The Effect of Process Variation on Pristine Carbon Nanotube Particle Dispersion within Glass-Fibre Reinforced Epoxy Polymer Composites and its Resultant Mechanical Characteristics

By

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July 2020

Abstract

The present work focused specifically on two fabrication processing methods, namely, vacuum-assisted resin transfer moulding (VARTM) and double vacuum-assisted resin transfer moulding (DVARTM) processing methods. DVARTM was essentially a modified VARTM process. The research focused on the effect of nanoparticle dispersion within the composite and the effect of process variation on its mechanical properties. The resultant composites consisted of E-glass fibre (GF) infused with an epoxy matrix doped with 0, 0.1, 0.3 and 0.5 wt% of pristine multi-walled carbon nanotubes (MWCNT). Dynamic mechanical analysis (DMA), tensile testing and a quantitative "burn-out" test analysis were conducted to show the effect of MWCNT dispersion due to the process variation. The overall graphical DMA analysis for the DVARTM method revealed trends consistent to specimens containing homogeneously dispersed nanoparticle content. At 30°C, the 0.5 wt% composite from the DVARTM method displayed a 34% stiffness increase compared to VARTM with the similar wt%. Glass transition temperatures (T_g), displayed a steady incremental increase in DVARTM from 0.1 to 0.5 wt% content. The VARTM method showed a steady increase in T_g for 0.1 and 0.5 wt% content with a decline in 0.3 wt% content. In the DVARTM method, the damping for 0.1 wt% decreased by 14.5% and 10%, compared to the 0.5 wt% and the control, respectively. The decreased damping indicated an enhancement to the filler-matrix interfacial bonding. The ultimate tensile strength (UTS) had a uniform increase with increasing weight percentages of MWCNT content for the VARTM method. Both methods experienced optimum UTS with 0.3 wt% MWCNT content. A "burn-out" test on various layers of the composite along the lengths and thickness directions was conducted for both methods. The resultant quantitative analysis of the residue on the GF after combustion suggested improved dispersion of MWCNTS for the DVARTM method in comparison to VARTM. The important finding in this study highlighted that enhancements to mechanical properties were achievable when using pristine MWCNTs along with process variation, as opposed to past studies which stated that pristine MWCNTs were non-effective unless functionalized.

Declaration

I, Prajan Ramdeen, hereby declare that the research contained herein is solely my work, except where indicated and that all references are reported accurately to the best of my knowledge. The study is submitted in fulfilment and accordance with the requirements for the degree: M Eng (Mechanical) offered within the Department of Mechanical Engineering at Durban University of Technology, South Africa. This work has not been submitted to any educational institution for assessment.

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FINAL APPROVED SUBMISSION

July 2020

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Acknowledgements

I am grateful to the Almighty for allowing me the opportunity to expand my knowledge and journey through the field of nanotechnology. I also wish to express my gratitude and blessings, above all the 'thank-you' notes below, to the following individuals for all their endeavours, strength, motivation and support during my study:

- Firstly, a big thank you to Denel Dynamics, South Africa for their financial support during the programme
- Thank you Durban University of Technology, South Africa, for their financial support from the postgraduate grant
- Thank you Prof K Kanny for all your understanding and support while under your dedicated supervision. I could not have asked for a better supervisor
- Thank you, Dr TP Mohan, for your guidance and direction with your expertise in the field of material science and your current research knowledge in nanotechnology
- Thank you to my beautiful son, Tej, for the love, support and forgiveness for the lost family time during the demanding periods of the study
- Thank you mum (S Ramdeen) and dad (G Ramdeen) for your extended support and help during unforeseen events during the programme
- A warm thank you to Avinash Ramsuroop for your assistance and time allocation given towards the testing and reporting of specimens
- Thank you VK Moodley, J Bux, S Chetty (Miss) for your friendship, support, motivation and help during my journey
- Thank you P Suthan, University of KwaZulu-Natal (UKZN), for your laboratory assistance and facilitation of results
- Lastly and most importantly, a greatly appreciated thank you attached with my sincere heart-filled blessings to my dear friend, Kirshwyn Naidoo, for loaning me his laptop during my laptop failure to complete this thesis

Dedication

I dedicate this dissertation to my beautiful son - Tej, mum, dad, brother, sister and fellow friends who sacrificially made this achievement achievable. Thank you!

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Chapter One – Introduction

This thesis takes an in-depth look into the fabrication of hybrid composite laminates containing multiple woven glass fibre (GF) reinforcement layers which are bonded within a thermosetting polymer-based epoxy matrix which is pre-doped with multi-walled carbon nanotubes (MWCNT). The fabrication involves two processing methods and the product variations are shown with the aid of mechanical testing.

1.1 Background

The combination of fillers and reinforcements to fabricate hybrid epoxy composites are commonly used in various applications, for example, the automotive and aerospace industries. The inclusion of fillers into reinforcements facilitates weight reduction, improved strength and enhanced thermo-mechanical properties. The literature depicts carbon nanotubes (CNTs) as an ideal filler choice for fibre-reinforced composite systems which complements the prior mentioned properties [1-3]. However, careful attention to CNT content is crucial in the achievement of optimal infusions. CNTs tend to aggregate naturally. Prolonged clustering of the tube form larger structures referred to as agglomerates. The extent of agglomeration affects the degree of dispersion of the CNTs within the composite. Past research showed that even with an addition of CNTs as low as 1 wt% to a matrix could drastically increase its viscosity. Consequently, higher filler loadings synergistically increased agglomeration. Composites containing CNTs beyond 0.5 wt% deteriorated its mechanical properties [4-6]. In addition to viscosity, the specific surface area (SSA) of CNTs similarly, has been found to influence agglomeration. Single-walled CNTs (SWCNTs) and double-walled CNTs were shown to have larger SSAs compared to MWCNTs. Larger SSAs created greater cross-linking between the CNTs and the matrix interphase. The improved interfacial bonding within the matrix simultaneously hindered the ability of the tubes to detangle and disperse homogeneously within the matrix. On the contrary, the smaller SSAs of MWCNTs potentially promoted better particle dispersion due to lowered cross-linking; however, this created weaker interfacial bonding with the matrix. Viscosity and SSA have thus

become crucial properties to consider during processing methods such as liquid transfer moulding, resin transfer moulding (RTM) and vacuum-infusion (VI) methods [7-10].

The vacuum-assisted resin transfer moulding (VARTM) method is a common, efficient and cost-effective process used to fabricate hybrid epoxy composites [11-14]. Efficient fabrications become possible when the following conditions are met: (a) strong interfacial bonding between CNTs and matrix; (b) good compatibility between the matrix choice and the type of CNTs considered; (c) adequate CNT dispersion and (d) appropriate orientation of the CNTs within the matrix [15-19]. Past research indicated that VARTM became challenging and unreliable when using large filler loadings mainly due to its influence on increasing the particle agglomeration. The increased agglomeration diminished the dispersion of particles within the fibre layers. Research in particle dispersion determined the optimum MWCNTs loading in VI processes to be effective at quantities <0.5 wt%. When this threshold was exceeded, it induced a 'filtering effect' and consequently retards or completely terminates the infiltration of the matrix into the fibre layers. Hence, the resulting composites had experienced either incomplete fibre wetting or dry spotting within and along the fibre layers as the matrix progressed in the shear direction while under vacuum [10, 19-22]. In another study, Gojny et al. experienced an absence of CNTs filtering through the fibre. However, the choice of the processing method (RTM) could have influenced the absence of filtration [10].

Homogeneous filler dispersion within the composites was shown to be imperative to obtain successful interfacial bonding within the composites. Ideal or near-ideal filler dispersion showed an enhancement to certain mechanical properties [23]. Particle dispersion was shown to be a significant area of concern in much of the research. Therefore, to countermeasure the above mentioned 'filtering effect', many techniques had been implemented to improve the filler (such as CNTs) dispersion before processing of the composites. Some common dispersion techniques included solvent addition, acoustic cavitation, mechanical agitation, sonication, 3-roll milling and CNT surface modification (also referred to as functionalization) or a combination of these techniques [6, 8, 24-28]. In the study by Gkikas [29], the researchers focused on sonication in CNT

dispersion. Their findings concluded that CNTs exposed to sonication for a duration of 1hr showed the best improvement to storage modulus and glass transition temperature (T_g). Other researchers such as Montazeri and Chitsazzadeh [30-31], reported that certain mechanical properties could be 'tailored' by exposure to sonication of CNTs at different power and time combinations. These combinations showed improvement in Young's modulus, tensile strength, dispersion and T_g. Their study concluded that prolonged sonication improved the filler dispersion state; however, the effect resulted in tube length reductions in MWCNTs.

Past research [32-37] often focused on improving the CNT-matrix interphase by surface modifications. In addition to MWCNT pre-treatment using sonication and surface modification, Fan et al. [25] successfully achieved a greater homogeneous dispersion state of MWCNTs within the reinforcement by simply modifying the VARTM method. This modification to the conventional VARTM introduced an additional vacuum bagging layer/step (referred herein as DVARTM).

1.2 Problem Statement

Two questions seemed to have emerged from the above-mentioned study [25] and in addition to the previous literature reviewed: (i) was the improvement due to the MWCNT surface modification? Or (ii) was it due to the variation in processing alone? A lack in knowledge exists in the processing comparisons as opposed to the usual focusing on the use of component comparisons.

1.3 Scope of the Study

In an attempt to clarify the doubt from the above-mentioned knowledge gap, the present study focuses on fabricating composites using VARTM and DVARTM processing methods. The study uses similar pre-treatment dispersion techniques as per the DVARTM process [25] with the exemption of any surface modifications to the MWCNT, thereby choosing pristine MWCNTs as the filler component. Furthermore and in addition to the prior objectives mentioned, this study also aims to establish a benchmark for processing techniques and to create enhanced clarity in the use of pristine

MWCNTs for future research and composite fabrication. The resultant mechanical properties generated from the composites dynamic mechanical analysis (DMA), tensile and flexural responses for both processing methods in comparison to control samples are presented.

1.4 Aim

a) To verify whether the modified VARTM method (DVARTM) improves the dispersion state of MWCNTs in the thickness and shear direction within the composite and

b) To verify for homogeneous dispersion using mechanical tests (Mechanical Analysis (DMA) and tensile tests).

1.5 Objectives

1.5.1   To fabricate a control sample consisting of matrix and GF reinforcement only

1.5.2   To fabricate hybrid composites containing 0.1, 0.3 and 0.5 wt % of MWCNTs using the VARTM processing method to identify parameters for comparison with the control.

1.5.2   To fabricate hybrid composites containing 0.1, 0.3 and 0.5 wt % of MWCNTs using the DVARTM processing method to identify parameters for comparison with the control.

1.5.3   To perform mechanical tests using Dynamic Mechanical Analysis (DMA) and tensile testing on both processing test specimens.

1.5.4   To compare mechanical results from both methods to the control.

1.6 Delimitation

The study is delimited with respect to two processing methods (VARTM and DVARTM) to fabricate the composites and pristine MWCNTs will be used as the filler component with a content of 0.5 wt% as a maximum.

1.7 Assumptions

Researchers such as Fan et al [25] indicated that the actual dispersion state of nanoparticles within the fibre reinforced hybrid composite was difficult to prove. Ideally, nanoparticle dispersion could best be shown by transmission electron microscopy (TEM), however, difficulty ensues in obtaining successful microtome sections with the presence of fibres within the composite. In this work, homogeneous dispersion states of MWCNTs were demonstrated in the composites which were produced. These homogeneous dispersion states were achieved using the modified VARTM method (DVARTM). As previously mentioned, this study embarks on two processing methods, namely, VARTM and DVARTM. In the present study, uniform MWCNT dispersion states will be assumed within all composites produced from DVARTM.

1.8 Structure of the Dissertation

This study will comprise of five chapters. This chapter dealt with the problems related to the usage of MWCNTs as the filler component and outlines the problems associated with vacuum infusion processing methods. The Chapter also describes the aim, objectives, delimitations and assumptions for the study.

Chapter Two will present the historical overview conducted by past researchers in this field of hybrid nanocomposites. The chapter will briefly outline how composites have been modified over the years and the processes that were used to fabricate them. The chapter will further discuss how fillers are combined with composites, the problems encountered with filler addition concerning their dispersion within the fibre layers and possible techniques that may countermeasure this effect.

Chapter Three will describe the research design and methodological approach used to prepare individual components of epoxy glass-fibre hybrid composites. In line with the guidelines of the respective ASTM standards, the testing and analytical procedures used will also be described.

Chapter Four will present a discussion on the test results obtained. The results obtained for both processing methods will be analysed in comparison to the control sample which comprises of neat epoxy and fibre only. The overall findings will be used to generate recommendations for future work in Chapter Five.

Chapter Five forms the final chapter of this dissertation and will provide a conclusion to this study based on the test results obtained for tensile strengths, Young's moduli, damping factors, stiffness and loss moduli. Recommendations for future work will be presented here which will be aligned to the overall results obtained in Chapter Four.

Chapter Two – Literature Review

The present research focuses on nanotechnology and its application in the area of hybrid polymer composites. This chapter introduces the reader to concepts pertaining to polymer hybrid composites and gaps in the literature. Apart from the gap identification, this literature review will also consist of a general overview of the role of composites in industries; components used in composite fabricating; a discussion on the mechanical properties resulting from enhancements to composite structures as compared to conventional materials; the components used to make up composite structures including the processing methods to combine them; properties of CNTs (the chosen nano-filler) for the study; a brief introduction to the fabricating of carbon nanotubes (CNTs); nature and characteristics of CNTs; benefits associated with CNT enhancements; hurdles encountered with CNTs as a filler component; the importance of CNT dispersion including dispersion techniques and lastly, a summary highlighting the chosen components and methodology employed to close the void in clarity within the research topic.

2.1 A Brief Introduction to Nanotechnology

Thus far, the world had been accustomed to matter being classified into various categories having specific properties such as colour, shape, molecular orientation, reactive tendencies with other elements, stability states, etc. However, the same materials, as we knew them, tended to deviate from the "norm" at very minute sizes – typically when scales such as $(1 \times 10^{-9}$ m) or nano-scale dimensions were approached. This phenomenon gave birth to a new horizon in science. The study of the behaviour and interaction of matter at nanoscale dimensions is what science presently terms as "nanotechnology". To date, nanotechnology is a relatively new and expansive science, which for 'now', seems to offer infinite possibilities and surprises for scientists and engineers worldwide. One sector of interest which researchers have thus been inspired to explore was within the field of polymer hybrid composite fabrications. The present study explores and expands on this sector of nanotechnology.

2.2 General Overview and the Role of Polymer Hybrid Composites

Polymer hybrid composites are formed by combining two or more different materials to form and behave as a single material. The resultant material could potentially take on properties from its counterparts by having specific or combined property enhancements or, at times, may acquire completely new properties within their systems. A composite can have a "simple" system usually formed by combining a matrix and reinforcement or they could implement a somewhat "complex" system comprising of a matrix, reinforcement and a filler component. Consequently, these two systems could be tailored and engineered to have specifically-desired property enhancements which could benefit certain applications. Also, the inclusion of fillers and reinforcements facilitates weight reduction, improved strength and enhanced thermo-mechanical properties. The most frequent structures currently being used in industries are laminates. These composites are used across various applications, for example, the automotive, marine and aerospace industries [1-5, 38]. However, hurdles within the design phase of composites still exist. From the ongoing research and the reviewed literature in this area, there is a clear indication that the fabrication and designing of composites are yet to be perfected. Therefore, subsequent improvements, component inclusions and variations to existing processing methods appear in the literature.

2.3 Components used in Composite Fabrications

Fabricating of composites, as previously mentioned, requires a combination of two or more components. The following sub-sections elaborate on the components used in simple and complex composite fabrications; a basic understanding of CNT manufacturing and a highlight of CNT properties pertinent to the study.

2.3.1 Reinforcements

"Simple" composite systems are comprised of a matrix and a reinforcing component, while "complex" systems are "simple" systems with one or more additional components. These components could be additional reinforcements or filler components. The matrix (usually a thermosetting polymer such as an epoxy) is the

weaker, more brittle component as compared to the stronger reinforcing component (normally fibres – refer to fig 2-1). Reinforcements aid in strengthening the composite structure by forging stronger bonding within the matrix. The reinforcement assists in dissipating any loads imposed on the matrix by acquiring the bulk of the stresses with which the composite is exposed to. Thus, sustaining the rigidity of the composite; enhancing the stiffness and occasionally create or enhance mechanical properties to the composite. Some mechanical property enhancements include high strength to weight ratios, improved thermal stability, improved corrosion prevention, higher resistance to fatigue, improved impact resistance and greater damage tolerance. Common examples of reinforcements include glass fibre (e.g. E-glass, S-glass, etc), carbon fibre, aramids such as Kevlar and Twaron and natural fibres such as jute, oil palm, coconut, banana, wood sisal, pineapple, flax, etc. (fig 2-1).

Glass fibre (GF) is commonly used in composite fabrication because of its availability and affordability. Composites can be made up of several layers of GF and held together within a thermosetting matrix. GF fabrics are also flexible which enhances their geometric tendencies within moulds. However, according to the literature, laminates are the preferred composite geometry [1-5, 38, 44-45]. This study incorporated GF as the primary reinforcement within the laminates which were fabricated.

Natural Fibers

Luffa

Palm

Jute

Banana

Rice Husk

Kenaf

Chicken feather

Cotton

Coir

Sisal

Flax

Abaca

Hemp

Ramie

Synthetic Fibers
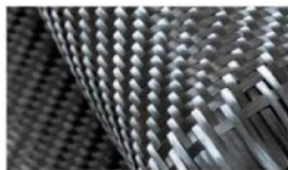
Carbon

Basalt
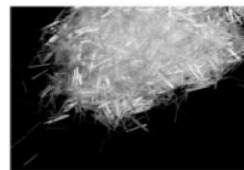
Glass

Kevlar

Figure 2-1: *Various types of natural and synthetic fibres[53]*

2.3.2 Matrix

There are several matrices available commercially. Most matrices are thermosetting polymers. From the literature reviewed, epoxies and polyester resins were the most common matrix choice. Polyester resins (also referred to as unsaturated polyesters) require a catalyst (or an accelerator) such as methyl ethyl ketone peroxide (MEKP) to initiate the polymerisation or curing process. These resins are advantageous to their use across multiple applications; quick curing times and long shelf lives at ambient temperatures. However, polyesters exhibit two major disadvantages: (i) they undergo self-polymerisation at elevated temperatures and (ii) have a high degree of shrinkage upon curing [46]. A wide variety of epoxies are also available commercially. These polymers are manufactured in a "two-part" system comprising of an epoxy and a hardener component. These two components need to be combined under a specified ratio which initiates an exothermic polymerisation process for the system to cure. Epoxies are the preferred choice for fibre reinforced composites. Many desirable properties are observed upon curing. These include low shrinkage, good corrosion and chemical resistance, good adhesion, dimensional stability, excellent thermal and mechanical properties, high tensile strength and high tensile moduli. However, the main disadvantage of epoxy is its brittleness. According to the literature, researchers had shown a keen interest to counter-measure this disadvantage by exploring and incorporating various reinforcements with epoxies [1, 47-48]. For this research, an epoxy system was selected despite the aforementioned shortcomings.

2.3.3 Nanofillers

Nanofillers are tiny particles having nanoscale dimensions. These fillers are incorporated within composites with the role of being either a primary or secondary reinforcement. The literature elaborates on the advantages, disadvantages as well as the challenges faced by previous researchers from their experience with using nanofillers in composites.

2.3.4 Classification of Nanofillers

According to Šupová et al. [6], nanofillers have at least one dimension that <100 nm and they could be grouped into one of the following categories:

a) When the aspect ratio (length to diameter) is at least 100 and the diameter is <100 nm then they are classified as being fibre or tube fillers.

b) In the case of layered materials having a thickness on the order of 1 nm and an aspect ratio of the other two sides at least 25 nm then these are classified as plate-like fillers.

c) If the particle is relatively equiaxed (equal dimensions in all directions) with their largest dimension being <100 nm then these particles are referred to as being three-dimensional nanofillers.

Particle shape is also a defining characteristic of nanofillers. The shape characteristic is distinguished by the particles divergence from its roundness and convexity. The divergence from roundness and convexity indicates how round or angular and how convex or concave the particle is, respectively. The term 'isometric' describes the external shape of the particle normally used to characterise a particle with more or less equal dimensions in all directions. These particles are generally approximated to be spherical for practical purposes.

The internal structure of the material is normally described by the term 'anisotropic'. (materials that have different magnitudes of physical properties when it is measured in different directions). These particles display significantly different protrusions in different directions. When these particles are centrally symmetric, the size and shape can be described by at least three numbers. These particles are generally considered as a triaxial case e.g. bioapatite platelets in bones. In many instances, anisometric particles may be considered as rotationally symmetric e.g. platelets or disks and rods or fibres. In this instance, two numbers are sufficient to describe the particle size and shape. To describe the shape and size in this case, the extension in the direction of the axis of rotation (maximum Feret diameter) and the maximum extension which is perpendicular

to the rotational axis (minimum Feret diameter) or an aspect ratio and an equivalent diameter will suffice.

Rotationally symmetric prismatic particle shapes often occur with the most common shape being either cylinders or spheroids. For cylinders, the height and diameter are sufficient to describe the size and shape. In spheroids, the size and shape can be described by using the extended height in the direction of the rotational axis and the diameter of the maximum extension from the rotational axis. These spheroids can occur either as flattened (e.g. disks or platelets) or elongated (e.g. rods or fibres). For both cylinders and spheroids, the aspect ratio is defined as the ratio of the height to its diameter.

2.3.5 Types of Nanofillers

Clay minerals and silica such as Cloisite® nanoclays, hydroxyapatite particles (found in biocomposites), inorganic nanoparticles and carbonaceous particles - for example, single, double and multi-walled carbon nanotubes (SWCNTs, DWCNTs and MWCNTs, respectively) were the typical nanofillers found in the literature. Of all the types of nanofillers, carbon nanotubes (CNTs) displayed many unique and desirable properties (addressed later in the thesis) over the other nanofillers. These properties make CNTs an ideal choice as a primary or secondary reinforcing component in fibre reinforced composite systems [1-6].

2.3.6 Basic CNT Manufacturing Methods and CNT Properties

CNTs can be synthesized by arc discharge, chemical vapour deposition (CVD), laser ablation, flame synthesis or electrolysis. The frequently used syntheses are arc discharge; CVD and laser ablation. The two most commonly produced CNTs, according to the literature, were SWCNTs and MWCNTs. A schematic representation of a graphene sheet and the two types of CNTs are presented in Fig 2-2 [49]. As shown in the diagram, SWCNTs could be simply imagined as a single graphene sheet bonded from end to end (either length-ends or both-breadth ends) thereby forming a seamless

cylinder. MWCNTs could be imagined similarly to SWCNTs but have multiple non-contacting concentric cylinders-within-cylinders with decreasing diameters. These diameters are interspaced at approximately 0.34 nm apart. The diameters of MWCNTs could range from 1 nm and were rarely found to exceed 100 nm. Diameters exceeding 100 nm are considered to be carbon fibre [49-50].
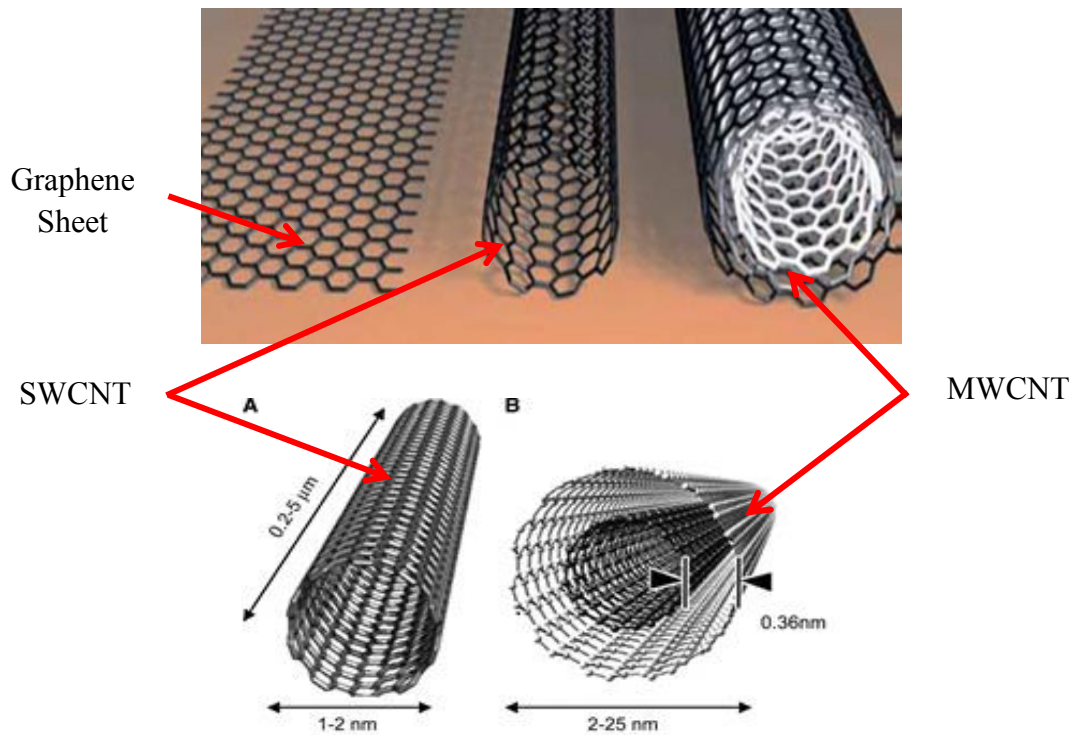
Figure 2-2: *Schematic of an ideal graphene sheet, SWCNT and MWCNT [49]*

2.3.7 Properties of CNTs

CNTs are known to have high strength and modulus, high thermal conductivity and stability, they are stronger than steel, have high chemical resistance, possess low densities and exceptionally high aspect ratios (length to diameter) ranging, up-to and at times exceeding one million [6, 20, 49]. Table 2-1, [52] displays some of the differences in properties in SWCNTs, DWCNTs and MWCNTs. CNTs exhibit anisotropic behaviour, meaning that they have unique properties along the different axes, thereby making SWCNTs different compared to MWCNTs. These properties make CNTs excellent candidates as reinforcements in composites. During the composite design

phase, the desired composite properties could be 'tailored' by selecting the appropriate CNTs that possess properties to suit a particular application(s). Although CNTs exhibit these enhanced properties they do have a setback whereby they have a natural tendency to agglomerate or cluster together [5-6, 20]. The effect of agglomeration thus poses a possibility to hinder the quantity of CNTs that could be added to a composite system (as discussed in the latter part of this review).

Table 2-1: Properties of CNTs

Property	SWNT	DWNT	MWNT
Tensile strength (GPa)	50–500	23–63	10–60
Elastic modulus (TPa)	~1	–	0.3–1
Elongation at break (%)	5.8	28	–
Density (g/cm^3)	1.3–1.5	1.5	1.8–2.0
Typical diameter	1 nm	~5nm	~20nm
Electrical conductivity (S/m)	~10^6		
Thermal stability	>700 ∘C (in air)		
Specific surface area	10–20m^2/g		

2.4 Processing Methods

Common processing methods used in the combination of filler, matrix and composite to fabricate hybrid composites include hand lay-up, resin transfer moulding (RTM) and vacuum-assisted resin transfer moulding (VARTM). The following subsections provide a general description of these processes.

2.4.1 Hand Lay-up

Hand lay-up is an open moulding method which entails the stacking of the reinforcement such as glass fibre, layer-upon-layer. The process starts with a fibre layer

which is coated (usually by brushing or rolling) with a matrix, such as epoxy. The matrix may be neat or optionally contain a filler component acting as secondary reinforcement such as CNTs or nanoclays. Fibre layers are added to the first layer and repeated with the same procedure as described above until the desired composite thickness is obtained. The hand lay-up method is a common method which utilizes the least amount of equipment and is the cheapest amongst the other mentioned methods. The negative aspect of this process usually produces uneven fibre-wetting, non-homogeneous filler dispersion (usually) and undesired void generation within the fibre layers. Uneven fibre-wetting is the result of poor distribution and impregnation of the matrix into and within the fibre voids.

2.4.2 Resin Transfer Moulding (RTM)

RTM is a closed mould method which incorporates a male and female mould. The female mould is lined with the reinforcement such as GF or carbon fibre which is then compressed and held by the male counterpart. The matrix which could be neat or doped with a secondary reinforcement is poured into a mould which is lined with the desired primary reinforcement. The matrix is usually poured in excess to "flood" the mould. The resin impregnates the fibre layers using gravity settling. The system is then left to cure before the moulds are separated. The matrix could also be transferred via forced pressure or be infused by differential pressure. Here, the differential pressure can be created by placing a vacuum at one end of the mould and a resin feed inlet at the opposite end. The resin can then be transferred or pulled through the fibres with the aid of this pressure gradient.

2.4.3 VARTM

Vacuum infusion is a low cost-effective closed mould method used in the fabrication of various composites and could be applied to complex shapes. Reinforcements such as fibre are first layered to form a desired thickness and shape. The entire system is then sealed off with a vacuum bag. A vacuum is introduced at one end of the bag by extracting the air within the system which causes compaction of the fibre layers onto the

surface of the mould. Once the vacuum is maintained, a matrix such as epoxy is introduced at the opposite end to the vacuum end. The pressure difference creates a driving force which enables the epoxy to be drawn through the fibre layers towards the vacuum end. Once complete wetting of the fibre is achieved, the vacuum can be turned off and the composite can be left to cure as per resin requirement before being de-moulded.

2.5 Limitations of Fillers and Processing methods

Past research has indicated many hurdles with the use of fillers as well as the setbacks with processing methods. The following subsections describe some of the limitations based on CNTs and processing methods such as hand lay-up, RTM and VARTM.

2.5.1 Limitations with CNTs as the Filler Component

As described in Chapter One, the biggest hurdle and limitation of CNTs is agglomeration. Agglomeration of CNTs occurs naturally because of their large SSA's as high as or even greater than 1000 m2/g. SSA's of this magnitude induce very high van der Waals forces between particles which end up promoting and assisting in maintaining the particle agglomeration [9-10]. Processing methods such as VARTM have a synergistic effect on incomplete fibre-wetting. When a vacuum is introduced in the VARTM method, the fibre stack becomes compressed and hence this further decreases the voids within the fibre. Some of these voids become too small and this hinders the resin flow and CNTs cannot seep through the fibre depth. When this occurs, the resin starts to accumulate at these "blocked zones", which causes further agglomeration [25]. This occurrence is also responsible for aiding in the "filtering effect", as mentioned in Chapter One. The aforementioned reasons that the maximum quantity of CNTs which could be infiltrated through the fibre was found to be 0.5 wt%.

2.5.2 Limitations of Hand Lay-up, RTM and VARTM

Like with most processes, VARTM also has limitations. In a study conducted by Afendi et al. [51], the objective of the research was to achieve a bubble-free resin system and

fabricate composites using the VARTM method. The following advantages and disadvantages were reported in their study:

Advantages:

i) VARTM was found to be effective for large structures requiring large loads and sandwich designs

ii) VARTM and RTM require closed systems and is preferred over hand lay-up. use closed systems are favourable since they reduce resin-to-skin exposure through handling, it omits volatile emissions such as styrene to the atmosphere during fibre-wetting and time to cure

iii) The closed systems minimise the generation of solid waste products which helps in sustaining a cleaner and healthier work environment

iv) In contrast to RTM, VARTM reduces tooling cost and offers more flexibility on large structures by minimising deformation and damage to the moulds and laminates. The minimisation fundamentally result from the entire enclosure being uniformly exposed to atmospheric pressure

v) VARTM method enhances mechanical properties since it allows for higher fibre content and low generation of voids

vi) Heating of the resin reduces the viscosity and improves degassing process and this also assists by easing the matrix flow through the reinforcement

Disadvantages:

i) Voids are normally caused by localised permeability variations between reinforcements and the matrix flow, leakage, boiling-off of volatile components or release of trapped dissolved gases in the matrix.

ii) reported that every 1% increment increase in void content resulted in a 10% reduction in mechanical properties such as flexural and interlaminar strengths along with a 5% effect on the flexural modulus. When the void content exceeded 5% the initiation of cracks became more complex.

iii)   Heating of the resin reduces the resin pot life which then reduces the rate of infusion, thus posing a disadvantage when fabricating large structures.

iv)   Void content is increased when the infusion is followed directly after degassing

2.6 Dispersion Techniques

The establishment of a homogeneous dispersion of matrix and or filler within the reinforcement renders optimum properties to composite structures [26, 38]. To sustain this attribute, researchers have experimented with many dispersion techniques over the years. Common dispersion techniques such as calendaring, sonication, ball mixing, functionalisation, extrusion, shear mixing and mechanical stirring were often used by researchers [1,7]. Afendi et al. [51] found that bubble nucleation and sparging reduced the dissolved gasses by 40-50% and left micro-bubbles present due to their difficulty in removing them. These micro-bubbles were shown to be separated by using a fine fibre medium. These dispersion methods affected improvements in infusion processes such as VARTM by causing increased fibre wetting by the matrix, thus reducing the void content within the composite. The key aspect to producing above satisfactory composites lies predominantly in the homogeneous distribution or dispersion of the filler component within the matrix. During processing, the tiny particles accumulate forming tiny clusters or aggregates which form strong bonds between them. The aggregates can eventually form larger clusters or agglomerates [25]. This effect is referred to as agglomeration. To make processing methods efficient, these tubes need to be untangled before processing. For this work, we have chosen to fabricate composite laminates using pristine MWCNTs and both VARTM and DVARTM methods as described below and in Chapter Three.

2.7 Process Modification

In the study by Fan et al. [25], the authors demonstrated that a greater homogeneous dispersion of MWCNTs was achievable within the reinforcement by modifying the VARTM method in addition to MWCNT pre-treatment using sonication and surface modification. This modification introduced an additional step that consisted of a double

bagging step to the conventional VARTM method (referred to herein as DVARTM). The DVARTM process is explained with greater detail in Chapter Three.

2.8 Summary

The literature reviewed, indicated that to achieve optimum composite structures that crucial attention needs to be paid to nano-filler dispersion within the structural systems. Also, the reviewed literature lacked sufficient comparisons of nano-filler dispersion from different processing techniques. This study is aimed at plugging this knowledge gap with a specific focus on whether or not processing technique variation would influence nano-filler dispersion and what effect if any, would it have on its mechanical properties. To achieve this, a choice had to be made for a composite structure, its constituents and the choice of processing techniques to be used to fabricate it.

Chapter Three - Research Design and Methodology

The primary objective of the present study was to use two processing techniques to fabricate glass-fibre (GF) reinforced composites which incorporated pristine MWCNTs as a filler component. The main purpose was to compare the filler dispersion states within each composite from both processes and also, to analyse the effect, if any, on the mechanical properties of the composites. To illustrate this, composites were processed using the conventional vacuum-assisted resin transfer moulding method (VARTM) and a modified version of VARTM which incorporated an additional bagging step. Alternatively, this process could be easily visualized as a double-bagged VARTM process (herein referred to as DVARTM). Filler-free composites consisting of only GF and epoxy were fabricated as control samples. Test samples were thereafter dimensioned and machined as per the ASTM testing standards guidelines. The samples from both processes were then mechanically tested. In general, the methodology applied to analyse the obtained test results was based on a comparison of individual samples from each process with equivalent weight percentages to that of the control. The contents to follow in this chapter will expand on a more detailed design of the research and the methodology used to produce the aforementioned composites.

3.1 Research Design

The design of the composites required the combination of raw materials consisting of E-glass fibre (GF) as primary reinforcement, multi-walled carbon nanotubes (MWCNTs) as secondary reinforcement (or filler component) and an epoxy system for the matrix. These components were combined using both the VARTM and DVARTM processing methods.

In Chapter Two, past research reflected that the VARTM processing method encountered difficulties when filler contents exceeded 0.5 wt%. However, the DVARTM successfully achieved infusions up to 2 wt% filler content [25]. To gain an equivalent comparison the maximum filler content for both the VARTM and DVARTM was selected to contain a maximum filler content of 0.5 wt% since this content restricted

the VARTM method. Choosing weight percentages too close to each other could have the possibility of masking slight changes. The cost of CNT's also influenced the selection process. Also, past research has shown that achieving infusions with high contents of CNTs exhibit infiltration setbacks. These setbacks were usually initiated between 0.3 to 0.5 wt% filler contents [10, 19-22]. Therefore, to keep manufacturing costs at a minimum and to generate a fairly good understanding of the MWCNT dispersion, a gradual incremental increase in MWCNT content was applied and restricted at the weight content threshold of VARTM. To satisfy the reasons mentioned, composites fabricated from each method contained six stacked layers of GF with each layer dimensioned to (30 x 30) cm^2 and doped with 0.1, 0.3 and 0.5 wt% MWCNTs. The control was fabricated as above, but with the absence of MWCNTs. The cured samples had undergone a further post-curing step before being cut-up and dimensioned into the required sample dimensions as per ASTM standards. The average overall trends of the material behaviour were thereafter determined using mechanical test analyses discussed herein.

Tensile tests were conducted to determine the ultimate tensile strength (UTS) of the material and dynamic mechanical analysis (DMA) to determine the glass transition temperature (T_g), loss modulus, stiffness, damping and degree of cure of the composites. A schematic overview of the research design is presented in figure 3-1. Here, this scheme shows the variation in MWCNT wt% and the outcome obtained from each test which will be used to characterise the composites. All test methods and sample preparations were conducted following the relevant ASTM standards as elaborated later in this chapter. All of the data and observations were reported on a quantitative basis.
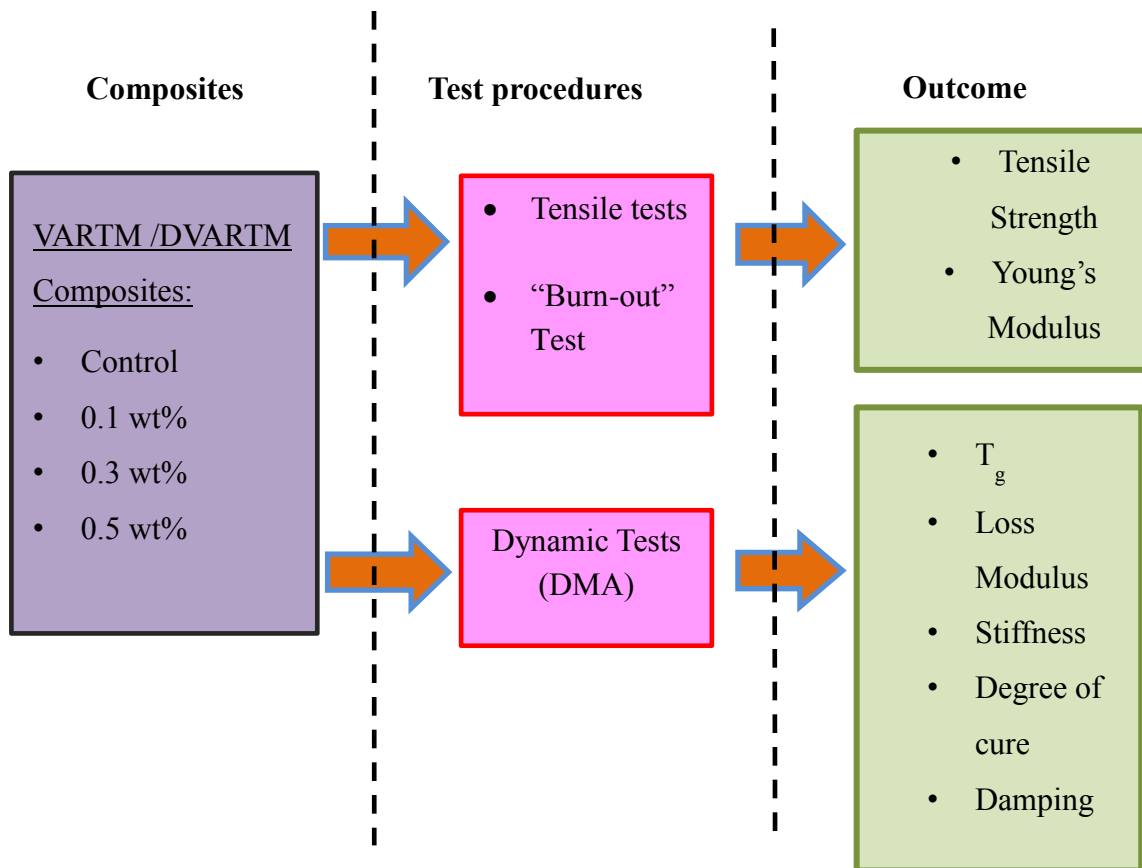
Figure 3-1: *Overall schematic of test procedures and their outcomes*

3.1.1 Raw Materials used

The materials used in this study were purchased from the following suppliers:

- Woven roving glass fibre, epoxy, hardener, release wax, peel ply fabric, vacuum bagging film and flow mesh were purchased from AMT Composites, South Africa
- MWCNTs were purchased from Capital Lab Supplies CC, South Africa
- Vacuum piping was purchased from Industrial Rubber and Piping Supplies, South Africa.
  i) Primary reinforcement:
    - Woven roving E-glass fibre (E-GF) was chosen as the primary reinforcement.

A few specifications of E-GF (can be found in Table 3.1 (a) and (b).

ii) Matrix:

- Epoxy - PRIME™ 20LV

- Hardener - PRIME™ 20 (slow hardener)

Cured properties of the epoxy/hardener system are shown in Table 3.2 from the manufacturers' datasheet.

iii) Nano-filler component:

A few of the important and relevant MWCNTs properties are reported in Table 3.3 according to the manufacturers' property datasheet.

Table 3-1 (a): Chemical composition of E-GF

Constituent	%
SiO_2	54-62
Al_2O_3	12-16
B_2O_3	5-10
CaO	16-25
MgO	0-5
$Na_2O + K_2O$	0-2
TiO_2	0-4
Fe_2O_3	0-0.8

Table 3-2 (b): *Mechanical properties of E-GF*

Property	Unit	Value
Density	g/cm^3	2.58
Tensile Strength at 23 °C	MPa	3445
Modulus of elasticity at 23 °C	GPa	72.3
Elongation	%	4.8

Table 3-3: *Cured properties of resin/hardener system*

Property	Unit	Value
Cure schedule	-	16hr (at 50 °C)
Tensile strength	MPa	73
Tensile Modulus	GPa	3.5
Strain to failure (%)	%	3.5
Cured density	g/cm^3	1.144
Linear shrinkage (%)	%	1.765
Barcol Hardness	-	27
Viscosity	cP	600 (at 25 °C) 640 (at 30 °C)
Gel time	hr:min	3:20 (at 25 °C) 2:20 (at 30 °C)

Table 3-4: Supplier properties of MWCNTs

Property	Unit	Dimension
Purity	-	>95% (MWCNTs)
Length	mm	3-10
Diameter	nm	4-12
Average interlayer distance	nm	0.34
Surface area	m^2/g	90-350
Bulk density	g/cm^3	0.05-0.17
Real density	g/cm^3	1-2

3.1.2 Composite Fabrication Overview

The schematic in fig 3.2 highlights six general steps which were used in the composite fabrication for both processing methods, that is, VARTM [13-16] and the modification, DVARTM, developed by Fan et. al [25]:

The required number of glass fibre layers was cut into the required areas and stacked one above the other, as shown in step 1. This was layered and set up as per the VARTM process (as detailed in Figure 3-3). The entire stack of layered fibre was weighed so that the epoxy and MWCNT quantities could be calculated. The mass of the epoxy used was in direct proportion to the mass of the stacked fibre (one to one ratio), that is, equivalent mass of epoxy to GF mass. The mass of the MWCNT content was calculated as a percentage of the total fibre mass.

- Step two incorporated the mixing of the epoxy and MWCNTs. The epoxy was initially heated before the addition of the MWCNTs and mechanically stirred, then placed into a heated ultrasonic bath to increase the particle dispersion and

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further mechanical stirring (the latter two steps were additional steps to the VARTM process for this study). At this stage, the mixture was continuously stirred while it was allowed to cool before the addition of the hardener.

- The hardener was prepared in the third step according to the manufacturers' specification as a ratio to the quantity of epoxy being used. Once the epoxy/MWCNT mixture cooled to the required temperature, the hardener was added and stirred to obtain a uniform mixture of epoxy/MWCNTs and hardener. At this stage, the infusion was ready to be done.

- Steps one to three were repeated to obtain the required MWCNT quantities within the composites for each processing method used in the infusion step four.

- Lastly, the resulting composites fabricated were demoulded (step five) and post cured according to specification from the epoxy manufacturer (step six).
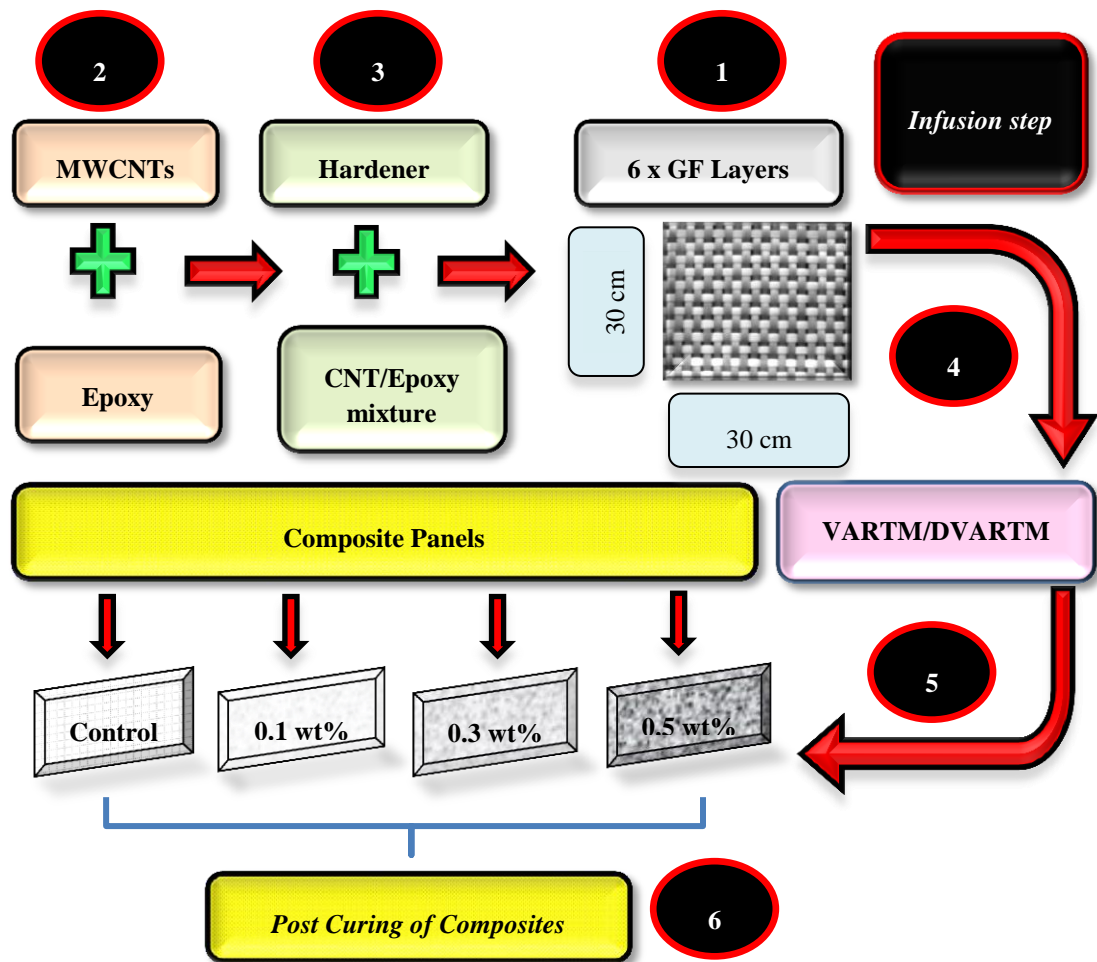
Figure 3-2: *Schematic of VARTM/DVARTM setup*

3.1.3 Processing Methods

Composite panels were produced using vacuum-assisted resin transfer moulding (VARTM) [13-16] and the modified double vacuum-assisted resin transfer moulding (DVARTM) [25] methods to contain 0.1, 0.3 and 0.5wt% MWCNTs, respectively. A detailed description of the setup follows for both methods that were used.

a) VARTM – Process Setup

Figure 3-3: *Physical setup of stacked layers in the VARTM process*

Figure 3-4: Schematic setup of the VARTM process

In Figures 3-3 and 3-4, the VARTM followed the following general layup:
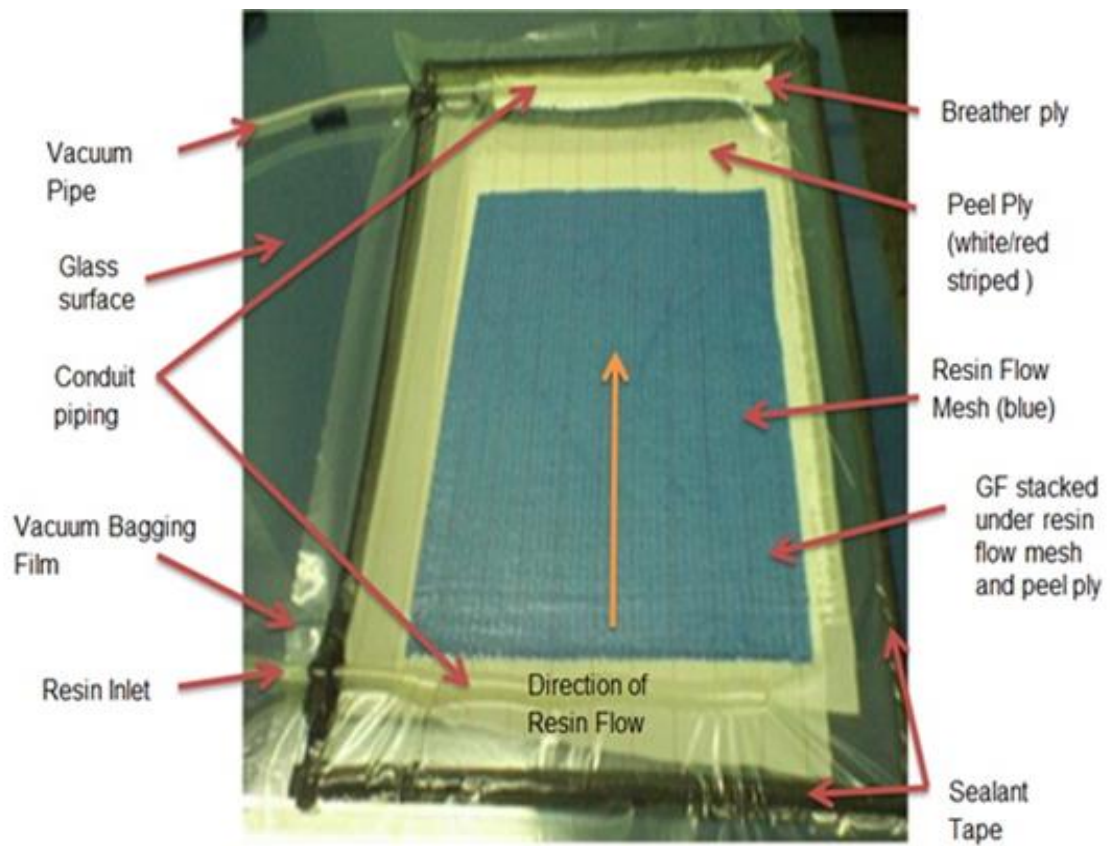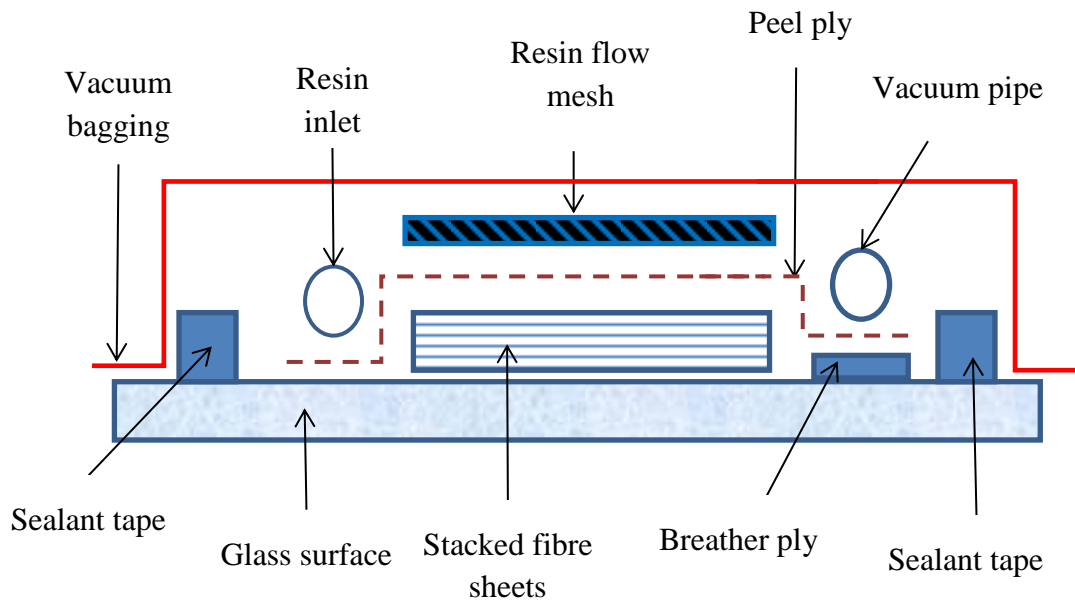
- The required number of fibre layers need to be dimensioned and stacked to obtain the desired thickness and placed on a cleaned waxed glass surface

- Peel-ply was then placed on top of the fibre bed. This served as a release mechanism when the composite has cured

- A flow mesh followed on top of the peel ply. The higher porosity of this layer aids in the distribution of the matrix by easing the flow across and within the fibre bed and towards the vacuum end.

- Breather ply was placed under the vacuum pipe to avoid the vacuum bagging film from forming a complete seal onto the glass once under vacuum

- Sealant tape was then applied around the perimeter of the entire setup

- A vacuum bag was then taped down onto the sealant tape to enclose the entire perimeter around the stacked layers

- At this stage, the enclosed area was ready to be vacuumed. Once the setup was under vacuum, the epoxy mixture was introduced via the inlet pipe and automatically fed through the fibre bed to the vacuum end. The vacuum was

turned off once the fibre bed was completely covered by the epoxy and left to cure at normal or ambient conditions.

b) DVARTM – (Modified VARTM Process)

As introduced earlier, Fan et al [25] modified the VARTM method. The initial lay-up followed the same setup as VARTM. The modification to the process can be seen in step 2 in Figure (3-5), [25]. A vacuum was applied to the stacked lay-up and then temporarily clamped and paused. The fibre bed was compressed and exposed to normal atmospheric pressure. At this stage, the resin was fed in excess into the system while still under vacuum. After the resin covers the entire stack of fibres another vacuum bag is enclosed over the initial bag. This allowed for a second vacuum to be introduced and applied over the first vacuum. The second bag allowed a reduction in atmospheric pressure that was acting on the first vacuum bag which caused a slight fibre bed expansion. The fibre bed expansion created more space to ease the resin infiltration. This modification deliberately enhanced the capillary settling effect of resin within the layers of the fibre bed. The second vacuum was released after 30 min and the fist vacuum was re-started to remove any excess resin. The first vacuum bag now applied atmospheric pressure to the now expanded bed to compress it further to increase further infiltration of MWCNTs. The composite was then left to cure.
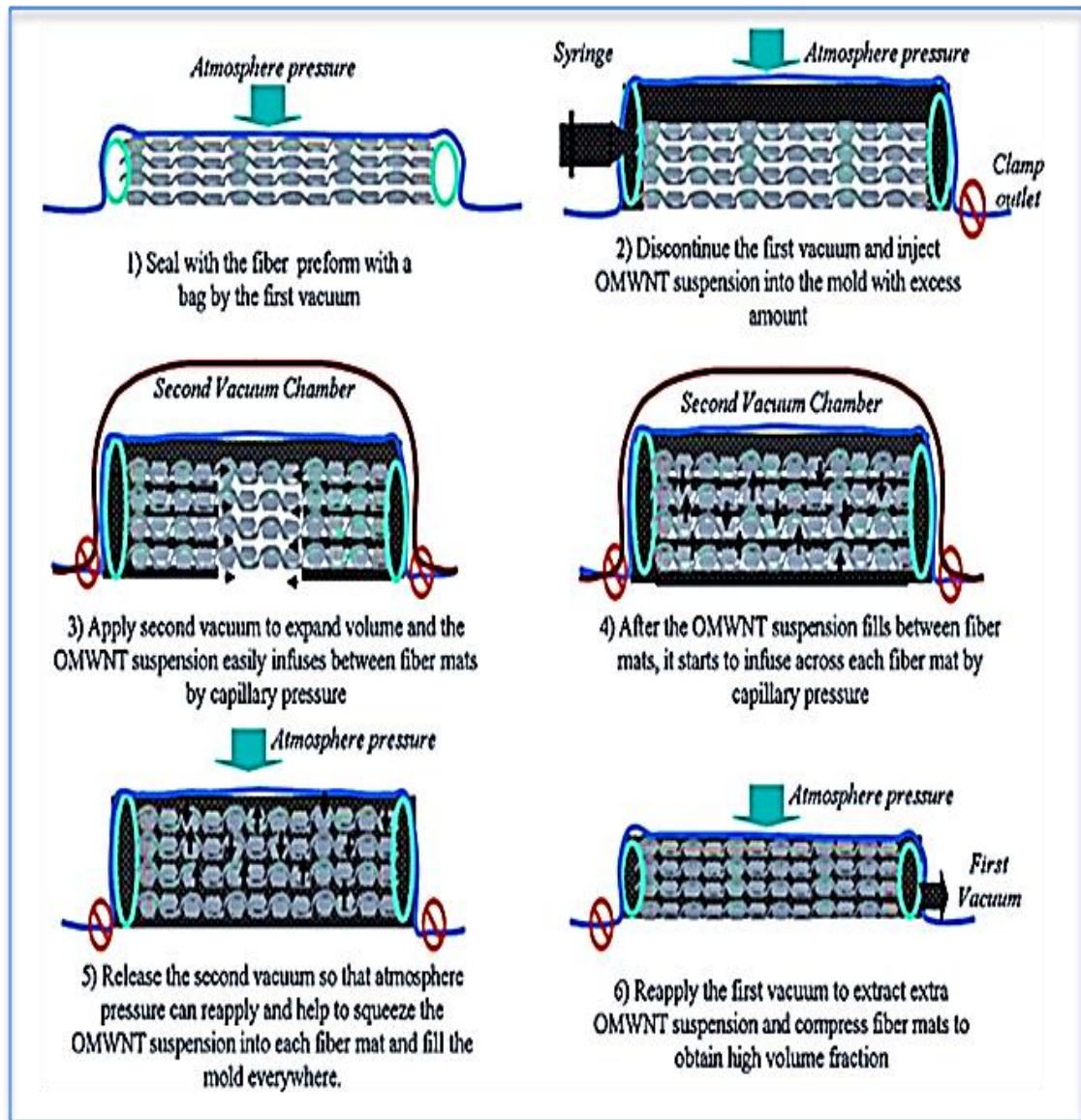
Figure 3-5: Schematic setup of the DVARTM process[25]

3.2 Methodology

The following subsections describe the processes used, sample preparations and testing methods which were used to gather and compare the data. The quantitative burn-out test results were used to generate a "representative" overall schematic of the distribution profile of MWCNT along the length and thickness of the composite for both processes as shown in Figure 4-2 and Figure 4-3.

These test samples underwent a series of tests which consisted of a burn-out test as well as dynamic and quasi-static testing standards and procedures. The composites were then further characterised using the data obtained from the tensile testing and the dynamic mechanical analysis (DMA). Tensile tests were conducted to determine the ultimate tensile strength (UTS) profiles and strain percentages of the samples. The glass transition temperature (T_g), stiffness and degree of cure for both processes were obtained from DMA.

3.2.1 VARTM and DVARTM Composite Fabrication

Six layers of E-GF having an area of (30 x 30) cm^2 were used as the primary reinforcement. As mentioned earlier, pre-treatment of the matrix (epoxy) containing the filler (MWCNTs) is crucial to obtain successful infusions. The epoxy and MWCNTs which made up the matrix was subjected to several pre-treatment phases. The first phase required the epoxy (PRIME™ 20LV) to be preheated to 65 °C to reduce the viscosity before the addition of the MWCNTs. A magnetic stirrer equipped with variable heat and stirring speed settings were used to achieve this. The neat epoxy was weighed according to the required wt% in a glass beaker. The required quantity of MWCNTs was also calculated and weighed as per wt% requirement for each sample and left aside temporarily. The neat epoxy solution was then placed onto the heating plate on the magnetic stirrer and was left to stir at 250 rpm with the temperature setting of ~65 °C. The temperature was controlled and monitored using a mercury thermometer which was suspended in the epoxy solution with the aid of a thermometer holder. Once the epoxy reached the required temperature, the next phase was to carefully introduce the weighed MWCNTs into the solution while still undergoing simultaneous stirring. The mixture was left to undergo mechanical stirring for 1hr while maintaining the temperature at ~65 °C. The next phase required sonication. Therefore, after the 1 hr stirring phase, the mixture was placed in an ultrasonic bath for a further 1hr at 40 ℃ to maintain a relatively low, manageable resin viscosity during the sonication duration. According to the resin specification and properties, the manufacturer recommended selecting an infusion temperature within the range of 24-35 °C to obtain successful infusions. Hence, after the 1 hr sonication phase, the mixture was removed and set aside to cool to a

selected temperature of ~30 °C. The above steps were repeated to produce composites containing 0.1, 0.3, 0.5 wt% MWCNTs using both processing methods. The control samples were also produced using the same selected infusion temperature as mentioned above. The composites were de-moulded 21 hrs after normal curing conditions and post-cured for a further 16 hrs at 50 °C, as per recommendation from the resin manufacturer.

3.2.2 Sample Preparation

a) Tensile Test Samples

Five test samples for each method were machined according to ASTM D3039/D3039M-00ε1 as demonstrated in figure 3-6. According to the figure the width (w) was 25mm, thickness (t) was 2.5mm and length (l) was 250mm:
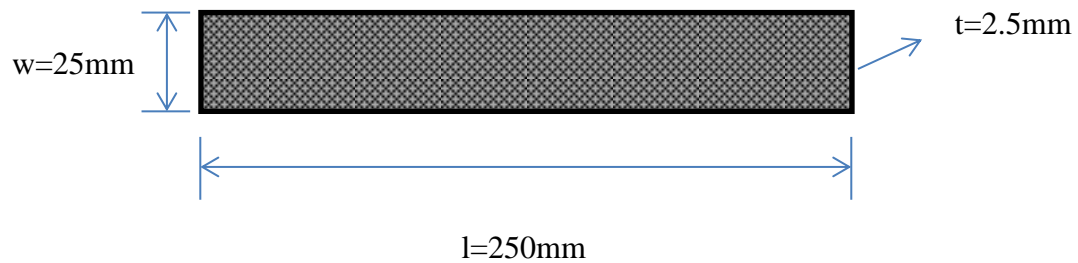

w=25mm

t=2.5mm

l=250mm

Figure 3-6: *Sample dimensions for tensile samples*

b) DMA Test Samples

Five test samples for each method were machined according to ASTM D4065 as demonstrated in figure 3-7. According to the figure the width (w) was 10mm, thickness (t) was 2.5mm and length (l) was 50mm:
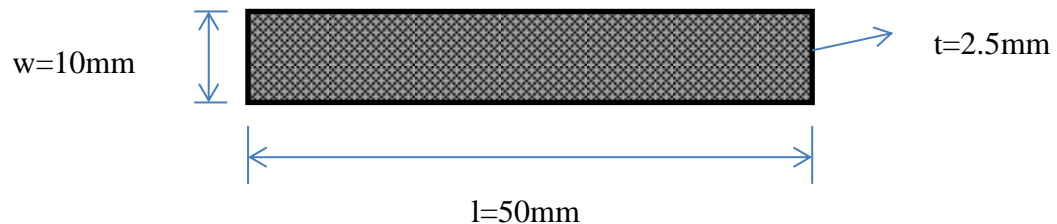

w=10mm

t=2.5mm

l=50mm

Figure 3-7: *Sample dimensions for DMA samples*

3.2.3 Tensile Tests

Tensile tests were conducted with MTS Landmark, Servo-hydraulic Test System which was purchased from IMP Innovative Solutions, South Africa. The machine was equipped with a load cell having a force capacity and a dynamic and static rating of 100 kN and 120 kN, respectively and a maximum pressure rating of 21 MPa. Samples were machined according to ASTM D3039/D3039M-00ε1. Samples were forced to failure using a crosshead speed of 5 mm/min under displacement mode at 25 °C and the following results were obtained for both processing methods:

a) Young's Modulus – this was derived from the samples stress and strain profiles

b) Ultimate tensile strength (UTS) – this was derived from the maximum peak loads that the samples were exposed to at their breaking point loads.

3.2.4 Dynamic Mechanical Analysis (DMA)

Dynamic testing was conducted using a dynamic mechanical analyser, model: DMA Q800. The data were generated and analysed using Universal Analysis 2000 software. Both the equipment and software were purchased from TA Instruments Inc., South Africa. The test method incorporated a dual cantilever beam setup with a temperature ramp rate of 3 °C from 25 °C to 150 °C at a fixed frequency of 1Hz. The test samples were exposed to three phases whereby the sample was heated, cooled and reheated. The results obtained were used to examine the following characteristics for both processing methods:

a) Glass transition temperature (T_g)
b) The stiffness of the material as a function of temperature
c) Loss moduli as a function of time were used to calculate the degree of curing of the samples and
d) Damping

Chapter Four discusses the results in further detail.

3.2.5 "Burn-out" Test

The cured composites were divided into 3 equivalent sections across its area (Figure 1). Five samples having an area of 1cm x 1cm were cut from each of the three sections (as shown by the squares in the shaded regions in Figure 1). The samples were further separated into three, approximately equivalent splits along the thickness layers of the composite. Each split was weighed to obtain their initial masses.
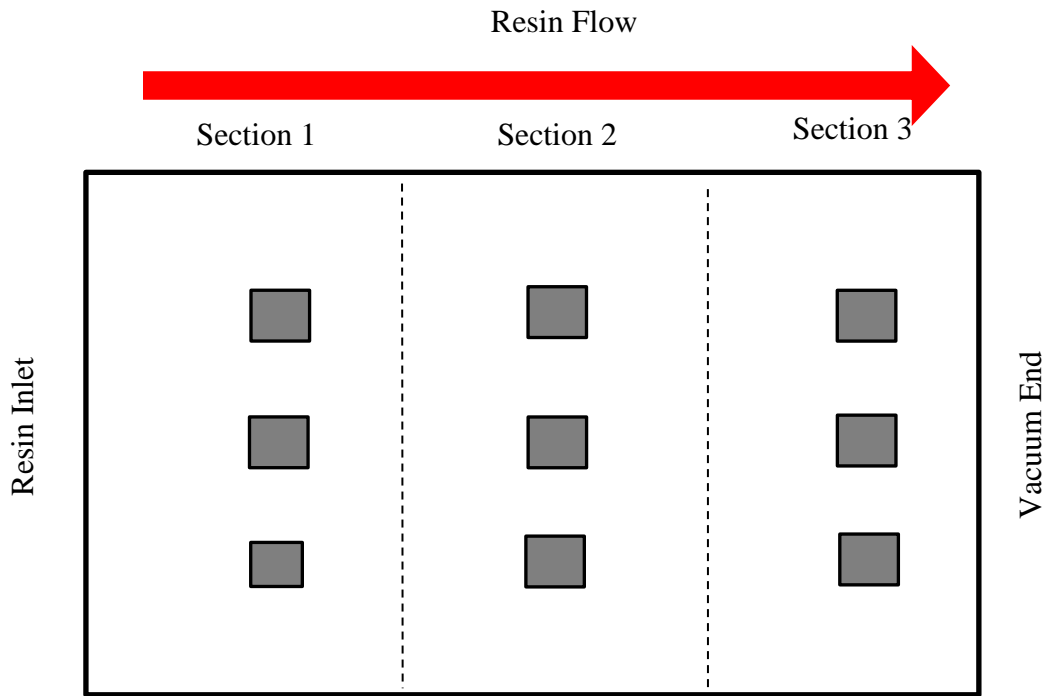
Figure 3-8: Plan view of the cured composite. The shaded regions represent the sectioned areas (1cm x 1cm) along the length of the composite, which were used in the "burn-out" test for both methods

The epoxy within the samples was burnt-off completely in an oven at 600°C for 4 hours with 30 min venting intervals. The sample was reweighed with the residue GF and combustion products were compared against their initial masses. The results were averaged and presented in the discussion

Chapter Four – Results and Discussion

In this chapter, the results of the dispersion states within the composites for both processing methods (VARTM and DVARTM) are discussed. Results for tensile, UTS, DMA and "burn-out" tests were explained.

4.1 "Burn-out" Test

The "burn-out" test was used to determine the amount of MWCNTs that infiltrated the fibre layers along its length and thickness. This method was used to gain a quantitative indication of the quantity of nanotubes that progressed within the fibre mat from the resin feed to the vacuum end of the composite during the infusion. In doing so, we could have an idea of the extent to which the CNTs infiltrated the fibre layers along its length and thickness layers. The data in Table 4-1 and 4-2 helps us visualize the 'filtering effect' as discussed in the literature [5-6,20]. For both processing methods, the residual average weight percentages of the GF, MWCNTS and epoxy combustion products to the total initial sample masses were reported.

In Table 4-1, the 0.1 wt% loading showed a decrease from 22% to 16% and 15% for layer 1 and 2 respectively. This is indicative of starvation of filler as it progressed to the vacuum end. In layer 3 we observed a 2% higher content as the layers above. This was probably due to the accumulation of the resin feed at the initial wetted fibre portions or due to a higher degree of agglomeration. The same rationale could be used to explain the other weight percentages for the filtering effect occurring across the fibre length and thickness layers and the effect caused by the higher percentages which could have influenced an increased degree of particle agglomeration. At 0.5 wt%, we can see that the last layer was starved quite considerably as compared to the lower wt% loadings, hence having a high degree of filtering. The VARTM method indicated that the CNTs tended to have preferential settling towards the thickness layers. On an overall basis, as the matrix progressed towards the vacuum end, the CNTs tended to seep into the fibre-bed depths along the shear direction. The CNTs started to accumulate and agglomerate thus causing an increase in viscosity and thereby hindering the flow of epoxy towards

the vacuum end. This resulted in a decrease in the concentration of CNTs along the length and thickness layers of the composite from the epoxy feed to the vacuum end.

Using the rationale described above, we observe that the DVARTM method also experienced a degree of filtering. On the overall, the DVARTM showed a relatively uniform distribution of filler across the length and thickness layers with exception of the 0.1 wt% filler content at layer 2, section 2 (30.3%/) and for the 0.5 wt% filler content at layer 2, section 2 (30.3%). These zones could have had a higher degree of localized agglomerates which could have influenced the lower weight contents for the layers below it. At 0.5 wt%, the DVARTM method still maintained a more or less uniform dispersion state. Figures (4-1 to 4-3) displays the exaggerated schematic of the overall filtering effect described previously. The contrast in shading shown in all figures represented the concentration of MWCNTs as it progressed from the resin feed to the vacuum end shown from the top and side views. The contrasted shaded regions represent the filler concentration profile across the respective plan and side-view fibre layers. The SEM image shown in Figure 4-1 represented the agglomeration within the composite.
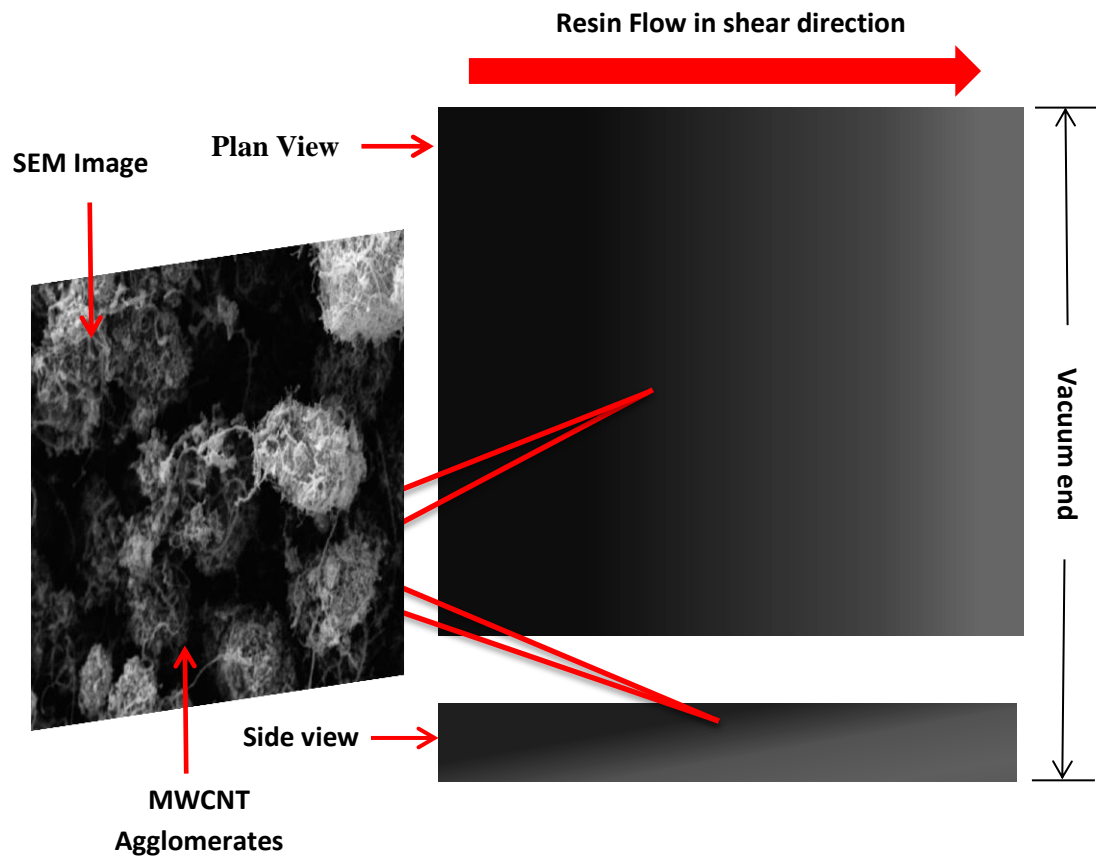
Resin Flow in shear direction

SEM Image

Plan View

Vacuum end

Side view

MWCNT Agglomerates

Figure 4-1: *SEM caption of agglomerated CNTs and the plan view displaying the filtering effect*

Table 4-1: *Average quantitative dispersion profile of MWCNTs in the VARTM method shown between the various fibre layers occurring along the thickness (layers 1-3) and shear directions (sections 1-3)*

wt%	Layer	MWCNT mass% calculation = Initial Mass - Post-combustion residue (%)		
		Section 1	Section 2	Section 3
	1	22.0	18.0	16.0
0.1	2	22.0	19.0	15.0
	3	24.0	13.0	10.0
	1	26.0	23.0	24.0
0.3	2	37.8	22.4	17.0
	3	18.9	14.8	13.0
	1	27.0	26.0	22.0
0.5	2	19.0	15.0	11.0
	3	8.0	7.0	4.0

Resin Flow in shear direction

Section 1   Section 2   Section 3
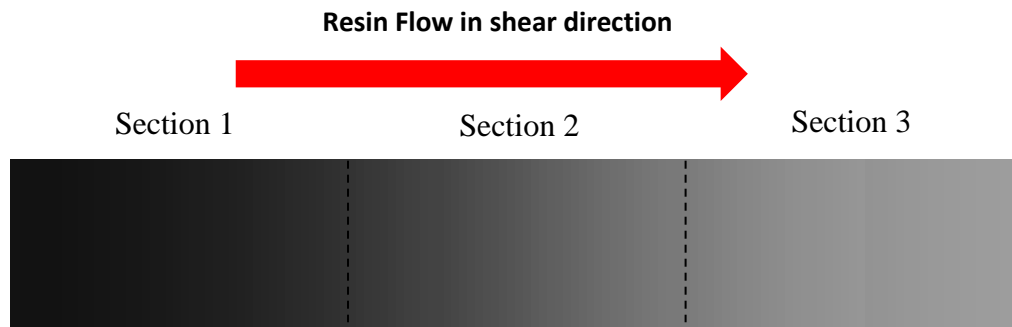
Figure 4-2: *Plan view schematic of CNT distribution along the length of the composite*

Resin Flow in shear direction

Layer 1

Layer 2

Layer 3

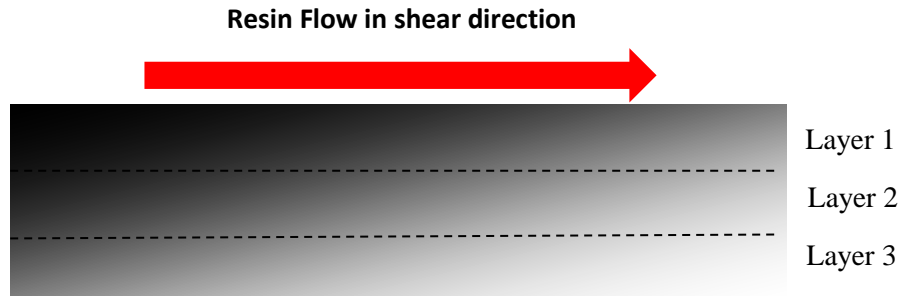***Figure 4-3:*** *Thickness view schematic of CNT distribution along the length of the composite*

Table 4-2: *Average Quantitative dispersion of MWCNTs in the DVARTM method shown between the various fibre layers the thickness (layers 1-3) and shear direction (sections 1-3)*

DVARTM				
wt%	Layer	MWCNT mass% calculation = Initial Mass - Post-combustion residue (%)		
		Section 1	Section 2	Section 3
0.1	1	17.1	21.3	20.9
	2	20.2	30.3	16.7
	3	19.0	15.1	11.0
0.3	1	22.0	19.0	27.0
	2	23.8	20.0	18.0
	3	15.7	11.0	9.0
0.5	1	28.0	21.3	26.0
	2	24.0	30.3	21.1
	3	17.0	13.0	12.0

4.2 Quasi-static tests

Quasi-static tensile testing was used to characterize the composite in terms of its ultimate tensile strength (UTS) and to obtain its Young's modulus.

4.2.1 Tensile Tests

The samples containing 0.1 wt% and 0. 5wt% showed that the UTS values were less than the neat epoxy and GF composites. This might have been due to poor interfacial bonding or increased agglomeration of the CNTs. From Figures 4-5 and 4-6, improvement in the UTS could be seen for all the samples in the DVARTM series compared to the control sample with the largest being for the 0.5 wt% loading. For the VARTM method, the largest tensile strength occurred in the 0.3 wt% loading. The ultimate tensile strength (UTS) analysis reported optimum results for 0.3 wt% MWCNT content in both methods.
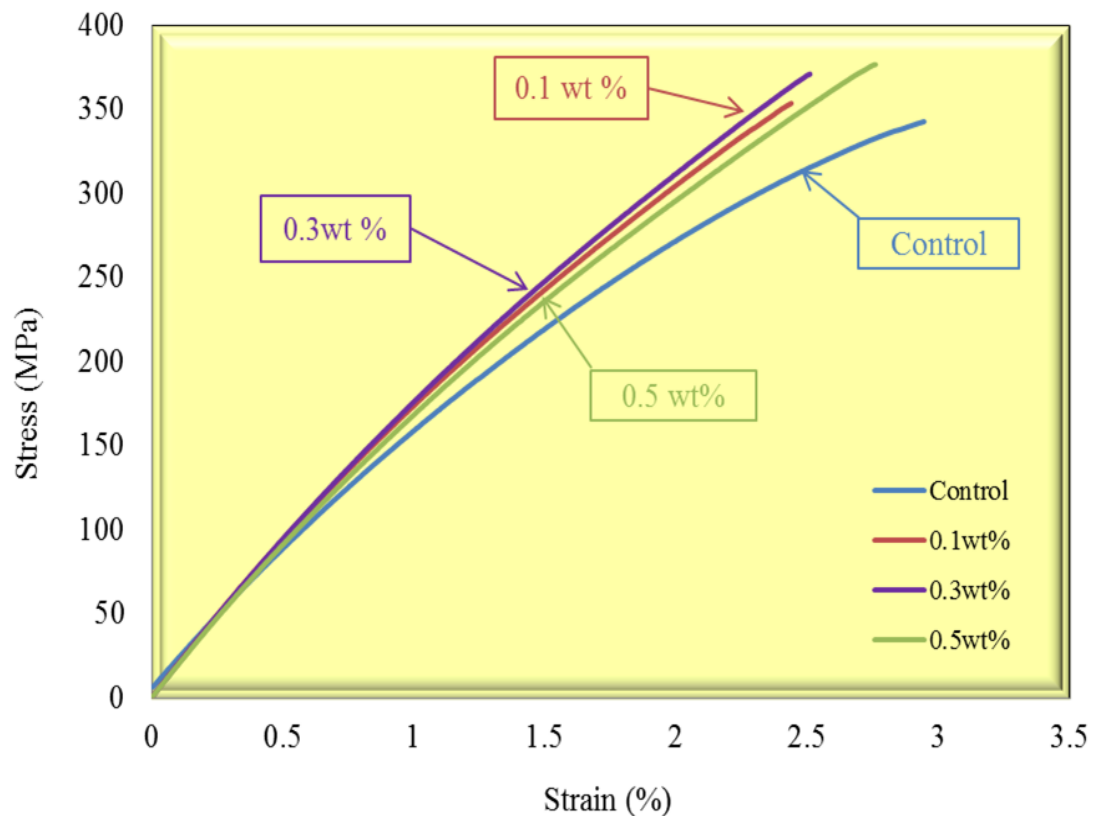

Figure 4-4: *Combined tensile test results for the VARTM series*

As discussed in the literature, the influence of improved filler dispersion, better interfacial molecular CNT-matrix bonding, decreased CNT agglomeration and or the orientation of the nanotubes within the composite, could generate a larger UTS. The results obtained for VARTM showed a uniform increase in UTS as the MWCNT wt% increased.

UTS decreased for both the 0.1 and 0.5 wt% in the DVARTM process as compared to the control. The lower UTS values obtained from both methods were indicative of increased brittleness (due to MWCNT dispersion), or greater localised stresses due to an increase in MWCNT agglomeration. The strain rate in VARTM (Figures 5 and 6) indicated a uniform increase in elasticity with increasing MWCNT weight content as compared to DVARTM. This effect could have been due to uniform filler dispersion or improved internal bonding between the nanotubes and the matrix.
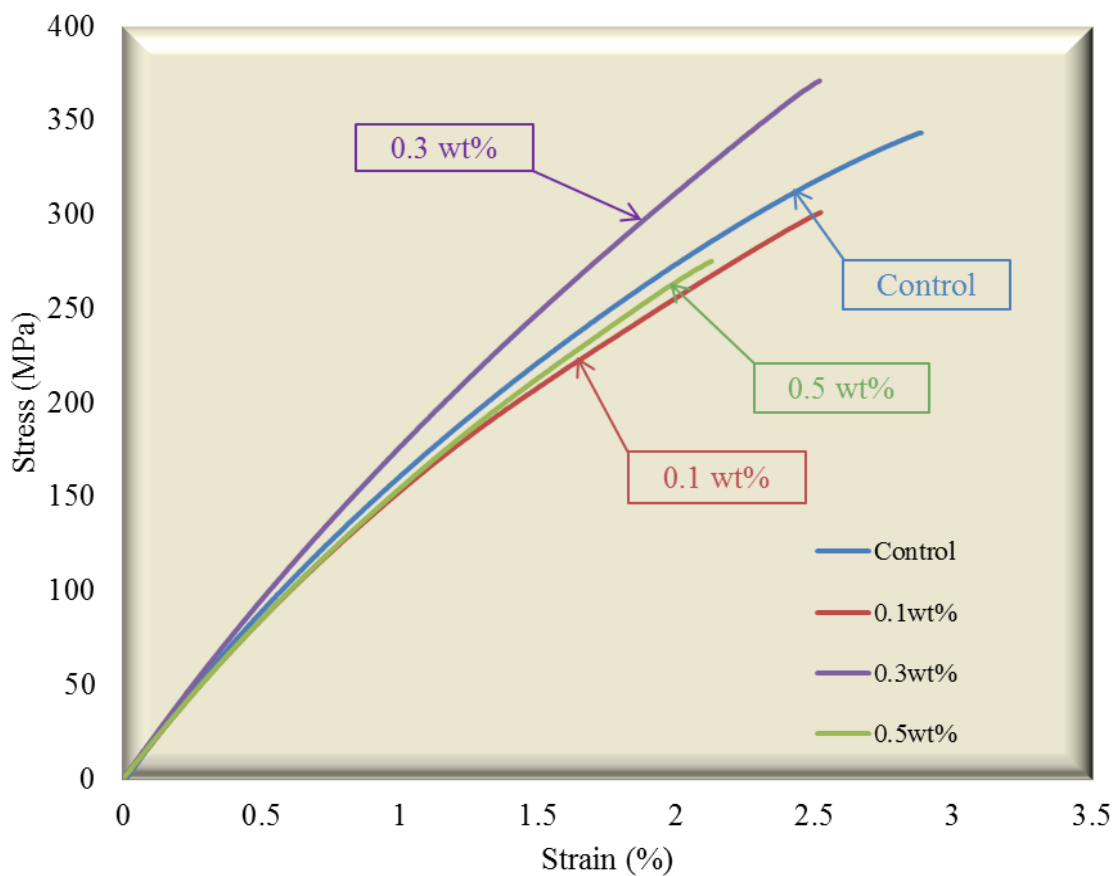

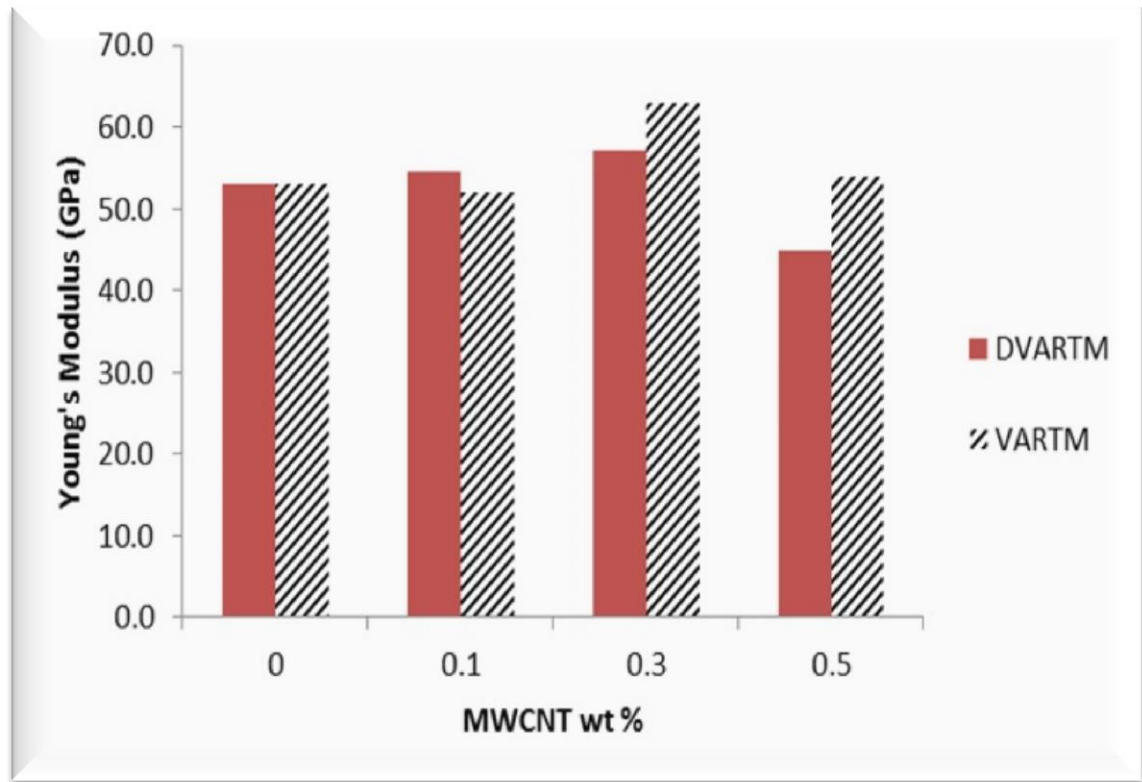**Figure 4-5:** *Combined tensile test results for the DVARTM series*

Figure 4-6: *Young's modulus comparison for the VARTM and DVARTM series*

4.3 Dynamic Mechanical Analysis (DMA)

DMA was used to evaluate the glass transition temperature (T_g) stiffness data, damping of the composite and the degree of cure

4.3.1 Determination of Glass Transition temperatures and Young's modulus

Glass transition temperature (T_g) was calculated using the tan δ vs temperature peaks. Figures 4-7, 4-8 and Table 4-3 showed a slight variation in T_g for both methods.

The 0.3 wt% MWCNT loading in the VARTM method reported the highest Young's modulus (Figure 7) which implied a good MWCNT dispersion within the matrix, according to Montazeri et al. [30]. The 0.1 and 0.5 wt% loading for VARTM showed no significant change in Young's moduli, which could have been attributed to a similar

MWCNT dispersion state within the matrices. Similarly, optimum Young's moduli values (Figure 4-6) were obtained from the 0.1 and 0.3 wt% (the highest being at 0.3 wt%) content in the DVARTM method (indicative of poor MWCNT dispersions within the matrix) [30]. The 0.5 wt% MWCNT content in DVARTM (compared to the control) reported a decrease in Young's modulus, which could have resulted from improved filler dispersion within the matrix. Hence, from the overall Young's moduli comparison, the DVARTM reported much better improvement in MWCNT dispersion in 0.3 and 0.5 wt% when compared to the VARTM method. DVARTM displayed a uniform increase in T_g, which is indicative of decreased molecular mobility and improved interfacial bonds between filler and matrices. The VARTM method reported higher T_g values for 0.1 and 0.5 wt% and a decrease from 0.3 wt%. This implied that the 0.3 wt% sample had increased molecular mobility resulting from weaker interfacial matrix-filler bonding. As mentioned previously, Montazeri et al. [30] found that poor dispersions of CNTs within the matrix could promote better Young's moduli values. This rationale was used to explain the results obtained from the tensile data below in fig 5 a and b and Young's modulus in Figure (4-6). The 0.3 wt% loading reported a lower T_g value (Figure 4-8) for the VARTM method along with the highest Young's modulus (Figure 4- 6). Using the same rationale, 0.1 wt% loading using the DVARTM method, reported a drop in T_g which also showed an optimum Young's modulus value (Figure 4-6). This implied that both 0.3% and 0.1 wt% loadings had poor dispersions within the matrix. On the other hand, it was also observed that 0.1 wt% in the VARTM method and 0.5 wt% reported larger peak values in T_g. This could also suggest that the distribution of the CNTs could have been more uniform in this loading and had created a better interface with the matrix. The tan δ − temperature analysis reported a slightly higher T_g value and also a slight shift in the T_g (an increase by ∼ 1 ℃) as compared to the neat composite (table 3). It could therefore be assumed that a better dispersion was present. This finding is also supported by Keusch et al. [42], who found that T_g has a direct proportionality relationship with interface bonding. In the DVARTM method, the damping for 0.1 wt% decreased by 14.5% and 10%, compared to the 0.5 wt% and the control, respectively. The decreased damping indicated an enhancement in the filler-matrix interfacial bonding.
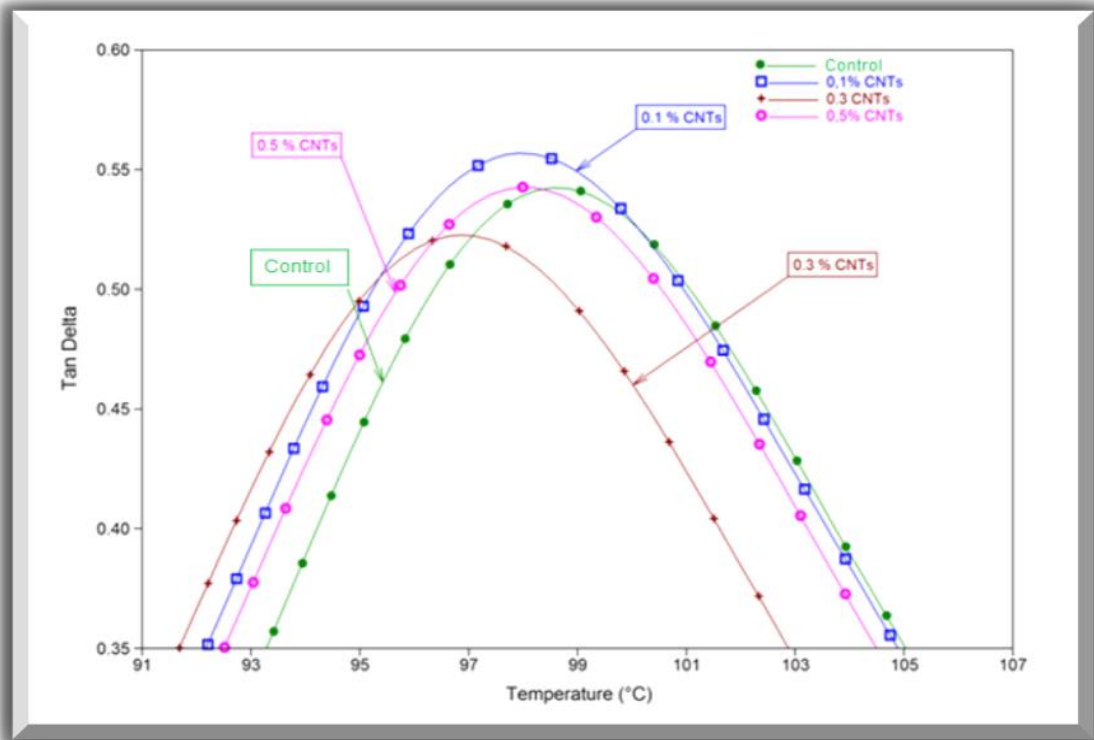
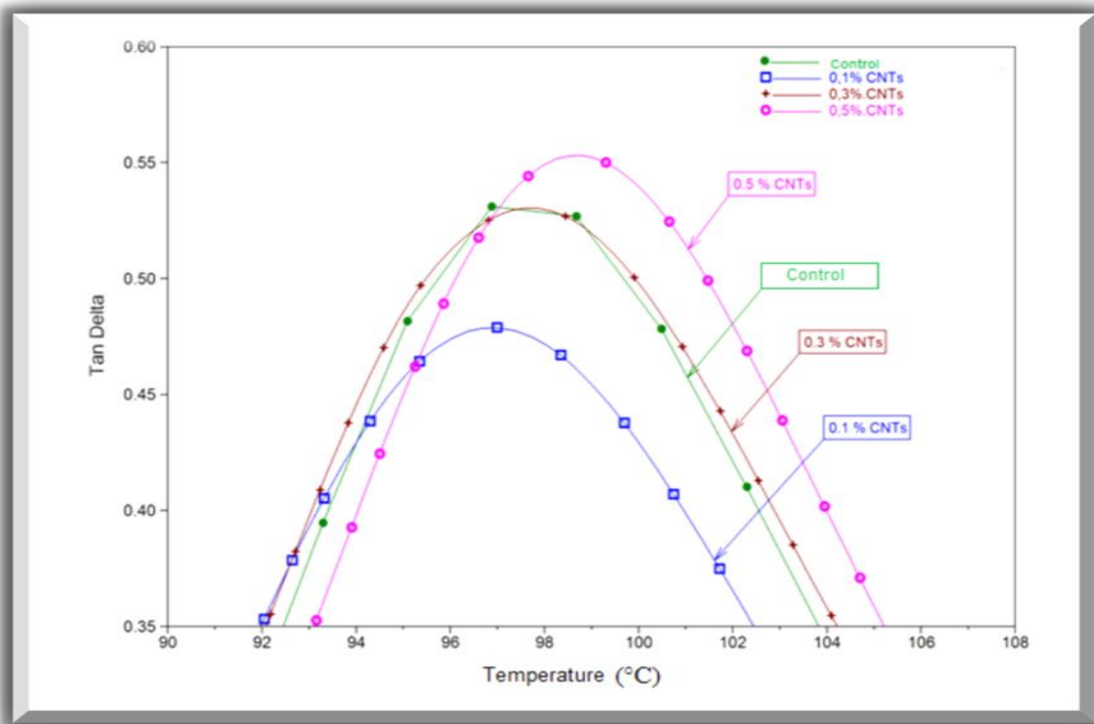**Figure 4-7:** *Damping of the VARTM series showing* T_g *at its peaks*

Figure 4-8: *Damping of the DVARTM series showing* T_g *at its peaks*

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Table 4-3: *Glass Transition summary for the VARTM and DVARTM series*

Glass transition temperature - T_g (°C)				
Method	**Control**	**0.1 wt %**	**0.3 wt%**	**0.5 wt%**
VARTM	98.8	97.8	96.8	98.1
DVARTM	98.8	96.8	97.7	98.7

4.3.2 Stiffness

In VARTM, the sample containing 0.1 wt% CNTs showed an approximately 6% increase in stiffness (Figure 4-9) and 0.5 wt% in DVARTM showed 34% improvement (Figure 4-10). The 0.3 wt% loading for the VARTM showed almost negligible improvement compared to the neat epoxy sample. The DVARTM method consequently showed a steady increase in stiffness with increasing CNT content compared to the VARTM method (Figure 4-9 and Table 4-4). From Table 4-4 and Figure 4-11, the VARTM samples containing 0.3 wt% and 0.5 wt% filler contents reported lower stiffness values when compared to DVARTM. This could be explained by the greater compaction created from single bagging or a larger distribution of the CNTs along the thickness direction of the stacked fibre mat. The 0.1 wt% filler loading displayed higher values than the control sample for DVARTM. When compared separately, the DVARTM results obtained a much more uniform increase in stiffness as the filler content increased. This suggested that random settling promoted a uniform increase in stiffness as the weight percentages were increased. The uniform stiffness increase is also indicative of uniform particle distribution for the DVARTM processing method. From fig 4-11, both 0.3 wt% loadings experienced almost equivalent magnitudes for its peak load for both methods.
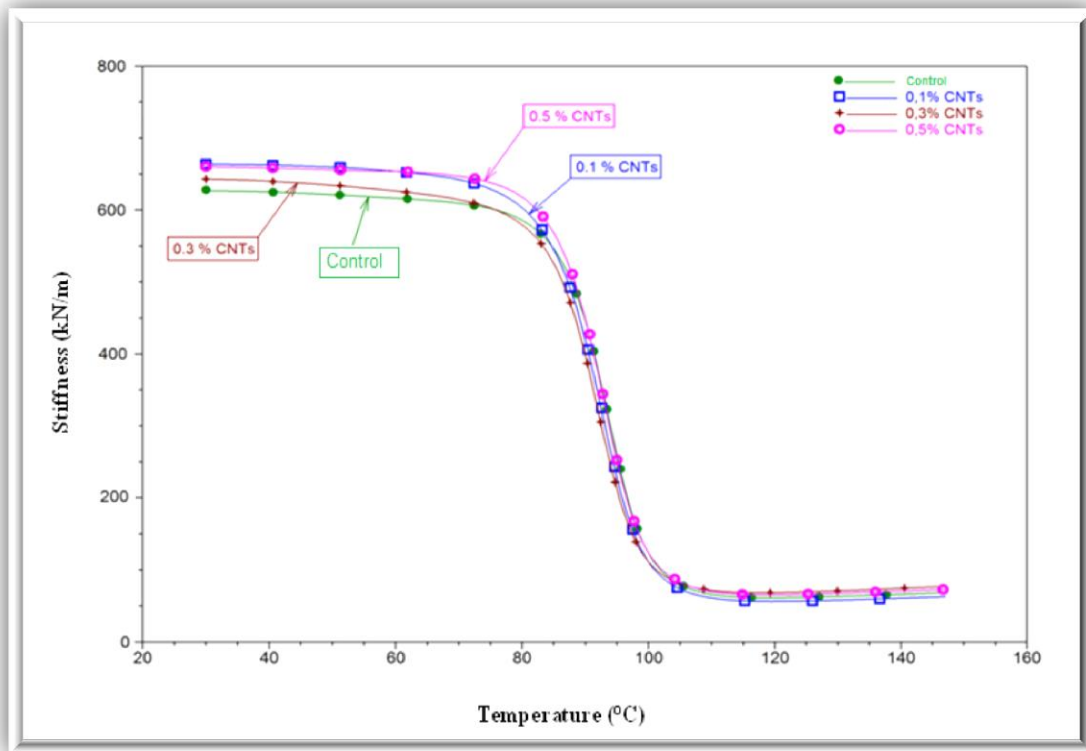
Figure 4-9: *The VARTM series for stiffness comparison as a function of time*
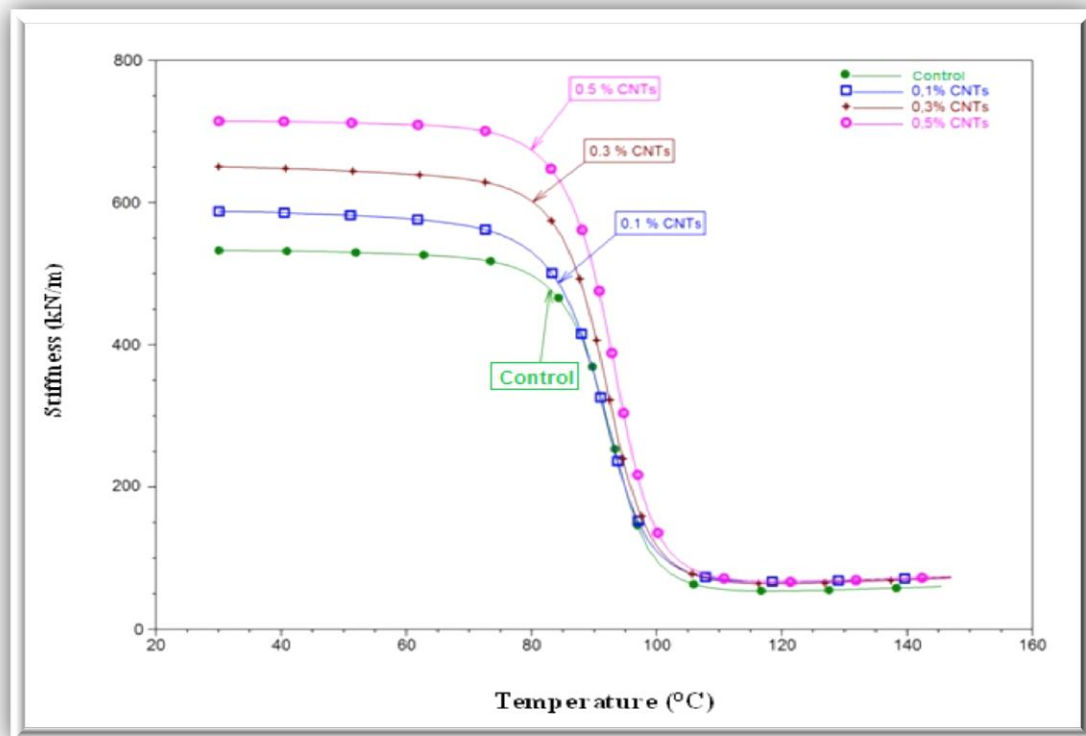
Figure 4-10: *The DVARTM series for stiffness increase as a function of time*

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Table 4-4: *Stiffness comparison of the VARTM and DVARTM series*

Stiffness (kN/m) at T= 30°C				
Method	**Control**	**0.1 wt %**	**0.3 wt%**	**0.5 wt%**
VARTM	627	664	643	661
DVARTM	532	587	650	714

Figure 4-11: *Linear stiffness comparison for the VARTM and DVARTM at T=30°C*

4.2.3 Degree of Cure

In this subsection, the loss modulus versus temperature curve of a single filler content loading in Figure 4-12 which was used as an example to explain how the degree of cure was obtained for all the 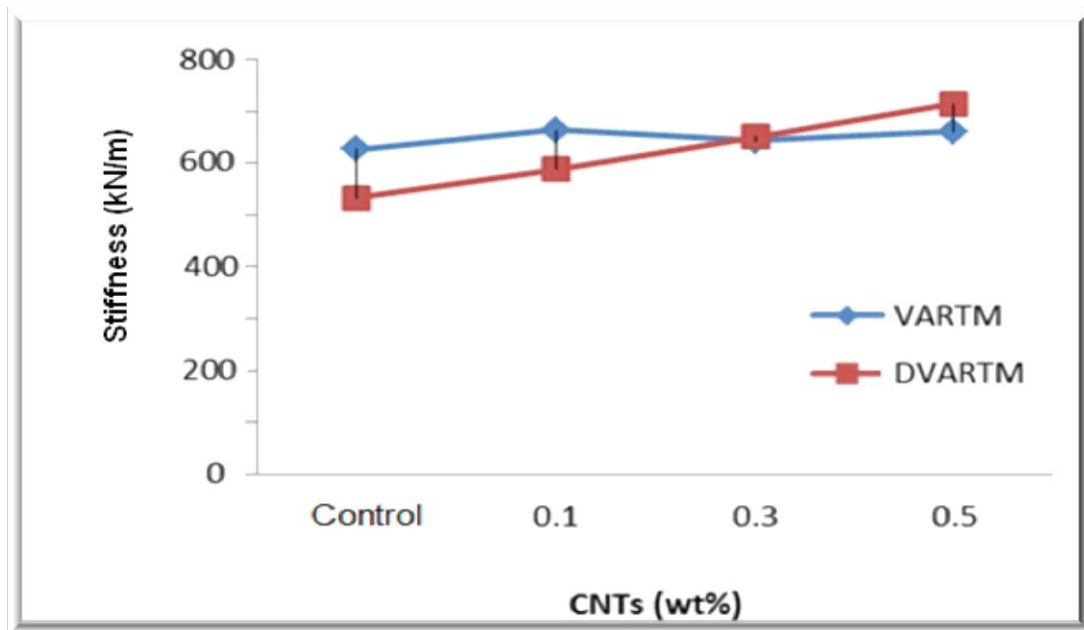other filler loads. The curve represents the three stages that the sample had been subjected to, i.e. heating, cooling and reheating which is shown by the three curves corresponding to Peaks A, B and C, respectively. To calculate the degree of cure (α), only the areas under both heated phases were needed, i.e. Peak A and C. These values were calculated for all samples using equation 1:

$$\alpha = [1\text{-}((A_{Peak\ A} - A_{Peak\ C})/A_{Peak\ A})] \times 100\%$$

...(1)

Where, A = area under the curve.

The difference in areas under these curves represents the degree of cure. Table 4-5 values were obtained using equation 1 for all the filler loadings for both methods. These results were also represented comparatively for both methods in Figure 4-13 to show a graphical trend. Cure rates are dependant on the cross-linking of the polymer molecules within the fibres. In the VARTM a steady increasing trend was observed as the filler content increased. This indicated that the filler dispersion was not homogeneous or that the agglomeration [5-6, 20] had impacted negatively on the cure rate. However, DVARTM displayed a uniform trend at approximately 97% for all three filler contents. The uniformity suggested uniform filler dispersion or having similar cross-linking profiles for DVARTM. The high cure rates obtained via DVARTM could have been the reason for the increase in the uniform stiffness obtained as previously mentioned.
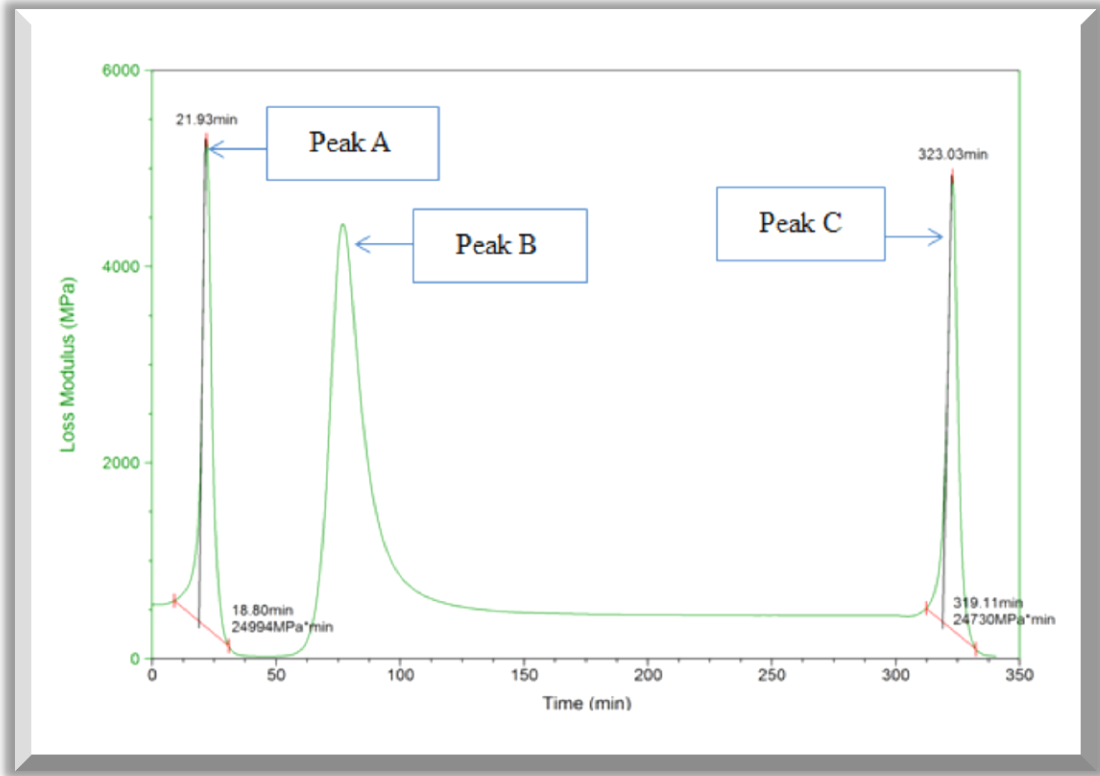
Figure 4-12: *Sample curve to illustrate the calculation for the Degree of Cure*

Table 4-5: *Degree of cure for the VARTM and DVARTM series*

Degree of cure, α (%)				
Method	**Control**	**0.1%**	**0.3%**	**0.5%**
VARTM	88.0	92.8	95.1	96.0
DVARTM	88.0	97.2	97.2	97.3
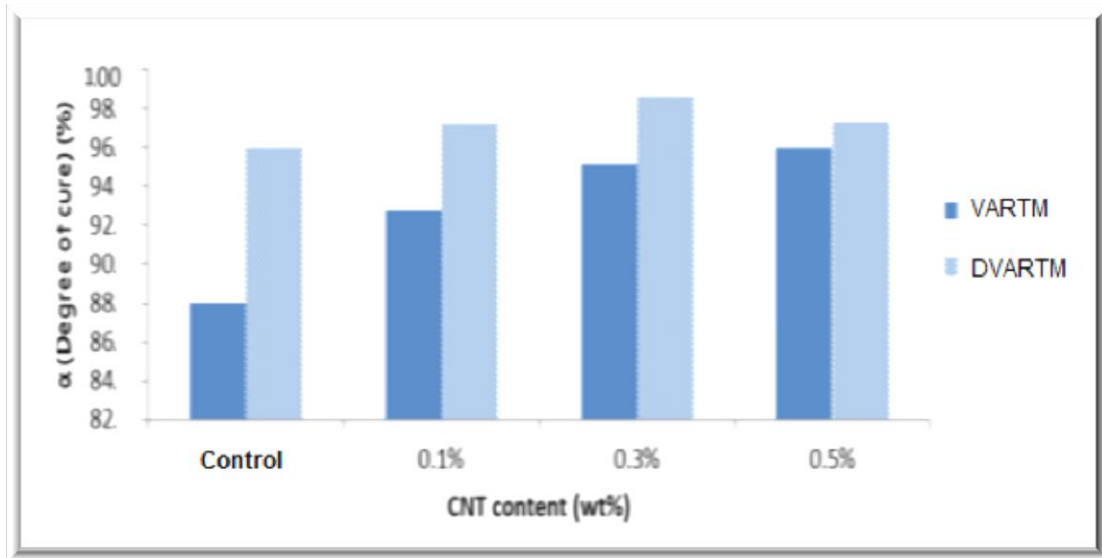
Figure 4-13: *Graphical comparison for both the VARTM and DVARTM series*

Summary

DVARTM displayed a much more uniform particle dispersion compared to VARTM which was observed from the stiffness curves which indicated a 34% increase for the 0.5wt% loading using the DVARTM method

- The "burn-out" test displayed the exaggerated theoretical schematic visualisation of the filtering effect experienced within the fibre layers from both the thickness and length perspectives
- Glass transition temperatures decreased for 0.3 wt% loading for the VARTM method and 0.1 wt% loading for the DVARTM method. This corresponded to an increase in the Young moduli for these percentages
- Ultimate tensile strengths showed small variations compared to the neat epoxy but showed a slightly increasing trend for the 0.1, 0.3 and 0.5 wt% loading for the DVARTM method. The VARTM method showed decreased loads for 0.1 and 0.5 wt% loadings and almost equivalent load capacity to the neat epoxy sample for the 0.3 wt% loading

- The values for the degree of cure for DVARTM indicated good interfacial bonding between the epoxy and matrix as compared to the VARTM method, with the best cure for the 0.3 wt% loading

Although CNT addition varied the mechanical properties slightly it did show that the selection of processing methods did have a significant effect overall.

Chapter Five – Conclusion and Recommendations

This Chapter finalises the dissertation with conclusions from the experimental work and presents some recommendations for future consideration.

5.1 Conclusion

DVARTM displayed a much more uniform particle dispersion compared to VARTM The following observations were encountered:

- The 0.5 wt% loading in the DVARTM method displayed a significant 34% increase in stiffness in comparison to the VARTM method

- Low T_g values are a result of poor dispersions within the matrix and hence improvement in Young's modulus (Figure 4-6). This was observed for 0.3 wt% in and 0.1 wt% in the VARTM and DVARTM processes, respectively (Figure 4-7 and 4-8)

- Besides 0.1 wt% in the VARTM method, both the 0.3 and 0.5 wt% loadings for DVARTM reported higher T_g values. This indicated an improved degree of cross-linking within the matrix.

- Ultimate tensile strengths showed small variations compared to the control but showed a slightly increasing trend for the 0.1, 0.3 and 0.5 wt% loading for the DVARTM method. The VARTM method showed decreased loads for both 0.1 and 0.5 wt% loadings and almost equivalent load capacity to the control sample for the 0.3 wt% loading

- The values for the degree of cure for the DVARTM indicated good interfacial bonding between the epoxy and matrix as compared to the VARTM method, with the best cure rate containing a 0.3 wt% loading

- The "burn-out" test displayed a significant drop in MWCNT content along the length and thickness layers in the VARTM method as compared to the DVARTM method. Both processes experienced MWCNT filtering indicated by the combustion residue in each section and layer shown (Table 4-1 and 4-2). However, this affected VARTM more than DVARTM. Although the filtering

effect was observed for both methods as the filler content increased, the DVARTM method displayed a better efficiency in achieving uniform distribution even with the increased filler loading. The decreased dispersion in VARTM at the higher wt% could have highly been attributed to an increased agglomeration state of the MWCNTs. The findings also suggested that the higher compaction of the fibre due to the single-bagging from VARTM could have also influenced the filler agglomeration as compared to double-bagging

Two processing methods (VARTM and DVARTM) were implemented to illustrate the effect of MWCNT filler dispersion variation within the composite fabrications. The result from the experimental data indicated a positive outcome to the overall effect on the mechanical properties of the composites. This suggests that when fabricating composite materials the processing methods cannot be overlooked and it strongly suggests that CNT surface modifications are not the only sole contributor to mechanical property enhancements. The effect of the incremental increase in MWCNTs did affect the mechanical properties and hence, we can conclude that the variation of processing does indeed impact on the mechanical properties.

5.2 Recommendations

Much of the literature focused on using CNT surface modifications to improve the cross-linking within the composite. This posed a gap in knowledge to the possible outcomes of the comparable processing methods. In this study, pristine MWCNTs were used as the secondary reinforcement in GF-epoxy hybrid composites. These findings could suggest an idea for future work whereby one could use this study as a benchmark and extend on the knowledge by varying some of the setup variables used in this study. For instance, MWCNT could be functionalized instead of being pristine or changed altogether (e.g. SWCNT, DWCNT, etc), the dispersion in the pre-infusion steps could be varied (e.g. sonication times – which by the way also varies properties as mentioned [30] in the literature, etc) or experiment on implementing more control on vacuum pressure (on the system while being processed via these two methods. This new knowledge could generate a further level of understanding from those modified

variables and see whether there had been any synergistic effect, or not, on the mechanical properties.

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List of Journal Articles and Conference Presentations

1. P Ramdeen, K Kanny. Effect of Temperature on Tensile Properties of Nanoclay Filled Hybrid Composites. Paper presented at the First International Conference for Composites, Biocomposites and Nanocomposites (ICCBN). ISBN: 978-1-919-858-25-8; 2-4 December 2013, Durban, South Africa

2. P Ramdeen, K Kanny. The Effect of Processing Methods of Carbon Nanotube/Glass Epoxy Hybrid Composites on its Impact And Hardness Properties. Paper presented at the Second International Conference for Composites, Biocomposites and Nanocomposites (ICCBN). ISBN: 978-0-620684-56-9; 28-30 October 2015, Durban, South Africa.

List of Submitted Journal Articles

P Ramdeen, T P Mohan and K Kanny. Process Variation and its Effect on Dispersion and Mechanical Properties of Polymer Hybrid Epoxy Glass Fibre Composites infused with Carbon Nanotubes. International Journal of Polymer Plastics Technology. Submitted for Review July 2020