

## **The effect of graphene oxide (GO) nanoparticles on processing of epoxy/glass fiber composites using resin infusion**

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### **Abstract:**

In this paper, the effects of graphene oxide (GO) nanoparticles on glass fiber composite processing by incorporating them into epoxy resin were investigated. GO was synthesized from graphite powder, and was mixed with epoxy resin. Three different GO contents of 0.05, 0.1 and 0.2 wt% were used. Epoxy/GO samples were tested for rheology and cure kinetics to evaluate the effects of GO content on important resin infusion processing parameters. The results show that adding GO to neat epoxy resin increased the viscosity and affected the resin cure reaction by reducing the resin gel time. After that, glass fiber composites were prepared using the resin infusion process. Samples with 0.2 wt% GO result in very slow resin infiltration time with premature resin gelation. 30% increase in flexural strength and 21% increase in flexural modulus are manifested by adding GO as the secondary reinforcement to glass fiber composites.

**Keywords:** Nanocomposites, Resin Flow, Resin infusion, Hierarchical composites

## **1.0 Introduction:**

In recent years, the rapid development of nano-technology and nano-science in automotive, biomedical and aerospace applications can produce materials with properties that are unachievable by traditional means. Recently, graphene, a two-dimensional, single-atom-thick structure of  $sp^2$ -bonded carbon atoms, has attracted tremendous research attention due to its high specific area and unique mechanical, electrical, and thermal properties [1, 2]. Since its discovery, the research community has shown great interest in this novel material due to its multifunctional properties. Accordingly, graphene has been used for research in developing electrodes, sensors, energy storing devices, solar cells, etc. Benefiting from its size and relatively large surface area, graphene sheets or platelets may serve as fillers for the enhancement of electrical and mechanical properties of composite materials. Hierarchical nanocomposites have demonstrated great potential to become next generation multifunctional structural materials [3-7]. Significant improvements in strength, fracture toughness and fatigue strength have been reported using graphene as fillers or reinforcements in nanocomposites [2-5]. Furthermore, the production cost of graphene can be much lower than that of carbon nanotubes (CNTs), one of popular nano-reinforcements in composite materials.

In the past few years, several methods, such as micromechanical exfoliation, chemical vapor deposition [8], chemical reduction of graphene oxide (GO) [9, 10], have been employed to prepare single or multi-layered graphene sheets. Among these methods, chemical reduction of GO is the most promising approach leading to large scale production of graphene. Although its effectiveness on the conversion of GO to restore the intrinsic graphene structure is still in debate, there is an emerging realization on the excellent properties of GO for material applications [11].

GO is easily obtained from natural graphite flakes by the strong oxidation and subsequent exfoliation based on Hummers method [12]. Compared to graphene, GO is heavily oxygenated with bearing hydroxyl, carbonyl, and epoxy groups on the basal planes and edges [13, 14]. Hence, GO is highly hydrophilic and readily exfoliated in water, resulting in the stable dispersion with most of single-layered sheets. In addition, GO sheets are mechanically strong with ultimate stress at around 60 GPa and Young's modulus about 250 GPa [15, 16]. The excellent mechanical properties combined with large aspect ratio and inexpensive sources have spurred intensive interests in GO for developing high-performance, cost-effective polymer composites [17]. To date, GO and its derivatives have been applied in various polymers to achieve the high reinforcement efficiency [18].

In addition to the material composition, specific steps in the fabrication process play an important role in determining the structure and the properties of composites. Generally, the fabrication of polymer/graphene composites involves the following four steps: 1) GO preparation, 2) dispersion of GO sheets in a suitable solvent, 3) mixing with the polymer and, 4) fabricating composites with a suitable technique. It is worth noting that the use of ultrasound has become a standard step in fabricating polymer/GO composites [19]. For instance, ultrasonication is required to exfoliate graphite oxide into single-layered GO sheets. It is also a common approach to break up GO agglomeration in order to achieve good GO dispersion in polymer matrices [20, 21]. Nano modified epoxy resins have shown great potential for the applications in fiber reinforced plastic (FRP) composites as matrices for resin infusion (RI) technology [22, 23].

The resin infusion process using vacuum assisted resin transfer molding (VARTM) is executed on single-sided molds, and has been utilized to manufacture medium to very large composite structures [24]. A classic rigid male or female mold can be used; the other side of the mold is a sealed flexible bag, which allows for the application of vacuum on the preform. The vacuum provides the compaction pressure and driving force for resin flow through the preform. A simple RI process consists of three basic phases, namely pre-filling, filling, and post-filling as described in Figure 1. In the pre-filling phase, the preform is compacted by the applied vacuum while the injection gate is still closed. The filling phase is initiated by opening the injection gate, the resin being sucked from the resin pot, saturating the preform. Once the preform is completely saturated with resin, the injection gate is closed and the preform is allowed to cure during the post filling phase. Resin infusion is a low cost process to achieve good mechanical properties of final composites. Furthermore, the porosity of final parts is low and the fiber volume fraction is higher and more homogeneous than with wet-hand lay-up [25].

Resin infusion process has widely been used in industries such as automotive, aerospace and marine [26-28]. The use of nanoparticles as secondary reinforcements is new to large scale industries and requires complete scientific understanding of their interactions with other reinforcing materials. To date, most of graphene based composites focused on small scale production to enhance electrical and thermal conductivity [10, 29]. With addition of 0.01–0.1 vol.% graphene fillers, the electrical conductivities of nanocomposites rise sharply by several orders of magnitude. To date, very limited research has been conducted to understand the processability of graphene in large scale advanced composite manufacturing. Some researchers have addressed carbon nanofibers (CNFs) and CNTs as fillers in polymer matrices using the RI

process [30-34]. The effects of nanoparticles on resin infiltration using CNFs and CNTs were also studied during such a composite manufacture [35]. However, the use of exfoliated graphene nanoparticles as a secondary reinforcement in glass fiber composite laminates has not been covered extensively. There are several methods used to introduce nanoparticles into composite materials, but among which one relatively easy method involves dispersing nanoparticles in the resin [30, 34-37]. However, the high surface area and aspect ratio of nanoparticles can result in an increase in resin viscosity [35]. Furthermore, during the resin infiltration, nanoparticle aggregation can occur within the fiber tows [10, 33, 38-41].

Due to its excellent processability and properties, epoxy resin is regarded as the most widely used polymer matrix for structural composites [40, 42]. It is an ideal polymer for further property enhancements by incorporating nano-scaled additives. During composites manufacturing in the RI process, matrix flow and cure reaction take place to produce void free, perfectly adhered fibers and matrices, which is considered to be the key for enhanced mechanical properties of final composite structures. Therefore, cure kinetics and rheological behavior of the matrix are critical parameters for manufacturing high-performance composite structures. The processing conditions of polymers with nanofillers should be different from those of neat polymer. The addition of nanofillers was found to influence the interaction of the matrix and fiber reinforcements by affecting the cure reaction of the matrix [43, 44]. Hence, complete understanding of resin flow and cure reaction of nano modified epoxy is important for successful design and manufacture of composite structures. Extensive studies related to cure kinetics of resins have been mentioned in the previous literature [45-51]. However, the effects of graphene

nanofillers on composites processing using liquid molding techniques such as RI process has not been investigated in details yet.

In this study, the effects of exfoliated GO on the processing characteristics of glass fabric composites fabricated by the RI process were investigated. The objective of this research is to investigate the rheological behavior and cure kinetics of GO mixed epoxy resin for manufacturing GO reinforced glass fiber composites using RI process and determining their flexural properties.

## **2.0 Experimental**

### *2.1 Materials*

Graphite powder with particle size less than 20 $\mu$ m, concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>), hydrochloric acid (HCl), potassium permanganate (KMnO<sub>4</sub>), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), were all obtained from Sigma-Aldrich Co. Ltd. All of the materials were directly used without further purification. The E-glass fibers (8 harness satin weave with an areal mass of 250 g/m<sup>2</sup>) were obtained from US composites, USA. All panels were fabricated using the RI manufacturing technique. The resin used was two-part epoxy supplied by Gurit<sup>®</sup>, UK. It include Prime<sup>™</sup> 20LV epoxy and a slow amine based Gurit<sup>®</sup> hardener (a resin-to-hardener ratio of 100:26 by mass). Prime 20LV has an initial mixed viscosity of 0.320 Pa.s, as stated by the manufacturer. A glass mold with the line injection and line vent was used to fabricate panels with dimensions of 25 × 15 cm<sup>2</sup>. This procedure was found to yield high-quality panels with good reproducibility.

## *2.2 Preparation of GO sheets*

GO was synthesized from graphite powder by the modified Hummers method. First, 10 g  $K_2S_2O_8$  and 10 g  $P_2O_5$  were dissolved in a 50 ml concentrated  $H_2SO_4$  solution at  $80^\circ C$ . 12 g graphite powder was then added to the acidic solution, and the resulting mixture was stirred at  $80^\circ C$  for 4.5 h. After cooling to room temperature, the solution was diluted with about 2 L de-ionized (DI) water, which was allowed to stand overnight. The supernatant was decanted, and the pretreated graphite was obtained by centrifugation and washed three times with DI water. The product obtained was dried in air at  $100^\circ C$  for 12 h. 2 g pretreated graphite powder was put into the 50 ml concentrated  $H_2SO_4$  solution with ice bath. 7 g  $KMnO_4$  were added gradually with stirring, and the temperature of the solution was kept below  $10^\circ C$ . The mixture was then stirred at  $35^\circ C$  for 2 h prior to adding 96 ml DI water. After the solution was stirred for additional 30 min, the reaction was then terminated by adding 300 ml DI water and a 30%  $H_2O_2$  solution (5 ml). The mixture was kept for centrifugation, further subjected to several cycles of suspension in 5% HCl solution, and separated by the centrifugation. In order to completely remove metal ions and acids, the graphite oxide underwent cycles of washing with DI water and separated using centrifugation until the pH value of the supernatant reached 6. The GO product was suspended in distilled water to give a viscous, brown dispersion at 15 mg/ml.

The graphite oxide suspension obtained was diluted to 5mg/ml, and was then ultrasonicated in a WiseClean ultrasonic bath (WUC-D22H, frequency of 40 kHz, power input of 300 W) at room temperature. The actual energy input into the GO suspension is related to the mass of bath water.

In this work, the calculated power input into the suspension is 30 W/L. The ultrasonication time varied from 0 to 5 h to alter the energy input into the solution. During a prolonged period of sonication, the bath water was heated and considerable evaporation occurs. Whenever the temperature of bath water became 5°C higher than room temperature, the hot water was replaced by fresh room-temperature water to keep the water level constant.

### *2.3 Preparation of GO/epoxy resin*

The original GO suspension was diluted to 1 mg/ml using ethanol. The mixtures were ultrasonicated in a bath for 30 min. The prepared GO suspension was mixed with epoxy resin under magnetic stirring. The epoxy mixture was then stirred at 100°C to remove the solvents. After complete solvent removal, the epoxy mixture was allowed to cool down to room temperature. Then the epoxy mixture was placed in a vacuum chamber for approximately 10 min in order to remove any air bubbles.

### *2.4 Resin Cure Kinetics*

Cure kinetics characterization was performed using a TA Instruments Q600 simultaneous TGA/DSC. For each DSC sample, about 50g epoxy resin batches, with GO contents of 0, 0.05, 0.1 and 0.2 wt%, and corresponding amounts of hardener were mixed. After weighing, the resin was mixed for about 5 min. Subsequently, a sample of approximately 10 mg was placed in an alumina pan. The sample was quickly weighed and placed inside the DSC chamber to minimize the ambient curing prior to the DSC tests. For dynamic scans, samples were heated at 2°C/min from room temperature to 250°C. Isothermal DSC tests were performed to investigate the progression of cure with time. Samples were held at 80°C for 1 h, cooled down to room



temperature, heated at 2 °C/min to 250°C to obtain the residual heat of reaction. Degree of cure,  $\alpha$  is a measure of the proportion of reaction completed, which is given by,

$$\alpha = \frac{H}{H_R} \quad (1)$$

Where  $H$  is heat of reaction and  $H_R$  is the total heat of reaction found from dynamic tests. The cure rate was calculated as;

$$\frac{d\alpha}{dt} = \frac{q - q_{baseline}}{H_R} \quad (2)$$

where  $q$  is the total heat flow and  $q_{baseline}$  is the reference obtained from the DSC graph. The degree of cure was determined after integrating equation (2) with respect to time  $t$ .

### *2.5 Resin Rheology*

Rheological tests of epoxy resin were performed using a TA Instruments Discovery Hybrid Rheometer with a peltier plate fixture of 25 mm disposable parallel plates. Similar to DSC tests, batches of about 50g epoxy resin, with GO contents of 0, 0.05, 0.1, and 0.2 wt% and the appropriate amount of hardener were mixed. Samples of approximately 2ml mixed resin samples were pipetted onto the rheometer bottom plate. Rheological tests were performed with 0.5 mm plate gap at a constant shear rate 2.5 s<sup>-1</sup>. Temperature sweep tests were completed for the determination of temperature-dependent viscosity evolution, which were performed on all samples from 23 to 95°C. Isothermal rheology tests were conducted at 80°C in order to determine the viscosity evolution with respect to time. This temperature was selected after investigating the dynamic DSC scans where peak temperature was about 82°C.

### *2.6 Composite Manufacturing*

A one-sided glass tool was coated with a mold-release agent to facilitate the easier removal of the part after curing. E-glass fabric was cut to 25 × 15 cm<sup>2</sup> with 8 layers to be stacked together.

On the top layer of the preform, a peel ply was laid. This peel ply enables the part separation from the vacuum bag. This lay-up was then covered by a vacuum bag tightly sealed to the mold, and connected to the resin and vacuum lines. Air was evacuated by a vacuum pump connected to resin trap. The resin was de-gassed for 5 min to remove air bubbles. The preform was then infused with resin under vacuum at a pressure of 1 atm. The resin flow fronts were monitored and recorded using a digital camera. The vacuum was maintained during the curing phase until the solidification was completed and the part was ready to be de-molded. The resin-infused panels were cured at room temperature for about 24 h and then post cured at 65°C for 7 h.

### *2.7 Flexural Tests*

Specimen were cut and flexural tests were conducted using a three-point bending rig mounted on an Instron 4505 universal testing machine (load cell capacity: 5 kN). All tests were performed under ASTM D7264. The crosshead speed was 1 mm/min with a support span to thickness ratio of 32:1. At least seven samples for each batch were tested for the good reproducibility. Average data were reported with standard deviations accordingly.

## **3.0 Results and Discussions**

### *3.1 GO Preparation*

The optical images of GO-water solution treated with different ultrasonication time are shown in Figure 2. Without the ultrasonication treatment, most of GO nanoparticles are precipitated at the bottom of the tube with a yellow-colored supernatant with limited exfoliation of graphite oxide. After ultrasonication, the precipitate of graphite oxide diminished significantly due to the exfoliation of graphite oxide into GO sheets. It is evident that both the amount of graphite oxide precipitation and the transparency of supernatant decrease with an increase of ultrasonication

time. At an ultrasonication time of 30 min (energy input 15 W·h/L), no precipitation was immediately observed. After keeping the solution for 7 days, only traces of graphite oxide precipitate were visible. The visible precipitation remainder was less than 2 wt%. However, by further increasing the ultrasonication time over 30 min, no apparent reduction in the precipitation amount was observed. The visible precipitation remainder is graphite particles without the full oxidization, which finally cannot be exfoliated by the ultrasonication process.

The morphology and thickness of GO sheets were examined by atomic force microscopy (AFM), and representative images are shown in Figures 3(a) and (b). The prepared GO sheets show irregular shapes with uniform thickness and the lateral dimension is in the range of 0.1 to 1  $\mu\text{m}$ . As indicated in Figure 3(a) marked by the red line, the typical sheet thickness is around 1.0–1.2 nm (Figure 3b), indicating that a single layer of graphene oxide is achieved. The GO sheets are slightly thicker than individual graphene, which is attributed to the presence of oxygen functional groups. For instance, epoxy and carboxyl generally exist on the GO surface and edges [52].

To observe the GO dispersion in epoxy matrices, the fracture surfaces of cured samples were examined using a Field Emission Scanning Electron Microscope (FESEM). As seen from Figure 4, the fracture surface of neat epoxy is characterized by a smooth surface after a brittle fracture. However, the fracture surfaces of GO modified epoxy sample at 0.2 wt% GO are remarkably different compared to those of neat epoxy. Many mini-ridges were observed on the fracture surfaces. This change from smooth to rough surface features on the composite fracture surface suggests that the GO sheets have induced the deflection of propagating crack fronts. This process

introduces off-plane loading that generates new fracture surfaces thus increasing the required strain energy for the continuation of fracture [3, 53].

### *3.2 Resin Cure Kinetics*

#### *3.2.1 Dynamic tests:*

The dynamic thermograms were obtained on each sample in Figure 5. A single exothermic peak was observed for the cure of pure epoxy system as well as for the 0.05, 0.1 and 0.2 wt% GO modified epoxy system. The total heat of reaction was found by the area under the curves for the respective reaction curves. The average total heat of reaction for pure epoxy was of 410J/g, whereas it was 438J/g for 0.2 wt% GO modified epoxy. The GO modified samples show some variations in time to reach the peak exotherm despite that similar temperature of 82°C was detected at each peak, Figure 5(b). It can be observed that peak temperatures for 0.1 and 0.2 wt% GO samples were reached slightly early as compared to those of 0 and 0.05 wt% counterparts, resulting in left shift of DSC curves in Figure 5(b). The results indicate that the addition of GO nanoparticles initiated the cure reaction earlier than neat epoxy. It is believed that thermal conductivity of GO may have played an important role by affecting the cure reaction. Furthermore, the reactive hydroxyl groups on the GO surface also participated in the opening of epoxide rings like an amino curing agent, which reacted with epoxy to form the ester bond, and facilitated the primary amine–epoxide reaction [48, 54]. Consequently, GO acted as a catalyst and played a certain role in the overall cure reaction of the epoxy. Compared to pure epoxy, the high heat of reaction from GO modified epoxy samples also confirmed this.

### 3.2.2 Isothermal Tests:

The catalytic effects of GO on the degree of cure of epoxy resin can be clearly observed in Figure 6. The GO modified epoxy exhibits a faster reaction rate, requiring less time to reach complete cure than for the pure epoxy system. This observation is consistent with the previous dynamic scans. The degree of cure for 0.2 wt% GO epoxy sample reached the value of 1 in about 15 min. The acceleration of cure reaction caused by the addition of GO can have a positive influence on composite processing by reducing the time required for curing and saving energy. On the other hand, early resin gelation can influence resin viscosity, and hence the flow by reducing the overall preform permeability. In order to process resins with the high GO content, high injection pressures will be required for molding operations such as resin transfer molding (RTM), high pressure RTM and compression RTM.

### 3.3 Resin Rheology

The viscosity curves for un-catalyzed resin samples mixed with different GO concentrations are demonstrated in Figure 7. It was evident that the addition of GO nanoparticles enhanced the viscosity as the GO content increased. The viscosity of GO modified epoxy system with the GO content of 0.2 wt% was approximately 75% higher than that of pure epoxy at room temperature, and was almost 28% higher at 70°C. This is possibly due to the thermal conductivity of GO nanoparticles to facilitate internal heat as the temperature increased. Figure 8 presents the viscosity versus temperature curves for each sample using catalyzed epoxy resin. At room temperature, 0.2 wt% GO modified epoxy samples show initial higher mixed viscosity than others. As the temperature increased to 50°C, the viscosities of all samples became similar until about 70°C, which started to deviate and rise sharply after 80°C. The 0.2 wt% GO modified epoxy sample started to gel faster than other samples, with pure epoxy being the slowest to gel.

The isothermal viscosity versus temperature curves at 80°C is displayed in Figure 9. These curves show an exponential increase in viscosity with time till the gelation of epoxy resin. The results are consistent with the DSC scans, which gives faster curing rate for 0.2 wt% GO modified epoxy samples. This is indicative of the premature gelation that may be encountered during the resin infiltration in the RI process.

### *3.4 Processing using Resin Infusion*

The photographs of RI manufacturing of all samples are depicted in Figure 10. Photos were taken every 2 cm of flow front advancement. The flow front position vs time graph is shown in Figure 11. It can be seen that 0.2 wt% GO modified epoxy sample did not infiltrate throughout the length and started to gel after 900 s. The mold filling time for 0, 0.05, and 0.1 wt% GO samples was around 1100, 805 and 860 s, respectively. The flow front of pure epoxy was leading up until the time reached 150 s mainly due to low initial mixed viscosity. As the flow front progressed, the cure reaction was initiated to generate internal heat, resulting in lowering the viscosity of GO mixed resin. This allows GO mixed resin to flow slightly faster than pure epoxy. The 0.2 wt% GO content was probably too high for RI processing under given conditions. As the cure reaction accelerated, the resin started to gel pre-maturely which resulted in increased viscosity with an incomplete injection.

### *3.5 Flexural Properties*

Figure 12 shows close ups of fully cured samples. The darkest sample has the GO content of 0.2 wt%. After samples were cut to the required dimensions, three-point flexural tests were conducted. Typical flexural stress versus flexural strain curves are shown in Figure 13(a), which suggests that with increasing the GO content from 0 to 0.2 wt %, the composites required more

strain before failure. As observed from Figure 13(b), the flexural moduli of glass fiber composites with 0.2 wt% GO reach the maximum level of 12.8 GPa, approximately 21% increase relative to that of pure epoxy/glass composites. The flexural strengths also have a similar trend with the maximum flexural strength of 400 MPa taking place at the GO content of 0.2 wt%. This results in the increase of flexural strength by 30% as compared to that of neat epoxy composites. The strength gains continued as a function of graphene oxide content across the full range of concentrations used in this study. Since high GO content affects the RI processing by increasing resin viscosity and lowering gel time due to high heat of reaction, GO content over 0.2 wt% for the RI process was not used. Improvements in other mechanical properties such as tensile, fracture toughness and fatigue using several GO contents were reported elsewhere [3, 4, 6, 55].

#### **4.0 Conclusions**

In this study, the effect of GO modified epoxy system on glass fiber composites processing was investigated. The cure behavior of GO modified epoxy resin with different GO contents was examined using dynamic and isothermal DSC analysis. The GO nanoparticles have shown influence on the key processing parameters used to manufacture composite structures using liquid molding techniques. The results of cure kinetics indicate that, compared to pure epoxy system, the GO modified epoxy exhibits an evident catalytic reaction that affects overall cure rate. Therefore, the enhanced curing behavior of GO modified epoxy resin has potential for a faster cure cycle in terms of time and energy conservation, despite the reduction of processing window for resin infusion. Additionally, the GO inclusion to epoxy resin system increased the viscosity of the mixed resin. As the time progressed, the viscosity decreased due to exothermic heat, the heat generated by 0.2 wt% GO sample was enough to cause pre-mature gelation,

resulting in unsuccessful mold filling, and further reducing the processing window at higher GO contents. The flexural test results show 21% increase in flexural modulus and 30% increase in flexural strength at 0.2 wt% GO. It can be confirmed that GO plays an important role as an effective secondary filler. However, the resin selection that is suitable for given processing conditions and part size needs to be carefully made to avoid any premature gelation during mold filling.

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## Figure Captions

Figure 1: Schematic of a typical resin infusion process

Figure 2: Optical images of GO water solution in a tube, treated at different ultrasonication time (Photos taken after 7 days) [14].

Figure 3: Characterization of individual GO sheets: a) typical tapping-mode AFM image of GO sheets, b) line profile for the sheet marked by the red line in the image.

Figure 4: The fracture surface of (a) pure epoxy and (b) GO modified epoxy (GO content: 0.2 wt%).

Figure 5: Dynamic DSC scans: a) heat flow versus temperature and b) heat flow vs. time of GO modified epoxy samples.

Figure 6: Degree of cure versus time for isothermal tests conducted at 80°C.

Figure 7: Viscosity versus temperature (un-catalyzed resin) of GO modified epoxy samples.

Figure 8: Viscosity versus temperature (temperature sweep)

Figure 9: Isothermal viscosity of GO modified epoxy samples at 80°C

Figure 10: Flow front progression at three different intervals during the resin infusion of composite samples at various GO contents: a) 0 wt% GO, b) 0.05 wt% GO, c) 0.1 wt% GO and d) 0.2 wt% GO.

Figure 11: Flow front position versus time to represent the flow front progression during the resin infusion.

Figure 12: Cured samples after resin infusion processing.

Figure 13: Flexural properties of Glass/GO composites: a) flexural stress versus flexural strain and b) flexural modulus.

## Figures

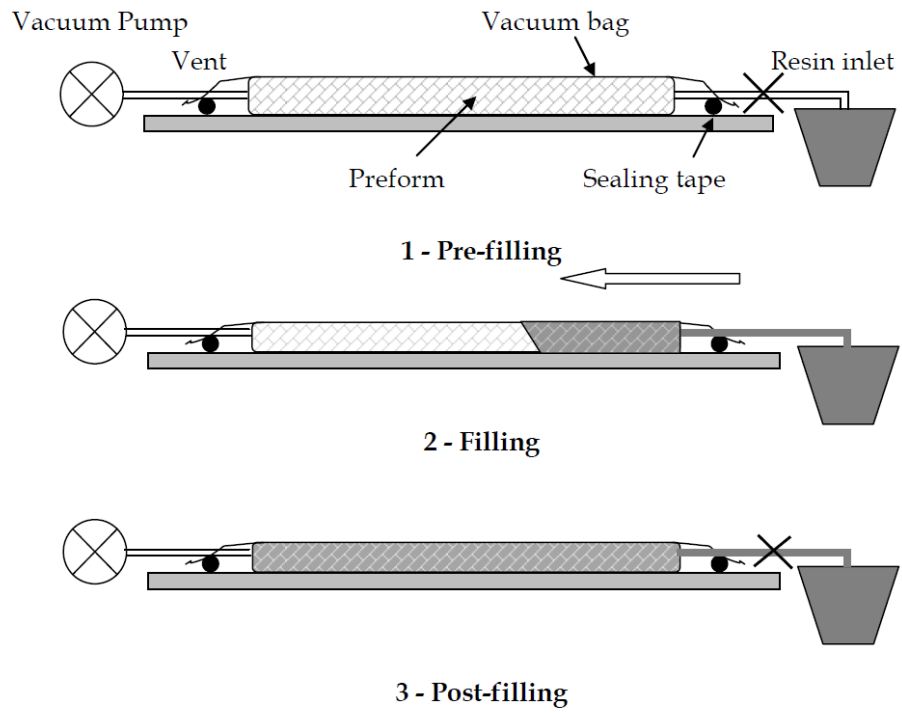


Figure 1



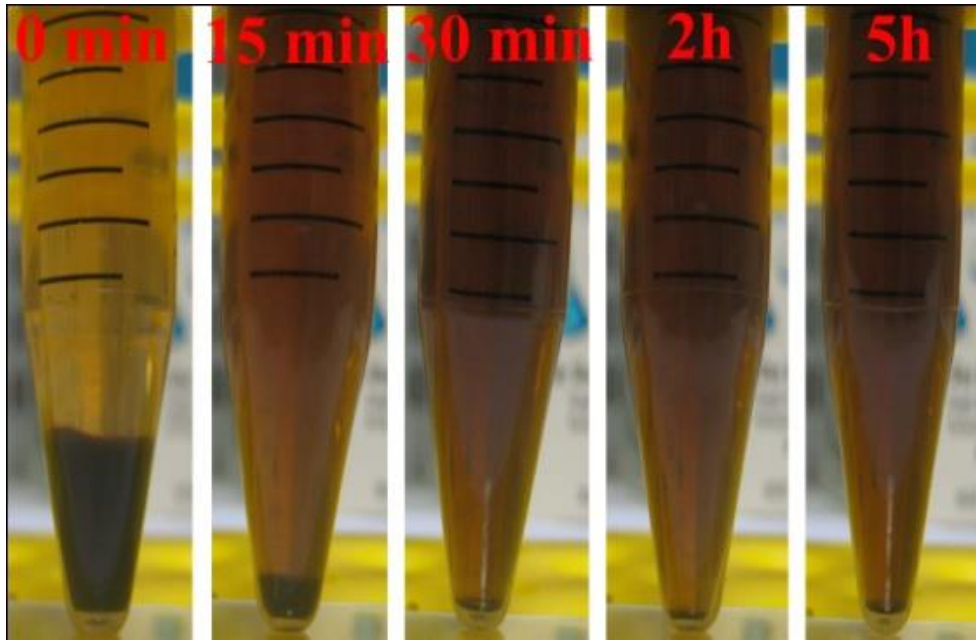


Figure 2

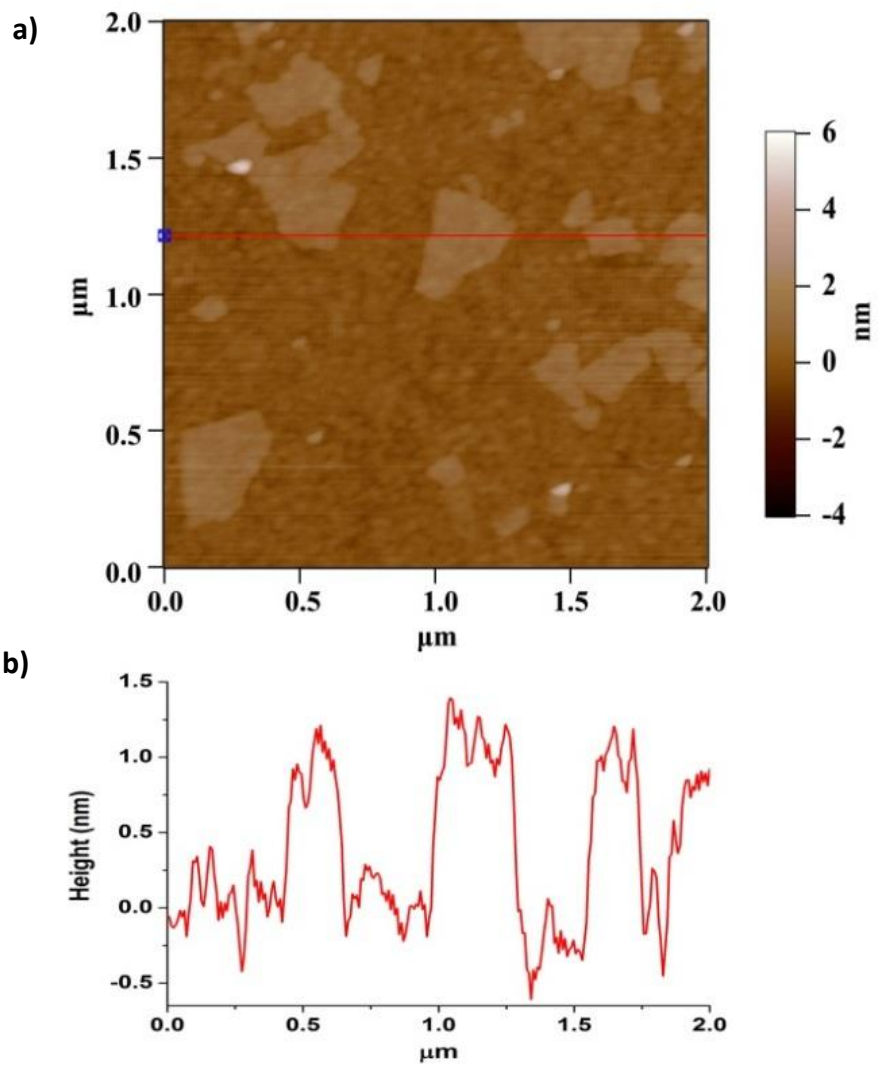
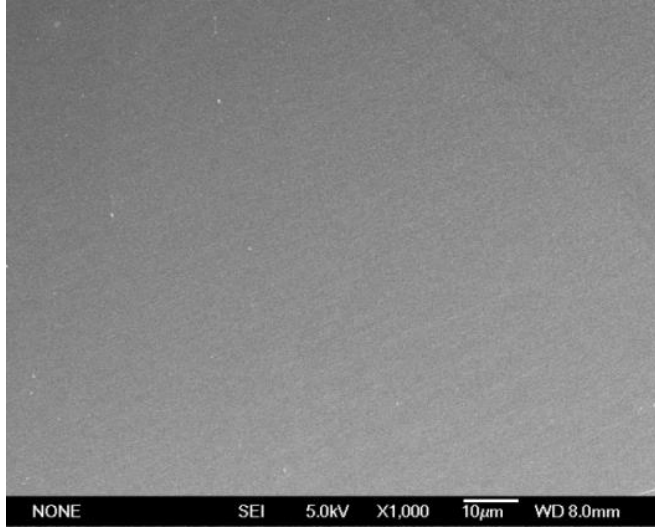


Figure 3

a)



b)

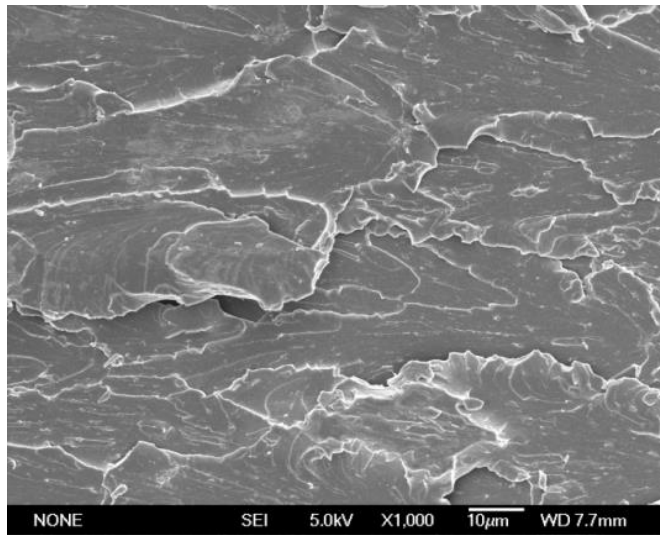


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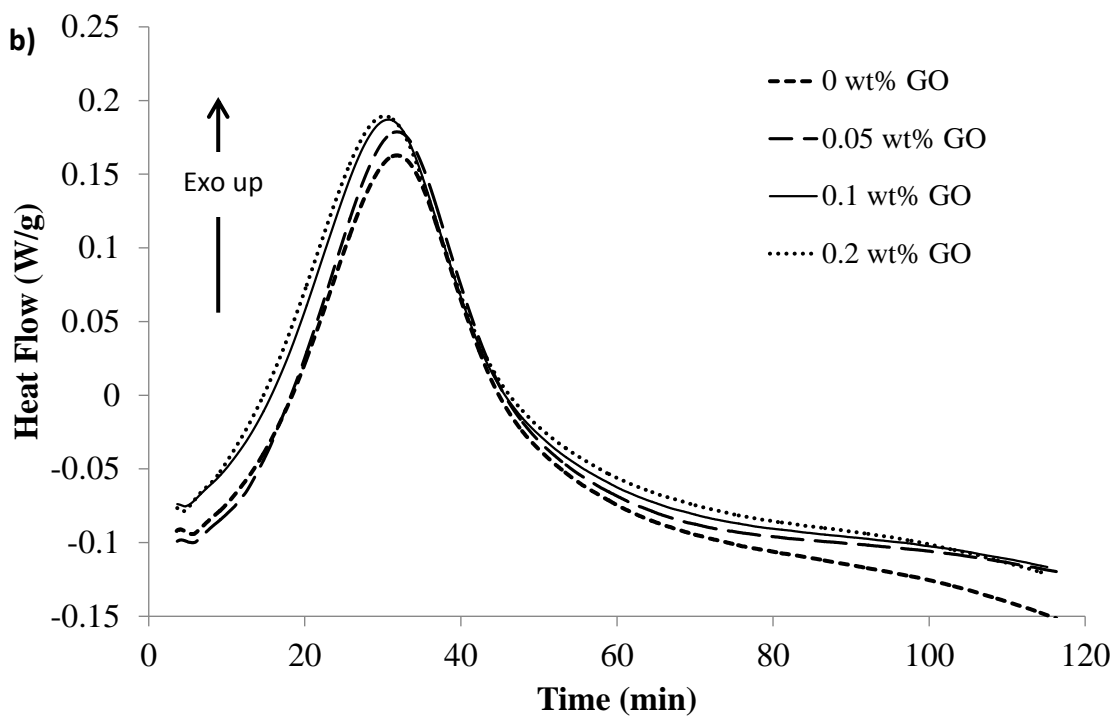
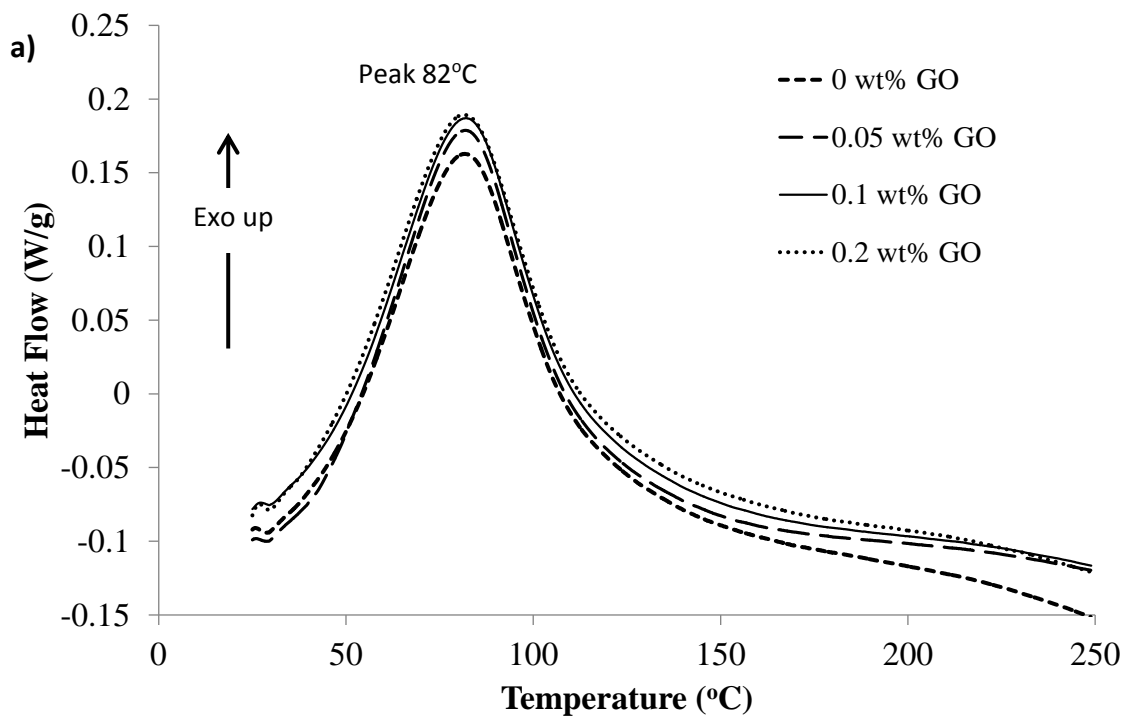


Figure 5

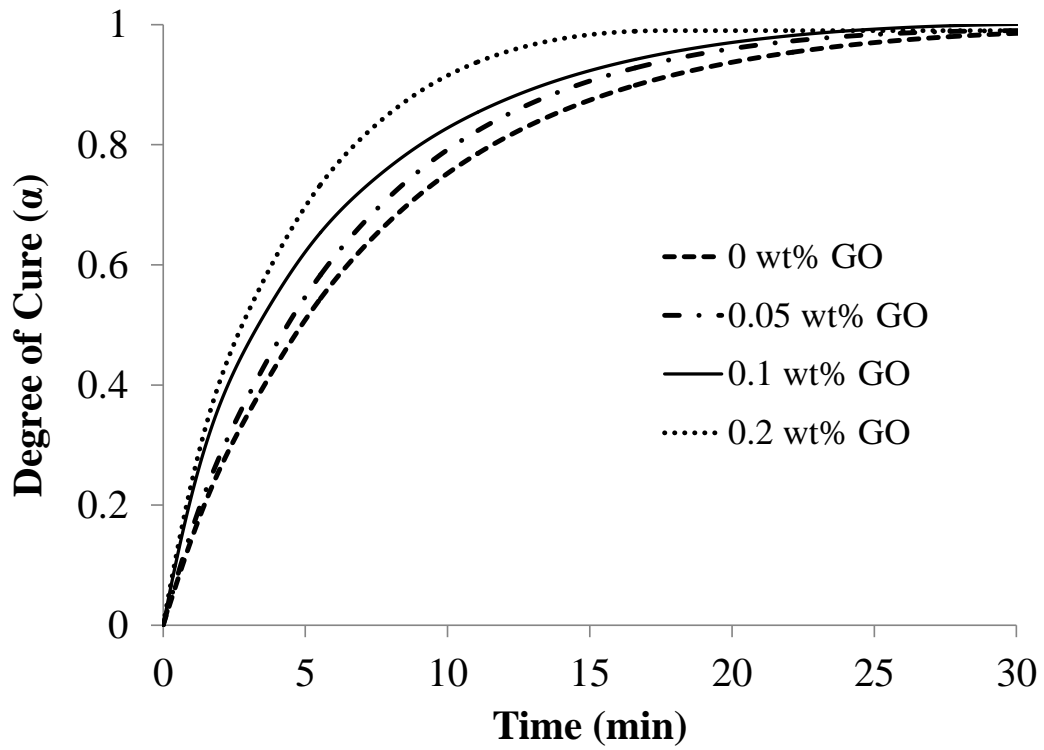


Figure 6

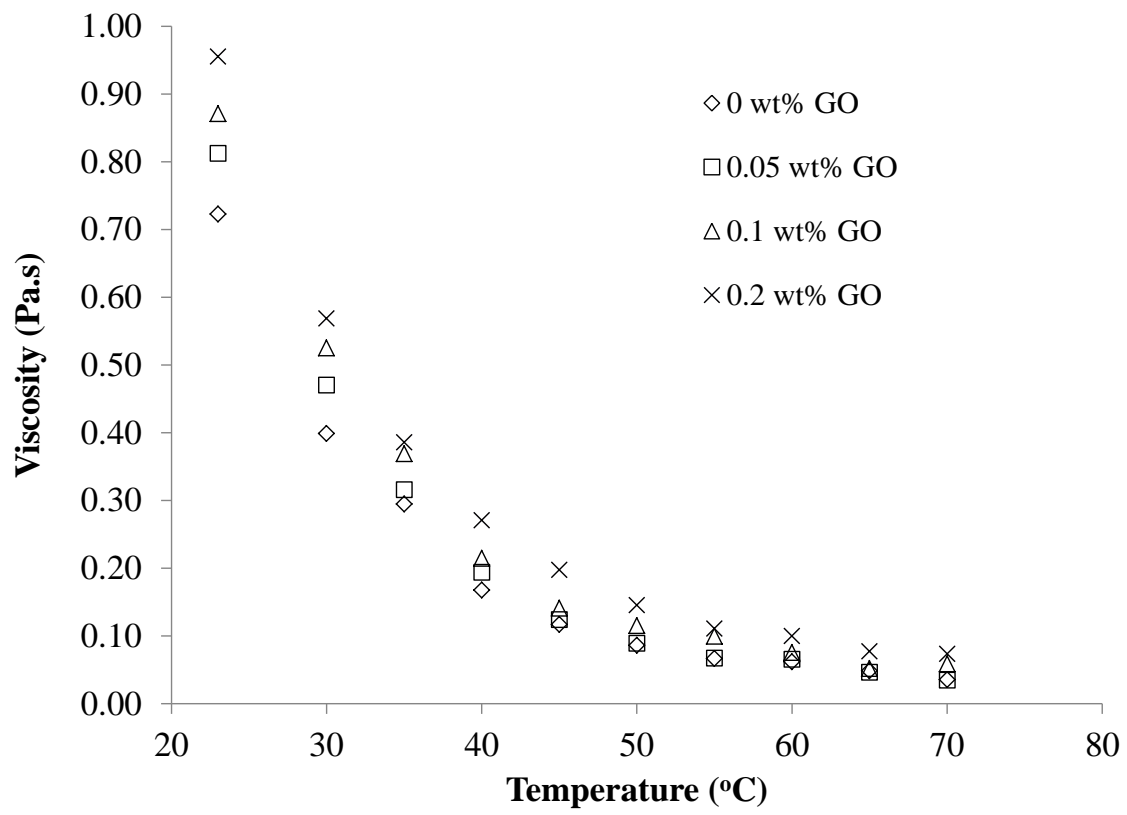


Figure 7

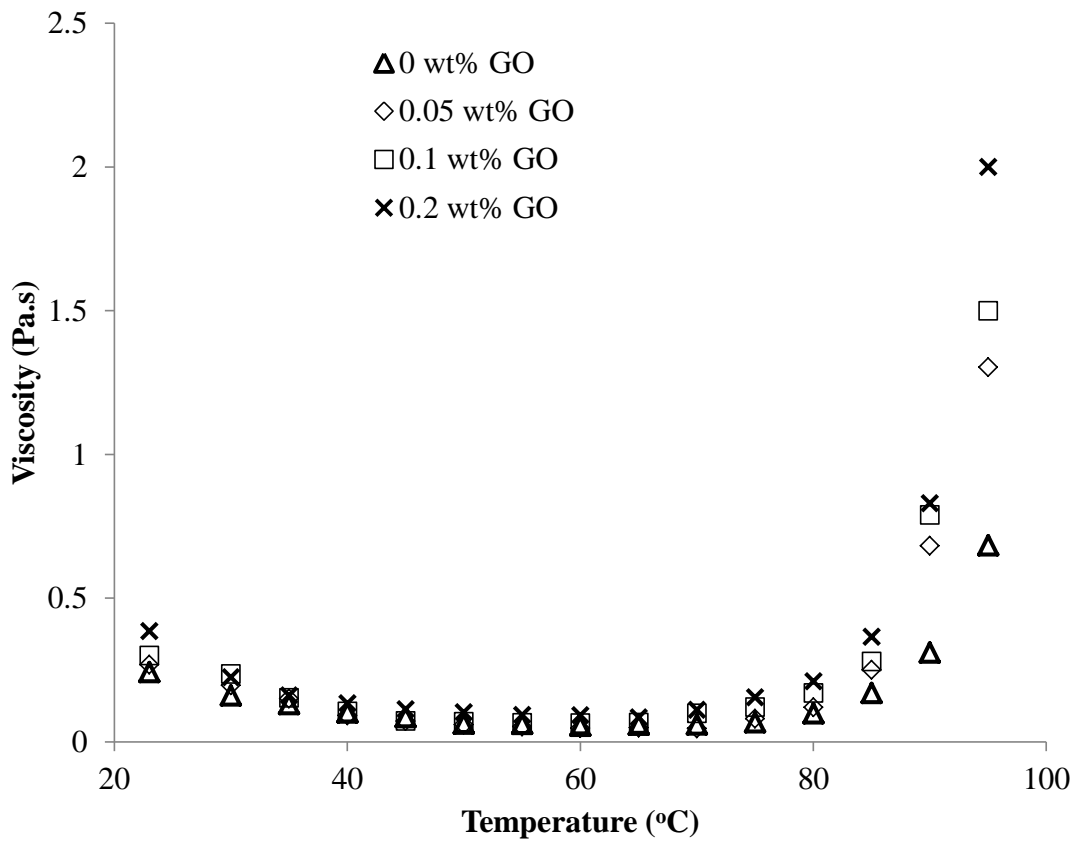


Figure 8

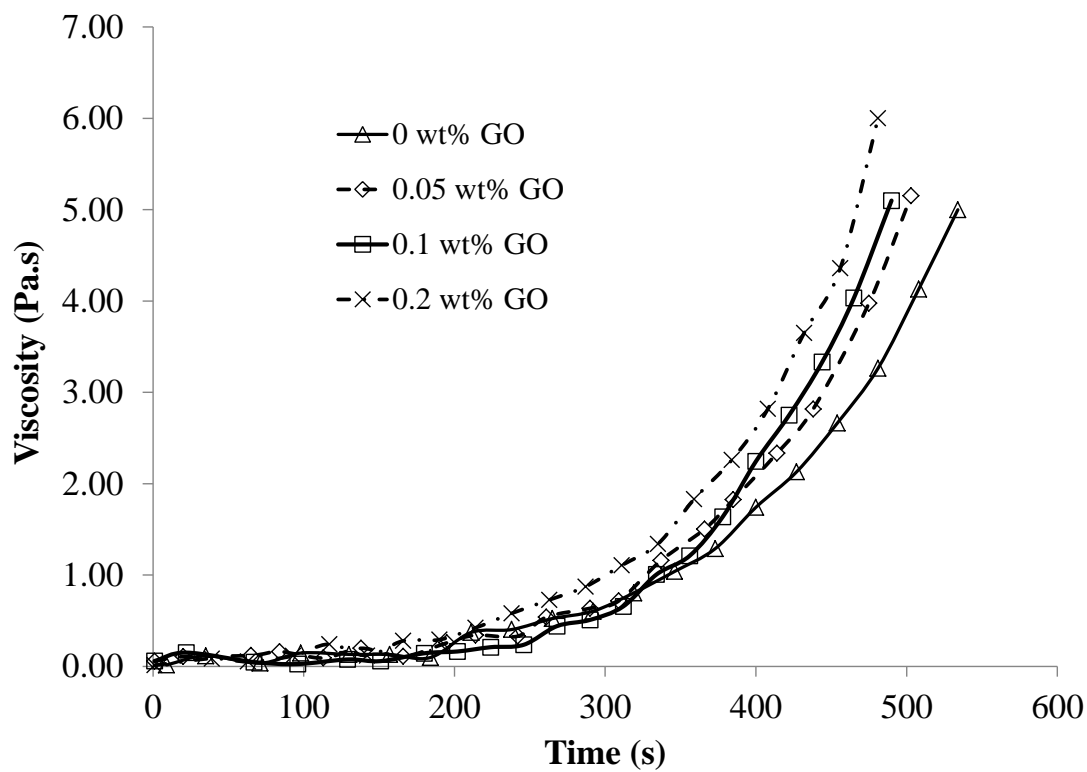


Figure 9



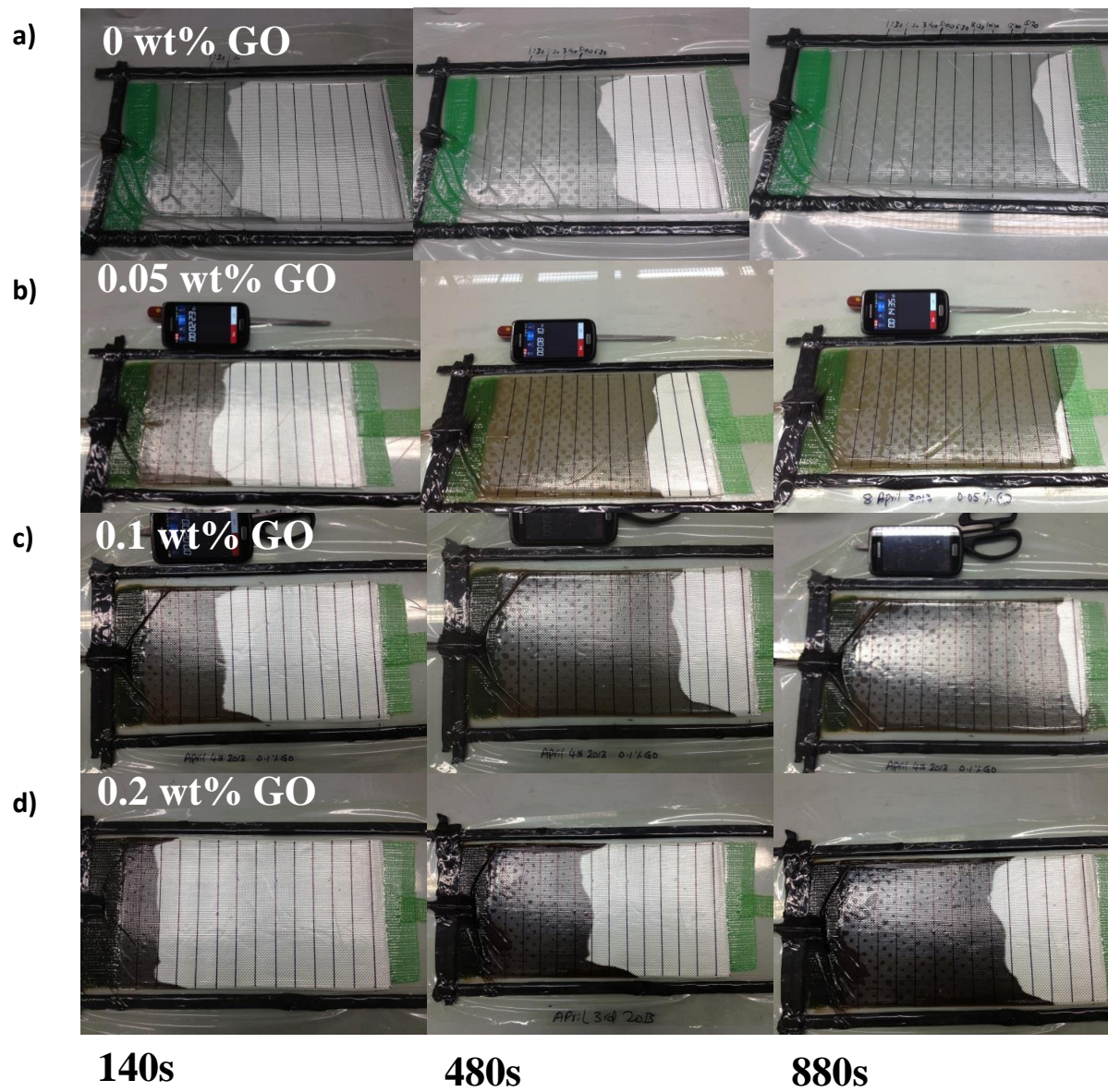


Figure 10

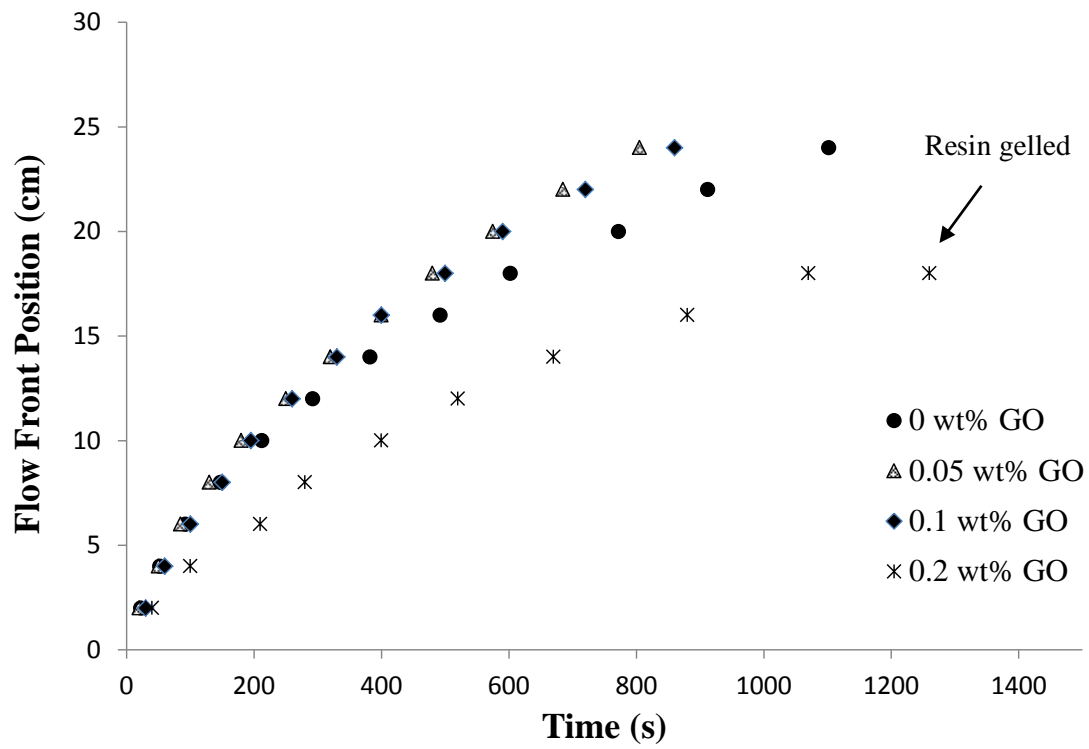


Figure 11

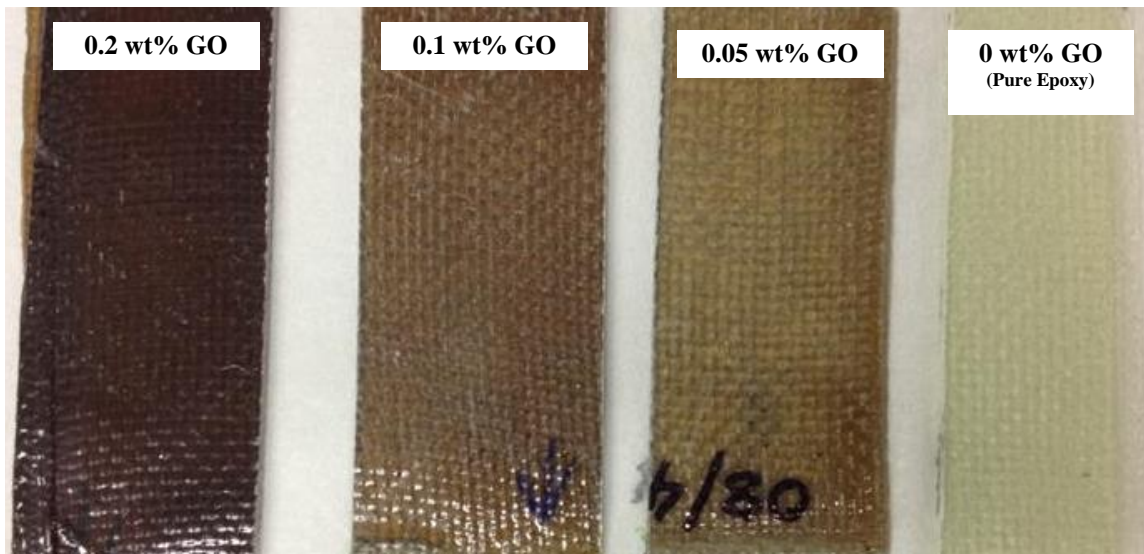


Figure 12

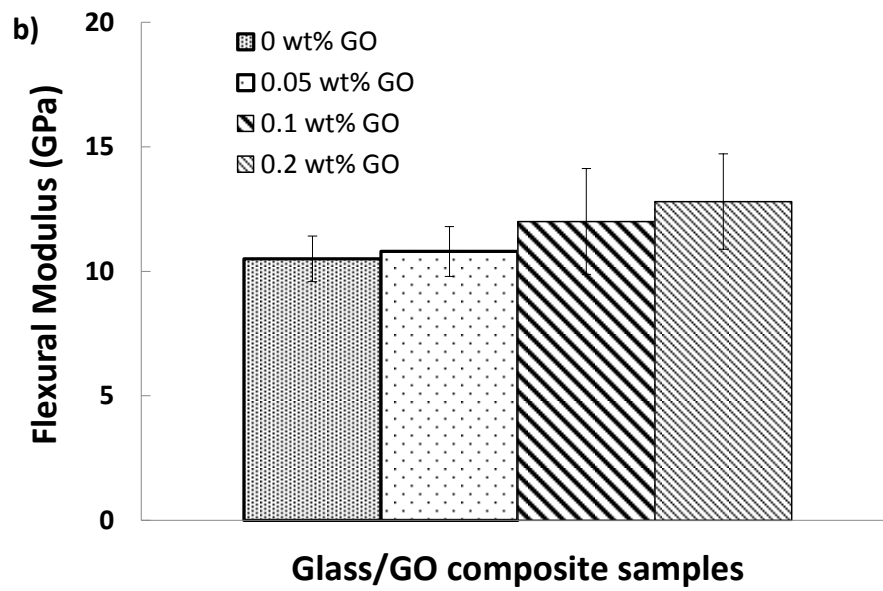
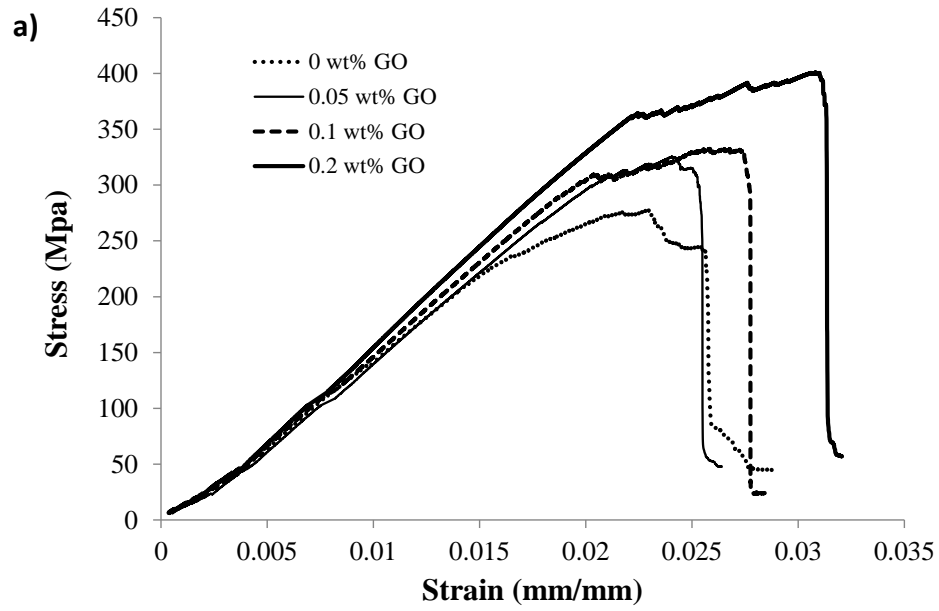


Figure 13