



## Fabrication and Characterization of a Polymer Matrix Composite Reinforced with Graphene Oxide for Electronic Packaging

W. Navas<sup>1</sup>, D. Cree<sup>1\*</sup>, and L. Wilson<sup>2</sup>

<sup>1</sup>Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

<sup>2</sup>Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

\* Corresponding author (duncan.cree@usask.ca)

### ABSTRACT

Most of the epoxy/graphene oxide (GO) composite studies have been conducted to determine the improvement on mechanical properties. The use of this material in electronic packaging also requires a knowledge of the composite thermal properties. GO produced in the laboratory was used as reinforcement (0.1-0.5 wt. %) in a bio-epoxy polymer. GO oxidation state, particle size and morphology, as well as mechanical (tensile and flexure) and thermal conductivity were evaluated. The oxidation state of GO was analyzed using Fourier Transform Infrared (FTIR) spectroscopy. FTIR indicated successful synthesis of GO from graphite flakes due to the presence of different functional groups attached. The mechanical properties were found to improve with the addition of low amounts of GO fillers compared to the pure bio-epoxy, while the thermal conductivity did not significantly vary with filler loading. Improvements in properties were achieved with considerably lower filler loadings than customary fillers. Further work is underway to determine the possibility of this composite material for use in electronic packaging.

**KEYWORDS:** graphene oxide, epoxy resin, characterization, mechanical properties, thermal conductivity

### 1 INTRODUCTION

The efficiency at which an electronic system functions not only depends on its electrical design and reliability, it is also determined by its packaging materials (Petch et al., 1999). Electronic packaging can be defined as the material enclosing an electronic element to provide mechanical protection, reduce or eliminate electromagnetic interference and ease heat dissipation (Chung, 1995). Traditionally, epoxy resins and other thermoset polymers have been widely used in this area because of their acceptable properties (Petch et al. 1999). As a result of the technological developments in this field of engineering, the mentioned conventional materials have been gradually replaced by composite materials due to the different advantages these types of materials possess in comparison to conventional materials (Jones, 1999). In the past few years, graphene oxide (GO) has caught attention within the scientific community. Several studies demonstrated by the addition of low amounts of this carbon-based material led to significant increments in mechanical properties of the resultant composite in comparison to the pure matrix (Tang et al., 2014; Galpaya et al., 2014; Liu et al., 2012). Additionally, GO offered a suitable dispersion capability in the matrix due to the different functional groups attached (Tang et al., 2014).

In this study, GO/epoxy composite materials were developed at different weight percentages of fillers. Tensile, flexural and thermal conductivity tests were performed on the obtained composites to

evaluate their mechanical and thermal properties. GO was synthesized using a modified Hummer's method and Fourier Transform Infrared (FTIR) spectroscopy was used to determine the oxidation of the graphite flakes. In addition, scanning electron microscopy (SEM) was used to observe the graphite and GO morphology and the fractured surfaces obtained from the tensile tests.

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Materials

Super Sap CPM/CPL, an epoxy resin containing bio-renewable sourced materials was acquired from Entropy Resins Inc. The composite fabrication process used a mix ratio of 100:40 by weight, epoxy to hardener. For the GO synthesis process, natural graphite flakes, 325 mesh ( $< 44\mu\text{m}$ ), 99.8% (metals basis) were acquired from Alfa Aesar (Thermo Fisher Scientific). The silicone rubber molds were fabricated using Mold Max 10T, a translucent condensation cure silicone rubber compound purchased from Smooth-On Inc., with a mix ratio of 100:10 by weight, part A to part B.

### 2.2 Graphene Oxide Synthesis

GO was synthesized through a Modified Hummer's Method starting from graphite flakes (Hummers and Offeman, 1958). For every batch of graphene oxide, 5 g of graphite flakes, 2.5 g of sodium nitrate ( $\text{NaNO}_3$ ) and 115 ml of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were added to a beaker and stirred for 45 minutes. Next, the solution was transferred to an ice bath and stirred for another 30 minutes. Then, 15 g of potassium permanganate ( $\text{KMnO}_4$ ) were slowly added. Thereupon, the solution was removed from the ice bath being careful to keep its temperature under  $20^\circ\text{C}$ . The solution was then transferred to a medium temperature bath (approximately  $35^\circ\text{C}$ ) and 230 ml of deionized water was added dropwise. After the water was completely added, the solution was transferred to an oil bath with a temperature of  $98^\circ\text{C}$  and stirred for additional 20 minutes. Subsequently, 400 ml of deionized water were added, until the solution turned to a light brown color and stirred for an additional 20 minutes. Finally, 50 ml of oxygen peroxide ( $\text{H}_2\text{O}_2$ ) were added to the solution.

After the synthesis was performed, a purification process was developed to obtain GO with an adequate purity. This technique consisted of different stirring and decantation processes after adding deionized water, hydrochloric acid (HCl) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in subsequent washes. When the purification process was completed, the solution was poured onto a flat surface and dried in a vacuum furnace at  $40^\circ\text{C}$ . Finally, the dried GO was grinded manually using a mortar and pestle.

### 2.3 Composite Preparation

GO powder was added to acetone and exfoliated through ultrasonic sonication for one hour, constantly verifying the temperature of the solution. This method was used to separate the different layers of GO that are stacked in a single layer. After this process, a CPM epoxy resin amount was added to the GO/acetone mixture, as shown in Table 1, and stirred mechanically for 30 minutes.

Table 1 Filler weight percentage in GO/epoxy composites

Graphene oxide (wt. %)	CPM epoxy (wt. %)	CPL hardener (wt. %)
0.0	71.5	28.5
0.1	71.4	28.5
0.3	71.2	28.5
0.5	71.0	28.5

The solution was placed under vacuum at a temperature of 60°C to allow the acetone to evaporate for approximately 12 hours. Once the acetone was evaporated, the solution was cooled down to room temperature for 5 hours. The CPL hardener was then added, and the solution was mechanically stirred for 10 minutes and vacuum degassed at a pressure of 71.1 cm Hg (28 in. Hg) for 30 minutes to remove air bubbles in the composite. The degassed solution was slowly poured into silicon molds casted in geometries according to ASTM standards as shown in Table 2. The molded composite specimens were cured at room temperature for 24 hours and then post-cured for 1 hour at 82°C.

## 2.4 Characterization

A JEOL JSM-6010 LV scanning electron microscope operated with an acceleration voltage of 10 kV was used to observe the graphite and GO morphology and tensile fractured surfaces. For this, the samples received a gold coating layer. The tensile specimens were tested using an Instron 600LX universal testing machine with a strain rate of 5 mm/min as the ASTM D638-14 standard suggested. The bending specimens were tested using an Instron 1137 universal testing machine with a crosshead speed of 2 mm/min. The support span length was 60 mm to procure a span-to depth ratio of at least 16:1. The thermal conductivity specimens were tested using a LaserComp Fox 314 heat flow meter. For this purpose, the upper plate was set to a temperature of 10 °C and the lower plate temperature was set to 35°C in order to have a 25°C temperature difference across the sample. Five specimens were tested of every weight percentage and an average value was reported.

Table 2 ASTM standards and specimen dimensions for the tests

<b>Mechanical or thermal property</b>	<b>ASTM Standard</b>	<b>Specimen dimension</b>
Tensile	D638-14	Dog bone shape samples. Length overall: 165 mm. Width overall: 19 mm. Width of narrow section: 13 mm. Length of narrow section: 57 mm. Radius of fillet: 76 mm. Thickness: 3.2 mm.
Flexural	D790-17	Width: 12.7 mm. Thickness: 3.2 mm. Length: 127 mm. Support span-to-depth ratio of 16:1.
Thermal conductivity	C518-17	Square cross-section specimen: 50.8 mm x 50.8 mm. Thickness: 25.4 mm.

## 3 RESULTS AND DISCUSSION

### 3.1 Scanning Electron Microscopy

The SEM micrographs of the natural pristine graphite powder are shown in Figure 1 (a) and the synthesised GO through modified Hummer’s method in Figure 1 (b). The graphite powders appear as solid particles with round edges and smooth surfaces. For GO powders, the material shows particles with

irregular shapes and surfaces. Also, GO present some particles consisting of single sheets and several sheets stacked on top of each other.

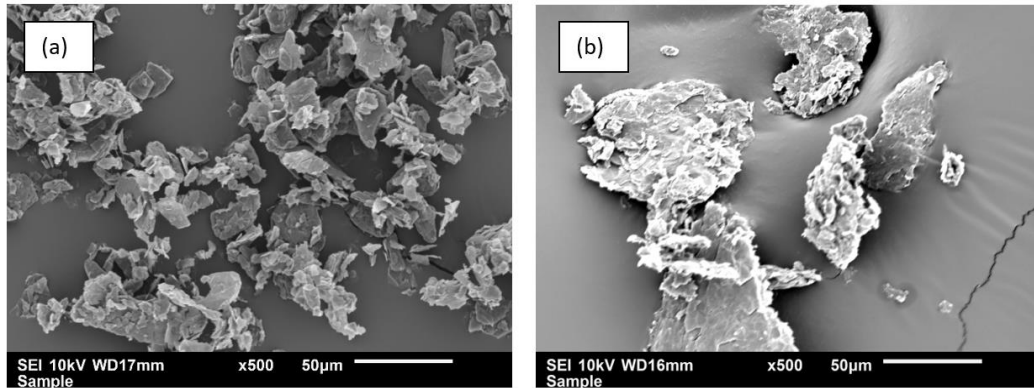


Figure 1: SEM images of (a) graphite powder and (b) GO powder

Figure 2 shows the typical tensile fractured surfaces of a pure epoxy specimen (Figure 2 (a)) and an epoxy/0.3 wt. % GO composite specimen (Figure 2 (b)). In Figure 2 (a) a smooth surface can be observed which is commonly found in epoxy made parts. The smooth surface indicates a crack initiation and propagation stage was absent, a phenomenon consistent with a brittle fracture. As observed in Figure 2 (b) the fractured surface and mechanism has been modified. A rougher surface with smaller fractured regions can be identified as a crack front pinning mechanism (Yasmin and Isaac, 2004; Li et al., 2013; Ramadan et al., 2017).

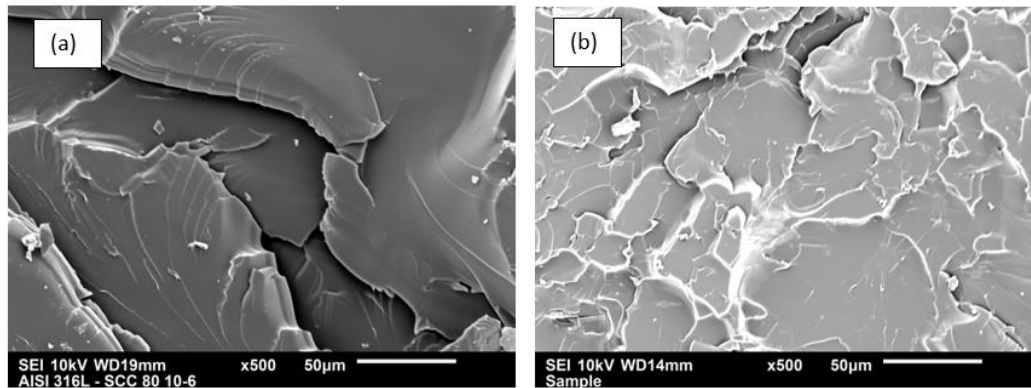


Figure 2: SEM images of typical fractured tensile samples of (a) pure epoxy specimen and (b) epoxy/0.3 wt. % GO

### 3.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR tests were performed to determine if the GO synthesis process was successful. The results obtained from both batches (1<sup>st</sup> and 2<sup>nd</sup> batch) of GO produced was compared to a graphite powder FTIR test. Figure 3 shows pure graphite did not show any peaks at any wavelength due it being an amorphous material. For both GO synthesized processes, several peaks can be observed confirming the presence of its functional groups attached. A wide peak is present in the range of 3400-3600  $\text{cm}^{-1}$  corresponding to O-H group (Li et al., 2013). The peak present at approximately 1700  $\text{cm}^{-1}$  corresponds to the carbonyl group (C=O), while the peak at approximately 1600  $\text{cm}^{-1}$  is attributed to C=C bonds. The peak at approximately 1200  $\text{cm}^{-1}$  matches the presence of a skeletal group (C-O-C) (Li et al., 2013).

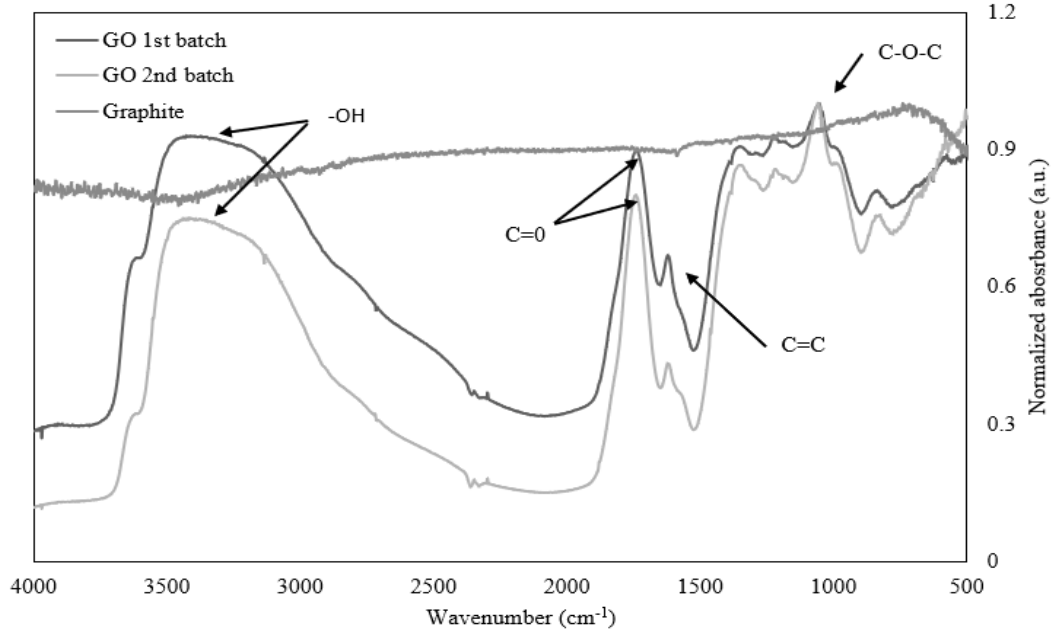


Figure 3: FTIR results for graphite and synthesized GO

### 3.3 Mechanical Properties

The tensile properties obtained for the epoxy/GO composites are presented in Figure 4. An improvement in tensile strength and tensile modulus was observed at all weight percentages (0.1, 0.3 and 0.5) of filler loadings as shown in Figure 4 (a) and Figure (b), respectively when compared to the properties obtained from pure epoxy samples. This increment can be attributed to a well dispersed GO reinforcement in the epoxy matrix. The tensile strength and tensile modulus for pure epoxy was determined to be  $63.37 \pm 3.1$  MPa and  $2.74 \pm 0.14$  GPa, respectively. The composites including 0.1, 0.3 and 0.5 wt. % improved in tensile strength by 8.75, 14.84 and 4.34 %, respectively. For the same composites, the tensile modulus improved by 4.08, 13.20 and 5.18 %, respectively.

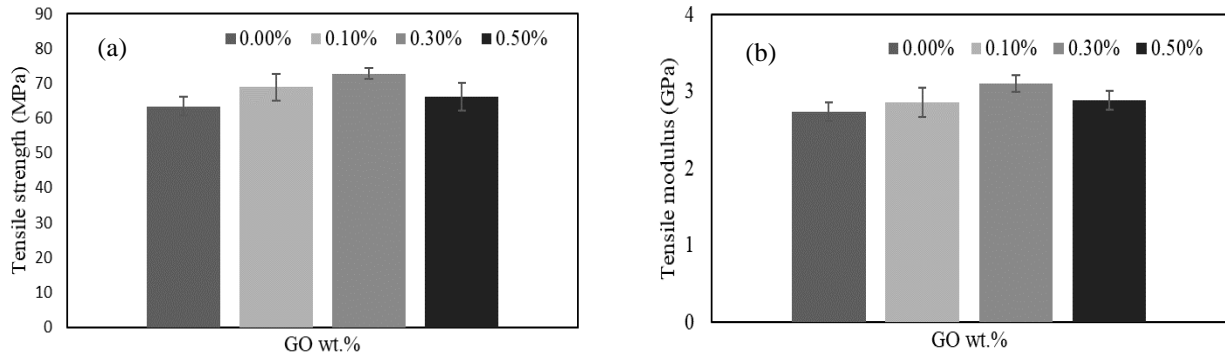


Figure 4: Tensile properties for epoxy/GO composites containing different amounts of filler loadings for (a) tensile strength and (b) tensile modulus

The flexural properties obtained for the epoxy/GO composites are presented in Figure 5. An improvement was observed for all weight percentages (0.1, 0.3 and 0.5 wt. %) for the flexural modulus when compared to the properties obtained from pure epoxy samples. However, for the flexural strength, an improvement was observed for two weight percentages (e.g. 0.1 and 0.3 wt. %), but had a slight decrease when 0.5 wt. % GO was added. As in the tensile tests, this increment can be attributed to a well dispersed GO reinforcement in the epoxy matrix. While the reduction in flexural strength for the last weight percentage can be attributed to the toughness that GO addition can cause to the epoxy resin (Tang et al., 2014). The flexural strength and flexural modulus for pure epoxy was determined to be  $95.33 \pm 2.6$  MPa and  $2.53 \pm 0.15$  GPa, respectively. The composites with 0.1 and 0.3 wt. % of GO improved in flexural strength by 6.17 and 12.58 %, respectively, but decreased by 0.67 % with the addition of 0.5 wt. % compared to pure epoxy. Similarly, the flexural modulus improved by 15.42, 32.03 and 15.65 %, respectively.

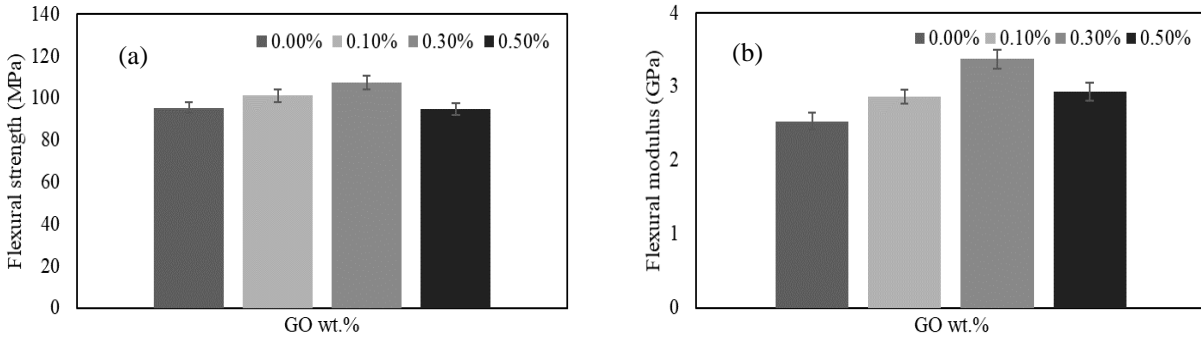


Figure 5: Flexural properties for epoxy/GO composites containing different amounts of filler loadings for (a) flexural strength and (b) flexural modulus

### 3.4 Thermal Conductivity

The thermal conductivity obtained for the epoxy/GO composites are presented in Figure 6. The thermal conductivity of the pure epoxy was not significantly affected with the addition of 0.1, 0.3 and 0.5 wt. % GO. A clear trend was not observed to determine if the addition of GO to pure epoxy can improve or reduce the material's thermal conductivity. The thermal conductivity for pure epoxy was determined to be  $0.050917 \pm 0.000295$  W/mK. The composites including 0.1, 0.3 and 0.5 wt. % had thermal conductivity reduced by 2.31 %, increased by 0.35 % and reduced by 0.29 %, respectively. Due to the high thermal conductivity that carbon presents (Web-1), an epoxy/GO composite material should have its thermal conductivity improved which could lead to a better heat dissipation in an integrated circuit.

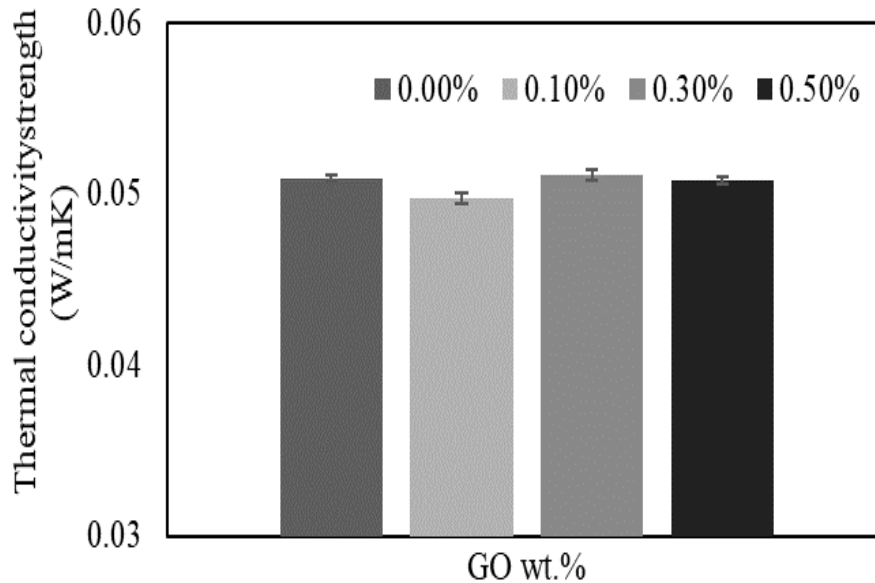


Figure 6: Thermal conductivity for epoxy/GO composites for different amounts of filler loadings

#### 4 CONCLUSION

In this research, epoxy/GO composites offered improved tensile and flexural properties when small amounts of reinforcement ( $\leq 0.5$  wt. %) were added to the epoxy resin matrix. The maximum improvement was obtained with 0.3 wt. % of GO. FTIR spectroscopy identified the synthesized GO was adequate to act as a particle reinforcement due to the presence of functional groups. The thermal conductivity did not show a clear pattern despite the addition of different weight percentages of GO which could be attributed to the significantly low amount of GO in the matrix. Additional work is required to determine the amount of GO required to change the thermal conductivity for use in electronic packaging.

#### 5 ACKNOWLEDGEMENTS

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Web-1: <https://phys.org/news/2013-07-competitor-diamond-thermal-conductor.html>, consulted 20 April 2019.