Resin Transfer Moulding Processing and Properties of Graphene-Enhanced Glass Fiber Laminate Composite

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ABSTRACT

Integration of graphene into conventional composites, more specifically at higher weight ratios, is challenging as the addition of graphene into the polymer often reduces the processibility of the material. In this work, resin transfer molding (RTM) is employed to fabricate graphene-enhanced glass fiber-reinforced polymer (GFRP) laminates. Few-layer graphene powder (GrapheneBlack™ 0X), produced in large scale by mechano-chemical exfoliation of natural graphite was supplied by NanoXplore Inc. Thermal stability, cure kinetics, rheological behaviour, the glass transition temperature (T_g), and tensile properties are first measured using neat resin samples with 0 wt%, 5 wt%, 10 wt%, and 15 wt% graphene. Coupons were then cut from the GFRP and resin panels to perform microscopy, three-point bending, Charpy, and electrical conductivity tests. As graphene content increases, the working time of the material decreases as its minimum viscosity increases, while the degradation temperature is not affected significantly. Overall, the T_g values remained consistent up to 10 wt% with both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) methods. The results of the tensile test show an enhancement of the Young's modulus of up to 40% at the expense of a reduction in strength and maximum tensile strain by 30% and 55%, respectively. Overall, the addition of graphene at the weight ratios explored in this project have shown to improve the electrical conductivity, the flexural modulus, and strength of the samples, while it seems to have a negative effect on the impact strength. From the microscopy results, it is observed that there are graphene agglomerates, which can be attributed to the reduced impact strength.

1.0 INTRODUCTION

The introduction of polymer-matrix composite materials into armour structures has brought several advantages including structural weight reduction and life cycle cost reduction. These materials, however, are asymptotically reaching their performance limits. New material developments hold the key for introducing or improving essential functionalities of armour structures, such as durability and flexibility while maintaining their strength and lightness. In addition, it would be possible to design structures that can dissipate bullet impact energy effectively, thus providing enhanced protection to the body. Graphene is a novel material that possess excellent properties that can be used to enhance structural and multifunctional properties of fiber-reinforced polymers. Current developments on reinforced nanocomposites with graphene filler have been surveyed by Vikas and Garima Mittal et al [1, 2]. Among many forms of graphene, nanoplatelets are the most common and their toughening effects have been investigated [3-5]. However, the graphene loadings in these studies are generally low (< 5 wt%) and the composite manufacturing methods are often limited in terms of scalability.

Resin transfer moulding (RTM) is a cost-effective, composite manufacturing process that is widely used in the industry to fabricate high quality parts with complex geometries [6]. In this work, RTM is used to manufacture graphene-enhanced glass fiber-reinforced polymer (GFRP) and resin panels. Few-layer graphene nanoplatelet powder is used in this process. This method achieves high graphene contents (up

to 10 wt%) and relatively large size (40 cm x 40 cm) parts. First, material characterization is performed to obtain an understanding of the resin and its processing window for RTM. Panels with 5 wt% and 10 wt% graphene contents are then manufactured and baseline panels are prepared. Microscopy, mechanical, and electrical conductivity tests are performed evaluate the effect of graphene in the material properties.

2.0 MATERIALS

Techno fusion 8000HT from Polymères Technologies (a two-part aerospace-grade room temperature epoxy resin system) is used in the RTM process. The recommended mixing ratio is 100:26 by weight of part A to part B, with a 24 hour room temperature cure. An additional post-cure is recommended for two hours at 120°C, and three hours at 150°C [7]. The graphene powder used in this paper is GrapheneBlack™ 0X provided by NanoXplore Inc. Table 2-1 shows the key technical data of this product [8]. The agglomerate size is measured using laser diffraction. The fiber used in this project is a plain weave, E-glass fiber with an areal density weight of 260 g/m^2.

Table 2-1: Graphene Black™ technical specification

Primary particle size	0.5-1 µm
Agglomerate lateral size	D_{50}=13 µm
Bulk density	0.14 g/cm^3
Mean platelet thickness	2-3 µm

METHODOLOGY/RESULTS

3.1 Material characterization on neat resin samples

As a first step, neat resin samples with 0 wt%, 5 wt%, 10 wt% and 15 wt% graphene are characterized to study the enhancement of the material properties. Through these characterization methods, a deeper understanding of the material is obtained to subsequently setup the processing parameters to manufacture panels using RTM. The description of each test and the results are included in the following sections.

3.1.1 Thermogravimetric analysis (TGA)

A TA Instruments Q5000 IR TGA is used to determine the degradation temperature of the resin. This temperature is then used to establish the high temperature test limits for differential scanning calorimetry (DSC). Neat resin samples that are 10–20 mg with 0 wt% and 15 wt% graphene are loaded in a small platinum crucible. A ramp of 10°C/min is performed from 20°C to 550°C in nitrogen, and from 550°C to 700°C under compressed air. The degradation temperature is selected before there is a significant mass loss percent of 5%. At 335°C, a mass loss of 2.3% and 4.1% is observed for the neat resin and graphene samples, respectively. The results are shown in Figure 3-1 . These results also show that the material will not experience significant degradation at the post cure temperatures (less than 1% mass loss).

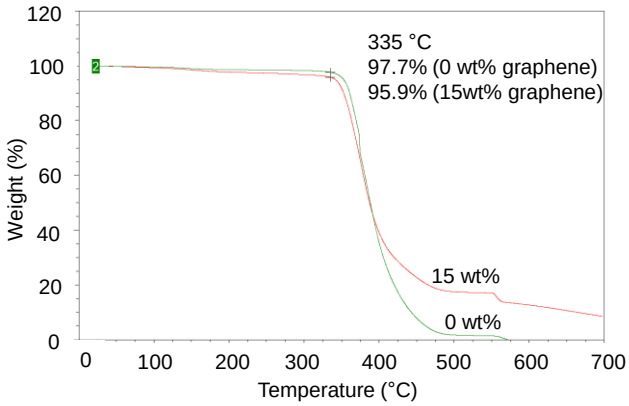

Figure 3-1: Thermogravimetric analysis results

3.1.2 Glass transition temperature (T_g)

A TA Instruments Q100 DSC and a Q800 DMA are used to measure the T_g of the resin samples. In DSC, the T_g of the material is identified by a step change in the specific heat. An isothermal at 20°C for 24 hours is performed for all of the samples. On the other hand, DMA traces the evolution of the elastic modulus of the resin. For these experiments, film samples are tested in tension in force control mode with a 1 Hz oscillating displacement of 15 µm. A 2 °C/min ramp is used to increase the temperature from 20°C up to 150°C. The tan δ peak (defined as the ratio of the loss and storage moduli G'' and G', respectively) is a measure of the midpoint between the glassy and rubbery state. This is the most sensitive technique available to measure the T_g [9]. Only one sample for each is tested for the scope of this work. Table 3-2 summarizes the results obtained with both techniques. With both methods, the T_g increases with higher graphene contents until reaching a peak at 10 wt%. The enhancement in T_g can be attributed to the restriction in chain mobility of the polymer due to the graphene being incorporated into the matrix [10].

Table 3-2: Changes of T_g with increasing graphene content evaluated with DSC and DMA

Graphene content (wt%)	T_g (°C) – DSC	T_g (°C) – DMA
0	100.1	92.4
5	101.1	106.7
10	100.6	110.0
15	81.6	106.9

3.1.3 Viscosity

For the rheology tests, a TA Instruments AR2000 rheometer is used to study the viscosity of the resin system. Neat resin samples with 0 wt%, 5 wt%, 10 wt%, and 15 wt% graphene contents are placed between two aluminum parallel plates. The gap between the plates is kept constant while the top plate rotates at a controlled strain rate. The minimum viscosity generally increases as graphene content increases. For RTM processing, it is desirable to use resins with low viscosity to reduce the amount of time required to fill the mould cavity under constant pressure injection. Ideally, it is desirable to infuse the resin within the viscosity range of 0.1 to 1 Pa [11]. From these results, the theoretical infusion window, or pot life, is defined as the time when the viscosity is between its minimum point and 1 Pa s. These results are summarized in Table 3-3.

Table 3-3: Minimum viscosity changes at different graphene contents

Graphene content (wt%)	Initial Viscosity (Pa s)	Pot life (minutes)
0	0.3	88
5	0.4	51
10	0.6	35
15	0.8	22

3.1.4 Tensile tests

Thin films are prepared by curing the resin between two glass plates treated with a release agent. Metal shims that are 200 µm thick are used to control the film thickness. Using a die punch (type 1BB), dog bone shape test coupons are prepared according to ISO 527-2. The elastic modulus, and the ultimate tensile strength (UTS) are found by testing these coupons in tension until failure. At least five coupons of each material are tested at a displacement rate of 0.5 mm/min on a MTS tensile machine with a load capacity of 1 kN. The results (Figure 3-2) show an increase in the Young's modulus with increasing graphene contents. Improvements of 14% and 34% are obtained at 5 wt% and 10 wt% graphene, respectively. The opposite trend is observed when measuring the UTS. At higher contents, the modulus and UTS seem to remain unchanged in comparison with the 10 wt% graphene batch.

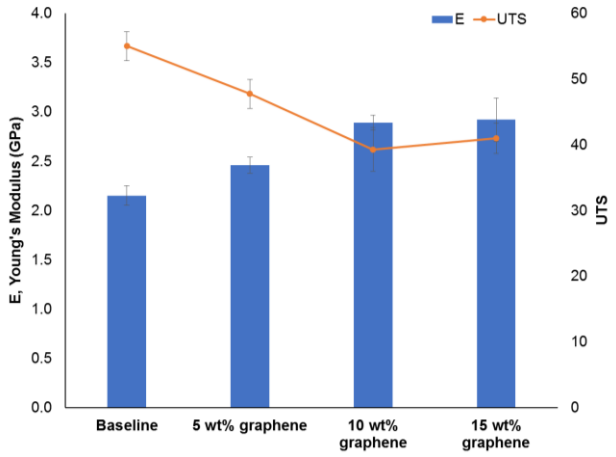

Figure 3-2: Tensile test results of resin thin films

3.2 Resin Transfer Molding Processing

To evaluate the microstructure, mechanical properties, and electrical conductivity of the samples, five panels are manufactured with RTM processing. Three GFRP and two neat resin panels with 0 wt%, 5 wt% and 10 wt% graphene are prepared (only 0 wt% and 10 wt% graphene contents are added to the resin panels). The details on the RTM process and each of the tests are presented in the following sections.

3.2.1 Resin transfer moulding process

With the knowledge obtained from material characterization, a strategy was devised to manufacture several

panels using RTM. A fiber glass dry preform is placed within a mould with two matching metal tools as shown in Figure 3-3**Figure**. The size of the mould cavity is 40 cm x 40 cm. The edge of the cavity is sealed with sealant tape to prevent resin race-tracking. For these enhanced panels, graphene is shear mixed with Part A of the resin (2000 RMP for 1 min, followed by 8000 RMP for 5 min). Prior to the addition of Part B, Part A is heated to 60°C for two to three hours to remove crystals formed during storage. The mixed resin is injected at a pressure of 290 kPa and vacuum is pulled at the outlet to prevent the formation of air bubbles in the part. Pure resin is injected at room temperature, and graphene-enhanced resin is injected at 35°C. The part is cured at room temperature for at least 24 hours, followed by a post-cure as per the resin supplier's specifications.

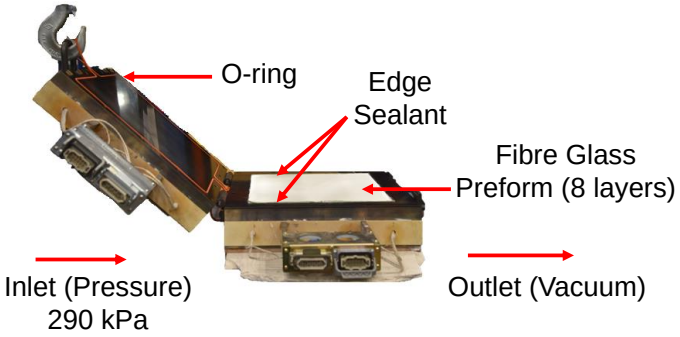

Figure3-3: RTM mould setup for flat panel manufacturing

3.2.2 Microscopy

Microscopy is performed using a Keyence VK 1000 laser scanning confocal microscope at 200X magnification. Coupons with a dimension of 20 mm by 20 mm are cold mounted using Epofix resin. These samples are then polished using SiC sandpaper, and a polishing cloth with 3 µm and 1 µm diamond suspension for the finishing step. Figure 3-4 shows a panoramic image of the 0 wt% and 5 wt% coupons, which is comprised of four images each. Graphene flakes can be observed mostly in the resin rich region, rather than in between the fibers. The graphene flake size (D_{50} = 13µm) is larger than the fiber diameter (approx. 7 µm), which interferes with inter-fiber dispersion.

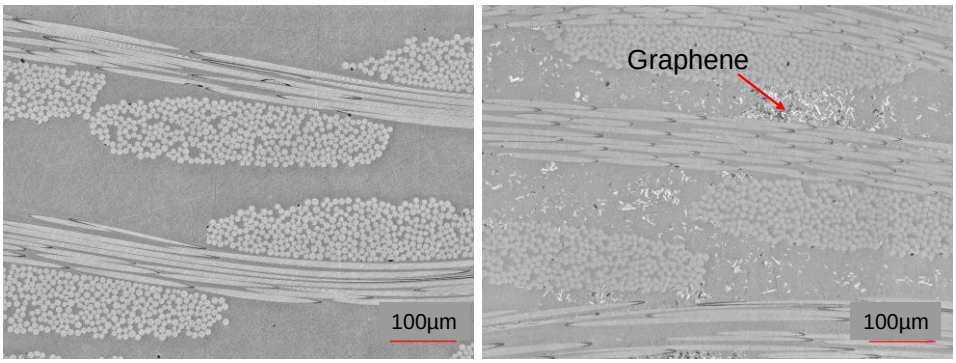

Figure 3-3: Micrographs of a) glass fiber-reinforced resin and b) glass fiber-reinforced resin with 5 wt% graphene

3.2.3 Three-point bending

Flexural properties of the materials are determined by three-point bending test per ASTM Standard D790-17 [12]. The coupons are 11 mm wide and 2 mm deep. The test span is 40 mm. As shown in Figure 3-5, the addition of graphene into pure resin brings modest improvement in flexural modulus. All GFRP panels exhibit significantly higher moduli. A peak modulus of 22.5 GPa is found at 5 wt% graphene content, which

subsequently drops to 21.4 GPa at 10 wt% graphene. These results suggest 10 wt% is beyond the optimal graphene content for modulus enhancement. Unlike the tensile results in the preliminary tensile test, there is no significant decrease in the flexural strength with the addition of graphene. This effect is likely due to the dominant effect of fiber reinforcement of the samples.

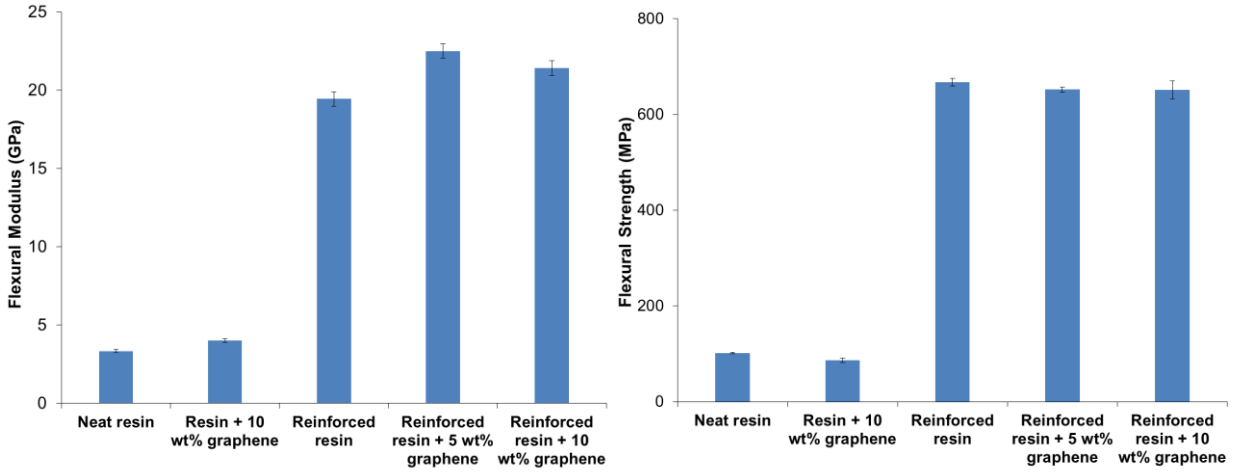

Figure 3-4: Three-point bending test results: flexural modulus (left) and flexural strength (right)

3.2.4 Charpy impact test

Charpy impact tests are performed according to ISO 179-1:2000 [13]. The test results are summarized in Figure 3-6. When comparing the neat resin with the GFRP samples without graphene, there is an improvement of the material's impact strength from 28 to 148 kJ/m^2. This effect is expected as the resin samples lack the fiber reinforcement and the matrix is brittle. After adding 5 wt% of graphene, there is a decrease in the toughness of the panels by 17%. At 10 wt% graphene, there is a marginal improvement to the impact strength. Overall, the addition of high graphene contents seems to have a negative effect on the impact strength of the material. The agglomerates observed in the samples (Figure 3-4, Section 3.2.2) can act as crack initiation sites, thus reducing the toughness of the material.

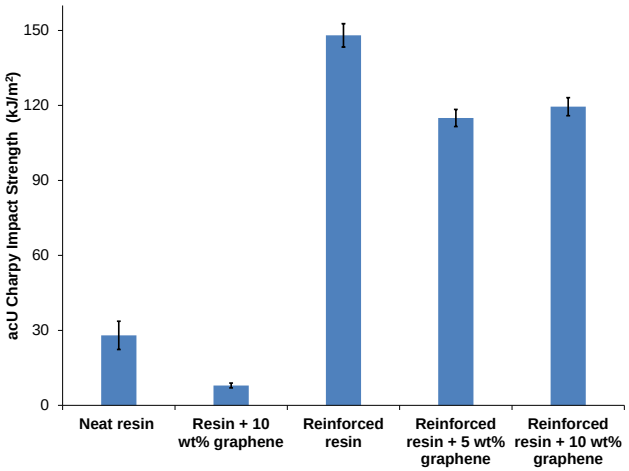

Figure 3 -5: Charpy impact test results

3.2.5 Electrical conductivity

Through-thickness and in-plane electrical conductivity are measured as shown 3-7. The hatched regions are covered with conductive silver paint, which act as electrodes when they are connected to a power source. Voltages of 10 V and 20 V are applied for both through-thickness and in-plane tests. Voltage is applied between the top and bottom surface, and between electrodes 1-2, 1-3 and 1-4, for through-thickness and in-plane samples, respectively.

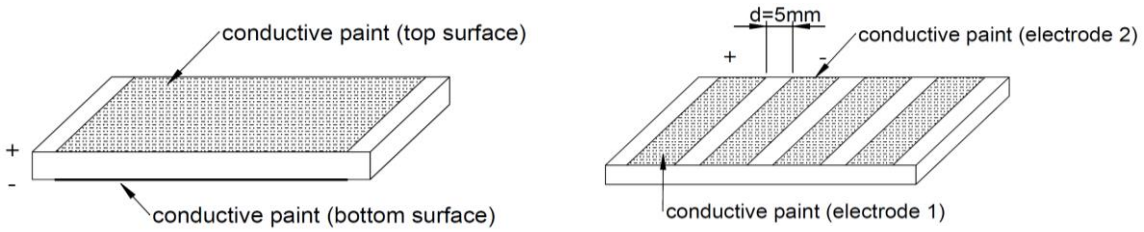

Figure 3-7: Schematic drawing of coupons used in through-thickness (left) and in-plane (right) electrical conductivity test

An improvement of nearly two orders of magnitude in the through-thickness electrical conductivity is observed on samples with 10% graphene, as shown in Figure 3-8. At these conductivity levels, graphene could be used to dissipate static charge in aircraft structures, military vehicles, and as protective gear when handling explosives. The in-plane test results did not show a significant improvement amongst all the panels, and hence these data is not shown in this paper. The limited enhancement in electrical conductivity can be attributed to the formation of agglomerates in the samples.

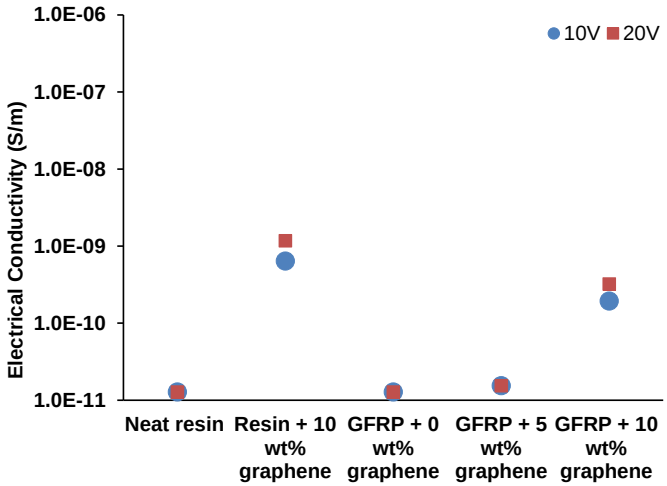

Figure 3-8: Through-thickness electrical conductivity test results

4.0 CONCLUSION

A two-part epoxy resin with graphene contents ranging from 0 wt% to 15 wt% is characterized to study the effect of graphene on the degradation temperature, T_g, and tensile properties. In addition, the optimum processing window in terms of viscosity is studied for RTM processing. Subsequently, GFRP and resin panels are fabricated via RTM and coupons are prepared to test the material properties. Improvements in the flexural modulus and strength, and electrical conductivity are observed. On the other hand, there is a deterioration of the impact properties with higher weight percentages. Improvements of the material properties are observed between the ranges of 5 wt% to 10 wt% graphene content. Therefore, it is

recommended to perform further experiments focusing on this range to find the optimum graphene content.

Agglomerations of graphene are found in the resin-rich region. Coarser fiber weave is expected to bring better inter-fiber dispersion, which could potentially improve its mechanical, and electrical conductivity properties. Other techniques such as functionalization can be used to reduce graphene agglomeration. It is expected that better graphene dispersion would result in further enhancement of the material properties. Since RTM provides great flexibility for the design of the part, this manufacturing process can be adapted into the production of existing or prospective armour structures to improve their performance.

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