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## SYNERGISTIC EFFECT OF GRAPHENE OXIDE AND TRIBLOCK COPOLYMERS ON EPOXY RESINS

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**Abstract** – Toughening epoxy resins is a recent trend in composite processing. The combination of rigid carbonaceous nanofillers such as graphene oxide (GO) with plasticizing additives could provide a synergistic effect on the thermal or mechanical properties of the composites. This work aims to study the combination of neat and silane-treated GO with poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (EPE). The dispersion, dynamic-mechanical and mechanical properties were evaluated. Addition of EPE aided the dispersion of both GO and GO-A in epoxy resin. EPE/GO modified epoxy resin showed lower rubbery modulus and better impact absorption properties, confirming their synergistic effect. Treatment with silane did not significantly alter the properties of the composites.

**Keywords:** *graphene oxide, triblock copolymer, epoxy resin, silanes, composites.*

### Introduction

Toughening epoxy resins is a growing trend. Their brittle nature – a result of their highly cross-linked network – can be improved by adding nanofillers. Graphene oxide (GO) has been successfully used to toughen epoxy resins, and surface treatment of GO with silanes also proved to be effective [1]. Recently, the family of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (PEO-PPO-PEO or EPE) has been suggested as a toughening agent. EPE possesses the ability to microphase separate when mixed with thermosetting resins by means of self-assembly or reaction induced phase separation or a combination of both, forming microstructures [2]. In addition to that, PEO blocks can form hydrogen bonds, potentially acting as coupling agents [3]. This way, a synergistic effect of both fillers could be achieved, increasing the toughening potential when both EPE and GO are combined. The aim of this study is to incorporate EPE triblock copolymers, and untreated and silane treated GO in epoxy resins, and to evaluate synergistic effects of the fillers on the dispersion, dynamic-mechanical properties, fracture toughness and impact strength of the composites.

## Experimental

### *Materials*

The triblock copolymer Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic® P-123), powder graphite and 3-aminopropyltriethoxysilane (APTES) were purchased from Sigma-Aldrich. Diglycidyl-ether bisphenol-A (DGEBA) epoxy resin (EP) grade HT1564 and hardener grade E150 were obtained from Advanced Vacuum.

### *Graphene oxide obtention and treatment*

Graphene oxide (GO) was obtained from powdered graphite by the Hummers method as described in previous literature [4]. GO was modified with APTES following previous methodology by the group [5]. APTES modified GO is herein named GO-A.

### *Composites preparation*

0.10 (wt%) of GO or GO-A were added to 25 mL of acetone and 25 g of epoxy resin, and sonicated for 1 h at 40% amplitude in a Sonics VibraCell VCX 500 sonicator (500 W) in an ice bath. Another 25 g of epoxy resin were added to the suspension and sonicated for another hour. Acetone was evaporated at 70 °C for 3 h under magnetic stirring and additional evaporation was done in a vacuum oven at 70 °C overnight. 5 wt% EPE was added to the resin and the mixtures were magnetically stirred at 70 °C for 20 min. Then, the mixtures were cooled and the hardener was added at 15:100 (hardener:resin), manually stirred and degassed in a vacuum oven. The composites were molded by casting the resin into rubber silicone molds, cured at room temperature for up to 72 h and later post-cured [5].

### *Characterization*

X-ray diffraction (XRD) was performed in a Shimadzu XRD-600 equipment ( $\text{CuK}\alpha = 0.1542 \text{ nm}$ , 30 mA, 40 kV,  $2^\circ < 2\theta < 40^\circ$ ,  $0.05^\circ$ ,  $2 \text{ s}^{-1}$ ). Dynamic-mechanical analysis was carried out in a Q800 AT TA Instruments equipment, in a single cantilever clamp, 30 °C – 200 °C, ramp of  $3 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ , 1 Hz frequency and 0.1% strain. Unnotched Izod impact testing was performed in a CEAST Resil-25 equipment with 2 J hammer energy (ASTM D256-10). Plane-strain fracture toughness ( $K_{IC}$ ) was evaluated using the single edge notched bend (SENB) test according to ASTM D5045-14. Tests were done in an EMIC DL-3000 equipment at  $1 \text{ mm}\cdot\text{min}^{-1}$ . One-way statistical analysis of variance was performed for impact and fracture toughness results, with a significance level of  $P < 0.05$ .

## Results and Discussion

XRD results are shown in Fig. 1. A peak at  $2\theta = 26.4^\circ$  is commonly reported for re-stacked graphene oxide. In this case, for both GO and GO-A dispersed in the resin with EPE, this peak is absent, showing apparent good dispersion of the nanoparticles in the resin and suggesting the intercalation of EPE in the galleries of graphene oxide. The same behavior has been reported by Hu et al., and according to them, the hydrophobic propylene oxide block is adsorbed on the particles' surfaces [6]. EPE may also have acted as a coupling agent due to a synergistic effect of PEO blocks bonding to the surface of GO, and PPO hydrophobic blocks aiding the dispersion and possibly the adhesion to the epoxy resin [3].

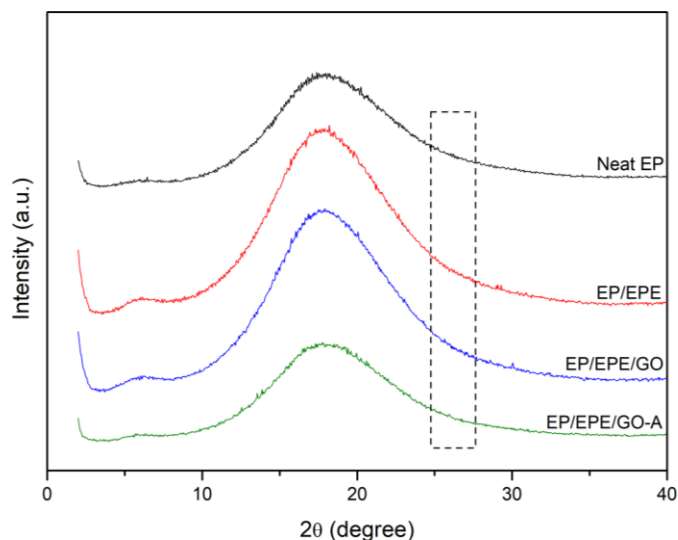


Fig 1. XRD spectra of the composites.

The storage modulus and the tan delta of the composites are presented in Fig. 2. The storage modulus of all the composites (Fig. 2a) is lower than the neat resin in the glassy region, which could be attributed to a lower rigidity due to the addition of EPE. This behavior was also found by Parameswaranpillai et al. [2]. In the rubbery region, the lowest modulus was observed for EP/EPE/GO composites and is related to a reduction in the crosslink density [5]. This could be beneficial to the impact and fracture toughness properties of the composites.

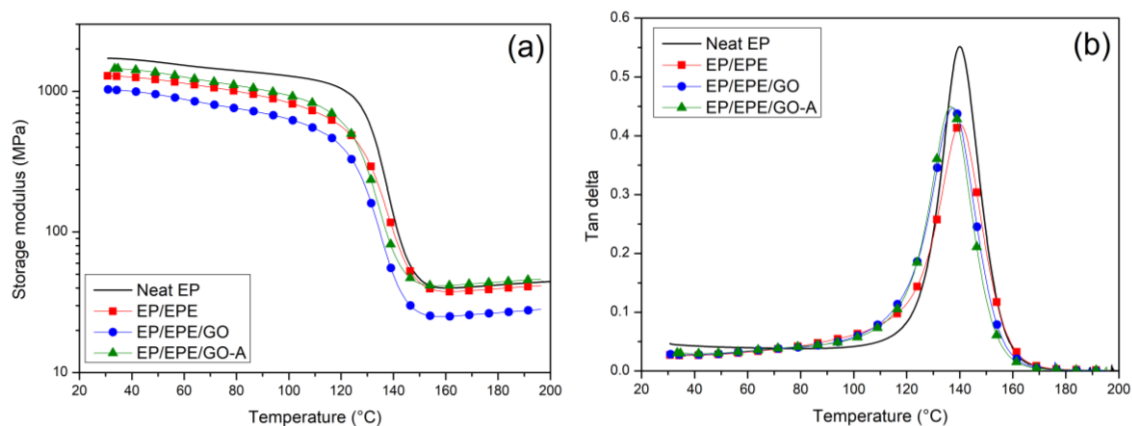


Fig 2. Storage modulus (a) and tan delta (b) of the composites.

The damping (tan delta) of the composites is shown in Fig. 2b. The peak height is lower in relation to that of the neat resin for all composites, indicating reduced chain mobility imposed by the reinforcement even with the addition of EPE. The reduction in peak height also implies that the EPE phase was miscible with the epoxy resin [2]. The glass transition temperature ( $T_g$ ) was obtained from the tan delta peak with respective values for neat EP, EP/EPE, EP/EPE/GO and EP/EPE/GO-A of 140 °C, 140 °C, 137 °C and 137 °C, thus not

significantly changing among the composites, perhaps because only a small amount of EPE was used.

The impact strength of the composites was evaluated and is shown in Fig. 3a. The best results were found for EP/EPE/GO. This agrees with the DMA data. A decrease in the cross-link density is often associated with better impact absorption behavior [5]. The plane-strain fracture toughness ( $K_{IC}$ ) of the composites is presented in Fig. 3b. Addition of only 5 wt% EPE increased the  $K_{IC}$  of the composites, and for EP/EPE/GO this property increases. Some authors report that well-exfoliated graphitic fillers could improve the fracture toughness of epoxy resins even in the presence of a rubbery phase [7]. This confirms the synergistic effects of EPE and GO on the impact absorption properties of the composites. Treatment with APTES increased both impact strength and fracture toughness of the composites in comparison to the neat resin perhaps due to better exfoliation, as seen in XRD analysis.

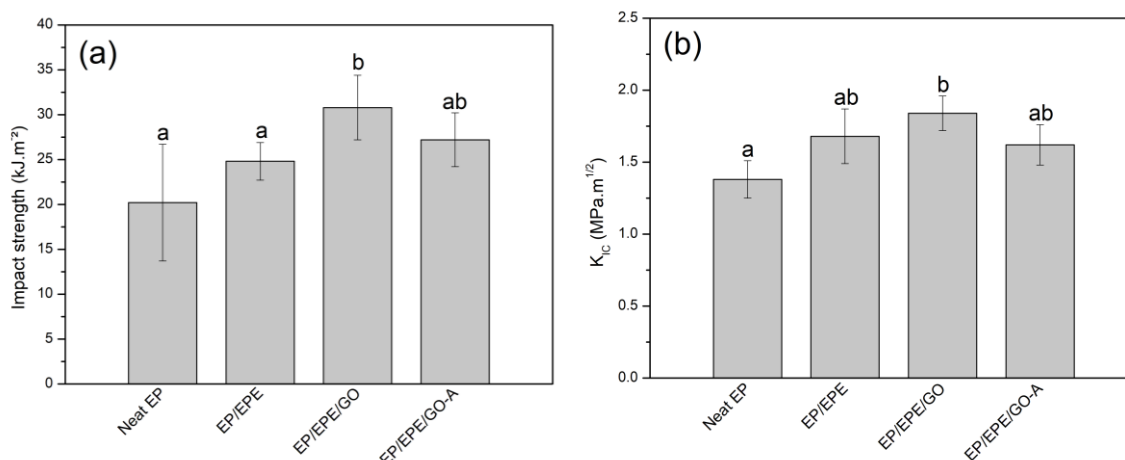


Fig 3. Impact strength (a) and plane-strain fracture toughness ( $K_{IC}$ ) (b) of the composites.

## Conclusions

The synergistic effects of EPE and GO or GO-A on the impact absorption properties of epoxy resins were evaluated. Good dispersion of both treated and untreated GO was achieved with the help of EPE. Lower rubbery modulus was found for EP/EPE/GO composites, and the glass transition temperature was maintained. Increased fracture toughness and impact strength were found for the combination of EPE and only 0.1 wt% of graphene oxide, confirming that a synergistic effect was obtained.

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