

Graphene reinforced phenolic foams

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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].

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.

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 (Figure 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, improve the flexural (34%) and compressive strengths (40%) of the ZGO-toughened PF foams (Figure 2) [1].

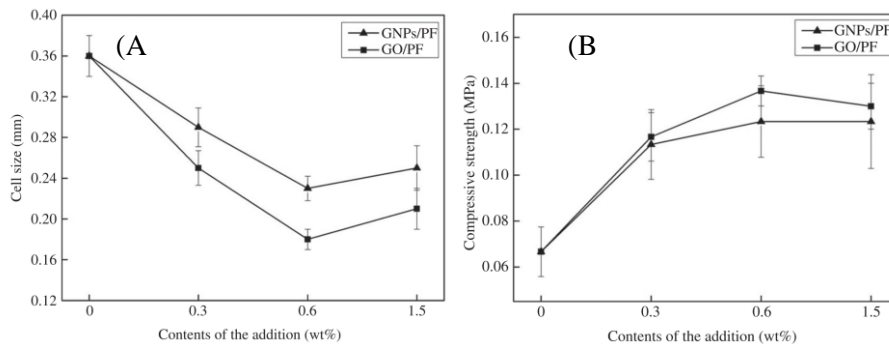


Fig. 1. Phenolic foams with addition (GNP or GO) nanofiller: (A) cell size distribution, (B) compressive strength properties [8].

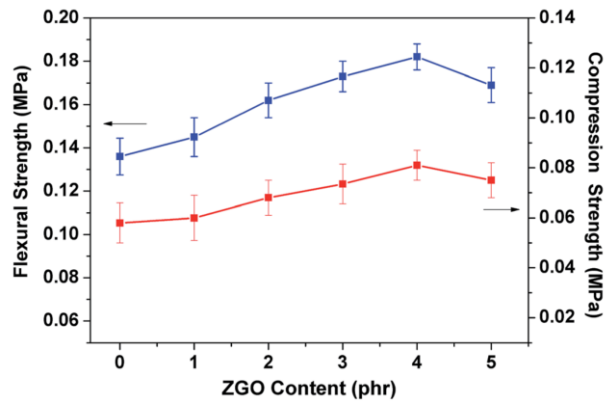


Fig. 2. ZrP/GO content on flexural and compressive strengths of PF foams with ZrP/GO modifier [1].

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 $T_{5\%(\text{mass loss})}=163^{\circ}\text{C}$ for pure PF to $T_{5\%(\text{mass loss})}=204^{\circ}\text{C}$ 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 (Figure 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 $T_{5\%(\text{mass loss})}=163^{\circ}\text{C}$ for pure PF to $T_{5\%(\text{mass loss})}=199^{\circ}\text{C}$ for 2 phr SGO nanomodifier in PF) [9].

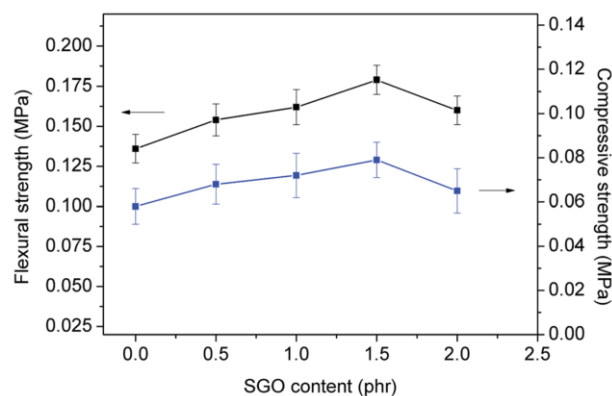


Fig. 3. SGO content on flexural and compressive strengths of PF foams [9].

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 the 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 0.9CoAl-LDH/GO/PF (79 kPa) increase by 55% in comparison to the pure PF foam (51 kPa) (Figure 4). Moreover, the flexural strengths of nanohybrid material 0.9CoAl-LDH/GO/PF (173 kPa) increase by 35% in relation to the pure PF (128 kPa) (Figure 4) [10].

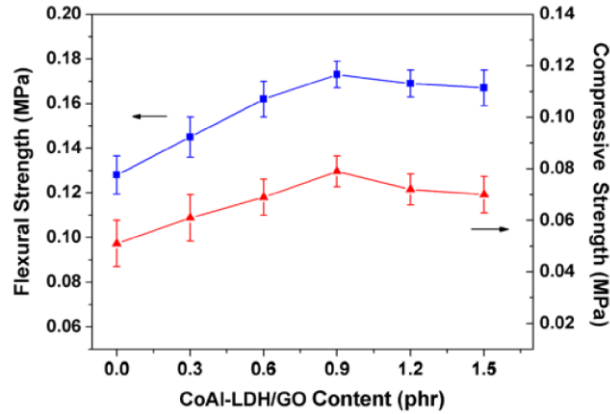


Fig. 4. CoAl-LDH/GO (GO: graphene oxide; LDH: layered double hydroxide; PF: phenolic) content on flexural and compressive strengths of PF foams [10].

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

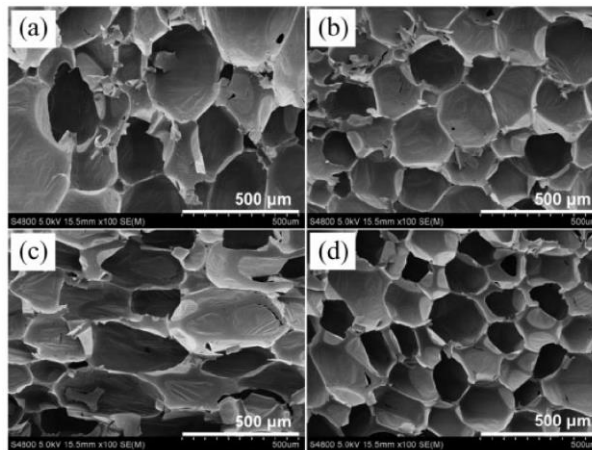


Fig. 5. SEM images of (a) neat PF foam, (b) 0.9GO/PF, (c) 0.9CoAl-LDH/PF and (d) 0.9CoAl-LDH/GO/PF [10].

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 materials were added into phenolic resin to prepare phenolic foam nanocomposites.

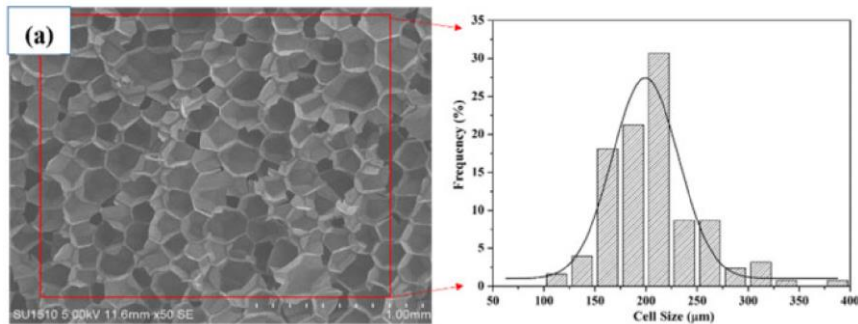


Fig. 6. SEM microphotograph of the pure PF surface and cell distribution [11].

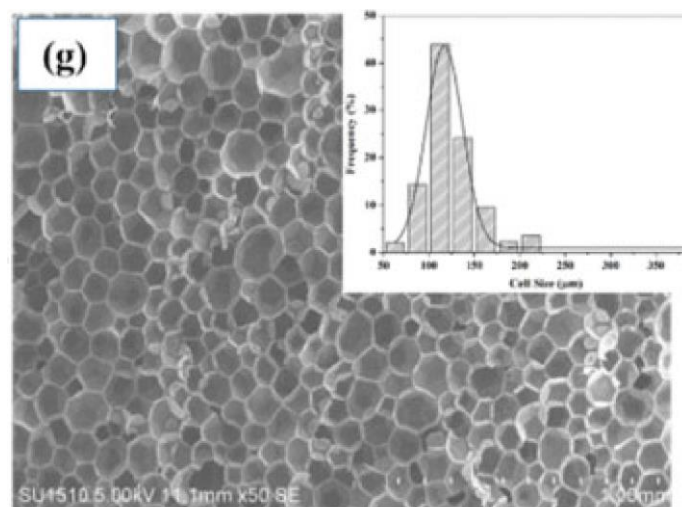


Fig. 7. SEM microphotograph of the PF/(1.0 wt% GO/SiO₂-80) material pure and cell distribution [11].

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

with a narrow cell distribution from 50-224 μm (Figure 7), in comparison to the pure PF foam with wider cell distribution and cell size about 200 μm (Figure 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), what was investigated by Zeng Y et al. [12]. EMI SE parameter which describe is 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 increase these parameter to about 23 dB which is connected with higher conductivity of this nanocomposite material (Figure 8a). Another modification based on GO/SiO₂ content highly increases EMI shielding. For material containing 1.5 wt% of GO/SiO₂ in PCF matrix the value of EMI SE increase 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 has a strong interaction with electromagnetic waves and this behaviour can significantly reduce the impact from electromagnetic field (Fig. 8b) [13].

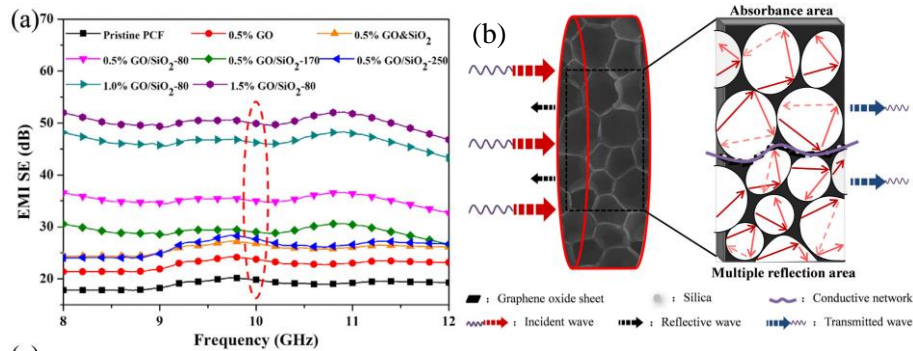


Fig. 8. (a) EMI SE as a function of frequency for PCF materials, (b) Schematic description of incident wave distribution in phenolic-based carbon foams [12].

The relationship between the cellular structure and the multipoles of the composites is shown in the Figure 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/Fe₃O₄ (rGO/Fe₃O₄) 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 about 200 μm. The introduction of 1.5 wt% rGO/Fe₃O₄ hybrid nanofiller into foam matrix reduced cell size to 130 μm (Fig. 9b).

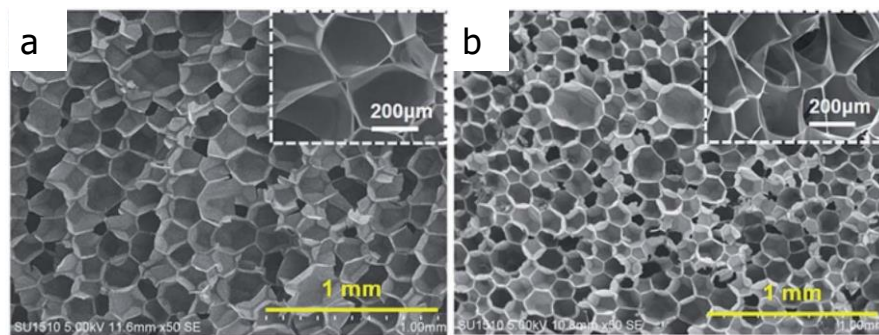


Fig. 9. SEM images of (a) pure carbon foam, (b) 1.5 wt% rGO/Fe₃O₄ hybrid-modified carbon foams [14].

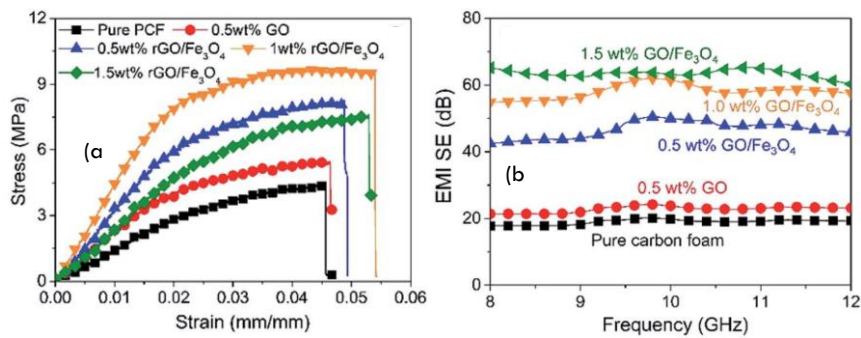


Fig. 10. Mechanical properties of the carbon foams: (a) stress–strain curves, (b) EMI SE [dB] of various carbon foams in the function of Frequency [GHz] [14].

Strain vs stress curves of the pure PCF foam and modified nanomaterials are showed in the Figure 10a. These results clearly prove that adding GO or rGO/Fe₃O₄ hybrid nanofillers into PCF foam improve mechanical properties. rGO/Fe₃O₄ hybrid nanofiller seems to be more effective in comparison to the GO.

Best results were obtained for the addition 1 wt% rGO/Fe₃O₄ hybrid nanofiller (Fig. 10a).

Figure 10b shows the EMI SE results for the carbon foams materials. Authors observed 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/Fe₃O₄) dramatically increased this parameter up to 65 dB. Enhanced EMI shielding performance is connected with Fe₃O₄ behaving as a magnetic material which possess strong interaction with the magnetic component of electromagnetic wave (Fig. 9b).

Some pro-ecological application 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 amount 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 increase with the addition of GnP nanofiller from PF wood matrix (re-PF/W)(thermal degradation $T_{\text{onset}}=212^{\circ}\text{C}$) to $T_{\text{onset}}=243^{\circ}\text{C}$ 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 Korea research group [16]. Noteworthy is the relatively simple method of obtaining nanocomposites according to the diagram shown in the Figure 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.

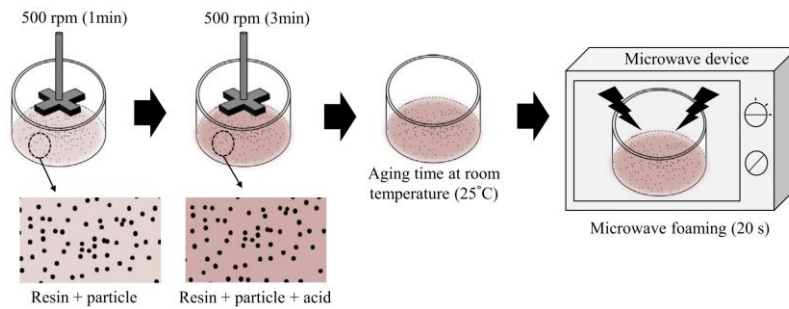


Fig. 11. Preparation of reinforced phenolic foam [16].

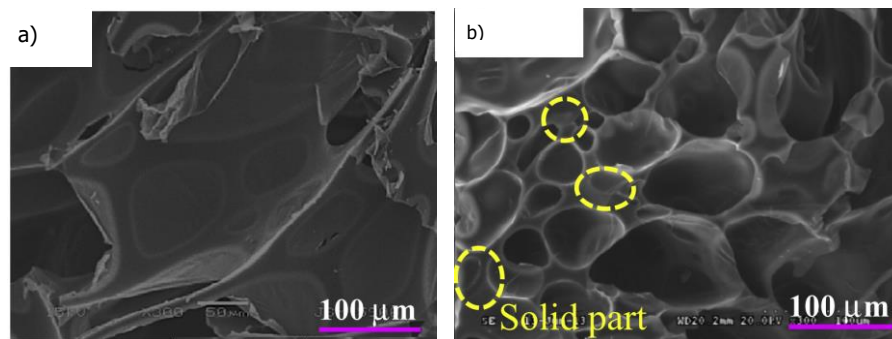


Fig. 12. SEM of the phenolic foams (a) - pure phenolic resin, (b) - Phenolic foam with 2.0 wt% Graphene [16].

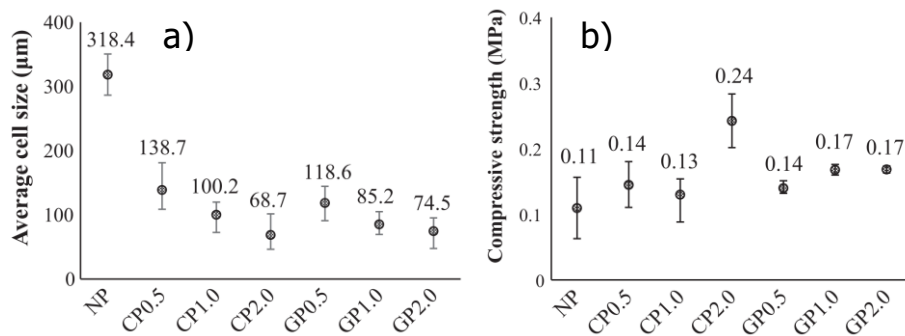


Fig. 13. Nanocomposite phenolic foams characterisation: (a) average cell size (b) compressive strength [16].

Based on phenolic foam's SEM images (Figure 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) (Figure 13). The carbon reinforced phenolic foams (CP - MWCNT, GP - Graphene), show smaller cell size for the both modified materials in comparison with the pure phenolic foams (Figure 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 amount 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 possess higher compressive strength in comparison to the large cell foams (Pure PF), because these materials have more ribs and walls within foam morphological structure [16].

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. [17].

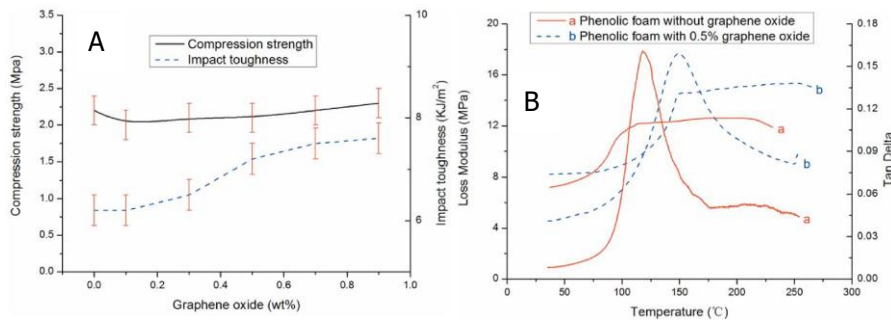


Fig. 14. (A) Compression strength and impact toughness of phenolic foam (PF) modified with graphene oxide (GO), (B) Loss modulus and $\tan \delta$ vs. temperature. Phenolic foam (a) without graphene oxide, (b) with 0.5% graphene oxide [17].

Mechanical parameters, for polymeric foam materials, are one of the most important factors influencing behaviour application in the environment. These nanocomposite materials (containing GO nanofiller) show small changes to strength improvement (within experimental errors) (Figure 14A) [17]. More noticeable changes are visible via impact toughness increase (up to 16% for 0.5 wt% GO in PF foam matrix) (Figure 14A). In the case of these systems, it is worth concluding that such small addition 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 (T_g) of graphene oxide reinforced phenolic foam compared with non-modified phenolic foams. Figure 14B presents T_g temperature of phenolic foam and PF with 0.5 wt% GO nanofiller increasing from $T_g=118^\circ\text{C}$ to $T_g=150^\circ\text{C}$ [17].

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. [18]. 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 $25 \text{ mW/m} \cdot \text{K}$) [18].

Phenolic foams modified using graphene derivatives can be also used as a high performance supercapacitors [19]. Li et al. [19] presents a new type of advanced energy storage device based on these materials.

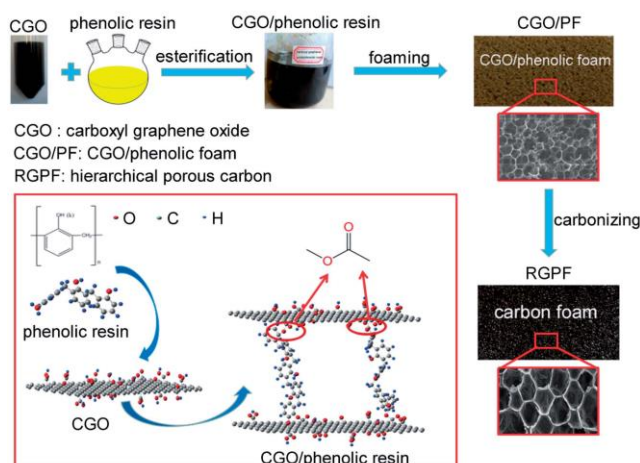


Fig 15. Synthesis of Carboxyl Graphene Oxide (CGO)/phenolic foam and hierarchical porous carbon foam (RGPF) materials [19].

The authors successfully prepared modified materials according to the synthesis of CGO/phenolic based on three steps method, where the CGO addition was in between 0.05% and 0.30% (Figure 15). Finally, porous carbon foam (RGPF) was prepared by carbonizing CGO/PF [19]. 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 conductive and used successfully for the electron transport. Prepared nanocomposites (especially RGPF with 0.2 wt% CGO) possess a high specific capacitance of 273 F/g in comparison to the non-modified PF material, where this parameter is equal to 114 F/g [19]. These

electrode materials (designed as RGPF-0.20%-800) also presented 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*-(methylenephosphonate) and reduced graphene oxide (rGO), which Liu L, et al.[20] introduced to phenolic foam (PF), were successfully in terms of increasing mechanical properties and thermal stability of PF.

This research presents one-step synthesis of a novel magnesium amino-*tris*-(methylenephosphonate) (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 behaviour 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 interesting modification of GO since it was obtained by reducing and functionalizing GO form) enhance the thermal stability of the phenolic foam more effectively than classic graphene oxide (GO) [20].

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 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) seem 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.

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