EFFECT OF MATERIAL AND MANUFACTURING PARAMETERS ON COMPRESSION RESIN TRANSFER MOULDING OF GRAPHENE-BASED MULTI-SCALE COMPOSITES

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1 Introduction

The advent of fast curing out-of-autoclave polymer systems along with the incorporation of low-cost fillers and particulate additives, are allowing for the production of non-structural automotive components with comparable mechanical properties to that of their denser metallic counterparts. The added benefit of lower rates of degradation also allows for longer operation life [1]. These new polymers systems are providing previously unserviceable manufacturing techniques, such as Compression Resin Transfer Moulding (CRTM), a new life that can keep up with the required rate of production necessary for the automotive sector [2]. Other than the immediately apparent benefits, the oddly synergistic effects of using such dissimilar materials in composites may reveal hidden added value where not initially considered. The concept of material multifunctionality is giving the entire engineering field something to consider when designing for the future. Historically, Fibre Reinforced Plastics (FRPs) were solely used as a material for structural design applications, but now scientist and engineers are looking at their potential applications for sensing and actuation [3]. The possibility to condense mechanical and electrical components into a single structure provides the ability to save weight and ease manufacturing. One way this is being achieved is through the use of Multi-Scale Composites (MSCs) [4].

This research manuscript delves into understanding the effect of material and manufacturing parameters on CRTM using a graphene-based MSC. A heated tool was used to compress a resin-wetted glass fibre preform to produce sample automotive body panels. The parts being produced are considered an MSC due to the resin system used being a graphene-based unsaturated polyester resin nanocomposite. To conclusively determine the degree of influence controllable material and manufacturing inputs had on the final desired material and manufacturing outputs, a Taguchi Method design of experiment (DOE) was employed. An experimental test matrix was produced with what were considered to be the most influential inputs, and sample test plates were created with these design configurations. This included sample target fibre volume fraction (V_{ff}), mould closure velocity (v_{cm}), mould temperature gradient (ΔT_m), resin nanoparticle loading (Graphene content by mass percentage) ($\%m_g$) and preform type (*Pref*). Each plate was then characterized using microscopy imaging and electrical conductivity techniques in order to objectively quantify its respective quality.

2 Methods

2.1 Design of Experiments

The CRTM process is described as an 8-Step procedure by Dransfeld and is depicted in Figure 1 [5].

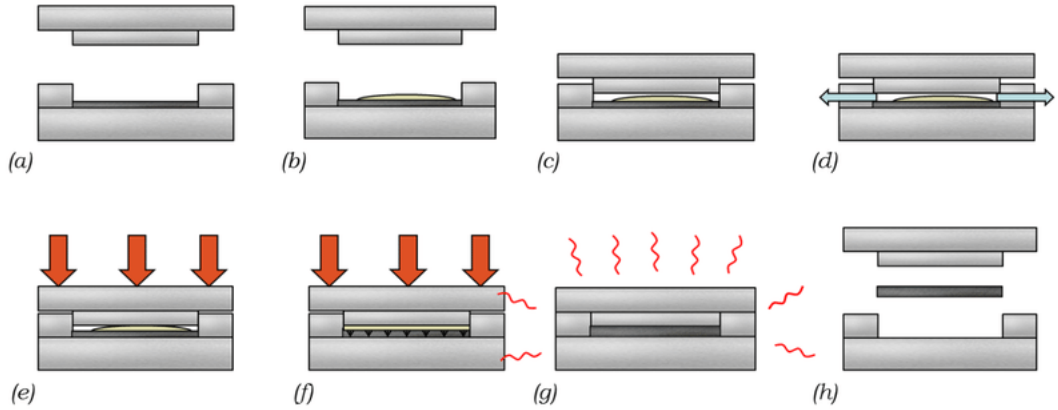

Figure 1. Principle of compression resin transfer moulding: (a) reinforcement is placed into mould, (b) resin is dosed, (c, d) cavity is closed to intermediate position and evacuated, (e, f) pressure on the mould impregnates the reinforcement through the thickness, allowing a particularly high dwell pressure, (g) curing and (h) demoulding [5].

Throughout these steps, there are multiple controllable and uncontrollable factors that can affect the quality of the final part. After a thorough literature review of the CRTM process, along with guidance from industry partners [6], a list of controllable input parameters used in the material system and manufacturing process were chosen as follows:

Table 1. Control factors and their corresponding levels

Control Factors		Symbol	Level				Units
			1	2	3	4	
A	Target Fibre Volume Fraction	V_{ff}	30	45	-	-	%
B	Mould Closing Velocity	v_{cm}	2	8	-	-	$mm \cdot s^{-1}$
C	Mould Temperature Gradient	ΔT_m	5	10	-	-	°C
D	Resin Nanoparticle Loading	$\%m_g$	0.0	0.3	1.5	7.5	%
E	Preform Type	*Pref*	R	U	-	-	-

where R stands for a randomly oriented glass fibre mat and U stands for a uni-directionally oriented glass fibre mat.

The resin used to incorporate the nanoparticles is an unsaturated polyester blend with styrene and low-profile additives, while the randomly oriented and uni-directional mats used are an Owen Corning Unifilo (000-0308) with areal weight of 450 g/m^2 and a Saertex mat (000-0118) with areal weight of 696 g/m^2, respectively.

Using Table 1, an orthogonal array matrix, shown in Table 2, was created. The required orthogonal array matrix for four 2-level control factors, with one 4-level control factor and no correlations is the L_8 matrix. The L_8 matrix is an eight-trial experiment which provides the minimum number of trials required to conduct ANOVA. Table 2 gives the final L_8 matrix showing the required trials with each control factor and corresponding level per trial, respectively.

Table 2. Taguchi L_8 Matrix

Trial	A	B	C	D	E
1	1	1	1	1	1
2	1	1	2	2	2
3	1	2	1	3	2
4	1	2	2	4	1
5	2	2	2	1	2
6	2	2	1	2	1
7	2	1	2	3	1
8	2	1	1	4	2

2.2 Plate Manufacturing

The setup used for the CRTM experiments was a custom instrumented hot press shown in Figure 2. The hot press was heated by four 500 W cartridge heaters from Watlow each in the upper and lower platens, and a Watlow SD series Proportional-Integral-Derivative (PID) temperature controller was used to control the temperature of each platen respectively. The fixture was mounted onto a 100 kN Instron universal testing machine and gap height was controlled through its respective software *Bluehill Universal*. The gap height was used to control the target fibre volume fraction within the mould therefore compaction pressure became an independent variable in the process. Using the instrument hot press, MSC test plates were manufactured according to a seven-step procedure:

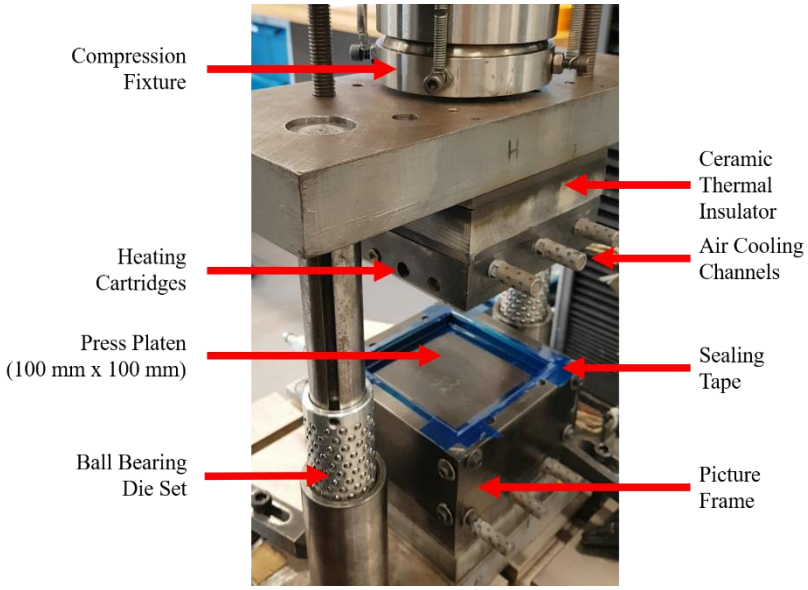

Figure 2. Instrumented hot press

Step 1. Create the Nanocomposite

The nanocomposite was created by mixing graphene powder with an unsaturated polyester resin using a high shear mixer as shown in Figure 3. The resin was mixed over ice to reduce its temperature while mixing to prevent evaporation of styrene.

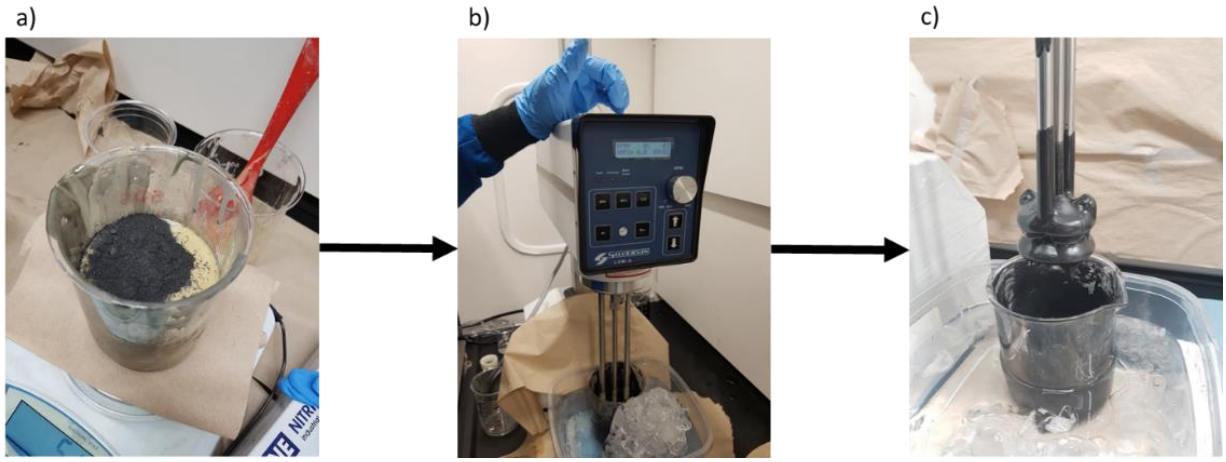

Figure 3. Creation of Nanocomposite - a) Unmixed graphene powder with unsaturated polyester resin b) Mixing nanocomposite in ice bath c) Final mixed nanocomposite

Step 2. Prepare Moulding Surfaces

Mould surfaces were prepared with high temperature polyester sealing tape to seal all internal joints, and then three coats of Chem Trend Chemlease 2726W was applied to all exposed mould surfaces.

Step 3. Measure Mould Surface Temperature

Top and bottom mould surfaces were measured with thermocouples to ensure that the set temperature and the actual mould temperature were the same. Depending on room temperature, the set temperature had to be adjusted to match that of the desired mould temperature.

Step 4. Place Preform into Mould

Proper fibre placement is paramount in CRTM as folds, kinks in the preform or any excess fibre in the flash gap, may cause fibre pinching and restricted flow within the mould and/or near the flash gap.

Step 5. Pour Nanocomposite over Preform

The resin was poured in the centre of the mould onto the preform as shown in Figure 4. An additional 10% of resin (by volume) compared to that of the desired fibre volume fraction for the part was added as to avoid dry spots. Excess resin flowed out of the flash gap and was easily removed during demoulding.

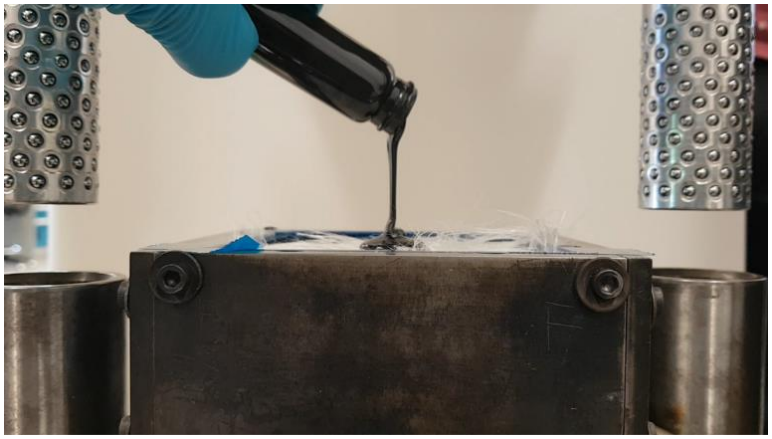

Figure 4. Pouring nanocomposite over preform during CRTM

Step 6. Mould Closure

The mould was closed a constant velocity to a desired final gap height enabling the desired target fibre volume fraction. This gap height was maintained for 10 minutes before the demoulding step.

Step 7. Demoulding and Visual Inspection

After removing each plate from the mould, sealing tape and excess flash were removed from the samples. The plates were then labelled with their designated trial number and an "X" was placed on the lower left corner on the upper side of the plate indicating each plate's orientation within the mould.

2.3 Direct Current Volumetric Electrical Conductivity

Using the Keithley Instruments Model 8009 resistivity test fixture, along with the ASTM D 257 - Standard Test Methods for DC Resistance or Conductance of Insulating Materials, the DC volumetric conductivity was measured. While applying a known DC voltage across the conductive surfaces of the testing fixture, the current response is measured. While testing, the sample must be handled carefully as surface debris and/or oils residues left from fingertips may affect the conductivity at the surface of the sample. By using a variety of samples with different nanoparticle loadings, and measuring each geometry of the sample being tested, an estimation of the percolation threshold can be found.

2.4 Optical Microscopy

After an initial inspection visual inspection of the manufactured 10cm x 10cm plates, each plate was cut using a wet saw into three axisymmetric regions: Region I - Furthest from centre, Region II - Offset from Centre and Region III - Centre. Each region was roughly 10mm in width and 70mm in length. Regions near the perimeter of the plate were removed as to avoid samples with large void content or anomalies produced by edge effects of the plate. A cross section from the midpoint of Region II was taken, potted, polished, and imaged using the Nikon L150 reflective microscope. Details highlighting void formations, matrix cracking, graphene dispersion and filtration effects were investigated.

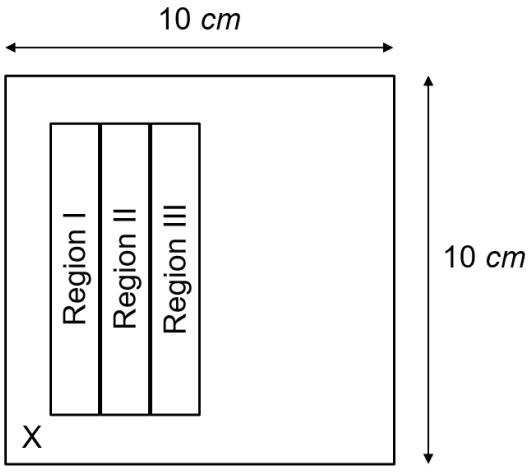

Figure 5. Regions of Plate

3 Results and Discussion

3.1 Visual Inspection – Macroscopic

Without any post-processing after manufacturing, the randomly oriented fibre plates and the uni-directional fibre plates appear as shown in Figure 6. It is clear to see that as the graphene content is increased, the plates become darker in colour. The most important aspect that must be taken away from the visual inspection are the manufacturing defects. These include the curvature seen in the uni-directional plates, and the effect of nanoparticle filtration across all samples.

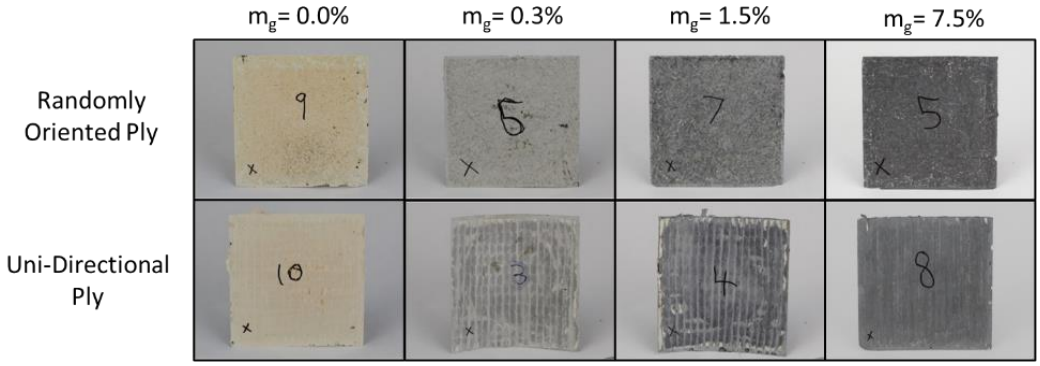

Figure 6. Manufactured Plates

3.1.1 Warp Defects

As shown in Figure 7, there is severe warpage in the uni-directional fibre plates, most excessively seen in the 0.3% graphene loading case, thus indicating high cure shrinkage in resin rich areas and/or poor fibre impregnation within the uni-directional tows. This did not happen in the randomly oriented fibres as the stochasticity of the fibre direction lends to a homogeneous part between the resin and the fibres. Void formation was predominately seen only at a micro-void level, meaning that the fibre tows were not fully saturated with the resin. It is assumed that as the resin's viscosity increased due to the addition of graphene, that the fibre tow was not permeable enough for the resin to fully wet the fibre. During compression, this effect is exacerbated as the fibre becomes compacted and it's permeability decreases even further. The resin then flowed along the path of least resistance which was between the fibre tows. From the naked eye, not many macro-voids were seen within the plates, however filtration effects were obvious.

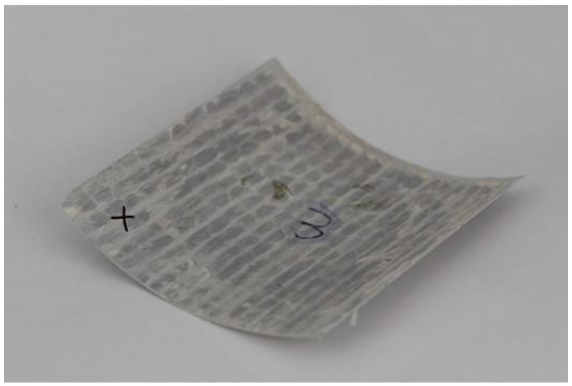

Figure 7. Warped Plate

3.1.2 Filtration Defects

Macro level nanoparticle filtration was seen both between and along fibre tows pre-dominantly in the uni-directional fibres. This filtration effect became even more apparent as the nanoparticle loading increased which inherently increased the resin viscosity. Inter-fibre filtration occurred along the entire length of the fibre while intra-fibre filtration seems to be most apparent furthest from the centre of the part. A test trial plate, produced additionally from the Taguchi test matrix, was shown to greatly highlight this filtration effect and is shown in Figure 8. The plate produced had a high graphene loading and high target fibre volume fraction.

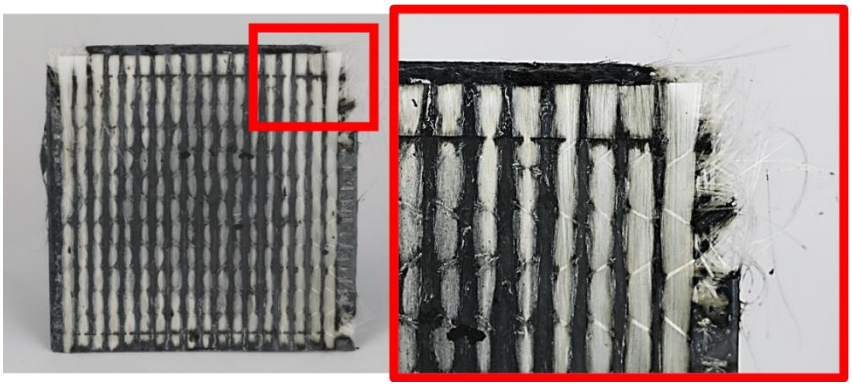

Figure 8. Graphene filtration both parallel to the fibre tow (intra-fibre) and transversely through fibre tows (inter-fibre)

3.2 Visual Inspection – Microscopic

3.2.1 Randomly Oriented Fibres

Common manufacturing defects such as void formations and surface defects were observed at all graphene loadings. As the nanoparticle loading increased, surface defects became less of a problem, while entrapment of air bubbles in the plate increased. This is most likely due to the increased viscosity of the resin not allowing for either proper fibre impregnation causing micro-voids, or air in the resin not being mobile enough to escape the high viscosity fluid causing macro-voids. The addition of nanoparticles also showed the consequential problem of graphene clustering and filtration. This was shown most clearly in the 7.5% nanoparticle loading resin and presented in Figure 9 with the graphene being the bright white spots.

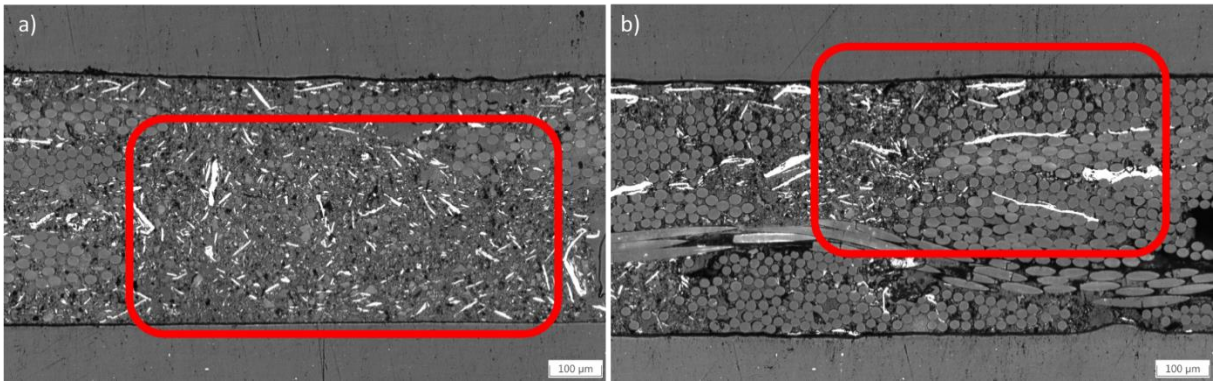

Figure 9. Randomly oriented fibre defects due to graphene loading – a) Graphene clusters b) Graphene filtration

3.2.2 Uni-direction Fibres

Similar void phenomenon was seen in the uni-directional fibre plates. Due to the architecture of the uni-directional fibre causing bending in the composite plate, severe matrix cracking in resin rich regions were observed. Also, due to the fact that not every fibre tow was perfectly equal, there was some variation in the impregnation of fibre tows within each manufactured plate. The low permeability of the fibre already caused problems with fibre wet out, but during compaction this problem was exacerbated. It is hypothesized that during compaction, the large tows became compacted quickly and little resin flowed within the tow, the smaller tows were able to be impregnated better and compacted well as the compaction reached its target fibre volume fraction gap height. This was proven as within the same plate, there are some well compacted areas but also some poorly compacted areas in which many micro-voids existed.

Similarly to the randomly oriented fibres, the introduction of the nanoparticle caused an increase in the viscosity of the resin which in turn further intensified the problem of fibre impregnation. There were numerous resin rich regions surrounding the fibre tow, predominantly near the surface of the plate and in between each fibre tow as shown in Figure 10.

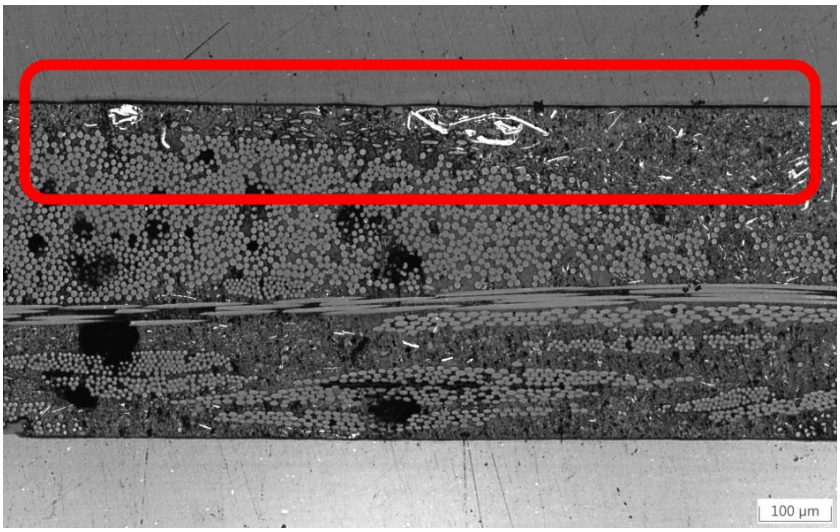

Figure 10. Poor fibre impregnation in uni-directional MSC plate - shown specifically is the 7.5% graphene loading case

3.3 Electrical Volumetric Conductivity

Due to the curvature of the uni-directional samples, only the randomly oriented plates were measured for electrical conductivity as the sample for this test is required to be flat. An electrification time of 60 sec at 100 V was set such that the material can be fully charged. It must be noted that for plates with graphene loadings at 7.5%, the voltage of 100 V produced too high of a current and the device was not operational. For this reason, plates with graphene loadings of 7.5% were tested at 1 V. The conductive testing surface is circular with a diameter of 54 mm, therefore the 6.0 cm x 7.0 cm composite plate easily covered this area to ensure that the entire surface of the plate was in contact with the testing fixture. Using the contact area, average plate thickness and the measured resistance, the electrical conductivity (σ_{DC}) can be evaluated using Equation (1).

$$\sigma_{DC} = \frac{I}{V}\frac{t_c}{A} \tag{1}$$

where *V* and *I* are the applied voltage and the measured current, respectively, t_c is the specimen thickness, and *A* is the conductive area. The effect of each control factor on the electrical volumetric conductivity is shown below in Figure 11.

Beyond a nanoparticle loading of 1.5% there is a drastic increase in the volumetric conductivity. This signifies that the percolation threshold is achieved somewhere between the 1.5% loading mark and the 7.5% loading mark. At a nanoparticle loading of 7.5%, the volumetric conductivity was measured to be 4.94×10^{-04} $(\Omega \cdot m)^{-1}$, on average. This is an increase in the volumetric conductivity by 8 orders of magnitude compared to that of all the other graphene loadings. Due to the large orders of magnitude change in the volumetric conductivity produced by the nanoparticle loading, the effect seen by other control factors are inconclusive. However, it is assumed that the remaining control factors do not play as significant of a role in the volumetric conductivity.

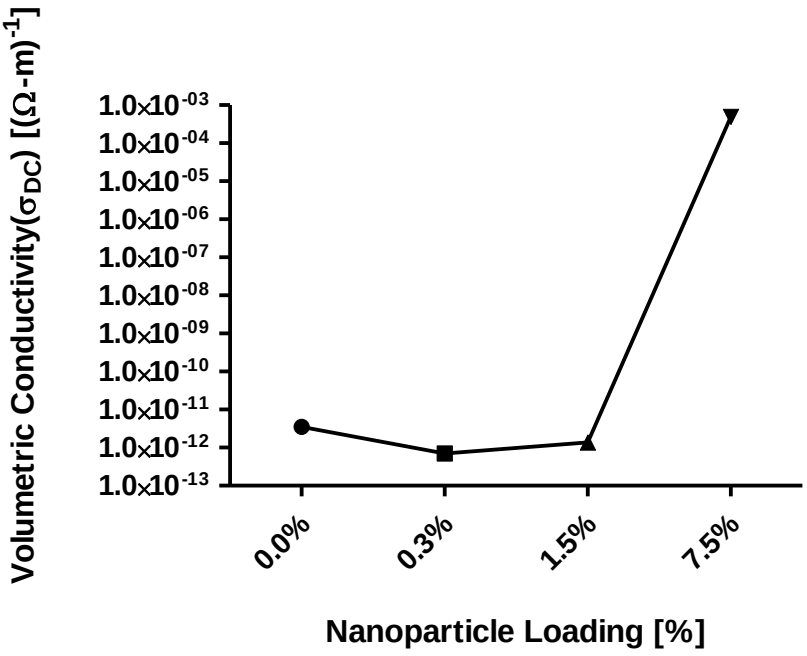

Figure 11. Nanoparticle loading effect on volumetric conductivity (σ_{DC})

4 Conclusion

The manufacturing of a graphene-based MSCs using the CRTM process was investigated. Looking at various material and manufacturing parameters, it was discovered that graphene greatly influences the conductive properties of the MSC but may also cause manufacturing defects that may not have been present without it. The introduction of graphene as a conductive filler greatly increases the viscosity of the impregnating resin reducing the allowable impregnation of resin as it flows due to compression.

One predominant limitation of the study was the inability to control the internal pressure within the mould. This may have been solved by controlling the size of the flash gap and/or by adding a “pinching zone” using a metallic

shim. Manufacturing defects such as dry spots or race tracking may be alleviated by controlling these parameters. It is hypothesized that by controlling the size of the flash gap, that the direction of resin flow can be better controlled. The same principle can be applied to using a metallic shim over the fibre bed, because during compression, the shim will compress the fibre differently depending on its shape and cause low-permeability regions within the mould, known as a “pinching zone”. Utilizing these pinching zones, resin flow can be better controlled.

5 ACKNOWLEGDMENTS

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6 REFERENCES

[1] Taub, Alan and De Moor, Emmanuel and Luo, Alan and Matlock, David K and Speer, John G and Vaidya, Uday. "Materials for automotive lightweighting". *Annual Review of Materials Research*, pp 327-359.2019.

[2] Hillermeier, Roman and Hasson, Tareq and Friedrich, Lars and Ball, Cedric. "Advanced thermosetting resin matrix technology for next generation high volume manufacture of automotive composite structures". *SAE World Congress and Exhibition*, pp 1176-1185. 2013.

[3] Li, Chunyu and Thostenson, Erik T and Chou, Tsu-Wei. "Sensors and actuators based on carbon nanotubes and their composites: a review". *Composites science and technology*, pp 1227-1249. 2008

[4] Mittal, G., Rhee, K. Y., Mišković-Stanković, V., & Hui, D. "Reinforcements in multi-scale polymer composites: Processing, properties, and applications.". *Composites Part B: Engineering*, pp 122-139. 2018.

[5] Dransfeld, Clemens and Masania, Kunal and Kramer, Erich and Siegfried, Marcel and Klauser, Stefan. "Fast impregnation of complex shapes for the manufacturing of high performance composites and its associated tooling". *11th International Conference Flow Processing in Composite Materials*. 2012.

[6] Phillips, David-Michael. “Effect of material and manufacturing parameters on compression resin transfer moulding of graphene-based multi-scale composites”. Montreal, Canada: McGill University. 2021.