Chapter 8
Thermal Stability of Phenolic Foams

Lakshmipriya Ravindran, M. S. Sreekala, S. Anilkumar, and Sabu Thomas

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].

L. Ravindran · S. Anilkumar
Postgraduate and Research Department of Chemistry, N.S.S. Hindu College, Changanacherry, Kerala 686102, India

L. Ravindran · M. S. Sreekala (✉)
Postgraduate and Research Department of Chemistry, Sree Sankara College, Kalady, Kerala 683574, India
e-mail: sreekala@ssc.edu.in

S. Thomas
School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O, Kottayam, Kerala 686560, India

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.

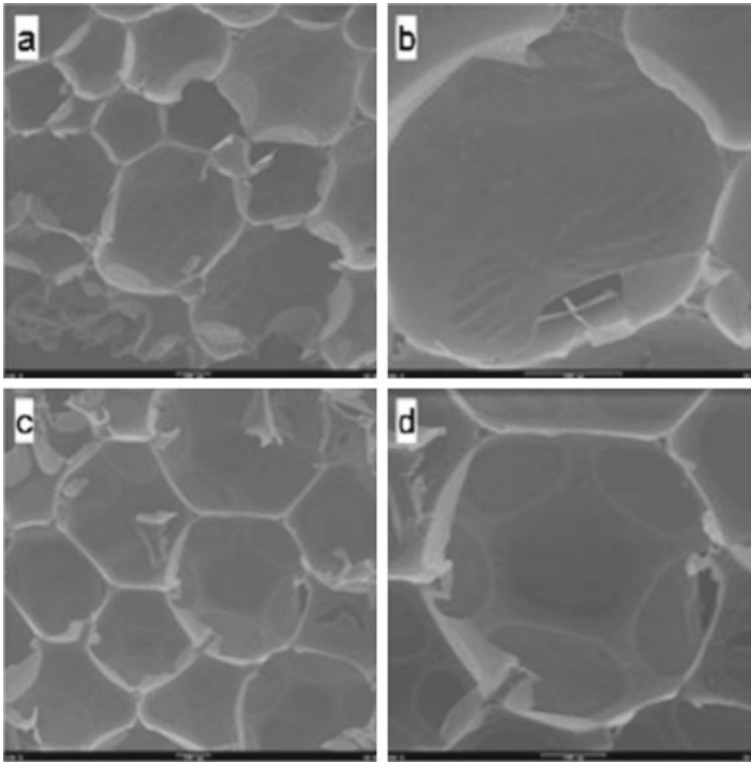**Fig. 1**   Global market of phenolic foam in 2023 [32]

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]
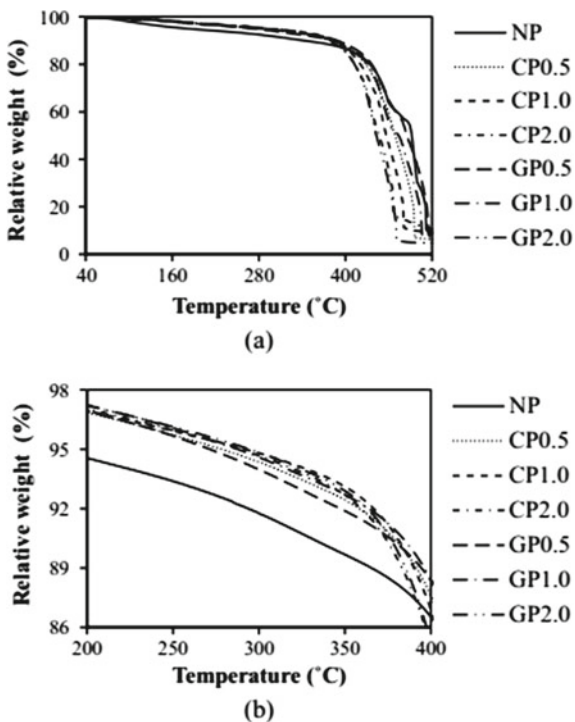
compared to pure PF foam, the cell distribution of MPF2s is more homogeneous. Based on the theory of thermal transfer, lower loading of silica sol in MPF0.5 cannot accelerate vibration of the molecular segment, which disrupts heat transmission. The results of the friability showed that the pulverization 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]
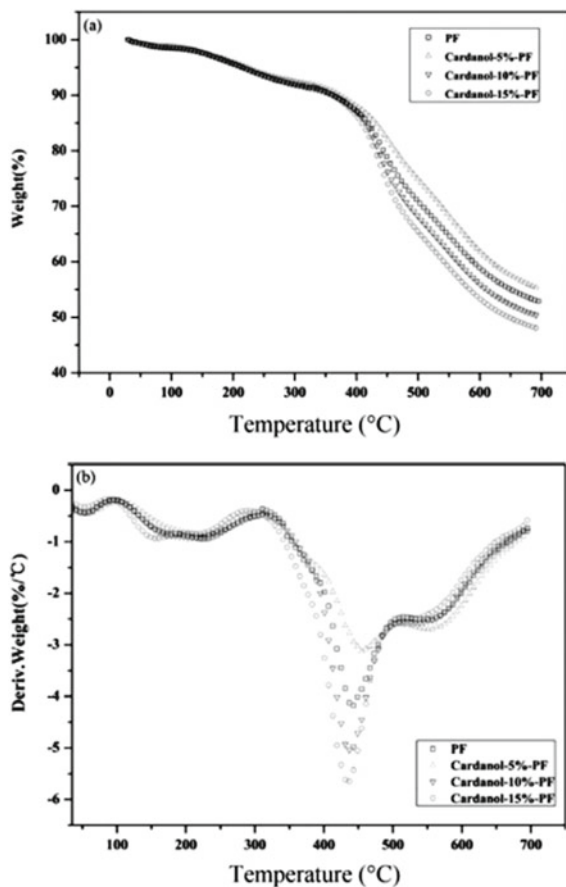
these trapped free radicals in the gas phase resulted in improved flame retardancy. However, the phosphaphenanthrene group generated a char residue that hinders further polymer combustion. Furthermore, these modified PF foam demonstrated superior mechanical properties than neat PF. With 4% PCC, the compressive 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
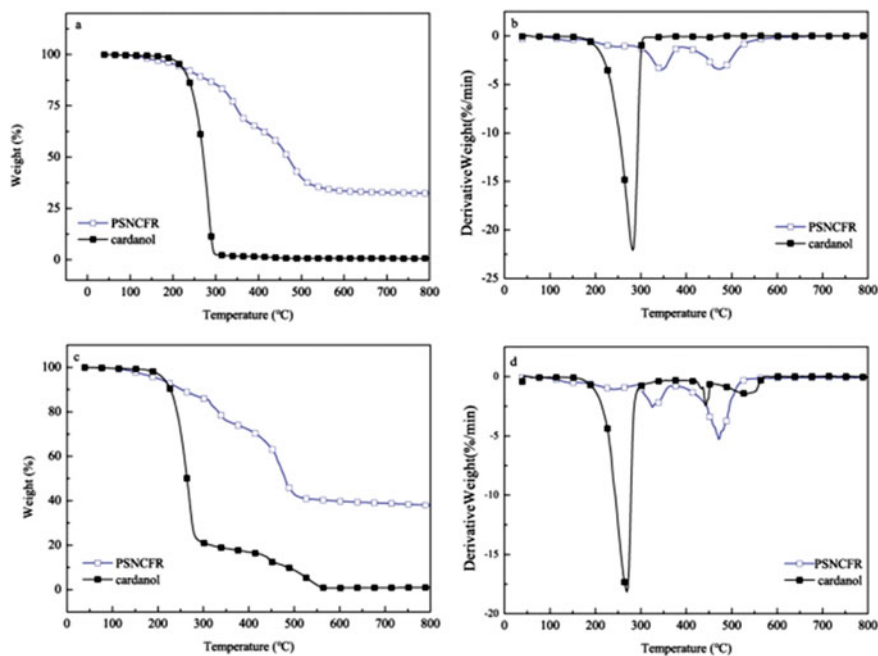

Fig. 5 **a** TGA and **b** DTG curves of cardanol and PSNCFR under N2, **c** TGA and **d** DTG curves of cardanol and PSNCFR under air [54]

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

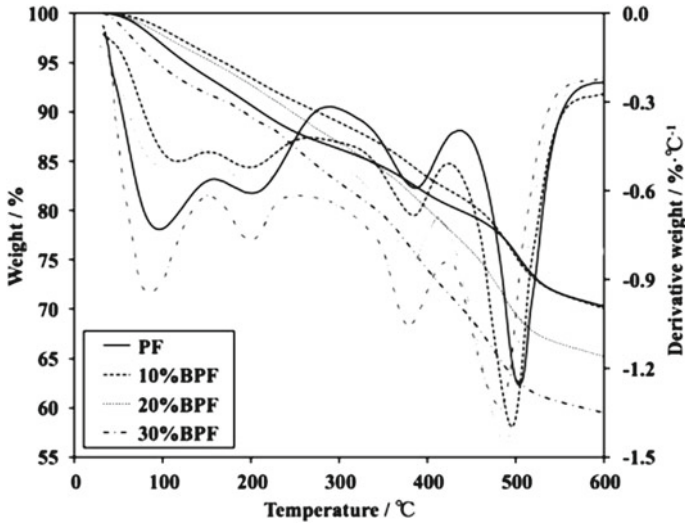**Fig. 6** Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of PF and BPFs [57]

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.

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