica-reinforced polymer composites. Mater Technol 47:285–293
7. Hamdani S, Longuet C, Perrin D et al (2009) Flame retardancy of silicone-based materials. Polym Degrad Stab 94:465–495
8. Preghenella M, Pegoretti A, Migliaresi C (2005) Thermo-mechanical characterization of fumed silica-epoxy nanocomposites. Polymer (Guildf) 46:12065–12072
9. Kang Y, Chen X, Song S et al (2012) Friction and wear behavior of nanosilica-filled epoxy resin composite coatings. Appl Surf Sci 258:6384–6390
10. Jajam KC, Tippur HV (2012) Quasi-static and dynamic fracture behavior of particulate polymer composites: a study of nano-vs. micro-size filler and loading-rate effects. Compos Part B Eng 43:3467–3481
11. Lin L-Y, Kim D-E (2011) Tribological properties of polymer/silica composite coatings for microsystems applications. Tribol Int 44:1926–1931
12. Tang L, Cheng J (2013) Nonporous silica nanoparticles for nanomedicine application. Nano Today 8:290–312
13. Periadurai T, Vijayakumar CT, Balasubramanian M (2010) Thermal decomposition and flame retardant behaviour of SiO2-phenolic nanocomposite. J Anal Appl Pyrolysis 89:244–249
14. Yang F, Nelson GL (2004) PMMA/silica nanocomposite studies: synthesis and properties. J Appl Polym Sci 91:3844–3850
15. Wang Y, Zhao Q, Han N et al (2015) Mesoporous silica nanoparticles in drug delivery and biomedical applications. Nanomedicine Nanotechnology Biol Med 11:313–327
16. Rao KS, El-Hami K, Kodaki T et al (2005) A novel method for synthesis of silica nanoparticles. J Colloid Interface Sci 289:125–131
17. Sinha RK, Sridhar K, Purohit R, Malviya RK (2019) Effect of nano SiO2 on properties of natural fiber reinforced epoxy hybrid composite: a review. Mater Today Proc 26:3183–3186
18. Krishnamoorti R, Vaia RA (2007) Polymer nanocomposites. J Polym Sci Part B Polym Phys 45:3252–3256
19. Bresson G, Ahmadi-Sénichault A, Caty O et al (2016) Thermographic and tomographic methods for tridimensional characterization of thermal transfer in silica/phenolic composites. Compos Part B Eng 104:71–79
20. Antunes M, Velasco JI (2014) Polymer-carbon nanotube nanocomposite foams. Polymer nanotube nanocomposites synthesis, properties and applications. Wiley, pp 279–332
21. Antunes M, Gedler G, Velasco JI (2013) Multifunctional nanocomposite foams based on polypropylene with carbon nanofillers. J Cell Plast 49:259–279
22. Laguna-Gutierrez E, Saiz-Arroyo C, Velasco JI, Rodriguez-Perez MA (2016) Low density polyethylene/silica nanocomposite foams. Relationship between chemical composition, particle dispersion, cellular structure and physical properties. Eur Polym J 81:173–185
23. Ibeh CC, Bubacz M (2008) Current trends in nanocomposite foams. J Cell Plast 44:493–515
24. Saiz-Arroyo C, Rodríguez-Pérez MÁ, Velasco JI, de Saja JA (2013) Influence of foaming process on the structure–properties relationship of foamed LDPE/silica nanocomposites. Compos Part B Eng 48:40–50
25. Lei S, Guo Q, Shi J, Liu L (2010) Preparation of phenolic-based carbon foam with controllable pore structure and high compressive strength. Carbon 48:2644–2646

26. Shen H, Lavoie AJ, Nutt SR (2003) Enhanced peel resistance of fiber reinforced phenolic foams. Compos Part A Appl Sci Manuf 34:941–948
27. Long H, Wang W, Li T, Ru H (2017) Hierarchically bimodal mesoporous silica fibers as building units for silica monolith with trimodal porous architecture. Ceram Int 43:2174–2181
28. Rodríguez F, Jaroniec M, López BL, Wickramaratne NP (2016) Aqueous synthesis of bimodal mesoporous carbons and carbon-silica mesostructures under basic conditions. Microporous Mesoporous Mater 226:299–308
29. Pilato L (2013) Phenolic resins: 100 Years and still going strong. React Funct Polym 73:270–277
30. Shah M, Fawcett D, Sharma S et al (2015) Green synthesis of metallic nanoparticles via biological entities. Materials 8:7278–7308
31. Ye L, Zhang Y, Song C et al (2017) A simple sol-gel method to prepare superhydrophilic silica coatings. Mater Lett 188:316–318
32. Mohanpuria P, Rana NK, Yadav SK (2008) Biosynthesis of nanoparticles: technological concepts and future applications. J Nanoparticle Res 10:507–517
33. Li Q, Chen L, Zhang J et al (2015) Enhanced mechanical properties, thermal stability of phenolic-formaldehyde foam/silica nanocomposites via in situ polymerization. Polym Eng Sci 55:2783–2793
34. Yuan J, Zhang Y, Wang Z (2015) Phenolic foams toughened with crosslinked poly (n-butyl acrylate)/silica core-shell nanocomposite particles. J Appl Polym Sci 132:1–8
35. Luo X, Yu K, Qian K (2018) Morphologies and compression performance of graphene oxide/SiO2 modified phenolic foam. High Perform Polym 30:803–811
36. Sui X, Wang Z (2013) Flame-retardant and mechanical properties of phenolic foams toughened with polyethylene glycol phosphates. Polym Adv Technol 24:593–599
37. Li X, Wang Z, Wu L (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. Rsc Adv 5:99907–99913
38. Bernal MM, Pardo-Alonso S, Solórzano E et al (2014) Effect of carbon nanofillers on flexible polyurethane foaming from a chemical and physical perspective. Rsc Adv 4:20761–20768
39. Yang C, Zhuang Z, Yang Z (2014) Pulverized polyurethane foam particles reinforced rigid polyurethane foam and phenolic foam. J Appl Polym Sci 131
40. Song SA, Lee Y, Kim YS, Kim SS (2017) Mechanical and thermal properties of carbon foam derived from phenolic foam reinforced with composite particles. Compos Struct 173:1–8
41. Zhuang ZH, He B, Yang ZG (2010) Preparation and characterisation of phenolic foam/HTAB-ATP nanocomposites. Plast rubber Compos 39:460–464
42. Rangari VK, Hassan TA, Zhou Y et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 103:308–314
43. Auad ML, Zhao L, Shen H et al (2007) Flammability properties and mechanical performance of epoxy modified phenolic foams. J Appl Polym Sci 104:1399–1407
44. Del Saz-Orozco B, Oliet M, Alonso MV et al (2012) Formulation optimization of unreinforced and lignin nanoparticle-reinforced phenolic foams using an analysis of variance approach. Compos Sci Technol 72:667–674
45. Wolfrum J, Ehrenstein GW (1999) Interdependence between the curing, structure, and the mechanical properties of phenolic resins. J Appl Polym Sci 74:3173–3185
46. de Carvalho G, Pimenta JA, dos Santos WN, Frollini E (2003) Phenolic and lignophenolic closed cells foams: Thermal conductivity and other properties. Polym Plast Technol Eng 42:605–626
47. Rojo E, Oliet M, Alonso MV et al (2014) Mechanical and interfacial properties of phenolic composites reinforced with treated cellulose fibers. Polym Eng Sci 54:2228–2238
48. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Lignin particle-and wood flour-reinforced phenolic foams: Friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos Part B Eng 80:154–161
49. Pizzi A, Celzard A, Fierro V, Tondi G (2012) Chemistry, morphology, microtomography and activation of natural and carbonized tannin foams for different applications. In: Macromolecular symposia. Wiley Online Library, bll 100–111

50. Guo Y, Hu L, Bo C et al (2018) Mechanical property of lignin-modified phenolic foam enhanced by nano-SiO 2 via a novel method. Chem Pap 72:763–767
51. Yang F, Nelson GL (2006) Polymer/silica nanocomposites prepared via extrusion. Polym Adv Technol 17:320–326
52. Wang R, Zhuo D, Weng Z et al (2015) A novel nanosilica/graphene oxide hybrid and its flame retarding epoxy resin with simultaneously improved mechanical, thermal conductivity, and dielectric properties. J Mater Chem A 3:9826–9836
53. Yang H, Wang X, Yu B et al (2013) A novel polyurethane prepolymer as toughening agent: Preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 128:2720–2728
54. Yang H, Yu Z, Wu P et al (2018) Electromagnetic interference shielding effectiveness of microcellular polyimide/in situ thermally reduced graphene oxide/carbon nanotubes nanocomposites. Appl Surf Sci 434:318–325
55. Zeng Y, Luo X, Yu K, Qian K (2019) EMI shielding performance of phenolic-based carbon foam modified with GO/SiO2 hybrid nanomaterials. Chem Phys Lett 715:166–172

Chapter 15
Synthesis of Bio-/lignin-Based Phenolic Foams for Insulation and Floral Applications

Hongwei Li, Bing Li, Zhongshun Yuan, Yongsheng Zhang, and Chunbao Charles Xu

1 Introduction

Phenolic foams are commonly used as insulation or floral materials [1, 2]. Phenolic foams typically contain closed-cell foams and open-cell foams. Closed-cell phenolic foams are generally applied as insulation polymer in military, civil, and marine fields due to the low thermal conductivity, high flame resistance, and low toxicity [2]. Open-cell phenolic foams, on the other hand, are usually used as floral foams, absorbent materials, and growing media for planting [1].

Specifically, phenolic foams are prepared by mixing two fractions: (1) a foamable phenolic resin, a surfactant, a blowing agent, and optional additives, which pre-mix well into a substantially uniform mixture; (2) a curing catalyst with or without a wetting agent. The mixing and reaction create sufficient heat for curing reaction to vaporize the blowing agent and form wetting property of the polymer, thereby foaming the mixture with or without water absorption property. This mixture finally becomes a phenolic foam after annealing with outside heating to prevent the heat release from inside of the mixture [3]. The main ingredient that influences foam properties is discussed as follows.

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1.1 Foamable Phenol Formaldehyde Resins

Phenolic resins are typically classified into novolaks and resoles [4]. Novolaks are synthesized by the reaction of formaldehyde and phenol under strong acidic conditions at a formaldehyde-to-phenol molar ratio (F/P) < 1.0. While resoles are conventionally alkaline-catalyzed phenol formaldehyde resins with an F/P > 1.0. Both types of resins are foamable resins that can be used for the preparation of phenolic foam. However, novolaks are usually solids at room temperature thus it is difficult to handle in the foaming process [1]. Therefore, liquid resole resins are predominantly used in the manufacture of phenolic foams.

Conventional phenol formaldehyde (PF) resoles are generally prepared by the reaction of formaldehyde and phenol under F/P of 1.5–2.5:1 under alkaline conditions [5]. Specifically, formaldehyde reacts with phenol and produces methylolphenols, which continues reacting with formaldehyde to form di-methylolphenols and even tri-methylolphenols. Meanwhile, these methylol phenols react among each other through condensation reaction before concluding a high molecular weight resole. A lower F/P ratio tends to produce foam with poor mechanical properties because the phenolic resin prepared contains insufficient condensed methylol phenols hence lower viscosity resulting in cell wall rupturing when making foam structure [6]. However, if the F/P ratio is too high, the viscosity of phenolic resins increases significantly, and the resin becomes semi-liquid or solid, leading to difficulties for homogeneous foaming mixture, making the phenolic foam preparation process more challengeable.

As shown in Fig. 1, the first part reaction of phenol, formaldehyde, and base catalyst, at around 70 °C, typically forms a mixture with a thick reddish-brown tacky color, which is rich in two substances containing *o*-methylol phenol and *p*-methylol phenol. The rate of the base-catalyzed reaction can be accelerated with

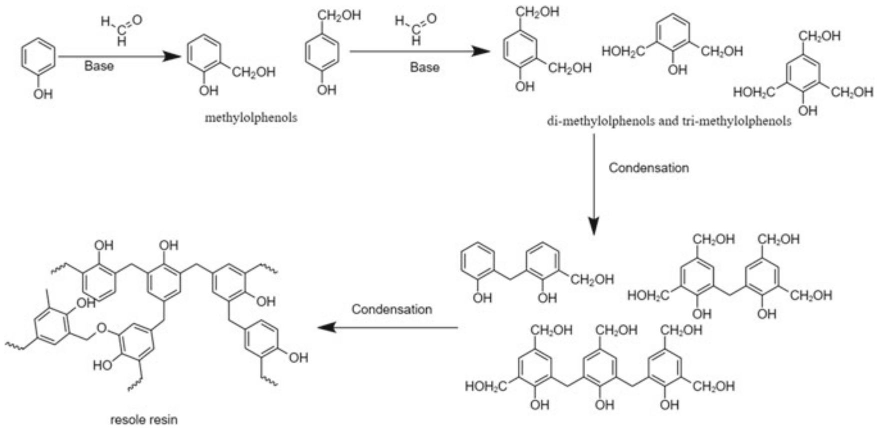

Fig. 1 Schematic chemical reactions of phenol formaldehyde resole resin

the spontaneously increasing of pH in the mixture, which could reach a maximum of pH 10. At this stage, phenoxide anion (C6H5O −) is formed, activating sites 2, 4, and 6 of the aromatic ring, following by the further reaction with formaldehyde, resulting in the formation of 2,4-dimethylolphenol, 2,6-dimethylolphenol, and 2,4,6-trimethylolphenol, respectively. Being thermosets, these methylol phenols crosslink with one another to form methyl and methylene ether bridges through condensation reactions at 120 °C, associated with the elimination of water molecules. At this stage, the resin is a three-dimensional network and typically of polymerized phenolic resole resins [7].

In addition, a preferred M_w (weight average molecular weight) range, M_n(number average molecular weight) range, and PDI (polydispersity index) range for foamable phenolic resoles are reported by the literature to be 700–2000 g/mol, 300 to 700 g/mol, and 1.8–2.6, respectively [5]. Typically, solid content of foamable phenolic resoles is in the range of 60%–99% by weight and initial viscosity of the resoles ranges from about 0.2 Pa·s to 300 Pa·s at 25 °C, more preferably, 0.4–25 Pa·s for easiest handling [8, 9].

In order to control the molecular weight and viscosity of foamable phenolic resoles, an acidic inhibitor is commonly added into the produced alkaline-based foamable phenolic resoles to stop further condensation reactions [6]. Typically, the pH of the resoles is neutralized and adjusted to a value in the range of 5.0–7.0. The commonly used acids include inorganic acid such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4), and organic acids such as acetic acid, oxalic acid, and formic acid, etc. It is reported that organic acids or weak acids are more benefitable than inorganic acids or strong acids in the preparation of foamable phenolic resoles [8]. Thus, acetic acid, formic acid, and oxalic acid are widely used as neutralizing acids for adjusting pH value of phenolic resoles.

1.2 Blowing Agent

The role of a blowing agent in the preparation of phenolic foams is to generate gas so the foaming mixture rises resulting in foam with cellular structure and various densities. During the foaming process by using the foamable phenolic resole under acid curing catalysts, the blowing agent absorbs the heat generated by the curing reactions and evaporates in the foaming mixture, resulting in expansion of the foaming mixture [4].

Conventionally, blowing agents such as fluorocarbons are popularly used in the preparation of phenolic foams. These polyhalogenated saturated fluorocarbon blowing agents produce a fine uniform closed-cell foam structure due to their relatively low heat transfer coefficient and excellent solubility in the foaming system, hence the improvement of thermal insulation performance and mechanical properties of the obtained phenolic foams [10]. However, the use of these fluorinated-based blowing agents decreased in recent years, due to the environmental concerns such as global warming and ozone depletion.

Instead, some low boiling point compounds are considered as environmentally acceptable blowing agents for phenolic foam preparation, mainly including hydrocarbons, ethers, and ketones. Commonly used hydrocarbon blowing agents include pentanes, hexanes, and other derivatives containing unsaturated $C = C$ bonds [4]. In the phenolic foam preparation, one blowing agent or a mixture of several compounds can be used. Some studies implied that mixtures of two or even more blowing agents were more effective for controlling foam cell size and structure hence the formation of a desirable phenolic foam [11]. For instance, Sudan et al. applied a mixture as blowing agent containing 25% n-hexane and 75% n-pentane and produced a satisfactory phenolic foam with closed-cell structure [12]. Raderet et al. found that the most reasonable addition of liquid volatile compounds as blowing agents was in the range from 1 to 15% (based on the weight of the phenolic resole) [13].

1.3 Surfactants

Surfactants are virtually used for regulation of cell structure and size. Surfactants play an important role in lowering foaming mixture surface tension and providing an interface between the extremely polar foamable phenol resole and the non-polar blowing agent such as pentane during the foaming process until gelation stage of the resole matrix occurs [4]. The foaming process usually conducted under acidic conditions thus the preferred surfactants are undoubtedly acid stable or non-hydrolysable and can mix well with water as well [14]. Commonly used surfactants in the preparation of phenolic foams include silicone-based polymers such as siloxane-oxyalkylene copolymers and DC-193, and “Tween” series such as Tween 20 and Tween 80. The amount of these surfactants used in the foaming system is typically at the range from 0.5% to 5% by weight of the foamable phenolic resole [9]. An insufficient addition of surfactant leads to failure of stabilizing the foam, while an excessive dosage of surfactant is not only wasteful but may also result in cell coalescence. This phenomenon is due to the relatively low surface tension of foaming mixture interface hence a larger cell structure, causing collapse of the phenolic foam structure.

1.4 Curing Agent

A curing agent is a chemical used during curing process and reacts with other ingredients to produce a polymer material with tridimensional network by cross-linking of polymer chains. The commonly used curing agents for the preparation of phenolic foams are both organic and inorganic acids. An acid catalyst is essential as a curing agent for the condensation of the phenolic resin during the foaming process. Phenolic foamable resins can be cross-linked through condensation reactions due to their free methylol groups in the structure under acidic conditions. During the foaming process, once a curing agent is added to the foamable resin containing a blowing agent, it will initiate exothermic reactions that generate highly enough heat for the evaporation of blowing agent, hence the rise and curing of the foaming mixture.

Typical organic acids used as curing catalysts in the manufacture of phenolic foams include toluene sulfonic acid, benzene sulfonic acid, xylene sulfonic acid, phenol sulfonic acid to name a few, while conventionally inorganic acids are hydrochloric acid, sulfuric acid, phosphoric acid, etc. [5, 15]. Organic acids are generally preferable for the preparation of phenolic foams, while inorganic acids especially hydrochloric acid are commonly known for the unavoidable severe corrosion issues associated with their remaining in the phenolic foams [4], so post-treatment of the foam is usually conducted to reduce the corrosivity of phenolic foam by using a neutralizing gas such as ammonia [1]. The most commonly used aromatic sulfonic acids in the manufacture of phenolic foams include xylene/toluene sulfonic acids and phenol sulfonic acid, which are believed to take part in the curing reaction with phenolic prepolymers and thus decreasing the acidity of the foam [1]. A high amount of curing catalyst might lead to so fast curing speed that results in insufficient time for foam growing, uneven distribution of the foaming mixture, and hence a poor foam structure. Whereas, a relatively low addition of curing agent would cause collapse of foam body due to too long of curing time. Therefore, these curing acids are generally added in a range of 10–25% of the total amount of the resin to achieve commercially acceptable curing time [5]. It has demonstrated that a mixture of two or more curing acids especially modified catalysts can be more effective for the production of phenolic foams [16, 17]. For instance, an aromatic acid and glycol mixture modified by incorporating of a dihydric phenol produced PF foams with improved moisture resistance [18].

A literature work has reported that the addition of a suitable amount of curing agent emulsifier could enhance not only the efficiency of catalyst to improve the homogenization of the foaming mixture but also the even dispersity of temperature to provide more consistent cell wall pressures among different cells, resulting in a desirable cell size [13]. Generally, the suitable emulsifiers include glycerine, higher molecular oils such as mineral oil, propylene glycol, ethylene glycol, etc. The preferable amounts of the curing agent emulsifier were found in the range of 1%–10% based on the total weight of the foamable phenolic mixture [13].

1.5 Wetting Agent

Phenolic foams are commonly used as supports in floral industry such as for cut flowers. These phenolic foams typically have good water attention and rapid wettability. Wetting agents are used in floral foam production to reduce the surface tension of water to allow it to spread and penetrate drops from exterior to interior of a foam structure, which could help increase water absorption capacity of phenolic foams [19].

There are a variety of chemicals that can be used as wetting agents, including polyoxyethylene sorbitan mono palmitate such as “Tween” series, Texapon N-25, polyglycol ether, alkyl phenoxy polyoxyethylene ethanol such as “Igepal”, sodium laureth sulfate, etc. [19–22]. These substances can help foam increase permeability for gas and ability to absorb liquids such as water rapidly.

The amount of a wetting agent in phenolic foaming system is usually under 5%. It was reported by Weissenfels and Engels et al. that 0%–1.2% addition of sodium laureth sulfate resulted in phenolic foams with not only increased water absorption capacity from 0 to 92% but also decreased closed cell content from 80% to only 10%. In addition, the foams prepared with sodium laureth sulfate exhibited good water retention ranging from 28% to 83.3% [21]. Smithers et al. observed that 4.4% of the wetting agent was excellent for maintaining the flower, and excessive addition was detrimental to the growth of plant while less than that might not give as complete water penetration into the foam structure [22]. Moreover, Basso et al. found that the cut flower stem remained upright and looked fresh with employment of a wetting agent in foam specimens compared with the classic foam prepared without a wetting agent [20].

1.6 Fillers

Phenolic foam has some serious drawbacks leading to severely limited structural applications [23, 24]. The high friability and brittleness of foam especially with lower foam density have resulted in serious problems such as debonding in foam structures, vulnerability to damage during transportation, and pollution of dustexfoliated from foam body.

There are mainly two ways for reinforcement of phenolic foams: chemical reinforcing and physical reinforcing. Chemical reinforcement is often conducted by reacting polymers containing active groups such as polyethyleneglycol [25, 26], dicarboxyl acid [27], polyether [28], amine-terminated polyether [29], polyurethane prepolymer [30], and cardinal [31] with the backbone of the phenolic resin by chemical reactions. Physical reinforcing of PF foam is mainly achieved through blending the resin with natural or synthetic materials, such as fibers [24, 32–34], rubbers [35], and fillers such as carbon black, mica, asbestos, talc, bamboo, and wood flours [24]. The addition of a finely ground filler in the foamable mixture could significantly improve the texture uniformity and homogeneity of foam body, but it can also lead to an increase in the foam density [24].

It was reported in many studies that the addition of fibers such as glass and aramid successfully increased the mechanical properties of phenolic foams [24, 36–38]. As shown in Fig. 2, phenolic foam reinforced with aramid fiber as a flexible fiber exhibited unique fracture behavior that was distinct from other prepared phenolic foams. The other foam with glass fiber, however, exhibited a significantly brittle rupture and a sharply drop of stress at the maximum loading. The foam reinforced by aramid fiber, instead showed a smooth decline in stress after the loading peak [39]. It was also observed that the shear testing of aramid fiber-reinforced foam specimens did not completely break despite strains of up to 50%. A similar observation for peel resistance of phenolic foam prepared with aramid fiber was reported by Shen et al.

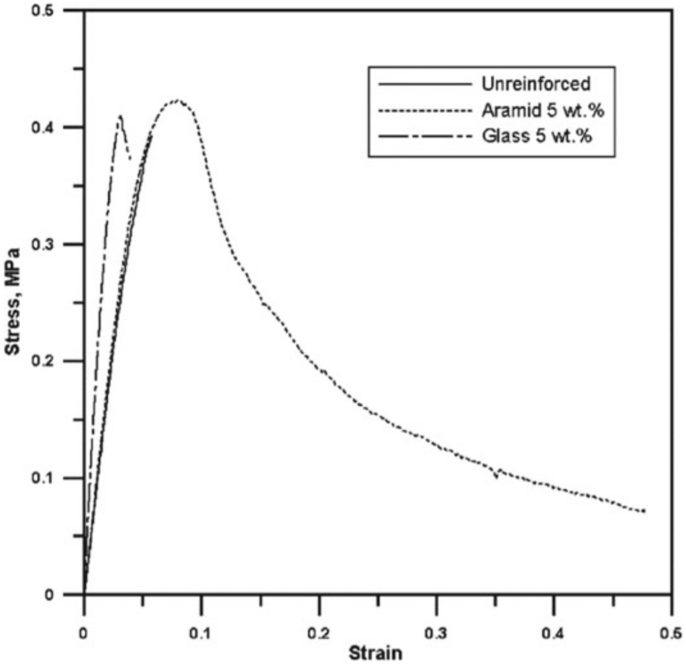

Fig. 2 Typical shear stress–strain relationships of phenolic foams. Shear plane and loading direction both are parallel to the foam rise direction. Reprinted with permission from Ref. [39]

[24]. Additionally, glass fiber reinforcement for phenolic foams was found to be the most effective way to improve foam physical properties including high mechanical performance, light weight, and excellent fire resistance. For instance, short chopped glass fibers introduced into phenolic foams led to an increase in foam toughness, strength, and dimensional stability [24, 39].

Bio-based materials such as wood fibers [40], cellulose fibers [41], and lignin [42] have also been used as environmentally friendly reinforcing materials for the performance improvement of polymeric materials. For example, addition of 1.5–8.5% wood flour produced phenolic foams with a density ranging from 120 kg/m^3 to 160 kg/m^3. It demonstrated that the reinforced phenolic foams showed better mechanical properties, e.g., increasing the compressive modulus and compressive strength of the foams by 30% and 54%, respectively, in compared with the unmodified PF foam [32].

2 Bio-Based Phenolic Foams

Nowadays, lignocellulosic biomass or lignin has been found to be a potential source of bio-phenols (derived from lignin) that can substitute partially or all petroleum-based phenol for the preparation of bio-based phenol formaldehyde resins [23, 43–45].

2.1 *Production of Bio-Phenols*

2.1.1 Biomass Feedstock

Lignocellulosic biomass mainly consists of three components (cellulose, hemicellulose, and lignin), and small quantities of organic extractives and mineral matters. In a woody biomass, lignin usually accounts for around 25–35 wt.% of the organic components [46]. Lignin is an amorphous natural polymer with similar phenolic hydroxyl groups as phenol. It is primarily composed of three main phenyl-propane units as its building block, i.e., syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H)), connected primarily through ether (mainly β-O-4 and α-O-4)and carbon–carbon linkages [44]. Therefore, lignocellulosic biomass or lignin can be a potential source of bio-phenolic compounds (bio-phenols) that can substitute petroleum-based phenol in the synthesis of phenolic resins [23, 43, 45].

A variety of lignocellulosic biomasses have been used for bio-phenol production. Table 1 shows the feedstocks that were used for production of bio-phenols. The most common types of feedstocks include woody biomass such as sawdust, forest

Table 1 Feedstock commonly used for production of bio-phenols

Feedstock	Bio-phenol	Refs.
White pine sawdust	Extracted lignin	[23]
Cornstalk	Liquefied bio-oil	[45]
Radiata pine sawdust	Liquefied with phenol	[47]
Wood waste	Liquefied with phenol	[48, 49]
Bagasse	Extracted lignin	[50]
Birch wood	Liquefied bio-oil	[51]
	Liquefied with phenol	[52]
Pine/birch wood sawdust	Liquefied bio-oil	[53]
Corn bran	Liquefied with phenol	[54]
Wastepaper	Liquefied with phenol	[55, 56]
Organosolv lignin	Direct use	[57, 58]
Lignosulfonate	Direct use	[59]
Spruce wood	Liquefied with phenol	[60]

residues, agricultural residues including bagasse, industrial residues such as waste papers and lignin.

2.1.2 Technologies for Production of Bio-Phenols

In the past few decades, numerous organosolv extraction and thermochemical conversion technologies were investigated for separation and production of bio-chemicals from biomass feedstock. Among these, extraction, phenolation, and direct liquefaction of lignocellulosic biomass have been extensively studied and they are considered as promising methods for the production of low molecular weight bio-phenols [23, 45, 48–50, 61].

Extraction of Lignin

Lignin can be separated from biomass by various methods, of which the organosolv process, or also known as delignification method with organic solvent, was considered as an environmental-friendly and cost-efficient method [62]. As described previously, lignin is an amorphous three-dimensional phenyl-propanol polymer linked mainly by ether and condensed C–C linkages [23]. Upon biological or thermochemical degradation, it could decompose to mono-phenolic products, as potential substitutes for pure phenol in the phenolic resins industry.

Wang et al. obtained bio-phenol by organosolv extraction of white pine sawdust in hot-compressed mixed solvents of ethanol and water. It was found that the reaction temperature had significant effect on the yield of lignin, and at 180 °C lignin yield reached 26%, which was almost the same as the total lignin content in the raw material. For lignin extraction, ethanol–water mixed solvents performed better than pure solvent of either ethanol or water, suggesting synergistic effects of these two solvents. The lignin yield was maximized in the mixed solvent at 50%–50% ethanol–water composition. Under the optimal conditions: 180 °C with ethanol–water mixed solvent (50:50, v/v), the lignin obtained has a purity of 83% with weight-average molecular weight (M_w) of 1150 g/mole. The extracted lignin was used for the preparation of bio-phenol formaldehyde (BPF) resins, and the obtained lignin could replace up to 75% petroleum-based phenol, although the thermal stability of the BPF resins reduced when the phenol replacement was over 50% [23].

Except for organosolv extraction, lignin could also be extracted in sodium hydroxide solution where it underwent extensive breaking of ether linkages such as α-aryl and β-aryl bonds [63]. Khan et al. extracted lignin from bagasse with 5 mol/L sodium hydroxide solution at 100 °C for 7 h, and the obtained black liquor was neutralized with sulfuric acid for precipitation of lignin products, resulting in 63.6% yield of lignin [50]. The same study also demonstrated that the bagasse-derived lignin could substitute 50% of petroleum-based phenol in preparation of bio-based phenolic adhesives. The prepared bio-resins showed comparable structure and thermal properties to a neat PF resin as a control.

Phenolation

Phenolation is a very effective modification method through which lignocellulosic biomass feedstock is treated with phenol assisted by an acid catalyst, leading to phenolated oils with combined phenol [64–66]. Specifically, in the presence of a strong inorganic acid, phenol could react with degraded lignin side chains to form phenolic compounds with increased reactivity, while hemicellulose and cellulose-derived sugars could form hydroxymethyl furfural compounds that could condense with phenol and formaldehyde by methylene bridges [65, 67].

Wang et al. found that bio-phenol yield in water solvent was much lower than that with pure phenol or phenol–water mixed solvents. Even though the bio-phenol yield was the highest in pure phenol solvent, it was preferable using phenol–water (1:4, wt/wt) mixed solvent for the phenolation of cornstalk, as the obtained bio-phenol could replace a high % of petroleum-based phenolin preparation of BPF resins [68].

However, the main limitation of the phenolation process is that it requires a large solvent-to-biomass ratio, at least 3:1 or 5:1 (w/w), in order to achieve a satisfactory phenolation efficiency. Therefore, the bio-based phenol substitution ratio in the phenolic resins was normally lower than 30% [64, 68].

Direct Liquefaction

Direct liquefaction was commonly conducted in the presence of water, organic solvents, or supercritical fluids [61, 69]. One of the most common solvents is water, because it is not only environmental-friendly and least pricey but also intrinsically contained in biomass. Meanwhile, organic solvents such as alcohols have also demonstrated highly effective in the biomass liquefaction process. Furthermore, it has been found that mixed-solvent systems of water-alcohol performed better than a monosolvent [70, 71] to achieve a higher yield of bio-phenols for phenolic resins synthesis.

Xu and Etcheverry et al. performed direct liquefaction of Jack pine powder in sub/super-critical ethanol and obtained a bio-oil product rich in phenolic compounds at a high yield of 63% [72]. Meanwhile, Xu's group reported direct liquefaction of white pine sawdust in alcohol or water or their mixed solvents. It was observed that the most efficient liquefaction conditions were: in mixed-solvent of ethanol–water (1/1, wt/wt) at 300 °C for 15 min, leading to 65% oil yield with biomass conversion > 95% [71]. Moreover, Xu's group successfully de-polymerized organosolv lignin by using the same liquefaction solvent (ethanol–water, 1/1, wt/wt), achieving the highest yield (92%) of de-polymerized lignin with M_w of 1193 g/mole. The lignin product known as bio-oil was then used as a substitute for petroleum-based phenol in the production of BPF resins. The bio-resins prepared with a phenol substitution ratio up to 75% showed mechanical and thermal properties comparable to the commercial PF resins but with reduced free formaldehyde content [73].

Although the direct liquefaction processes mentioned above using alcohol or water or their mixtures as solvents are effective, these processes are commonly conducted under high operating pressures and temperatures (300–350 °C). Thus, it leads to negative impact on industrial applications of the direct liquefaction processes when taking economical and practical factors into account. Therefore, it is desirable to develop direct liquefaction methods under relatively low operating conditions for the sake of energy-efficient and cost-effective production of bio-phenols. Mahmood et al. successfully depolymerized hydrolysis lignin (HL) in water–ethanol mixed-solvents at 250 °C for 1 h, leading to a high yield of depolymerized HL (DHL), around 71%. The obtained DHL had a Mw ~1000 g/mole with suitable phenolic (215 mg KOH/g) and aliphatic (227.1 mg KOH/g) hydroxyl numbers [74]. Furthermore, high-boiling alcohols such as ethylene glycol and glycerol were also used for the liquefaction of lignocellulosic biomass at a lower operating at temperature (150–280 °C) and low pressure [75]. Biomass liquefaction in high-boiling alcohols involves biomass dehydration, volatilization of alcoholic solvents, and biomass alcoholysis [76]. It was found that the introduction of glycerol/polyethylene glycol solvent (1/9, g/g) inliquefaction of woody biomass resulted in up to 95% liquid yields and the liquefied bio-oil has a hydroxyl number of 216 mgKOH/g [77]. This liquefied biomass in high-boiling alcohol has been commonly investigated and used as a bio-polyol for the production of polyurethane materials [74, 78], whereas there is no research reported thus far on production of bio-phenol formaldehyde (BPF) foams using bio-phenols from liquefaction of biomass.

2.2 *Preparation of BPF Foams*

For the preparation of BPF foams, a foamable BPF resin is mixed with one or more blowing agent, surfactant, curing catalyst, and/or a wetting agent. The foaming ingredients are typically different for different applications of foams.

2.2.1 BPF Insulation Foams

PFfoam is a promising material for insulation of transport vehicles and buildings due to its superb fire-resistant and smoke properties and less toxicity (FST) with a high ignition temperature around 595 °C [79, 80]. Owing to the better sustainability and potential cost benefits, BPF insulation foams have gained increasing popularity. Table 2 summarized several successful trials using bio-phenols for the preparation of foamable BPF resins under various phenol/formaldehyde molar ratio (P/F) for production of BPF insulation foams.

BPF Insulation Foams with Lignin

Hu et al. synthesized a foamable resole using bio-phenols (30% replacement) derived from modified lignosulfonate. The foamable resole (prepared at P/F molar ratio

Table 2 BPF foams for insulation applications

Bio-phenol	P/Fmolar ratio	Other ingredients in foam recipe	Ref
Kraft lignin	1:1–1:1.6	Pentane and hexanes, p-toluene sulfonic acid, polyether polysiloxane-copolymer, distilled water, and glycerol	[11]
Liquefied wood	NG[a]	Poly(ethylene ether) of sorbitan monopalmitate, hydrochloric acid, diisopropyl ether	[47]
Phenolated lingo sulfate	1:1.7	Sulphuric acid, N-pentane, Tween-80	[81]
Depolymerized hydrolysis lignin	1:1–1:1.3	Polyether polysiloxane-copolymer, hexanes, p-toluene sulfonic acid, distilled water, glycerol	[82]
Liquefied bamboo	NG[a]	Tween-80, p-toluene sulfonic acid, phosphoric acid, n-pentane	[83]

[a] NG: Not given

of 1/1.7), together with other ingredients containing N-pentane (blowing agent), Tween-80 surfactant, and sulphuric acid (curing catalyst) were mixed and achieved a BPF foam. The BPF foam sample exhibited desired foam density in the range from 50 kg/m^3 to 55 kg/m^3 and mechanical property comparable to that of a conventional PF foam [59]. Similarly, Hu et al. [81] prepared BPF foam samples with phenolated lignosulfonate with 20% phenol replacement. TGA results showed that the weight loss of the BPF foam sample was 9.6% lower than the conventional PF foam sample, suggesting improved thermal stability of the obtained BPF foam. More interestingly, the BPF foam exhibited almost 9-time increase in compressive modulus and sevenfold increase in compressive strength, compared with the conventional PF foam sample.

Hydrolysis lignin, a by-product from hardwood fractionation, could also be used for BPF foam preparation. Li et al. reported that hydrolysis lignin was successfully used in the preparation of BPF insulation foams after having been depolymerized under a mild temperature (200–300 °C) condition [82]. The depolymerized hydrolysis lignin (DHL) replaced 30% and 50% phenol for the preparation of BPF foamable resin. BPF insulation foams were prepared with the foamable resins and other additives including a surfactant, a blowing agent, a curing catalyst, etc. It was found that BPF foam prepared with the resin at 30% phenol replacement has a similar foam density value of 40 kg/m^3 as a neat PF foam, while BPF resins with 50% phenol replacement resulted in a foam of a much greater density (108 kg/m^3). It is also observed by Li et al. [82] that the foam sample with a higher density shows a much higher compressive strength (0.405 MPa) than that (0.152 MPa) of the meat PF foam. Figure 3 shows optical and SEM images of the typical foams collected by Li et al. [82]. As presented in the figure, the foam samples became darker as the percentage of

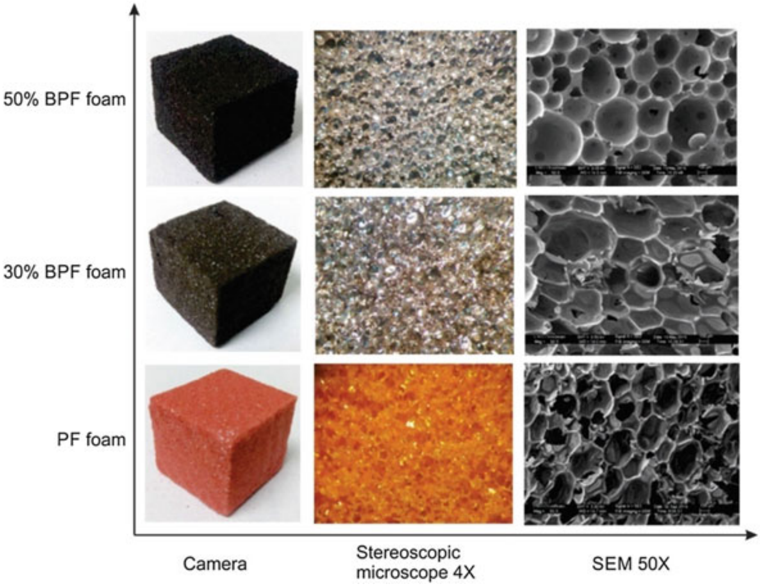

Fig. 3 Optical photos and SEM of BPF insulation foams with depolymerized hydrolysis lignin. Reprinted with permission from Ref. [82]

bio-phenols in the resin increased from 30 to 50%. Also, the cells of all foam samples are mostly closed although some perforations are present in some foams. It was also observed that the BPF foams at 30% and 50% phenol replacement display a cell size of 435 µm and 308 µm, respectively, while the reference PF foam has an average cell size of 308 µm. Furthermore, thermal analysis results showed that thermal conductivity of all BPF foam samples is in the range of 0.033–0.040 W/(m·K) that meets the requirements as insulation foams [84], and the BPF foams were thermally stable up to 200 °C.

Unmodified kraft lignin was used for production of BPF foams for insulation materials for construction of buildings by Li et al. [11]. In this study, raw and unmodified kraft lignin replaced 10–50% phenol in the foamable BPF resin and the obtained foam samples exhibited relatively low density in the range of 20 kg/m^3 to 80 kg/m^3, excellent compressive strength up to 1 MPa, and low thermal conductivity below 0.048 W/(m · K). In addition, the effects of bio-phenol replacement ratio and the blowing agent composition (mixture of pentane and hexanes) on the BPF foam structure were compared and are presented in Fig. 4. As shown in the figure, under the same bio-phenol replacement, the foam cell structure is different when changing composition of the blowing agent. Generally, the pore size decreased and became more uniform while increasing of hexane content in the blowing agent. Interestingly, when the bio-phenol substitution level reached 40–50%, the amounts of large pores reduced, compared with the BPF foam at 30% phenol replacement (Fig. 4).

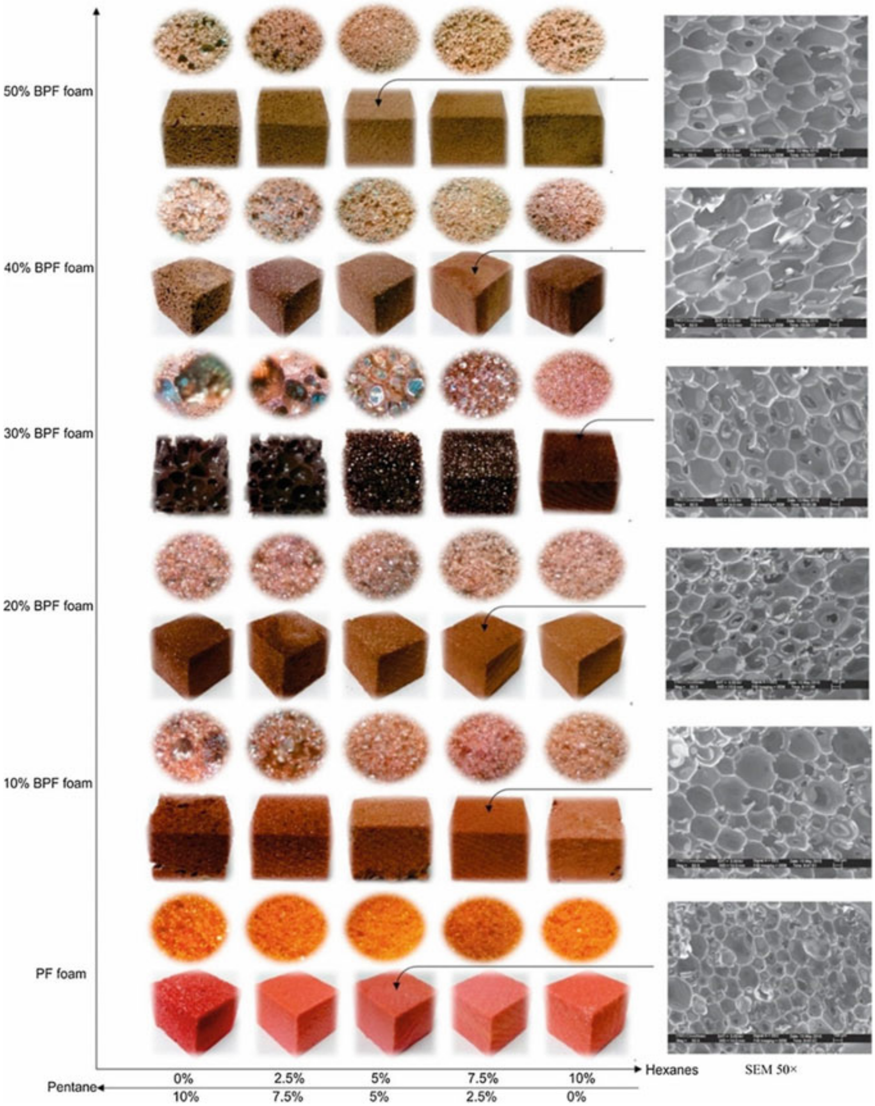

Fig. 4 Foam structure of BPF foams prepared with various amount of unmodified kraft lignin and blowing agent. Reprinted with permission from Ref.[11]

BPF Insulation Foams with Liquefied Biomass

Liquefied woody biomass has been used as a bio-phenol for the preparation of BPF foams through a rapid liquefaction process by Lee et al. [85]. The obtained liquefied product had a M_w in the range of 400 g/mole–600 g/mole. Using the same liquefaction conditions, Lee et al. [47] prepared bio-phenol by using liquefied phenolated radiata

Table 3 Viscosity of foamable resin mixtures containing conventional PF resin and various % BPF resin[47]

BPF resin (%)	Conventional PF resin (%)	Viscosity of the foamable resin mixture (Pa · s)[a]
0	100	50
20	80	80
40	60	100
60	40	200
80	20	350
100	0	540

[a] Measured at 25 °C and 60% RH

pine sawdust and also investigated the influence of bio-phenol on the mechanical properties of the obtained BPF foams with the substitution ratio of bio-phenol to phenol ranging from 0 to 100%. BPF foams were successfully prepared with the bio-phenol-based resin, combined with diisopropyl ether as a suitable foaming agent (with a relatively higher boiling temperature), hydrochloric acid as a catalyst and poly (ethylene ether) of sorbitan monopalmitate as a surfactant. The conventional PF foam prepared with 0% bio-phenol has a density as low as17 kg/m^3, compressive strength and elastic modulus of 49 kPa and 1.47 MPa, respectively. However, it was found difficult to prepare a low-density foam with BPF resins such as liquefied pine sawdust-based resins at 50–100% phenol replacement due to the high viscosity of the bio-phenols and the BPF resins (as shown in Table 3), leading to the high density of foam sample in the range of 19–66 kg/m^3, accounting for their better mechanical properties than those of the conventional PF foam due to their higher density.

Bamboo powder was also successfully used in the preparation of phenolic foams [83]. The raw material was liquefied using phenol as the solvent with 3 wt.% acidic catalyst and then reacted with formaldehyde under an alkaline condition to obtain foamable BPF resin with viscosity in the range of 2–4 Pa·s. BPF foams were then prepared with the foamable BPF resin, tween-80, p-toluenesulfonic acid, phosphoric acid, and n-pentane. The density of the prepared foam samples was in the range of 20–82 kg/m^3 with excellent compressive strength up to 0.57 MPa.

2.2.2 Preparation of BPF Floral Foams

Various synthetic materials including PF foams have been used as plant growth media sustaining seed germination and plant growth. PF floral foams, as pictured in Fig. 5, are open-cell hydrophilic absorbent materials used as support of floral arrangements with cut flowers, while these materials could absorb and retain water so that the flowers remain fresh for a longer time [86]. PF or UF foamed products are commonly used as floral foams for cut flowers in the floral industry for many years.

PF floral forms can be produced by mixing a foamable PF resin with soluble additives including a surfactant, a foaming agent, a catalyst and a wetting agent.

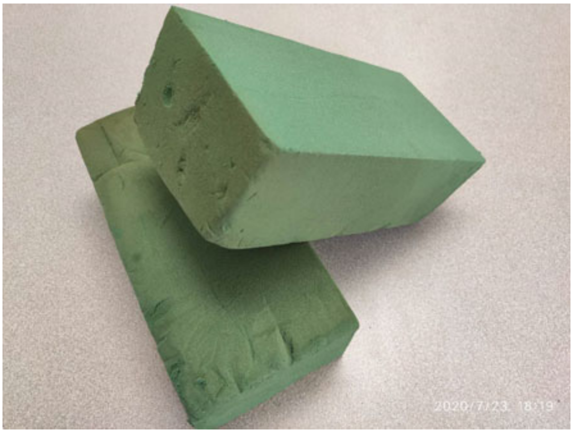

Fig. 5 Photo of a commercial PF floral foam

Foamable PF resins generally have viscosity of 1–2 Pa·s. A wetting agent (such as Tween 40 or Tween 60) is essential for a floral foam for achieving significant water absorption capacity by carrying water into the interior of the foam pores [21, 22]. Pilato produced a PF foam product by mixing a foamable PF resin using pentane and phenol sulfonic acid as the blowing or foaming agent and catalyst, respectively, Texapon N-25 as a wetting agent in the amount of around 3–4 wt.%. The PF floral foam prepared has a density of 16–32 kg/m^3 and can be used as supports for cut flowers [19].

Due to the non-biodegradability of the PF/UF floral foams, the used floral foams are disposed either by incineration or landfills, which pose environmental issues. As such, in recent decades, there is a growing need for biodegradable floral foam materials. However, to the best of our knowledge, very few researches were reported on producing bio-phenolic foams using lignin or lignocellulosic biomass except for a few reports as introduced below. Lignin particles were used as a filler in the preparation of hydrophilic urea–formaldehyde (UF) foams [87]. Pan et al. adopted lignin as a stabilizer to establish a stable Pickering oil-in-water emulsion, and the prepared UF foam was successfully used as a new adsorbent for absorption of three typical phenolic compounds. However, the lignin content in the foam sample was only 3–7.5%. Zhang et al. [88] reported a bio-PF floral foam using phenolated crop residues (replacing less than 10–20% phenol due to the poor reactivity of the bio-phenol) and Basso et al. reported bio-phenolic floral foams using tannin [20]. Bio-phenolic foams are believed to have more biodegradability than the petroleum-based PF/UF foams [88]. It is thus economically and environmentally significant to develop new and BPF floral foams with bio-phenols derived from forestry and agricultural residues to substitute over 50% of phenol. The most challenging part of preparation of BPF floral phenolic foams at a high phenol replacement ratio would be to ensure the foams have a sufficient open cell content to attain enough water absorption capacity and rate.

3 Market Evaluation of Phenolic Insulation and Floral Foams

The phenolic insulation foam market has a promising future with opportunities especially in construction and building, and HVAC systems globally. This market is expected to attain a value of $1.6 billion by 2024 with a compound annual growth rate (CAGR) of 6.6% in the period of 2019 to 2024. The phenolic insulation foam market size is expected to grow rapidly mainly driving by the growth of buildings in the construction with energy efficiency, rising concerns related to GHG (greenhouse gas) emissions, and excellent insulation efficiency of phenolic foam [89].

The flower spending was estimated to be $ 35.2 billion in 2017, and it is expected to reach $44.4 billion in 2023 [90]. According to Entrepreneur India [91], the floral foam market size was USD 17.58 billion in 2016 and is projected to reach USD 22.39 billion by 2021, at a CAGR of 4.95% from 2016 to 2021. The world's largest floral foam Products maker and supplier, FloraCraft®, realized a 60% increase in revenue in 2015 and had a portfolio of 3,500 SKUs in floral foam production in any 1 year [92].

4 Challenges and Future Work of Preparing BPF Foams

Even though BPF foams have been successfully prepared with lignin and lignocellulosic biomass, there are still some challenges before commercialization. Table 4 summarized some current challenges for the preparation of BPF foams and presented some potential solutions for improvement. First and foremost, the bio-phenol replacement in the BPF foams is very low. Until now, the bio-phenol replacement ratio is up to 50%, which was only achieved with lignin-based bio-phenols [11] but cannot be higher due to their high viscosity, while the ratio is much lower when using biomass-derived bio-phenol due to their lower reactivities [32]. In order to solve this problem, further researches should be focused on improving the chemical and physical properties of bio-phenols, for example, by oxypropylation which can not only improve the reactivity but also decrease the viscosity of bio-phenols. Second, phenolic foams prepared with bio-phenols usually exhibit uneven and irregular cell distribution [11, 20]. This is mainly caused by the incompatibility of ingredients between blowing

Table 4 Current challenges of preparing BPF foams and potential solutions

Current challenges	Potential solutions
Bio-phenol replacement lower than 50%	Improve reactivity of bio-phenols by oxypropylation reaction
Uneven and irregular cell structure	Apply both non-ionic and anionic surfactants into the foaming system
Relatively low water retention capacity	Introduce a cell opener and modify the dosage

agent and surfactant. This could be solved by introducing both non-ionic and anionic surfactants into the foaming system and obtain a suitable proportion of each surfactant. Last but not least, except open cell structure, water retention capacity is also very important for a floral foam. Specifically, a high open cell content ensures a good aeration, but an excess in porous structure induces a low water retention capacity in foams [20]. To solve this problem, a suitable cell opener is needed, and the amount should be determined in the near future work.

5 Conclusion

Ingredients such as phenolic resin, blowing agent, surfactant, wetting, and curing agent play an important role in the properties of phenolic foams. Bio-phenols derived from renewable sources (lignin or lignocellulosic biomass) can potentially replace phenol in preparation of phenolic foams for insultation and floral foams. The available conversion methods for producing bio-phenols include lignin extraction, phenolation of biomass with neat phenol, and direct liquefaction of lignocellulosic biomass or lignin. Insulation foams have been successfully prepared using various types of lignin products (i.e., lignosulfonate, hydrolysis lignin, and kraft lignin) and liquefied lignocellulosic biomass such as woody biomass. The bio-phenol formaldehyde (BPF) foams exhibited uniform structure, relatively low density, and comparable mechanical properties to conventional PF foams. Additionally, bio-phenols are also a potential source for preparing floral foams although not much researches have been reported to date. The most challenging part of the preparation of BPF floral phenolic foams at a high phenol replacement ratio would be to ensure the foams have a sufficient open-cell content to attain enough high-water absorption capacity and rate.

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References

1. Klempner D, Sendijarevic V, Aseeva RM (2004) Handbook of polymeric foams and foam technology, 2nd edn. Hanser Publishers, Munich Cincinnati
2. Amen-Chen C, Pakdel H, Roy C (2001) Production of monomeric phenols by thermochemical conversion of biomass: a review. Bioresour Technol 79:277–299
3. Calvo-Flores FG, Dobado JA (2010) Lignin as renewable raw material. Chem Sus Chem 3:1227–1235
4. Gardziella A, Pilato L, Knop A (2000) Phenolic resins: chemistry, applications, standardization, safety, and ecology, 2nd edn. Springer, Berlin Okumura, New York

5. Coppock V, Zeggelaar R, Takahashi H et al (2007) A phenolic foam, European Patent, 1922356B1.
6. Carlson JD, Kifer EW, Wojtyna VJ et al (1985) Phenol formaldehyde resoles for making phenolic foam. US Patent, 4539338 A
7. GardziellaA PilatoL, Knop A (2000) Phenolic resins: chemistry, appplications, standardization, safety and ecology, 2nd edn. Springer, New York, USA
8. Okumura S, Awano S, Kinoshita M et al (1992) Foamable phenolic resin composition and process for preparation thereof. US Patent, 5137931 A
9. Gusmer FE (1981) Method of preparing closed cell phenol-aldehyde foam and the closed cell foam thus prepared. US Patent, 4303758 A
10. Alessandro WD (1968) Foaming phenol-formaldehyde resins with fluorocarbons. US Patent, 3389094
11. Li B, Yuan Z, Schmidt J et al (2019) New foaming formulations for production of bio-phenol formaldehyde foams using raw kraft lignin. Eur Polym J 111:1–10
12. Sudan K (1991) Semi-flexible or flexible phenolic foam composition. US Patent, 5057546 A
13. Rader SL (2000) Method for making a closed-cell phenolic resin foam, foamable composition, and closed-cell phenolic resin foam. US Patent, 6013689 A
14. Beale JH, Moss EK (1981) Phenolic foam and surfactant useful therein. US Patent, 4247413 A
15. QuarlesJohn RW, Baumann A (1967) Phenolic foam compositions. US Patent, 3298973 A
16. Meunier PJ, Lunt J, Macpherson EJ (1991) Modified phenolic foam catalysts and method. US Patent, 4883824 A
17. Simic D, Zupancic H-U, Cherubim M (1977) Process for the production of flame-resistant phenolic resin foam plastics. US Patent, 4001148 A
18. Lunt J, MacPherson EJ, Meunier PJ (1986) Closed cell phenolic foam. US Patent, 4883824 A
19. Pilato LA (1980) Floral foam product and method of producing the same which incorporates a flower preservative and a bacteriocide. US Patent, 4225679 A
20. Basso M, Pizzi A, Al-Marzouki F et al (2016) Horticultural/hydroponics and floral natural foams from tannins. Ind Crops Prod 87:177–181
21. Weissenfels F, Engels W (1984) Method for the preparation of highly absorbent phenolic resin foams. US Patent, 4426462 A
22. Smithers V (1956) Absorbent material for floral arrangements. US Patent, 2753277 A
23. Wang M, Xu CC, Leitch M (2009) Synthesis of phenol-formaldehyde resol resins using organosolv pine lignins. Eur Polym J 45:3380–3388
24. Shen H, Lavoie AJ, Nutt SR (2003) Enhanced peel resistance of fiber reinforced phenolic foams. Compos Part A Appl Sci Manuf 34:941–948
25. Hu XM, Wang DM, Cheng WM et al (2013) Effect of polyethylene glycol on the mechanical property, microstructure, thermal stability, and flame resistance of phenol-urea-formaldehyde foams. J Mater Sci 49:1556–1565
26. Wang FY, Ma CCM, Wu WJ (2001) Kinetic parameters of thermal degradation of polyethylene glycol-toughened novolac-type phenolic resin. J Appl Polym Sci 80:188–196
27. Choi MH, Byun HY, Chung IJ (2002) The effect of chain length of flexible diacid on morphology and mechanical property of modified phenolic resin. Polymer 43:4437–4444
28. Yang H, Wang X, Yuan H et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 19:1–10
29. Samanta BC, Maity T, Dalai S et al (2006) Amine-terminated poly(ethylene glycol) benzoate (ATPEGB)-modified epoxy: mechanical and thermal properties. J Adhes Sci Technol 20:491–502
30. Yang H, Wang X, Yu B et al (2013) A novel polyurethane prepolymer as toughening agent: Preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 128:2720–2728
31. Cardona F, Kin-Tak AL, Fedrigo J (2012) Novel phenolic resins with improved mechanical and toughness properties. J Appl Polym Sci 123:2131–2139

32. Del Saz-Orozco B, Alonso MV, Oliet M et al (2014) Effects of formulation variables on density, compressive mechanical properties and morphology of wood flour-reinforced phenolic foams. Compos B Eng 56:546–552
33. Wei D, Li D, Zhang L et al (2012) Study on phenolic resin foam modified by montmorillonite and carbon fibers. Procedia Eng 27:374–383
34. Huang Y, Wang C, Huang Y et al (2010) Enhancing specific strength and stiffness of phenolic microsphere syntactic foams through carbon fiber reinforcement. Polym Compos 31:256–262
35. Kaynak C, Cagatay O (2006) Rubber toughening of phenolic resin by using nitrile rubber and amino silane. Polym Test 25:296–305
36. Desai A, Auad ML, Shen H et al (2008) Mechanical behavior of hybrid composite phenolic foam. J Cell Plast 44:15–36
37. Ben G, Shoji A (2005) Pultrusion techniques and evaluations of sandwich beam using phenolic foam composite. Adv Compos Mater 14:277–288
38. Ben G, Shoji A, Souma M (2005) Development and evaluation of FRP sandwich beams containing glass fibers into phenolic foam core. In: Thomsen O, Bozhevolnaya E, Lyckegaard A (eds) Sandwich structures 7: Advancing with sandwich structures and materials. Springer, Dordrecht, pp 1007–1016
39. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Compos Part A 34:899–906
40. Guigo N, Mija A, Vincent L et al (2010) Eco-friendly composite resins based on renewable biomass resources: Polyfurfuryl alcohol/lignin thermosets. Eur Polym J 46:1016–1023
41. Abdelmouleh M, Boufi S, Belgacem M et al (2007) Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading. Compos Sci Technol 67:1627–1639
42. Park Y, Doherty WOS, Halley PJ (2008) Developing lignin-based resin coatings and composites. Ind Crops Prod 27:163–167
43. Cheng S, D'cruz I, Yuan Z, et al (2011) Use of biocrude derived from woody biomass to substitute phenol at a high-substitution level for the production of biobased phenolic resol resins. J Appl Polym Sci 121:2743–2751
44. Ramires EC, Megiatto JD, Gardrat C et al (2010) Valorization of an industrial organosolv-sugarcane bagasse lignin: characterization and use as a matrix in biobased composites reinforced with sisal fibers. Energy Fuels 107:612–621
45. Wang M, Xu CC, Leitch M (2009) Synthesis of phenolic resol resins using cornstalk-derived bio-oil produced by direct liquefaction in hot-compressed phenol-water. J Ind Eng Chem 15:870–875
46. Kleinert M, Barth T (2008) Phenols from Lignin. Chem Eng Technol 31:736–745
47. Lee S, Teramoto Y, Shiraishi N (2002) Resol-type phenolic resin from liquefied phenolated wood and its application to phenolic foam. J Appl Polym Sci 84:468–472
48. Alma MH, Altay BM, Shiraishi N (2001) Cocondensation of NaOH-catalyzed liquefied wood wastes, phenol, and formaldehyde for the production of resol-type adhesives. Ind Eng Chem Res 40:5036–5039
49. Lee S, Ohkita T (2003) Rapid wood liquefaction by supercritical phenol. Wood Sci Technol 37:29–38
50. Khan MA, Ashraf SM, Malhotra VP (2004) Development and characterization of a wood adhesive using bagasse lignin. Int J Adhes Adhes 24:485–493
51. Maldas D, Shiraishi N (1997) Liquefaction of biomass in the presence of phenol and H_2O using alkalies and salts as the catalyst. Biomass Bioenergy 12:273–279
52. Alma M, Yoshioka M, Yao Y et al (1998) Preparation of sulfuric acid-catalyzed phenolated wood resin. Wood Sci Technol 32:297–308
53. Shiraishi N, Hse C (2000) Liquefaction of the used creosote-treated wood in the presence of phenol and its application to phenolic resin. In: Wood Aashesives 2000, session 3B: advances in wood Ashesive formulations, pp 259–266
54. Lee S (2003) Phenolic resol resin from phenolated corn bran and its characteristics. J Appl Polym Sci 87:1365–1370

55. Lee S, Teramoto Y, Shiraishi N (2002) Acid-catalyzed liquefaction of waste paper in the presence of phenol and its application to Novolak-type phenolic resin. J Appl Polym Sci 83:1473–1481
56. Ono H, Yamada T, Hatano Y et al (1996) Adhesives from waste paper by means of phenolation. J Adhes 59:135–145
57. Çetin NS, Özmen N (2002) Use of organosolv lignin in phenol–formaldehyde resins for particleboard production: I. Organosolv lignin modified resins. Int J Adhes Adhes 22:477–480
58. Çetin NS, Özmen N (2002) Use of organosolv lignin in phenol-formaldehyde resins for particleboard production: II. Particleboard production and properties. Int J Adhes Adhes 22:481–486
59. Hu L, Zhou Y, Liu R et al (2013) Synthesis of foaming resol resin modified with oxidatively degraded lignosulfonate. Ind Crops Prod 44:364–366
60. Alonso Ma V, Oliet M, Rodríguez F et al (2005) Modification of ammonium lignosulfonate by phenolation for use in phenolic resins. Bioresour Technol 96:1013–1018
61. Wang Y, Wang H, Lin H et al (2013) Effects of solvents and catalysts in liquefaction of pinewood sawdust for the production of bio-oil. Biomass Bioenergy 59:158–167
62. Barros A, Dhanabalan A, Constantino CJ et al (1999) Langmuir monolayers of lignins obtained with different isolation methods. Thin Solid Films 354:215–221
63. Chakar FS, Ragauskas AJ (2004) Review of current and future softwood kraft lignin process chemistry. Ind Crops Prod 20:131–141
64. Jiang X, Liu J, Du X et al (2018) Phenolation to improve lignin reactivity toward thermosets application. ACS Sustain Chem Eng 6:5504–5512
65. Alma MH, Basturk MA (2006) Liquefaction of grapevine cane (Vitis vinisera L.) waste and its application to phenol-formaldehyde type adhesive. Ind Crops Prod 24:171–176
66. Funaoka M, Matsubara M, Seki N et al (1995) Conversion of native lignin to a highly phenolic functional polymer and its separation from lignocellulosics. Biotechnol Bioeng 46:545–552
67. Yamada T, Ono H (2001) Characterization of the products resulting from ethylene glycol liquefaction of cellulose. J Wood Sci 47:458–464
68. Wang M, Xu CC, Leitch M (2009) Liquefaction of cornstalk in hot-compressed phenol-water medium to phenolic feedstock for the synthesis of phenol-formaldehyde resin. Bioresour Technol 100:2305–2307
69. Ramsurn H, Gupta RB (2012) Production of biocrude from biomass by acidic subcritical water followed by alkaline supercritical water two-step liquefaction. Energy Fuels 26:2365–2375
70. Feng S, Yuan Z, Leitch M et al (2014) Hydrothermal liquefaction of barks into bio-crude-Effects of species and ash content/composition. Fuel 116:214–220
71. Cheng S, D'cruz I, Wang M, et al (2010) Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents. Energy Fuels 24:4659–4667
72. Xu C, Etcheverry T (2008) Hydro-liquefaction of woody biomass in sub- and super-critical ethanol with iron-based catalysts. Fuel 87:335–345
73. Cheng S, Yuan Z, Leitch M et al (2013) Highly efficient de-polymerization of organosolv lignin using a catalytic hydrothermal process and production of phenolic resins/adhesives with the depolymerized lignin as a substitute for phenol at a high substitution ratio. Ind Crops Prod 44:315–322
74. Mahmood N, Yuan Z, Schmidt J et al (2015) Hydrolytic depolymerization of hydrolysis lignin: effects of catalysts and solvents. Bioresour Technol 190:416–419
75. Rezzoug SA, Capart R (2003) Assessment of wood liquefaction in acidified ethylene glycol using experimental design methodology. Energy Convers Manag 44:781–792
76. Zou X, Qin T, Huang L et al (2009) Mechanisms and main regularities of biomass liquefaction with alcoholic solvents. Energy Fuels 23:5213–5218
77. Kurimoto Y, Tamura Y (1999) Species effects on wood-liquefaction in polyhydric alcohols. Holzforschung 53:617–622
78. Kurimoto Y, Takeda M, Koizumi A (2000) Mechanical properties of polyurethane films prepared from liquefied wood with polymeric MDI. Bioresour Technol 74:151–157

79. Kim J, Lee JH, Song TH (2012) Vacuum insulation properties of phenolic foam. Int J Heat Mass Transf 55:5343–5349
80. Knop A, Pilato L (1985) Phenolic resins: chemistry, applications, and performance: future directions. Springer, Berlin
81. Hu L, Zhou Y, Zhang M et al (2012) Characterization and properties of a lignosulfonate-based phenolic foam. BioResources 7:554–564
82. Li B, Wang Y, Mahmood N et al (2017) Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin. Ind Crops Prod 97:409–416
83. Zhang J, Du M (2013) Bamboo powder liquefaction and resinification: application on the phenolic foam. Mater Sci Forum 743–744:306–311
84. Li H, Feng S, Yuan Z et al (2017) Highly efficient liquefaction of wheat straw for the production of bio-polyols and bio-based polyurethane foams. Ind Crops Prod 109:426–433
85. Lee S, Yoshioka M, Shiraishi N (2000) Preparation and properties of phenolated corn bran (CB)/phenol/formaldehyde cocondensed resin. J Appl Polym Sci 77:2901–2907
86. Landrock AH (1995) Handbook of plastic foams: types, properties manufacture and applications. Noyes Publications, New Jersey
87. Pan J, Luo J, Cao J et al (2016) Competitive adsorption of three phenolic compounds to hydrophilic urea-formaldehyde macroporous foams derived from lignin-based Pickering HIPEs template. RSC Adv 6:93894–93904
88. Zhang W, Ma Y, Xu Y et al (2013) Lignocellulosic ethanol residue-based lignin-phenol-formaldehyde resin adhesive. Int J Adhes Adhes 40:11–18
89. Phenolic Insulation Market Report: Trends, Forecast and Competitive Analysis (2020). https://www.lucintel.com/phenolic-insulation-market.aspx. Accessed 16 April 2021
90. FloraCraft invests in growth while remaining rooted in Michigan (2020). https://mibiz.com/sections/manufacturing/floracraft-invests-in-growth-while-remaining-rooted-in-michigan. Accessed 16 April 2021
91. Entrepreneur India (2020). https://www.entrepreneurindia.co/project-and-profile-details/Floral%20Foam%20(Phenolic%20Foam)%20with%20Resin%20Manufacturing. Accessed 20 May 2020
92. How the World's Largest Maker and Supplier of Floral Foam Products Increased Production (2015). https://www.industryweek.com/cloud-computing/article/21966292/how-the-worlds-largest-maker-and-supplier-of-floral-foam-products-increased-production. Accessed 16 April 2021

Chapter 16
Foams in Wood Composites

Ali Shalbafan

1 Introduction

Wood composites (WCs) or wood-based products (WBPs) are general terms describing various types of products produced by a combination of wood elements and adhesives under heat and pressure. It can be used for different applications; from interior to exterior furniture, and from industrial scale to small home project, which enabling more design options without sacrificing structural requirements. Production of wood composites has considerably increased in the world from 66.6 million m^3 (1970) to 408 million m^3 (2018) [1]. The share of wood composites production in various continents in 2018 is illustrated in Fig. 1. As shown, about 60% of WPBs are only produced in Asia (mainly in China), followed by Europe with a 22% production share.

The WBP industries are transforming via recent advancements in adhesives formulations, production technologies accompanied by online control techniques and measuring systems [2–4]. Furthermore, the WBP production is also growing rapidly from both a steadily increasing demand for existing products and an increasing demand for new products to be used in new applications. In this context, the trends such as the production of lightweight furniture made of wood composites and innovations in new coating techniques and materials are expected to drive the furniture market in the forthcoming years [5–7].

The furniture industry is known as the main branch of wood industries, which plays an important role in the world's socio-economic growth [8]. To this end, WBPs used in the furniture application are very important indices affecting further and sustainable development of the industry [9]. Weight reduction of WBPs used for furniture manufacturing is generated much interest in recent years. In general, lightweight furniture has several advantages for both panels and furniture manufacturers, designers,

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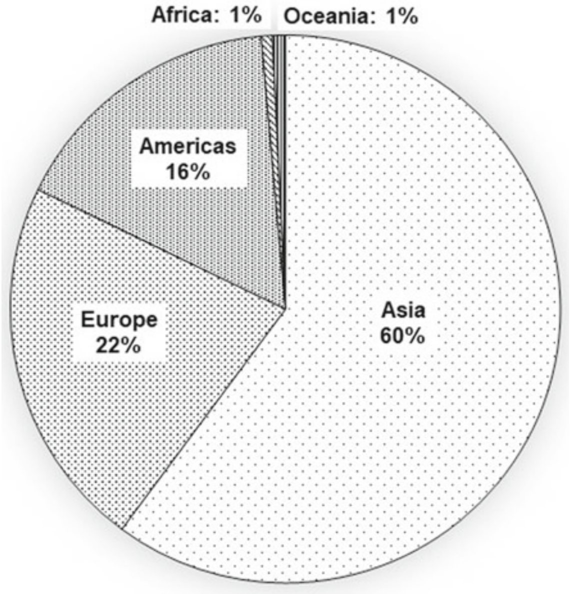

Fig. 1 The share of wood composites' production in various continents [1]

and consumers such as the low weight, high resource efficiency, more flexibility in design (using thick elements with lower weight), easy handling, and lowering both transportation and raw material costs [10–13]. In addition, the availability of raw wood is decreased, which results in increased prices of wood [14]. This is mainly driven by both increasing demand for wood as a renewable energy source and by increasing prices for fossil-based energy. Importantly, concerns about greenhouse gas emissions and a possible future shortage of fossil-based resources are leading to a growing demand for wood as a renewable and green material for energy source [6, 15, 16]. This implies that the WBP industry is confronted with a competition for raw materials and increasing prices for both materials and energy [14]. It is also assumed that the cost for wood biomass and energy will still continue to increase [15]. In this context, the density reduction of WBPs is known as a technological option to decrease the competitiveness of the wood industry with the growing wood energy market while fulfilling the customer demand for lightweight flat-packed furniture [17, 18].

Several concepts were implemented during recent decades to develop lightweight composites used for furniture application. All of these strategies used for the reduction of composite density are categorized into three major groups entitled technology, materials, and sandwich concept [17]. Less compaction of the wood-furnish mat (lightweight fiberboard and dual-density boards) and hollow-tube profile fabrication of composite (tubular boards) are the two technological methods for the reduction of composite weight. There have also been several attempts in the field of materials' selection used to produce lighter boards, e.g., low-density wood species, annual or perennial plants (agriculture residues like maize, sunflower, hemp, etc.), mixing of polymer beads or starch granulates in the board's core layer and foamable adhesives [7, 19, 20]. Nevertheless, all of these techniques have certain restrictions or disadvantages that require resolution. However, multi-layered composites with a lighter core layer than their surface layers, entitled sandwich, can reach remarkable weight reductions and material saving while still meet the industrial requirements [21].

2 Sandwich Composites

Sandwich is a common concept in nature which even has an older history than mankind. In other words, resource efficiency (materials and energy) is a basic principle in nature leading to minimizing the weight [22]. The elder branches of the tree, the bones of humans' skeletons, and the birds' wings are some examples of the sandwich structures with foam-like and honeycomb-like core materials, which are also illustrated in Fig. 2 [23–25]. The materials science and production technologies of sandwich composites have gained an impressive momentum in recent decades. Furthermore, sandwich composites are extensively used in many engineering applications including aerospace, automotive, and furniture due to their lightweight and good mechanical strength [26].

A sandwich panel is a special class of composite products, which is made of a thick and lightweight core to absorb shear stresses covered by two thin and stiff skins to absorb tensile and compression stresses when the composite is under bending forces [21, 22]. Due to the increment of sandwich composite application in the furniture industry, the European Committee for standardization recently defined a sandwich board for furniture as follows (CEN/TS 16,526 [27]): "a laminar composite product consisting of at least two skins positioned on either side of a core, which is

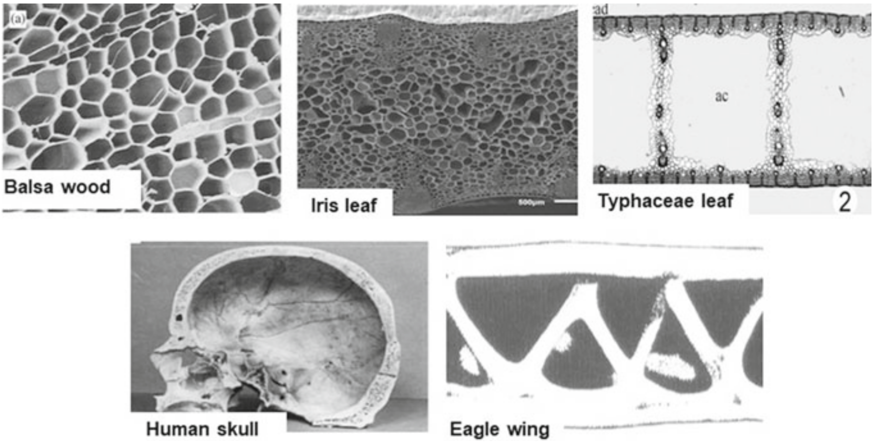

Fig. 2 Some examples of the sandwich concept in nature [23, 28]

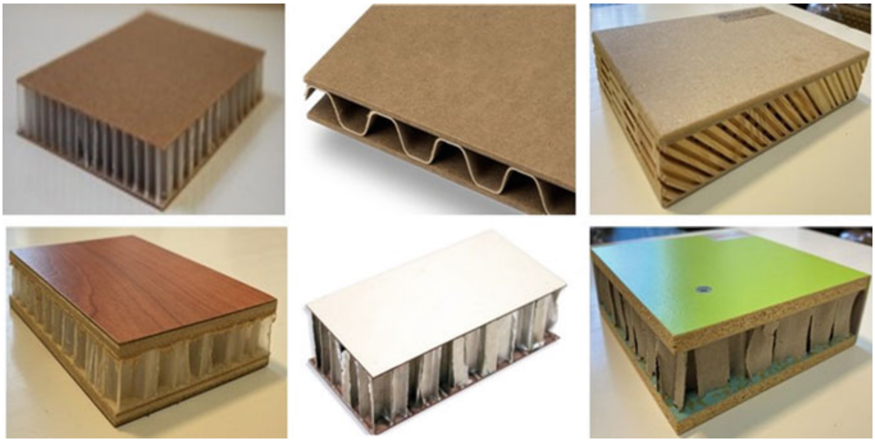

Fig. 3 Some examples of sandwich composites made by non-homogeneous core structure

firmly connected to the skins (e.g., by bonding, by core-generated adhesion) so that the three (or more) components act compositely when under load. Wood or other lignocellulosic materials constitute at least one of the components".

Sandwich composites are presented the required performance comparable to those monolithic composites while still saving weight. The cross-section of a monolithic composite is broken up by inserting a lightweight material as the core layer of sandwich composites [21, 26]. Generally speaking, the core layer of a sandwich (also named cellular solids) can be divided into two major groups; either non-homogeneous or homogeneous structures/materials [28]. The former group contains a honeycomb, a web, or a corrugated structure having adequate shear strength and modulus [17]. There are vast varieties of materials with different strength properties, which can be used for the manufacturing of non-homogeneous core materials such as plastic, metal, paper, and wood. Figure 3 shows some examples of sandwich composites made by non-homogeneous core structures.

Sandwich composites made of paper-based honeycomb were used for several decades in the furniture industry mainly as doors [29]. Notably, the high production cost of honeycomb cores and produced panels often prevented their massive application in lightweight furniture [30]. Although a lot of efforts have been put, from both industries and researchers, into the improvement of production technology of sandwich composites with non-homogeneous cores in the past, but there are still various challenges and drawbacks for their massive applications in the furniture industry. Low mechanical strength, special technologies needed for fitting, edge connections, and edge-banding are some limitations for these types of composites that are due to their hollow structures of the core. In addition, for the standard thicknesses used in the furniture industry, particleboard and medium density fiberboard (MDF) are more preferred than honeycomb panels due to their lower prices. Hence, a great challenge of the recent years in wood-based panel and furniture manufacture was to come up with lightweight concepts for standard thickness range (below 24 mm) [30].

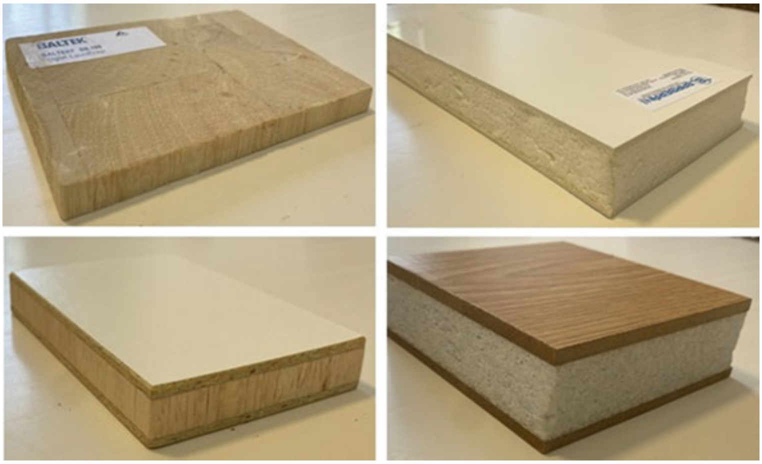

Fig. 4 Some examples of the sandwich composites made by homogeneous core structure

Homogeneous core layers are more preferred due to the lowering difficulties regarding edge-processing, integration of connectors, and fittings difficulties compared with those of non-homogeneous ones. Two major groups of materials can be used as homogeneous core layer: wood strips and foams (Fig. 4). The sandwich made of low-density wood strips as the core layer is typically named block board (also called lumber-core or multi-layered wood products). Here, the narrow (width of about 28–38 mm) side-glued strips of low-density wood species like Balsa (Ochroma lagopus), Cottonwood (Ceiba spp.), Poplar (Populus spp.), or Pine (Pinus spp.) are sandwiched between two thin sheets of veneer or other types of wood-based products (e.g., plywood, particleboard, and fiberboard). Wood and wood-based products are natural and hydrophilic polymer material, their dimensional stability is essentially affected by their swelling and shrinkage with changing moisture content below the fiber saturation point and by thermal expansion [29]. Hence, different dimensional stability of face and core layer materials in block boards have to be considered in final application, which may result in unwanted deformations with changing of moisture content and/or temperature [31].

The second approach to produce homogenous core in sandwich composite is the application of foam. Foam cores are often polymeric; however, metallic and mineral foams can also be used for engineering applications [32]. An overview of different varieties of sandwich composites with homogeneous and non-homogeneous cores and corresponding production processes for manufacturing of foam core panels is illustrated in Fig. 5.

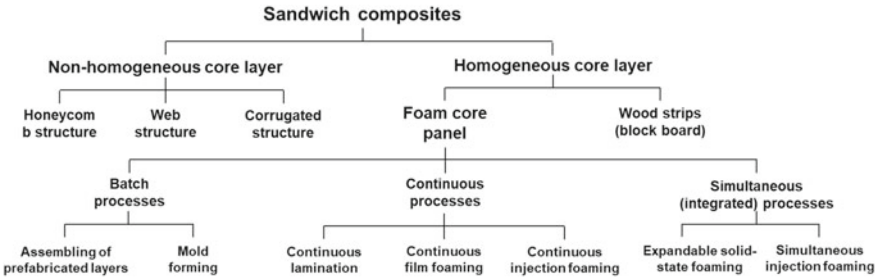

Fig. 5 An overview of different varieties of sandwich composites and corresponding production processes for manufacturing of foam core panels

3 Foam Core Panels

Foam is an object generally described as a dispersion in which a large ratio of gas bubbles by volume is diffused in a liquid, solid, or gel to form open or closed cell structures [33]. In other words, a foam is one made up of interconnected network of solid struts or plates, which form the edges and faces of the cells. Solid foams can be made from polymers, metals, glass, or ceramics [28]. Among all, polymeric foams are the most commercialized kind and have grown as a substantial industry since early of 1960s that almost affects every aspect of human lives [34]. After the polymers are synthesized, the foams are shaped and used for many applications like cushioning, insulation, and absorption properties.

In sandwich structures, the polymeric foams are extensively used as the core materials to produce foam core composites/panels. Two main procedures were mainly described to manufacture foam core panels; discontinuous (batch) processes and continuous processes, which were more described in the following sections. Notably, several new methods were developed or are under development such as simultaneous production processes of foam core panels, which were also described below.

3.1 Discontinuous (Batch) Processes

The basic production of foam core panels was first initiated by batch process where the prefabricated faces and polymeric foams were used. The three layers (two faces and one core layers) were separately glued, assembled together and then putting under pressure and heat, if required depending on the type of resin used [35]. Schematic of the production process steps is presented in Fig. 6. The main advantage of this process is its flexibility regarding the type of materials used as surface and core layers. Almost any type of material existed as a sheet form can be utilized to produce foam core panels by this process [22, 28].

Another batch process to manufacture foam core panels is the mold forming (also named discontinuous injection process) where the mold bottom is covered by the

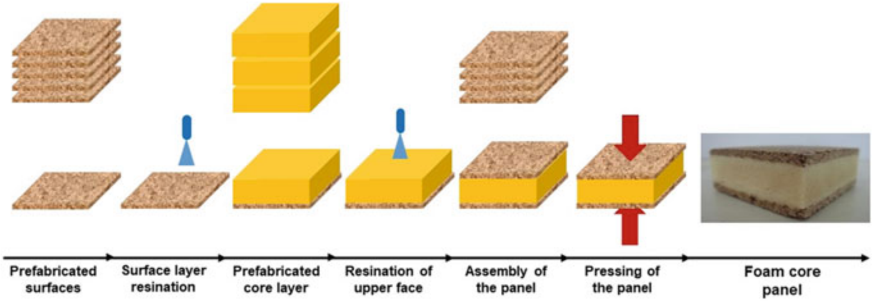

Fig. 6 Production steps of the discontinuous production process

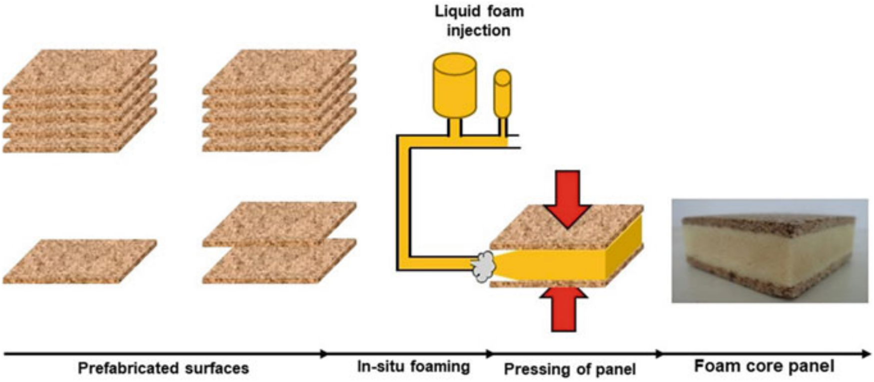

Fig. 7 Production steps of the discontinuous injection process (mold foaming)

lower face layer, and the upper face layer is located in the final position supported by spacers. Then, the required amount of liquid-foam components is injected in between the two prepared surface layers via a nozzle [26]. The production process steps are shown in Fig. 7. The surface layers in this process were still prefabricated while the foam is shaped in-situ in the panel. Here, the application of resin on surface layers is not needed due to in-situ foaming. Although, the production process is rather shorter than previous batch process, but the whole production process can still be relatively slow to stabilize the foam. The main advantage of this process is the possibility to produce complicated shapes of panels for special applications [35].

3.2 Continuous Processes

Continuous processes are gained more and more interests in the wood industry for mass production of wood composites. Several strategies were already developed and are under development for continuous production of foam core panels such as continuous lamination, film foaming, and injection foaming. In all of these processes, the prefabricated surface layers are mostly the coiled up sheets (like thin boards, foils, or impregnated paper) moving in an endless manner to manufacture an endless panels. The main differences between various continuous production processes are back to shaping of their core layer [26, 35]. In continuous lamination, the prefabricated foam sheets are consecutively enclosed between the two surface layers to form an endless product (part A of Fig. 8). In film foaming process, an expandable polymeric film

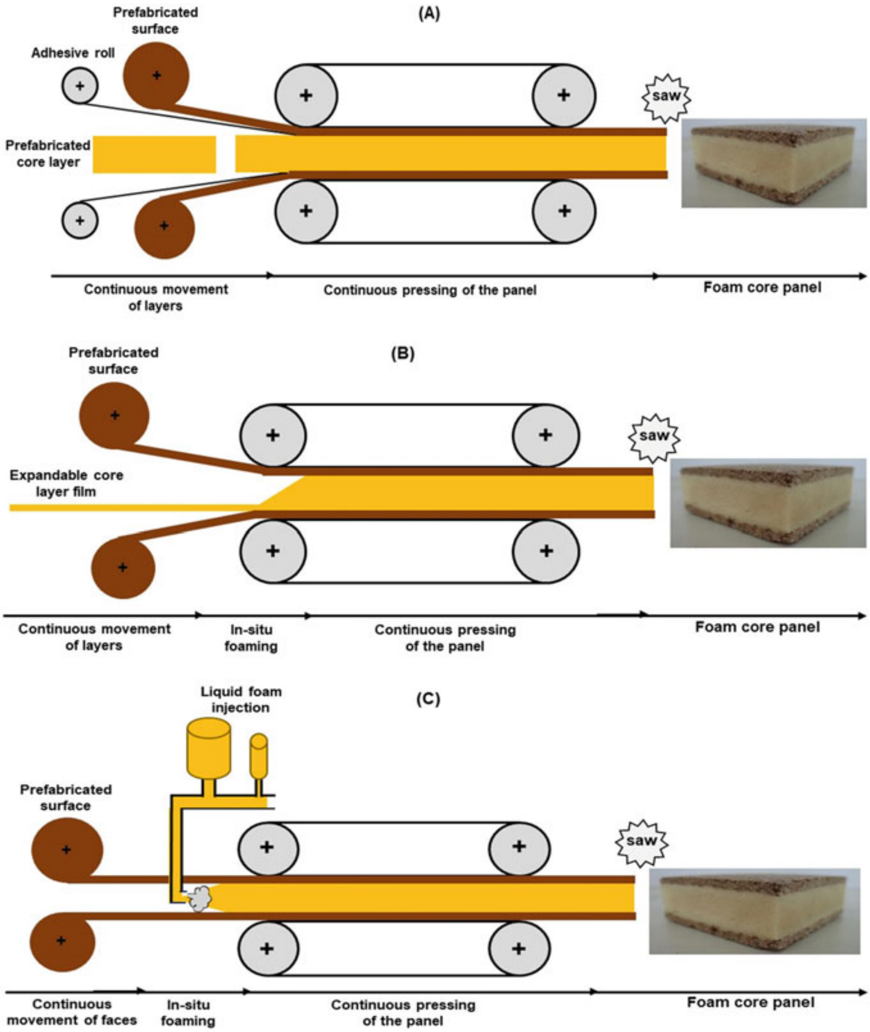

Fig. 8 Production process steps of various continuous processes; **A** continuous lamination, **B** continuous film foaming, and **C** continuous injection foaming

impregnated with a blowing agent is successively feed and foamed (in-situ foaming) between the two facings to shape the core layer (part B of Fig. 8). In injection foaming process, a foaming liquid is successively injected (in-situ foaming) between the two endless face layers to create the core layer (part C of Fig. 8). Notably, the application of adhesive between the face and the core layers would not be needed, if the core layer is formed by an in-situ foaming process. Figure 8 shows the differences between the production process steps of various continuous processes.

A reasonable comparison is needed to perform a selection between batch and continuous process. The main feature of batch processes is that all the layers are completed at a unit prior they transfer to the next step. Batch process is advantageous for the production of low-volume high-added value products, or for production of the seasonal orders, which are not easy to forecast. Another advantage of batch production is the lower initial capital investment; hence, it is especially profitable for small businesses or trial runs of new products [36]. But, continuous processes are more industrially preferred than batch processes for mass production of similar products, since a consistency of products quality can be achieved. Furthermore, the continuous process is more economical due to less production steps and accordingly having higher efficiency in time, material, and labor [17]. The difficulties of edge-processing and integration of fittings are also minimized with having polymeric foams as the core layer compared with hollow sections in honeycomb sandwich composites.

3.3 Simultaneous (Integrated) Processes

One of the disadvantages of the abovementioned processes is that they do not have a process similar to the conventional production process that existed in the wood-based panel industries like particleboard or fiberboard. The surface layers in all of those aforementioned processes should be separately manufactured via another production line. In other words, a lack of simultaneous production of all layers (face and core layers) together at one time (process) is evident. This has been considered for some years and a novel process was developed to manufacture foam core panels using an integrated approach [37]. In this process, the resinated woody materials and expandable polymeric materials (as a film or granules) can be used as the surface and core layers, respectively. No additional glue has to be applied during mat formation in the interface of surface and core layers due to the in-situ foaming. The prepared mat should be then transferred into the press. The integrated pressing process consists of three consecutive stages entitled; pressing, foaming, and stabilization stages to produce endless foam core panels. The produced panel is composed of wood composite for the surfaces and expanded polymeric foam as core layer [38]. The production steps of this simultaneous production process are presented in Fig. 9.

The core layer materials should fulfill some features to be applicable for the in-situ foaming during the simultaneous production process. The polymeric materials

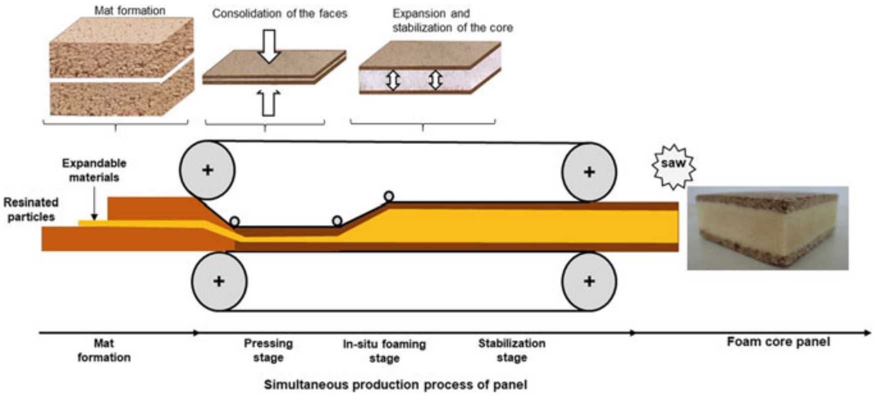

Fig. 9 Production steps of the simultaneous production process of foam core panel with expandable solid-state materials

should be able to expand, be expandable under heat, expand when a certain activation temperature (about 100 °C) level is reached, have a solid-state shape (powder, granulate or as film) to allow mat formation before expansion, not be too tacky to allow easy and uniform felting/scattering, and be pressure resistant in its un-expanded state [17]. Although, these characteristics narrow the selection range for the core layer materials, but there are still some polymeric materials, which fulfill these requested characteristics (refer to Sect. 4.1).

The features of the core layer polymer, e.g., their thermoset or thermoplastic nature, set challenges in the simultaneous production process. An internal cooling for panel stabilization would be necessary for the thermoplastic polymers at final production stage in the press [18, 39]. It was stated that the core layer materials should have an expandable solid-state shape (either as a film/sheet or granule) to be used for simultaneous manufacturing process of foam core panels [11]. Although, the thermoset polymers do not require cooling for stabilization, but such thermosetting granules having an expandable solid state to meet the requirements for a simultaneous process are not yet available on the market [40]. Hence, another simultaneous production process was developed with the ability to use thermosetting liquid foam where no cooling would be necessary to stabilize the panel [41–43]. Figure 10 illustrates the production process steps of simultaneous process of foam core panels using in-situ foaming of liquid foam. In this process, the mat consists of two surface layers composed of resinated wood constituents. After consolidation of the surface layers during the first pressing stage, the surface layers will be separated in-line depending on the separation techniques used. Various separation techniques can be carried out after the bottom layer formation and prior to surface layer formation using either un-resinated wood particles or water spray technique [44]. Conventional fine un-resinated woody materials (about 400 g/m^2) can be used as separation materials between the two surface layers. The amount of sprayed water on top of the bottom

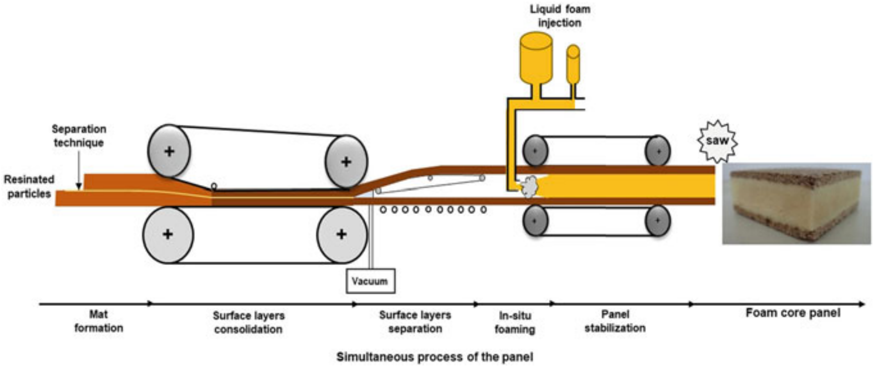

Fig. 10 Production steps of simultaneous production process of foam core panel with liquid thermosetting foam

layer can be about 60 g/m^2 to rise the steam mass (during the surface layers consolidation stage) in between both surface layers for their lateral separation [45]. Finally, the liquid foam can be injected between the separated layers to shape the endless foam core panels. No additional adhesive is also needed between the surface and core layers due to the in-situ foaming of core layer. The main advantage of this process is no need for internal cooling during panel stabilization stage. This is an important criterion to produce foam core panels in already existing WBP lines while slight modifications would also be needed [11, 46].

4 Polymeric Foams

Polymeric foam, also known as cellular solid or porous polymer, is an important class of materials, which has many advantages, such as low density, good heat and sound insulation property, high specific strength, and corrosion resistance [28]. Polymeric foams are extensively used in various industrial applications, such as automotive, packaging, composites fabric, energy absorptions, and furniture [34]. In furniture industry, the selection of production process to manufacture foam core panel is highly dependent on the foam characteristics (e.g., thermoset or thermoplastic, liquid shape, or solid-state (before foaming), etc.). Hence, the potential of various polymeric foams for the simultaneous production process of foam core panels is discussed here.

4.1 Expandable Bead Foams

Polymer bead foaming technology has raised the market for plastic foams by enlarging their applications because of the breakthrough in the production of low-density foamed components even with complex geometrical structure [40]. Foams produced from expandable beads or granules compose of numerous particles, which are fused together to create three-dimensionally shaped products. Expandable bead has a core–shell structure, which consists of thermoplastic polymers as the shell encapsulating an expanding (blowing) agent in a gas or liquid form. When heated, the thermoplastic shell softens while the expanding agent inside the shell increases its pressure, resulting in a dramatic increase of the granule volume. The various thermo-mechanical behaviors of different polymer beads make it possible to select an optimal type of beads for each process and application.

Currently, various beads made of different base polymers are available in the market such as microspheres (MS), polystyrene (EPS), polyethylene (EPE), polypropylene (EPP), and thermoplastic polyurethane (TPU) as well as blend-systems. Among all, only microsphere (MS) and polystyrene granules (EPS) have the criteria of being used as the core layer material in foam core panels produced by simultaneous production process shown in Fig. 9. As mentioned earlier, the core layer materials for this process should have a solid-state shape and being expandable under heat. However, unlike MS and EPS, which is supplied as expandable pellets, suppliers can only provide EPP, EPE, and TPU beads in an expanded form. In addition, the EPS and MS have an activation temperature about 100 °C, which is needed for simultaneous production process [17]. Figure 11 shows various types of foam core panels using expandable microspheres and polystyrene granules as core layer for application in furniture industry [11, 18]. A comparison of those panels showed that the panels produced by EPS had higher bending strength and internal bond strength compared with those produced by MS [11].


Foam core panels made of expandable microspheres beads

Foam core panels made of expandable polystyrene beads

Fig. 11 Foam core panels produced with expandable microsphere and expandable polystyrtene beads via simultaneous production process [17, 18]

The effect of various process parameters such as press temperature, press time, and foaming time on the characteristics of produced foam core panels was evaluated [5, 47]. The results showed that the surface quality, foam structure, and interface between the foam core and the surface layers have considerable effects on the physical and mechanical properties of the panels. An improved interface and denser surfaces were created by the lower pressing temperature and the longer pressing time. The results also indicated that the foaming conditions are crucial parameters influencing the properties of both foam and foam core panels. Smaller foam cell sizes and higher foam cell density were achieved by higher pressing temperature and shorter foaming time. In general, the properties of foam core panels can be widely changed to fulfill minimum requirements set by industrial users. With a proper design, furniture made of lightweight foam core panels can achieve weight reduction of up to 50% compared with those made of conventional wood-based panels (e.g., particleboard and fiberboard), while still maintaining comparable strengths [38].

As said earlier, manufacturing of foam core panels via simultaneous process is depended on the polymer type used for the core layer material (e.g., thermosetting or thermoplastic). Both microspheres and polystyrene have a thermoplastic nature. Thermoplastic is the one that does not undergo chemical change in their composition, when heated, and so can be molded several times. Furthermore, the thermoplastic foams, when expanded, need to be cooled down below their glass transition temperature (T_g) for stabilization. This implies that the panels with a thermoplastic foam as the core layer can only be produced using a simultaneous production process if the continuous press would have a cooling section close to the outlet side. Considering this issue, these types of panels cannot be produced in the most exciting production lines since most of the already existing continuous presses have no cooling sections. The glass transition temperature of the polymers has an important influence on the stabilization time. Here, the polystyrene has a higher glass transition temperature (103 °C) compared with microspheres (85 °C) resulting a considerable reduction of cooling time in EPS board [48]. The shorter the cooling time, the higher the production capacity.

4.2 Thermosetting Foams

Another set of polymer is the thermosets or thermosetting polymers, which melt and take shape only once. When thermosetting polymers are solidified, they cannot be melted for reshaping. A chemical reaction usually occurs in the thermosetting polymers that are irreversible [49]. The starting material for making thermosetting foams, prior to hardening, is usually *malleable* or liquid, and is often designed to be *molded* into the final shape. Acrylic, polyesters, *vinyl esters*, epoxy, polyurethanes, and phenolic resins are some examples of thermosetting polymers. Among all, polyurethane and phenolic resins have unique characteristics to be used as the core layer of foam core panels manufactured via a simultaneous production process. Hence, some special characteristics about these foams are mentioned below.

4.2.1 Polyurethane Foam

Polyurethane (PU) is a thermosetting polymer composed of organic units joined by urethane links and is well suited for in-situ foaming since decades. PU is manufactured through an exothermic reaction between the hydroxyl groups of a polyol (PO) with the NCO functional groups of isocyanate (ISO) ingredients. PU has a wide application range for adhesive, sealants, coatings, and foams. Among PU consumption, foams correspond to about 67% of the global PU consumption [42]. Various types of PU foams such as soft, elastomer, and rigid one can be produced, depending on the initial foam ingredients [41]. Rigid PU foams are more favored for manufacturing foam core panels. Rigid foam is mostly produced within a density range of around 40–1000 kg/m^3, depending on the PO structure [50].

Although the production process of conventional PU foams is a well-known technology, but still new production techniques have to be developed in the future depending on the necessity to develop novel products with new functionality and shapes [42]. In this context, a simulated one-step production process has been developed (illustrated in Fig. 10) for the production of foam core panels using rigid PU as the core layer and particleboard/fiberboard as the surfaces [44]. The results showed that the mechanical properties (e.g., bending strength and internal bond strength) were mostly influenced by the surface layer thickness, while the water absorption and edge screw withdrawal were influenced by PU foam cell structure. The effect of ingredient ratios of rigid PU foam on its cell structure and panel properties was also investigated [45, 46]. It was observed that the foam cell density, as the most important factor influencing the foam characteristics, was higher in the foam with higher ISO and polyether-PO content. Bending strength, internal bond, and screw withdrawal resistance of the foam core panels were significantly enhanced when the ISO and polyether-PO content were increased in the foam formulation. Changing of foam ingredient ratios did not change the thickness swelling, while the water absorption was influenced by foam ingredients ratios.

Various aspects of foam core particleboard produced by simultaneous production process with liquid PU foam are shown in Fig. 12. Typical micrograph (part C of Fig. 12) of the foam core panel shows that the foams consist of well-defined closed cells of spherical and polyhedral shapes. Furthermore, an intensified interface between the face-core layers was observed in produced panels implying a good adhesion between the PU foam and the wooden layers [46]. PU foam was penetrated between the wood particles of surface layers (part D of Fig. 12) creating a strong mechanical interlocking between the face and core layers of foam core panels, which was also enhanced the panels bending stiffness. Further analysis showed that the cell density of PU foam increased with higher concentration of blowing agent in the foam formulation, which influences the panels' properties [45].

Energy conservation in building is an urgent need for sustainable economic development. To this end, exterior wall insulation exhibits a vital role in building energy consumption via affecting cooling and heating energy uses [51]. Structural insulating panel (SIP), as a well-known sandwich composite, has been significantly used for commercial buildings and houses worldwide for more than 50 years. SIP consists

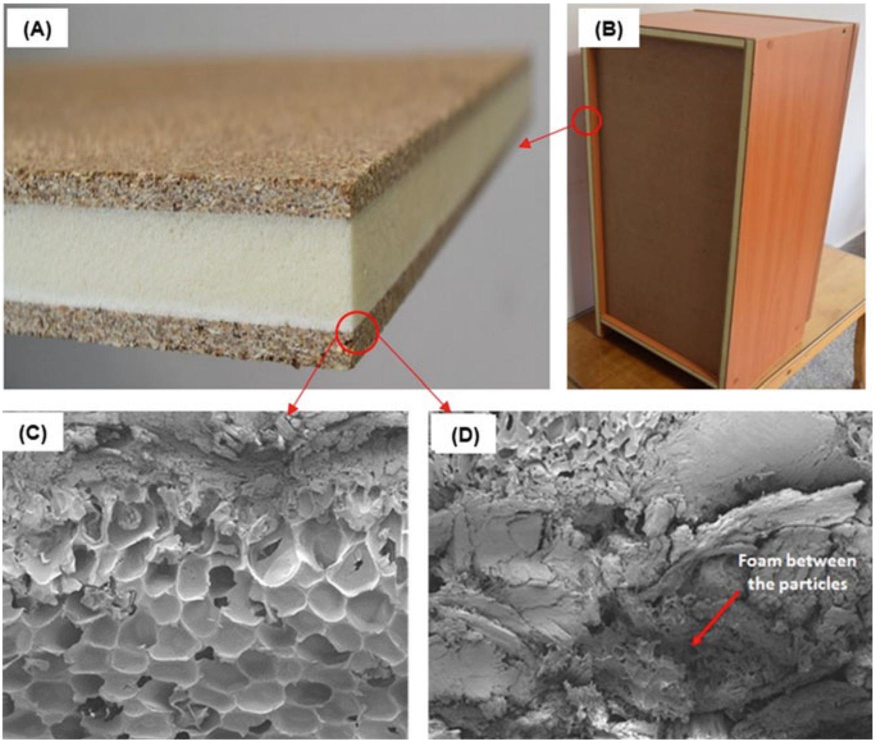

Fig. 12 Foam core panels produced with liquid injection of polyurethane via simultaneous production process; **A** foam core particleboard, **B** a produced box with foam core particleboard, **C** face-core layers interface of foam core panel, **D** penetrated PU foam between the wood particles [46]

of an insulated polymeric foam (mainly polyurethane and polystyrene) as the core layer sandwiched between two layers of structural boards [52]. The structural board as surfaces can be thin metal sheets, wood-based panels (e.g., plywood and oriented strand board (OSB)) and mineral-bonded boards (cement and magnesium oxide-based boards). Among all, the SIP consists of OSB as surface layers and polyurethane as core layer was attracted extensive attention due to its both unique structural and insulation performances [53]. The most common methods of producing SIP's are batch and continuous processes. In addition, a German company produced SIP's using simultaneous production process described in Fig. 10 [54]. The final panel was made of PU foam as the core layer and OSB as the surface layers (Fig. 13). Mass production, higher thermal insulation, preferable panel-sized construction, and less production cost were mentioned to be the advantages of this novel SIP compared with those conventional ones.

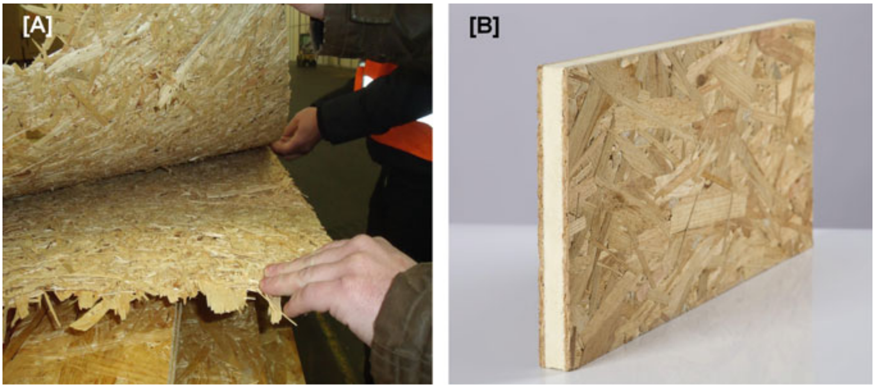

Fig. 13 Structural insulated panel produced by simultaneous process according to Fig. 10 [54]: **A** separated OSB layers after the first pressing stage, **B** structural insulated panels made of OSB and PU foam

4.2.2 Phenolic Foam

Phenolic foam, as a versatile material, has diverse applications where moisture resistance, thermal and fire performances as well as structural strength are key performance criteria. They are mostly used in building and engineering applications for heating, ventilating, roofing, flooring, cavity walls, and air conditioning applications [43]. Phenolic foams show an extraordinary strength to weight ratio being lightweight but still strong. They have a rigid characteristic with a closed cell structure made of phenolic resin. The impressively high level of closed and the fine cells structure makes phenolic foam as an ideal thermal insulator [55]. The foam is produced in various forms such as blocks, flexible and rigid-faced laminate and composite panels as well as for specialized applications (e.g., fire-proofed doors and molded products).

Today, homes are burn faster than ones in the past, and the furniture plays a major role to control or accelerate flaming [56]. The application of petroleum-based materials in furniture, drapes, and rugs can cause serious problems in case of fire. Although, the general benefits of foam core panels for furniture applications are obvious, but the polymeric foam as the core layer may implies some restrictions. The fire safety of this type of innovative panels might become a crucial aspect preventing the further acceptance of panels into the market [57, 58]. It should be considered that both surface and core layers play an important role to classify the fire performance of foam core panels [59]. The fire resistance of foam core panels should at least meet the requirement of conventional wood-based panels such as particleboard or fiberboard. A research showed that the foam core panels compared with conventional particleboard generally had much higher heat release rate what reduced their burning times approximately to half [57]. They also showed higher heat of combustion and smoke production due to the polystyrene component of lightweight panels. Although, the flammability properties of foam core panels were dramatically improved using intumescent fire retardant paper underneath the veneers, but an inherent fire resistance of polymeric foam would be an essential need [59]. Being based on petroleum materials, phenolic foam has outstanding fire performances and extremely low smoke emission when exposed to a flame source. Zero or very low flame spread, negligible smoke emission, and a very low level of toxic gas emission give exceptional fire performances to phenolic foams [60]. Most of the European fire certifications can be achieved by phenolic foams having an appropriate form and structure. On the basis of fire resistant, researchers compared some polymers and figured out that the phenolic foam had the highest fire resistance compared with other thermosetting polymers [61].

The use of phenolic foams in furniture applications can be grown, as these are more stable in case of fire. Phenolic resins have been widely used as binder in wood composites since century, even with consideration of its limitation like brittleness and shrinkage. They keep hold of industrial and commercial interest due to the very low formaldehyde emission, good resistance in water and humid conditions, high mechanical performance, and thermal stability [62]. Furthermore, the fiber-reinforced phenolic composites are also rapidly rising in both commercial purposes and research fields [51]. But, the application of phenolic resin for sandwich panels was limited due to its corrosive properties and low adhesion with metal surfaces. However, these limitations have been dominated with recent improvements in foam chemistry and formulations [63]. Notably, the phenolic resins have a good adhesion with woody materials and can create a strong interface between the face and core layers. The phenolic foam core panel, with its unmatched fire resistance and strong adhesion to wood surfaces, shows promising aspects for lightweight furniture, which has not yet been evaluated.

5 Strategies Toward Bio-Based Foams

Main motivations for the development of bio-based polymers and foams are raising the cost and predictable future scarcity of petrochemicals as well as the sustainable development concerns, which was gained more importance due to the strong public concern regarding polymer waste [43]. Moreover, extensive researches were performed for the development of bio-base polymeric foams, which would be capable to be applied for the production of foam core panels.

5.1 Bio-Based Expandable Bead Foams

Most of the polymer beads are not met the prerequisites for expandable bead foaming like the ability for welding or fusion, hence, the modification of such polymer inappropriate feature is in major focus to research. The aim is to make more polymers applicable for bead foaming and accordingly increasing their possible applications [40]. Polylactic acid (PLA) has attracted extensive attention and provides effective solutions for the development of bead foaming. Although, an improvement in the mechanical properties and especially an enhanced thermal stability of PLA beads has been conducted, but a critical requirement of PLA application for the production process of foam core panels is not yet completely fulfilled. As mentioned earlier (Sect. 4.1), an important criterion for the core layer materials applicable for in-situ foaming in simultaneous production process is the bead expansion when a certain activation temperature (about 100 °C that is needed for adhesive curing of face layers) level is reached [17]. PLA has quite low glass transition temperature (Tg) of about 55–68 °C, depending on the type and crystallization degree. Furthermore, the significant reduction of PLA glass transition temperature during impregnation with physical foaming agents such as pentane and CO_2 makes the situation more critical [64].

The applicability of PLA beads for the simultaneous production process of foam core panels was investigated using CO_2 as a non-inflammable and non-VOC (volatile organic compound) blowing agent and resinated wood particle as facings [65]. According to Fig. 14, the production process was not successfully succeeded. Different failure modes were observed during production process, which were due to the very low Tg of the PLA beads. To overcome these challenges, the PLA was blended with poly-methyl methacrylate (PMMA) as a miscible and more durable polymer having higher Tg [66]. Although the Tg of PLA-PMMA blend was improved (reaching about 70 °C after CO_2 impregnation), but still was lower than the required level needed for panel production. The panel production of such PLA-PMMA blend was only possible with very low pressing temperature of about 120 °C that is not desirable for industrial panels' manufacturers [48]. Briefly, the glass transition temperature (Tg) of developed polymer beads has still to be increased to name the important technological requirement of the core layer material. Mechanical properties of various bead foams, based on microspheres, polystyrene, and PLA-PMMA, used for in-situ production of foam core panels were analyzed [48]. According to the results, EPS and PLA-PMMA foams showed higher and almost identical tensile and compression young's modulus, while the compression modulus was higher for microsphere foam.

Cellulose is known as the most abundant biopolymer on plant, which can be produced from a variety of raw materials such as cotton, wood, recycled paper, and bacteria [67]. Organic cellulose esters such as cellulose acetate (CA), cellulose acetate butyrate (CAB), and cellulose acetate propionate (CAP) are the major types of cellulose-based polymers. They are manufactured via reaction of cellulose with organic acids, anhydrides, or acid chlorides. Cellulose acetate butyrate (CAB) is one of the oldest thermoplastic polymers in the world, which showed promising potentials for beads foaming [68]. Researchers were developed a bio-based and a biodegradable blend made of cellulose acetate butyrate (CAB) with polybutylene succinate [69]. The CAB-based beads were impregnated with pentane as the blowing agent prior to application. Then, the CAB-based beads were successfully used to produce foam core panels with simultaneous production process where the process parameters were adjusted to the bead foams' properties. In summary, researches showed that the future of lightweight foam core panels having bio-based polymeric beads as the core layer looks bright to replace conventional petroleum-based foams.

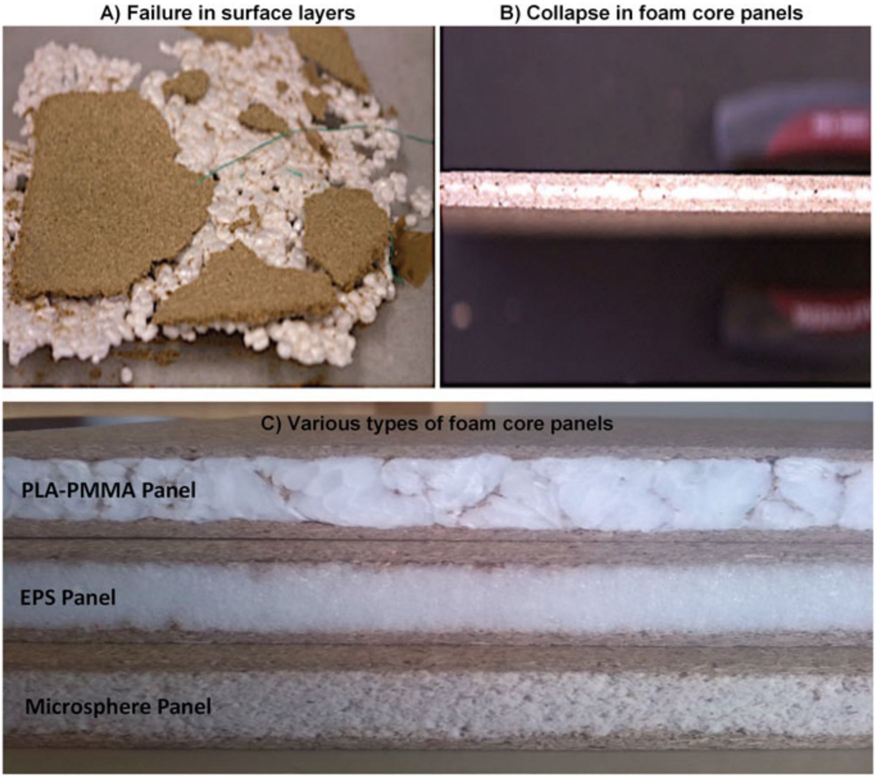

Fig. 14 Foam core panels using PLA impregnated with CO_2 produced by simultaneous production process, **A** failure in surface layers during panel production, **B** collapsing of core layer, **C** panels with various polymer beads as core layer [48, 65]

5.2 *Bio-Based Polyurethane Foam*

Polyol (PO) and isocyanate (ISO) are the two major ingredients to shape PU foam, which are mostly based on petroleum feedstocks. Due to the environmental issues and scarcity of petroleum in the future, a lot of efforts have been focused toward development of bio-based PU foam via substitution of polyol and isocyanate derived from bio and renewable materials. As a result of that, the biomass feedstocks have been extensively used to manufacture renewable POs for the PU industry [50]. According to a recent published report, the global market for green and bio-based POs was valued at USD 2.63 Billion in 2015 and is projected to reach USD 4.71 billion by 2021 [70]. This can be explained by growing preference for the use of materials that have a lower carbon impact and are recyclable or derived from non-polluting resources [42].

So far, it was proved that bio and green POs are an obvious alternative for replacing fossil POs. However, the isocyanate used for the PU formation is still mainly dependent on fossil resources, which is a toxic substance in its liquid form. Notably, less studies were focused on the substitution of isocyanate derived from alternative materials compared with those with POs. Non-isocyanate PU is a novel type of PU produced by reaction of cyclo-carbonates and amines instead of toxic ISOs. They can be more preferred due to their enhanced porosity, water absorption, thermal, and chemical resistance in comparison to those conventional PUs [71]. The results have recently demonstrated the replacing of typical petroleum-based ISOs with this type of materials [72].

Critical steps for the successful implementation of the bio-based ingredients to shape PU foam can be their applicability for in-situ foaming, properties of the resultant foam as well as the sandwich composites. Among various features, the ability of bio-based PUs foams to adhere with wooden surface layers can be the most relevant characteristics for furniture industry [47]. The isocyanate functional groups can not only react with the polyol, but as well with the hydroxyl groups at the wood surface creating a covalent bonding [73]. Such bonding mechanisms cannot be happened at non-isocyanate PU foam creating a doubt for its final characterization as core layer for foam core panels. It should be considered that the bio-based PUs should not only have superior performance but also enhanced durability as the core layer of sandwich composites.

5.3 Bio-Based Phenolic Foam

The development of bio-based phenol formaldehyde is an important research area since years. Several methods and materials were reported in literature to substitute both petroleum resources of phenol and formaldehyde [43, 74]. Lignin is well known as the second most abundant renewable and bio-degradable polymer on plant after cellulose, which contains phenolic functional groups suitable for substituting phenol during resin synthesis [75]. An important step to further progress of bio-based phenolic foam is development of green technologies to extract and preparation of lignin from biomass prior to application. Among all technologies, solvent-based liquefaction of biomass (solvents like water, alcohols, supercritical fluids, etc.) shows promising aspects having high biomass conversion to produce bio-based phenolic materials while still keeping comparable features with that conventional phenolic resin, i.e., low molar mass phenolic materials with high substitution ratio [76]. Although, the potential of several types of biomass was analyzed, oxidative degraded lignin presents better performances than that of untreated lignin having mechanical properties similar to those of conventional foams. Furthermore, phenolated lignin showed an excellent potential as it raised the compressive strength and at the same time decreased the friability because of the linear alkyl side chains in lignosulfonate structure, and to the more regular cells with a lower cell size of the foam microstructure [43].

Although, some literatures are presented about the reduction of formaldehyde emission from phenolic foams, there are still plenty of opportunities for the development of formaldehyde-free foams based on phenolic components [77, 78]. In general, sandwich composite using a core made of bio-based phenolic foam could be a lightweight and fire-proofed structural products for the future, especially for furniture applications. Nevertheless, the technological aspects and durability of these bio-based materials and products have still to be studied.

6 Conclusions and Outlook

Weight reduction of WBPs as furniture elements is an important issue nowadays due to both increased competition for raw wood materials and raising customer demand for lightweight furniture. Application of sandwich idea, having a lightweight and thick material sandwiched by two thin and stiff sheets, in WBP industries was offered as an applied solution through the development of foam core panels used for furniture applications. Although, the conventional methods (e.g., discontinuous and continuous processes) to produce foam core panels were implemented for panels manufacturing, but they were not extensively favored by WBP industries since they do not have a production process similar to those conventional wood-based panels. Innovative simultaneous (integrated) production processes were recently developed to simplify the multi-step production processes of foam core panels. Notably, the integrated approaches can be carried out by a conventional production line for wood composite (e.g., particleboard) with some modifications.

The production steps in simultaneous production process are influenced by characteristics of the polymer used (e.g., thermoplastic or thermoset, solid, or liquid form) as the core layer. Polymer bead foaming technology was successfully implemented to produce lightweight foam core panels, but a cooling stage was necessary to stabilize the foam due to its thermoplastic feature. When thermosetting polymers are foamed, they do not need cooling for stabilization, but they have to be injected between the two surface layers due to their liquid state prior to foaming. To confirm and support general advantages of lightweight foam core panels, the possible restriction due to their fire performance has to be considered. To this end, phenolic foam, as a versatile and fire resistance component, has great potential to be used as the core layer of foam core panels for lightweight furniture elements.

There are still a lot of research topics regarding foam core panels for further investigation. As an outlook, the quality of face-core layer interface, especially in panels produced with new developed foam materials, has to be investigated. Furthermore, development of expandable thermosetting beads for foaming would be an important issue for further industrialization of foam core panels. Although using bio-based polymers as the core layer like polylactic acid (PLA) and cellulose derivatives can give a great ecological advantage, but has to be considered that they have a thermoplastic nature, which needs cooling for stabilization stage. Thermosetting bio-based polymer applicable as the core layer of foam core panels would be of high interest. In final conclusion, researches showed that the future of lightweight foam core panels having bio-based foam materials as the core layer looks bright for the replacement of conventional wood-based panels such as particleboard and fiberboard.

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References

1. FAO (2018) Food and Agriculture Organization of the United Nations - Global forest products. Facts and figures. http://www.fao.org/3/ca7415en/ca7415en.pdf
2. Thoemen H, Irle M, Sernek M (2010) Wood-based panels: an introduction for specialists. Brunel University Press
3. Hemmilä V, Adamopoulos S, Karlsson O, Kumar A (2017) Development of sustainable bio-adhesives for engineered wood panels-A review. RSC Adv 7:38604–38630
4. Matuana LM, Heiden PA (2005) Wood composites. Encycl Polym Sci Technol 12:521–546
5. Shalbafan A, Welling J, Luedtke J (2013) Effect of processing parameters on physical and structural properties of lightweight foam core sandwich panels. Wood Mater Sci Eng 8:1–12
6. Teischinger A (2010) The development of wood technology and technology developments in the wood industries-from history to future. Eur J Wood Wood Prod 68:281–287
7. Monteiro S, Martins J, Magalhaes FD, Carvalho L (2016) Low density wood-based particleboards bonded with foamable sour Cassava starch: preliminary studies. Polym 8:354
8. Cordella M, Hidalgo C (2016) Analysis of key environmental areas in the design and labelling of furniture products: application of a screening approach based on a literature review of LCA studies. Sustain Prod Consum 8:64–77
9. Azizi M, Mohebbi N, De Felice F (2016) Evaluation of sustainable development of wooden furniture industry using multi criteria decision making method. Agric Agric Sci procedia 8:387–394
10. Burnett MP, Kharazipour A (2017) Mechanical behaviour of a lightweight, three-layered sandwich panel based on the raw material maize. Holzforschung 72:65–70
11. Shalbafan A, Luedtke J, Welling J, Thoemen H (2012) Comparison of foam core materials in innovative lightweight wood-based panels. Eur J Wood Wood Prod 70:287–292
12. Khojasteh-Khosro S, Shalbafan A, Thoemen H (2020) Preferences of furniture manufacturers for using lightweight wood-based panels as eco-friendly products. Eur J Wood Wood Prod 78:593–603
13. Jafarnezhad S, Shalbafan A, Luedtke J (2018) Effect of surface layers compressibility and face-to-core-layer ratio on the properties of lightweight hybrid panels. Int Wood Prod J 9:164–170
14. O'Brien M, Bringezu S (2017) What is a sustainable level of timber consumption in the EU: Toward global and eu benchmarks for sustainable forest use. Sustain 9:1–18
15. Paletto A, Bernardi S, Pieratti E, et al (2019) Assessment of environmental impact of biomass power plants to increase the social acceptance of renewable energy technologies. Heliyon 5:e02070
16. Buonocore E, Häyhä T, Paletto A, Franzese PP (2014) Assessing environmental costs and impacts of forestry activities: a multi-method approach to environmental accounting. Ecol Modell 271:10–20
17. Shalbafan A (2013) Investigation of foam materials to be used in lightweight wood based composites. Dissertation. Hamburg University, Hamburg, Germany
18. Lüdtke J (2011) Entwicklung und Evaluierung eines Konzepts für die kontinuierliche Herstellung von Leichtbauplatten mit polymerbasiertem Kern und Holzwerkstoffdecklagen. Dissertation, Hamburg University, Hamburg, Germany

19. Nelis PA, Mai C (2019) The influence of low-density (Paulownia spp.) and high-density (Fagus sylvatica L.) wood species on various characteristics of light and medium-density three-layered particleboards. Wood Mater Sci Eng. https://doi.org/10.1080/17480272.2019.1659850
20. Dziurka MT (2013) Characteristics of lightweight particleboards with the core layer supplemented with rape straw and expanded polystyrene. For Wood Technol 82:250–254
21. Allen HG (1969) Analysis and structural design of sandwich panels. Pergamon Press, Oxford, UK
22. Zenkert D (1995) An introduction to sandwich construction. Engineering Materials Advisory Services, England
23. Corrêa FF, Pereira MP, Madail RH et al (2017) Anatomical traits related to stress in high density populations of Typha angustifolia L. (Typhaceae). Brazilian J Biol 77:52–59
24. Gibson LJ (2005) Biomechanics of cellular solids. J Biomech 38:377–399
25. Thomsen OT, Bozhevolnaya E, Lyckegaard A (2005) Sandwich structures 7: advancing with sandwich structures and materials. Proceedings of the 7th International conference on sandwich structures, Aalborg University, Aalborg, Denmark. Springer Science & Business Media, Aalborg, Denmark
26. Davies JM (2008) Lightweight sandwich construction. Wiley, New Jeresy
27. CEN/TS 16526 (2013) Sandwich boards for furniture (SWB-F). Factory made products. Definition, classification and test methods for determination of performance characteristics. European Committee for Standardization, Brussels, Belgium
28. Gibson LJ, Ashby MF (1997) Cellular solids. Structure and properties., Second edi. Cambridge university press, London, UK
29. Kollmann FFP, Kuenzi EW, Stamm AJ (1975) Principles of wood science and technology: II. Wood based materials. Springer Science & Business Media, Berlin, Germany
30. Thoemen H (2008) Lightweight panels for the European furniture industry: some recent developments. COST E49 conference: Lightweight wood-based composite; properties and usage; Bled; 23rd – 25th June., pp 1–14
31. Rindler A, Vay O, Hansmann C, Müller U (2017) Dimensional stability of multi-layered wood-based panels: a review. Wood Sci Technol 51:969–996
32. Xiong J, Du Y, Mousanezhad D, et al (2018) Sandwich structures with prismatic and foam cores: a review. Adv Eng Mater 21:1800036 (1–19)
33. Hill C, Eastoe J (2017) Foams: from nature to industry. Adv Colloid Interface Sci 247:496–513
34. Lee S-T, Scholz DPK (2008) Polymeric foams: Technology and developments in regulation, process, and products. CRC Press
35. Karlsson KF, TomasÅström B (1997) Manufacturing and applications of structural sandwich components. Compos Part A Appl Sci Manuf 28:97–111
36. Georgiadis GP, Elekidis AP, Georgiadis MC (2019) Optimization-based scheduling for the process industries: From theory to real-life industrial applications. Processes 7:438 (1–35)
37. Lüdtke J, Welling J, Thömen H, Barbu MC (2010) Lightweight wood-based board and process for producing it. United States Patent Office, US20100098933A1
38. Shalbafan A, Luedtke J, Welling J, Fruehwald A (2013) Physiomechanical properties of ultra-lightweight foam core particleboard: Different core densities. Holzforschung 67:169–175
39. Klyosov AA (2007) Wood-plastic composites. Wiley, New Jersey
40. Raps D, Hossieny N, Park CB, Altstädt V (2015) Past and present developments in polymer bead foams and bead foaming technology. Polym 56:5–19
41. Ionescu M (2005) Chemistry and technology of polyols for polyurethanes. iSmithers Rapra Publishing, United Kingdom
42. Gama NV, Ferreira A (1841) Barros-Timmons A (2018) Polyurethane foams: past, present, and future. Materials (Basel) 11:1–35
43. Mougel C, Garnier T, Cassagnau P, Sintes-Zydowicz N (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polym 164:86–117
44. Shalbafan A, Chaydarreh KC, Welling J (2016) Development of a one-step process for production of foam core particleboards using rigid polyurethane foam. BioResources 11:9480–9495

45. Shalbafan A, Choupani Chaydarreh K, Welling J (2021) Effect of blowing agent concentration on rigid polyurethane foam and the properties of foam-core particleboard. Wood Mater Sci Eng 16:85–93
46. Choupani Chaydarreh K, Shalbafan A, Welling J (2017) Effect of ingredient ratios of rigid polyurethane foam on foam core panels properties. J Appl Polym Sci 134:44722
47. Shalbafan A, Welling J, Luedtke J (2012) Effect of processing parameters on mechanical properties of lightweight foam core sandwich panels. Wood Mater Sci Eng 7:69–75
48. Shalbafan A, Rhême M, Thoemen H (2017) Ultra-light particleboard: characterization of foam core layer by digital image correlation. Eur J Wood Wood Prod 75:43–53
49. Pascault J-P, Sautereau H, Verdu J, Williams RJJ (2002) Thermosetting polymers. CRC Press
50. Ashida K (2006) Polyurethane and related foams: chemistry and technology. CRC Press
51. Liu J, Wang L, Zhang W, Han Y (2020) Phenolic resin foam composites reinforced by acetylated poplar fiber with high mechanical properties, low pulverization ratio, and good thermal insulation and flame retardant performance. Materials (Basel) 13:148 (1–14)
52. Agarwal S, Gupta RK (2017) Plastics in buildings and construction. In: Applied plastics engineering handbook. Elsevier, pp 635–649
53. Samali B, Nemati S, Sharafi P et al (2019) Structural performance of polyurethane foam-filled building composite panels: a state-of-the-art. J Compos Sci 3:40
54. Langguth S (2018) Light structural panel (LSP) - next generation building material. In: 11th European wood-based Panel Symposium, 10th – 12th 2018. Hamburg, Germany
55. Mao J, Chang J, Chen Y, Fang D (1998) Review of phenolic foam. Ind Eng Chem Res 15:38–43
56. Ogle RA, Schumacher JL (1998) Fire patterns on upholstered furniture: Smoldering versus flaming combustion. Fire Technol 34:247–265
57. Shalbafan A, Dietenberger MA, Welling J (2013) Fire performances of foam core particleboards continuously produced in a one-step process. Eur J Wood Wood Prod 71:49–59
58. Dietenberger MA, Shalbafan A, Welling J (2014) Foam core particleboards with intumescent FRT veneer: Cone calorimeter testing with varying adhesives, surface layer thicknesses, and processing conditions. In: 25th annual conference on recent advances in flame retardancy of polymeric Materialsm 19–21st May, 2014, Stamford, Connecticut, USA
59. Dietenberger MA, Shalbafan A, Welling J (2018) Cone calorimeter testing of foam core sandwich panels treated with intumescent paper underneath the veneer (FRV). Fire Mater 42:296–305
60. Pilato L (2010) Phenolic resins: a century of progress. Springer, Berlin
61. Saba N, Jawaid M, Paridah MT, Al-Othman OY (2016) A review on flammability of epoxy polymer, cellulosic and non-cellulosic fiber reinforced epoxy composites. Polym Adv Technol 27:577–590
62. Gomez-Bueso J, Haupt R (2010) Wood composite adhesives. Phenolic resins: a century of progress. Springer, Berlin, pp 155–187
63. Asim M, Saba N, Jawaid M et al (2018) A review on phenolic resin and its composites. Curr Anal Chem 14:185–197
64. Yoon Y, Plummer CJG, Thoemen H, Månson J-AE (2016) Liquid CO_2 processing of solid polylactide foam precursors. J Cell Plast 52:153–174
65. Yoon Y (2016) Heat expandable biopolymers for one-step production of foam core sandwich composites. École Polytechnique Federale de Lausanne, Zurich, Switzerland
66. Yoon Y, Plummer CJG, Månson J-AE (2015) Solid heat-expandable polylactide-poly (methyl methacrylate) foam precursors prepared by immersion in liquid carbon dioxide. J Mater Sci 50:7208–7217
67. Figueiredo JA, Ismael MI, Anjo CMS, Duarte AP (2010) Cellulose and derivatives from wood and fibers as renewable sources of raw-materials. In: Carbohydrates in sustainable development I. Springer, pp 117–128
68. Zepnik S, Hildebrand T, Kabasci S, et al (2013) Cellulose acetate for thermoplastic foam extrusion. Cellul Conversion Rijeka InTech 17–44
69. Lüdtke J, Roch H, Haiduk FK (2017) Biobasierter Hybrid-Sandwichwerkstoff aus Holz und Celluloseschaum. Holztechnologie 58:18–22

70. Green and Bio Polyols Market by 2021 (2018) Markets and markets press release. https://www.marketsandmarkets.com/PressReleases/green-and-bio-polyols.asp
71. Guan J, Song Y, Lin Y et al (2011) Progress in study of non-isocyanate polyurethane. Ind Eng Chem Res 50:6517–6527
72. Grignard B, Thomassin J-M, Gennen S et al (2016) CO_2-blown microcellular non-isocyanate polyurethane (NIPU) foams: from bio-and CO 2-sourced monomers to potentially thermal insulating materials. Green Chem 18:2206–2215
73. Solt P, Libowitzky S, van Herwijnen HWG, Konnerth J (2020) Improved method for analyzing cohesive strength development of pMDI. Wood Sci Technol 54:7–17
74. Cui Y, Hou X, Wang W, Chang J (2017) Synthesis and characterization of bio-oil phenol formaldehyde resin used to fabricate phenolic based materials. Materials (Basel) 10:668
75. Glasser WG (2019) About making lignin great again-some lessons from the past. Front Chem 7:565
76. Li B, Feng SH, Niasar HS et al (2016) Preparation and characterization of bark-derived phenol formaldehyde foams. RSC Adv 6:40975–40981
77. Li W, Lin Q, Yan M, Zou Y (2003) Reducing the contents of free phenol and formaldehyde in phenolic foam. J Appl Polym Sci 90:2333–2336
78. Hartman Jr JJ, Lenox RS, Putt DL (1998) Phenolic foams having a low formaldehyde evolution. United State Patent Office (US5705537A)

Chapter 17
Wood Flour-Reinforced Phenolic Foams (WFPF)

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1 Introduction

Global environmental, social and legal initiatives for sustainable development, circular economy, and climate neutrality are leading to development of renewable products for more sustainable materials. The introduction of more and more restrictive environmental regulations by the European Union and highly developed countries is leading to the growth of interest about wood polymer composites (WPCs) [1, 2]. Many branches of modern industries are interested in exchange of usage of inorganic fillers for natural, biodegradable, and renewable materials. This is due to the high consumption of high-density, expensive, and non-degradable fillers such as carbon and glass fibers. Moreover, the use of these materials is connected with high abrasive wear of machinery (expensive machines and their maintenance), harmful influence on the environment, and health of the workers. The most serious dangers from exposure to fibers for human are skin and eyes irradiation and respiratory system diseases. Recent research suggests the possible lung carcinogenicity of inhaled glass fibers. Nevertheless, 90% of produced polymer composites consist of glass fiber or/and carbon fiber [3].

In the last decades to overcome these problems, industry and scientists are trying to apply less expensive and less hazardous wood-based fillers. This interest can be observed in the increasing number of articles, books, and patents associated with incorporation of these materials. Looking at wood as an alternative option for other fillers, it is estimated that potential of wood origin fillers is huge. Global Forest Resources Assessment 2020 made by FAO reports that 31% of the total land area is covered by forests, what is equivalent to 0.52 ha per person. More than 54% of the world's forests are in five countries—Brazil, Canada, Russian Federation, China, and

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the United States [4]. Proper management of such a large amount of raw materials can lead to the development of a sustainable industry. It is necessary to process not only full-valuable products but also by-products. One of the most popular side product during wood processing is wood flour. About 50% of this waste is generated from processing of solid wood pieces in sawmills during production of wood panels, plywood, particle boards, and furniture [5]. Minimalization of the negative impact on the environment and human living can be caused by the implementation of effective utilization of this type of waste. In last years, a lot of researchers proposed effective methods of application of wooden wastes in a wide range of materials—especially in wood polymer composites [6].

2 Wood and Wooden Fillers

Wood is a material that a has huge impact on the social and economic life of human population all over the world. These materials played a huge role in the evolution of man and history of mankind. Wood is an orthotropic, natural composite (in micro and macroscopic levels) mainly composed of hemicellulose (15–25%), cellulose fibers (40–50%) forming cellular structures, which are connected by lignin (15–30%) forming middle lamella. As can be seen in Fig. 1, wood cell wall shows specific structure, which gives wood unique properties such as lightweight, good stability, elasticity, hardness, toughness, and high load-bearing capacity [7].

Due to the excellent mechanical properties, biodegradability and free availability of wood and products produced during the processing are widely used in building and constructions and manufacturing of household products (furniture, sports kit, paper, auto parts). The wood structure, chemical compositions, and acoustic, physical, mechanical, and thermal properties are different in various wood species even the

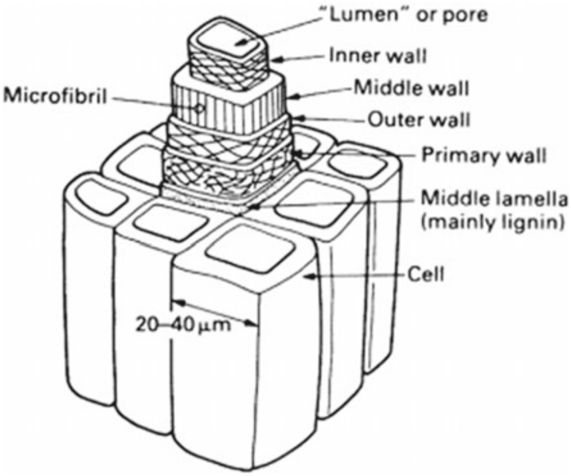
Fig. 1 Molecular structure of a wood cell wall [3]

Table 1 Chemical composition and properties of selected wood species from literature sources [5, 9, 10]

Wood species	Cellulose [%]	Hemicellulose [%]	Lignin [%]	Others [%]	Density [g/cm^3]	σ_{max} [MPa]	E [GPa]
Softwood							
Pine	44–46	25–28	27–29	4–5	0.35	12–27	0.1–0.5
Spruce	44–46	25–27	27–29	–	1.5	85	18–40
Cedar	37	19	34	3 0.35		12–27	0.1–0.5
Fir	41–46	27–35	28–30	2–3	0.33	78	14
Larch	38.5	27.2	21	–	0.56	100	11
Hardwood							
Teak	49	30	30	–			
Maple	47	30	21	2 0.54		108	9.58
Beech	44–46	30–35	21–23	–	0.56	86	9.5
Poplar	44–46	33–36	18–21	– 0.33		154	5.9
Oak	42–47	20–27	25–27	3–4 0.63		78	10.4
Sal	40–50	15–25	15–30	–	0.72	40	1.5
Mango	40	11.5	36	–	0.52	24	1.17
Apple wood shell	40	26	30	0.9 –		–	–
Bamboo	26–43	30	21–31	–	0.6–1.1	140–230	11–17
Birch	40	26	33	–	0.62	137	4.8

same species growing in different conditions [8]. Depending on the wood composition and anatomy, it can be divided into two groups—hardwood and softwood. Table 1 shows division into these two groups, chemical composition and properties of most popular wooden species [5, 9, 10].

2.1 Production of Wood Flour

Wood flour is mostly generated from various scraps from wood processors. To obtain the high-quality wood flour, it has to be free from dirt, bark, and other impurities and should be composed of a specific species (or a mixture of species group) of wood. Availability of different kinds of wood flour depends on the continent, country, or even region of clean raw materials from the wooden industry. For example, in the

United States, the most commonly used wood flour is derived from pine, oak, and maple.

Nowadays, there is no standard method of producing wood flour, some general points can be discussed. The most important issues in this process are size reduction and size classification. Initial grinding of the larger raw materials may be conducted using equipment such as a hog, chipper, or hammer mill. Pre-grounded material can be pulverized by crushing in roller mill, beating with hammers, impactors or grinding in attrition mills. This process results in receiving particles containing fibers and their fragments [11].

Depending on the intended application, wood can be treated to obtain different shape and size of grain [12]. Grinding wood into small particles to form wood powder called wood flour is necessary for many applications. Depending on the energy, mechanism of grinding, and wood properties, it is possible to obtain wood flour with fine particle size, high specific surface area, various particle shapes, or even with low crystallinity. It has been proposed that wooden biomass is finely grinded when product size is less than 100ηm. On the other hand, in few studies, particles with size up to 1 mm is acceptable in further production of wood flour-reinforced composites. During wood grinding, a number of different stress types in wood structures occur. Most likely stress types are presented in Fig. 2 [10]. The process of size reduction of wood is a highly energy-consuming process. This is due to viscoelastic nature of wood. The amount of energy may be lowered by appropriate pretreatment of wood, selecting the appropriate grinding technique, and grinding medium.

The obtained wood flour is characterized by different aspect ratios, especially length to diameter. Low aspect ratios allow wood flour to be more easily metered and fed than individual wood fibers, which tend to bridge. However, the low aspect ratio limits the reinforcing ability. After pulverization, the wood flour can be classified by size using vibrating, rotating, or oscillating screens. Moreover, separation of wood particles by air flow is also used, especially with finely ground wood flour. Separation by size can be described by the actual size of the powder or by mesh of the wire cloth sieves used to classify. The most popular manufactured wood flours used as fillers in thermoplastics are in the size range of 180–425 mm (80–40 US standard mesh). Typical wood flour supplied for the further processing content between 4 and 8% of moisture and must be dried before use [11]. Figure 3 represents the scanning electron micrographs of different types of WFs—initial (00), dry pulverized at mill-plate gap 200 μm (200), dry pulverized at mill-plate gap 350 μm (350), wet pulverized at

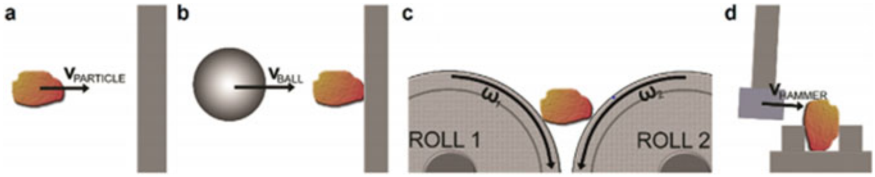

Fig. 2 Illustration of different stress types during grinding: **a** single impact, **b** double impact, **c** slow compression, **d** shearing impact [10]

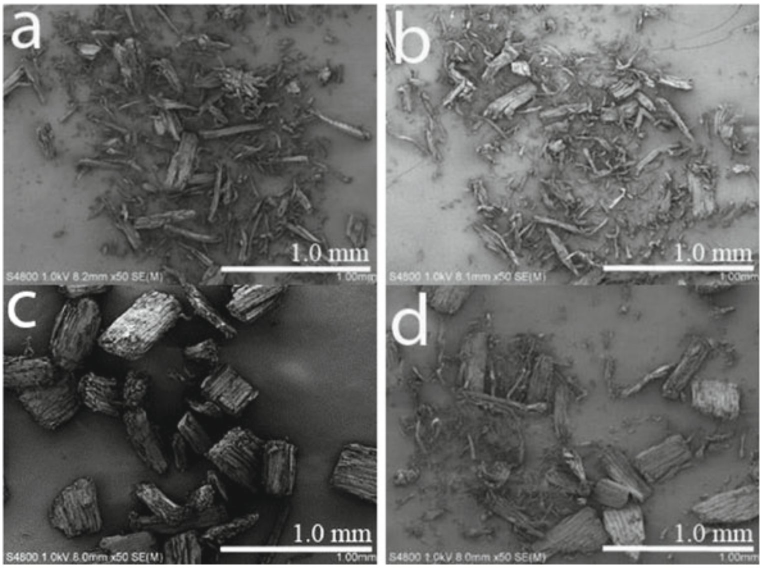

Fig. 3 Scanning electron microscopic images of short cypress flour (CWF_S) and long cypress flour (CWF_L), **a** CWF_S00, **b** CWF_S200w, **c** CWF_L00, **d** CWF_L200w [13]

mill-plate gap 200 μm (200w), and wet pulverized at mill-plate gap 350 μm (350w), respectively.

2.2 *Impact of Wood Flour on Material Properties*

Depending on the origin and type of processing, the types of wood flour may differ from each other with particle size, size distribution, chemical composition, and content of additives. Each parameter mentioned above could have a huge impact on the properties of the product. Very fine wood flours can cost more (increase of material price) and may increase melt viscosity more than coarser wood flour. On the other hand, composites made with smaller powders typically have a more uniform appearance and a smoother finish. If the filler is grounded too fine, the fiber bundles become wood dust. These fragments no longer resemble fiber or fiber bundles and may not cause such a significant enhancement.

Wood flour originating from the softwood has higher in comparison to the hardwood cellulose content, what leads to higher adhesion between two phases—wood particles and polymer matrix. On the other hand, materials with softwood filler have lower mechanical properties. Hardwood fillers with a lower cellulose content have poorer interfacial adhesion but better mechanical properties [14, 15].

3 Methods of Wood Flour Management

Before concern for the environment began, wood powder was a mainly waste stream from wood processing plants such as sawmills and furniture factories. In the last few decades, many common applications of wood flour have been found. Due to its unique properties and chemical composition, wood powder has a wide range of applications not only in material production.

One of the most popular applications of wood flour is combustion and co-firing. This process is conducted in specially designed boilers and furnaces, often with the addition of coal. Nowadays, 64% of wood and wood waste are subjected to this form of processing. Before combustion wood should be pulverized, which is a very energy-consuming process. In this process, the key parameters are particle size, shape, and density. Currently, the state-of-the-art for this method is obtaining wood pellets in the process of torrefaction. This process combined with pelletization changes wood properties to provide a better fuel quality for combustion and gasification applications. Torrefaction produces a relatively dry product, which reduces or eliminates its potential for organic decomposition. The possibility of replaceing or supplementing coal with biomass in coal-based power plants with existing equipment is considered [16, 17]. Nevertheless, according to the normative acts about hierarchy in waste management, priority is given to preparing wastes for re-use and recycling than for energy recovery (Directive 2008/98/EC). Importantly, the opinion that energy recovery and reprocessing into materials to be used as fuels is a form of material disposal, not form of recycling, becomes more and more popular. For this reason, new methods of wood waste managing are being developed [18, 19].

Another management method of wood flour is the conversion to chemicals and biofuels. Liquefaction, saccharification, and gasification are the three most popular approaches to utilizing lignocellulosic biomass. These methods are based on thermal processing of wooden biomass under high pressure, generally with addition of auxiliary substances such as solvents, catalysts, mixture of gases, enzymes, or even bacteria [10]. This type of processing allows obtaining valuable intermediates in the production of synthetic chemicals. These products include conversion of biomass into simple sugars via acidic or enzymatic hydrolysis and further fermentation to methanol, ethanol, or butanol [20], preparation of bio-polyols [21] to production of bio-polyurethanes and their composites [22] or generation of syngas (mixture of hydrogen and carbon monoxide) during gasification [23]. The other uses of wood flour include lignophenol production [24], which is a valuable intermediate used for further production, obtaining absorbers and ion exchangers to remove organic pollutants and heavy metals from aqueous systems.

4 Wood Plastic Composites

Polymer composites reinforced with wood fiber or flour are generally known as wood plastic composite—WPC. These composites are made of wood fibers/flour (or other cellulose-based fillers, such as bamboo, peanut hulls) and preferably waste plastics. As the material of matrix, the most frequently used plastics are polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS). The search for more environmentally friendly solutions led to the gain in importance of biodegradable plastics produced from renewable resources. Examples of such materials include polylactic acid (PLA), starch acetate, non-biodegradable bioplastics such as bio-derived PE and polyamide [25]. The plastics mentioned above are chosen due to their low temperature of processing, which is between 150 and 220 °C, what prevents wood from decomposition during processing. While temperature arises over 200 °C, wooden materials are starting to release volatile products [26]. Degradation of the least stable ingredients of wood (hemicellulose and extractives) starts at 210 °C [27]. Cellulose and lignin have more stable structure and starts to degrade over 270 °C. Processing of the composites filled with these substances over 220 °C leads to the generation of volatile degradation products. This effect causes foaming of product and decrease of material properties [28]. Moreover, both materials before processing should be dried and kept sealed, because more than 1% of moisture in material could lead to foaming of the product. The presence of water may cause generation of micro voids and lead to porous structure with irregular shapes, what will result in deterioration of mechanical properties of the product [29].

Nowadays, the most popular method of production of WPC is two-step extrusion. First, the prepared blend is subjected to pelletizing, and then obtained pellets are used to extrude into a final product. Pelletized material is more homogeneous and it is easier to control moisture content. In order to facilitate the production, installations enabling the processing of untreated wood in a single-stage process were developed. The main ingredients in the composition of WPC are wood flour and plastic matrix. In commercial WPC products, the addition of wood flour reaches up to 70%. This amount varies due to material of matrix, application and required appearance. Moreover, to enhance properties, extend product life, improve processing, or facilitate material maintenance, a number of different types of additives are used during processing. The most popular additives during processing are coupling agents, which can improve the dispersion of the wood inside matrices, bonding on the matrix/reinforcement border and reduces the rate of water uptake. Due to possible incompatibility between matrix and reinforcement, coupling agents should work as a connection of their surfaces. The most popular coupling agents are: silanes, titanites, and functionalized polymers (e.g. polyolefins). Other additions include lubricants, foaming agents, pigments, fire retardants, antioxidants, biocides, and UV stabilizers. It should be remembered that the addition of these substances may be associated with an increase in the price of the received material [29].

4.1 Properties of WPC

Due to subjection of WPCs to the thermal and mechanical loadings, this kind of material should be characterized by appropriate flexural, impact and compressive strength, hardness, resistance to aging, and thermal stability. Listed properties greatly depend on the type of matrix and type of reinforcement. The most important properties of woof flour that affect are content of wood flour, aspect ratio, geometry of filler, type of wood (softwood/hardwood), and interfacial properties between phases.

The major advantage of wood polymer composite over wood is the possibility of forming composite to every projected shape. Designed properties of WPCs hardly depend on their predicted application. Unlike wood, this material needs no application of additional preservatives on surface, what makes it environmentally friendly and material requires less maintenance. The addition of filler also provides WPCs excellent resistance to splitting and cracking. Moreover, it looks and behaves like wood but it does not have the same rigidity as wood.

The use of waste from the wood industry in these materials may reduce the rate of deforestation due to obtaining full value products with possibility of modification of material properties by modification of composition. The right mix and proportions of wood, matrix, and additives can lead to receiving materials with the better or equivalent properties to wood. Unfortunately, due to the addition of non-biodegradable plastic binder of wood (phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins, polyurethane), these materials are only partially biodegradable. To obtain fully biodegradable materials, it is suggested to use plastics such as PLA or thermoplastic starch.

5 Reinforced Phenolic Foams

Phenolic foams are getting more and more popular material all over the world. Nowadays, scientists are looking for materials that will meet more restrictive requirements. Due to unique combination of properties, phenolic foams (PF) have a number of engineering applications. These materials are used in energy adsorption, insulation, fire protection, and lightening of structures. The most important advantages of this material include high thermal stability, low thermal conductivity, and tremendous fire resistance. Moreover, generation of toxic gases during combustion process is very low and material shows no dripping behavior. Unfortunately, phenolic foams have a number of disadvantages such as brittleness and tendency to pulverization, what limits wider application. In order to solve this problem, scientists in their research present methods to improve the properties of these materials [30].

Two methods of improving the properties of these materials have been distinguished. The first one relies on the appropriate choice of method of production. For example, free rise/closed mold method will influence on homogeneity and density of obtained foam. The second one is based on the modification of formulation of foam to improve properties of the product. Such methods include modification of the foam composition, which affects its chemical and physical structure and includes the addition of other components to the material to improve their properties. The most common modifications include addition of fillers (fibers, particles, etc.) to the materials to improve flexural and compressive strength of material, addition of nucleating agents to increase density of the material, or addition of flame retardants [30].

Moreover, fillers are not only added to increase mechanical properties but also for reduction of material price. In the case of phenolic foams, the main purpose of addition of fillers is to increase compressive strength and decrease excessive friability. The most popular additives are glass fiber, aramid fiber, multiwall carbon nanotubes, and other organic and inorganic fillers intentionally added to the material. Recently, scientists are interested in preparation of phenolic foams using common and natural fillers such as wood flour, cellulose fiber, or even lignin. Addition of these substances is associated with a slight decrease in thermal stability and fire resistance, improvement of mechanical properties, and increase of viscosity.

6 Wood Flour Reinforced Phenolic Foams

Currently, there are only a few studies describing the influence of wood flour on the properties of phenolic foams. However, due to the unique properties of PF filled with wood flour, there is a possibility that this material will become more popular in the near future.

In some research [31], wood flour derived from *Pinus Radiata* was incorporated in phenolic foam matrix. Wood flour was obtained by milling wooden chips in a mill and then sieved to a size lower than 0.15 mm. To obtain phenolic foams, the authors used a petrochemical system with addition of hardener (ACE 1035), catalyst (phenol-4-sulfonic acid), and blowing agents (Tween® and n-pentane). The ratio of phenolic:surfactant:catalyst:blowing and agent:hardener was 100:2:4:1.1 and 3.9:20 (by weight). Selected substances were mixed with mechanical stirrer and then obtained mixture was poured into a mold. Material was cured for 1 h at 80 °C and then further post-cured for 24 h at 105 °C. To study the influence of variables on the reinforced PF properties, the author changed the weight fraction of wood flour (1.5–8.5 wt.%) and blowing agent amount (1.5–3.5 wt.%) in the composition.

Author has shown a decrease of density of WRPF with an increase in amount of wood flour and blowing agent. This can be due to the performance of wood flour as a nucleating agent, which promotes generation of bubbles in the foam. Moreover, a greater addition of blowing agent caused an increase in the quantity of gas. This effect caused a decrease in the density of foams. This effect was also observed when lignin nanoparticles were added to the matrix [32]. On the other hand, the addition of glass or aramid fibers in phenolic foams did not show this effect but some works showed that it is necessary to add more blowing agents to maintain previous density [33]. It is also shown that with an increase in amount of blowing agent and wood flour, compressive strength and modulus decrease. Contour maps of change of properties

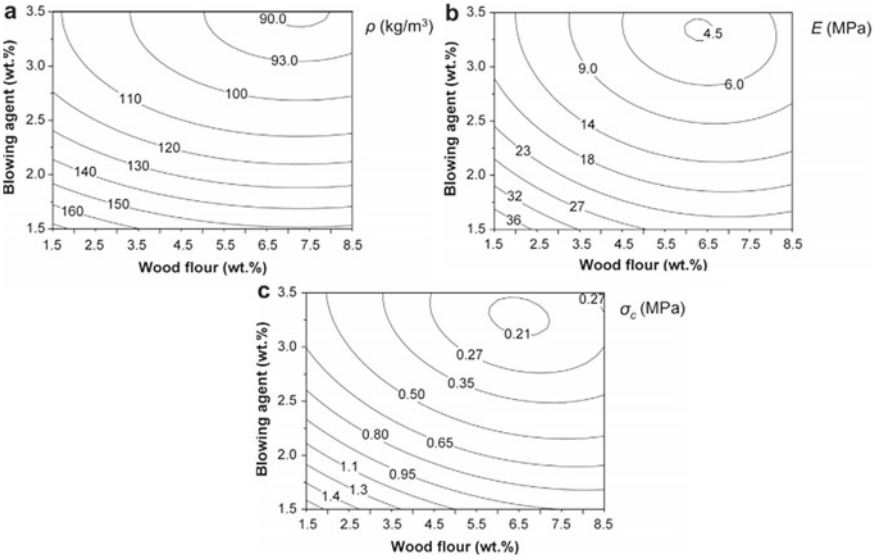

Fig. 4 Contour maps for WRPF **a** apparent density (kg/m3), **b** compressive modulus (MPa), and **c** compressive strength (MPa) [31]

with different amount of filler and blowing agent are shown in Fig. 4. Author noticed that changes in mechanical properties of obtained composites are differed depending on the material density. This can be caused by change of cell wall thickness, which can be responsible for reinforcing effect of fiber.

The microstructure of these materials has been determined using scanning electron microscopy. It was noticed that wood flour can be found inside cell walls and among cells. Due to the hydrophilic nature of wood and phenolic foam, the compatibility between these two phases is very good. This is confirmed by the absence of voids in the obtained material. Moreover, observation of the cellular structure of the obtained composites with different addition of reinforcement and blowing agent showed that mean cell size decreases with lower addition of wood flour (0.05–5 wt.%). Higher addition (5–9.95 wt.%.) of wood flour barely changes the cell size distribution. On the other hand, the addition of more blowing agent is associated with a continual increase in cell size. SEM images for WRPFs formulated with the addition of blowing agent and wood flour are shown in Fig. 5.

The other work [34] compared the effects of wood flour and lignin particles on the friability, thermal stability, and effect of hygrothermal aging on structure and properties of material.

High friability is one of the biggest disadvantages of phenolic foams. Literature indicates that average friability varies between 15 and 40% depending on chemical structure and used additives. In this work, it is shown that the addition of small amount of wood flour does not significantly influence on friability but higher addition is associated with strong increase of this parameter. This effect is caused by generation

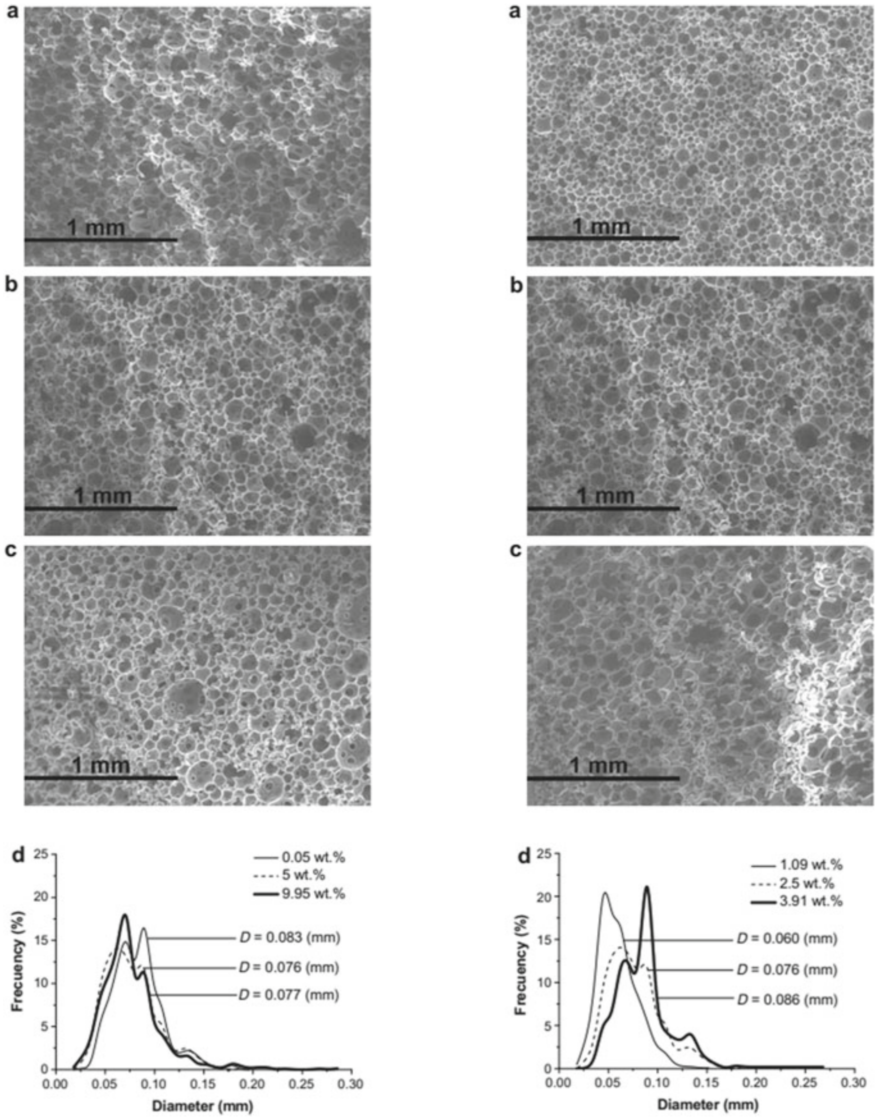

Fig. 5 SEM images for WRPFs formulated with 2.5 wt.% of blowing agent and **a** 0.05, **b** 5, and **c** 9.95 wt.% of wood flour and **d** cell size distributions, SEM images for 5 wt.% WRPFs formulated with **a** 1.09, **b** 2.5, and **c** 3.91 wt.% of blowing agent and **d** cell size distributions [31]

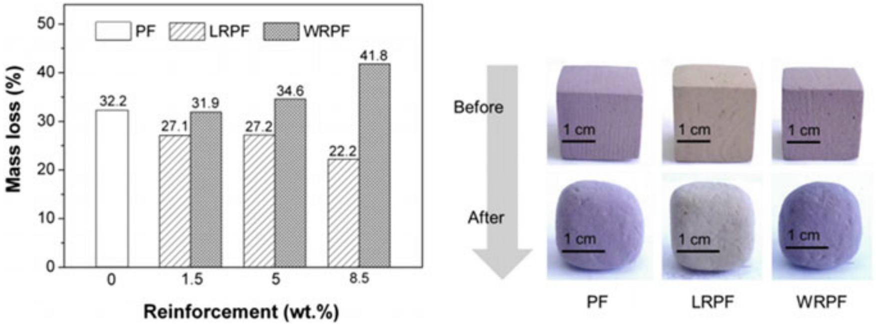

Fig. 6 **a** Mass loss during friability test for unreinforced and reinforced phenolic foams, **b** Friability test specimens of unreinforced phenolic foam, 8.5 wt.% lignin particle and 8.5 wt.% wood flour-reinforced phenolic foams [34]

of defects (cracks etc.) and modification of crack propagation, which favors higher wear of material during friability tests. On the other hand, the addition of lignin particles caused a decrease in friability. The observed change of parameters may be caused by the modification of the cell edge thickness and cell size of the foam cells caused by the addition of fillers. The values of weight loss for these materials are shown in Fig. 6.

Thermal stability of the material was studied by thermogravimetry (TGA). Obtained thermograms were characterized by a three-stage course. The first step (below 150 °C) is related to the moisture and volatile products (formaldehyde, phenols, etc.) losses. The second step (between 150 and 500 °C) is associated with degradation of the polymer, while polymer bonds brake and formaldehyde and water particles are generated. During the last step of degradation at temperatures over 500 °C, generation and release of carbonaceous substances occur. It was also shown that addition of lignin particles negligibly changed $T_{5\%}$ and ash content ($ASH_{900\,°C}$), however, $T_{25\%}$ decreased. Authors observed that wood flour reinforced foams had higher $T_{5\%}$ and ash content but $T_{25\%}$ has been significantly lowered. Although both substances modified thermal stability of materials, significant reinforcement effect is visible only in the temperature range of 250–500 °C in which wood flour particles and lignin decompose faster than phenolic foam.

Regarding hygrothermal aging, authors noted that strain–stress curves of the materials after aging were more similar to the plastic foams but unaged materials showed the nature of brittle foams. It can be concluded that water shows a plasticizing effect on polymeric material. This effect is confirmed by decrease in mechanical properties of the materials after aging in comparison to the unaged materials. Compressive modulus and strength before and after hygrothermal aging for PF, 8.5 wt.% LRPF and 1.5 wt.% WRPF are shown in Fig. 7. For reinforced materials, a greater decrease in properties is observed, but still, these samples have better properties than an aged material without any filler. SEM micrograms of samples subjected to the

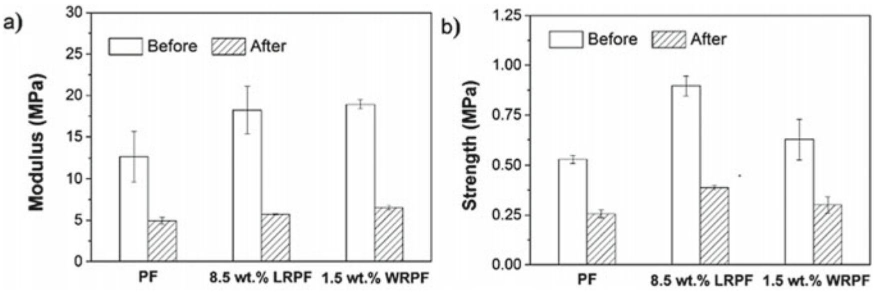

Fig. 7 Compressive mechanical properties for unreinforced and reinforced phenolic foams before and after hygrothermal aging: **a** Modulus, **b** Strength [34]

hygrothermal aging showed that all foams maintained similar cell size to the unaged materials.

The other paper [35] investigated the thermal stability, changes in chemical structure during thermal degradation, and the kinetics of thermal degradation of a wood flour reinforced phenolic foam.

Changes in chemical structure during thermal degradation were studied by FTIR analysis. The tests of phenolic foams, reinforced foams, and reinforcement have been conducted in room temperature, 225 °C, 375 °C, 500 °C, and 800 °C. For the phenolic foam, the spectrum obtained at room temperature was similar to the spectrum at 225 °C, indicating that the foam did not undergo changes in its chemical structure below 225 °C. Significant differences were noticed at 375 °C, when intensity of band at 1200 cm^{-1} was reduced. This can be due to pyrolysis of phenolic structures present in obtained materials. Furthermore, band at 800 cm^{-1} fully disappeared, which indicates consumption of low molecular weight structures and phenolic monomers. At 500 °C, it was noticed that band at 1200 cm^{-1} fully disappeared, which is associated with fully degradation of phenolic structures, and the intensity of band at 1581 cm^{-1} was significantly reduced. It was noticed that the FTIR spectrum of the wood reinforced material was similar to the spectrum of the PF foam. This indicates that the amount of wood flour was not high enough to cause significant structural changes during the pyrolysis process.

The thermal stability and degradation process of reinforced foams and wood flour were analyzed using the thermogravimetric analysis (TGA). For the wood flour, the study proved degradation of each component at different temperature ranges. Obtained thermograms showed that hemicellulose degrades first (between 250 and 300 °C), then degradation cellulose (between 300 and 400 °C). The third main component of wood flour—lignin degrades between 250 and 450 °C and shows a maximum degradation rate at approximately 350 °C.

The study showed that the phenolic and reinforced phenolic foams degrade differently. Again, it was confirmed that three peaks found in the DTG curve for temperatures less than 900 °C indicate three different degradation stages of the samples. Due to moisture release during measurement, results below 150 °C have been removed from all the thermograms. The results of previous studies about degradation of unreinforced and reinforced phenolic foams have been confirmed. Again, the first degradation stage occurred between 150 and 250 °C, and it is attributed to the volatilization of molecules of low molecular weight; however, it was added that responsible for this phenomenon is emission of monomeric phenol and formaldehyde, present in the structure of the foam during the curing/manufacturing process.

In the second stage of degradation, it was added that the mass loss that occurred during this stage is mainly due to the release of formaldehyde and water. It is caused by bond breaking (mostly methylene ether) and conversion into more stable structures. In this stage, the authors conclude that the mass loss could be associated with the decomposition of the material and transformation into carbonaceous structures and products low molecular products, such as water, carbon monoxide, carbon dioxide, methane, and phenol. The generation of CO_2 can be attributed to the breaking of the bridges connecting phenolic rings and of the bond joining the hydroxyl radical to the aromatic ring. It is considered that these reactions can take place at high temperatures (>500 °C) under an inert atmosphere. The radicals generated during these reactions can react with each other, leading to the formation of compounds whose functional groups are oxidized and giving rise to aldehyde groups, which can also easily oxidize carboxyl groups [36, 37].

Obtained by MFK methods, the values of activation energies are in a range of 110–170 kJ/mol. For almost all conversion ranges, the activation energies obtained for the reinforcement are constant and are about 162 kJ/mol. The results obtained using Flynn-Wall-Ozawa MFK and Kissinger–Akahira–Sunose methods showed high correlation coefficients when compared to the data. Research has also shown that the 2-Gaussian DAEM model is suitable for thermal degradation of manufactured phenolic foams and activation energy values vary between 108.6 and 175.6 kJ/mol.

7 Conclusions

Phenolic foams can be very useful materials; however, their common use is limited by disadvantages such as their high friability and low mechanical properties. A way to reduce or eliminate the drawbacks of this material may be the addition of particle reinforcement, especially wood flour. The use of this type of reinforcement not only has a pro-ecological character but also, as proved in the studies described above, has the potential to obtain materials with the desired characteristics. With this type of treatment, it is possible to obtain a material with increased compressive strength and Young modulus, reduced amount of foaming agent, and modified abrasion. It should also be remembered that the addition of wood flour increases the density of the material, which may limit its use. There is also a high possibility of an increase in the flammability of the obtained materials. Change of this parameter has not been extensively examined and requires attention in future research. Moreover, there is a lack of studies describing the biodegradability, decomposition of this material, and the effect of aging (UV, thermal, etc.) on the properties of this type of material.

References

1. John MJ, Anandjiwala RD (2008) Recent developments in chemical modification and characterization of natural fiber-reinforced composites. Polym Compos 29:187–207
2. Ou R, Xie Y, Wolcott MP et al (2014) Effect of wood cell wall composition on the rheological properties of wood particle/high density polyethylene composites. Compos Sci Technol 93:68–75
3. Olakanmi EO, Strydom MJ (2016) Critical materials and processing challenges affecting the interface and functional performance of wood polymer composites (WPCs). Mater Chem Phys 171:290–302
4. FAO. Food and Agriculture Organization of the United Nations (2020) Global Forest Resources Assessment 2020: key findings, p 16
5. Khan MZR, Srivastava SK, Gupta MK (2020) A state-of-the-art review on particulate wood polymer composites: Processing, properties and applications. Polym Test 89:106721
6. Hetzer M, De Kee D (2008) Wood/polymer/nanoclay composites, environmentally friendly sustainable technology: a review. Chem Eng Res Des 86:1083–1093
7. Fahim M, Chand N (2008) Wood reinforced polymer composites. Woodhead publishing series in composites science and engineering. Cambridge, p 180–196
8. Wong AHH., Kim YS, Singh AP, Ling WC (2005) Natural durability of tropical species with emphasis on Malaysian hardwoods – variations and prospects. Int Res Gr Wood Prot 32
9. Jiang W, Kumar A, Adamopoulos S (2018) Liquefaction of lignocellulosic materials and its applications in wood adhesives—a review. Ind Crops Prod 124:325–342
10. Karinkanta P, Ämmälä A, Illikainen M, Niinimäki J (2018) Fine grinding of wood – overview from wood breakage to applications. Biomass Bioenerg 113:31–44
11. Schwartz E.B, Russell J (2010) Functional fillers for plastics, 2nd ed. WILEY-VCH, pp 269–288
12. Pelaez-Samaniego MR, Yadama V, Lowell E, Espinoza-Herrera R (2013) A review of wood thermal pretreatments to improve wood composite properties. Wood Sci Technol 47:1285–1319
13. Haque M, Goda K, Ito H et al (2019) Fatigue performance of wet and dry pulverized wood flour reinforced PP composites. J Compos Sci 3:20
14. Geng Y, Li K, Simonsen J (2006) Further investigation of polyaminoamide-epichlorohydrin/stearic anhydride compatibilizer system for wood-polyethylene composites. J Appl Polym Sci 99:712–718
15. Gardner DJ, Han Y, Wang L (2015) Wood–plastic composite technology. Curr For Reports 1:139–150
16. van der Stelt MJC, Gerhauser H, Kiel JHA, Ptasinski KJ (2011) Biomass upgrading by torrefaction for the production of biofuels: a review. Biomass Bioenerg 35:3748–3762
17. Tumuluru JS, Sokhansanji S, Hess R et al (2011) A review on biomass torrefaction processand product properties for energyapplications. Ind Biotechnol 7:384–401
18. Cesprini E, Resente G, Causin V, et al (2020) Energy recovery of glued wood waste – a review. Fuel 262:116520
19. Ramage MH, Burridge H, Busse-Wicher M et al (2017) The wood from the trees: the use of timber in construction. Renew Sustain Energy Rev 68:333–359
20. Fan LT, Lee Y-H, Beardmore DR (1981) The influence of major structural features of cellulose on rate of enzymatic hydrolysis. Biotechnol Bioeng 23:419–424
21. Gosz K, Kowalkowska-Zedler D, Haponiuk J, Piszczyk Ł (2020) Liquefaction of alder wood as the source of renewable and sustainable polyols for preparation of polyurethane resins. Wood Sci Technol 54:103–121
22. Olszewski A, Kosmela P, Mielewczyk-Gryń A, Piszczyk Ł (2020) Bio-based polyurethane composites and hybrid composites containing a new type of bio-polyol and addition of natural and synthetic fibers. Materials (Basel) 13:2028
23. Dai J, Saayman J, Grace JR, Ellis N (2015) Gasification of woody biomass. Annu Rev Chem Biomol Eng 6:77–99
24. Funaoka M (2003) Lignin: its functions and successive flow. Macromol Symp 201:213–222

25. Mahesh V, Joladarashi S, Kulkarni SM (2020) A comprehensive review on material selection for polymer matrix composites subjected to impact load. Def Technol
26. Nabi Saheb D, Jog JP (1999) Natural fiber polymer composites: a review. Adv Polym Technol 18:351–363
27. Sapieha S, Pupo JF, Schreiber HP (1989) Thermal degradation of cellulose-containing composites during processing. J Appl Polym Sci 37:233–240
28. Guo G, Rizvi GM, Park CB, Lin WS (2004) Critical processing temperature in the manufacture of fine-celled plastic/wood-fiber composite foams. J Appl Polym Sci 91:621–629
29. Matuana LM, Stark NM (2015) The use of wood fibers as reinforcements in composites, 1st edn. Woodhead Publishing, Cambridge, pp 648–688
30. Mougel C, Garnier T, Cassagnau P, Sintes-Zydowicz N (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer (Guildf) 164:86–117
31. Del Saz-Orozco B, Alonso MV, Oliet M et al (2014) Effects of formulation variables on density, compressive mechanical properties and morphology of wood flour-reinforced phenolic foams. Compos Part B Eng 56:546–552
32. Del Saz-Orozco B, Oliet M, Alonso MV et al (2012) Formulation optimization of unreinforced and lignin nanoparticle-reinforced phenolic foams using an analysis of variance approach. Compos Sci Technol 72:667–674
33. Desai A, Nutt SR, Alonso MV (2008) Modeling of fiber-reinforced phenolic foam. J Cell Plast 44:391–413
34. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Lignin particle- and wood flour-reinforced phenolic foams: Friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos Part B Eng 80:154–161
35. Domínguez JC, Del Saz-Orozco B, Oliet M et al (2017) Thermal properties and thermal degradation kinetics of phenolic and wood flour-reinforced phenolic foams. J Compos Mater 51:125–138
36. De Carvalho G, Frollini E (2002) Lignin in phenolic closed cell foams: thermal stability and apparent density. J Macromol Sci - Pure Appl Chem 39 A:643–656
37. Hu L, Zhou Y, Zhang M, Liu R (2012) Characterization and properties of a lignosulfonate-based phenolic foam. BioResources 7:554–564

Chapter 18
Lignin Nanoparticle-Reinforced Phenolic Foams

Masoumeh Kiyanfar, Hoda Daneshvar, Seyyedeh Fatemeh Hosseini, and Mir Saeed Seyed Dorraji

1 Introduction

Foams consist of two phases: a continuous solid phase (matrix) and a discontinuous gaseous phase (cells). For the formation of foams, gas bubbles diffuse in the matrix and make open and close cells. This process directly influences the properties of the final yields such as the cell size distribution, cell type, and density of foams [1, 2]. Foam preparation conditions, materials used in its preparation, and structural parameters are effective factors in the structure and characteristics as well as the final application of foams. Phenolic compounds are widely used for the preparation of various products, including adhesives and foams. Phenolic foams (PFs) are one of the most commonly used polymeric foams [3].

Polyurethane, polyvinyl chloride, or polystyrene foams compared to PFs have less brittleness and friability, higher density, and better thermal and mechanical properties. However, they have low heat resistance and generate toxic gases during combustion. These features limited their applications where fire resistance is critical so that PFs are suitable substitutions for industrial applications especially in the area of the insulating material. Therefore, PFs attracted more attention compared to the other commercial polymeric foams because of their advantageous properties such as low flammability and outstanding fire, chemical resistance, low fire propagation speed, low smoke density, nontoxicity, high thermal stability over a broad range of temperatures, low cost, and non-dripping during combustion [4–13]. Phenolic foam's specific features make them attractive for several applications such as insulation, decontamination, fire protection, packaging, structural and domestic elements, agriculture, horticulture, and energy absorption. Phenolic resins are produced by an exothermic reaction of phenol with formaldehyde. It is a polycondensation reaction and depends

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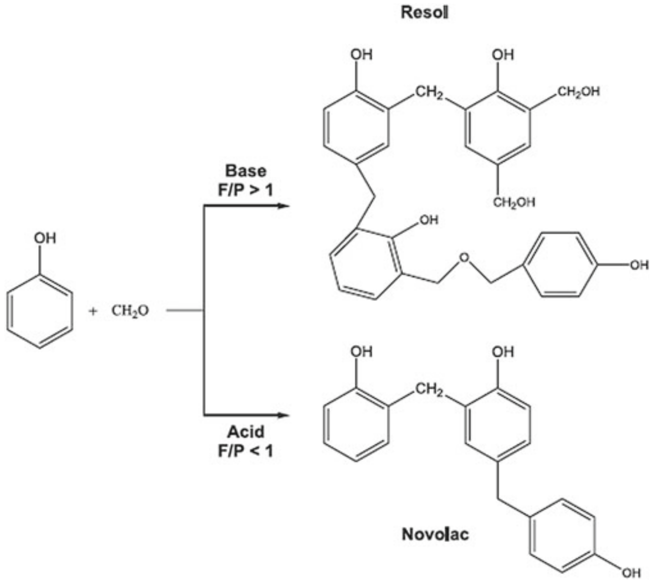

Fig. 1 Synthesis conditions for producing resol and novolac resins. Reproduced from [9] with permission from Springer

on the pH of the mixture, catalyzer, and reactant molar ratio. In the presence of acidic catalysts, two types of resin could be produced which depends on the ratio of formaldehyde to phenol (F/P, Fig. 1). If the molar ratio of F/P is less than one, it leads to the production of novolac-type resin, and if it is higher than one, it leads to the production of resol-type resin. Resol-type resins have methylol groups and they are the most used to produce foam [4, 9].

After preparing phenolic resins, the next necessary step in preparing PFs is the production of gases as an expansion agent. Gases can be obtained by evaporating a low boiling point solvent or by thermal decomposition of chemical blowing agents [9]. An emulsifier is also used to emulsify the expansion agent, and stabilize the forming foam. Other materials involved in the phenolic foam formation are a catalyst and optionally some additives for improving its final features [14].

It is noteworthy that the brittleness, friability, and pulverization tendencies are the weaknesses of PFs that restrict their applications [15]. Therefore, researchers have focused on improving the mechanical properties of PFs such as compressive strength, flexural strength, and friability, without deteriorating its excellent fire resistance. In recent years, the use of various fillers to improve the properties of phenolic foams has attracted much attention. On the other hand, the emphasis on producing the biocompatible products has led to investigate the effect of various bio-based reinforcements like inert natural filler (e.g., wood flour, lignin) and natural fibers (e.g., cellulose, kenaf) into the PFs [12, 16].

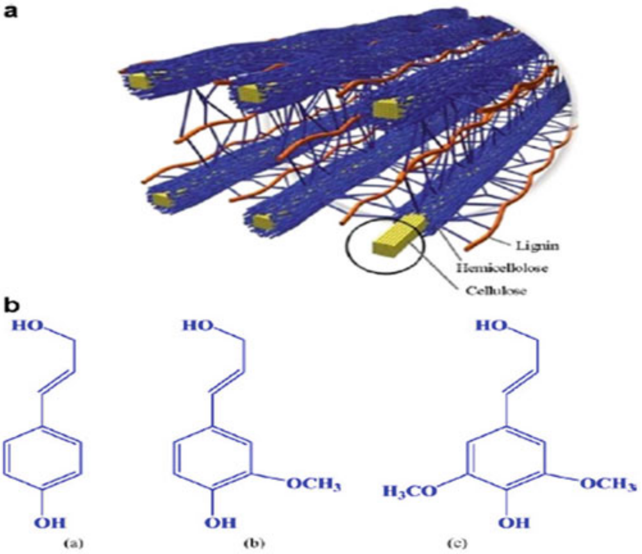

Fig. 2 **a** Cellulose strands surrounded by hemicellulose and lignin. **b** Monolignol monomer species: **a** p-coumaryl alcohol (4-hydroxyl phenyl), **b** coniferyl alcohol (guaiacyl), **c** sinapyl alcohol (syringyl). Reproduced from [22] with permission from Elsevier

In addition, the overconsumption of petroleum and other fossil fuels and also rising environmental concerns have led to increase efforts to find green and new sustainable raw material resources [17, 18]. It has been found that by biomass chemical substitution, the reduction in the use of phenol and the associated environmental pollution, and improvement in its performance can be observed [19]. Lignocellulosic biomass can be considered as one of the worldwide accessible substitutes for fossil fuels [20]. The cell walls of natural lignocellulosic biomass are composed of cellulose, hemicellulose, and lignin (Fig. 2). Researchers use lignocellulose directly or indirectly in the synthesis of foams. For example, in the synthesis of bio-foam, nanoparticles of lignin are directly added into the polymeric matrix to improve its mechanical behavior or they convert it to bio-polyols, which are used in the formation of foams [12, 21]. The amount of lignin used in the foams is less than 37% [3]. There are many phenolic hydroxyl groups in the lignin molecule, which leads to more activity of the C3 and C5 positions of guaiacol and p-hydroxyphenyl groups [6].

Lignin is the most available biopolymer, after cellulose [23, 24]. It is an amorphous polymer and is present in many different plants. The type of plant (hardwood/softwood/grass) and the extracting process affect its overall properties as well as its applications [25, 26]. Lignin is widely generated as by-products in different industries such as pulp and paper-making, ethanol production from biomass, etc. In the process of bioethanol production, the annual consumption of 225 million tons of dry biomass can produce 62 million tons of lignin [27]. Generally, the functional groups, elemental composition, and molecular weight of lignin isolated from various resources are different [28]. In recent years, only a small portion of industrial lignin is used for processes other than heat generation such as value-added products [29].

The similarity of lignin structure to phenol led researchers to study the substitution of phenol by lignin in the synthesis of lignin-based phenolic resins [30–32]. Lignin-based materials have more attractive properties compared to synthetic materials such as high abundance, low weight, inexpensive, eco-friendly, and reinforcing capability [33]. Some of the lignin-producing processes are, namely, Kraft, sulfite, soda, organ solve, hydrolysis, and steam explosion [3]. The insolubility of lignin in water limits its use in an industrial scale. Fortunately, it is now possible to prepare lignin nanoparticles dispersed in water. Researchers could successfully use the aqueous lignin nanoparticles as an improving agent in PFs [34–36]. The presence of different polar functional groups in lignin (alcohols, ketones, and aldehydes) is effective in their compatibility with the polymer matrixes [37]. The conversion of lignin into nanoparticles improves its properties compared to the raw material. Lignin nanoparticles have a higher surface area and more available functional groups (e.g., thiols, aliphatic hydroxyl, and phenolic). These features make it easier to modify the lignin surface and improve its blending properties. Also, they increase the potential applications of lignin in different fields [38].

2 Preparation of Lignin Nanoparticle-Reinforced PFs

To prepare lignin nanoparticle-reinforced phenol–formaldehyde foams, first phenol–formaldehyde resins consisting of nano-lignin are synthesized and then they are converted into the foams by incorporating other components. Phenol and formaldehyde are reacted together in an acidic or alkaline medium to form phenolic resins. Also, lignin nanoparticles are mixed with the resol resin in this step. Phenolic resins act as a solid matrix in which gas diffuses into it. Other basic components that are used in this synthesis include a blowing agent, surfactant, catalyst, and curing agent [39, 40]. The blowing agent expands that its evaporation can form a cellular structure. Some of the blowing agents are n-pentane, cyclopentane [41], hexane [42], and petroleum ethers [10]. Having the lowest boiling point (36 °C), n-pentane is the most common blowing agent for the preparation of PFs [14, 43].

The curing agent affects the final density of the foam. Therefore, depending on the desired density, the blowing agent can be used with/without the curing agent. During the foam formation process, surfactants are also used to control the characteristics of the foam by making a stable and homogeneous emulsion between the phenolic matrix and the blowing agent. Tween 40 and Tween 80 are the most used surfactants [44–46]. Catalysts increase the curing process rate. Also, they reduce the gelation time and take part in the foam expansion. Recently, acids like p-toluene sulfonic acid [47] and phenol sulfonic acid [13], compared to sulfuric acid or hydrochloric acid [13] are more used. When all of the components are mixed, the mixture is poured into a mold and is held for 1 h in a pre-heated oven at 80 ºC and post-cured for 24 h at 105 °C [40].

3 Microstructure of Lignin Nanoparticle-Reinforced PFs

The foaming process basically consists of two main steps: (a) bubble nucleation and (b) bubble growth. In the nucleation process, a new phase (bubble phase) is generated from the initially homogeneous polymer–gas mixture. In the second process, the bubble nuclei grow into final bubbles. Both processes are affected by many physical properties such as viscosity, gas solubility, surface tension, and glass transition temperature. Therefore, a change in any of these factors can affect the foam-forming process, the microstructure, and properties of foams [48]. Considering nanoparticles, they can greatly alter the physical properties of the polymer mixture and also the microstructure and density of the foams. Therefore, gaining a clear understanding of these changes is critical to study the properties of the foams. Del Saz-Orozco et al. [39] investigated the effect of formulation parameters, namely, stirring speed and blowing agent content on the microstructure of unreinforced and lignin-reinforced PFs. As shown in Fig. 3, the cell size distribution of PFs (containing 2.5 wt.% blowing agent, without lignin nanoparticles) changes by altering the stirring speed. The SEM images revealed the increase in stirring speed results in finer cells in nanocomposite foam structure. Particularly, the mean cell size decreased from 0.103 to 0.07 mm when the stirring speed increased from 609 to 750 rpm. The authors stated that at elevated stirring speeds, the surface tension of the formulation mixture decreased which favors the nucleation of bubbles in the foaming process and decreased the mean cell size in the foam structure [49].

The SEM images also reveal that the effect of blowing agent content is not as significant as the stirring rate; however, when the blowing agent content was decreased, the mean cell size increased. The possible explanation could be the higher gas supply in the formulation mixture at higher blowing agent content [50].

As illustrated in Fig. 4, the mean size of the cells in the foam decreased as the lignin nanoparticle percentage decreased from 0.05 to 9.95 wt.%. It is reported that lignosulfonates can have surfactant properties decreasing the surface tension of the formulation mixture, which the same as stirring speed favors the nucleation of bubbles in the foaming process resulting in finer cell size [49, 51].

In another study conducted by the same group later in 2015 [52], the effect of hydrothermal aging (the samples were placed in an environmental chamber at 38 °C and 97% of relative humidity for 2 weeks) on the morphology and cell size distribution of unmodified PFs and lignin-modified PFs (8.5 wt.%) was investigated. The results suggested that hydrothermal aging did not affect cell size distribution. It can be seen in Fig. 5 that both unmodified and modified foams exhibited similar diameters before and after aging.

Moreover, the same as their previous study, the cell size of the foam decrease from 0.085 to 0.061 mm after the addition of lignin nanoparticles.

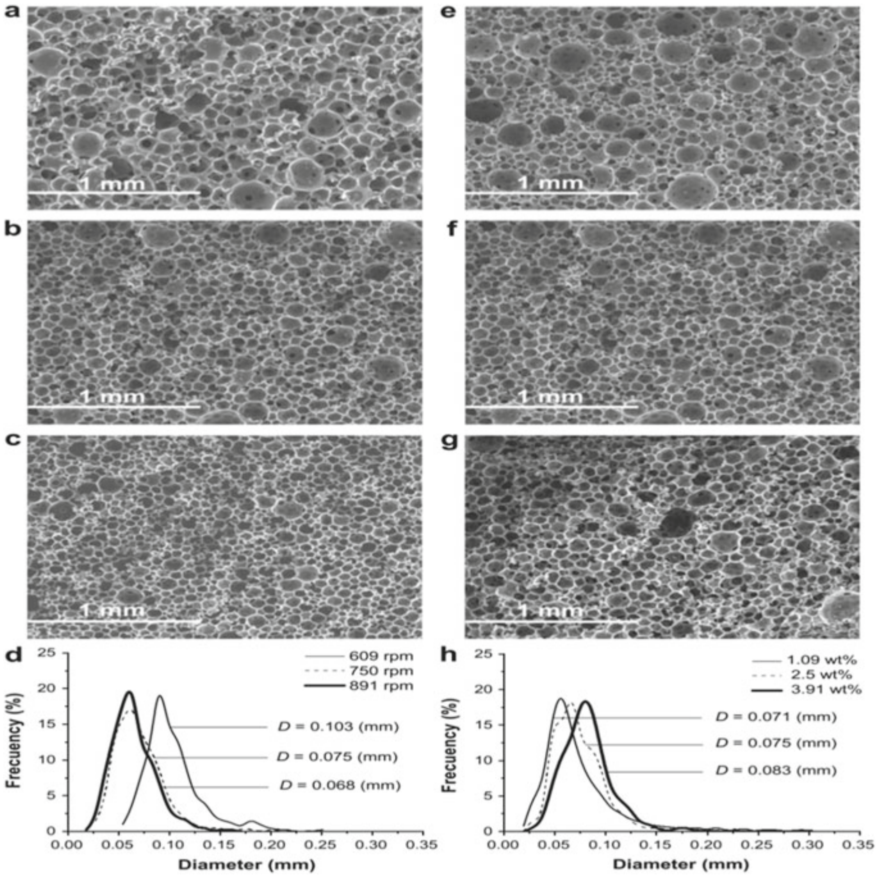

Fig. 3 SEM images of PFs formulated at stirring rate of **a** 609, **b** 750, **c** 891 rpm, and **d** their respective cell size distribution. SEM images of PFs formulated with **e** 1.09, **f** 2.5, **g** 3.91 wt.% blowing agent and stirring rate of 750 rpm and **h** their respective cell size distribution. Reproduced from [39] with permission from Elsevier

4 Physical Properties

4.1 Mechanical Properties and Friability

PFs are one of the best options to use in structural and insulating applications, especially when the fire resistance is crucial, mostly because of their high thermal stability, low thermal conductivity, and significant fire-resistant properties [53]. Nevertheless, as a severe drawback, the low mechanical properties of PFs compared to polymeric foams should be overcome to fabricate tougher PFs. The aromatic structure and rigidity of lignin nanoparticle make it an exceptional candidate to be used as a reinforcing component in polymer composites. In this context, Del Saz-Orozco et al.

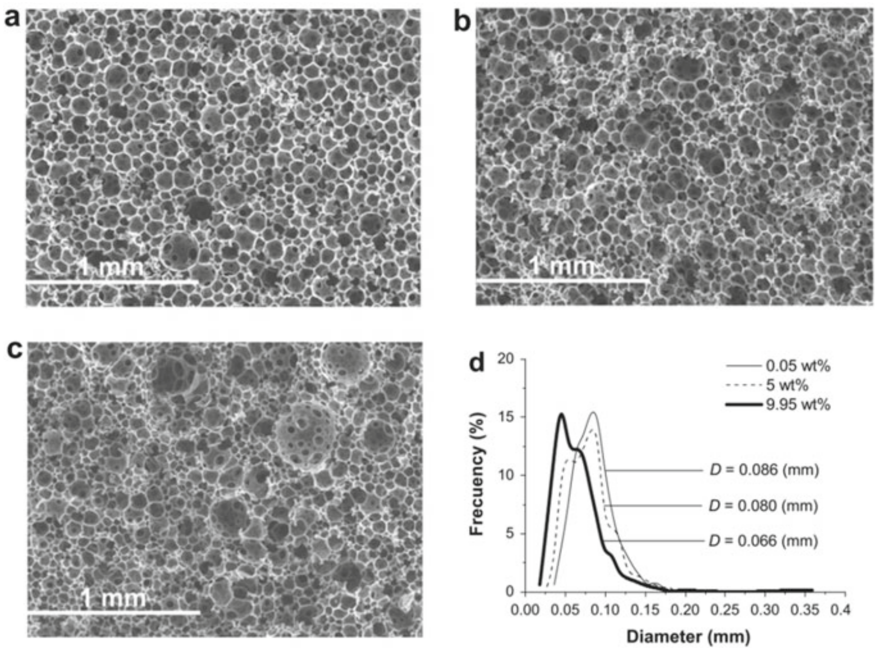

Fig. 4 SEM images of lignin nanoparticle-reinforced PF containing **a** 0.05, **b** 5, **c** 9.95 wt.% lignin, and **d** their respective cell size distribution. Reproduced from [39] with permission from Elsevier

[39] applied the ANOVA method to determine the influence of the formulation variables of lignin nanoparticle-reinforced phenolic foam (LRPF) such as stirring speed, blowing agent amount, and lignin nanoparticle percentage on the mechanical properties and density of the prepared foams. Based on the results of the experiments the modulus and strength of LRPFs were enhanced compared to pure PFs up to 128% and 174%, respectively. Moreover, the amount of needed blowing agents reduced by 31% with the use of lignin nanoparticles as a reinforcing agent, which reduced the used chemicals and fabrication costs.

In their next work, Del Saz-Orozco et al. [52] studied the effect of LRPF and wood flour-reinforced phenolic foam (WRPF) on the friability of PFs, and the effect of hydrothermal aging on mechanical properties. Friability is of great importance as it indicates the capacity of being easily disintegrated in small particles, and materials with high friability can generate a considerable amount of dust during work which is dangerous for human health.

The values of mass loss for the PF and LRPF and WRPF (reinforced with 8.5 wt. %) were measured to be 32.2%, 22.2%, and 42.8%, respectively. Besides, PF/8.5 wt.% LFPF and 8.5 wt.% WRPF before and after the friability test are shown in Fig. 6. The presence of lignin particles decreased mass loss of the phenolic foam which can be due to the agglutinating properties of lignin nanoparticles, which increases the toughness of the material [22]. Interestingly, wood flour adversely affects the

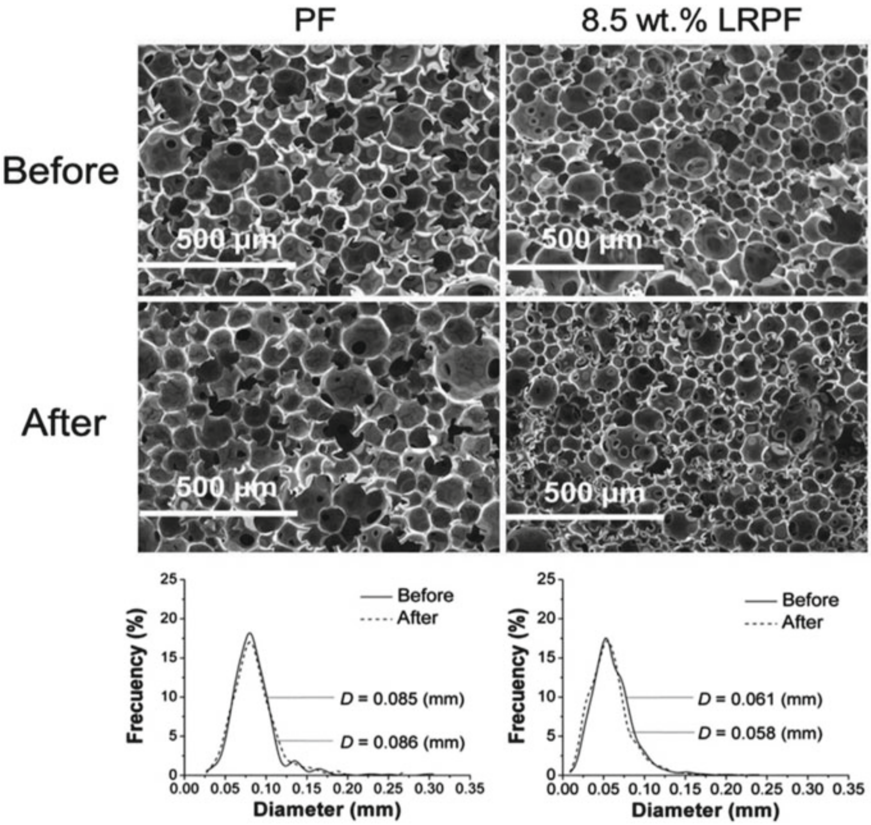

Fig. 5 SEM images and cell size distribution of pure PF and lignin-reinforced PF before and after hydrothermal aging. Reproduced from [52] with permission from Elsevier

friability and increased by 30% concerning PF. This could be a result of defects in the material such as cracks, which can favor the mass loss of the foam during the friability test.

To make sure that PFs are the right choice to use in the insulating application, investigating their behavior under moister and pressure is essential. The strain–stress curves of unreinforced and 8.5 wt.% lignin nanoparticle-reinforced PFs, before and after the hydrothermal aging, are shown in Fig. 7.

The LRPF and PF transformed from rigid brittle foams to plastic foams after hydrothermal aging as it is evident from strain–stress curves [54]. This change in behavior could be the result of the plasticizing effect of water on polymeric materials [55]. It can be seen that the mechanical properties for both modified and unmodified PFs decreased after hydrothermal aging. In particular, the change in compressive modulus after hydrothermal aging was 61% and 69% for PF and LRPF, respectively. The reduction of stress values after hydrothermal aging in LRPF was also due to a weakened interface of matrix reinforcement as a result of the interaction

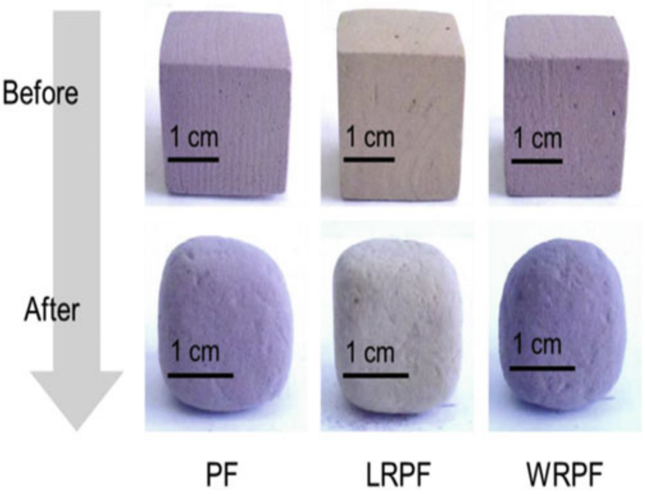

Fig. 6 Friability test of PF and reinforced PF containing 8.5 wt% lignin nanoparticle and wood flour. Reproduced from [52] with permission from Elsevier

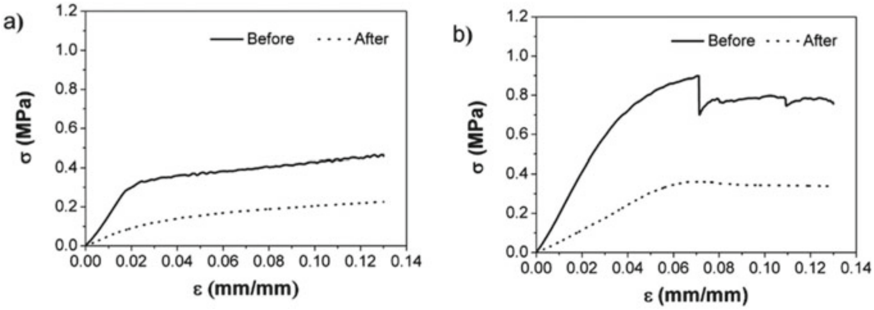

Fig. 7 Strain–stress curves of **a** PF and **b** LRPF before and after hydrothermal aging. Reproduced from [52] with permission from Elsevier

between water molecules and the lignin particles. Although the reduction in mechanical properties of lignin-reinforced foams was higher than for the unreinforced foam after hydrothermal aging, modulus and strength of the reinforced foams were significantly improved after the addition of lignin nanoparticle. The modulus and the strength of 5.72 and 0.388 MPa were achieved for LRPF which were considerably improved compared to PF with modulus and strength of 4.95 and 0.256 MPa. The best overall performance before and after hydrothermal aging was obtained when 8.5 wt.% of lignin particles were incorporated in PFs.

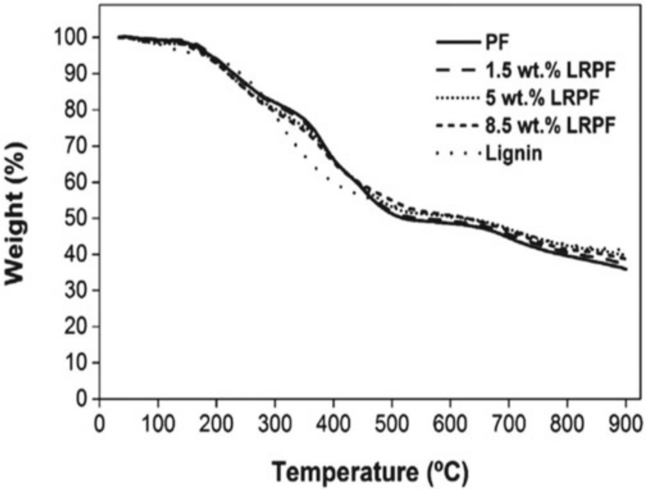

Fig. 8 Thermograms of PF and LRPF with different weight fractions. Reproduced from [52] with permission from Elsevier

4.2 *Thermal Stability and Degradation*

As mentioned before, PFs are mainly used in insulating applications. Therefore, thermal stability in a broad range of temperature and fire-resistance properties are important features to study [52]. Del Saz-Orozco et al. [52]studied the thermograms of PF and LRPFs containing several reinforcement weight fractions as shown in Fig. 8. The similarity thermograms of both foams are because they have similar polyphenolic chemical structure [56]. It can be seen that thermal degradation happens in three steps. The first step occurs at temperature below 150 °C and corresponds to the loss of volatile compounds and moisture.

The second step which takes place between 150 and 500 °C is due to the degradation of the polymer, cleavage of weak polymer bonds, and the release of water. And last the release of carbonaceous substances which happens [7, 40]. Moreover, T5%, T25%, and Ash 900 °C of PF were measured, and in the temperature range between 250 and 500 °C, LRPF degrades significantly faster than PF. In short, it was noted that lignin nanoparticles did not significantly influence the thermal stability, except for the range of 250–500 °C.

5 Conclusion

In this study, the developments and general views concerning the fabrication of lignin/PF nanocomposites and the influence of nanoparticles on mechanical, thermal, and structural properties of PFs have been discussed in detail. It can be concluded from the above studies that the use of lignin nanoparticles as an improving agent in the PF structure can significantly increase their mechanical and thermal stabilities, compared to the pure PFs. In addition, the microstructure of the PFs improves with an increase of lignin nanoparticle loading. It can be explained by the good dispersion of lignin nanoparticles in PF matrix and creating the strong crosslink between nanoparticles and resin.

Briefly, the lignin nanoparticles/PF composites present both serious challenges and excellent potential, so it can be considered as a research field for years to come. Moreover, the outstanding progress in the applications and improvement of these foams will strongly depend on how we can solve the challenges.

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References

1. Imeokparia DD, Suh KW, Stobby WG (2002) Cellular materials. EPST, Wiley, New York
2. Gibson L, Ashby M (1997) The mechanics of foams: basic results. Cellular solids. Structure and properties. Cambridge University Press, United Kingdom. http://ocw.raf.edu.rs/courses/materials-science-and-engineering/3-054-cellular-solids-structure-properties-and-applications-spring-2014/lecture-notes/MIT3_054S14_L1_intro.pdf
3. Mimini, V, Kabrelian V, Fackler, et al (2018) Lignin-based foams as insulation materials: a review. Holzforschung 73(1):117–130
4. Del Saz-Orozco B, Alonso MV, Oliet M et al (2014) Effects of formulation variables on density, compressive mechanical properties and morphology of wood flour-reinforced phenolic foams. Compos B Eng 56:546–552
5. Ma Y, Wang C, Chu F (2017) Effects of fiber surface treatments on the properties of wood fiber-phenolic foam composites. BioResources 12(3):4722–4736
6. Zhang N, Hu L, Guo Y et al (2020) Mechanical property of lignin-modified phenolic foam enhanced by whisker silicon. J Dispers Sci Technol 41(3):348–354
7. Auad ML, Zhao L, Shen H et al (2007) Flammability properties and mechanical performance of epoxy modified phenolic foams. J Appl 104(3):1399–1407
8. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Compos Part A-Appl Sci Manufact 34(9):899–906
9. Pilato L (2010) Phenolic resins: a century of progress. Springer, Heidelberg
10. Liu L, Fu M, Wang Z (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 54(7):1962–1970
11. Gao M, Yang YL, Xu ZQ (2013) Mechanical and flame retardant properties of phenolic foam modified with polyethyleneglycol as toughening agent. Open J Adv Mater Res 803:21–25
12. Vickers NJ (2017) Animal communication: when i'm calling you, will you answer too? Curr biol 27(14):R713–R715
13. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Compos B Eng 75:367–372
14. Li Q, Chen L, Li X, et al (2016) Effect of nano-titanium nitride on thermal insulating and flame retardant performances of phenolic foam. J Appl 133(32)
15. Li Q, Chen L, Zhang J et al (2015) Enhanced mechanical properties, thermal stability of phenolic formaldehyde foam/silica nanocomposites via in situ polymerization. Polym Eng Sci 55(12):2783–2793

16. Shen H, Lavoie AJ, Nutt SR (2003) Enhanced peel resistance of fiber reinforced phenolic foams. Compos Part A-Appl Sci Manufact 34(10):941–948
17. Shukla SK, Maithani A, Srivastava D (2014) Studies on the effect of concentration of formaldehyde on the synthesis of resole-type epoxidized phenolic resin from renewable resource material. Des Monomers Polym 17(1):69–77
18. Rybarczyk MK, Peng H-J, Tang C et al (2016) Porous carbon derived from rice husks as sustainable bioresources: insights into the role of micro-/mesoporous hierarchy in hosting active species for lithium–sulphur batteries. Green Chem 18(19):5169–5179
19. Lihong H (2012) Progress of bio-based phenolic foam. New Chemical Material, China
20. Norgren M, Edlund H (2014) Lignin: recent advances and emerging applications. Curr Opin Colloid Interface Sci 19(5):409–416
21. Gu R, Sain MM, Konar SK (2013) A feasibility study of polyurethane composite foam with added hardwood pulp. Ind Crops Prod 42:273–279
22. Doherty WO, Mousavioun P, Fellows CM (2011) Value-adding to cellulosic ethanol: lignin polymers. Ind Crops Prod 33(2):259–276
23. Notley SM, Norgren M (2010) Surface energy and wettability of spin-coated thin films of lignin isolated from wood. Langmuir 26(8):5484–5490
24. Bertini F, Canetti M, Cacciamani A et al (2012) Effect of ligno-derivatives on thermal properties and degradation behavior of poly (3-hydroxybutyrate)-based biocomposites. Polym Degrad 97(10):1979–1987
25. He Z-W, Yang J, Lü Q-F, Lin Q (2013) Effect of structure on the electrochemical performance of nitrogen-and oxygen-containing carbon micro/nanospheres prepared from lignin-based composites. ACS Sustain Chem Eng 1(3):334–340
26. Mu W, Ben H, Ragauskas A, Deng Y (2013) Lignin pyrolysis components and upgrading—technology review. Bioenergy Res 6(4):1183–1204
27. Wang H, Pu Y, Ragauskas A et al (2019) From lignin to valuable products–strategies, challenges, and prospects. Bioresour Technol 271:449–461
28. Upton BM, Kasko AM (2016) Strategies for the conversion of lignin to high-value polymeric materials: review and perspective. Chem Rev 116(4):2275–2306
29. Agarwal A, Rana M, Park JH (2018) Advancement in technologies for the depolymerization of lignin. Fuel Process Technol 181:115–132
30. Del Saz-Orozco B, Oliet M, Alonso M, et al (2012) Study of lignin nanoparticle-reinforced phenolic composite foams formulation using an experimental design. In: Paper presented at the 15th international conferance on composite materials, Venice, Italy, 24–28 June 2012
31. Glasser WG, Barnett CA, Muller PC et al (1983) The chemistry of several novel bioconversion lignins. J Agric Food Chem 31(5):921–930
32. Xiao S, Feng J, Zhu J et al (2013) Preparation and characterization of lignin-layered double hydroxide/styrene-butadiene rubber composites. J Appl 130(2):1308–1312
33. Singha A, Thakur VK (2010) Mechanical, morphological, and thermal characterization of compression-molded polymer biocomposites. Int J Polym Anal Charact 15(2):87–97
34. Wei Z, Yang Y, Yang R et al (2012) Alkaline lignin extracted from furfural residues for pH-responsive Pickering emulsions and their recyclable polymerization. Green chem 14(11):3230–3236
35. Nypelö TE, Carrillo CA, Rojas OJ (2015) Lignin supracolloids synthesized from (W/O) microemulsions: use in the interfacial stabilization of Pickering systems and organic carriers for silver metal. Soft Matter 11(10):2046–2054
36. Richter AP, Brown JS, Bharti B et al (2015) An environmentally benign antimicrobial nanoparticle based on a silver-infused lignin core. Nat Nanotechology 10(9):817–823
37. Sahoo S, Seydibeyoğlu M, Mohanty A et al (2011) Characterization of industrial lignins for their utilization in future value added applications. Biomass Bioenergy 35(10):4230–4237
38. Zhao W, Simmons B, Singh S et al (2016) From lignin association to nano-/micro-particle preparation: extracting higher value of lignin. Green chem 18(21):5693–5700
39. Del Saz-Orozco B, Oliet M, Alonso M et al (2012) Formulation optimization of unreinforced and lignin nanoparticle-reinforced phenolic foams using an analysis of variance approach. Compos Sci Technol 72(6):667–674

40. de Carvalho G, Frollini E (2002) Lignin in phenolic closed cell foams: thermal stability and apparent density. J Macromol Sci A 39(7):643–656
41. Jing S, Li T, Li X, et al (2014) Phenolic foams modified by cardanol through bisphenol modification. J Appl 131(4)
42. Zhou J, Yao Z, Chen Y et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym compos 35(3):581–586
43. Li X, Wang Z, Wu L et al (2016) One-step in situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 6(78):74903–74912
44. Lee SH, Teramoto Y, Shiraishi N (2002) Resol-type phenolic resin from liquefied phenolated wood and its application to phenolic foam. J Appl 84(3):468–472
45. Hu L, Zhou Y, Liu R et al (2013) Synthesis of foaming resol resin modified with oxidatively degraded lignosulfonate. Ind Crops Prod 44:364–366
46. Hu L, Zhou Y, Zhang M et al (2012) Characterization and properties of a lignosulfonate-based phenolic foam. BioResources 7(1):0554–0564
47. Li Q, Chen L, Li X et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Compos Part A Appl Sci Manuf 82:214–225
48. Lee LJ, Zeng C, Cao X et al (2005) Polymer nanocomposite foams. Compos Sci Technol 65(15–16):2344–2363
49. Housel T (2004) Flexible polyurethane foam. In: Eaves D (ed) Handbook of polymer foams. Rapra Technology Ltd, United Kingdom, pp 85–122
50. Yun MS, Lee WI (2008) Analysis of bubble nucleation and growth in the pultrusion process of phenolic foam composites. Compos Sci Technol 68(1):202–208
51. Landrock AH (1995) Handbook of plastic foams: types, properties, manufacture and applications. Elsevier, Netherlands
52. Del Saz-Orozco B, Alonso MV, Oliet M et al (2015) Lignin particle-and wood flour-reinforced phenolic foams: friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology. Compos B Eng 80:154–161
53. Guo Y, Hu L, Bo C, Shang Q et al (2018) Mechanical property of lignin-modified phenolic foam enhanced by nano-SiO_2 via a novel method. Chem Pap 72(3):763–767
54. Gibson LJ, Ashby MF (1999) Cellular solids: structure and properties. Cambridge University Press, United Kingdom
55. Wan Y, Luo H, He F et al (2009) Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. Compos Sci Technol 69(7–8):1212–1217
56. Alonso M, Oliet M, Pérez J, et al (2004) Determination of curing kinetic parameters of lignin–phenol–formaldehyde resol resins by several dynamic differential scanning calorimetry methods. Thermochim Acta 419:161–167

Chapter 19
The Role of Polyurethane Chemistry on the Properties of Phenolic Foams Applied in the Thermal Insulation Industry

Chiacchiarelli Leonel Matías

1 Introduction

Phenolic foams (PFs) represent the material of choice whenever fire resistance is a fundamental design requirement. The combination of a very low-flame spread velocity, almost null smoke or toxic gas emissions, no liquid dripping when subjected to high temperatures, and high insulation value represent the key distinct properties that differentiate PF with respect to other insulation materials available in the industry [1, 2]. According to the European Phenolic Foam Association (EPFA), the main applications of PF are insulation, mining, and floral.

The use of urea–formaldehyde PF in housing and industrial structures was introduced in the 1960s in northern Europe [3, 4], while in the 1970s, Canada and the USA continued this path. However, the emissions of formaldehyde gas provoked by poor industrial application standards in the interior of residential houses caused a severe setback in the residential industry in Canada and the USA. Another issue was raised in the 1990s, where the application of PF in decking caused corrosion in metallic structures. Recent research programs led mostly by the Department of Energy of the USA [1] are aimed at the development of PF with a higher pH and improved adhesive as well as mechanical properties. The recent transition of the construction industry from traditional wet construction systems to industrialized building systems (IBS) will lead the way to increased growth of the PF industry in sandwich structures [5]. The main advantage of this approach is that the structural panel is manufactured continuously in an industrial environment. Due to the fact that it is possible to introduce high-quality standards and to maintain this in a localized manufacturing

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facility, future initiatives in the development of PF applied in sandwich construction will certainly pave the way to a new growth stage. One of the key issues to catalyze this growth is related to the highly friable nature of PF. The use of polyurethane chemistry is a key aspect to reduce the friability of PF without a simultaneous deleterious effect on flammability performance. To achieve this objective, reactive routes based on the use of isocyanate prepolymers represent the state-of-the-art. Other methodologies based on the use of composites and nanotechnology will also be discussed in this chapter, emphasizing the interplay between these strategies and the cure kinetics, friability, flammability, and environmental impact of PF and PUF.

Another relevant application of PF is in underground mining [1]. During normal operations, if mineworkers stumble into an unstable crumble rock face or lair, it is frequent to use foams so as to eliminate a plausible accident. To this effect, PF foams are usually sprayed in situ so as to increase structural stability. The main advantage of PF applied in this industry is related to the fact that when it is accidentally ignited, no volatile emissions are released. Finally, PF is also used for the growth of flowers and all sorts of floral arrangements. It is important to highlight that, due to the niche nature of these last applications, in this chapter our discussion will be centered on PF applied in thermal insulation.

In contrast to PF, polyurethane foams (PUF) also find widespread uses in industry, such as spray-up thermal insulation as well as structural panels [6, 7]. Even though both PF and PUF share a common chemical precursor, that is, benzene, initial R&D efforts were not focused on using both systems synergistically. This has led to the development of parallel industries known as the phenolic and polyurethane foam industries. Nowadays, the R&D efforts focus on the development of PF with improved toughness retaining as well as high fire resistance. To achieve this goal, it is important to apply a synergistic approach using polyurethane chemistry as an ally. For example, the introduction of isocyanate prepolymers and glycols in the molecular structure of PF can help to improve toughness without altering significantly other relevant properties.

The main objective of this chapter is to highlight how PF properties can be tailored using the flexibility of polyurethane chemistry. To this effect, Sect. 2 will deal with a brief introduction on polyurethane chemistry, emphasizing the principal concepts and ideas which are frequently used by polyurethane specialists. Due to the fact that this book is specialized in phenolic foams, the reader can consult specific aspects of PF chemistry in other chapters. The following section will focus on correlating the properties of PF and PUF, particularly on the areas of formulations, blowing agents, cure kinetics, friability, environmental impact, and flammability. Section 4 will deal with how reactive routes are applied in PF chemistry. The section starts laying out the main principles associated with the use of reactive routes and how those are related to polyurethane chemistry. Then, study cases are presented so as to illustrate the main application of those principles. Finally, the chapter finalizes with a conclusion section so as to emphasize the main concepts that were studied in this chapter.

2 A Brief Introduction to the Polyurethane Chemistry

The polyurethane chemistry was born when Dr. Otto Bayer, around the year 1938, reacted a diisocyanate with a natural polyester polyol, that is, castor oil [7]. Nowadays, the polyurethane industry represents one of the most relevant polymeric commodities and their applications range from flexible to rigid foams, coatings, thermoplastic and thermosetting polymers, adhesives, sealants, as well as other applications. This versatility is based mostly on the chemistry of the diisocyanate precursor, where its facile reaction with a wide range of functional groups has led to such different applications and uses.

Polyurethanes are obtained through the reaction of two main chemical precursors, diisocyanates (from now on isocyanates) and polyols. Blowing agents (BAs), catalysts, surfactants as well as other additives are usually employed and dispersed within the polyol component. In industry, both physical and chemical BAs are usually employed. The physical BAs rely on the evaporation of a low melting point liquid (such as a hydrocarbon) and the chemical BAs are based on the reaction of isocyanate with water, forming carbon dioxide during PUF cure [7]. Hence, polyurethane chemistry can be significantly altered mostly by chemical BAs, because the in situ formation of CO_2(g) can compete with the chemical reactions of the polyol with the isocyanate precursor [6]. In PUFs, catalysts are usually employed to increase the gelling and blowing reactions [8]. In this regard, tin-based catalysts are frequently employed to increase the cure kinetics of reactions between isocyanates and hydroxides (polyol). On the other hand, amine-based catalysts are usually responsible to improve the kinetics of blowing reactions, such as the formation of CO_2(g) from isocyanate and water. Typical formulations of PUFs usually employ both catalysts, whereas the specific concentrations are carefully determined so as to have the right balance between the gelling and blowing reactions. Surfactants are a key aspect for the development of a closed and homogeneous cell structure. These usually don't have a substantial effect on polyurethane chemistry, but instead, have a preponderant role in the formation of a PUF with a high content of closed cells.

From an industrial point of view, polyurethanes are usually two-component systems, where component A is usually a mixture of different types of isocyanates and component B represents the polyol and all the remaining additives and catalysts. The preferred isocyanate used for the thermal insulation industry is polymeric methylene diphenyl diisocyanate (pMDI). Due to the fact that MDI is solid at room temperature, eutectics are usually employed to obtain a pMDI with low viscosity, that is, within the range of 200–400 cp (at 25 °C). The main characteristic of pMDI is the isocyanate number (NCO_{number}), which is a measurement of how many isocyanate groups are available to react on a weight basis. This value should not be confused with the isocyanate index, which is referred to as the stoichiometric relationship between isocyanate and hydroxide (or other reactive) groups present in the component B. On the other hand, the polyol is usually a blend of a wide range of monomers characterized mainly by its molecular weight, functionality, and viscosity. A higher molecular weight polyol is usually employed to mitigate the effect of a highly crosslinked structure, which will inevitably lead to fragile material. This characteristic is of paramount importance for the reactive modification of PF precursors. Further details will be explained in Sect. 4. The functionality has also a relevant impact on the final properties of the material. Due to the fact that both PF and PUF are crosslinked polymers (thermosetting), polyols with functionality above 2.0 are mostly employed. The chemical nature of the functionality is also relevant; hydroxides being the main radical group that is used to react with the isocyanate moiety. Viscosity plays a fundamental role, particularly when processing technology is taken into account. In this regard, polyols with either low, medium, or high viscosities can be employed (200–4000 cp). A summary of the properties of the precursors frequently used for PUF systems is depicted in Table 1.

Polyurethanes can be prepared using the one-shot [9], quasi-prepolymer [10], and prepolymer techniques [11]. The distinction between these three types of techniques is fundamental, especially when PFs are taken into consideration. Further details about the relationship between these techniques and PF synthesis will be discussed in the next section. The one-shot technique [6] is usually employed for the preparation of either flexible or rigid polyurethane foams (RPUF). In this method, the precursors need to be of relatively low viscosity (<1000 cp) so as to achieve good physical mixing using conventional or high-pressure dosing equipment. The properties of a typical PUF precursor used for the one-shot technique are reported in Table 1. As it can be deduced, the isocyanate component (A) has a high $\mathrm{NCO}_{\mathrm{number}}$ (29.0%), which is an indication that no reaction has taken place so as to change the properties of this component. With respect to the polyol (B), in this case the hydroxide number (#OH) and functionality indicate that the polyol has been formulated for in situ spray foaming.

The quasi-prepolymer technique is based on the use of precursors which are the reaction products of a blend of polyols with a large excess of isocyanate. The term adduct is usually employed to identify this intermediate, which has a lower $\mathrm{NCO}_{\mathrm{number}}$, between 15 and 29 wt%. The main objective of this technique is to circumvent one of the great disadvantages of isocyanates, that is, the unstable nature of isocyanate moieties. These are prone to react with water, forming both carbon dioxide and polyamines. In addition, a reduced volatile organic content (VOC) can also be achieved, reducing the environmental impact of the formulation. Further details can be consulted in Table 1.

Finally, the prepolymer is an isocyanate adduct with a lower $\mathrm{NCO}_{\mathrm{number}}$, between 1 and 14 wt%. These are usually synthesized by the slow addition of specific polyols to isocyanates in reactors under a controlled atmosphere (dry nitrogen gas) and temperature (around 60 °C). The resulting monomers are usually applied in urethane elastomers, coatings, adhesives, sealants as well as toughening agents of PF (Sect. 4). The main advantage of using this approach relies on the fact of a reduced cured exotherm, which leads to a widespread family of versatile polymers. These materials are also reacted with chain extenders, i.e., long aliphatic monomeric species which serve to increase molecular weight and to cause significant toughness improvements. In PF chemistry, it is usual to apply this technique, whereas the main disadvantage

Table 1 Physical properties of typical PUF and PF systems

Property	PUF (spray-up)[1]		PUF prepolymer (elastomer)[2]	PUF (quasi-prepolymer)[3]	Phenolic foam[4]	
	CA (isocyanate)	CB (Polyol)	CA (isocyanate)	CA (polyol)	CA (phenolic resin)	Catalyst
NCO_{number} (%)	30–32.5	–	5–7	16.5–22.5	–	–
HCl acidity (ppm)	<200	<100	<150	<100	–	–
Viscosity (cp)	150–300 (25 °C)	200–500 (25 °C)	1000–4000 (50 °C)	3000–10,000 (50 °C)	2000–8000(25 °C)	<10 (25 °C)
Density (g/m^3)	1.20–1.22	1.10–1.15	1.10–1.15	1.10–1.15	1.1–1.2	1.8–2.3
#OH	–	250–300	–	–	–	–
Functionality	2.1–2.9	>3.0	>2.5	>3.0	–	–
pH	–	–	–	–	8.50–9.50	<4.0
Dry solid content (%)	>99.9	>93	>99.9	>99.9	75–80	Liquid
Free phenol (%)	0	0	0	0	4.5–6.5	0
Free formaldehyde (%)	0	0	0	0	<1.40	0

of using it relies on its impact on fire performance (Sect. 3). Specific details of an isocyanate prepolymer are reported in Table 1.

3 Correlating Cellular Structures Based on Polyurethane and Phenolic Chemistry

The phenolic chemistry is based on the chemical reaction of a phenol and formaldehyde in either acidic (Novolak) or basic conditions (resole). One of the key features is that the reaction can be performed either in acidic or basic conditions by changing the molar ratio of the phenol and formaldehyde precursors (P/F ratio). When the P/F ratio is less than 1, the molecular structure of the resulting phenolic resins is very stable (Novolak), whereas its subsequent use as a precursor for other materials is based solely on the use of catalysts. Taking into account the molecular structure (Fig. 1A) of the resulting precursor, Novolak resins can also be understood as low molecular weight and highly aromatic polyols [12], giving rise to a highly friable structure. Hence, the use of Novolak resins in the formulation of PF is not frequently employed, because it increases the crosslinking and aromatic content, giving rise to an extremely friable PF [1].

On the other hand, when the P/F ratio is higher than 1, the resulting molecular structure of the phenolic resin is not stable (resole), giving rise to resole-type precursors (commonly known in the industry as resins). The main reason associated with

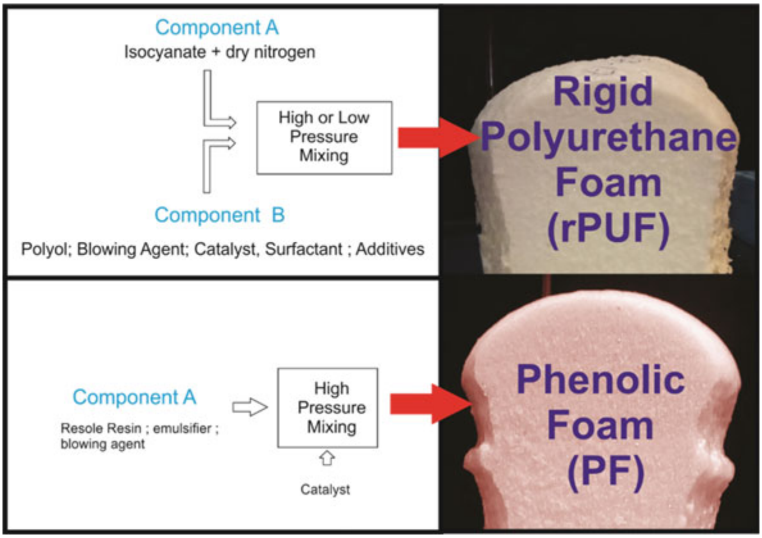

Fig. 1 Rigid polyurethane foams (rPUF) and phenolic foams (PF) obtained from its chemical precursors

this characteristic is the presence of unstable methylol groups, which can further react without the addition of specific catalysts and those can crosslink solely by a slight temperature increase. This is a key feature for the plausibility of using this precursor for the preparation of phenolic foams (PFs). Taking into account that this precursor is the most relevant precursor of PF, the subsequent discussion will focus on resole precursors (resins). Further details can be consulted elsewhere [1].

The resins used for PF are mostly obtained from the resole chemistry. In this regard, the P/F lies within the range of 1:1.3 to 1:2.1 [1], and hydroxide salts are employed as catalysts so as to achieve a highly crosslinked network (Table 1). The typical viscosity of such resins lies within the range of 1500–12,000 cp. Hence, it can be understood that, from a processing point of view, PFs have precursors with a moderate to high viscosity. In contrast, polyurethane precursors used for spray foam applications have working viscosities well below those values (200–400 cp). It is important to notice that the solid content is a key aspect to consider to actually contrast polyurethane and PF precursors. Indeed, in both cases, processing viscosity can be effectively reduced by the use of non-reactive diluents [1, 6]. However, the use of such diluents has been a cause of severe critics, due to the fact that non-reactive diluents can be extremely toxic. Nowadays, strict emissions control enforced by the United Nations Environment Program (UNEP) is currently being deployed worldwide so as to reduce environmental impact.

3.1 Systems Based on PF and PUF Precursors

The resulting monomers obtained from the synthesis of precursors used to manufacture either phenolic or polyurethane foams are usually not suitable by themselves to this effect. Then, blends of different components are usually employed so as to circumvent the disadvantages of each precursor and improve processing properties as well as reduce toxicity or emissions. These are denominated systems or formulations.

For the case of PFs, these are based on catalyzed one-component systems (Fig. 1). In this regard, a typical formulation is composed of the resole phenolic resin, an emulsifier, and a blowing agent (BA). The resin is inherently unstable, due to the presence of methylol groups which can react and crosslink the molecular structure of the precursor solely by temperature. The emulsifier is used to improve the miscibility of the BA and the resole resin and to avoid phase separation. Nowadays, the vast majority of PF are prepared using pentane as a BA and ethoxylated ricin-based emulsifiers which enhance emulsion stability [1]. When the manufacture of the PF is desired, an aqueous acid catalyst is added to this component and the temperature is raised in the mold so as to achieve higher cure conversions. Typical processing temperatures of PF are well above 60 °C, reaching in some cases up to 140 °C [1]. Even though higher amounts of catalysts can be added into the system to improve cure kinetics, most systems need much higher temperatures to achieve good conversions.

In contrast, PUF formulations are two-component systems (Fig. 1). One component is a mixture of isocyanates (A) while the second component is composed of one or more polyols, catalysts, blowing agents as well as surfactants and other additives (B). To manufacture the foam, the systems are usually formulated so that equals amounts (in volume) of component A are mixed with equal amounts of component B. The cure can be performed in a wide range of temperatures. It is possible to formulate the system so as to have a cure temperature as low as 5 °C, but most PUF systems cure at 20–25 °C. No post-cure is necessary to achieve the final mechanical properties.

3.2 Blowing Agents

The cure reaction of both PF and PUF is exothermic, which gives rise to the possibility of using this energy for the volatilization of physical foaming agents. In contrast to PUF, the expansion of the polymeric mass during cure for PF is exclusively from the expansion of physical blowing agents (BAs). As already explained in Sect. 2, the isocyanate precursor has the capability of producing carbon dioxide gas through its chemical reaction with water. The boiling temperature of the BA must be slightly higher than 25 °C and the BA in the liquid state must have a suitable solubility with the precursor as well as low flammability and toxicity. The earlier adoption of BA based on chlorofluorocarbons (CFCs) has led, nowadays, to stringent worldwide regulations regarding the use of BAs with low ozone depletion potential (ODP) as well as low global warming potential (GWP). Then, the main difference between PF and PUF is that the former uses mostly physical BAs, whereas the latter can use either chemical or physical ones. Within the PF industry, the most common BA is pentane as well as liquid carbon dioxide. Even though it is known that pentane has a high explosive risk, the vast majority of industrial production of PF are performed under strict industrial conditions, particularly when pentane is used as the exclusive BA. In contrast, PUF is more flexible in this regard, whereas its application can be performed in situ (spray foam) as well as in industrial conditions.

3.3 Cure Kinetics

The underlying behavior of thermosetting polymers which undergo the cure process is mostly influenced by how the molecular structure of the precursors evolves to a final crosslinked network. In this regard, resole phenolics undergo both polyaddition and polycondensation reactions. However, it is important to highlight that temperature is a key variable that controls the preponderance of both reactions [1, 2, 13]. If the reaction evolves at temperatures below 60 °C, polyaddition of methylol groups will certainly be the most relevant reaction mechanism [1]. On the other hand, when the reaction temperature is higher than 60 °C, polycondensation might play a relevant role in cure kinetics. At the first sight, the occurrence of both phenomena might be intranscendental. However, it is important to highlight that polycondensation reactions in phenolic chemistry indicate the formation of a subproduct, which in this case is water. As already noticed in the previous section, the cure enthalpy is frequently employed to aid the volatilization of blowing agents, which, in turn, lead to the formation of a cellular structure. If the cure reaction generates liquid H_2O, the cure enthalpy will also be used to heat the liquid H_2O produced in situ. This combined effect will lead to a decrease in the efficiency of the foaming process [1, 14]. In addition, if the PF main application is insulation, the high conductivity of liquid H_2O will have a deleterious effect on the thermal properties of the final PF structure.

On the other hand, PUF chemistry is exclusively based on polyaddition kinetics. This indicates that the reaction between the precursors does not generate undesirable subproducts. However, as already noticed in the previous section, the volumetric expansion during cure is based on the use of both physical and chemical BAs. Indeed, small additions of water are intentionally added in the formulation of the polyol precursor so as to purposely cause the formation of carbon dioxide, which causes volumetric expansion. PUF cure kinetics is mainly dependent on temperature, polyol functionality, catalyst, filler content, and blowing agent [7]. An increase in temperature causes an overall increase of cure kinetics, but it is not frequent to use higher temperatures in this regard [6]. Instead, catalysts have the main role in PUF cure kinetics. The concentration added is specified according to the location of the manufacturing site as well as the desired final structure. For example, for spray-up PUFs, a higher content of tin-based catalysts is usually employed if the application is performed for temperatures in the range of 0–20 °C. On the other hand, the polyol functionality also has a fundamental role in PUF cure kinetics [15]. If a highly functional polyol is employed, cure kinetics will be certainly faster, and reduced amounts of catalysts will be employed to achieve the desired final mechanical properties. The BA can also have a role in PUF cure kinetics [16]. Due to the fact that physical BA relies on the absorption of heat to volatilize, a higher content of BA will certainly decrease the PUF cure kinetics. If this aspect is not taken into account, an incomplete cure will lead to an unstable PUF structure.

3.4 Friability

Polymeric cellular foams can be extremely fragile. In this regard, when the cell walls and struts do not have enough deformation to rupture, the overall cellular structure tends to break down into small pieces, forming dusty fragments after the application of small forces caused by handling or manipulation. This effect is usually noted as friability (brittleness, pulverization) and it is measured by the tumbling box technique following the guidelines of ASTM C421 [17]. However, it is frequent in the literature to evaluate foam pulverization using other tailored methods [10, 18, 19]. The main parameter measured is weight loss as a function of how the abrasion experiment is being performed (pulverization ratio). If a higher weight loss is measured, then the foam is said to have a higher friable or fragile nature.

Phenolic foams have always been extremely friable. The high aromatic content of the PF precursor (Fig. 2), its low molecular weight, and the highly crosslinked network after cure are the main causes of a very friable cellular structure. To circumvent this important issue, several strategies have been tested [14]. The first one is the reactive route, which is related to a change in the molecular structure of the PF precursor. However, the main drawback of this strategy has to do with the impact of such modification on the flammability of the resultant PF. Indeed, if conventional reactive routes are implemented, the flammability might be significantly reduced. Due to the relevance of this issue, further details on this will be discussed in Sect. 4. Another strategy is based on the development of particulate composites [20], whereas both granular particulates and fibers [19, 21–24] can be used in the precursor to reduce friability. This approach has been extensively studied in the literature and this chapter will focus mostly on the reactive route.

On the other hand, for the case of PUF, friability can always be modified through a change in the molecular structure of the polyol component. However, when it comes to polyurethane foams with high flame resistance, the polyisocyanurate foam (PIR) is widely employed (Table 1). The molecular structure of PIR is based on the trimerization of the isocyanate precursor, forming a highly crosslinked structure without the need of high weight content of polyol in the network [25]. The PIRs are known for being highly flame-retardant and heat-resistant [25]. However, the initial developments led to extraordinary friable foams which were of no practical or industrial use [25]. This changed after Ashida developed urethane-stabilized PIR foams. The first PIR foams were commercialized by Nisshinbo Inc. of Tokyo, Japan using the technology disclosed by the Ashida patent [26].

3.5 Environmental Impact and Renewable Content

When it comes to the evaluation of the environmental impact of a product, it is important to perform a lifecycle analysis, which is the most comprehensive and suitable tool so as to evaluate the whole value chain of the product under analysis [27, 28]. Our discussion will only focus on the industrial production of the precursor, how it is processed in the industry to obtain a final product, and the properties of the final product by itself.

The industrial production of both PF and PUF chemical precursors shares a common origin. Indeed, both phenolic resins and isocyanates are obtained from the same hydrocarbon, benzene [7]. In addition, this chemical is obtained from crude oil, a non-renewable resource. The first aspect to notice is that for the case of phenolics, most of the weight content of the formulation is solely obtained from benzene using the cumene process [1]. Indeed, both phenol and acetone are synthesized from benzene and propylene using this path. Phenols are also obtained from renewable resources, such as coal tar or the liquid byproducts of gaseous processes. However, the main drawback of these renewable paths is that the phenols obtained are of low purity.

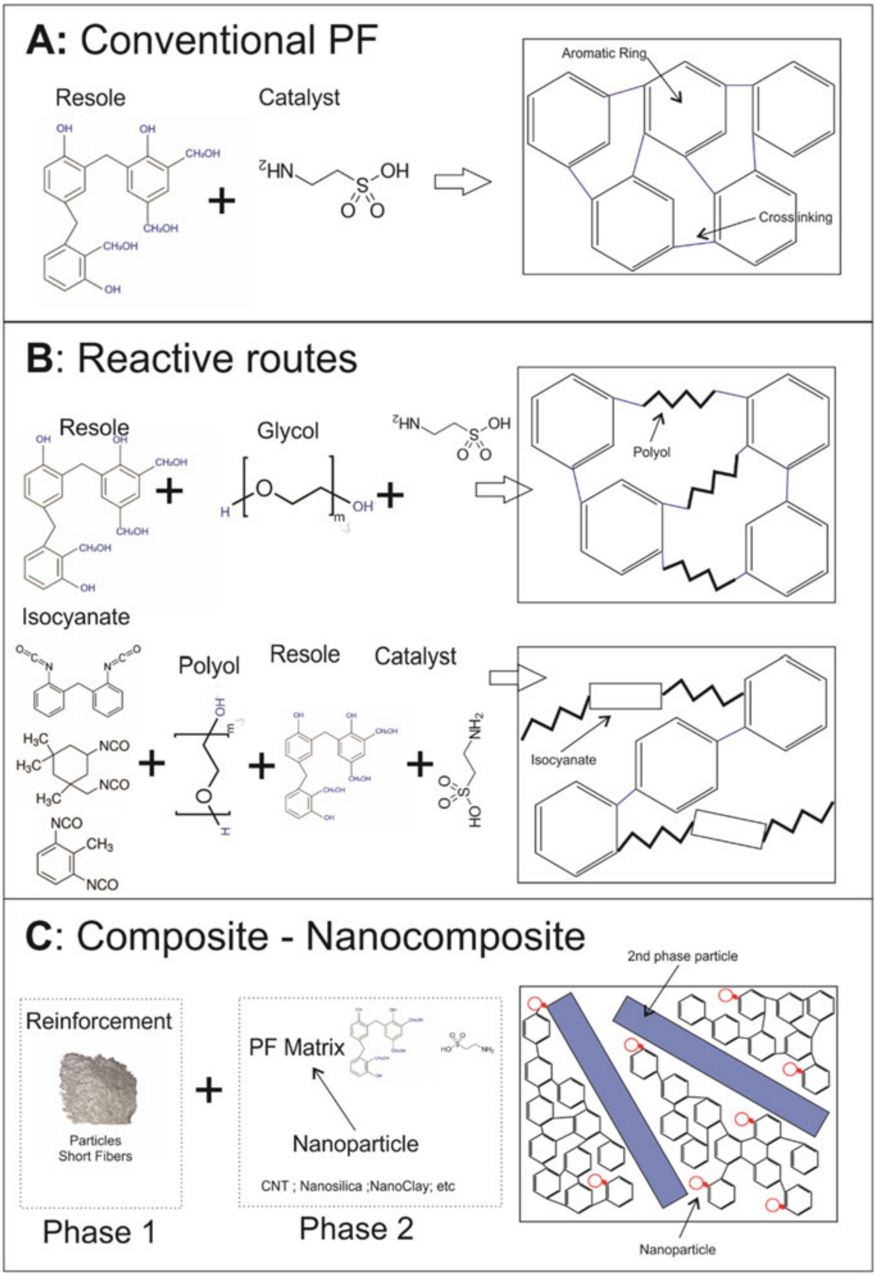

Fig. 2 Conventional **A** PF route, reactive routes **B**, and composites and nanocomposite routes **C** used for the preparation of PF

Another relevant PF precursor is formaldehyde. As already noticed above, resoles are synthesized using a stoichiometric excess of formaldehyde. Even though the objective of the chemical process is to completely react the aldehyde, leaving only unreacted methylol groups, this is not usually the case and the PF precursors are usually characterized to evaluate its free formaldehyde content [29]. It is important to notice that formaldehyde has been classified by the Environmental Protection Agency (EPA, USA) as a "probable human carcinogen". This precursor is the main reason why PF participation in the thermal insulation market has been reduced significantly. Nowadays, formaldehyde is mainly produced from methanol, which is obtained from natural gas. Renewable resources, such as syngas, can be used to obtain methanol.

For the case of PUF, the development of isocyanates from renewable resources has not been studied extensively either in academia or in the industry [5]. In this regard, a non-isocyanate route [30–32] to polyurethanes has emerged as a possible substitute for the use of the isocyanate moiety as an intermediate in the manufacture of polyurethane foams. On the other hand, the polyol component can be completely obtained from renewable resources, such as soybean, sunflower, castor, and other natural oils [5, 33–36].

When it comes to the environmental impact of insulation applied in residential structures, it is important to highlight the history of insulation materials used in this field. One of the first insulation foams applied in residential buildings was the urea–formaldehyde foam (UFFI). The initial development of UFFI goes back to 1933 [3, 4, 37, 38]. The residential use in northern Europe flourished during the 1960s and, then, in the USA during the 1970s. The UFFI is based on the in situ application of a mixture of urea, formaldehyde, and aqueous acid catalysts. Due to the highly unstable nature of formaldehyde and to the lack of stringent industrial application standards, the application of UFFI inside residential homes in the 1970s led to the release of a significant amount of that gas in household environments. In turn, this led to an increasing health impact on house owners. The increasing relationship between health issues and UFFI led to the banning of the use of UFFI in Canada and the USA in 1980 and 1982, respectively.

One of the most relevant aspects regarding the use of PF and PUF is the processing technologies involved in the transformation of the liquid polymer into foam. Even though the use of industrialized building systems (IBS) has led to the development of sandwich structures using either PF or PUF as a core material, the in situ application of foams still remains a convenient way to insulate either commercial, industrial, or residential buildings. The processing technology used to apply foams in situ has evolved significantly from the initial application of sprayed foams in the 1930s. The main concept behind this technology is the atomization of two components that are simultaneously sprayed onto the surface which needs to be insulated. The main advantage of this technology is that it can be applied to any surface, improving its insulation properties dramatically and also generating a sealed environment, which reduces convective air circulation from the outside atmosphere. All these improvements can be obtained at a low cost, which can be amortized through an increase in energy efficiency. However, the main drawback of this technology has to do with the fact the unreacted precursors are sprayed on the surface and it is generally assumed that those precursors will react completely forming either PF or PUF foams. This is certainly not the case and external auditors are needed to control that no toxic emissions are present after the application of the foam. For example, the use of spray foam polyurethane (SPF) insulation in residential houses in the USA usually involves the fact that the owners have to leave their residency for at least a couple of days so as to perform the foam application. Due to the fact that the formulation of PUF systems involves the use of amines as catalysts, it has been reported that if the application of SPF is not performed under standard procedures, then the toxic amines or unreacted isocyanates might remain in the atmosphere of the house. This has led to several complaints of house owners, and in some cases, a complete removal of the insulation material had to be performed.

3.6 Flammability or Fire Resistance

Fire propagation is a key aspect when cellular foams are applied in infrastructural applications. The performance evaluation tests are strongly related to regulations imposed by each country or state. For example, in the UK, phenolic insulation foams must be tested according to the BS476 standard. In the USA, the Ohio State University (OSU) 65/65 heat release standard is usually employed, and in Argentina, the DIN4012B2 is required by state law. Nonetheless, all these methods share a common scientific basis. The key aspect is to quantify the amount of heat released over time of a material subjected to a specific ignition or burning scheme. For example, the DIN4012 standard involves suspending the sample vertically and igniting it at the lower end. The speed at which the flame propagates is estimated and the emission of toxic gases as well as the dripping of burned material can also be quantified. All these measurements must comply with the specific regulation of each country and it is common to test not only the foam by itself but to analyze how the material behaves in real applications, where the foam can be combined in a sandwich structure with composite or steel facings.

Nowadays, PF is still the highest performance material whenever flammability is taken into account. Its use in infrastructure is highly associated with local regulations. As a matter of fact, the UK applies the highest standards in the world regarding foam flammability requirements. Hence, PF has found widespread application in that country. However, in the rest of the world, PIR foams or even conventional PUR foams with anti-flame additives are also widely used. To aid the worldwide development in this field, limiting oxygen index (LOI) and UL94 experiments are frequently reported in the literature. The LOI experiments are obtained following the guidelines of ISO 4589. In this analysis, a long sample is tested vertically and it is located inside a tight glass container. The atmosphere of the container is controlled by changing the volume mixture of nitrogen and oxygen gases. The LOI index is then obtained for the minimum oxygen concentration within the chamber which sustains the combustion of the polymeric foam. An LOI index below 21% is a characteristic of flammable material, and flame-retardant materials usually have indexes above approximately 27% [1].

4 Synergistic Reactive Routes to Improve the Properties of PF Using the Polyurethane Chemistry

When it comes to analyzing how to improve the properties of PF, it is important to establish benchmark parameters. Taking into account that our discussion is centered on thermal insulation panels applied to IBS, the minimum properties of the foam shall be deduced from the requirements associated with that application.

The first important properties are obtained from compressive and flexural mechanical tests. The compressive strength (σ_c) of foamed materials is measured following the guidelines of ASTM 1621. In a typical compressive mechanical test, the stress–strain curve presents three stages. The initial is a linear-elastic response followed by a plateau regime, finalizing with a densification stage at higher deformations [39]. This measurement is usually performed at 25 °C and the sample is oriented at the direction of cell growth. It is important to highlight that foams are anisotropic materials whereas the principal direction is oriented parallel to cell growth. To obtain the compressive strength, two methods are usually employed. The first one is to use directly the peak stress measured when the linear-elastic response finalizes and the second one is to report the stress at 10% deformation. Taking into account this last definition, foam cores for thermal insulation should have compressive strengths above 1.0×10^{-1} MPa [40]. Another frequently employed mechanical test is three-point bending [14]. The most relevant parameter obtained from this test is flexural strength, which is the stress associated with the yielding point of the stress–deformation curve. A higher flexural strength indicates that the foam will be able to tolerate higher loads within its linear-elastic regime. In addition, the flexural strain at break is also an indication of the maximum deformation that the foam will be able to tolerate before rupture. Even though several research groups have studied the flexural properties of the foams, it is important to highlight that the foams are mostly applied in sandwich construction. Hence, the evaluation of the flexural properties of the foam alone is not as relevant as to evaluating the sandwich structure. Another important factor in this test is the span to length ratio (SLR). In order to compare the results of one work with another, it is important to use similar SLR values. A low SLR value will cause a relative increase of shear stress with respect to applied flexural bending stress [41]. Comparison of mechanical properties deduced from this mechanical test should be based upon similar SLR values.

With respect to flammability performance, the results of both UL94 and limiting oxygen index (LOI) experiments are usually reported. As a reminder, flame-retardant materials need to have LOI values above 27%. The higher the LOI value, the better the material will behave with respect to flame propagation. It is important to highlight that the minimum requirements of this property are strictly related to state regulations.

The final decision associated with the use of the foam in the industry is related to the approval of certified tests performed by third-party institutes specialized in this area. However, in R&D studies, the LOI technique is usually employed so as to compare the results obtained from laboratories all around the world. The heat release rate measured with the cone calorimeter test is also widely employed; however, this chapter will focus only on LOI indexes.

With respect to friability, even though the standard experiment is the tumbling box, this technique is not frequently employed in R&D studies. Indeed, most of the researchers perform different experiments to assess the friability of a specific foam, which is based on erosion caused by a specific cyclic state of stress. The pulverization ratio, which is a weight relationship describing the weight loss associated with that experiment, is usually regarded as the friability indicator. Hence, it is difficult to establish a benchmark in this particular measurement, and the analysis will be centered on relative measurements.

One of the most relevant properties of PF applied in thermal insulation applications is their insulation value. The cellular nature of polymeric foams has the advantage of generating a microstructure will small and closed cells, such as the ones depicted in Fig. 3. This structure is composed of struts and cell walls, and within each cell, gases are entrapped, preventing convective among the whole volume of the foam. The thermal conductivity (λ) is defined and measured as the heat energy passing through a plate of standard dimensions. In polymeric foams, the thermal conductivity has the contribution [7] of radiate, solid, gas, and convective heat transfer. The most relevant value is the gas conductivity (λ_{gas}) and its value defines the overall conductivity of a polymeric foam [5]. Hence, the composition of the gas within the cell is a key aspect to take into account. In addition, if the gas within the cell diffuses or permeates outside the cell, a change of thermal conductivity will be measured (aging effect).

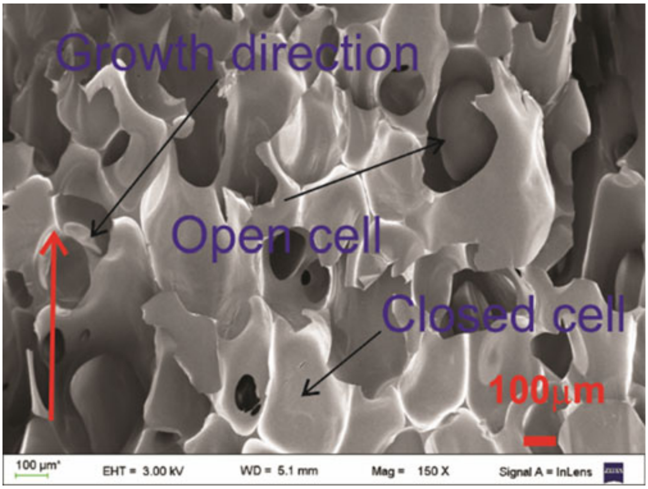

Fig. 3 Typical geometry of PUF polymeric cellular structures

Indeed, the most relevant features of thermal insulation foams are their initial λ value and variation as a function of time (thermal aging). Typical values of thermal conductivity for either PF or PUF are reported in Table 2. For the benchmark, a λ value less than 25 mW m^{-1} K^{-1} should be achieved. Another relevant property is closed-cell content. In order to achieve a negligible increase of thermal conductivity as a function of time (thermal aging), the cells need to be closed. If the processing technology or the system creates a foam with a high content of open cells, the internal gases will tend to migrate and generate convective flow, reducing significantly the thermal insulation value of the foam. Higher closed-cell contents of around 85% can achieve this requirement [7].

The strategies that are used in the literature to improve the previously mentioned properties are based mostly on changing the molecular structure of the polymer (also known as reactive routes) and through the preparation of composites (Fig. 2). The reactive route is the main scope of this chapter (Fig. 2b). Hence, further details of this technique will be discussed below. The other route is related to the composite field (Fig. 2c). Composites are a class of materials that have the main purpose of using polymers, ceramics, and metals synergistically [42]. The constituents of a composite material are reinforcement, matrix, and interface. The three main families of composites materials are based on the structure of the matrix constituent. Polymeric matrix composites (PMC), ceramic matrix composites (CMC), and metal matrix composites (MMC) are the three main families associated with polymeric, ceramic, and metallic matrices, respectively. In phenolic and polyurethane foams, the matrix is then polymeric. On the other hand, the reinforcement can be either particles or short fibers with different aspect ratios [19, 21–23, 43–60]. Another relevant possibility relies on the use of nanotechnology (Fig. 2c). Any constituent can be nanostructured using a wide range of nanoparticles, which gives rise to the nanocomposites field [61, 62]. It is important to emphasize that any constituent can be nanostructured; hence, when the term nanocomposite is used, either the reinforcement or the matrix could be nanostructured. Another important aspect relies on the type of nanoparticles employed. If the surface functionality of the nanoparticle alters the chemistry of the matrix being studied (phenolic or polyurethane), then the nanoparticle will be treated as a reactive route because the molecular structure of the polymer is being changed by the incorporation of nanoparticles. Several articles have been published on this topic [63–74] and further details of this approach will be discussed below.

4.1 Principles Associated with the Development of Synergistic Routes

First, it is important to emphasize the most relevant aspects of the PF and PUF chemistry and how those can be combined synergistically. As already noticed in the previous section, the resole PF is solely based on the polyaddition and condensation of methylol groups. In this regard, the chemical properties of this PF precursor are

Table 2 Summary of physical properties of the study cased developed in this work

System	Route	Toughener concentration (wt. %)	Apparent density (kg m^{-3})	Compressive strength (MPa)	Friability (pulverization ratio, %)	LOI index (%)	Thermal conductivity (mW m^{-1} K^{-1})	Closed cell content (%)
rPUF [5]	In situ	0	25–35	>0.3	<2.0	<20 [83, 84]	24–28 0.10^{-3}	>90
rPIR [5]	In situ	0	35–40	>0.3	<2.0	<25 [84]	24–28 0.10^{-3}	>90
PF-PEG; MW 600–400 [76]	Reactive	0–4	60–70	0.10–0.15	2.2–5.8	25–31	N.M	30–80
PF BPEG; MW 200–600 [18]	Reactive	0–6	25	0.05–0.11	2.1–3.5	35.5–39.0	N.M	N.M
PF-PPEG; MW 400–600 [75]	Reactive	3–10	36.5–45	0.11–0.15	N.M	40–51	N.M	N.M
PF-PSIP [11]	Reactive prepolymer	2–5	32.6–60.2	0.12–0.35	1.75–5.0	43–47	N.M	N.M
PF-GF-PTDI [44]	Reactive prepolymer composite	0–10	47.7–58.2	0.15–0.28	N.M	41–52	N.M	N.M
PF-GO-LDH [65]	Reactive nano	0–1.5	40	0.05–0.08	6–14	38–39.5	N.M	N.M
PF-NSi-GO [66]	Reactive nano	0–2	16	0.06–0.07	1.5–5.5	38–41.0	N.M	N.M
PF-Bio-oil MMT [69]	Reactive nano renewable	0–8	55.5–62.5	0.14–0.17	5–9	29.8–39.7	N.M	N.M
PF-CNT [81]	Reactive nano	0–2.0	48.7–103.2	0.11–0.24	N.M	N.M	57–91	N.M
PF-RGO [82]	Nano	0.08–0.15	58.8–70.0	N.M	N.M	N.M	89–113	N.M

much more similar to the structure of a polyol rather than an isocyanate. Indeed, the resole precursor can be understood as a highly aromatic polyol with a tailored molecular weight. The high specific content of benzene rings and the highly crosslinked nature of the resulting PF are the main reasons why PFs are highly friable (fragile). From this argument, the simplest reactive route can be deduced. That is, to decrease the aromatic content and increase molecular weight by adding an aliphatic chain into the molecular structure of the resole precursor (toughening). This route is straightforward and it might severely affect flammability performance, altering one of the key design features of PF. One of the most applied techniques has been the use of aliphatic monomers [13, 18, 75, 76], such as polyethylene glycol (PEG), incorporated directly in the formulation of resole PF. In order to attenuate a poor flammability performance, boron and phosphorous have been incorporated into the molecular structure of those aliphatic monomers [18]. This approach can be considered simple and straightforward, not having substantial changes in the chemistry of the resole precursor. Finally, let’s compare this approach using the principles of polyurethane systems. In polyurethanes, the main contributor to aromatic content is the isocyanate precursor (hard segment), while in some exceptional cases aromatic polyols are also the source. The molecular structure which has the highest aromatic content is polyisocyanurate foams (PIR), where the isocyanate precursor trimerizes, obtaining highly crosslinked and friable materials [25]. In this case, if a reduction in friability is desired, the common strategy is associated with a change in the molecular structure of the polyol. As it can be understood from these statements, in both systems, PF and PUF, similar chemical strategies are implemented so as to reduce friability. Another example of this strategy involves the use of either epoxy, phenoxy, and dicyandiamide [77] groups.

A second strategy employed by several researchers is to exploit the versatility of isocyanate chemistry so as to achieve complex molecular structures. In literature, the term prepolymer or quasi-prepolymer is usually used to identify this path. The main idea of this route is related to the reaction of any isocyanate precursor with other monomers so as to create a tailored molecular structure. Finally, this tailored molecule is inserted within the PF resole precursor, and the crosslinking reaction proceeds using similar cure procedures. The first important aspect to consider is the type of isocyanate being used. Two main types of isocyanates are available: aliphatic and aromatic [6]. The aliphatic isocyanate, such as isophorone diisocyanate, is the best choice because it does not have aromatic rings; hence, it is unlikely to increase the fragile nature of the PF matrix. However, the main drawbacks rely on its high cost and low reactivity. Aromatic isocyanates, such as pMDI or toluene diisocyanate (TDI), are frequently employed in the literature as a starting point for the development of molecular structures which can improve the properties of PF. The main drawback of this isocyanate is its high aromatic content, which means that the use of aliphatic polyols with medium or high molecular weight and low functionality is mandatory. Otherwise, the properties of the final material will not be improved. It is important to highlight that the use of TDI as a starting material might generate an increase in the volatile organic content (VOC) of the PF precursor. In this regard, only prepolymers are suitable to achieve this objective. As already noticed earlier, quasi-prepolymers have a high NCO_{number}, then higher VOCs should be expected (Table 1).

Another aspect to consider with respect to this route is that the tailored molecule which is synthesized has to be hydrophilic or at least with a high hydrophilic character. Otherwise, even though after using surfactants or emulsifiers, the resulting PF precursor might not be a colloidal stable dispersion, leading to phase separation and to the impossibility of producing PF with suitable thermomechanical properties. This characteristic is not easy to achieve, because the isocyanate precursor is highly hydrophobic. Hence, the synthesis path will have to involve the formation of hydrogen liable groups so as to reduce its hydrophobic character.

Finally, it is important to discuss the role that nanotechnology can have in the change of molecular structure of PF. There are several nanoparticles that can be applied in this field so as to obtain substantial improvements of either mechanical properties, flammability, or insulation value [5, 63, 65–69]. One important feature of nanoparticles is their geometry. Spherical nanoparticles, such as nanosilica, have diameters within the orders of 5–10 nm and are frequently dispersed in the matrix as aggregates (tactoids) [78]. Nanoclays are lamellar nanostructures that have a thickness of around 0.1–0.5 nm and usually conglomerate into a layered structure that needs to be exfoliated in the matrix being reinforced. Finally, carbon nanotubes (CNT) are tubular structures with diameters ranging in the order of 10 nm with variable lengths [79]. However, the most relevant feature that needs to be considered when using nanoparticles is surface functionality. The extremely high area per unit weight of nanoparticles indicates that the interface will have a fundamental role when it comes to analyzing the performance of a nanoparticle as a reinforcement. Hence, taking into account the previous analysis, it can be inferred that nanoparticles that have a suitable surface functionality (such as hydroxide groups) can be considered as an alternative reactive route toward the synthesis of nanostructured PF. On the other hand, if the nanoparticle does not have any surface functionality which cannot covalently react forming a network, then the nanoparticle will behave as a second phase (Fig. 2c).

4.2 Study Cases

The reactive route based on the incorporation of aliphatic chains using PEG was studied by Hu et al. [76] for the development of urea–formaldehyde PF (Table 2). The main scope of the study was centered on evaluating the effect of PEG molecular weight (from 600 to 4000) and concentration (up to 4 wt%). The reported apparent density fell within the range of 60–70 kg m^{-3}, whereas its variation followed a non-monotonous increase as a function of PEG weight content. The compressive strength of the pristine PF was superior to the benchmark (Sect. 4.1) and it reached a maximum with a PEG concentration of 2 wt% and a molecular weight of 1000. This reflected the presence of a compromise relationship between this property, PEG weight content, and molecular weight. Intermediate values of these properties were the most appropriate to increase compressive strength. A similar trend was also deduced from friability measurements (pulverization ratio). This ratio decreased as a function of PEG weight content and molecular weight, with a minimum located at a PEG content of 2 wt% and a 1000 molecular weight. The LOI indexes showed clearly how the gradual increase of PEG content in the PF caused a deterioration of the fire performance of the foam. Comparing the reported values with the benchmark, it can be deduced that for PEG contents higher than 2 wt%, the LOI index fell below the benchmark value (27%). These results clearly reflect the compromised relationship between adding aliphatic chains into the PF molecular structure and its concomitant reduction of flammability performance. A summary of the properties of this work and all the others reported in this section can be consulted in Table 2.

Liu et al. [18] studied the incorporation of a borate PEG into a resole PF precursor (Fig. 2a). Starting with a PEG monomer, boric-acid-assisted esterification was implemented so as to introduce boron into the molecular chain of the aliphatic monomer (borate-PEG). Then, the strategy was based on the reduction of the aromatic content of the resole PF precursor so as to reduce friability as well as the incorporation of boron backbones so as to attenuate the concomitant flammability reduction. The reported compressive strength of the pure PF was 0.06 MPa (apparent density 25 kg m^{-3}), which was significantly lower than the minimum required by the benchmark. The incorporation of PEG with a molecular weight of 200, 400, and 600 proved to increase that value, but only for the case of a borate-PEG with a molecular weight of 400, the compressive strength accomplished the minimum established by the benchmark. Friability measurements indicated that the incorporation of PEG and borate-PEG in the molecular structure contributed to a reduction of the pulverization ratio. LOI and UL94 tests were performed and in all cases, the values were higher than the benchmark.

Yang et al. [75] studied the incorporation of phosphorous-functionalized PEG (PPEG) monomers using phenyl dichlorophosphate as the precursor. The reported PF had apparent densities which varied in the range of 36–46 kg m^{-3} as a function of increasing PPEG weight content (0–10 wt%). The compressive strength of all the PF prepared in this work surpassed the value established by the benchmark, proving also that an increase of PPEG also caused significant improvements. LOI and UL94 tests corroborated that both the pristine PF and the PPEG-PF foams achieved and surpassed the minimum requirements of the benchmark. Comparing the results obtained in this work and those obtained by Liu et al. [18], it is important to mention that in this last case, the foam density was fixed at 25 kg m^{-3}.

Another work of the same group [11] reported the implementation of a reactive route exploiting the chemistry of polyurethane systems (Fig. 2b). A prepolymer obtained from TDI and the reaction of phosphorus and silicon-containing polydimethylsiloxanes (PSPUP) was incorporated in a PF system with the objective of improving its compressive strength, pulverization ratio, and fire performance. The apparent density of the PF ranged from 32.6 kg m^{-3} for the pristine PF to 60.2 kg m^{-3} for the PF modified with 5 wt% of PSPUP. In all cases, the compressive strength of the foams surpassed the minimum established by the benchmark. It is important to emphasize that the incorporation of the polyurethane prepolymer caused substantial improvements in both the compressive and the specific compressive strength. As already noticed by Lobos et al. [80], the comparison of different foams is valid only when specific properties are reported. An additional advantage of this approach was associated with the dramatic reduction of the pulverization ratio, whereas its reduction was proportional to the PSPUP weight content. Finally, in all cases, the LOI indexes were much higher than the benchmark, indicating that the prepolymer route did not adversely affect fire performance.

A synergistic approach combining the polyurethane prepolymer (Fig. 2b) reactive route and the composite one (Fig. 2c) using chopped fiberglass as reinforcement was studied by Yuan et al. [44]. Due to the fact that chemical flame retardants usually have a highly aromatic structure, it is important to increase their molecular weight so as to avoid further embrittlement of the PF matrix. In this regard, the study presented the preparation of a polyurethane prepolymer (DOPU) reacting a phosphaphenanthrene oxide (DOPO-BQ) with isophorone diisocyanate (IPDI). The isocyanate moieties of IPDI reacted with the hydroxyl functionalities of the DOPO-BQ, producing a precursor with increased molecular weight and reduced aromatic content. On the other hand, chopped fiberglass (GF) was used to combine both an increase of compressive strength and fire performance. A fixed concentration of GF (0.5 wt%) was implemented for all the synthesized foam and the effect of increasing amounts of DOPU (up to 10 wt%) was the main variable under scrutiny. Under these conditions, the reported density ranged between 47.7 and 58.2 kg m^{-3}, increasing as a function of higher DOPU content. With respect to the compressive strength, all the foams analyzed in this work had values that were better than the benchmark. The incorporation of both GF and DOPU up to 10 wt% caused a monotonous increase of the compressive strength. Even though the specific compressive strength was not reported, our calculations based on the experimental results indicated that the specific compressive strength increased significantly as a function of DOPU content. LOI tests indicated that for all the foams prepared in this work, the values were much higher than the benchmark, even for the case of no incorporation of DOPU into the molecular structure of the PF. This suggested that the small addition of GF had a relevant effect on the fire performance of the PF.

A reactive route based on the use of nanotechnology was studied by Wang et al. [65]. The approach was centered on the use of a nanohybrid based on graphene oxide (GO) immobilized with layered double hydroxides (CoAl-LDH/GO). The functionalization of GO with the LDH helped to create a reactive route as well as to avoid the poor fire performance of GO. The PF was synthesized with a fixed apparent density of 40 kg m^{-3}. The reported compressive strength presented improvements as a function of increasing weight content of the CoAl-LDH/GO, reaching a peak value at 0.9 wt%. Comparing the results with the benchmark, it can be deduced that, in all cases, the reported values were inferior to the minimum established by the benchmark. On the other hand, the reported pulverization ratio was significantly reduced as a function of increasing CoAl-LDH/G weight content, indicating that the reactive path produced a less friable PF. Finally, all the reported LOI indexes showed values well above the benchmark, indicating that all the PF developed in this work had excellent fire performance. Similar results were also obtained in another work published by the same group using nanosilica instead of LDH [66].

A reactive route based on the use of nanotechnology and renewable resources was recently published by Xu et al. [69]. The strategy of this work was centered on an increase of the renewable content of the PF precursor through the use of biomass obtained from the pyrolysis of Larix gmelinii. In addition, montmorillonite (MMT) lamellar nanoparticles were also used in the PF system. Taking into account that the MMT nanoparticles had hydroxyl functionality, the strategy used by the researchers can be classified as a reactive route. Indeed, the authors corroborated that the MMT was covalently bonded to the PF matrix. The reported apparent density ranged between 55 and 62.5 kg m^{-3} and its variation was mainly due to the incorporation of MMT in the PF system (up to 8 wt%). The compressive strength of the foams prepared in this work was higher than the benchmark, and a substantial increase of the specific compressive strength was found as a function of increasing MMT content, peaking at a 4 wt%. The friability analysis revealed that small contents of MMT (<4 wt%) caused a decrease in the pulverization ratio. On the other hand, higher MMT loadings caused a significant increase of this property, increasing friability above benchmark values. The LOI index showed that in the PF prepared in this work, the reported values were better than the benchmark. In addition, the LOI index reached a plateau of approximately 37% even for a low MMT concentration (2 wt%).

The properties of PF foams nanostructured with multi-wall carbon nanotubes (MWCNT) or graphene were studied by Song et al. [81]. The reported apparent density ranged between 48.7 and 103.2 kg m^{-3} and its variation was a strong function of nanoparticle type and content. The highest density was attained when MWCNT was used at 2 wt%, while the lowest density was measured at MWCNT of 0.5 wt%. The incorporation of graphene in the PF matrix caused a similar apparent density variation, whereas the lowest apparent density was measured at 1 wt%. The reported compressive strength of all the foams studied in this work was higher than the benchmark. In addition, the incorporation of nanoparticles caused an increase of the compressive strength, however, reducing significantly the specific compressive strength of the resulting foam. This work also highlighted the measurements of processing viscosity and final thermal conductivity of the PF. In this regard, it is important to emphasize that the incorporation of nanoparticles caused a significant reduction in thermal conductivity. However, the reported λ values are still high compared to other PF foams available in the industry.

A recent work applying nanotechnology to produce nanocomposite foams based on PF precursors was performed by Sandhya et al. [82]. To avoid the use of poisonous reducing agents, such as hydrazine, the starch potato was used to chemically reduce graphene oxide (GO). The reported apparent density ranged from 58.8 to 70.0 kg m^{-3}, whereas its variation changed non-monotonously as a function of reduced graphene oxide (RGO) content (from 0.08 up to 0.15 wt%). The reported thermal conductivity ranged between 0.089 and 0.113 W m^{-1} K^{-1}. The incorporation of RGO into the microstructure permitted a change in thermal conductivity so as to produce foams with tailored electrical properties.

5 Conclusions

The path to the new generation of PF is based on synergistic strategies using the tools that have been laid out in this chapter. To achieve a PF with improved friability (reduced pulverization rate), it is crucial to use the polyurethane chemistry for the development of additives that can be incorporated into the PF precursor, decreasing the overall degree of aromatic content of the final polymeric network without affecting other properties. Several study cases have been analyzed which emphasize how it is possible to increase specific compressive strength, attain a high fire performance, and reduce friability significantly by the use of reactive routes based on the versatility of the isocyanate chemistry. Combining this reactive route with the use of composite and nanocomposite technology can give rise to PF with outstanding properties. These aspects have been emphasized by establishing a benchmark and by comparing the results available in the state-of-the-art with respect to the benchmark.

Even though substantial R&D efforts have been devoted to study the thermomechanical properties, fire performance, thermal degradation, and friability, it is important that future efforts should focus on how to increase the thermal insulation value of PF. To this effect, further studies should deal with the new safe blowing agents with low ODP as well as GWP values. In addition, further aging studies which reflect the performance of PF as a function of time should also be conducted. New materials based on PF precursors should have a higher solid content so as to achieve a decrease of organic volatile emissions in the manufacturing process. Finally, the change from using precursors obtained mostly from oil and gas has already been taking place and future PF precursors will certainly contain a higher content of renewable resources, leading the way to a sustainable industry.

References

1. Pilato L (2010) Phenolic resins: a century of progress, 10th edn. Springer, New York
2. Asim M, Saba N et al (2018) A review on phenolic resin and its composites. Curr Ann Chem 3:185–197
3. Norman G R, Pengelly LD, et al (1986) Respiratory function of children in homes insulated with urea formaldehyde foam insulation. CMAJ: Can Med Assoc J 10:1135–1146
4. Harris JC, Rumack BH et al (1981) Toxicology of urea formaldehyde and polyurethane foam insulation. JAMA 3:243–246
5. Chiacchiarelli L (2019) Sustainable, nanostructured, and bio-based polyurethanes for energy-efficient sandwich structures applied to the construction industry. In: Verma, D (ed) Biomass, biopolymer-based materials, and bioenergy,1st edn. Elsevier, United Kingdom, pp 135–160
6. Szycher M (1999) Szycher's handbook of polyurethanes, 2nd edn. CRC Press, New York
7. Randall D, Lee S (2003) The polyurethanes book, 2nd edn. Wiley, New Jersey
8. Chiacchiarelli LM, Puri I et al (2012) Cure kinetics of a highly reactive silica–polyurethane nanocomposite. Therm Acta 3:172–178
9. Gimenez RB, Leonardi L et al (2017) Improved specific thermomechanical properties of polyurethane nanocomposite foams based on castor oil and bacterial nanocellulose. J Appl Polym Sci 25:730–746

10. Ding H, Wang J et al (2015) Preparation and properties of a novel flame retardant polyurethane quasi-prepolymer for toughening phenolic foam. J Appl Polym Sci 35:324–333
11. Yang H, Wang X et al (2013) A novel polyurethane prepolymer as toughening agent: preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 5:2720–2728
12. Ionescu M (2005) Chemistry and technology of polyols for polyurethanes, 1st edn. Rapra Technology Limited, United Kingdom
13. Wang FY, Ma CM et al (2001) Kinetic parameters of thermal degradation of polyethylene glycol-toughened novolac-type phenolic resin. J Appl Polym Sci 2:188–196
14. Mougel C, Garnier T et al (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer 1:86–117
15. Herrán R, Amalvy JI et al (2019) Highly functional lactic acid ring-opened soybean polyols applied to rigid polyurethane foams. J Appl Polym Sci 4:59–65
16. Park S-B, Choi S-W et al (2016) Effect of the blowing agent on the low-temperature mechanical properties of CO2-and HFC-245fa-blown glass-fiber-reinforced polyurethane foams. Comp Part B: Eng 3:317–327
17. Zieleniewska M, Leszczyński MK et al (2016) Development and applicational evaluation of the rigid polyurethane foam composites with egg shell waste. Polym Degrad Stab 2:78–86
18. Liu L, Fu M et al (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 7:1962–1970
19. Yang C, Zhuang ZH et al (2014) Pulverized polyurethane foam particles reinforced rigid polyurethane foam and phenolic foam. J Appl Polym Sci 1:342–356
20. Mallick P (2007) Fiber-reinforced composites: materials, manufacturing, and design, 3rd edn. CRC Press, New York
21. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Comp Part A: Appl Sci Manfact 9:899–906
22. Huang YJ, Wang CH et al (2010) Enhancing specific strength and stiffness of phenolic microsphere syntactic foams through carbon fiber reinforcement. Polym Compos 2:256–262
23. Kaynak C, Cagatay O (2006) Rubber toughening of phenolic resin by using nitrile rubber and amino silane. Polym Test 3:296–305
24. Desai A, Auad ML et al (2008) Mechanical behavior of hybrid composite phenolic foam. J Cell Plast 1:15–36
25. Ashida K (2006) Polyurethane and related foams: chemistry and technology, 1st edn. CRC Press, New York
26. Ashida K, Yagi T (1996) French Patent 1,511,865
27. Tingley DD, Hathway A et al (2017) The environmental impact of phenolic foam insulation boards. Proc Inst Civ Mat 2:91–103
28. Kylili A, Seduikyte L, et al (2018) Life cycle analysis of polyurethane foam wastes. In: Harson J (ed) Recycling of polyurethane foams, 1st edn. Elsevier, pp 97–113
29. Li W, Lin Q et al (2003) Reducing the contents of free phenol and formaldehyde in phenolic foam. J Appl Polym Sci 9:2333–2336
30. Guan J, Song Y et al (2011) Progress in study of non-isocyanate polyurethane. Ind Eng Chem Res 11:6517–6527
31. Kathalewar MS, Joshi PB et al (2013) Non-isocyanate polyurethanes: from chemistry to applications. RSC Adv 13:4110–4129
32. Delebecq E, Pascault J-P et al (2013) On the versatility of urethane/urea bonds: reversibility, blocked isocyanate, and non-isocyanate polyurethane. Chem Rev 1:80–118
33. Lligadas G, Ronda JC et al (2010) Plant oils as platform chemicals for polyurethane synthesis: current state-of-the-art. Biomacromol 11:2825–2835
34. Meier MA, Metzger JO et al (2007) Plant oil renewable resources as green alternatives in polymer science. Chem Soc Rev 11:1788–1802
35. Mosiewicki MA, Aranguren MI (2013) A short review on novel biocomposites based on plant oil precursors. Eur Polym J 6:1243–1256

36. Mosiewicki MA, Aranguren MI (2016) Recent developments in plant oil based functional materials. Polym Int 1:28–38
37. Thun MJ, Lakat MF et al (1982) Symptom survey of residents of homes insulated with urea-formaldehyde foam. Environ Res 2:320–334
38. Frigos E, Filley WV et al (1981) Asthma induced by dust from urea-formaldehyde foam insulating material. Chest 6:706–707
39. Chiacchiarelli LM, Cerrutti P et al (2019) Compressive behavior of rigid polyurethane foams nanostructured with bacterial nanocellulose at low and intermediate strain rates. J Appl Polym Sci 137:20–32
40. Davies JM (2008) Lightweight sandwich construction, 1st edn. John Wiley & Sons, New York
41. Chiacchiarelli LM, Escobar MM et al (2015) The role of the interphase on the shear induced failure of multiwall carbon nanotubes reinforced epoxy nanocomposites. J Appl Polym Sci 4:23–37
42. Mazumdar S (2001) Composites manufacturing: materials, product, and process engineering, 1st edn. CRC Press, New York
43. Shen H, Lavoie AJ et al (2003) Enhanced peel resistance of fiber reinforced phenolic foams. Comp Part A: Appl Sci Manufact 10:941–948
44. Yuan H, Xing W et al (2013) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 2:273–279
45. Huang Y-J, Vaikhanski L et al (2006) 3D long fiber-reinforced syntactic foam based on hollow polymeric microspheres. Comp Part A: Appl Sci Manufact 3:488–496
46. Huang Y-J (2009) Fiber-reinforced syntactic foams, 1st edn. University of Southern California, United States
47. Liu J, Li X et al (2018) Mechanical and thermal properties of modified red mud-reinforced phenolic foams. Polym Int 5:528–534
48. Xiao W, Huang Z et al (2017) The mechanical and thermal characteristics of phenolic foam reinforced with kaolin powder and glass fiber fabric. Mater Sci Eng 274:120–134
49. Zuluaga CL, Du J et al (2018) Lignin modifications and perspectives towards applications of phenolic foams: a review. BioResources 4:9158–9179
50. Zhuang XW, Li SH et al (2011) Preparation and characterization of lignin-phenolic foam. Adv Mater Res 4:1014–1018
51. Del Saz-Orozco B, Alonso MV et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Comp Part B: Eng 13:367–372
52. Li C, Ma H et al (2020) Preparation and properties of melamine-formaldehyde rigid closed-cell foam toughened by ethylene glycol/carbon fiber. Cell Polym 5:1234–1340
53. Sreekala M, Czigány T et al (2003) Investigation of oil palm and pineapple fiber reinforced phenol formaldehyde composites by acoustic emission technique. Polym Polym Compos 1:9–18
54. Balakrishnan P, Geethamma V, et al (2018) Polymeric biomaterials: state-of-the-art and new challenges. In: Martin N (ed) Fundamental biomaterials: polymers, 1st edn. Elsevier, pp 1–20
55. Sreekala M, Kumaran M et al (2004) Environmental effects in oil palm fiber reinforced phenol formaldehyde composites: Studies on thermal, biological, moisture and high energy radiation effects. Adv Compos Mater 34:171–197
56. Sreekala M, Thomas S et al (2005) Dynamic mechanical properties of oil palm fiber/phenol formaldehyde and oil palm fiber/glass hybrid phenol formaldehyde composites. Polym Compos 3:388–400
57. Sreekala M, Kumaran M et al (2000) Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance. Appl Compos Mater 5–6:295–329
58. Sreekala M, George J et al (2002) The mechanical performance of hybrid phenol-formaldehyde-based composites reinforced with glass and oil palm fibres. Compos Sci Technol 3:339–353
59. Joseph S, Sreekala M et al (2002) A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibres and glass fibres. Compos Sci Technol 14:1857–1868

60. Castillo-Lara JF, Flores-Johnson EA et al (2020) Mechanical Properties of Natural Fiber Reinforced Foamed Concrete. Materials 14:3060
61. Agarwal R, Saxena N et al (2000) Effect of different treatments on the thermal behavior of reinforced phenol–formaldehyde polymer composites. J Appl Polym Sci 3:603–608
62. Chiacchiarelli LM, Cerrutti P et al (2020) Compressive behavior of rigid polyurethane foams nanostructured with bacterial nanocellulose at low and intermediate strain rates. J Appl Polym Sci 20:48701–48711
63. Rangari VK, Hassan TA et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 1:308–314
64. FortunatiE YW et al (2016) Lignocellulosic nanostructures as reinforcement in extruded and solvent casted polymeric nanocomposites: an overview. Eur Polym J 13:295–316
65. Wang Z, Li X (2018) Synthesis of CoAl-layered double hydroxide/graphene oxide nanohybrid and its reinforcing effect in phenolic foams. High Perform Polym 6:688–698
66. Li X, Wang Z et al (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. RSC Adv 121:99907–99913
67. Auad M, Nutt S et al (2007) Synthesis and properties of epoxy-phenolic clay nanocomposites. Exp Polym Lett 13:346–355
68. Hu X, Cheng W et al (2016) Flame retardant, thermal, and mechanical properties of glass fiber/nanoclay reinforced phenol–urea–formaldehyde foam. Polym Compos 8:2323–2332
69. Xu P, Yu Y et al (2019) Preparation and characterization of bio-oil phenolic foam reinforced with montmorillonite. Polymers 9:1471–1483
70. Zhu Y, Wang Z (2016) Phenolic foams, modified by nano-metallic oxides, improved in mechanical strengths and friability. Iran Polym J 7:579–587
71. Zhou J, Yao Z et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym Compos 3:581–586
72. Li Q, Chen L et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Comp Part A: Appl Sci Manufact 14:214–225
73. Yang Z, Yuan L et al (2013) Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes. J Appl Polym Sci 3:1479–1488
74. Li X, Wang Z et al (2016) One-step in situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 78:74903–74912
75. Yang H, Wang X et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 3:9831–9845
76. Hu X, Wang D et al (2014) Effect of polyethylene glycol on the mechanical property, microstructure, thermal stability, and flame resistance of phenol–urea–formaldehyde foams. J Mater Sci 4:1556–1565
77. Gao M, Wu W et al (2016) Phenolic foam modified with dicyandiamide as toughening agent. J Therm Anal Calorim 1:189–195
78. Kenny JM, Torre L et al (2015) The effect of processing routes on the thermal and mechanical properties of poly (urethane-isocyanurate) nanocomposites. J Appl Polym Sci 45:243–272
79. Hussain F, Hojjati M et al (2006) Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. J Compos Mater 17:1511–1575
80. Lobos J, Velankar S (2016) How much do nanoparticle fillers improve the modulus and strength of polymer foams? J Cell Plast 1:57–88
81. Song SA, Chung YS et al (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 3:85–93
82. Sandhya P, Sreekala M et al (2020) Thermal and electrical properties of phenol formaldehyde foams reinforcing with reduced graphene oxide. Polym Compos 10:4329–4339

83. Modesti M, Lorenzetti A (2002) Flame retardancy of polyisocyanurate–polyurethane foams: use of different charring agents. Polym Degrad Stab 2:341–347
84. Günther M, Lorenzetti A et al (2018) Fire phenomena of rigid polyurethane foams. Polymers 10:1166–1173

Chapter 20
Phenolic Foams: The Insulating Materials to Reduce the Frost Penetration, Skidding, and Flooding Risk of Road and Airfield Pavements

Shohel Amin and Mohamed Heweidak

1 Introduction

The polymeric foams are formed using distinctive techniques including injection and extrusion molded foam process and the use of supercritical fluids over solid counterparts and the molding process made it light with enhanced structural stability [19, 44, 54]. The PFs are classified into three groups based on the potential end-user applications such as structural, flexible, and speciality foams. The structural or rigid foams, for example, rigid polyvinyl chloride and polyurethane foams are used in both construction and appliances as these have higher stiffness modulus and low thermal conductivity resulting in higher energy efficiency. The flexible foams including flexible polyurethane and polystyrene foams are used in cushion packaging and energy absorption applications for their low stiffness modulus and open-cell structure [32]. Speciality foams including PF are designed to meet predetermined cellular size and specific properties to perform functions in various applications.

The applications of PF in polymeric industries observe a growth from 5% to 6.5% during the last 5 years for their better performance in fire resistance, thermal insulation, filtration, absorbing practices, and environmental safety and cost [1, 32]. The ability to dissipate the kinetic energy makes the PF as a soft ground arrestor in airfield pavement to avoid over running of aircraft and ensure safety. In addition, the PF has a potential as a geotextile layer in permeable pavement systems (PPS) to minimize the flooding risks and a thermal insulation layer in tunnels and pavements to avoid

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frost damage. The PF can improve the mechanical properties of foamed tar pavement optimizing its stability and resilience. This chapter discusses the applications and benefits of PF in materials of roads and airfield pavements.

2 Physical Properties of Phenolic Foams

The cell morphology is crucial for the functionality of PF as its cellular structure provides versatile applications in market areas such as thermal insulation, absorbent materials, safety applications, and fresh flower support. The chemical process and constituents employed to produce PF determine two significant cellular structures: (1) open-cell foam with high liquid absorption and retention capacity within its structure and (2) closed-cell foam used as thermal insulation material in construction [46].

The main constituents to manufacture the PF are phenolic resins, acid catalyst, inorganic filler, and blowing agents [18]. Phenolic resins comprise of approximately 80% solid and a combination of volatile components including phenol, water, and formaldehyde [46]. The catalyst component stimulates the process of converting phenolic resins to foam. Sulfonic acids such as phenol and xylene have proven efficiency in foam curing over inorganic acid catalyst where corrosion problems are exhibited. Inorganic fillers enhance PF properties, for example, calcium carbonate produces PF with densities over 50 kg/m^3 [46]. The blowing agents such as aliphatic hydrocarbon and fluorocarbons (HCFC-141b and HCFC-22) are the principal materials for defining the properties and morphology of PF [46, 49]. The closed-cell PF has the ability to maintain its properties for long periods as long as blowing agents are confined within the foam structure while water evaporation and formulation of formaldehyde (CH_2O) primarily control the production of open-cell PF such as floral foam [11, 27]. Utilization of fluorocarbons (PFCs) as the blowing agents in closed-cell PF exhibits poor performance in terms of mechanical properties such as density and thermal conductivity comparing to the tetrafluoroethane blowing agent (CFC-114) [27, 46].

Each product of PF has identical physical properties that allow its utilization for a particular function (Table 1). Closed-cell PF with low thermal conductivity (0.018–0.02 W/mK) and high compression strength (2.8–7 kg/cm^2) is suitable for insulation applications [11, 46]. The open-cell floral or absorbent foams possess an excellent ability in absorbing and retaining liquids within the foam structure for long periods but with lower compression strength and friable structure (Table 1).

Table 1 Physical properties of PF [21, 46]

PF applications	Density (kg/m^3)	Compression strength (kg/cm^2)	Thermal conductivity W/mK	Closed/opened cell content	Water absorption
Insulation	32–50	2.8–7	0.018–0.02	More than 90% closed	Very low
Floral and absorbent	16–32 0.4	0.7–1.2	0.02–0.025	Less than 5% closed	Very high
Orthopedic	8–12	0.2–0.3	Low thermal conductivity	Open/closed	Low
Foamed concrete for ground arrestor systems	200–800	4.2–5.6	0.1–0.66	Up to 75 % open	Very low

3 Airfield Soft Ground Arrestor, Skid Resistance, and Safety

The highest rate of aircraft accidents (more than 25% of all commercial aircraft accidents annually) occurred due to runway excursion [12]. The runway excursion mainly occurs during aircraft take-off or landing in the form of runway overruns resulting from inappropriate aircraft handling techniques, aircraft malfunction, poor visibility, and airfield pavement condition. The Ascend World Aircraft Accident recorded 141 runway excursion accidents (85% of these accidents occurred during landing) during the period 1998–2007 that led to 550 casualties [14]. A total of 28 overrun aircraft accidents occurred in the United States during the period 2008–2017 and 4 of those accidents resulted in 17 casualties [3]. The aircraft overrun accidents have had a long history, which urges the aviation industries to find out the best practices eliminating the disastrous consequences of aircraft overrun.

The International Civil Aviation Organization (ICAO) recommends 305 m length safety area beyond the runway. Some airports find it difficult to comply with the ICAO standard due to the topographical locations and urge alternative solutions to overcome this problem. The runway arrestor systems are widely used techniques to effectively decelerate aircraft speed and ensure safe stopping. There are two techniques commonly used in the runway arrestor systems, active arresting system, and passive ground system. The active arresting systems such as deck cables and large net barriers are mostly developed for jet aircraft [20, 24, 45]. Active arresting systems are not adequate for passenger aircrafts as deck cables are not economically feasible and the large net barrier obstructs aircraft passengers from using emergency egress. In addition, the net barrier adversely affects the aircraft wing flaps due to the applied load by the net barrier system. The passive ground system applies engineering materials to prevent the aircraft overrun and eventually reducing the length of runway safety area [20].

Several studies in the United Kingdom tested soft ground materials including gravel, sintered fuel, and aerated concrete during the period from 1968 to 1971 [4, 35]. The urea–formaldehyde foam was used as ground arrestor material and the trial was proceeded by Comet 38 aircraft in 1974. There was no damage in aircraft engine turbine due to the efficiency of foam in reducing the predictable peak drag force acting over leading and trailing wheels [20]. Cook et al. [6] compared various materials such as water, gravel, soft soil (clay and sand), PF, and foamcrete to determine the advantages and disadvantages of materials in terms of workability, maintenance cost, resistance to erosion. Cook et al. [6] recommended the PF as a ground arrestor material for its stable mechanical properties and its ability to decelerate the commercial aircraft with a coefficient of friction equals to 0.4 denoting a good braking action. Cook et al. [6] examined the performance of PF as a ground arrestor with compressive strength of 380 kPa and 50 cm depth. The analytical models estimated the stopping distance of aircraft entering the PF arresting system with 50 knots and 60 knots speed. The Boeing 727 safely stopped at 128 m and 165 m distance with 50 knots and 60 knots speeds, respectively [6].

The aircraft stopping distance inside the bed arrestor subjects to deceleration rate, materials strength and thickness, aircraft weight, and landing gear loads [10]. The increase in foamed concrete bed depth can significantly offset the aircraft load but landing gears subjects to additional loads. The rebounding force over landing gear was not evidently defined by Cook et al. [6]. Cook et al. [6] argued that PF had rebounding properties that might exhibit additional force over landing gear resulting in the damage of landing gear [22]. The Federal Aviation Administration (FAA) and Engineering Arresting Systems Corporation (ESCO) jointly worked on improving the rebounding characteristics of PF employing the crushable lightweight concrete to disperse the energy instead of returning to aircraft body [23]. The bed arresting system consists of precast blocks formed from closed cell concrete foam that is bonded by silicon sealer [22]. A protective layer is provided as a waterproof paint to improve the durability of material subjected to severe weather conditions [36]. The crushable concrete foam is the only engineering material arresting system (EMAS) that is accredited and recommended by FAA and is used in 59 runways at 40 airports [37]. However, the bed arrestor system with concrete foam requires at least 4–12 weeks to install and is expensive [22, 36]. The concrete foam causes a cloud of dust during aircraft landing that enters inside the aircraft engine risking the aircraft operation [15]. Moreover, the humid weather adversely impacts the foam reducing its long-term performance and requires maintenance for moisture infiltration and membrane peeling [22]. The foamed concrete arrestor does not perform safely for all types of aircrafts, for instance, the landing gear of puddle jumper aircraft may experience fatal damage when crash into the ground arrestor system [51].

Several studies examined the application of alternative materials for improving the ground arrestor system [10, 15, 22, 51]. Yang et al. [15] investigated the use of polyurethane foam as a ground bed arrestor due to its low strength and energy dissipation capacity. Yang et al. [15] asserted the importance of ground arrestor material's strength on aircraft crash ignoring other factors such as material durability, cost, and maintenance as well as stopping distance of aircraft inside the arrestor bed. A study examined the performance of tire-honeycomb material as a ground arrestor against the friction between the material and aircraft undercarriage and compared the results with traditional EMAS [51]. Yang et al. [51] argued that the manufacturing tire-honeycomb material was more environment friendly due to low haze production and effective in stopping overrunning aircraft. The FAA approved EMASMAX® and greenEMAS® as the EMAS. The EMASMAX® is nontoxic and composed of lightweight blocks made from cellular cement material with higher durability and fire and extreme weather resilient. The greenEMAS® is manufactured from recycled glass, bonded together with high-strength plastic, covered by cement layer, and treated by topcoat sealant [12]. The Zodiac Aerospace has installed EMASMAX® bed arrestor at 112 runways in 67 airports in the USA [12, 42]. There were 15 incidents recorded in U.S airports until April 2019 where overrun aircrafts safely stop within EMAS with almost no passengers injured and undamaged aircraft body [50].

4 Frost Penetration Below Highways and Airfield Pavements

Frost penetration, which occurs due to seasonal freeze–thaw cycles, reduces the life service of highways and airfield pavements [20, 25, 41]. The freeze–thaw cycles saturate the subgrade soil with excessive water and affect the mechanical properties of subgrade soil beneath the pavement structure without the existence of a proper drainage system [26]. During the cold season, the formation of ice lenses in the unbounded layer increases the bond between the particles of subgrade soil and subsequently improves the bearing capacity of the soil. The fine particles in subgrade soil, high thermal conductivity, the moisture content in pavement, and ice formation in the pavement subsurface are the main factors of frost heave. However, the workability of pavement may be weakened due to thermal cracks and uneven frost heave [26]. The increase of temperature causes ice thawing resulting in soil saturated with water. The impact of ice thawing may cause potential settlement of pavement structure under heavy traffic loads due to poor drainage system and structural inadequacy [26]. In northern Sweden, around 40% of road network was inaccessible during the frost thawing period in the year 1994 and the Swedish national road administration estimated that the annual maintenance and reconstruction cost was approximately 25% of the road construction budget [26].

Several studies measured the frost penetration depth in the pavement structure [5, 16, 20, 40]. Equations 1–4 show that soil thermal conductivity is one of the major determinants of frost penetration.

$$X = \sqrt{\frac{48K(FI)}{L}} \text{ Freitag and McFadden [33]} \tag{1}$$

$$X = \lambda\sqrt{\frac{48K(FI)}{L}\text{Aitken and Berg [35]}} \tag{2}$$

$$FI = \frac{diLi}{24n\lambda} + R \text{ Bianchini and Gonzalez [34]} \tag{3}$$

$$X = a(FI)^b \text{ Baladi and Rajaei [32]} \tag{4}$$

where X is the frost penetration depth; FI is the freezing index; K is the thermal conductivity; n is the factor that transfers air FI to surface FI; λ is the correction coefficient; d is the layer depth; R is the thermal resistance; L is the latent heat; a and b are constant.

During the late 1960s, several studies in cold regions examined the application of insulation materials including polymeric foams to reduce the frost penetration depth in pavement foundation [2, 33]. Penner [2] examined the impact of installing extruded polystyrene and polyurethane foams between the subsoil and gravel base to evaluate the pavement performance in Ontario, Canada. Penner [2] observed that the insulation foams reduced the frost heave at a significant level. In Alaska, Esch [33] investigated the usage of 5 cm of urethane foam and 8 cm of styrofoam as the subgrade insulation layer and identified that the frost penetration depth was reduced by 48.5% and 81%, respectively. However, Esch [33] observed that the polyurethane foam, a mixture of urethane and styrofoam in liquid state, had lower structural strength and thermal conductivity. A recent study monitored the impact of extruded polystyrene foam on the frost heave for 3 years in France and asserted its ability to reduce the frost penetration [13].

The application of polyphenolic foam in reducing the frost damage at Galongla tunnel located in China was experimented applying the finite element method (FEM) [8]. Thermal sensors were installed at 10 sections along the tunnel axis at depth of 370 cm. Tan et al. [8] compared the polyphenolic foam and concrete as insulation layers to study temperature distribution in rock surrounding tunnel lining. The polyphenolic foam performed better in sustaining very low temperature in rock layer for 1 year and thus avoid freezing–thawing damage. Li et al. [43] examined the thermal conductivity of three insulation foam materials such as polyurethane, phenolic, and floquet in dry, wet, and freezing conditions using the hot disk thermal physical property analyzer. The relationship between thermal conductivity and gray volume moisture content ratio (*Gv*) was applied to evaluate the impact of water content on insulation foams. The average thermal conductivity for phenolic and polyurethane materials under dry conditions was 0.040 W/(m.K)and 0.029 W/(m.K), respectively [43]. The experiments revealed that thermal conductivity increased with an increase in of iced mass moisture content. Although the PF is applied in wider range as the thermal insulator, the application of extruded polystyrene foam to reduce the freezing–thawing damage is more advantageous. For example, in Norway, polystyrene foam is one of the common insulation materials used in pavements [28]. The insulation materials such as foam glass aggregate are used as the alternative materials to extruded polystyrene foam in cold regions of Europe since the materials are economical and have been manufactured as an environmentally friendly solution [].

5 Permeability and Sustainable Drainage System

Impermeable pavement surfaces hinder the infiltration of stormwater runoff and cause surface runoff of pollutants such as nutrients, heavy metals, and motor oil to the water bodies resulting in risk to marine life and human health if untreated [17, 34, 48]. Impermeable pavement surfaces also increase the volume of stormwater runoff that overburdens the capacity of drainage networks and eventually causing floods particularly in urban areas [34, 48]. Sustainable drainage system (SuDS) is a contemporary challenge that considers permeable pavement system (PPS) as the environmentally and economically beneficial approach for minimizing flood risks [38]. The most practiced PPS in the United Kingdom is a geotextile layer beneath the pavement structure because geotextile materials retain stormwater pollutants and enhance the process of biodegradation within the pavement structure [29, 39, 47]. Several materials such as polyethylene, polypropylene, and polyester are used to manufacture the geotextile layer that acts as the filtration or separation layer of PPS [29, 30, 47]. The three-dimensional structure of OASIS® PF can increase the material ability to absorb and attain stormwater up to a saturation limit [9, 47].

Nnadi et al. [47] examined the hydraulic properties of OASIS® material with 1.3 cm and 2 cm thicknesses under rainfall intensities of 100 mm/ hr, 200 mm/hr, and 400 mm/hr and stated that OASIS® material retained stormwater. Nnadi et al. [47] identified that one-centimeter increase of depth in OASIS material would increase its stormwater storage capacity by 37%. A similar study was conducted by Heweidak and Amin [31] examining the infiltration rate and steady-state behavior, water storage capacity of different thicknesses of OASIS® material, and the effect of OASIS® material in deferring the water peak flow during rainfall intensities of 100 mm/hr, 243 mm/hr, 400 mm/hr, and 563 mm/hr. Heweidak and Amin [31] stated that a 35 mm thickness of OASIS® layer could absorb approximately stormwater with rainfall intensity of 100 mm/hr for 15 min duration, and a 10 mm increase of OASIS® layer thickness can increase the water storage capacity by 12%. The PF can effectively retain rainwater delaying water peak flow that minimizes the flooding risk (Table 2). The PF materials have structural strength bearing static loads, but pavement surface

Table 2 Properties of absorbent PF [32]

Material	Density (kg/m$^{3)}$	Polymer density (kg/m$^{3)}$	Expansion ration	Cell diameter (microns)	Void fraction %	Volume of foam In^3	Volume of solid In^3
Absorbent PF	32.04	1188.57	37.1	250	97.3	64	1.73

is subjected to both dynamic and static loads [31]. The PF layer may increase the probability of void clogging that affects the performance of PPS [53].

6 Conclusions

The low thermal conductivity, effective energy absorption, and liquid absorption of PF provide a wider range of its application in building and infrastructure materials. This chapter discusses the applications and benefits of PF in materials of roads and airfield pavements. The PF as an EMAS in airfield pavements demonstrates an efficient material to safely stop the aircraft within the PF bed arrestor system. However, the drag force generated from the aircraft undercarriage leads to serious damage to landing gear. The EMASMAX, approved EMAS by FAA, improves the rebounding properties of the bed arrestor in the airfield pavement. The EMASMAX is composed of cementitious cellular foam with sufficient capacity to dissipate the energy instead of returning to aircraft and the cellular cementitious foam is recyclable and environment friendly. The commercial availability of EMASMAX is very limited causing a higher cost of installation and maintenance. Foam glass could be an alternative EMAS but it possesses high strength. The cementitious foams are subjected to moisture infiltration, membrane peeling and freeze–thaw effects.

The PF has low thermal conductivity but the XPS is commonly utilized as an insulation layer in pavement structures in Nordic countries and Canada. The XPS has some technical difficulties such as weak joints due to geometry and possible loss of material efficiency over time as a result of XPS chemical decomposition. The application of PF to reduce frost penetration in pavement structures can be a sustainable solution as PF reduces the environmental impacts through recycling waste materials.

The experimental results of PF application in PPS argue its efficiency in minimizing flood risk, however, further studies require to understand its performance under dynamic traffic loads with extreme rainfall intensities. The manufacturing process and residual after the life cycle of PF hinder its applicability in road and airfield pavements. The contaminated waste of PF is non-recyclable and sends to the depot. Future studies require to addressing the material durability, response to vehicles and aircraft loads and speed, the environmental impacts, and the installation and maintenance costs.

References

1. Advanced market analysis (2020) Phenolic foam market segmented into XX submarkets. Available via: https://www.advancemarketanalytics.com/reports/31925-global-phenolic-foam-market [Accessed 23 May 2020]
2. Atkin GW, Berg RL (1968) Digital solution of modified Berggren equation to calculate depths of freeze or thaw in multilayered systems. Special report 122. Cold Regions Research and Engineering Laboratory, Engineer Research and Development Center, USA. Available via http://hdl.handle.net/11681/11899
3. Ayres M, Shirazi H, Carvalho R et al (2013) Modelling the location and consequences of aircraft accidents. Safety Sci 51(1):178–186
4. Bade E (1968) Soft-ground arresting of civil aircraft, Ministry of Technology, Royal Aircraft Establishment, Farnborough
5. Baladi G, Rajaei P (2015) Predictive modeling of freezing and thawing of frost susceptible soils. Final Report, RC-1619. Michigan Department of Transportation. Available via https://www.michigan.gov/documents/mdot/RC1619_500351_7.pdf
6. BarnesJ (1971) Development of a model technique for investigating the performance of soft-ground arresters for aircraft, CiteseerX.
7. Bianchini A, Gonzalez C (2012) Pavement-transportation computer assisted structural engineering (PCASE) implementation of the modified berggren (ModBerg) equation for computing the frost penetration depth within pavement structures. TR-12–15. Geotechnical and Structural Laboratory. U.S. Army Corps of Engineers
8. Boutonnet M, Lerat P, Saint-Laurent D et al (2003) Thermal aspect of frost-thaw pavement dimensioning: in situ measurement and numerical modeling. Paper No. 03–2657, pp 1–23. 82nd Annual Meeting. Transportation Research Board. Washington, DC
9. Brownstein JB (1998) An investigation of the potential for the biodegradation of motor oil within a model permeable pavement. Unpublished PhD thesis, Coventry University, UK
10. Cook RF (1993) Soft-ground arresting system for commercial aircraft, Universal Energy Systems, Dayton, 1993 Final Report
11. Coppock V, Zeggelaar R, Takahashi H et al (2013) Phenolic foam. US patent no. 20130072589A1
12. Eaves D (2004) Handbook of polymer foams. Shawbury: Rapra Technology.
13. Esch D (1969) Subgrade insulation for frost heave control construction, instrumentation, and first year summary. State of Alaska, Department of Highways Materials Division. Available at http://www.dot.state.ak.us/stwddes/research/assets/pdf/esch_jun1969.pdf
14. FAA (Federal Aviation Administration) (2020) Fact sheet—engineered material arresting system (EMAS). Avaliable via https://www.faa.gov/news/fact_sheets/news_story.cfm?newsId=13754 [Accessed 12 July 2020]
15. Federal Aviation Administration (2005) AC 150/5220–22A engineered materials arresting aystems (EMAS for Aircraft Overruns)
16. Freitag DR, McFadden T (1997) Introduction to cold regions engineering. The American Society for Civil Engineers
17. Frydenlund TE, Aabøe RO (2003) Foam glass—a new vision in road construction. In: Paper presented in proceedings of the 22nd PIARC—C12 technical committee on earthworks, drainage and subgrade. Durban, South Africa, 2003
18. Gardziella A, Pilato L, Knop A (1999) Phenolic resins, 2nd edn. Springer-Verlag Berlin Heidelberg New York in 2000, Springer
19. Gong W, Fu H, Zhang C et al (2018) Study on foaming quality and impact property of foamed polypropylene composites. Polym 10(12):1375
20. Hartzer R (1993) From sandbags to MAAS, aircraft arresting systems, Air Force Civil Eng Mag
21. Heweidak M, Amin S (2019) Effects of OASIS® phenolic foam on hydraulic behaviour of permeable pavement systems. J Environ Manage 230:212–220

22. Heymsfield E, Halsey TL (2008) Sensitivity analysis of engineered material arrestor systems to aircraft and arrestor material characteristics. Transp Res Rec J Transp Res Board 2052(1):110–117
23. Ho CH, Romero P (2009) Investigation of existing engineered material arresting system at three U.S. Airports. In: 50th Annual Transportation Research Forum 2009. 50th Annual Transportation Research Forum 2009, vol. 1, pp. 510–524, 50th Annual Transportation Research Forum 2009, Portland, OR, United States, 3/16/09
24. Horne T (2019) from the editor: overrun the perils of too high, too fast. Available via: AOPA.https://www.aopa.org/news-and-media/all-news/2019/april/pilot/from-the-turbine-editor-overrun. Accessed 22 Jul 2020
25. Janoo VC, Berg RL (1996) PCC airfield pavement response during thaw-weakening periods—a field study. Special Report 96–12. CRREL, US Army Corps of Engineers
26. Johnson AE (2012) Freeze-thaw performance of pavement foundation materials. Iowa State University, Ames, Iowa, Master of Science
27. Landrock AH (1995) Handbook of plastic foams: types, properties, manufacture, and applications. Park Ridge, N.J., U.S.A.: Noyes Publications
28. Li Y, Sun Y, Zhuang Y et al (2020) Thermal conductivity characteristics of thermal insulation materials immersed in water for cold-region tunnels. Adv Mater Sci Eng 2020:1–15
29. Newman AP, Nnadi EO, Duckers LJ et al (2011) Further developments in self-fertilizing geotextiles for use in pervious pavements. Water Sci Technol 64(6):1333–1339
30. Nnadi EO, Coupe S, J, Sañudo-Fontaneda LA et al (2014) An evaluation of enhanced geotextile layer in permeable pavement to improve stormwater infiltration and attenuation. Int J Pavement Eng 15(10):925–932
31. Nnadi EO (2009) An evaluation of modified pervious pavements for water harvesting for irrigation purposes. Unpublished PhD Thesis. Coventry University, UK
32. Obi BE (2017) Polymeric foams structure-property-performance: a design guide. William Andrew, Oxford
33. Penner E (1967) Experimental pavement structures insulated with a polyurethane and extruded polystyrene foam. In: Proceedings-International Conference on Low Temperature Science, Hokkaido University, Sapporo, Japan
34. Pratt C, Newman A, Bond P (1999) Mineral oil bio-degradation within a permeable pavement: long term observations. Water Sci Technol 39:103–109
35. Rastegar J, Ge J (2005) Roadway for decelerating and/or accelerating a vehicle including an aircraft. US patent no. 6969213B2
36. San-Filippo WK, Delong H (2002) Engineered materials arresting system: an alternative solution to runway overruns. In: Sproule W, Jansen S (eds) Proceedings of the 27th international air transport conference 2002. p 257e65
37. Santagata E, Bassani M, Sacchi E (2010) Performance of new materials for aircraft arrestor beds. Transp Res Rec J Transp Res Board 2177(1):124–131
38. Scholz M (2013) Water quality improvement performance of geotextiles within permeable pavement systems: a critical review. Water 5(2):462–479
39. Scholz M, Grabowiecki P (2009) Combined permeable pavement and ground source heat pump systems to treat urban runoff. J Chem Technol Biotechnol 84(3):405–413
40. Simonsen E, Isacsson U (1999) thaw weakening of pavement structures in cold regions. Cold Reg Sci Technol 29(2):135–151
41. Skybrary (2019) Engineered materials arresting aystem. Available online https://www.skybrary.aero/index.php/Engineered_Materials_Arresting_System_(EMAS) Accessed 12 Jul 2020
42. Steyn WJ, Lombard S, Horak E (2016) Foamed concrete-based material as a soft ground arresting system for runways and airfields. J Perform Constructed Facil 30(1):1943–5509.0000692
43. Tan X, Chen W, Wu G et al (2013) Numerical simulations of heat transfer with ice–water phase change occurring in porous media and application to a cold-region tunnel. Tunneling and underground space technology 38:170–179

44. Wang G, Zhao G, Zhang L et al (2018) Lightweight and tough nanocellular PP/PTFE nanocomposite foams with defect-free surfaces obtained using in situ nanofibrillation and nanocellular injection molding. Chem Eng J 350:1–11
45. White DJ, Vennapusa KR, Zhang Y et al (2016) Assessment of seasonal variations in concrete pavement foundation layers—multiple test sections in Iowa. In: Trans Project 09–352 Report. Iowa State University. Ames, IA
46. White JC, Agrawal SK (1993) Final report soft ground arresting system for airports, federal aviation administration, Washington, DC
47. Wilson S, Bray B, Cooper P (2004) Sustainable drainage systems, 1st edn. CIRIA, London, UK
48. Woods-Ballard B, Kellagher R, Martin P et al (2007) The SUDS manual, no C697. London, UK: Construction Industry and Research Association (CIRIA)
49. Wypych G (2017) Handbook of foaming and blowing agents. Chemtec Publishing, Toronto
50. Yang X, Xing Y, Zhang Z et al (2017) Theoretical analysis and multi-objective optimisation for gradient engineering material arresting system. Int J Crashworthiness 22(5):541–555
51. Yang X, Zhang Z, Xing Y et al (2017) A new theoretical model of aircraft arresting system based on polymeric foam material. Aerosp Sci Technol 66:284–293
52. Yong CF, Deletic A, Fletcher TD et al (2008) The clogging behaviour and treatment efficiency of a range of porous pavements. In: Proceedings of the 11th International Conference on Urban Drainage (ICUD). Edinburgh, Scotland
53. ZODIAC Aerospace (2011) EMASMAX™ aircraft arresting systems for runway overrun protection ICAO—global runway safety symposium montreal. Available via https://www.icao.int/safety/RunwaySafety/GRSS2011/Documentation/Docs/ESCO%20Zodiac%20Aerospace%20Solutions%20Workshop%20Presentation.pdf
54. Zhou D, Xiong Y, Yuan H et al (2019) Synthesis and compressive behaviours of PMMA microporous foam with multi-layer cell structure. Compos Part B Eng 165:272–278