

A comprehensive review on phenol-formaldehyde resin-based composites and foams

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Funding information

Department of Science and Technology, Ministry of Science and Technology, India, Grant/Award Number: 487/DST/FIST/15-16

Abstract

This article covers the introduction to polymer composites, phenol formaldehyde resin, phenol formaldehyde composites, and foams along with their properties and applications. The previous research in the fields of phenol formaldehyde composites, nanocomposites, and PF foams is also covered in depth. Various combinations of nanomaterials and processes have been investigated in the field of structural composites to meet the requirements of industries such as automotive, aerospace, military, civil, and construction. Due to their different features and possibilities when compared to equivalents composed of other polymers, particularly thermosets, phenol-formaldehyde reinforced composites are commonly used for large load bearing structural applications. Composite properties can be improved by using nanoparticles, which are materials that have been developed as a result of advances in nanotechnology. This research focuses on a literature review of nanofillers' use to improve the structural properties of phenol-formaldehyde composites and foams published in the last two decades. The use of nanomaterials to modify composites is examined in depth.

KEYWORDS

foams, macro-composites, nano-composites, nano-reinforced foams, phenol formaldehyde resin

1 | INTRODUCTION

In comparison with non-reinforced polymers, polymer composites, especially nano composites, are gaining attention due to their exceptional properties. The field of nanotechnology is fast growing nowadays. Nanofillers prepared from different sources and methods show unique properties in relation to the macro substances. Due to the high interfacial area of the nanofillers, polymer nanocomposites exhibit excellent mechanical, thermal, and electrical properties compared to their host matrix. The major advantage of polymer nanocomposite is that, it is capable of improving its chemical and

physical properties with a minimal amount of reinforcement. By choosing appropriate nanofillers, it is able to design polymer nanocomposites with desired properties.

“Nano sandwiches” is an article published by Chemistry in Britain in 1988 suggests “Nature is a master chemist with incredible talent”. Natural nanocomposites include bones, shells, and wood, which are created by combining natural reagents and natural polymers such as protein, carbohydrates, and others in nanometer dimensions. Nylon-6 polymer nanocomposite synthesized by Toyota Central Research Laboratories in Japan in the 1990s showed a pronounced improvement in thermal and electrical properties for the corresponding polymer

nanocomposite. They used clay mineral sheets in layered silica as a filler in Nylon-6. The nature of the nanocomposites does not merely depend on the polymer matrix and the nanofillers but also on their morphology and interfacial interaction.

The significant difference between macroparticles and nanoparticles is the huge difference in their physical and chemical properties. Nano particles have larger surface area compared to macro particles.^[1,2] Because surface and surface properties are the primary determinants of physical and chemical interactions, composites with nanoparticles have very different properties than those with macroparticles of the same composition. Nanoparticles in a polymer matrix play a crucial role in determining the mechanical properties of polymer nanocomposites. Poor dispersion of nanoparticles will degrade the properties of the polymer nanocomposites. Good adhesion at the interface will improve properties such as interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance.

Nonetheless, to the best of our knowledge, no literature report has been published on nano/macro-reinforced phenol formaldehyde composites and foams and the reinforcing effects on their properties. Many of the reviews focus on the on a single filler or a single composite attribute of interest. This review gives a thorough literature survey concerned with the enhancement of PF composite's and foam's properties by nano-reinforcements. The focus of this review is only on PF-based composites and foams. With general perspectives on the phenolic nano/hybrid composites, foams development and curing process, followed by characterization of their properties.

1.1 | Polymer composites

Polymer composites are polymer materials that contain reinforcement, in which the polymer functions as a matrix resin that allows the reinforcement bundles to penetrate and thus bond to the reinforcement. Polymer composites are commonly used in aerospace and defense applications. One or more of the following components make up a composite: reinforcement and matrix. Metallic, ceramic, or other polymeric materials can be used as a matrix and reinforcement in the composite. The use of thermosetting and thermoplastic resins as the matrix of polymer composites has become increasingly popular. Polymer composites are mostly used in the automotive and aerospace industries. The field of polymer has a few important issues to consider, and a single polymer will not be able to match the demands of advanced applications. As a result, polymer composites have captivated the future of the global world.

It has been shown that natural fiber-reinforced polymer (NFRP) composites may partly replace traditional synthetic fiber-reinforced based composites since they are biodegradable, harmless, and have an intrinsic lightweight property.^[3-6] On the other hand, the poor impact strength and high moisture absorption of natural fibers have limited their application. Natural fibers are modified by chemical treatments, such as alkali treatments, in order to overcome such difficulties. The term "hybrid composites" refers to composites containing more than one type of reinforcement. The term "hybrid" refers to the combination of two or more different materials into a single system. Based on the geometry of the reinforcing components, composites are further classified as particle-reinforced, fiber-reinforced, and sandwich or laminated structures. Fiber-reinforced plastic (FRP), also known as fiber-reinforced polymer, is a composite material that consists of a polymer matrix with fiber reinforcement. Glass, carbon, and aramid fibers, as well as natural fibers such as basalt, jute, sisal, flax, and coir, are commonly used. Due to a combination of the specific features of the parent materials, these hybrid/composite systems can have better functional performance than their individual constituents. Improved electrical, mechanical, chemical, optical, and thermal properties can be attained exorbitantly by developing hybrids and composites.

Mishra et al.^[7] found that improvement in the mechanical characteristics of composites could be brought about treating sisal fiber with a 5% NaOH concentration solution. The impact of alkaline treatment on the tensile characteristics of curaua fiber composites was investigated by Gomes et al.^[8] They concluded that fracture strain in alkaline-treated fiber composites was greater than in untreated fiber composites. The impact of alkaline treatment on the tensile characteristics of sugar palm fiber reinforced epoxy composites was examined by Bachtiar et al.^[9] The tensile modulus was enhanced compared to untreated epoxy composites. Furthermore, treating the reinforcing fiber with silane coupling agents could increase the performance of natural fiber composites. By reacting with the hydroxyl groups on the surface of fibers, silane chemicals alter their surface properties, making polymer resin impregnation easier. Silane chemicals may also limit hydrogen bonding between fibrous molecular chains, resulting in greater polymer resin dispersion and fiber impregnation. In addition, the interaction between hydrophobic polymer matrix and hydrophilic fiber may also be enhanced, lowering mechanical property deterioration as well. Islam et al.^[10] coated CNT on jute fiber to improve the thermal stability of the fiber. He found that CNT addition increased the crystallinity and mechanical performance. Microcrystalline cellulose was dispersed in epoxy/jute composite at the fiber-matrix interface to improve the static-dynamic mechanical properties and

thermal behavior.^[11] They observed that MCC addition significantly improved all the properties. Li et al.^[12] fabricated an epoxy hybrid composite that contains ramie fabric and carbon nanotubes. Apart from impact fracture toughness, it was discovered that introducing multiwalled carbon nanotubes improved the mechanical and fracture properties of ramie fiber-reinforced epoxy composites. Natural fibers' distinct chemical compositions and multi-scaled nanosized microstructures have brought about new techniques for improving the mechanical properties of natural fiber-reinforced composites to light.

Sever et al.^[13] investigated the influence of α -Methacryloxypropyltrimethoxy silane on the mechanical characteristics of Jute/Polyester composites at different concentrations. When compared to the untreated sample, 0.3% of α -Methacryloxypropyltrimethoxy silane was shown to be sufficient to improve the mechanical characteristics of composites. Khan and Hassan^[14] found that treating jute textiles with γ -aminopropyl trimethoxy silane before fabricating jute/polycarbonate composites improved the mechanical characteristics and promoted dimensional stability when compared to untreated composites. Dilfi et al.^[15] concluded that combining alkaline and 3-glycidoxypropyltriomethoxy silane treatments enhanced the mechanical performance of jute/epoxy composites.

1.2 | Polymer nanocomposites

In order to address the limitations of polymers, various dimensional fillers are often used.^[16] The use of nanofillers has been extensively employed to enhance the physico-mechanical characteristics of polymers.^[17,18] The structure may have an isotropic or strongly anisotropic sheet-like or needle-like appearance depending on the nano dimension. When it comes to developing intriguing polymer nanocomposites, new nanofillers and polymeric materials may be combined in imaginative new ways for the advancement of nanoscience and nanotechnology. Polymer nanocomposites may normally be classified into three primary classes based on the size of the nano-scale fillers. Layered silicate,^[19] graphene,^[18,20] and MXene^[21,22] are two-dimensional (2D) nano-scale fillers found in polymer matrices in the form of sheets from hundreds to thousands nanometers long and thick.

It is possible to classify the polymer nanocomposites made with 2D nanofillers as layered polymer nanocomposites. Nanotubes and fibers, such as halloysite nanotubes or carbon nanotubes^[23] or halloysite nanotubes^[24] in the second group, all have diameters of less than 1 nm. All three dimensions in nanometers are represented in the third category of nanocomposites,^[17,25] semiconductor

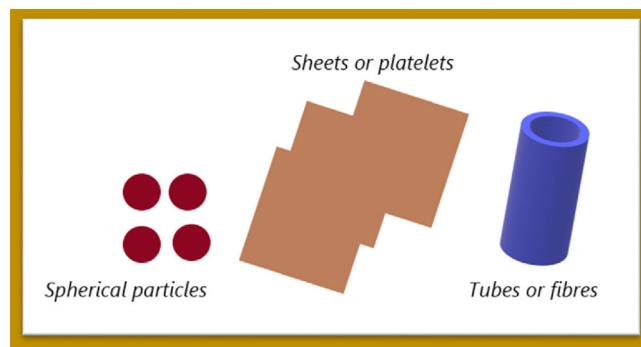


FIGURE 1 Shows schematic representation of various nanoscale fillers

nanoclusters^[26] and quantum dots^[27] fall into this category. Homogeneous dispersion of both isotropic and anisotropic fillers may result in a high specific interfacial area per unit volume. Moreover, this is a morphology, which is heavily influenced by nanoscale behavior. Polymer nanocomposites offer better mechanical and physical characteristics, in part because of the wide interface between polymers and nanofillers. In Figure 1, several nanomaterials are shown in varied shapes and sizes.

1.3 | Phenolic resin

Phenol-formaldehyde resin was formulated by Leo Bakeland in 1907.^[28] It is also known as “Bakelite” and was the first synthetic plastic to be made. The non-conductive properties of PF resin make it ideal for use in electrical insulators, circuit board output molding compounds, coatings, and adhesives. From the beginning, bakelite has been utilized as a matrix in the production of composites. The phenol-formaldehyde resin has exceptional chemical and physical qualities compared to other synthetic polymers. Formaldehyde and phenol may be used to synthesize PF resins, which are thermosetting polymers. Reinforcing PF resin with nanofillers provides exceptional quality. However, PF is very brittle and prone to buckling, even though it has excellent thermal stability, insulating properties, flame retardance, and ablation capabilities. Filling with nano and macro fillers, as well as tougheners like rubber and elastomers, may lower both the characteristics.^[29–32]

It is impossible to replace phenolic resins in a wide range of applications, including insulators, hardwoods, adhesives, and composite materials along with molding compounds and casting, due to their thermal stability and ablative properties. Even though PF resin has a wide range of applications, its color, brittleness, poor initiation, crack resistance etc., limit its applications. The

condensation reaction between phenol and formaldehyde produces phenolic resins (Figure 2). Under acidic conditions, phenol reacts with formaldehyde in less than equimolar amounts, giving novolac resins containing aromatic phenol units mainly connected by methylene bridges (Figure 3). These are the polymers that are stable under thermal conditions. Curing of novolacs can be done by cross-linking with donors, including hexamethylene tetraamine-containing HCHO groups. Resoles are the phenolic resins used most commonly for composites (Figure 4). Under alkaline conditions, phenol's reaction with a greater than equimolar amount of formaldehyde gives resoles. They are simply polynuclear phenols, or hydroxymethyl phenols.

1.3.1 | Structure

A. Phenolic Resin

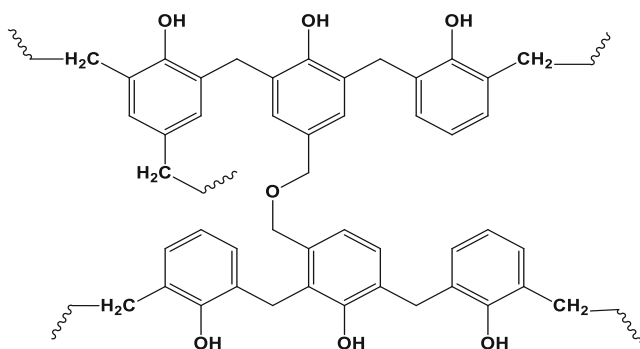


FIGURE 2 Structure of phenolic resin

B. Novolac

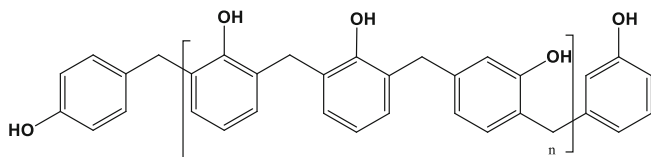


FIGURE 3 Structure of novolac

C. Resole

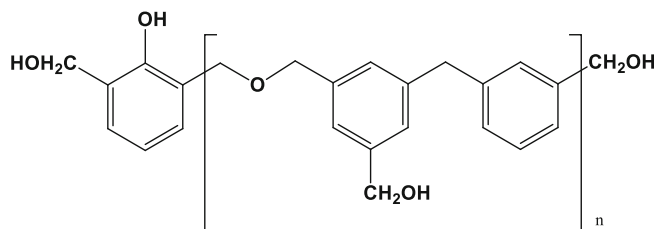


FIGURE 4 Structure of resole

1.3.2 | Applications

Phenol formaldehyde resin has many applications in different industries. Phenolic resins are primarily used in the manufacture of circuit boards, as well as in the adhesive industry, etc. It is also needed in manufacturing electrical equipment, caps, buttons, furniture, knobs, cameras, ash trays, etc. This is also used in laminated materials such as boards, rods, and tubes made from cloth, paper, wood, etc. There are many different types of base materials that can be impregnated with phenolic resin and then laminated together under high pressure using heat. Phenolic foam is a rigid substance used in a wide range of applications where the main performance requirements are thermal strength, moisture tolerance, and fire protection. Phenolic foam resins are used in a range of applications, particularly for heating, cooling, and air conditioning in the building and electronics industries. The use of phenolic foams in the insulation field is increasing as they are more stable in the case of fire resistance and almost no emissions are released.

1.4 | Phenol-formaldehyde nanocomposite

The ablative applications of phenol-formaldehyde resin are mainly due to its excellent thermal stability, flame retardant properties, high decomposition rate, and char retention capacity. But the major disadvantages associated with phenolic resin are its brittleness and its lack of antioxidant properties. The incorporation of inorganic and organic fillers can be a perfect solution to meet these problems. SiO₂-RGO hybrid nanofiller was used to reinforce phenolic resin and found to have better thermal stability.^[33] A remarkable improvement in mechanical and thermal characteristics was seen in the nanocomposites produced.

When graphene oxide was added to the nano composite, it dramatically improved its characteristics.^[34] Conducting PF nanocomposites were prepared by the incorporation of graphene oxide via in-situ polymerization. During in-situ polymerization, the non-conducting graphene oxide was reduced in the presence of phenol, and the reduced graphene oxide (RGO) prepared from this method showed high conductivity. The resultant nanocomposite exhibited a percolation threshold of about 0.17 vol.%. With the incorporation of 2.3 vol.% graphene oxide, there was a shrinking increase at the decomposition temperature of 76°C. By reinforcing with 1.7 vol.% of graphene oxide, there was an increase in flexural properties (strength and modulus) by 317% and 57%, respectively. This efficient method paved the path for making high performance conducting PF composites.

For biosensing applications, phenol formaldehyde resin modified with MnO_2 nanoparticles was used for sensing glutathione in blood serum.^[35] They developed a unique MnO_2 -modified PFR (phenol-formaldehyde resin) nanoprobe for the fast and selective sensing of glutathione (GSH). The MnO_2 -PFR nanocomposite was processed in PFR colloidal solutions by the in-situ synthesis of MnO_2 nanosheets. It was possible to quench the fluorescence of PFR in this nanocomposite due to the close enough gap between PFR and MnO_2 nanosheets, and therefore fluorescence resonance energy transfer (FRET) occurred. Due to the decomposition of the MnO_2 to Mn^{2+} , this quenching effect caused by MnO_2 might have been restored in GSH's presence. Compared to other biomolecules and electrolytes, the developed nanocomposites displayed high GSH selectivity. In fact, it displayed an impressive enhancement of fluorescence to GSH, and a detection limit of 7.6 nM was observed, showing the high sensitivity of GSH in aqueous solutions.

Using an in-situ polymerization technique nano-silica was dispersed in novolac resin and analyzed for its flame retardant properties by Periadurai et al.^[36] They found that nanocomposite materials prepared exhibited a high decomposition temperature and high char content. The LOI value of nanocomposite was found to be 43, while that of neat is 38. Through structural analysis (NMR, mass spectrometry, and FT-IR), they observed good chemical linkage between the nanofiller and the resin. The addition of nano-silica increased the ablation properties of the carbon fiber-phenolic matrix.^[37] Improvement in mechanical and thermal stability was also observed and, at higher filler loadings, (5%) both bending strength and ablation decreased.

By integrating nanofillers like reactive rubber nanoparticles (RRNP) and nano-clay into the phenol-formaldehyde resin, Solyman et al.^[38] developed PF nanocomposite with the addition of reactive rubber nanoparticles (RRNP) and modified nano-clay, phenol formaldehyde nanocomposites were prepared before curing. The hardness of the PF nanocomposite increased because of the good interfacial interaction between the matrix and the filler (RRNP) and modified nano-clay. The functional groups present in nano clay and the PF matrix interacted well, which attributed to the enhancement in mechanical properties. Furthermore, there was an enhancement in the thermal stability of the fabricated PF nanocomposite by 10%–20%. Using functionalised nano-clays and reactive rubber nanoparticles, a novel PF nanocomposite was synthesized. The PF-RRNP and PF-Cloisite 30B nanocomposites were prepared using the nanoindentation technique. Due to the presence of chemical bonding between RRNP and the PF matrix, the fabricated nanocomposites showed a substantial decrease in

the indentation depth and an improvement in the hardness of the prepared substrate. Furthermore, results of thermal studies showed that these nanocomposites were 10%–20% more thermally stable than neat PF matrix. Increasing loading of Cloisite 30B suggested an upward shift in load–displacement curve for all nanocomposites. Because of the interfacial interaction between the polar groups in the matrix and the polar nano-clay sheets, the mechanical properties significantly improved. Declination in nano depth indentation is a useful indicator that the nano clay sheets were evenly distributed and associated within the matrix.

To create the graphene oxide–lignin (GO–L) hybrid nanofiller, lignin and graphene oxide were hybridized using the ultrasonic technique. Phenol formaldehyde nanocomposite was reinforced with this hybrid nanofiller.^[39] The dispersion of the GO–L hybrid in the polymer matrix was prevented, resulting in nanocomposite materials with much improved characteristics compared to those formed from single-component nanofillers (like GO or L). Nano-reinforcements significantly improved the storage modulus. Because of the strong interfacial contact and the synergistic effect of the two different types of lignins, the nanocomposites had higher E values than those of the individual components. The PF/GO–L nanocomposites' total heat flow rate was also raised throughout the curing process.

An in-situ covalent approach has been attempted for the construction of phenol formaldehyde-graphene nanocomposite (GPF) by π – π interactions.^[40] This method not only improved the dispersion of graphene oxide in the PF matrix but also enhanced filler matrix interactions. On the carbon steel, the newly synthesized GPF was then coated to test its anti-corrosion performance under the irradiation of the γ -ray. Both GPF and PF were irradiated with specific dosages of γ -ray to further investigate the anti-corrosion behavior of GPF coatings under γ -ray irradiation. The mechanism and progress of the radical scavenging process were studied by using electron spin resonance spectroscopy (ESR). The result of the ESR analysis suggested that the highly dispersed GO could serve as an enhanced radical scavenger in the resin matrix and effectively slow down the rate of radiolytic oxidation in the radiation environment. In addition, the electrochemical measurements showed that under radiation conditions, graphene may retain the properties of corrosion resistance.

Hatami et al.^[41] reported the fabrication of PF nanocomposite with homogeneously dispersed cerium oxide nanoparticles. Sono-chemical aided synthesis was used for the preparation of the PF-CeO₂ nanocomposite by mixing it with the surface-treated cerium oxide by in-situ polymerization of polymer materials. The well-trapped

nanoparticles in the PF matrix were not agglomerated since there was less interaction of the organic functional units present in the polymer matrix with surface-treated nanoparticles. The benefit of this approach is that the surface-based nanoparticles are specifically enclosed within the polymer matrix, resulting in a well-dispersed system. The PF-CeO₂ nanocomposite structures were analyzed and, from XRD, FT-IR, FE-SEM, and AFM findings, it was found that the CeO₂ nanoparticles were in a separate state and evenly dispersed in the polymer matrix. With the incorporation of CeO₂, the amorphous nature of pure PF had changed to a semi-crystalline nature since CeO₂ is crystalline in nature. From AFM analysis, a homogeneous dispersion of the CeO₂ in the matrix of polymers was also obviously measurable. Thermal study of nanocomposite using the measurement of TGA curves indicated improvements in thermal stability with CeO₂ reinforcement relative to the pure polymer. Morphological analyses using FE-SEM showed that the CeO₂ nanoparticles were uniformly scattered deep into the PF matrix. A comparison of the properties of phenol-formaldehyde nanocomposites reinforced with lignin micro (LMP) and nanoparticles (LNP) with two separate weight compositions (5% and 10%) was carried out by Yang et al.^[42] The interfacial interaction of lignin in the matrix was tested by means of morphological analysis. This analysis not only provided the level of adhesion between LNP and the PF matrix but also established the dispersion level of LNP. The thermal stability of the composites and rate of curing were investigated with thermogravimetric (TGA) and thermo-mechanical (TMA) analysis and differential scanning calorimetry (DSC) respectively. They have also checked the shear strength of the prepared adhesives by joining wooden strips.

From SEM results, it was clear that LNP was better dispersed than LMP in resole resin. Because of the presence of a large number of phenyl propane units, both LMP and LNP particles will definitely improve the thermal cure cycle. The lower curing temperature and heat curing were due to the formation of methylol substituents by reaction of phenyl propane units present in lignin (which acts as an active substitution of phenol units) with formaldehyde, and which were thereby further reduced into methylene bridges. Due to the higher surface area and LNP reactivity, the reaction between formaldehyde and lignin phenolic units would be more desirable than micro lignin particles. With the addition of 5 wt.% lignin, there was an increment in adhesive strength due to the increment in crosslink density. This work opened the backdoor to substituting a cost-effective and environmentally benign lignin residue for conventional wood adhesives.

Wu et al.^[43] synthesized graphene nanosheets by means of one-pot hydrothermal process using autoclave. Utilizing these graphene nanosheets (GNS), they have prepared PF nanocomposites. The researchers also conducted an in-depth analysis of the mechanical and thermal characteristics of composites made of phenol formaldehyde and carbon nanotubes, as well as phenol formaldehyde and graphene nanosheets. Their findings demonstrated the improved performance of graphene nanosheets compared to carbon nanotubes. By comparing the mechanical properties, they found that when both filler loads were 0.6 wt.%, the tensile strength for graphene nanosheets improved by 77%, 141%, 109%, and 115% and for carbon nanotubes by 55%, 86%, 62%, and 45%, respectively. Additionally, each of these two carbon materials could improve the thermo-stability of the PF composite. At a weight loss of 10%, the thermal degradation temperature was raised to 255.6°C for phenol formaldehyde-graphene nanosheet composites and to 253.5°C for phenol formaldehyde-carbon nanotube composites from 233.6°C for pure samples. The addition of 0.6 wt.% each of sufficient quantities of carbon nanotubes (CNT or GNS) could increase the PF's tensile and compressive properties, which were confirmed by experimental results. By the impregnation of water-swollen CNF films with PF resin super flexible phenolic films were made.^[44] To improve the mechanical, wet strength, and hygroscopic properties, PF was evenly impregnated and adhered to CNF. It was reported that the impregnation of CNF films in phenolic resin had improved the mechanical properties of the CNF films. It was achieved by freeze-drying the film and soaking it in different concentrations of PF resin for prolonged hours. It was then air dried and compressed at 130 °C at 30 MPa of pressure. They have studied morphology, mechanical properties, and oxygen permeation properties of the prepared nanocomposite.

According to the experimental results, incorporating 8% PF into CNF improved the mechanical properties of CNF-PF films, with the resulting tensile strength and hardness being 248 MPa and 26 N/mm², respectively. Moreover, at moderately high humidity, the moisture absorption of CNF films was decreased. Improved wet strength was observed for the CNF films with the addition of PF. They reported that more than 15% of PF content increased the brittleness of the film. Less PF content increased the toughness of the film. Moreover, the oxygen permeation properties of films decreased by 35% with the addition of PF resin. CNF-PF films with high durability and reduced absorption of moisture have found excellent applications in the packaging industry and electronic devices, and more assessment is required for these applications.

Three types of nanocellulose (laboratory prepared, commercial, cellulose nanocrystals) were used for preparing PF nanocomposite by Liu et al.^[45] By using nanoindentation, they have analyzed layers on the cell wall and changes in the mechanical properties of the prepared nanocomposite. The nano-materials derived from cellulose would improve the mechanical characteristics of both adhesives and cell walls, as well as their overall stability. Commercial cellulose had the most evident reinforcing impact on the elastic modulus (E) and stiffness inside the glue line, particularly within the glue line. With the adjustment, the E and hardness were attained in the S2 layer away from the glue line at 13.0 and 0.436 GPa, respectively, in the S2 layer. In the experiment, the unreinforced matrix had an E of 7.31 GPa and a hardness of 0.256 N/mm².

Cherian et al.^[46] fabricated PF composites by reinforcing with macro, micro, nano fibrils of cellulose extracted from banana fibers. He reported aging studies and mechanical properties of the prepared composite. The nanofibrils and nanocomposites offered robust and sufficient insulation, and they were often more resistant to all aging processes as compared to microfibrils. The composite's PF matrix was not much weakened by long-term aging when analyzed as it displayed no noticeable water absorption or reduction in strength. During the aging cycle, composites made of macrofibril experienced full-strength loss. In all aging tests, the degradation of the mechanical properties was fairly limited when compared with microfibril and macrofibril composites. Alkali treatment improved the strong bonding between fibers and matrices. Due to its hydrophobic nature, the fiber modification using silane coupling agent decreased the fiber-matrix interaction, resulting in the least interaction with the hydrophilic matrix.

Recently a research group studied ablative properties of phenolic resin reinforced with mesoporous silica synthesized from tetraethyl orthosilicate (TEOS).^[47] They also prepared a nanocomposite of phenolic resin with carbon black as the filler and found that silica interacted well with phenolic resin. This was characterized by DSC and TEM. The sample with silica reinforcement showed lower erosion rates and back-face temperatures. SEM images showed the morphology of the charred plates. Carbon black improved carbonaceous residue production by raising the residual mass in the TGA experiments, but due to poor compatibility with phenolic resin, the cross-linking degree and T_g decreased. An example of the strong interaction between particles and matrix was that the silica particles were observed to increase the cross-linking density and T_g. Both types of particles decreased the risk of erosion during the ablation experiments. To achieve a significant increase in the ablation resistance of

the composites, high loadings were needed. Besides, with the addition of both black carbon and silica dust, the level of insulation improved. The best results were obtained with composites containing 20% silica particles; the mesoporous structure and thermal tolerance were responsible for the high ablation behavior.

To improve the tribological, mechanical, and thermal properties of PF nanocomposites, Cu nanoparticles were hybridized on the surface of graphene (Cu/RGO nanohybrid) using a simple *in situ* reduction process.^[48] Effective synergistic effects were achieved by increasing the dispersion of the Cu/RGO nanohybrid in paraffin oil. As a consequence of the good dispersion and interfacial compatibility of Cu/RGO nanohybrid in PF matrix, this Cu/RGO filling PF nanocomposites showed better mechanical performance and higher thermal stability than single RGO or nano-Cu and could prevent the generation and propagation of cracks, bear much more shear stress and suppress the movement and decomposition of PF chain segments. The friction coefficient and wear rate of PF nanocomposites were lowered by 23.7% and 32.5%, respectively, with the addition of 2.0 wt.% Cu/RGO nanohybrid (Figure 5).

1.5 | Phenol-formaldehyde composite

In history, plant fibers are considered the oldest known biopolymer. Ancient people extracted natural fibers from wild plants for many applications. Later on, agriculture became the major source of plant fiber. Long before they began to polish metal or earthenware, ancient civilizations experimented with plant fibers, particularly in weaving fabrics. Among the most crucial aspects of the use of fibers in ancient times may be observed in the production of fabric. Humans encountered colder temperatures in their new environments thousands of years ago, due to their spread from Africa to Asia and Europe, and they needed to shield their bodies from severe storms and cold weather. People began to experiment with plant fibers as a textile material in addition to pelts of animals and wool to cope with the winter conditions due to this situation. They started collecting fibers from forests, especially from the bark and leaves. However, the advent of cotton and hemp transformed the world's future. Then, due to the massive rise in manufacturing, fibers from grown plants made a lot of things easier. Weaving history began when weavers discovered that spinning each fiber improved fiber strength.

The proportion of fiber/matrix interface produced, as well as the type and degree of interactions between the polymer matrix and the fibers, are the key determinants of interfacial adhesion in natural fiber-based composites.

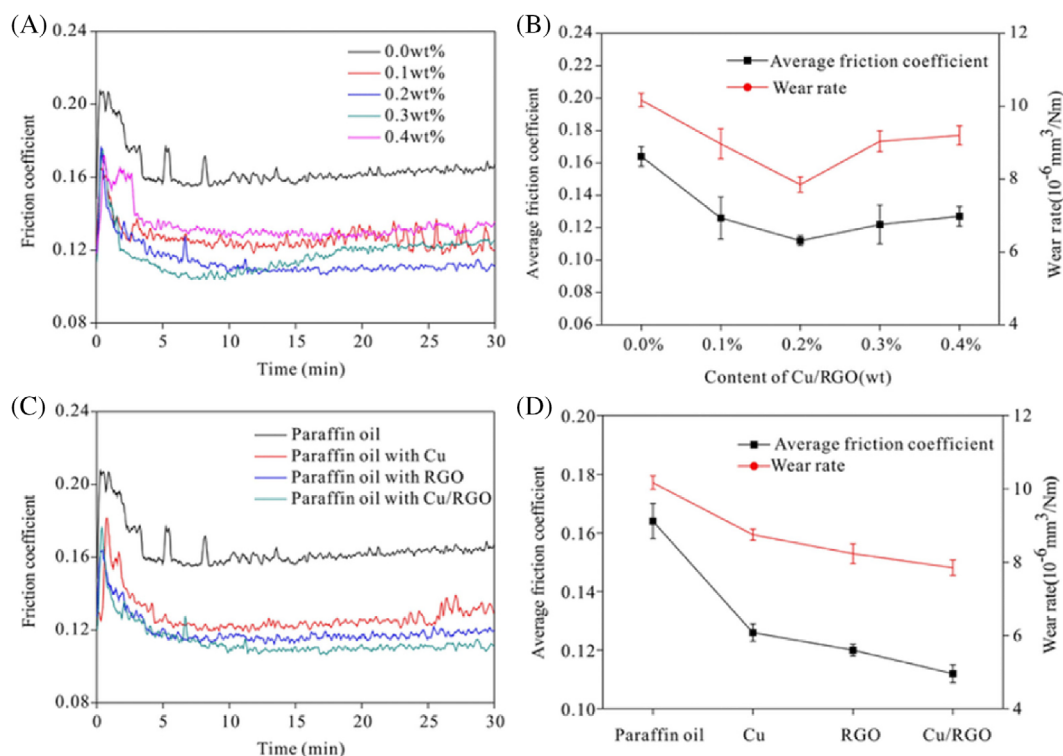


FIGURE 5 Tribological properties of Cu/RGO nano-modified paraffin oil (A) and (B) and 0.2 wt.% nano-modified paraffin oil (C) and (D).^[48]

Developing specialized treatments and techniques that increase fiber dispersion while providing optimal exposure of reactive and/or functionalized fiber surfaces to the matrix without weakening fiber structure could improve the quantity and quality of the fiber-matrix interaction. This is one of the most significant obstacles to the commercialization of natural fiber reinforced composites with improved structural characteristics. Matrix modification with nanofillers appears to be more eco-friendly than fiber surface treatment procedures and has the potential to produce large-scale tailored composites. Nano-filled matrices improve interfacial adhesion and mechanical performance of laminates by allowing for more efficient stress transfer.^[49] This minimizes local stress concentration around the fiber-matrix interlayer and improves interfacial adhesion and mechanical performance. A significant possibility for the creation of novel biocomposite materials with novel functional features will undoubtedly be one of the most important factors in the deployment of natural fiber reinforced composites in industrial applications.

Because of growing environmental concerns and the need to produce sustainable materials, the use of bio-fibers to substitute glass fibers as reinforcement in composites for engineering applications has gained favor in recent years.^[50,51] The exponential expansion of bio-

composites is suggestive of their widespread use in the future as structural materials for the next generation, and their rapid growth. Bio-fibers are a cost-effective option because of their low density. These are non-abrasive and biodegradable materials. Furthermore, they are easily accessible, and their particular mechanical characteristics are equivalent to those of glass fibers utilized as reinforcement.^[52] They are also cost-effective.

As a result of their higher biocompatibility, reusability, and degradability compared to synthetic fibers, natural fibers (such as coconut fibers, silk, flax fibers, and flax seed fibers) and some synthetic fibers (such as glass fibers) are often used to reinforce polymer or hybrid or natural resin matrix composites.^[53] Epoxy resin could be blended with *Lannea coromandelica* (LC, Anacardiaceae plant gum) to create hybrid *lannea coromandelica* epoxy matrix composites (LCE) that are biodegradable and environmentally friendly. Pineapple/Silk/Flax fiber mats with 2%, 4%, and 6% volume fraction of bentonite nanoclay in each composition reinforcement in hybrid LCE resins prepared by compression hand molding process and hybrid LCE resins are made using this approach. Hybrid composites' mechanical properties improved by three to four times when compared to LCE resin. DMA findings showed that untreated and treated hybrid composites had the highest storage modulus and the lowest

damping factor compared to hybrid LCE resin. According to biodegradability studies, LCE resin composites reinforced by pineapple and glass (P/G/P) fiber mats could be biodegraded at a 4% volume fraction of nano filler. The mechanical properties of a hybrid phenol formaldehyde (PF) composite produced from Areca Fine Fibers (AFFs) and Calotropis Gigantea Fiber were examined by Sanjeevi et al.^[54] When compared to other hybrid composites, the 35 wt.% hybrid composites had improved mechanical characteristics in both wet and dry circumstances. The addition of fibers improved the mechanical characteristics of neat PF in general. The water absorption increased as the fiber content rose, but after 120 h of immersion, all of the composites reached equilibrium.

The influence of stacking order on the mechanical, physical, and biodegradability features of treated coconut leaf sheath/jute/glass fabric reinforced phenol formaldehyde hybrid composites was investigated.^[55] According to the findings, the inclusion of coconut leaf sheath with glass fiber in hybrid composites had a stronger influence on tensile and hardness qualities than previously thought. The adherence of coconut leaf sheath fibers to the matrix improved significantly after treatment with NaOH solution. Water absorption plots for various durations of immersion revealed that coconut leaf sheaths with glass hybrid composites outperformed pure natural fiber reinforced composites in terms of water absorption. Due to a rise in the proportion of water absorption, the thickness swelling of hybrid composites increases. According to a SEM study of the tensile cracked surface, the failure of hybrid composites was owing to weak interfacial adhesion between fiber and matrix.

Compared to other natural fibers, sisal fiber is an effective reinforcing agent in the PF matrix. Maya et al.^[56] developed sisal fiber with an ideal fiber length of 40 mm and a fiber loading of 54 wt.% was found to improve the mechanical characteristics of the PF composites. Sisal-PF, which had 54 wt.%, had a superior fiber matrix interaction. The composites' flexural and impact strengths were investigated, and they were found to rise when the fiber percentage was raised. The composites' aging investigations revealed a similar pattern to those of unaged samples. Water absorption test findings demonstrated that composites with 54 wt.% fiber loading have superior matrix interaction and contain fewer voids. This is also attributed to superior fiber matrix interaction. Hasan and colleagues created polymeric resin biocomposites based on natural fibers such as energy reeds and rice straw.^[57] The observed findings show that as the energy reed loading in composite systems grows, so do the mechanical characteristics and moisture stability. When compared to rice straw, the biocomposite made from 100% energy reeds had superior mechanical qualities.

The thermomechanical characteristics of composite materials improved as energy-reduced fiber loading in the composite system increases.

Venkatarajan et al.^[58] investigated the impact of combining Areca Fine Fibers (AFFs) with Calotropis Gigantea Fiber (CGF) to make a PF biocomposite. Glass fibers (GFs) were used to construct hybrid composites in order to analyze and compare their mechanical characteristics. The overall weight percentages of the CGF/AFF/PF hybrid composites were 25%, 35%, and 45%. When compared to the other hybrid composites (25 and 45 wt.%), the hybrid composite with 35 wt.% had superior mechanical characteristics. When compared to CGF/GF/PF and AFF/GF/PF hybrid composites, the CGF/AFF/PF hybrid composites had the best mechanical characteristics. However, as compared to GF/PF (35 wt.%) composites, it displayed a lesser degree of mechanical characteristics. Table 1, shows the recent literature survey on PF and PF/natural fiber composites.

1.6 | Application of phenol formaldehyde composites

In the last few decades, phenolic resin-based composites have found considerable use in engine components, adhesives, digital instrumentation casings, and pump-related parts. As a result of their high durability, good thermal tolerance, easy handling, vibration dampening capabilities, and moisture resistance, phenolic composites are used as, brake linings, clutch plates, brakes pads, and its components. In a work of Naik and colleagues, PF-sisal fiber composites were developed.^[67] During transformer assembly, laminates that are ecologically benign, strong in mechanical strength, and electrical insulators have been produced for the use. The electrical and aerospace sectors, as well as others, can benefit from the use of these laminates. Rajan et al.^[68] fabricated PF composites for automotive applications by reinforcing with slag waste. The composites that contained 65 wt.% slag waste and 5 wt.% phenolic resin showed the highest friction coefficient (0.406), the lowest fade (20.44%), and the lowest frictional fluctuation (0.209), but they also showed the highest levels of wear (10.80 g) and disc temperature rise (618°C). Composite with the lowest slag waste content of 50 wt.% combined with the highest phenolic resin of 20 wt.% showed higher recovery performance (120.63%), lowest wear (4.45 g), and disc temperature rise (536°C). However, it exhibited the lowest friction coefficient (0.315) and friction stability (0.79), in addition to the highest friction variability (0.60) and fluctuations (0.238).

Moubarik et al.^[69] developed PF adhesive with improved mechanical properties by incorporating cactus

TABLE 1 Recent studies on PF and PF/natural fiber composites

PF nanocomposites	Observations	PF/natural fiber composites	Observations
Tao et al. ^[59] (2019)	Tensile strength-189% improved	Cai et al. ^[60] (2022)	Tensile strength-57 MPa
Abdullah et al. ^[61] (2021)	Internal bonding strength improved	Hasan et al. ^[62] (2021)	Insulation properties-0.000494 W/m.K
Senthilkumar et al. ^[63] (2020)	Better fire performance	Madhu et al. ^[64] (2022)	Superior mechanical properties
Rahman et al. ^[65] (2018)	Tensile strength-43 GPa	Sekhar et al. ^[66]	Tensile strength -44.82 MPa

seed powder. These adhesives showed better adhesion than conventional adhesive. The impact of PF loading on the wear rate and anticorrosion behavior of composite coatings was explored in depth.^[70] The results revealed that adding PF to the PVB (polyvinylbutyral) coating improves its wear resistance significantly, with the minimum wear track width dropping from 301 μm to 154 μm under dry friction environment. The homogeneous and compact framework generated by PVB and PF, which has exceptional flexibility, dimensional stability, and good barrier qualities, can be attributed to the better performance of prepared composite.

Hasan et al.^[62] developed phenol formaldehyde polymeric (PF) resin-based insulation panels by incorporating coir fiber. Composite nanocomposite of Fe_3O_4 nanoparticles (NPs) and PF resin was used in the laminated veneer lumber LVL structure in order to expedite preheating of the billet using microwaves (MW).^[71] An increase in the initial temperature of the core layer caused the MW preheated LVL's with 3% Fe_3O_4 to reach 100°C faster. Cui et al.^[72] prepared the asymmetric structure of janus phenol-formaldehyde resin (PF) and periodic mesoporous organic silica (PMO) nanoparticles utilizing PF microspheres as seeds and PMO for branch growth. By combining chemical and physical features, the hydroxyl groups on the PF surface and the large specific surface area of PMO promote the effective adsorption of heavy metal ions and organic dyes. Panigrahi et al.^[73] developed ablative composites using silica fiber, glass microsphere and PF resin which can be used in solid motor nozzles for rockets and missiles, as well as space re-entry vehicles. With a density of 36% lower, the created composites had 50% lower thermal conductivity and 50% lower thermal diffusivity than typical silica phenolic composites.

1.7 | Phenolic foam

Owing to their tremendous ability, polymeric foams are being used recently in numerous applications, like thermal and sound insulating materials, packaging, purifiers,

and structural components.^[74] Due to the weightless structures, they allow energy savings during transport^[75] and high performance insulation.^[76] Both of these activities tend to reduce the effect on the environment. Phenolic foams were first used in the early 1940's as a replacement for balsa material in the German industry.^[77] Because of less fragility and friability of other polymers, such as polyurethane, polyvinyl chloride, polystyrene foams, PF foams became less prevalent over time.^[78,79]

However, with the new fire restrictions, industrialists were not satisfied with the above-mentioned foams because of their low resistance to fire and the elimination of toxic gases during combustion. The effective fire retardant behavior of phenolic foams was then rediscovered.^[80,81] The major problems associated with PF foams are their brittleness and friability. Research has been focused on improving the mechanical qualities of PF foam, such as compressive strength, flexural behavior, and friability, in order to retain the high fire retardance capabilities of PF foam.^[82,83]

Because of their particular properties, they may be employed in highly specialized applications, such as decontaminating water and creating space shuttles. As a result of which, the country's economy will boom, and the demand for insulation is also soaring across the globe. There are usually two or three phases in the fabrication of polymeric foams. Polymers such as rubber, thermoplastics, and thermosets are examples of solid-phase materials that include gaseous phase elements. Foams may be classified as flexible, semi-flexible, semi-rigid, or rigid based on how hard the polymer basis is. Chemical structure and polymer matrix features such as crystallinity and density of cross-linking have a role here. Dense materials have distinct physical and mechanical properties.

Foams, in addition, can allow a wider variety of applications compared to dense solids due to their broad range of properties^[84]:

- Lightweight structures with rigid components can be developed due to low densities. Because of low thermal conductivity, cost-effective insulation can be assured.

- Foams being less rigid, they can be used for energy-absorbing applications.

Among commercial foams, PF is considered a rigid thermosetting foam because it has good thermal stability, excellent thermal insulating properties, outstanding fire resistance and zero dripping behavior, and emits fewer toxic gases during combustion.^[85] Yet, as stated earlier, PF's brittleness and pulverization tendencies severely limit their applications.^[86] The structure and volume of each component of the formulation can be modified such that the final properties of the foam can be tailored.^[28,87–90] Fibers are used, for example, to strengthen the compressive and flexural properties.^[91] Alternatively, the addition of polyethylene glycol helps to improve the deformation of the cell walls^[83] and a nucleating agent or small particles can be added to increase cell density.^[92,93] Furthermore, by the application of flame retardant materials, the fire resistance quality of the phenolic foams are improved.^[94] The second route goes by the choice of production method. The use of an open mold would prefer an inhomogeneous density, resulting in the formation of a high open cell content, while the use of a closed mold can result in a more regulated density and probably a high closed cell content.^[81]

Mechanical, physical, or chemical processes may be used to produce phenolic foam.^[74] Commonly used foaming approaches are:

- Blowing-agent thermal decomposition that produces N₂, CO₂ or both as the temperature rises due to exothermic reaction or ambient heating.
- Gaseous materials during exothermic polymerization producing volatile gases (e.g., isocyanate facilitates CO₂ formation reacting with water).
- Volatilization of low-boiling solvent like, fluorocarbon, methylene chloride, pentane or ether in the foam mixture after an exothermic reaction or by ambient heating.
- Mechanically agitation of gaseous molecules in a polymer network, such as a liquid, solution, or suspension, that either cures by utilizing a catalyst, by heating, or both, to trap the bubbles.
- Expansion of beads filled with gas by ambient heating or exothermic reaction
- The expansion of a dissolved gas in a polymer medium such as CO₂ by reducing the pressure of the system.
- Incorporation of hollow microspheres into the foaming mixture, such as hollow glass or hollow plastic beads.

The widely used technique for PF foam production is the volatilization of a solvent with a low boiling point. According to reports, volatilization of gases happens

during exothermic polymerization reactions or the heating-induced disintegration of chemical blowing agents.^[81] The preparation of PF foam includes an emulsifier, blowing agent, catalyst, curing agents, and some additives. The additives can be plasticizers or fibers,^[95] micro or nanoparticles.^[96] Formed foam is controlled by the battle between two mechanisms, namely the expansion of the blowing agent and the simultaneous curing of the resin, both of which take place at the same time. Therefore, the phenolic resin's viscosity and reactivity are two main parameters influencing the formulation of phenolic foam.

Often, emulsifiers are of considerable significance as they help regulate the consistency and properties of the foam. Their purpose is to create a consistent and uniform oil-in-water emulsion between the polymer material and the blowing agent, which will control the foam cell's features. An emulsifier's key task is to maintain emulsion consistency in the foaming cycle, which involves the temperature rise, the evolution of viscosity, and the blowing agent's change of state.^[81,89] Blowing agents addition by physical or chemical methods are considered to be the reason for the foaming of the phenolic resin.

During PF foam formulation, carbon dioxide (CO₂) is evolved. This is generated by carbonate reaction with the acid catalyst or by isocyanate-water reaction in limited amounts.^[81,97] When the temperature increases, the formation of gas bubbles in the phenolic matrix happens and there is evaporation of blowing agents through physical processes. The structure of the foam cell, such as open or closed-cell foam, is generated depending on the kind of blowing agent used. The sort of blowing agent to use is determined by the ultimate demand as well as the category of foam cell that is required (Figure 6). Open-cell formation has been induced by large volatile hydrocarbons. Their high flammability and open cell structure make them easier to be removed from the foam and lower the risk of explosion during the foaming process. Pentane^[85,96] is the most commonly used blowing agent in the processing of PF foam and the use of other hydrocarbons like cyclopentane,^[99] hexane^[90] and petroleum ethers^[82] are less frequently stated (Table 2).

In order to speed up the resin's curing reaction by reducing the gelation time and assisting in the expansion of the foam, catalysts are needed. Organic acids, such as p-toluene sulfonic acid^[93] and phenol sulfonic acid,^[100] are preferred these days over extremely corrosive inorganic acids, namely sulfuric acid or hydrochloric acid.^[101] To boost the flame retardancy and to raise the reaction rate of the foam, organic acid mixtures containing small amounts of inorganic acids are mainly used.^[102] In addition to the introduction of additives or fillers, various PF formulations can be prepared according to the intended

FIGURE 6 Photographs of closed and open cell foam.^[98]

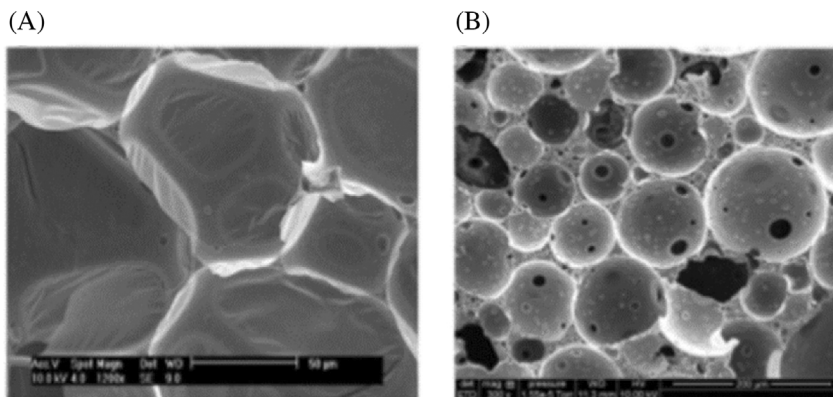


TABLE 2 Major foaming agents used for PF foam formulation, excluding chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC)

Foaming agent	Boiling point (°C)
n-pentane	36
Petroleum ether	49
Cyclopentane	42–62
Hexane	68
Diisopropyl ether	69

use. In addition to the introduction of additives or fillers, various PF formulations can be prepared according to the intended use. Therefore, the effect of each variable on the final characteristics of the PF must be taken into account.

1.8 | Nanofiller reinforced phenolic foam

Phenolic foam reinforced with nano clay cloisite was prepared by V.K. Rangari et al.^[97] to improve the mechanical, thermal, and morphological properties. They employed a novel sonochemical method for the preparation of foam. The incorporation of nano clay cloisite improved crosslinking, thereby increasing mechanical properties by 60%. An improvement in glass transition temperature was also observed. Silica sols were perfectly dispersed in phenolic resin followed by the addition of foaming agent, surfactant, and curing agent for phenolic foam preparation.^[86] An in-situ polymerization technique was employed for the uniform dispersion of silica sols in the phenolic matrix. From FT-IR analysis, they found that silica chemically bonds with the PF matrix. Because of the highly crosslinked structure of silica inside the matrix, the mechanical, thermal, and friability properties of the foam increased tremendously. The cell wall thickness increased, and the cells were uniformly

distributed. The tensile strength, compressive strength, and compressive modulus were increased by 57%, 47%, and 39%, respectively.

Sample thermal insulation was tested and associated with modifier effects and subsequent cell structure. Because the mean cell size of phenolic-silica foam (MPF) 0.5 was smaller, the thermal conductivity of MPF 0.5 decreased by 8.86%, and the cell size distribution was thinner than that of neat PF. In fact, more homogeneity in MPF2's cell distribution than in pure PF was found. Furthermore, heat propagation based on the thermal transfer principle was possible when there was low silica sol content in MPF0.5 and it hindered the vibration of molecular fragments (Figure 7). From TGA, it was revealed that the MPF samples are thermally more stable than the neat matrix. In comparison, the rate of pyrolysis was lower, and the char yield was more than pure PF. The tests of the friability indicated that there was a substantial decrease of 59% in the pulverization ratio of MPFs, and the sample MPF2 had the lowest pulverization ratio (1.3%) relative to neat PF.

As a reinforcement, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) grafted -glycidoxy propyl trimethoxy silane (GPTS) modified wood fiber (DGMWF) was used to improve the fire retardant behavior of phenolic foam.^[103] The morphology, mechanical properties, thermal stability, and fire-retardant properties of the prepared foam were analyzed (Figure 8). The addition of 4% and 6% of DGMWF to phenolic foam enhanced the bending strength compared to neat foam. Due to the better dispersion of 6% DGMWF in PF foam, it exhibited higher tensile strength. Due to the reduced toughening effect, the tensile strength also reduced. The addition of DGMWF improved the limiting oxygen index (LOI) due to the synergetic effect of silicon and phosphorus. The morphological analysis clearly indicated the reduction in cell diameter due to the better interfacial interaction between DGMWF and the phenolic resin.

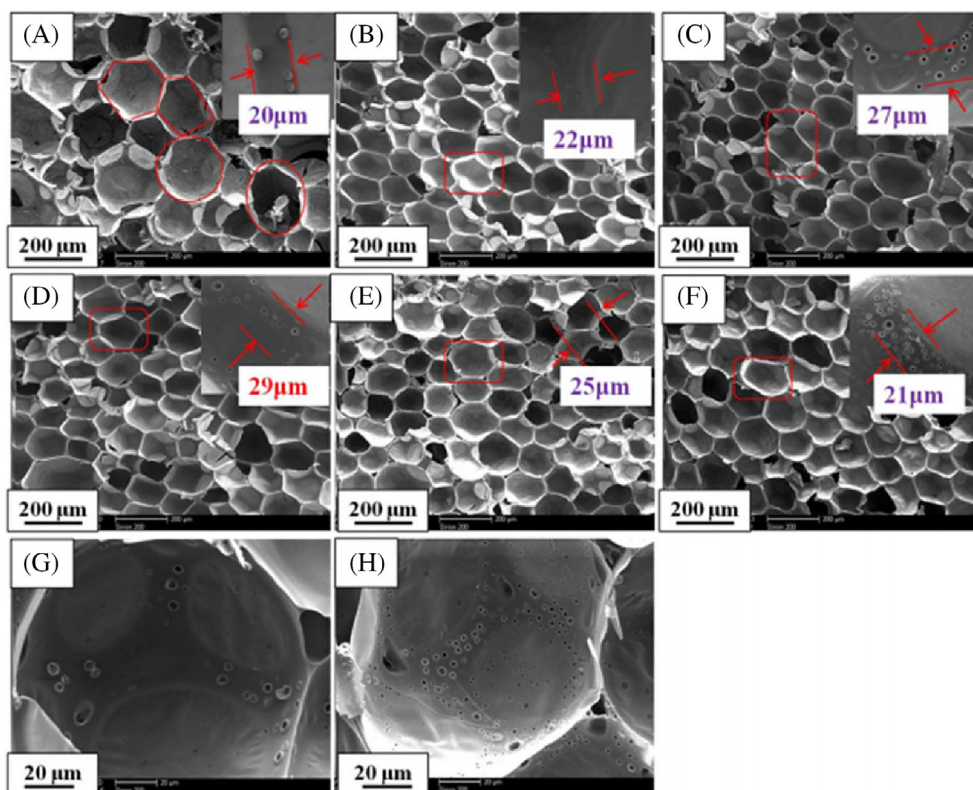


FIGURE 7 SEM images of neat and reinforced PF foams.^[86]

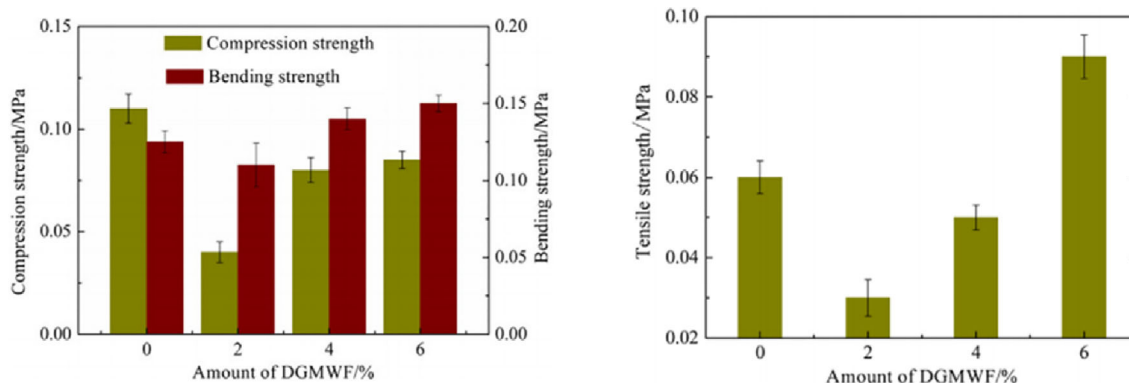


FIGURE 8 Mechanical properties of modified wood fiber reinforced phenolic foam.^[103]

To boost the efficiency of phenolic foam, a 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and Itaconic acid (ITA) additive compound were added to ethyl cellulose (EC), and DOPO-ITA-modified EC (DIMEC) was obtained, which was utilized to reinforce phenolic composites and phenolic foams (CPF).^[104] Relative to EC, DIMEC's crystallinity was significantly reduced, and the peak positions of diffraction remained the same. Thermal stability also reduced by 24°C. The residual carbon (600°C) level increased by 25.7%. By increasing the concentration of DIMEC/P, the DIMEC carbon phenolic resin activation energy (E_a) values slowly improved. CPFs' mechanical properties, fire

retardation, and residual carbon (800°C) improved compared to PF. The CPF cell size was smaller, and the distribution of cells was almost the same.

Novel novolac aerogels were prepared by the addition of graphene oxide (GO) and heat transfer as well as the structural properties were studied.^[105] To achieve this objective, sol-gel polymerization of novolac resin under solvent-rich conditions was employed to generate aerogels with varying GO loadings. Microstructural and thermal characterizations were used to investigate the involvement of GO nanosheets in the structure and morphology of nanocomposite aerogels. Furthermore, the thermal degradation kinetics of nanocomposite aerogels

were used to examine the impact of GO nanosheets on the heat transmission mechanism. The investigations on the kinetics of nanocomposite aerogels at high temperatures were used to analyze processes connected with their structure using GO nanosheets.

Through understanding these processes, it is possible to monitor and formulate the thermal degradation of organic nanocomposite aerogels. The structural, thermal, and morphological properties of Novolac/GO nanocomposite aerogels produced using a sol-gel polymerization process were studied. The exfoliation of GO nanosheets was confirmed by XRD studies. FTIR findings were used to explore the interfacial bonding between nanosheets of GO and macromolecules of novolac. The development of covalent C-O-C bonding between GO nanosheets and polymer chains was found to be the key interaction mechanism between GO nanosheets and novolac. Furthermore, there was exfoliation of GO nanosheets and novolac entered as colloidal structures inside GO, as evidenced by morphological studies. The microstructural studies found that, due to two parallel impacts (the increase in the size of secondary nanoparticles and pore size), the density of nanocomposite aerogels increased with the increased loading of GO nanosheets. Because of the extremely high aspect ratio of GO nanosheets, the actual surface area of nanocomposite aerogels increases as the nanofiller loading increases, even though the porosity content decreases. This is due to the fact that the highly loaded-GO material has a higher actual surface area than the low-loaded-GO material. The addition of GO sheets resulted in an improvement in the thermal conductivity of nanocomposite aerogels, which was due to their microstructural characteristics. When it comes to the transport of heat at high temperatures, the processes of re-radiation and conduction are the most common. Heat re-radiation and the formation of heat transfer barriers are enhanced by reduced-GO nanosheets. Due to the fact that these nanosheets may serve as suitable materials for quick energy carrier transfers, reduced-GO nanosheets can increase the heat transfer of nanocomposite aerogels by increasing their surface area. When exposed to high temperatures, nanocomposite aerogels with GO loadings lower than the percolation threshold demonstrated better heat transmission. While this was true, when the content of GO nanosheets surpassed the level of percolation, the conduction process took over as the primary mechanism of action.

Mehdiseraji et al.^[106] synthesized hydrophobic aerogels based on a phenol-formaldehyde-silica hybrid by the use of a solvent saturated vapor environment and ambient pressure drying (APD). In addition to providing a simple, rapid, and low-cost condition for the creation of PF-silica aerogels, this approach may also be used to

overcome the hydrophilicity limitation that is present in hydrophilic PF-silica aerogels. The second purpose of this effort is to create a link between the microstructure of aerogel and the characteristics of a solvent saturated vapor atmosphere (SSVA), which is currently being investigated. PF/silica aerogels have been investigated for their microstructure, physical characteristics, and hydrophobicity. The molar ratio of TEOS and MTES (methyltriethoxysilane), polymerization duration, and catalyst volume have all been calculated to determine their effects. The colloidal microstructure of the hybrid aerogel was discovered after being changed into a polymeric morphology with an intermediate core-shell arrangement.

Li et al.^[93] investigated the electrical properties of carbonized foams prepared from phenolic foam (PF)-multi-walled carbon nanotubes (MWCNTs) via in-situ polymerization. Excellent dispersion of MWCNTs in the PF matrix was observed from TEM results. Results from scanning electron microscopes showed that PF-MWCNT foams displayed lower cell size, improved cell wall thickness, and cell density relative to neat PF foam. The integration of MWCNTs enhanced PF's mechanical properties considerably. Compared to pure PF, all reinforced PF foams exhibited less thermal conductivity. Relative to pure PF, the thermal conductivity of 2 wt.% MWCNT nanocomposites decreased dramatically to 27%.

In addition, a three-dimensional open-cell carbon skeleton structure was observed for both carbonized reinforced and neat PF, and the MWCNTs were uniformly distributed on the skeleton surface. By creating a conductive network of MWCNTs, the electrical behavior of foams and carbonized foams was greatly increased. Compressive strength and modulus, tensile strength and modulus, improved dramatically by 242% and 167%, 265%, and 126%, respectively, in PF-2 wt.% MWCNT nanocomposites compared to neat PF. The PF/MWCNT nanocomposite was found to have lower pulverization ratios than pure PF. Higher thermal stability for PF nanocomposites was revealed by TGA tests. The addition of MWCNTs can boost PF's mechanical and thermal insulating and electrical properties.

In order to improve the compressive properties of phenolic foam, Delsaz-Orozco et al.^[100] integrated viscose cellulose fibers into PF foam. In addition, the influence of cellulose fibers on the thermal degradation of modified foams was also analyzed. The greatest compressive mechanical properties were obtained for 2 wt.% cellulose fiber reinforced phenolic foam. Relative to neat PF foam, the compressive strength and modulus were improved by 21% and 18% for 2 wt.% loaded cellulose fiber-phenolic foam. The inclusion of the cellulose fibers reduced the phenolic foam's thermal stability significantly. As both fibers and matrix displayed hydrophilic behavior, the

cellulose fibers demonstrated strong interfacial bonding with the phenolic matrix. The incorporation of cellulose fibers into the phenolic foam resulted in improved foam cell density and reduced cell size due to strong binding, which improved the viscosity of the mixture and promoted the nucleation of bubbles. The mechanical properties and thermal stability of the materials affected the molecular composition of the foams. Reinforced phenolic foam with a 2 wt.% loading of cellulose fiber showed better performance.

Some of the researchers focused on strengthening PF foam and carbon foam derived from PF foam's electrical properties by the incorporation of hybrid nanofillers (MWCNTs and nano-Fe₃O₄) via in-situ polymerization.^[107] Using heat treatment methods, novel carbon foams with an open cell structure derived from these reinforced PF foams underwent EMI shielding analysis. In contrast, neat and reinforced foams showed a closed-cell microstructure, which was revealed by SEM results. But the carbon foams had an open-cell structure, while for carbon foam with MWCNT (C-PFC) and carbon foam with 2% MWCNT and nano-Fe₃O₄ (C-PFC2F), a large number of MWCNTs were attached and made interconnecting conductive networks. As the thickness of the prepared foam increased, the EMI shielding also improved. In addition, PF's electrical conductivity and EMI shielding effectiveness (SE) were enhanced with the application of MWCNTs, whereas the application of nano-Fe₃O₄ greatly improved the conductivity of PF foam with 2% MWCNT (PFC2) along with an improvement in EMI SE. It was inferred that by incorporating MWCNTs and Fe₃O₄ nanoparticles into the closed shell-PF foam concurrently, an enhancement in electrical and EMI shielding properties would be observed. It was reported that the incorporation of MWCNTs was the key contributor to the PF's electrical properties, while their electrical and EMI shielding output was contributed mainly by nano Fe₃O₄ to the PF foam.

Nano-SiO₂ application in composite materials has recently gained significant attention.^[108] A new approach to processing was developed in which instead of other organic alcohols, phenol was used to prepare nano-SiO₂. Higher formaldehyde reactivity was displayed by phenol mixtures with nano-SiO₂ than pure phenol. In fact, applying just 0.1 wt.% of nano-SiO₂ to resin raised PF foam modified lignin's compressive strength by 153%. A secure, interconnected network structure was formed by nano-SiO₂, connecting each part of the matrix like a bridge. For use in high-temperature insulating materials, phenolic foams were reinforced with two types of carbon nanoparticles: MWCNTs and composite particles (CPs; MWCNTs with polyimide).^[109] In the reinforcement of phenolic foams, MWCNTs and composite particles (CPs;

MWCNTs with polyimide) were used. The mechanical and thermal characteristics of the carbon foam precursor were enhanced as a result of the reinforcements. Polyimide is used in CPs to improve the dispersion of MWCNTs in phenolic resin, hence boosting the carbon yield of the precursor foam. Polyimide is also used to improve the dispersion of MWCNTs in phenolic resin. A thermally conductive route was also produced during the carbonization process, which allowed the heat to be delivered evenly to the interior section of the precursor foam. This was accomplished by partially dissolving the MWCNTs in the CPs in a solvent before use. Carbonizing the phenolic precursor foams at 1000 °C for 8 hours was used to produce the carbon foams in a nitrogen environment. The mechanical strength of carbon foams based on phenolic foams is lower due to the glassy material formed during the carbonization process. Phenolic foam with 2 wt.% carbon particles (PF 2.0 CP) demonstrated a uniform cell morphology and cell density that was 19.4 times higher than PF. It is observed that PF 2.0 CP and carbon foam with 2 wt.% carbon particles's (CF 2.0 CP) compressive strength and modulus were improved by 130% and 205%, which were higher than PF and CF's. Because of the high cell density, PF 2.0CP's thermal conductivity was 50.5% lower than PF's. Higher thermal conductivity was exhibited by CF 2.0CP (96%) than the others since a thermally conductive pathway was created by entangled MWCNTs on the CPs and also the polyimide being converted into the graphitic structure after carbonization.

While preserving the excellent flame retardant properties of PF foams, attempts were made to enhance the mechanical properties and friability of PF foams using two nano-oxides, namely nano Al₂O₃ and nano ZrO₂.^[110] The two nano-oxides had a significant effect on the mechanical properties and pulverization ratio of PF foams. In comparison, the LOI, UL 94, and cone calorimetry analyses were used to measure the flame retardant properties of modified foams. For modification of phenolic (PF) foams, two nano-metallic oxides, that is, nano-Al₂O₃ and nano-ZrO₂, were used. A significant improvement in the flexural, compressive, and impact strengths was observed by the incorporation of sufficient quantities of nano-oxides into the PF foams. In comparison, the introduction of the pulverization ratio of nano-ZrO₂ decreased the pulverization ratio of the PF foams more significantly than nano-Al₂O₃. In terms of LOI values, the modified foam improved by more than 37%. From the cone calorimetric results, peak heat release levels were less than 50 kW/m² for the modified foams. The TGA tests showed that, relative to pure PF foam, the char yield of the reinforced foams with the nano oxides was increased at higher temperatures.

For making EMI shielding materials, several researchers investigated the effects of different forms of

graphene on composite foam.^[111] However, the industrial use of these products is minimal due to the difficulties in their extensive production. By using graphene as a conducting filler, it is possible to explore the excellent properties of graphene in low-cost carbon foams. A novel technique was adapted for the production of two forms of carbon-reduced graphene oxide (RGO) composite foams, namely: the application of RGO into PF resin and carbonized into carbon foam and RGO into phenolic resin-based carbon foam. A polyurethane (PU) template was used with a mixture of phenol formaldehyde resin and RGO for making carbon foams. The findings showed that the introduction or decoration of RGO dramatically enhanced mechanical efficiency, electrical conductivity, EMI shielding, and carbon foam surface area. During processing, RGO promotes the graphitization process by creating internal tension between the carbon material and the RGO filler. The carbon foam with 1.0 wt.% RGO (sample thickness of just 2.0 mm) improved shielding effectiveness (SET) from 23.2 to 50.7 dB (in the X-band frequency region). The decoration of 1.0 wt.% RGO on carbon foam resulted in a SEA (absorption component) that outperformed the SET (275%). The porous material improved microwave absorption due to multiple scattering and reflections and as a result of the carbon-RGO composite foam's high surface area ($97 \text{ m}^2/\text{g}^{-1}$). In fact, the electrical and thermal properties improved along with the RGO content of the composite foam. They claimed that this innovative RGO painted carbon foam offers a new approach for the production of high-performance lightweight EMI shielding materials for applications in the fields of electronics for the next generation and aerospace.

By penetrating molten Si into liquid PF resin, carbonaceous Si foam with a millimeter pore size was made by the pyrolysis of SiC-based foams.^[112] They have studied the effects of heating rate on the structure and properties of pyrolyzed carbon foams and SiC foams during the foaming process. This study proposed a unique method for the preparation, pyrolysis, and reactive infiltration of macro-porous SiC-based foams, consisting of SiC-filled PF foam. The heating rate probably influenced the cell expansion and size of the cell. A porosity of approximately 72.5%, a mean pore size of approximately 0.5 mm, and a compressive strength of approximately 8.61 MPa were obtained for synthesized composite porous foam. By eliminating Si residue, a compressive resistance of 5 MPa has been achieved for flat porous SiC ceramics.

Gamma-aminopropyl triethoxysilane was used to modify low molecular weight PF resin in order to enhance its electrical properties and bonding strength.^[113] Compared to alcohol-based PF resins, this is a simple and eco-friendly process for the manufacturing of PF resin in an aqueous state. Measurement of volume resistance and

bonding force before and after soaking in hot water was done. To obtain an insight into the changes in the observed material properties, the resin structure and curing behavior were analyzed. Water resistance, volume tolerance, and bonding strength have been enhanced in reinforced PF resin after curing. The 5% silane coupling agent (KH550) exhibited the highest-pressure tolerance and physical and mechanical properties. The DSC study found that the temperature of curing of both resins was high, at about 130°C , with comparable cure times. The curing speed of KH550-modified LPF resin was mild and was more speedy than other foams, thereby minimizing the consumption of energy.

Composites based on reinforcing multi-walled carbon nanotubes (MWCNTs)-lignin-phenolic foams (L20PFs) were fabricated via in-situ polymerization.^[114] Uniform cells were formed by means of decreasing average cell size, which was attributed to the heterogeneous nucleating behavior of MWCNTs. Moreover, MWCNTs were distributed on the cell's porous walls, which were able to transfer certain loads through the foam's interface improved the mechanical properties of the same. The mechanical properties, with compressive and flexural forces exhibited by MWCNTs doped PF, were 0.326 and 0.483 MPa, respectively. The heat release rate (HRR), total heat release rate (THR), and mass loss rate (MLR) were reduced by the addition of MWCNTs, and besides, the limiting oxygen index (LOI) of PFs was enhanced to 44%. It was because the MWCNT formed a thick and incompletely combusted black carbon coating that hinders the entrance of external heat and air into the composite material and acted as a flame retardant composite. There was a marginal reduction in thermal conductivity due to the addition of MWCNT.

Zhang et al.^[115] successfully developed phenolic foams reinforced with silicone whiskers and lignin (LWSPF). A fine dispersion of silicone whiskers and lignin was achieved in the LWSPF system. The performance of the composite materials was enhanced by the addition of silicone whiskers and lignin. This was because of the uniform and decreasing cell size of the foam cells. For silicon whisker (0.6%) and lignin (10%), the char yield was improved by 55.6% compared to the neat PF char yield. The formation of stable Si-O chemical bonds and the even whisker dispersion have improved the system's structure, thermal stability, and mechanical performance. The LWSPF's bending and compression strengths improved by 81% and 82%, respectively, as compared to neat PF.

Using the hydrothermal process, a nanohybrid, graphene oxide (GO) immobilized with layered double hydroxide (CoAl-LDH/GO) was synthesized.^[116] The immobilization of the nanoparticles of CoAl-LDH on GO was well observed from morphological analysis, and the

thermal stability of GO increased significantly on immobilization as revealed by TGA results. There was a significant increase in the compressive and flexural capabilities of the PF foams with a sufficient volume of CoAl-LDH-GO nanohybrid integrated into the PF foams, compared to those of GO or CoAl-LDH-modified PF foams at the same loading. In comparison, the CoAl-LDH/GO-modified PF foam exhibited lower friability compared to the GO-modified foam and greater flame retardance.

In order to boost the thermal insulation, flame retardancy, and mechanical properties of phenolic foam, titanium nitride (TiN) nanoparticles were reinforced by in situ polymerization of phenolic resin with additives and by chemical foaming to make PFTN nanocomposites.^[96] In relation to physical properties, the role of TiN nanoparticles on the porosity, density of cells, and morphology of (PF)/TiN nanocomposites (PFTNs) were investigated. The following findings were obtained, depending on the experiments: SEM findings confirmed a uniform morphology. Narrow cells with small cell sizes were obtained for PFTNs compared to pure PF. All of the foam samples passed a V-0 rating, indicating that these foams have excellent flame retardant efficiency. In fact, the LOI values of PFTN's were enhanced by the addition of TiN nanoparticles, which was higher than neat PF's. The thermal stability of the PFTNs in the atmosphere of nitrogen and air had improved significantly, indicating that nano-TiN had an effective role in enhancing the thermal stability of PF.

Furthermore, mild nano-TiN content improved the mechanical performance of the PF to some extent, but at 4 wt.%, nano-TiN content the same got reduced. The thermal insulating efficiency of the PFTNs was improved through the addition of TiN nanoparticles. The pure PF's thermal conductivity increased with temperature within the -22 to 60°C range. In comparison, the PFTNs' thermal conductivity steadily improved with temperature changes in the range from -20 to 20°C . However, the thermal conductivity of the PFTNs decreased when the temperature rose (30 – 60°C). At different temperatures, PFTN exhibited lower thermal conductivity than neat PF. A reduction in thermal conductivity of 23.7% at 220°C and 19.4% at 20°C was observed for PFTN1 relative to pure PF, since PFTN1 has a more uniform distribution of cells, less cell size, narrower cell size distribution, and higher porosity. The radiant barrier, PFTN4, had lower thermal conductivity at 60°C due to the high additive content of TiN nanoparticles. So, it was concluded that better flame retardancy and lower thermal conductivity were achieved by the introduction of TiN nanoparticles.

Using an easy and cost effective method, graded porous carbon materials have been synthesized by foaming and carbonization of phenolic resin-carboxyl graphene oxide composite.^[117] The fabricated foams consisted of macropores,

mesopores, and micropores due to the foaming process, ester group degradation, and polymer carbonization was confirmed by morphological analysis. The rational distribution of hierarchical porous structures facilitates the transport of electrons and ions by achieving excellent electrical conductivity, by decreasing the distance of ion transport and increasing the charge accommodation. As a result, reinforced foam (RGPF-0.20%-800) had a high specific capacitance of 273 F/g at a current density of 0.1 A/g in KOH electrolyte, higher than PF-800.

Jin et al.^[118] fabricated three-dimensional Co-Ni alloy particles encapsulated in N-doped porous carbon foam by pyrolysis of the phenolic resin and metal ion foam. This was the first-time melamine foam was used as a base, phenolic resin as a matrix, and an alloy as a structural member. The large surface area of the 3D foam skeleton structure improved multiple reflections and incident wave diffraction, and facilitates multiple polarization processes. Due to the engineered configuration of the different materials, the absorbers obtained a property that fitted well with impedance such that further incident waves entered the substrate and then turned into other types of energy. These composites were known to be ideal candidates for electromagnetic protection devices with relatively high absorption and large bandwidth. This approach will surely pave the way for the massive production of porous carbon foam for the absorption of electromagnetic waves.

By incorporating the GO-SiO₂ hybrid nanomaterials into phenolic resin by an in-situ preparation process, Zeng et al.^[119] succeeded in manufacturing ultra-efficient EMI shielding carbon foam and attained fairly good performance. Efficient conductive networks were formed using 1.0 wt.% GO/SiO₂ reinforcement in PF since it favored microstructure, the smaller diameter of cell, and a narrow range of distribution, which were confirmed by SEM findings. EMI shielding properties showed that by increasing the volume of nanoparticles, the electromagnetic interference shielding effectiveness (EMI SE) of a certain thickness of the foam also increased. The excellent property of 3D GO-SiO₂ to form a matrix interface protected more than 99% of electromagnetic radiation waves when the modified carbon foam was reinforced with 1.5 wt.% GO-SiO₂. This system has an EMI SE value of up to a limit of 50 dB. This feather-weight and high-performance electromagnetic shielding system can be used in industrial applications.

1.9 | Application of phenol formaldehyde foams

Wang et al.^[120] fabricated a unique PF foam which can act as interlayer for brazing carbon fiber reinforced carbon composites (C/C). Ding et al.^[121] prepared a superior

flame retardant phenolic foam by incorporating phosphorus- and nitrogen-containing polyurethane quasi-prepolymer (PNPUQP). In comparison to the pure foam, the modified foam that contained 3 wt.% PNPUQP displayed the maximum specific strength in compression and flexibility. The as-prepared modified foams displayed a considerable rise in the LOI values, which is suggestive of an improvement in the flame retardancy. El Bouhtoury et al.^[122] developed PF foams which is free of formaldehyde for removing heavy metals from waste water. Copper, cadmium, zinc, and lead ions each attained their maximum adsorption capabilities of 46.5, 41, 29.1, and 100.9 mg/g, respectively. Lead ions had the highest adsorption capacity. Another breakthrough application of PF foam is in the microbial fuel cells [MFC].^[123] The research group have used carbonized PF foam as anode in the cell. Because of its superior electrochemical performance as well as its possibility of being fabricated in large quantities, the carbonized phenolic foam anode material was worthy of consideration for the potential application of MFCs in the future. A unique flame retardant based on PF foam by the incorporation of demethylated lignin functionalized halloysite nanotubes.

2 | CONCLUSIONS

Incorporation of a small amount of nano dispersed fillers/natural fibers into polymers leads to better mechanical, thermal, electrical, tribological and other physical properties. The property improvements depend on the form of the filler, its size, shape, alignment and volume fraction. The chemical and physical properties often depend on the process used to produce nanocomposites of polymers. The fusion of particles and polymer chains on comparable longitudinal scales provides various advantages and tremendous enthusiasm for the prospect of constructing stable, engineered material structures intelligently. Although these materials will certainly have enhanced properties for a broad variety of applications, profound knowledge of the mechanisms associated with these enhanced properties is necessary to make effective use of them. In this review, we described a few important properties of the major components in PF nano/hybrid composites. We have highlighted several reports on other fields of research, past and present, in the field of polymer science on which we can develop our understanding of the “nano” effect in polymer nano/hybrid composites.

3 | FUTURE SCOPE

Following research and industrial application, phenolic resin composite/foam with low or no free aldehyde

and/or phenol content are still required for environmental protection. Replacing fossil fuel derived phenol with bio-oils need much more attention.

ACKNOWLEDGMENTS

The authors thank the support from DST, New Delhi for the facilities provided to Sree Sankara College, Kalady under the DST-FIST program (No. 487/DST/FIST/15-16).

FUNDING INFORMATION

The authors declare that they have not received any funds.

CONFLICT OF INTEREST

The authors declare that they have no competing interests.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this review article as no new data were created or analyzed in this study.

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How to cite this article: L. Ravindran, S. M. S., A. Kumar S., S. Thomas, *Polym. Compos.* **2022**, *43*(12), 8602. <https://doi.org/10.1002/pc.27059>