Chapter 13
Graphene Reinforced Phenolic Foams

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1 Introduction

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

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

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

2 Graphene Derivatives in Phenolic Foam Modification

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

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

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

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

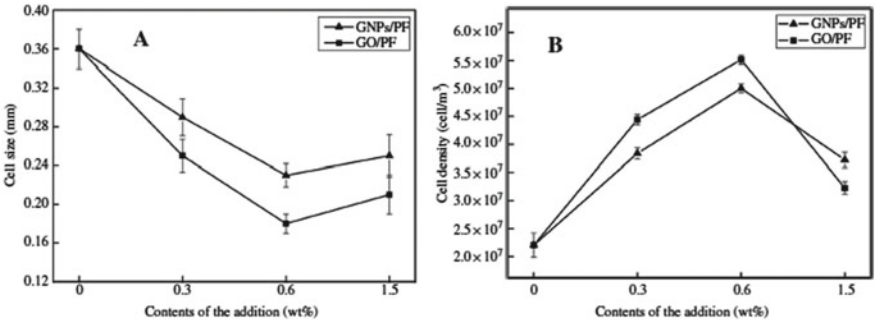
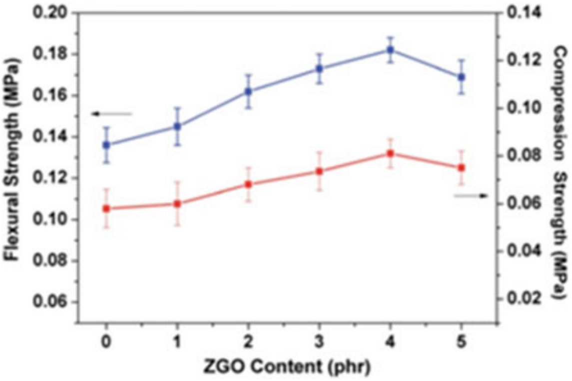


Fig. 1 Phenolic foams with addition (GNP or GO) nanofiller: **a** cell size distribution, **b** compressive strength properties [8]

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



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

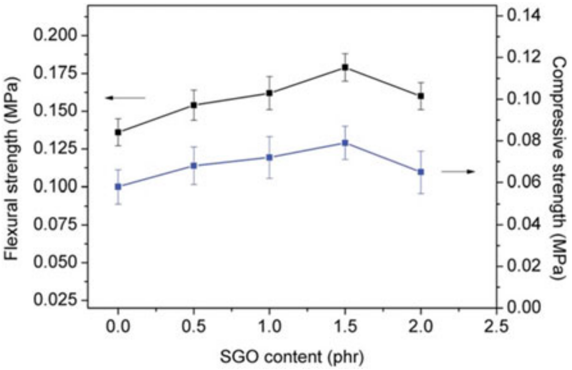
Li X et al. [9] also investigated materials based on phenolic foams modified by graphene-based hybrid nanoparticles (SGO) consisting of GO sheets and SiO2 nanospheres. In their study, the incorporation of 1.5 phr SGO into PF foam leads to a 32% increase in the flexural, a 36% increase in compressive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

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

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

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

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



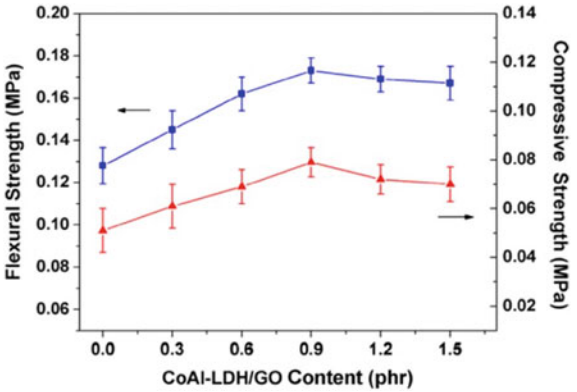


Fig. 4 CoAl-LDH/GO (GO: graphene oxide; LDH: layered double hydroxide; PF: phenolic) content on flexural and compressive strengths of PF foams [10]

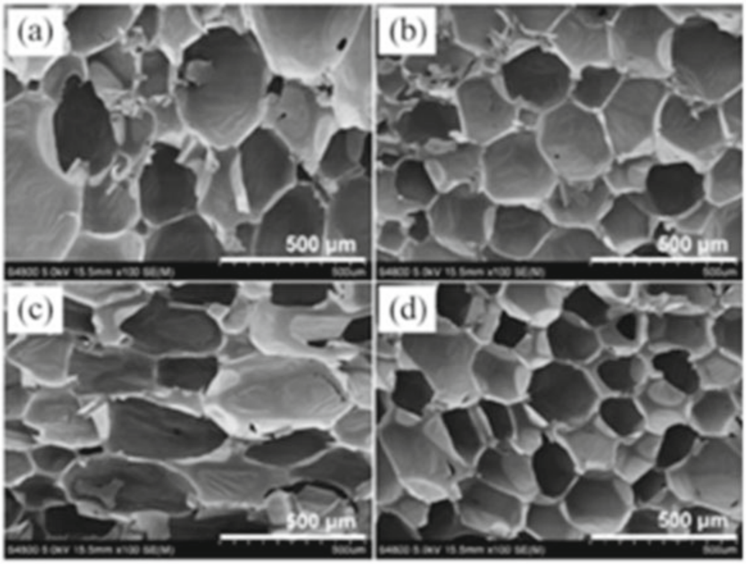


Fig. 5 SEM images of **a** neat PF foam, **b** 0.9GO/PF, **c** 0.9CoAl-LDH/PF and **d** 0.9CoAl-LDH/GO/PF [10]

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

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

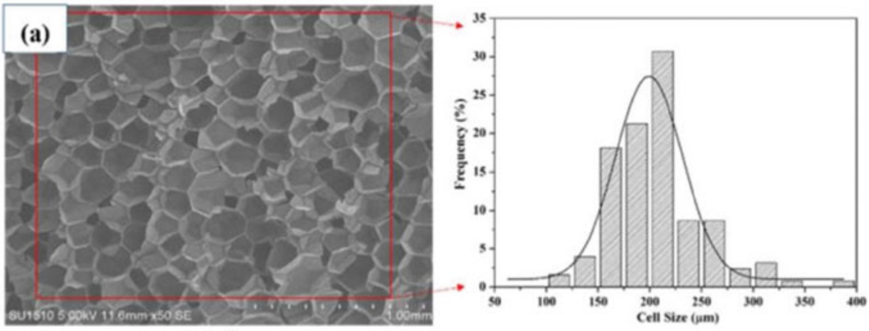
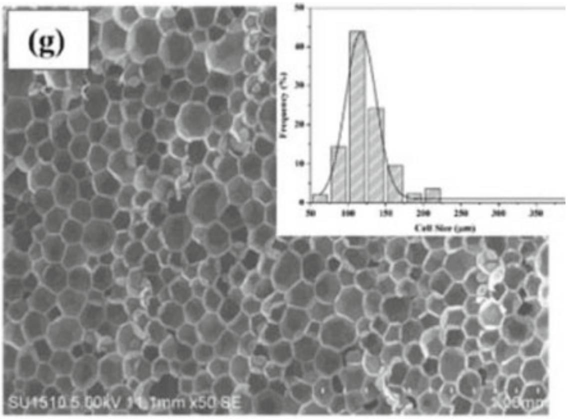


Fig. 6 SEM microphotograph of the pure PF surface and cell distribution [11]

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



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

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

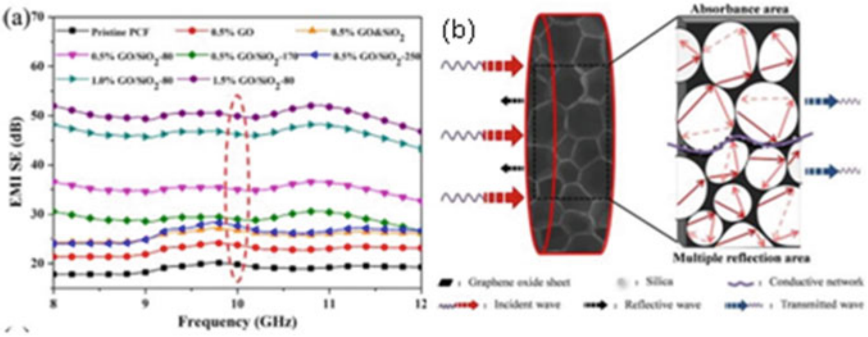


Fig. 8 **a** EMI SE as a function of frequency for PCF materials, **b** Schematic description of incident wave distribution in phenolic-based carbon foams [12]

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

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

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

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

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

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

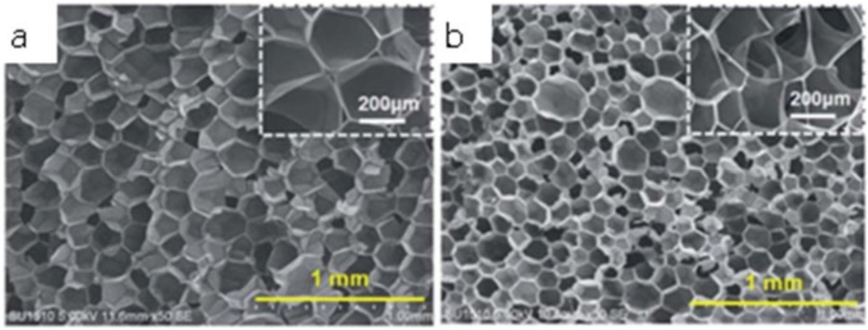


Fig. 9 SEM images of **a** pure carbon foam, **b** 1.5 wt% rGO/Fe_3O_4 hybrid-modified carbon foams [14]

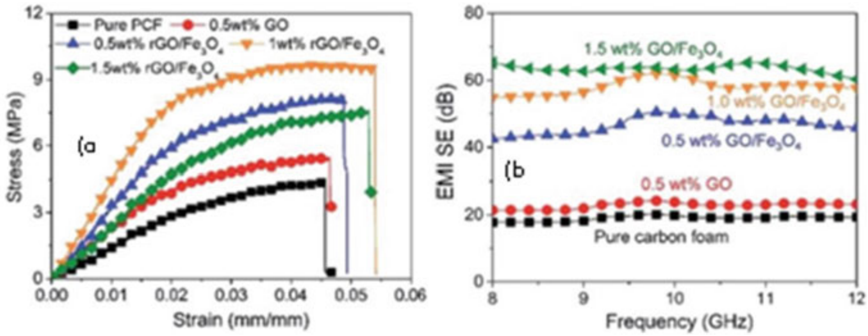


Fig. 10 Mechanical properties of the carbon foams: **a** stress–strain curves, **b** EMI SE [dB] of various carbon foams in the function of Frequency [GHz] [14]

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

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

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

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

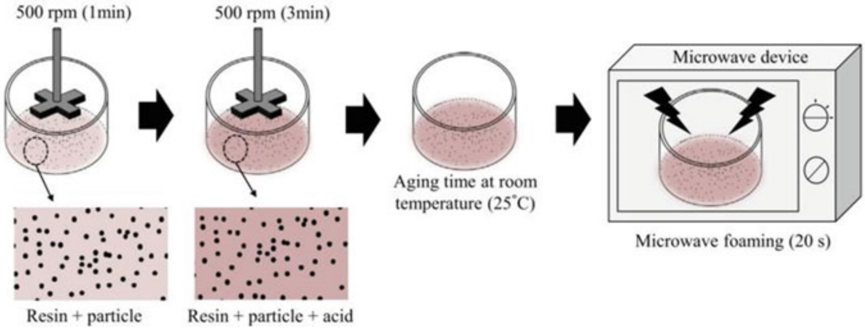


Fig. 11 Preparation of reinforced phenolic foam [2]

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

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

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

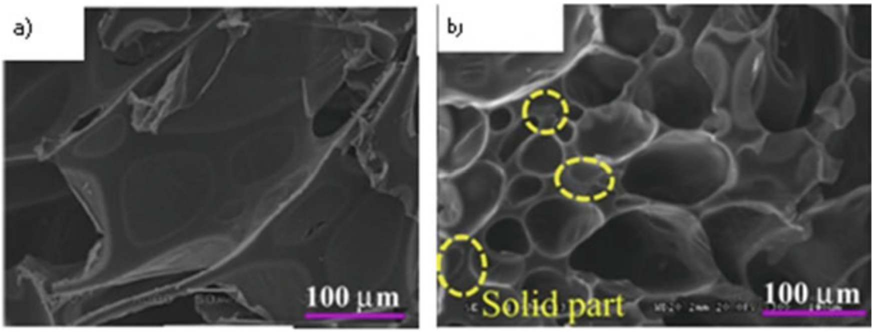


Fig. 12 SEM of the phenolic foams **a** pure phenolic resin, **b** Phenolic foam with 2.0 wt% Graphene [2]

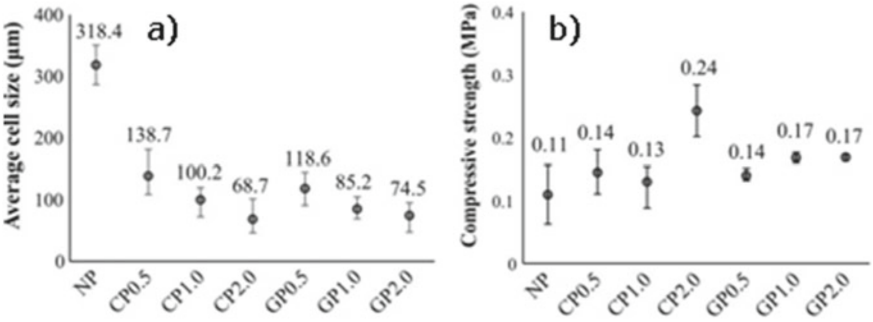


Fig. 13 Nanocomposite phenolic foams characterization: **a** average cell size **b** compressive strength [2]

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

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

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

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

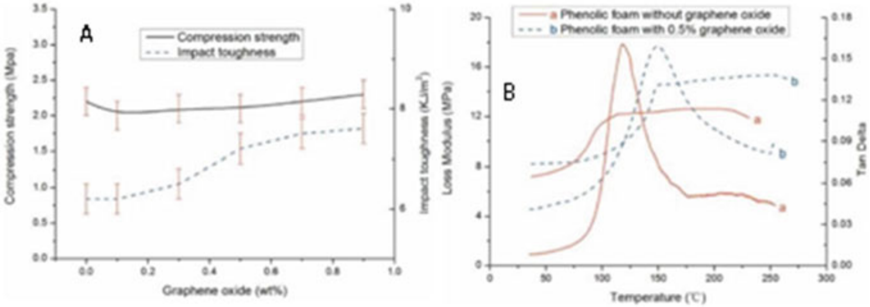


Fig. 14 **a** Compression strength and impact toughness of phenolic foam (PF) modified with graphene oxide (GO), **b** Loss modulus and tan δ vs. temperature. Phenolic foam **a** without graphene oxide, **b** with 0.5% graphene oxide [16]

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

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

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

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

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

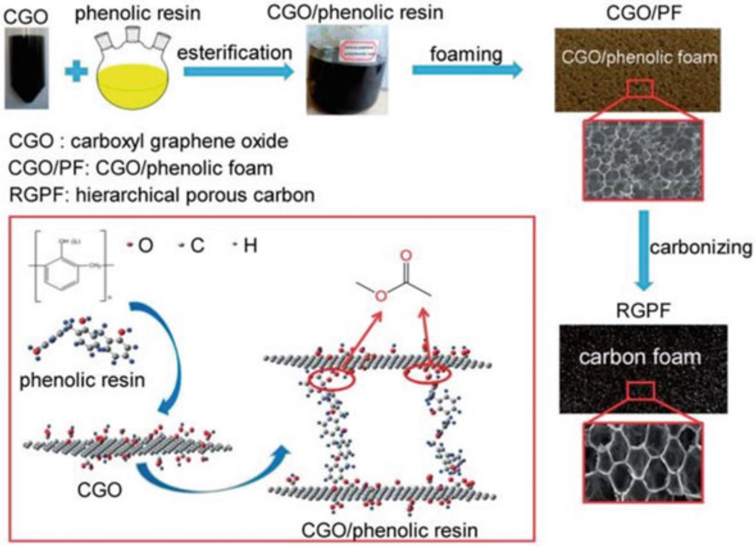


Fig. 15 Synthesis of Carboxyl Graphene Oxide (CGO)/phenolic foam and hierarchical porous carbon foam (RGPF) materials [18]

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

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

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

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

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

3 Conclusion

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

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

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

References

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

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