

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.

P. K. Sandhya · S. Thomas

School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala 686560, India

M. S. Sreekala (✉)

Post Graduate Research Department of Chemistry, Sree Sankara College, Kalady, Kerala 683574, India

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.

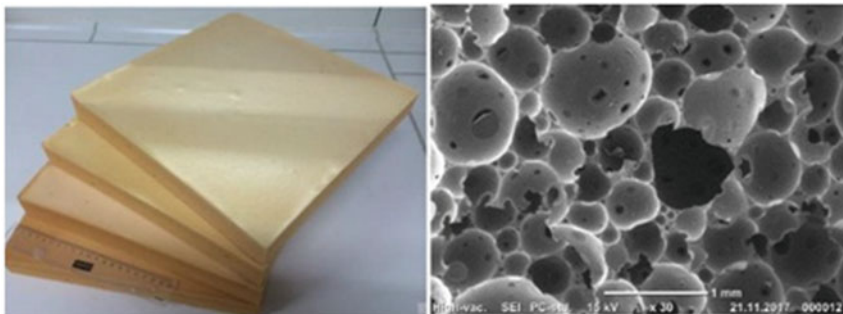


Fig. 1 a Phenolic foam panels (300 mm × 300 mm × 40 mm) b SEM image of phenolic foams possessed interconnected macroporous structure [2]

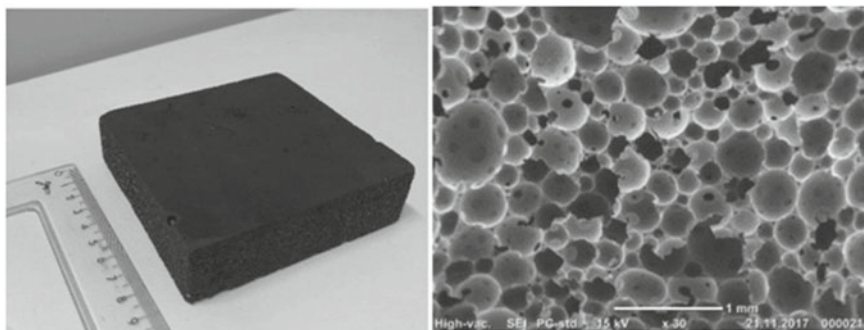


Fig. 2 a Monolithic carbon foam produced by pyrolysis of phenolic foams b Macroporous structure of carbon foam [2]

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

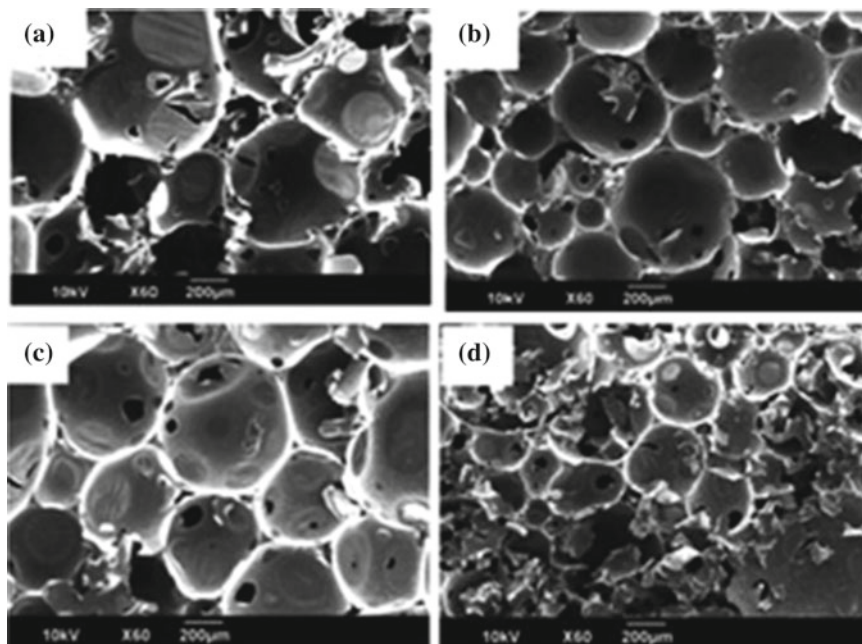


Fig. 3 SEM images of neat PF foam **a**, 0.08 wt% RGO **b**, 0.12 wt% RGO **c**, and 0.15 wt% RGO **d** [27]

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-SiO₂ and an increase in mechanical properties of PF foam is observed.

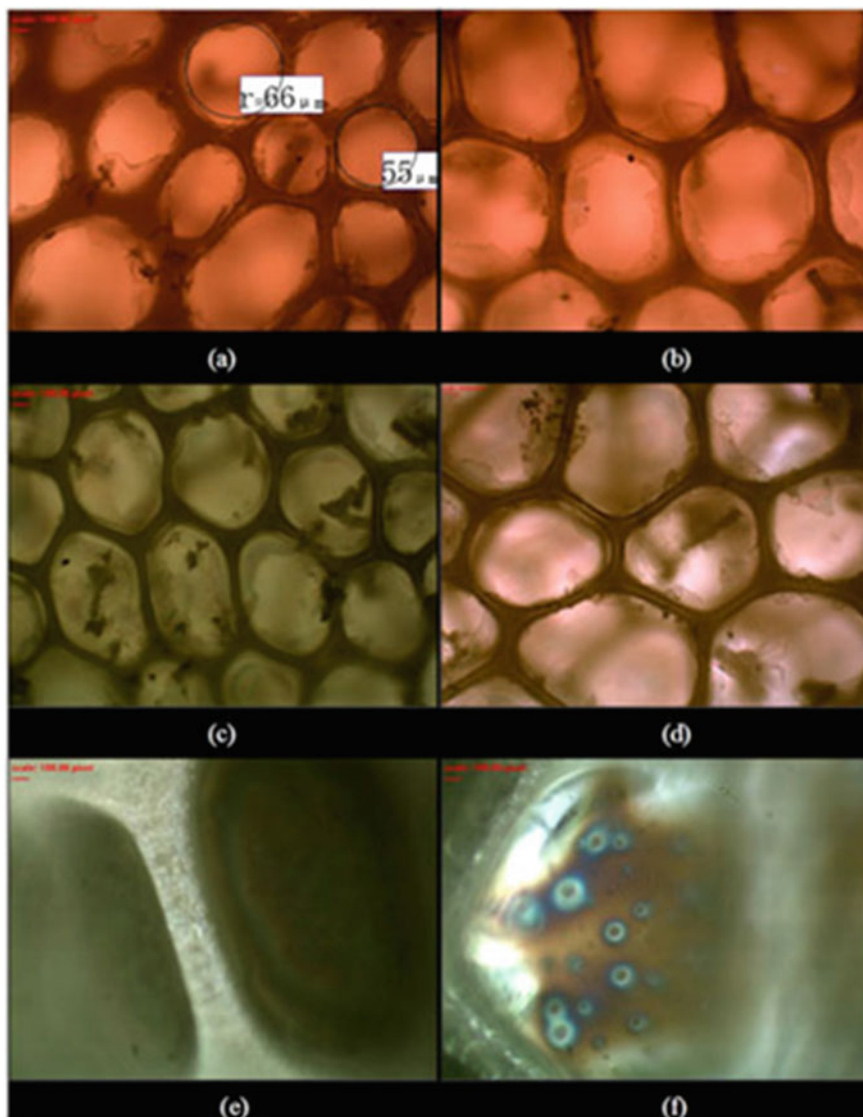


Fig. 4 Optical microscopic images of pure phenolic foams (**a** $\times 100$ transmission; **e** $\times 400$ reflection), PEGP200 (**b** $\times 100$ transmission), PFPEGP400 (**c** $\times 100$ transmission; **f** $\times 400$ reflection), and PFPEGP600 (**d** $\times 100$ transmission) [14]

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. Domínguez 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-pentadecylphenol 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-Fe₃O₄-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.

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