



Material Characterization of Graphene Enhanced Composites for Resin Transfer Moulding

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ABSTRACT

Graphene possesses excellent mechanical, thermal and electrical properties and it can impart multi-functionality to conventional composites. In this paper, different graphene contents ranging from 0% to 15% weight ratios are added to a two-part room temperature epoxy resin. This resin is characterized in terms of thermal stability, rheological behaviour, and glass transition temperature (T_g). Resin Transfer Moulding (RTM) is used to fabricate glass fiber composite panels with and without graphene (up to 10 wt%). Additional neat resin samples and neat resin samples with 10 wt% graphene are also manufactured. Microscopy, three-point bending, and electrical conductivity tests are performed. From the material characterization results, the resin is thermally stable until 335°C prior to degradation. Overall, the T_g and the viscosity of the resin increase with higher graphene contents until reaching a peak which is between 10-15 wt%. The material at the maximum content of graphene gels after 630 minutes, providing a very broad window to infuse the resin. Overall, the addition of graphene at the % weight ratios explored in this project have shown to improve the flexural modulus and electrical conductivity of the samples. The microscopy images show non-homogenous graphene dispersion across the resin and the fibres which may limit the property enhancement of the composite. The recommendation is to use finer graphene flakes or coarser fibre weave to improve inter-fibre dispersion, which is expected to improve both the mechanical performance and electrical conductivity of the material.

KEYWORDS: Material Characterization, nanocomposites, resin transfer moulding, graphene

1 INTRODUCTION

Graphene research only recently started in 2004 when Geim and Novoselov of the University of Manchester discovered and isolated a single atomic layer of carbon for the first time [1]. Graphene is a defect-free carbon-based monolayer of sp^2 hybridized carbon atoms packed into a 2D honeycomb structure [2]. This carbon-based material exhibits a wide range of mechanical, electrical, optical, thermal, physical and chemical properties [3-5]. Graphene is known to be the strongest material known to mankind, even stronger than diamond, lightweight, flexible, transparent (graphene absorbs only 2.3% of light transmitted through it), electrically and thermally conductive (better than copper), non-toxic and chemically inert [6]. By adding graphene to composites, it is possible to improve significantly the properties of these materials. A manufacturing process used to add graphene into composite structures is Resin Transfer Moulding (RTM).

In this paper, a two-part room temperature epoxy resin is first characterized with different contents of graphene ranging from 0 wt% up to 15 wt%. Subsequently, RTM is used to manufacture two baselines (fibre glass and neat resin), two glass fibre-reinforced polymer (GFRP) panels with 5 wt%, and 10 wt% graphene, and an additional neat resin panel with 10 wt% graphene. Samples are cut and microscopy, three-point bending and electrical conductivity tests are performed. An evaluation is performed and recommendations are provided on the processing parameters for RTM composite manufacturing with graphene along with its recommended weight percentage to obtain improve its material properties.

2 EXPERIMENTAL

In this paper, two-part room temperature epoxy resin Techno fusion 8000 HT from Polymères Technologies is characterized and used to infuse fibre glass panels using RTM. This is a low viscosity, long pot life resin which makes it ideal for this process. The recommended mixing ratio is 100:26 by weight of part A to part B, with a recommended cure of 24 hours at room temperature, followed by a post cure two hours at 120 °C and then three hours at 150 °C [7]. For this work, GrapheneBlack 0X (from NanoXplore Inc.) is also used.

2.1 Material characterization methodology

As a first step to evaluate the effect of graphene in GFRP, the thermal stability, viscosity and glass transition temperature (T_g) of the two-part resin is characterized as described in the following subsections.

2.1.1 Thermal degradation

The first test performed is thermogravimetric analysis (TGA). A TA Instruments Q5000 IR TGA is used to determine the degradation temperature of the resin. This temperature establishes the high temperature limit of the material to ensure that the heat released during differential scanning calorimetry (DSC) is due to cure and not degradation. A neat resin sample and a sample with 15 wt% graphene of approximately 10-20 mg are loaded in a small platinum crucible. For the experiments, a ramp is performed from 20°C up to 550 °C under nitrogen and from 550 °C to 700 °C under compressed air at 10 °C/min. The degradation temperature is selected before there is a significant mass loss percent of 5%. For the neat resin and graphene samples, there is a mass loss of approximately 2.4% and 4%, respectively at 335 °C. The addition of a high content of graphene does not significantly change the degradation temperature of the material. This temperature is used as the limit in the subsequent DSC tests.

2.1.2 Glass transition temperature

The T_g of the resin samples is measured using a TA Instruments Q100 DSC and a Q800 dynamic mechanical analyser (DMA). 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. The $\tan \delta$ 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 [8]. Table 1 summarizes the results obtained with both techniques with 0 wt%, 5 wt%, 10 wt%, and 15 wt% graphene. With both methods, the T_g increases with higher graphene contents until reaching a peak at 10 wt%.

Table 1: T_g of the two-part epoxy resin with different graphene contents

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

2.1.3 Viscosity

A TA Instruments AR2000 rheometer is used to study the viscosity of the resin with and without graphene prior to processing with RTM. Similar as before, 0 wt%, 5 wt%, 10 wt% and 15 wt% graphene contents are tested. Overall, viscosity increased with higher graphene percentages while the gel time decreased. Gel time is defined as the point where the resin viscosity goes to infinity. Table 2 summarizes the rheology results. For all cases, it took less than 5 minutes to reach minimum viscosity.

Table 2: T_g of the two-part epoxy resin with different graphene contents

Graphene content (wt%)	Gel time (min)	Minimum Viscosity (Pa s)
0	770	0.3
5	700	0.4
10	700	0.6
15	630	0.8

2.2 Resin Transfer Moulding Manufacturing

Five panels are manufactured with different graphene contents ranging from 0 wt%, 5 wt% and 10 wt% using RTM. A dry fibre glass preform is placed between two flat mould surfaces. Sealant tape is placed at each edge of the preform to prevent race-tracking. Part A of the resin is placed on a hot steering plate at 60°C for two to three hours prior to the infusion to remove the formation of crystals prior to the addition of Part B. Graphene is shear mixed with Part A for the panels containing this nanoparticle. Resin is injected at the inlet at a pressure of 290 kPa. At the outlet, vacuum is pulled as the resin front advances to reduce air entrapment and assist the injection of the resin. The setup is shown in Figure 1. The laminate is cured inside of the mould for 24 hours at room temperature and subsequently post cured as per the manufacturer's specifications [7]. From the viscosity results, the resin will flow three minutes after mixing until reaching gelation at around 630 minutes, which provides an ample injection window.

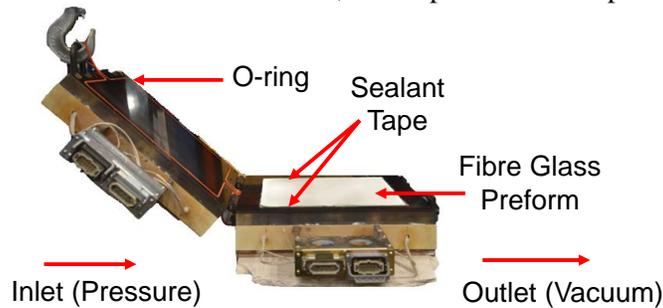


Figure 1: RTM mould setup for flat panel manufacturing

The manufactured panels are used to perform a series of tests which include microscopy, three-point bending and electrical conductivity. The test matrix is summarized in Table 3. These tests are performed to evaluate the impact of graphene on the material performance.

Table 3: Summary of panels manufactured with RTM with tests performed

Panel Code	Type	Graphene (wt%)
a	Resin	0
b	Resin	10
c	Fibre + Resin	0
d	Fibre + Resin	5
e	Fibre + Resin	10

2.2.1 Microscopy

Microscopy coupons with dimensions of 20 mm by 20 mm are cold mounted using Epofix resin. For polishing, 500, 800 and 1200 grit SiC sandpaper is used, followed by polishing cloth with 3 μm and 1 μm diamond suspension for the finishing step. The cross-sections are then examined under Keyence VK1000 laser scanning confocal microscope at 200X magnification.

2.2.2 Three-point bending

ASTM Standard D790-17 is followed to determine the flexural properties of the materials with and without graphene, and the neat resin samples [9]. The coupons are 11 mm wide by 2 mm deep. The test span is 40 mm. The crosshead motion rate is 1.33 mm/s as calculated according to Equation 1 in ASTM D790-17:

$$R=ZL^2/6d \quad 1)$$

Where R is the rate of crosshead motion, L the support span, d the depth of beam and Z is the outer fibre straining rate.

2.2.3 Electrical conductivity

Electrical conductivity is highly dependent on the manufacturing process of the sample, the measurement technique, and the anisotropy of graphene. In this paper, only one measurement technique and one process (RTM) is evaluated. However, both through-thickness and in-plane electrical conductivity are measured to account for the anisotropy of graphene. Silver conductor paint is applied uniformly on the samples as shown in Figure 2: Coupon surfaces are sanded to ensure good contact between the sample and electrodes. To measure the through-thickness electrical conductivity, a voltage of 10 V and 20 V is applied on the top and bottom surface. For the in-plane test, the same voltage is applied but only between electrodes 1-2, 1-3 and 1-4. The current is measured simultaneously for both tests while voltage is being applied.

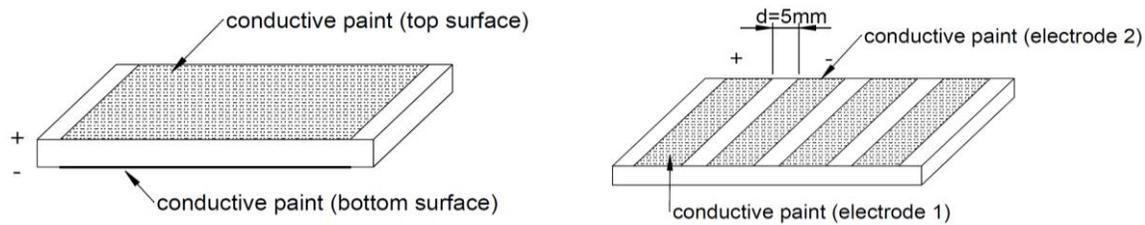


Figure 2: Schematic drawing of coupons used in through-thickness (left) and in-plane (right) electrical conductivity test

2.3 Microscopy, mechanical, and conductivity tests

Each of the following sections provide details on the results for each of the tests as outlined previously in the test matrix in Table 3.

2.3.1 Microscopy

The microscopy results are processed, resulting in pictures comprised of four stitched panoramic images each. These are shown in Figure 3. It can be observed that graphene flakes appear mostly in the resin rather than within the fibres. This could be a result of the graphene flake size ($D_{50} = 13 \mu\text{m}$) being larger than the fibre diameter ($\sim 7 \mu\text{m}$), thus making inter-fibre dispersion difficult. Such conglomerates may also result in a reduced impact strength where clusters of graphene can act as crack initiation sites.

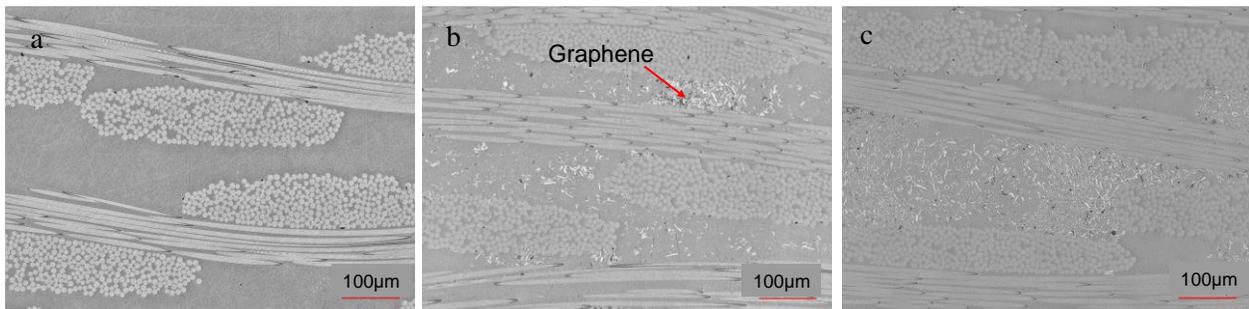


Figure 3: Micrographs of a) 0 wt% graphene with glass fibre, b) 5 wt% graphene with glass fibre and c) 10 wt% graphene with glass fibre

2.3.2 Three-point bending

The flexural modulus of each panel is shown in Figure 4. Flexural modulus is significantly higher in the GFRP panels, as one would expect. Incorporating graphene into pure resin adds modest improvement in modulus (from 3.3 GPa to 4.0 GPa).

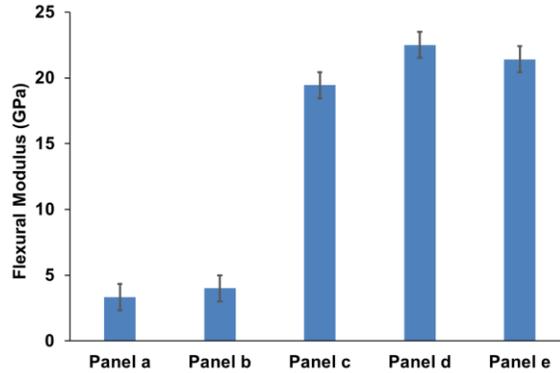


Figure 4: 3-point bending test results

Results from the GFRP (Panel *c-e*) imply that the optimal graphene content in terms of flexural modulus lies between 5-10 wt%. It is observed in the results that the improvement in flexural modulus is not linearly correlated to the graphene content. At 5 wt% graphene content (Panel *d*), the flexural modulus reaches a peak value at 22.5 GPa, a 15% improvement when compared to Panel *c* (19.4 GPa), and then the value drops to 21.4 GPa at 10 wt% graphene.

2.3.3 Electrical conductivity

Under both the 10 V and 20 V test conditions, there is an improvement on the electrical conductivity of the samples with 10 wt% graphene (Panel *b* and *e*) by a magnitude of two in the through-thickness direction. Although this level (10^{-7} S/m) of electrical conductivity is still not in the conductor range, it can be used for static charge dissipation. Graphene could be used to reduce the risk of static charge accumulation in applications such as aircraft structures and automobile spoilers. The in-plane test results show there is no significant difference in electrical conductivity amongst all the panels.

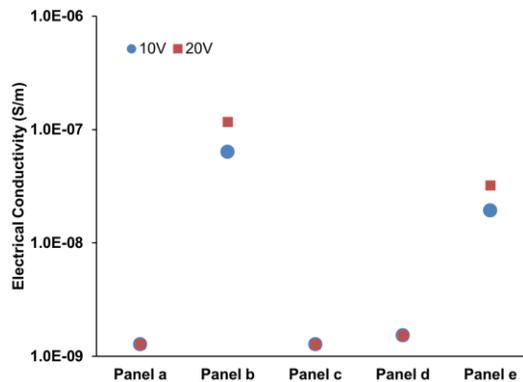


Figure 5: Through-thickness electrical conductivity results

3 RECOMMENDATIONS

Agglomerations of graphene flakes are found in the resin-rich region. Such dispersion characteristic may limit the enhancement performance brought by graphene. Finer graphene flakes or a coarser fibre weave are expected to bring better inter-fibre dispersion, which could improve its performance in mechanical and electrical conductivity tests. Improvements of the material properties are observed up to 10 wt% graphene, so it is suggested to explore additional weight percentages that are between 5-10 wt%. It is also recommended to perform additional tests such as Charpy to verify the full effects of graphene on the impact strength, and thermal conductivity.

4 CONCLUSIONS

Graphene is successfully impregnated into GFRP to up to 10 wt% using RTM processing. As expected, flexural modulus and strength significantly improved by adding glass fibres into the composite. There optimal graphene content to improve the flexural modulus of the material lies between 5-10 wt%. There is an indication for this batch of tests that graphene does not significantly improve the flexural strength. On the other hand, adding 10 wt% of graphene shows a significant improvement on the electrical conductivity of the material. Further optimization can be achieved by improving the dispersion characteristics of graphene by using finer graphene flakes or coarser fibre weaves, which would yield an overall improvement in these mechanical properties.

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