

GRAPHENE OXIDE REINFORCED BIO-EPOXY POLYMERS

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Abstract— The majority of epoxy/graphene oxide (GO) composite studies have been conducted on synthetic epoxies. This work presents the results on GO filler loadings of 0.1, 0.2 and 0.3 wt. % to a green bio-epoxy polymer. GO was synthesized from oxidation of graphite flakes. The epoxy/GO composites were prepared using a solution mixing route. Scanning electron microscopy (SEM) was used to examine the graphite and GO powder morphology and composite fractured surfaces. Fourier transform infrared (FTIR) spectroscopy was used to identify functional groups on the produced GO material. Tensile strength of pure and modified bio-epoxy composites was evaluated. SEM showed differences in fractured surfaces which implies the GO material was able to modify the bio-epoxy polymer. The FTIR results confirmed oxidation of the graphite was successful. The tensile strength and modulus improved by 23 % and 35 %, respectively as compared to the pure bio-epoxy with only 0.3 wt. % GO filler. Additions of GO to bio-epoxy revealed a significant enhancement in tensile strength and stiffness could be achieved with considerable lower filler loadings than traditional fillers.

Keywords-*graphene oxide; bio-epoxy; composite; mechanical properties*

I. INTRODUCTION

Synthetic epoxy polymers are used in a number of industries such as aerospace, automotive and consumer products due to their lightweight, corrosion and chemical resistance. Cured epoxy composites tend to be brittle and have low impact strengths which can have limitations on certain applications. Fillers are added to polymers to reduce component costs. Mineral fillers in thermoset polymers help to improve impact toughness, modulus and hardness of the

composites. However, these fillers tend to decrease the tensile strengths of the polymer composites. It has been reported much less graphene oxide (GO) fillers are required compared to traditional fillers to improve mechanical properties [1].

Graphite, a carbon based three-dimensional crystalline material was discovered by KW Scheele in 1779. Each layer of carbon atoms are covalently bonded, while the bonding between the layers or sheet are weakly bonded with Van der Waals bonds [2]. By exfoliating the sheets of graphite, graphene a two-dimensional material is formed. Graphene was discovered in 2004 and is defined as a single flat sheet of graphite where its carbon atoms are arranged in a hexagon structure [3]. Although studies have shown graphene can improve properties of polymer composites, graphene has a smooth, non-reactive surface which prevents a good bond to form, limiting the load transfer from the polymer matrix to the graphene sheets [4]. Compared to graphene, GO obtained from oxidizing graphite contains a number of GO sheets stacked on top of each other. The GO sheet can be exfoliated into single sheets by sonication in water, solvents and polymers. The advantage of using GO in polymers is the presence of functional groups on the surface and edges of the GO sheets. Significant improvements in mechanical properties can be obtained by adding GO to epoxy resin. For example, when GO was added to a synthetic epoxy in loadings of 0.1 wt. %, 0.2 wt. % and 0.5 wt. %, tensile strength improved by 7 %, 9 % and 11%, respectively and tensile modulus increased by 8 %, 20 % and 24 %, respectively [1].

This study investigates the mechanical tensile strength of a green bio-epoxy composite containing GO fillers in loadings of 0.1-0.3 wt. %. The aim of the work was to evaluate the morphology of the GO filler and fractured surfaces of the

modified and unmodified composites and verify appropriate oxidation of the graphite. The initial results of this work are provided.

II. EXPERIMENTAL

A. Materials

Super Sap CPM/CPL a bio-based epoxy was purchased from Entropy Resins Inc., San Antonio, USA. The resin was mixed with a ratio of 10:4 by weight, bio-epoxy to hardener. Natural graphite flakes, -325 mesh (44 μ m), 99.8% (metals basis) were provided by Alfa Aesar Thermo Fisher Scientific.

B. Graphene Oxide Preparation

GO was prepared according to the modified Hummer's method which oxidizes graphite using sulfuric acid, sodium nitrate and potassium permanganate. The solution was purified with multiple rinsing using millipore water, 30 % hydrochloric acid and ethanol until a pH of \sim 7 was reached. The product was finally vacuum dried at 40 $^{\circ}$ C for 12 hours to produce a GO film. The film was then made into powder using a mortar and pestle.

C. GO/Epoxy Resin Composite Preparation

The GO powder was added to acetone in separate batches in weight fractions of 0.1 wt. %, 0.2 wt. % and 0.3 wt. %. The GO powder was homogeneously dispersed and exfoliated in acetone by sonication for 1 h. The GO/acetone mixture was added to the bio-epoxy resin and mechanically stirred for another 1 h. The resin was placed in an oven at 40 $^{\circ}$ C under vacuum overnight to evaporate the acetone. The hardener was added and mechanically stirred for 10 min. followed by vacuum degassing at room temperature for 30 min. The mixture was then poured into silicone molds and cured for 24 h at room temperature followed by a post-cure at 82 $^{\circ}$ C for 1h. Tensile specimens are shown in Fig.1.

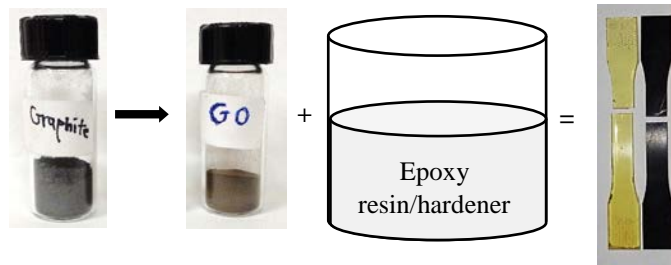


Figure 1. Schematic route for preparation of epoxy and epoxy/GO composites.

D. Measurements and Characterization

Graphite and GO powder morphology and tensile fractured surfaces were observed by scanning electron microscopy (SEM) using a JEOL JSM-6010 LV (Tokyo, Japan) operated at 10-15 kV. The samples were coated with a thin layer of gold. Fourier transform infrared (FTIR) spectroscopy was performed on as received graphite and as synthesized GO. The FTIR spectra were conducted on a Bio-Rad FTS-40

spectrophotometer. The spectra for each analysis was obtain in reflectance mode with a resolution of 4 cm^{-1} over the spectral range between 500 and 4000 cm^{-1} . The samples were made into powdered form and compressed into tablets of KBr in a weight ratio of 1:10 (sample powder: KBr). Tensile strength tests were conducted using an Instron 1137 universal testing machine with a 10 kN load cell. Tensile strength was evaluated at a strain rate of 5 mm/min according to ASTM D638-14 on dog-bone specimens measuring 165 x 13.0 x 3.3 mm^3 (l x w x t). Five specimens were tested for each composite and averaged.

III. RESULTS AND DISCUSSION

A. Scanning Electron Microscopy Analysis

The different morphologies of the starting graphite and synthesized GO sheets are shown in Fig. 2. The majority of natural graphite has a flake-like structure, with some having smooth, rounded edges stacked together forming solid dispersed materials as shown in Fig. 2 (a). The graphite flakes also show a flat plate-like morphology with sizes less than 44 μ m and thicknesses of several micrometers. After chemical oxidation, the GO material has an irregular, layered, plate-like structure as shown in Fig. 2 (b). The flakes appear to be thinner with fewer layers than the initial graphite flakes possibly due to exfoliation from the sonication process.

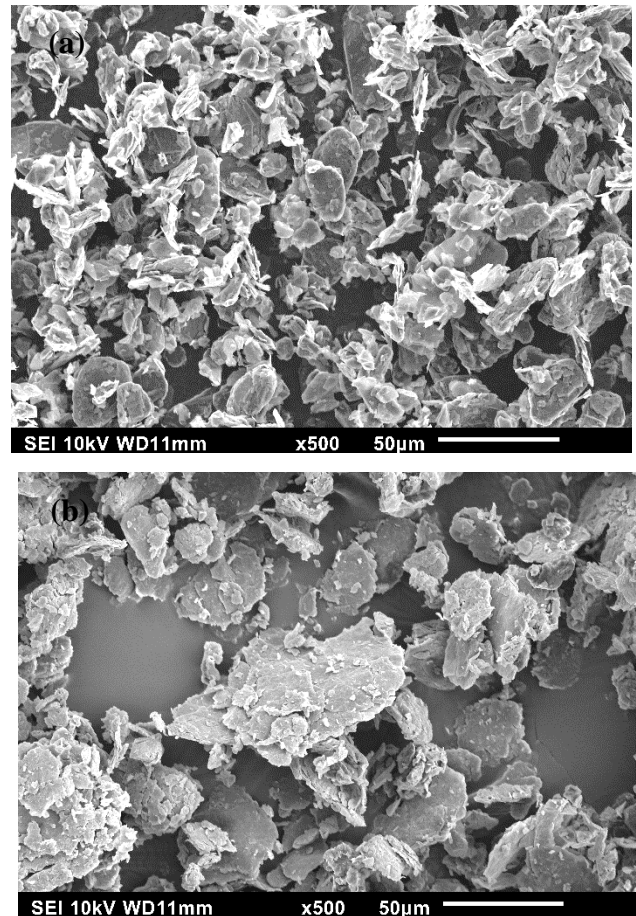


Figure 2. SEM image of (a) graphite powder and (b) GO powder.

The SEM images of the fractured tensile surfaces are shown in Fig. 3. Pure epoxy is shown in Fig. 3 (a) with its typical smooth plate-like featureless surface. Some cracks are present indicating brittle fracture (low ductility). With the addition of 0.3 wt. % GO reinforcement into the bio-epoxy polymer, the fractured surface becomes altered as shown in Fig. 3 (b). The surface appears to be rougher and more irregular with smaller failure surfaces. The image shows additional white regions which exhibits a more ductile fracture. The dispersion and possible agglomeration of GO sheets in the bio-epoxy matrix are difficult to visualize using SEM. One proposed method would be to etch the composite in sulfuric acid to reveal the GO sheets and their locations [6].

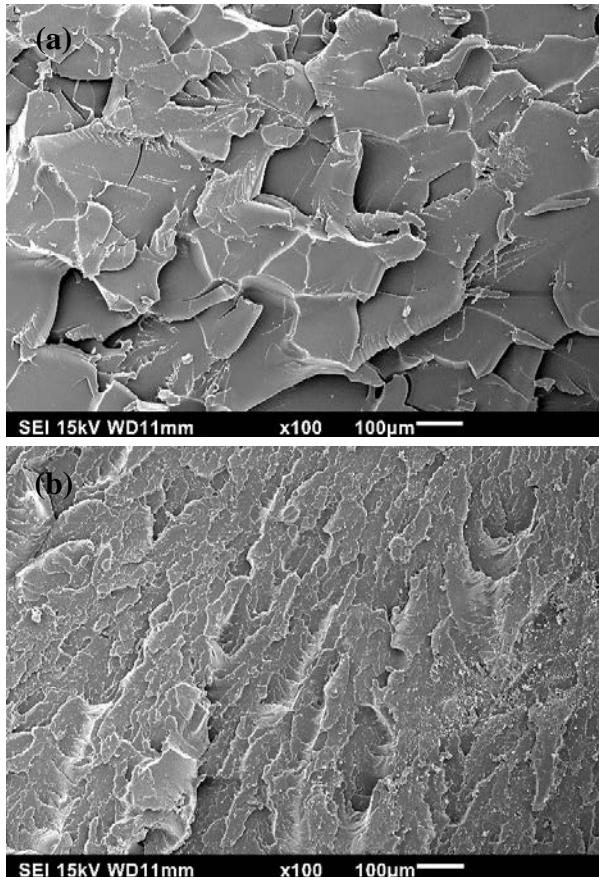


Figure 3. SEM images of fractured tensile surfaces of (a) pure epoxy and (b) epoxy/0.3 wt. % GO composite.

B. FTIR Analysis

FTIR tests were carried to confirm successful oxidation of graphite as shown in Fig. 4. Natural graphite powder did not show any significant peaks. In contrast, GO contains different functional groups as observed by characteristic feature peaks in the FTIR spectrum. A broad peak at 3400-3600 cm^{-1} signifies O-H stretching vibration of the hydroxyl groups [1] and water absorption at 3200 cm^{-1} [5]. The absorption peak at 1720-1732 cm^{-1} is attributed to stretching vibration of the carbonyl (C=O)/carboxyl (COOH) groups [1, 5]. The peak at 1620-1622 cm^{-1} is attributed to the vibration of adsorbed water and vibrations from skeletal un-oxidized graphitic domain

(some regions did not oxidize) which can be assigned to the aromatic C=C bonds [5]. The 1200-1237 cm^{-1} peak is the C-OH stretching from carboxylic groups [5], while the peak at 1050-1057 cm^{-1} is attributed to the skeletal C-O or C-C stretching from carbonyl, carboxylic and epoxy groups [5]. FTIR confirmed GO was successfully synthesized based on the presence of the oxygen-containing functional groups (O-H, C=O, COOH, C-OH and C-O).

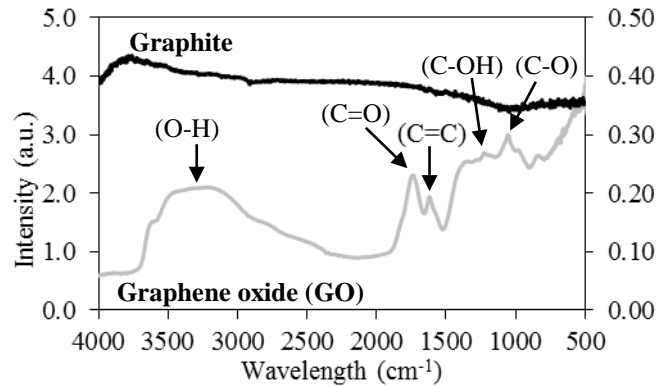
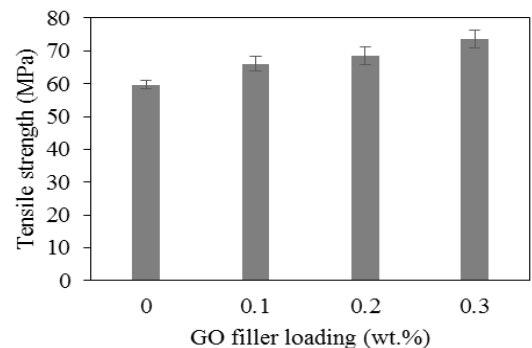


Figure 4. FTIR results for graphite (left scale) and graphene oxide (right scale).

C. Mechanical Properties

When GO was mixed into the bio-epoxy, the composites turned black in color as shown in Fig.1. This occurred for all bio-epoxy/GO composite loadings, even with 0.1 wt. % GO. This change in color was also observed for epoxy composites containing 0.5-2 wt. % GO and was attributed to the addition of the GO material [6].

The tensile strength and modulus results are shown in Fig. 5 with error bars representing the standard deviations. The pure bio-epoxy had a tensile strength and modulus of 59.68 MPa and 2.6 GPa, respectively. The composites showed an improvement compared to the pure bio-epoxy for all GO filler loadings. The most significant improvement was at a loading of 0.3 wt.% GO where the tensile strength and modulus reached 73.55 MPa and 3.5 GPa, respectively which are increases of 23 % and 35 %. The large surface area and functional groups on the surface and edges of the GO sheets have an affinity to the bio-epoxy matrix [7]. This improved interaction translates to a strong interfacial adhesion and load transfer between the matrix and the GO reinforcements.



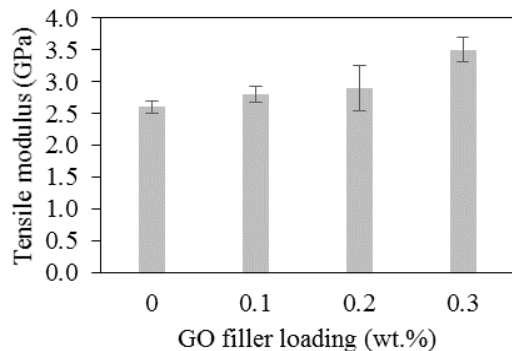


Figure 5. Tensile strengths and tensile modulus results for pure epoxy and epoxy/GO composites.

IV. CONCLUSION

Epoxy/GO composites have successfully been produced using a simple solution mixing method. SEM showed the fractured surfaces of the tensile samples were altered from the addition of GO. FTIR verified the presence of oxygen based functional groups on the surface of the GO material and confirmed successful oxidation of graphite using the modified Hummer's method. Both tensile strength and tensile modulus showed a steady increase with the addition of GO. With a 0.3 wt. % loading, the tensile strength improved by 23 % whereas the modulus increased by 35 % over the pure bio-epoxy. Therefore, a reinforcing effect has been observed with the addition of very small amounts of synthesized GO material. Based on the results, adding GO to a green bio-epoxy polymer is seen as a positive approach to enhance its tensile strength properties much more than traditional fillers of the same weight percentages. This composite would be able to compete in industries where synthetic epoxies are currently used.

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REFERENCES

- [1] L. Zheng, R. J. Young, R. Wang, F. Yang, L. Hao, W. Jiao, and W. Liu, "The role of functional groups on graphene oxide in epoxy nanocomposites," *Polymer* vol. 54, no. 21, pp. 5821-5829, 2013.
- [2] J. C. Charlier, X. Gonze, and J.P. Michenaud, "Graphite interplanar bonding: electronic delocalization and van der Waals interaction," *Europhys. Lett.*, vol. 28, no. 6, pp. 403-408, 1994.
- [3] A. Imran, O. M. L. Alharbi, A. Tkachev, E. Galunin, A. Burakov, and V. A. Grachev, "Water treatment by new-generation graphene materials: hope for bright future," *Environ. Sci. Pollut. Res.*, pp. 1-15, 2018.
- [4] J. L. Yan, G. J. Chen, C. A. O. Jun, Y. Wei, B. H. Xie, and M. B. Yang, "Functionalized graphene oxide with ethylenediamine and 1, 6-hexanediamine," *New Carbon Mater.*, vol. 27, no. 5, pp. 370-376, 2012.
- [5] G. Dilini, M. Wang, G. George, N. Motta, E. Waclawik, and C. Yan, "Preparation of graphene oxide/epoxy nanocomposites with significantly improved mechanical properties," *J. Appl. Phys.*, vol. 116, no. 5, pp.1-10, 2014.

- [6] X. Weiwei, Y. Liu, and S. Guo, "Composites of graphene oxide and epoxy resin assuming a uniform 3D graphene oxide network structure," *RSC Adv.*, vol. 6, no. 90, pp. 86904-86908, 2016.
- [7] C. Sanjukta, J. W. Wang, W. S. Kuo, N. H. Tai, C. Salzmann, W. L. Li, R. Hollertz, F. A. Nüesch, and B. T. T. Chu, "Mechanical reinforcement and thermal conductivity in expanded graphene nanoplatelets reinforced epoxy composites," *Chem. Phys. Lett.*, vol. 531, pp 6-10, 2012