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

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1 Introduction

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

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

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

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

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

2 Fillers in Hybrid Composite Foam

Phenolic foam (PF) was first introduced in the early 1940s, yet the material has not been entirely commercialized due to its brittleness and friability. Later in the early twentieth century, with the emergence of industrial revolution, rigid thermosetting foam has gained its attention due to the growing demand for cheap foam thermal insulation materials. Closed-cell PF is suitable for thermal insulation applications, while the open-cell foam was common for sound insulation applications. Since then,

an effort has been made by researchers to tailor PF cell size, shape, and distribution for various purposes. To reconstruct pure PF according to the desired properties, numerous approaches have been conducted, namely, chemical modification on phenolic resin, physical blending between phenolic and other polymer resins, altering formulation and ingredients, and addition of filler in the open- and closed-cell PF system [7, 21].

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

2.1   Hybrid Fiber

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

In the fire exposure experiments, the thermal conductivity of the hybrid composite appeared to be 0.26 W/m.K through the 38 mm core thickness direction. In terms of strength, the hybrid honeycomb post-fire flexural strength decreased by 16% from 20.5 to 3.4 MPa and the stiffness decreased by 49% from 226 to 110 Pa.m^4 after 1 h of

exposure to fire. This was also indicated by the hybrid composite PF flexural strength as it decreased by 54% of the original strength caused by core shear failure. Interestingly, the PF hybrid composite core sandwich structure produced with carbonized phenolic aramid/glass hybrid composite face was able to retain about 50% of the original strength after post-fire exposure which concluded that the hybrid composite mat sandwich with PF has the ability to replace epoxy, vinyl ester, or polyester resin. The failure mode for the entire honeycomb hybrid system was derived from delamination and cracking between the composite face and core on the fire-exposed side.

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

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

By taking advantage on the inherited properties of glass fiber and aramid fiber, an experiment was conducted to determine the hybrid short fiber mechanical properties

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

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

2.2 Hybrid Particulates

The tailor-made properties of particulate hybrid composite foams allow the production of foams with distinct properties. The rule for developing uniform and regular cells in PF is by homogeneously dispersing particulate fillers in phenolic resin. The inclusion of filler in the PF formulation may stabilize the emulsion by Pickering. These fillers also act as nucleating agents in creating more bubble nuclei when exceeding the free critical nucleating energy. In comparison to the filled fiber, the addition of particle filler can severely increase the viscosity of the filled phenolic resin. However, it is insignificant to compare with fiber systems due to its isotropic properties. Higher viscosity results in better cell uniformity and generates smaller cell

size during foam expansion but on the downside it constructs a higher foam density. If the viscosity is too high, the foam will be completely inhibited from further expansion. There are a number of single filler systems from microns to nano-sized particles added in PF, such as clay, glass beads, and gypsum. These fillers come in various sizes, shapes, surface chemistry, and specific surface areas which may impart an outstanding performance on foam stiffness, compressive strength, flexural strength, and fire properties. To achieve more than one of these properties, hybrid particulate fillers have proven to be a promising solution [21].

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

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

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

of optimum nanoclay loading helps to boost mechanical properties and increase the flame resistance of the foam [31].

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

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

Inspired by previous work on hybrid carbon-based fillers for application in heat, electricity, and magnetism, Zeng et al. [36] extended their research using the three-dimensional structure of graphene oxide/SiO_2 (GO/SiO_2) hybrid nanomaterials in PF to cater the EMI shielding performance. The configuration of the effectiveness of the

foam electromagnetic shield was connected to the foam cellular structure. The presence of 1 wt% GO/SiO$_2$ nanomaterials clearly enhanced the cell structure, narrowed the range of cell distribution, and reduced the density of the foam which in turn assisted an efficient conductive network. The build-up porous structure of the carbon foam was identified to create a number of interfaces which simultaneously enhanced multiple reflections and absorptions of electromagnetic waves. The penetrating electromagnetic waves were then reflected in the matrix and propagated over a greater distance in random direction electromagnetic waves. They also discovered that the EMI SE of the carbon foam increased higher than ∼40 dB when a small amount of GO/SiO$_2$ was added. The value increased up to ∼50 dB as the concentration of GO/SiO$_2$ was added up to 1.5 wt% [36].

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

3 Mechanical Properties of Hybrid Composite Phenolic Foam

Recently, various industries have focused on phenolic foam (PF) due to its excellent fire resistance, low density, low water absorption, and good thermal insulation [2]. Nevertheless, the drawbacks of PF foam are its high brittleness and low mechanical strength which limit its applications in some areas which require high mechanical properties. Generally, PF exhibits lower mechanical strength and brittleness compared to other commodity plastic foams [21]. Therefore, increased mechanical strength and reduced friability are crucial to highlight its potential in various applications. The mechanical strength of PF depends on the interaction of filler with the matrix, type of filler, shape of filler, and size of filler. Moreover, by using hybrid fillers, the compatibility between the fillers, mixed ratio, or weight fraction and filler dispersion could have a significant effect on the final properties of the composite

foam. For example, Luo et al. [4] reported that the compressive strength of graphene oxide/SiO$_2$ (GO/SiO$_2$)-modified phenolic foam was better for SiO$_2$ with a diameter of 80 nm compared to 170 nm and 250 nm. Small particles with higher surface area could provide heterogeneous nucleation sites, thus producing PF with a uniform cell structure. In the same study, the compressive strength of PF increased from 0.3 wt% up to 1 wt% GO/SiO$_2$ and decreased by 1.5 wt%. Desai et al. [3] also reported that the PF reinforced with glass and aramid fiber at a ratio of 3:1 has higher compressive strength than 1:3 ratio.

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

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

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

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

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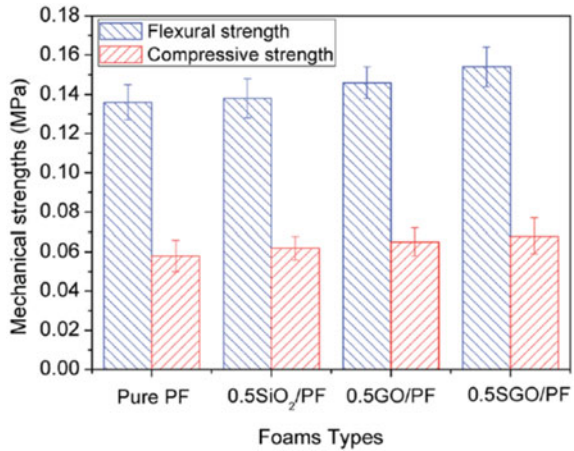

The flexural and compressive strengths of the composite foam became better with the addition of SGO compared to unfilled PF foam. It can be seen from Fig. 1 that hybrid phenolic composite foam showed higher flexural strength and compressive strength compared to unfilled and single filler reinforced PF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

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

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

Fig. 2 Flexural and
compressive strength of pure
and reinforced phenolic
foam [8]
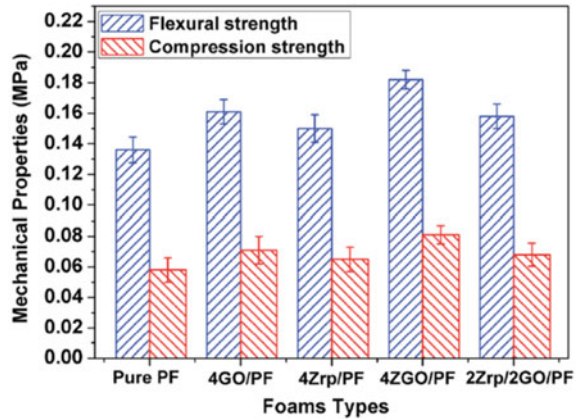
resins. Nevertheless, Zrp showed poor dispersion in the PF by producing non-uniform
cell structures, thus damaging the mechanical strength of 4ZrP/PF and 2ZrP/2GO/PF
as shown in Fig. 2.

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

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

can be improved and tailored to specific requirements of particular applications by varying the filler parameters such as size, specific surface area, shape, type, and weight fraction.

4 Conclusion

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

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