INFLUENCE OF SILANE TREATMENTS ON THE PROPERTIES OF GRAPHITE NANOPLATELET/EPOXY NANOCOMPOSITES

Alessandra Lavoratti [(1)], **Ademir J. Zattera** [(2)] **and Sandro C. Amico** [(1)]

(1) Postgraduate Program in Mining, Metallurgical and Materials Engineering (PPGE3M), Universidade Federal do Rio Grande do Sul (UFRGS), Brazil

(2) Postgraduate Program in Engineering of Processes and Technologies (PGEPROTEC), Universidade de Caxias do Sul (UCS), Brazil

Abstract
Epoxy resins are used in composite applications due to their good mechanical properties. To further enhance their performance, the use of nanofillers such as graphite nanoplatelets (GrNP) has been proposed, which can be surface treated for extra improvement. This study aims to evaluate the influence of GrNP content and treatment on the mechanical and dynamic-mechanical properties of GrNP/epoxy composites. GrNP was treated with (3-glycidyloxypropyl)trimethoxysilane and (3-aminopropyl)triethoxysilane, and later dispersed in epoxy resin aided by sonication. Composites reinforced with 0.25 wt% GrNP displayed increased tensile strength compared to the neat resin. Silane treated fillers showed an improvement in tensile strength and dynamic-mechanical properties compared to both neat resin and GrNP/epoxy composites at the same wt% of reinforcement, evidencing that the silane treatment was advantageous.

1.   INTRODUCTION

Epoxy-based materials are widely employed as coating agents, structural adhesives, in microelectronics and as matrix for composites. Improvement in mechanical and thermal properties can be achieved by incorporating a number of different fillers in epoxy resins [1]. Recently, graphitic nanofillers have been introduced as a new class of material for reinforcing epoxy resins, such as carbon nanotubes and graphene oxide. Some of the limitations of these materials include the increase in viscosity of the systems, which could render epoxy resins difficult to use in liquid moulding processes such as resin infusion and resin transfer moulding. Moreover, they are difficult to disperse and often expensive [2].

Graphite nanoplatelets (GrNP) have been suggested as promising particles for reinforcing epoxy resins. They consist on several stacked platelet-like structures with a thickness of a few nanometers and possess a good balance between mechanical and electrical characteristics due to their high surface area and platelet morphology. They have similar reinforcing potential to carbon nanotubes, for example, but with only moderate increase in viscosity of the systems, which makes them suitable for liquid moulding processes [2]. In addition, they can be functionalized with silanes to increase their compatibility with epoxy resins.

Some studies report the functionalization of carbon nanotubes and graphene oxide with (3-glycidyloxypropyl)trimethoxysilane (GPTMS) and (3-aminopropyl)triethoxysilane (APTES) [3], but few studies have addressed functionalization of GrNPs with silanes. As such, the aim of this study is to evaluate the dynamic-mechanical and tensile properties of GrNP/epoxy nanocomposites focusing on the effect of filler functionalization with silanes.

2. EXPERIMENTAL

2.1 Materials

Graphite nanoplatelets were purchased from Strem Chemicals (MA, USA). Bisphenol A diglycidyl ether (DGEBA) based epoxy resin and hardener grade HT1564/E150 were obtained from Advanced Vacuum (SP, Brazil). The resin had a viscosity of 1,200–1,400 mPa.s. GPTMS and APTES silanes were supplied by Sigma-Aldrich (MO, USA). Ethanol 99.5%, acetone and glacial acetic acid were purchased from Neon Química (SP, Brazil) and Anidrol (SP, Brazil). All reactants were used as received.

2.2 GrNP modification

GrNP (0.5 g) was dispersed into 50 mL of ethanol using a SONICS Vibracell VCX-505 (500 W) tip sonicator for 1 h, at 40% amplitude and net power output of 500 W. Hydrolysis of the silane was done using a 75:25 (v/v) ethanol:water solution. GPTMS or APTES silane (1.5 mL) was added to the solution, which was acidified with glacial acetic acid (pH 4-5). GrNP/ethanol was added to the silane and stirred for 4 h at 70 °C. Excess silane was removed by centrifugation (Novatecnica NT-820) at 4000 rpm for 5 min. The silane-functionalized GrNPs were dried in a vacuum oven for 12 h at 80 °C, and are named GrNP-G and GrNP-A after GPTMS and APTES treatment, respectively.

2.3 GrNP nanocomposites

GrNPs were studied at 0.25 wt% content. GrNPs were added to 50 mL of acetone and sonicated for 1 h in an ice bath. The acetone/GrNP suspension was added to 100 g of epoxy resin and sonicated for another hour. The mixture was magnetically stirred at 80 °C for 3 h to remove acetone. The remaining solvent was removed by placing the sample in a vacuum oven at 80 °C for 12 h. After cooling to room temperature, the hardener was added to the epoxy/GrNP mixture (15 parts of hardener to 100 parts of resin in weight). The hardener was manually mixed for 5 min and the mixture was degassed in a vacuum oven at -0.8 bar for 30 min.

The composites were casted into rubber silicone moulds, cured *in situ* for 48 h at room temperature and post-cured in an oven following 2 h at 70 °C, 2 h at 90 °C, 2 h at 120 °C and 15

h at 150 °C, according to the manufacturer's data. The composites were named after the wt% of GrNP and silane used, e.g. GrNP_0.25-G.

2.4 Characterization

X-ray diffraction (XRD) analyses were performed in a Shimazdu XRD-600 equipment (CuKα = 0.1542 nm, 30 mA, 40 kV, $2° \leq 2\theta \leq 50°$, $0.05°.2$ s−1) for GrNP powders and for the nanocomposites. Morphology of GrNPs and their composites was evaluated by field emission gun scanning electron microscopy (FEG-SEM).

Dynamic-mechanical analysis was done in a TA instruments Q800 AT equipment, with clamp single cantilever from 30 °C to 200 °C, at 3 °C.min^{-1}, frequency of 1 Hz and deformation amplitude of 0.1%.

Tensile testing was performed according to ASTM D638 with Type I test specimens in an EMIC DL-3000 (200 kgf load cell) at 1 mm.min^{-1}, with a 50 mm extensometer. Five test specimens were used in each case. One-way statistical analysis of variance (ANOVA) of the results of tensile strength, modulus and strain at break was carried out, and a significance level of $p<0.05$ was adopted.

3.   RESULTS AND DISCUSSION

The GrNPs were successfully functionalized with silanes, as demonstrated in previous studies [4]. XRD data obtained for GrNP is displayed in Figure 1 and shows a peak at $2\theta = 26.4°$, with a d-spacing of 0.3381 nm, associated with the stacked crystalline graphitic sheets. Functionalized GrNPs show a weaker and broader peak, possibly related to some intercalation of silane molecules, as reported in [3]. The crystallite size found for neat GrNP was L= 18 nm, and the calculated number of single sheets is ca. 41 layers, according to Pavoski et al. [5]. For the GrNP-G and GrNP-A, the crystallite size was smaller 15 nm, with 35 layers for both silanized GrNPs.

The peak at $2\theta = 26.4°$ is present for GrNP_0.25 sample in Figure 1b, evidencing GrNP as restacked platelets in the nanocomposites. For functionalized GrNPs at similar content (0.25 wt%) this peak disappears, perhaps due to better exfoliation of GrNP-G and GrNP-A [6].

FEG-SEM micrographs in Figure 2 show the morphology of GrNPs. Both untreated and treated fillers display small stacks within the nanometric scale. GrNP-G are seemingly more exfoliated, in agreement with XRD results, which is advantageous in terms of dispersion in the epoxy resin.
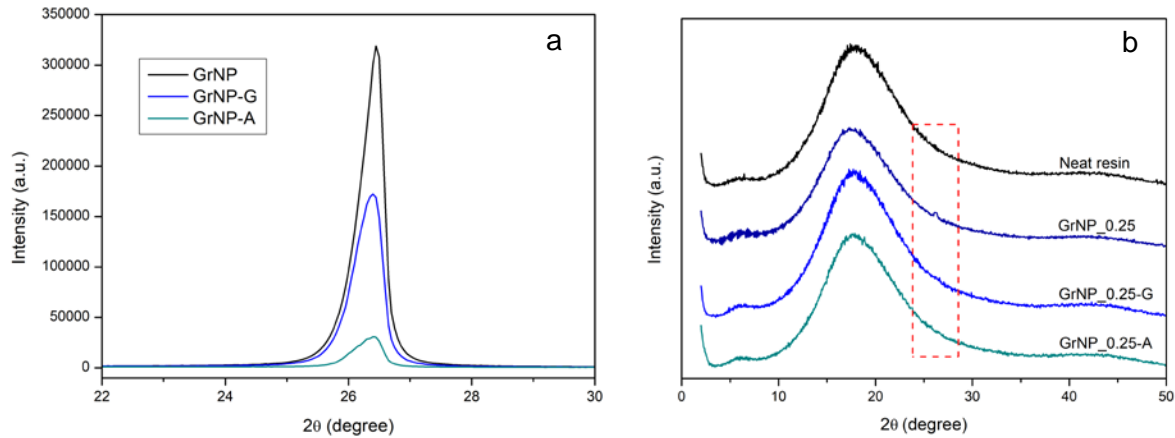
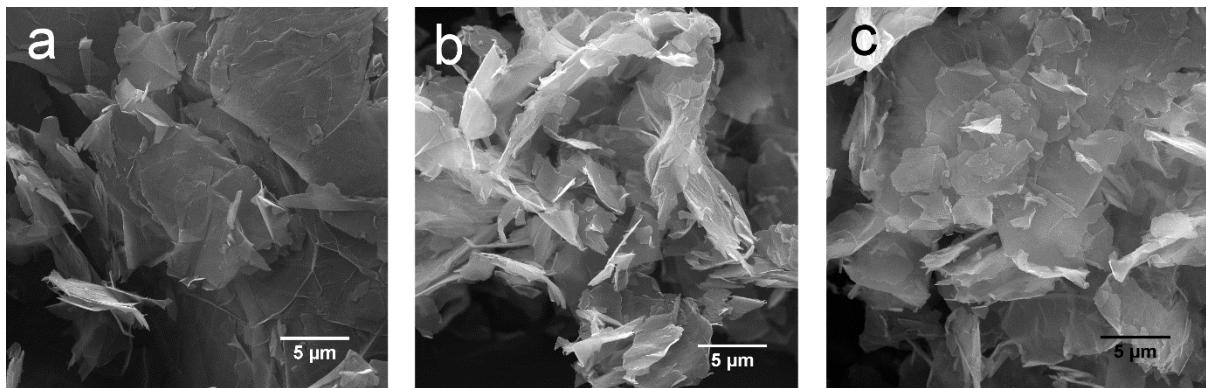Figure 1: XRD spectra of GrNP powders (a) and GrNP nanocomposites (b).

Figure 2: FEG-SEM micrographs of GrNP (a), GrNP-G (b) and GrNP-A (c) (×10.000).

The dynamic-mechanical results for neat epoxy and the nanocomposites are displayed in Figure 3. No significant difference was observed in modulus in the glassy region. But functionalization of GrNPs increased stiffness in the rubbery region, which could be an indicative of better adhesion at the interface due to the compatibility of the silanes with epoxy resin [7].
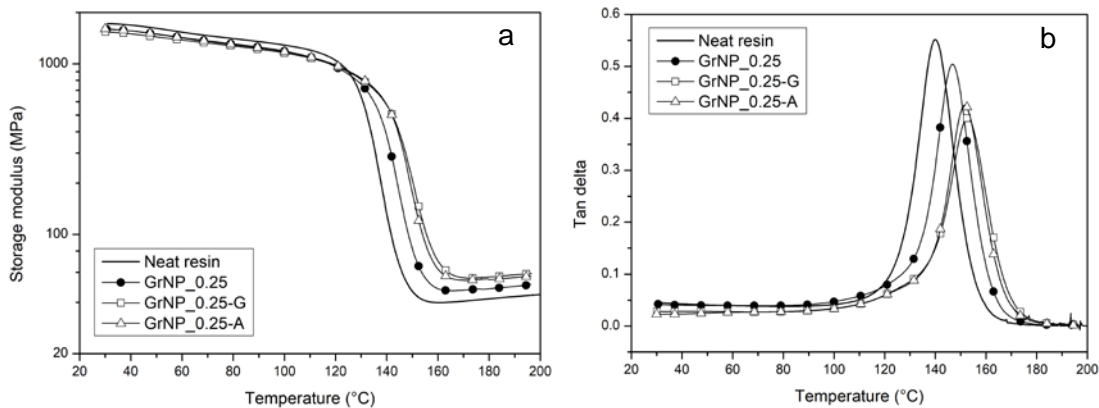

Figure 3: Storage modulus (a) and damping (tan delta) (b) of GrNP/epoxy nanocomposites.

Damping (tan delta) of the samples is shown in Figure 3b. Peak height of all nanocomposites is lower than that of the neat resin. The glass transition temperature (T_g) of the composites was 140

°C, 146 °C, 152 °C and 151 °C for the neat resin, GrNP_0.25, GrNP_0.25-G and GrNP_0.25-A, respectively. The shift to higher temperatures of the tan delta peak is related to the restriction of molecular mobility due to better adhesion [2].

The mean tensile strength, elongation at break and modulus results of the composites are listed in Table 1. Tensile strength increased with 0.25 wt% filler content, suggesting good interaction of the GrNP with the epoxy resin. An increase in tensile strength is noticed when using GrNP-G and GrNP-A compared to the GrNP_0.25. Treatment may improve stress transfer at the interface and increase interfacial area by facilitating dispersion, with a larger interfacial volume [8].

Elongation at break increased compared to the untreated GrNP, but not in relation to the neat resin considering the statistical results. Tensile modulus increased with the addition of untreated and treated fillers to the neat polymer due to the introduction of a rigid filler into the matrix. No increase in modulus can be observed within statistical significance for silanized nanocomposites. For intercalated structures, modulus increases with the degree of dispersion, exfoliation, for higher aspect ratio and larger d-spacing [9]. As such, it is possible that an optimal dispersion was not yet achieved.

Table 1: Tensile strength, elongation at break and modulus of GrNP/epoxy nanocomposites.

Sample	Tensile strength (MPa)	Elongation at break (%)	Modulus (GPa)
Neat resin	52.8 ± 4.8^a	3.88 ± 0.15^a	2.09 ± 0.19^a
GrNP_0.25	59.3 ± 2.3^b	3.35 ± 0.39^b	2.75 ± 0.21^b
GrNP_0.25-G	64.3 ± 2.5^d	4.11 ± 0.42^a	2.65 ± 0.18^b
GrNP_0.25-A	63.5 ± 2.8^d	4.44 ± 0.50^a	2.60 ± 0.28^b

The FEG-SEM micrographs from the tensile fractured composites are shown in Fig. 4. Small platelets can be seen in all samples, especially for the treated samples, which is also in agreement with XRD results. Additionally, good adhesion at the interface can be seen for the silane treated GrNPs, which corroborates the dynamic-mechanical and tensile strength results.
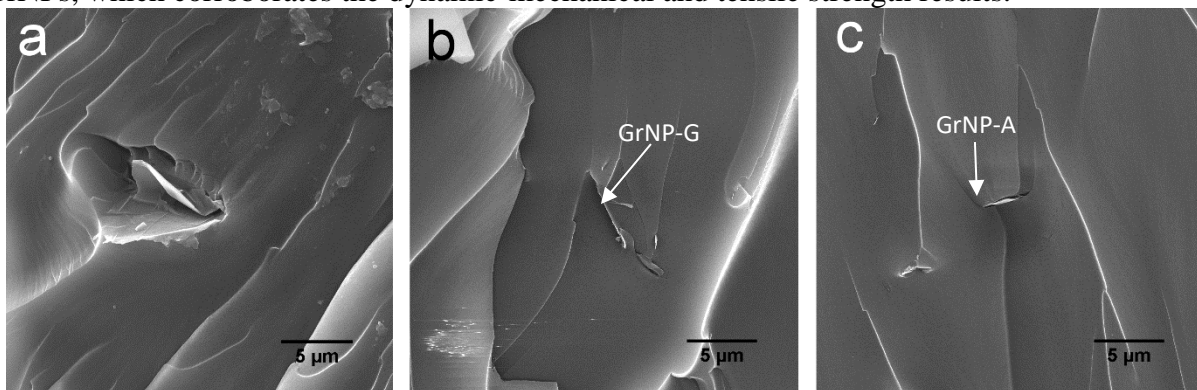

Figure 4: FEG-SEM micrographs of GrNP (a), GrNP-G (b) and GrNP-A (c) nanocomposites (×10.000).

4.   CONCLUSIONS

GrNP/epoxy nanocomposites were successfully obtained using sonication only and the silane treatment promoted better dispersion of the GrNPs in the epoxy matrix;

Addition of untreated fillers was able to increased tensile strength, but better overall mechanical and dynamic-mechanical properties were obtained only after functionalization of GrNPs.

In conclusion, the silane treatment of GrNPs was favorable. Better dispersion and better overall properties could be achieved. Nevertheless, the nanocomposites could still benefit from further improvement in processing.

ACKNOWLEDGEMENTS

REFERENCES

[1] Kang, W. S., Rhee, K. Y. and Park, S. J., 'Influence of surface energetics of graphene oxide on fracture toughness of epoxy nanocomposites', *Compos. Part. B* **114** (2017) 175-183.

[2] Prolongo, S. G., Moriche, R., Jimenez-Suárez, A., Sánchez, M. and Ureña, A., 'Advantages and disadvantages of the addition of graphene nanoplatelets to epoxy resins', *Eur. Polym. J.* **61** (2014) 206-214.

[3] Li, Z., Wang, R., Young, R. J., Deng, L., Yang, F., Hao, L., Jiao, W. and Liu, W., 'Control of the functionality of graphene oxide for its application in epoxy nanocomposites', *Polymer* **54** (2013) 6437-6446.

[4] Lavoratti, A., Zattera, A.J. and Amico, S.C., 'Modificação de nanoplaquetas de grafeno com agentes de acoplamento silano para aplicação em nanocompósitos', in '14° Congresso Brasileiro de Polímeros', Águas de Lindóia, September, 2017.

[5] Pavoski, G., Maraschin, T., Fim, F. C., Balzaretti, N. M., Galland, G. B., Moura, C. S. and Basso, N. R. S., 'Few Layer Reduced Graphene Oxide: Evaluation of the Best Experimental Conditions for Easy Production', *Mater. Res.* **20** (2017) 53-61.

[6] Zhang. Y., Wang, Y., Yu, J., Chen, L., Zhu, J. and Hu, Z., 'Tuning the interface of graphene platelets/epoxy composites by the covalent grafting of polybenzimidazole', *Polymer* **55** (2014) 4990-5000.

[7] Jabbar, A., Militký, J., Wiener, J., Kale, B. M., Ali, U. and Rwawiire, S., 'Nanocellulose coated woven jute/green epoxy composites: Characterization of mechanical and dynamic mechanical behavior', *Compos. Struct.* **161** (2017) 340-349.

[8] Wan, Y. J., Tang, L. C., Gong, L. X., Yan, D., Li, Y. B., Wu, L. B., Jiang, J. X. and Lai, G. Q., 'Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties', *Carbon* **69** (2014) 467-480.

[9] Azeez, A. A., Rhee, K. Y., Park, S. J. and Hui, D., 'Epoxy clay nanocomposites – processing, properties and applications: A review', *Compos. Part. B.* **45** (2013) 308-320.