INFLUENCE OF NANOPARTICLES ON THE PHYSICAL PROPERTIES OF FIBER REINFORCED POLYMER COMPOSITES

THESIS

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Abstract

Conventional fiber reinforced plastics (FRP’s) have long been important if not indispensable in many crucial applications such as transportation, renewable energy, defense applications, as well as many others. Composite materials are of interest to these industries due to their attractive properties including high strength to weight ratio and high modulus to weight ratio. Comprehensive research has been conducted on conventional composite materials to optimize their processing parameters as well as optimize their mechanical behavior and reliability. Although composites provide excellent mechanical properties, certain applications demand improved mechanical behavior as well as the presence of additional properties. Recent developments in polymers have developed nanocomposites, which are composites reinforced by nanoparticles. In these materials, the nanoparticles have shown great enhancements in mechanical properties, thermal properties, and electrical properties. Nevertheless, these composites lack the strength for applications where FRP’s are currently used. The addition of nanoparticles as reinforcement to conventional composites shows great promise to not only enhance the existing properties of these composites, but also add many other properties that would maximize their applications.
The promise of substantial multifunctional improvements to the behavior of conventional composites does not come without a cost. The effective reinforcement of the desired properties is a direct function of nanoparticle selection and proper dispersion of such nanoparticles. The objective of this research proposal is to develop long fiber reinforced polymer nanocomposites that combine conventional composites with the added benefits of nanocomposites.

One of the main challenges involved in the successful enhancement of properties through the addition of nanoparticles is to overcome the problem of poor dispersion in the polymer matrix. Therefore novel state-of-the-art methods of incorporating and dispersing nanoparticles must be developed.

Current methods to produce nanoparticle reinforced composites are very limited. One method involves the direct dispersion of nanoparticles in the polymer matrix, then molding the composite through the related process. This approach dramatically increases the polymer’s viscosity, making the polymer extremely difficult if not impossible to process.

The entire approach of this research, involving the incorporation of nanoparticles into the fiber perform is unique. This method involves the sonication of the nanoparticles in a solvent solution under specific sonication frequency and amplitude as well as specific exposure time to optimize dispersion. The solution is then sprayed onto a layer of fiber perform which is on a specialized fluid flow processor to incorporate such nanoparticles through multiple layers of fiber mats.
The approach undertaken has shown important improvements in specific properties of the composites, but not to the theoretical potential of improvement. Further development of processing parameters as well as the mechanics of the method itself need to be improved substantially.

The mechanical property improvement was studied to determine the enhancement to tensile strength, flexural strength, interlaminar shear strength, impact strength, fatigue life, and behavior under stress concentration caused by geometric discontinuity. A series of testing samples for each specific property testing were produced and tested according to the corresponding ASTM standards.
Dedicated to My Father, My Mother and My Brother
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Table of Contents

INFLUENCE OF NANOPARTICLES ON THE PHYSICAL PROPERTIES OF FIBER REINFORCED POLYMER COMPOSITES ................................................................. 1

THESIS ............................................................................................................................... 1

Abstract ............................................................................................................................... ii

Acknowledgements ............................................................................................................ vi

Vita.................................................................................................................................... vii

Publications ................................................................................................................... vii

Fields of Study ............................................................................................................. viii

Table of Contents ............................................................................................................... ix

List of Tables ................................................................................................................... xiv

List of Figures ................................................................................................................... xv

Chapter 1: Introduction ...................................................................................................... 1

1  Polymer Composites ................................................................................................... 1

1.1  Resins ................................................................................................................... 2

1.2  Fibers .................................................................................................................... 3
Chapter 2: Analysis of the Effect of Nanoparticles on Mold Filling in a Vacuum Assisted Resin Transfer Molding System ................................................................. 41

1  Introduction............................................................................................................ 41

2  Experimental.......................................................................................................... 42

2.1  Mold Filling Analysis.......................................................................................... 45

3  Results and Discussion .......................................................................................... 49

4  Conclusions............................................................................................................ 57

References ..................................................................................................................... 58
List of Tables

Table 1. Tensile properties of CNF-modified epoxy (Zhou Y. P., 2008) ......................... 26

Table 2. Flexural properties of neat and nanophased carbon/epoxy and carbon/CNF/epoxy composites (Zhou Y. P., 2008) .......................................................... 34

Table 3. Tensile properties of neat and nanophased carbon/epoxy composites (Zhou Y. P., 2008) ............................................................................................................................ 36

Table 4. Permeability and porosity values of reinforcement with various CNF loadings 52

Table 5. Thermal properties of UP-CNF Nanocomposites ............................................... 67

Table 6. Specifics for cross-flow assisted spraying samples ............................................ 94
List of Figures

Figure 1. Tensile behavior of fiber-reinforced plastics and other structural materials (Sheldon, 1982) ................................................................. 10

Figure 2. Common particle reinforcements/geometries and their respective surface to volume ratios (Thostenson, 2006) ............................................. 12

Figure 3. Scheme of three main types of layered silicates in polymer matrix (Alexandre, 2000) .............................................................. 13

Figure 4. Schematic of (a) single-wall and (b) multi-wall nanotubes (Hussain, 2006) ................................................................. 16

Figure 5. Tensile strength comparison of common engineering materials (Lau, 2002) .......................................................... 16

Figure 6. Schematic of various types of graphitic nanofibers (al., 2005) ................. 18

Figure 7. Interlaminar shear strength (ILSS) of the nano-reinforced Glass Fiber Reinforced Polymer (GFRPs) (EP-epoxy, CB-carbon black and DWCNT-double wall carbon nanotubes) (Gojny, 2005) .............................................................. 22

Figure 8. Stress-strain curves for epoxy and CNT/epoxy (Zhou Y. P., 2008) .............. 23

Figure 9. Effect of CNT content on strength and modulus of neat and nanophased epoxy (Zhou Y. P., 2008) ................................................................. 24

Figure 10. Effect of CNF content on tensile stress-strain curves of epoxy (Zhou Y. P., 2008) ................................................................................. 25

Figure 11. Effect of CNF content on tensile strength and modulus of epoxy (Zhou Y. P., 2008) ................................................................. 26
Figure 12. S-N curves of epoxy and nanocomposite (Zhou Y. P., 2008) ......................... 28
Figure 13. Effect of CNF contents on fatigue life of neat and nanophased epoxy (Zhou Y. P., 2008) ............................................................................................................................ 28
Figure 14. Load-displacement curves in fracture test (Zhou Y. P., 2008) ......................... 29
Figure 15. Effect of CNF content on fracture toughness of neat and nanophased epoxy (Zhou Y. P., 2008) ............................................................................................................ 30
Figure 16. Resistivity of some polypropylene/VGCNF composites. Approximate resistivity values required for static discharge, electrostatic painting and radio frequency interference shielding indicated. Data from three different types of fibers are plotted and compared to a simple superposition model for graphitized or as grown fibers (Tibberrs, 2001) ........................................................................................................................................ 32
Figure 17. Flexural stress-strain curves (Zhou Y. P., 2008) ............................................. 34
Figure 18. Tensile stress-strain curves (Zhou Y. P., 2008) ............................................... 36
Figure 19. S-N curves of neat and nanophased composite (Zhou Y. P., 2008) ............... 37
Figure 20. Schematic of experimental set-up for VARTM ............................................. 44
Figure 21. Composite samples prepared by the pre-mix and pre-bind methods .......... 46
Figure 22. SEM image of 5wt% CNFs pre-binding on GF mat ...................................... 51
Figure 23. Comparison of mold filling profile with various CNF contents................. 51
Figure 24. Filling time vs. (flow length)$^2$ plots for permeability calculation .......... 52
Figure 25. Experimental and calculated flow length of various CNF loadings: (a) 0, (b) 3.5, and (c) 5 wt% .............................................................. 53
Figure 26. Flexural properties of UP-CNFGF hybrid composites: (a) flexural strength; (b) flexural modulus. (all samples tested in transverse direction to long fiber longitudinal axis)................................................................................................................................. 54

Figure 27. Mold filling data fit to the simple capillary .......................................................... 54

Figure 28. Mold filling data fit to the Kozeny-Carman model ............................................. 55

Figure 29. SEM images of the cured composite sample: (a) CNFs at the fracture surface of the tested composite sample; (b) glass fiber, CNFs, and resin at the interface of the phases .................................................................................................................................. 55

Figure 30. Schematic of experimental set-up for VARTM .................................................. 67

Figure 31. Flexural properties of UP-CNFGF nanocomposites: (a) flexural strength; (b) flexural modulus .............................................................................................................................................. 68

Figure 32. Pictures of UP-CNFGF-GF hybrid composites: (a) 3.5 wt% CNF pre-mixing sample; (b) 3.5 wt% CNF pre-binding sample (resin flow is left to right) ..................................................... 68

Figure 33. SEM image of CNFs pre-bonded on glass fibers .............................................. 69

Figure 34. Flexural properties of UP-CNFGF-GF hybrid composites: (a) flexural strength; (b) flexural modulus. (All samples are tested in the transverse direction to the major long fiber axis) ................................................................................................................................. 70

Figure 35. SCRIMP setup for Epoxy resin – Three carbon fiber/epoxy composite panels being prepared simultaneously. .............................................................................................................. 80

Figure 36. (a) Effect of carbon nanofibers and silver oxide on the thermal conductivity of epoxy/carbon fiber composites. (b) Effect of carbon nanofibers and silver oxide on the conductance of epoxy/carbon fiber composites ........................................................................................................... 81
Figure 37. (a) Effect of heat treated carbon nanofibers on the thermal conductivity of epoxy/carbon fiber composites. (b) Effect of heat treated carbon nanofibers on the conductance of epoxy/carbon fiber composites

Figure 38. (a) Effect of synthetic diamond and heat treated carbon nanofibers on the thermal conductivity of epoxy/carbon fiber composites (b) Effect of synthetic diamond and heat treated carbon nanofibers on the conductance of epoxy/carbon fiber composites

Figure 39. (a) SEM of heat treated carbon nanofibers on continuous carbon fiber (b) SEM of Silver oxide particles on continuous carbon fiber mats

Figure 40. Effect of various carbon based nanoparticles on the conductivity and conductance of epoxy/carbon fiber composites

Figure 41. Schematic representation of cross-flow assisted spraying

Figure 42. Schematic of experimental set up for VARTM (SCRIMP)

Figure 43. Flexural strength of the composite samples

Figure 44. Flexural strength improvement of the composite samples

Figure 45. Flexural modulus of the composite samples

Figure 46. Flexural modulus improvement of the composite samples

Figure 47. SEM image of the Pure VE sample cross-section (50 µm scale bar)

Figure 48. SEM image of the Pure VE sample cross-section (10 µm scale bar)

Figure 49. SEM image of the Pure VE sample cross-section (5 µm scale bar)

Figure 50. SEM image of a method (1) sample cross-section (5 µm scale bar)

Figure 51. SEM image of a method (2) sample cross-section (10 µm scale bar)
Chapter 1: Introduction

1 Polymer Composites

Polymeric materials have long been used in many areas, such as transportation, packaging, structural components, defense industry, wind energy, and other applications. Presently polymers are the fastest growing materials in the world.

A composite is a material that consists of two or more components with different chemical or physical characteristics, which remain separate and distinct on a macroscopic level within the finished structure and that might serve different functions. Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials, namely matrix and reinforcement. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart special mechanical and physical properties to enhance the matrix. The combination of these two constituents produces a synergistic effect resulting in a material with properties unavailable from the individual constituents. The preparation of composites with two or more constituents is one of the most important approaches to meet the demand of design, strength and cost requirements for a particular application.
These composite materials possess better chemical or physical properties than pure polymeric materials, namely higher strength and modulus, low specific gravity, improved chemical and corrosion resistance, as well as other functionalities.

1.1 Resins

In general, there are two main types of polymer resins: thermoplastics and thermosets (Schwartz, 1982). These two polymer types differ in their molecular structure as well as their behavior.

In thermoplastic materials, the individual molecules have a linear structure and there is no chemical linking between them. These molecules associate through weak Van der Waals forces, dipole-dipole interactions, hydrogen bonding and even stacking of aromatic rings. Thermoplastics can be softened and made to flow with the application of heat and pressure as the weak interaction between the molecules can be temporarily broken down. When the material is then cooled, the molecules restore the secondary bonding between them and the material then solidifies. Due to this ease of manufacture and formability, thermoplastic materials are widely used in a variety of products, and their use in composite products has become more and more popular.

Thermoset polymers are the most widely used materials for composite applications. In this type of polymer, the molecules are chemically linked together, forming a three-dimensional network structure. Curing of thermoset materials can be done through the application of heat or through a chemical reaction. This cross-linking
results in molecules with higher molecular weight, leading to a higher melting point. Once the cross-linking has occurred, the thermoset material cannot be melted or made to flow. This implies that thermoset materials cannot be recycled, except as a filler material. Thermoset materials have much higher thermal stability when compared with thermoplastic materials, a great advantage for high demand applications.

1.2 Fibers

Conventional composites generally consist of fillers in the form of long fiber reinforcements. These reinforcements are in the form of inorganic, organic, or metallic fibers of relatively high strength and modulus embedded in or bonded to a polymer matrix. Fiber reinforcements are the most widely used fillers while fiber reinforced polymer Composites (FRPC) are the most widely used composite materials. In general, the fibers are the principal load-carrying members, while the surrounding matrix keeps them in the desired location and orientation as well as acting as a load transfer medium between the fibers themselves.

There are three important categories of fiber reinforcements used in FRPC: glass, carbon and aramid. Glass fiber reinforcement was tested in military applications at the end of World War Two (Gunter, 2006), carbon fiber production began in the late 1950’s and was used by the British industry beginning in early 1960’s. Aramid fibers were being produced around this same time by Dupont under the trade name Nomex. Presently, glass
fibers are used widely across all industries, although carbon fiber and carbon fiber aramid composites are mostly found in aerospace, automotive and sporting good equipment.

1.2.1 Glass Fiber

Glass fiber or fiberglass is a material made from extremely fine fibers of glass, and it is the largest reinforcement measured in sales. Glass fiber was invented in 1938 by Russell Games Slayter of Owens-Corning as a material to be used as insulation (Lowenstein, 1973). Ever since then, glass fiber has become widely used as insulation and composite reinforcement material. Based on the composition and the application, glass fibers can be classified in several types. The most commonly used glass fiber type for composite applications is E-glass, due to its relatively good mechanical properties and high electrical insulation. S-glass is also used in composite materials where high tensile strength is desired, however this material comes at a much higher cost. R-glass is also used in composite materials with high mechanical requirements such as fatigue life and high chemical resistance. The typical fiber diameter for glass fiber is 9-17 µm and the specific gravity is about 2.5. The tensile strength of glass fiber is in the order of 2000-4800 MPa and the elastic modulus is in the order of 50-90 GPa, much higher than that of polymers (Biron, 1973).
1.2.2 Carbon Fiber

Carbon fiber if graphite fiber is another major fiber reinforcement type used in FRPC. One of the most common methods of manufacturing carbon fiber is the oxidation and thermal pyrolysis of polyacrylonitrile (PAN), so called PAN-based carbon fibers. This material consists of extremely thin fibers about 5-10 µm in diameter and comprised mostly of carbon atoms. The carbon atoms are bonded together in microscopic crystals that are mostly aligned parallel to the long axis of the fiber. This alignment makes the fiber show very high tensile properties. The tensile strength of carbon fiber is in the order of 3000-5800 MPa and the elastic modulus is in the order of 500-600 GPa (Lowenstein, 1973). Compared with glass fibers, carbon fibers have lower density but higher tensile strength and elastic modulus. These properties make carbon fiber an ideal reinforcement for composite materials used in aircraft components, high-performance vehicles, sporting equipment, wind generator blades, and other high demand, high performance applications.

1.2.3 Aramid and Other Fibers

Aramid fibers are a class of heat-resistant and strong synthetic fibers. They are used in aerospace and military applications, for ballistic rated body armor fabric, and as an asbestos substitute. The name is a shortened form of aromatic polyamide. In this
material the chain molecules are highly oriented along the fiber axis, exploiting the strength of the chemical bond, exhibiting high mechanical properties.

Other fibers such as Kevlar, boron, or metal materials can also be used in FRPC, however the high cost of the material and the complicated manufacturing process as well as processing of the composite material itself has limited their popularity when compared to glass fiber or carbon fiber.

1.3 Fillers

Fillers are used in polymers for a variety of reasons, namely to reduce cost, improve processing, control density, thermal conductivity, thermal expansion, electrical properties, magnetic properties, flame retardance, and to improve mechanical properties.

Each filler type has different properties depending on particle size, shape and surface chemistry (Rothon, 2002). The most commonly used fillers for thermoset resins are calcium carbonate, kaolin, and alumina hydrate. Other commonly used filler include clay, carbon black, mica, silica, glass micro-spheres, and glass whiskers.

In general, the fillers can change the performance of polymer composites by changing the color, viscosity, barrier properties, curing rate, electrical and thermal properties, surface finish, shrinkage, etc.
1.4 Processing

There are many processing techniques for manufacturing FRPC. The main processing techniques are hand lay-up, pray-up, autoclave/vacuum bag, match molding process, compression molding, filament winding, and liquid composite molding (RTM and VARTM). Each of these methods has their specific characteristics, and they are meant for different types of composite parts. This study is primarily based on thermosetting FRPC made of epoxy, vinyl ester, and unsaturated polyester resins. The most commonly used processes for these materials are introduced as follows.

1.4.1 Autoclave/Vacuum Bag Molding

This process consists of laying-up individual sheets of prepreg material in an open mold. Prepreg material usually consists of unidirectional tape or a woven fabric pre-impregnated with a partially cured resin. The material is then covered with release film, bleeder/breather material and a vacuum bag. A vacuum is then pulled on the part and the entire mold is placed into an autoclave (heated pressure vessel). The vacuum assists in removing any trapped air from the laminate, while the pressure and temperature are applied to cure the part. This process is mainly used by aerospace industry because it allows precise control over the molding process, precise control over laminate dimensions and better overall composite quality.
1.4.2 Match Molding Process

This process is a simplified version of the autoclave/vacuum bag molding process. The autoclave/vacuum bag molding process requires a strong initial investment for the autoclave equipment; however the same curing procedure can be replicated by the match molding process by means of replacing the autoclave with a heated hydraulic press. In this case, the material is also placed in a two part mold, and then covered with release film, bleeder/breather material and a vacuum bag. A vacuum is then pulled on the part. The top portion of the mold is then assembled on top of the laminate and the entire mold is placed in the heated hydraulic press. The heated hydraulic press provides the desired pressure and temperature necessary for adequate curing of the part.

1.4.3 Liquid Composite Molding (RTM and VARTM)

Liquid composite molding has become increasingly popular due to its low cost, good composite quality, and the ability to manufacture high performance composites with complicated geometry. The main processes in this category are resin transfer molding (RTM), structural reaction injection molding (SRIM), vacuum-assisted resin transfer molding (VARTM) and others.

In RTM, pre-shaped fabric reinforcements called performs are placed in a mold cavity. The mold is then closed and heated to a desired temperature. Pressurized resin is then injected into the mold cavity. The resin will flow through the fiber perform,
expelling any trapped air and impregnating the perform. The composite is then cured and removed from the mold.

VARTM is a variant of RTM. In the VARTM process, the resin is driven into the reinforcement purely by vacuum and both mold filling and curing may be done at ambient temperature. William Seeman patented a method of manufacturing FRPC using a variant of the VARTM process. This method is called Seeman Composite Rein Infusion Molding Process (SCRIMP). This process consists of using a soft mold half, namely a vacuum bag, a highly permeable medium and a peel ply to remove the highly permeable medium after molding. This process allows for shorter cycle time and reduced cost.

1.5 Performance

FRPC are the most widely used composite materials. These materials are highly desirable due to their outstanding mechanical properties and excellent performance when compared to other materials.

There are several noticeable advantages which include design flexibility, dimensional stability, thermal stability, improves chemical and corrosion resistance, high strength to weight ratio, high modulus to weight ratio, high internal damping, low specific gravity amongst others (Lowenstein, 1973).

Fiber-reinforced epoxy composites have higher strength and modulus than unreinforced epoxy (Sheldon, 1982). Referring to Figure 1, it can be observed that 60 % by volume carbon fiber epoxy composites have better mechanical properties than steel.
These excellent properties with the added advantage of weight savings make composite materials ideal for use in high performance applications such as the space shuttle, military aircraft, and artificial satellites (Kamal, 1973).

Figure 1. Tensile behavior of fiber-reinforced plastics and other structural materials (Sheldon, 1982)
In the last 20 years, there has been a strong emphasis on the development of polymeric nanocomposites, where at least one of the dimensions of the filler material is in the order of a nanometer (Hussain, 2006). The final composite does not have to be in nanoscale, but can be micro- or macroscopic in size (EN-AVT-129, May 2005). In general, the unique combination of the nanomaterial’s characteristics, such as size, mechanical properties, and low concentration necessary to modify the polymer matrix properties have generated much interest in the field of nanocomposites. Another aspect that makes polymer nanocomposites is the fact that they can be fabricated and processed in ways similar to that of conventional polymer composites, making them particularly attractive from a manufacturing point of view.

Nanocomposites exhibit light-weight, good dimensional stability, enhanced heat and flame resistance, improvements in strength and modulus as well as barrier properties with far less loading than conventional composite counterparts (Monk, 1997) (Wang, 1998), however these properties depend on several factors such as type of nanoparticle, surface treatments, polymer matrix, synthesis methods, and polymer nanocomposites morphology (Koo, 2006).
2.1 Nanoparticles

The transition from microparticles to nanoparticles yields dramatic changes in physical properties (Hussain, 2006). Nanoparticles in general have high surface area for a given volume (Luo, 2003). Common nanoparticle geometries and their respective surface area to volume ratios are shown in Figure 2.

![Figure 2. Common particle reinforcements/geometries and their respective surface to volume ratios (Thostenson, 2006)](image)

Typical materials currently under study include nanoparticles, nanoplatelets, nanotubes, nanofibers, fullerenes, and nanowires. In general, these materials can be classified by their geometries (Schmidt); in general, there are three classes, namely particle, layered, and fibrous materials (Schmidt) (Thostenson, 2006).
2.2 Nanoplatelets

The two main types of nanoplatelets particles most commonly used in polymer nanocomposites are layered silicate (Nanoclay) clay and graphite (Graphene). A material will be characterized as nanoplatelets if it has a nanometer thickness and a high aspect ratio (30-1000) plate like structure (Alexandre, 2000). Figure 3 represents three main types of nanocomposites for layered silicate materials.

Figure 3. Scheme of three main types of layered silicates in polymer matrix (Alexandre, 2000).
In general, the morphology of polymer-clay composites can be divided into three categories, namely phase separated (microcomposite), intercalated nanocomposites, and exfoliated nanocomposites (Alexandre, 2000) (Koo, 2006) (Thostenson, 2006) (Messersmith, 1994). In the phase separated (microcomposite), the clay nanoplatelets keep their crystal structure and the particle is in the microscale. In an intercalated (nanocomposite) stage, few polymer molecules penetrate into the silicate layers, with fixed interlayer spacing. In the exfoliated (nanocomposite) stage, the nanolayers are delaminated and individually dispersed in the continuous polymer matrix.

The most desired structure for a nanoplatelet/polymer nanocomposite is for the nanofiller to be in the exfoliated state, as this provides maximum interfacial contact and best dispersion resulting in optimum nanocomposite performance (Koo, 2006).

Natural flake graphite (NFG) is also formed of individual graphite nanoplatelets called graphene layers. The structure of NFG is comprised of individual graphene layers where the carbon atoms are linked by covalent bonds, and these graphite sheets are stacked together by much weaker Van der Waals forces (Pan, 2000). The NFG can be separated down to 1 nm thick sheets, with an aspect ratio in the order of 200-1500 and with a modulus in the order of 1 TPa.
2.3 Nanotubes and Nanofibers

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are the most widely used fibrous nanoparticles used in polymer materials.

CNTs are rolled are graphitic sheets rolled into seamless tubes (i.e., arrangements of carbon hexagons into tube-like fullerenes) and have diameters ranging from about a nanometer to tens of nanometers with lengths up to centimeters (Hussain, 2006). Nanotubes have received much attention due to their exceptional mechanical, thermal and electrical properties since their discovery in 1991 by Iijima (Iijima S., 1991) (Iijima S. a., 1993). There are two types of CNTs, namely single-walled carbon nanotubes (SWNTs), which their name implies are formed by a single layer of carbon atoms in a cylindrical structure; and multi-walled carbon nanotubes (MWNTs) which exhibit a structure of concentric nanotubes forming one tube defining a multiwall nanotube as seen in Figure 4. CNTs present tensile modulus and strength values for single- and multiwall nanotubes ranging from 270 GPa to 1 TPa and 11 GPa to 200 GPa respectively (Lau, 2002). Figure 5 shows a comparison of the tensile strength for common engineering materials.
Figure 4. Schematic of (a) single-wall and (b) multi-wall nanotubes (Hussain, 2006)

Figure 5. Tensile strength comparison of common engineering materials (Lau, 2002)
CNFs are another type of fibrous nanomaterial. They have similar characteristics to CNTs and can serve as substitutes to these materials. Recent studies have shown that CNF-polymer nanocomposites have similar properties to CNT-polymer nanocomposites. CNFs are a unique type of vapor-grown carbon fibers that fill the gap in physical properties between conventional carbon fibers (5-10 µm) and carbon nanotubes (1-10 nm). The reduced diameter of the nanofiber provides a larger surface area with surface functionalities in the fiber (Jayaraman, 2004). Typical CNFs are not concentric cylinders; the length of the fiber can be varied from about 100 µm to several centimeters, and the most common structure of CNFs is the truncated cones, but there are wide ranges of morphologies (cone, stacked coins, etc). Figure 6 shows several different structures for CNFs.
Figure 6. Schematic of various types of graphitic nanofibers (al., 2005)
The structure of a polymer nanocomposite will be determined by the processing conditions, therefore preparation and processing are the crucial to achieving good properties in the final nanocomposite. In general, there are four common methods to prepare polymer nanocomposites, namely high-shear mixing, solution blending, melt blending, and in-situ polymerization. These processes are described as follows:

2.4.1 High-shear Mixing

This process is achieved by mixing solid nanofiller with the liquid polymer resin using high-shear equipment. During this process, shear forces are used to force the de-agglomeration and dispersion of the nanofiller. High-shear mixing is a relatively simple approach to preparing polymer nanocomposites, however proper dispersion is not always achieved as the shear forces may not be high enough to disperse the nanoparticles effectively in the polymer matrix.

2.4.2 Solution Blending

This process utilizes a solvent to dissolve the polymer and hence reduce its viscosity. This allows better dispersion of the nanoparticles as it facilitates dispersion
through the application of ultrasonic forces, high shear mixing or other dispersion methods. This technique has been widely used with water-soluble polymers.

2.4.3 Melt Blending

This method has particular application with thermoplastic materials as the procedure involves the mixing of a molten polymer with nanoparticles through high shear forces induced generally by a twin screw extruder. The disadvantage is that during blending such as extrusion, the fibrous nanoparticles may break under the high shear forces and lose their high aspect ratio (Shen, 2006).

2.4.4 In-situ Polymerization

In this process, the nanoparticles are first mixed with a monomer. The nanoparticles are dispersed in the monomer with the assistance of ultrasonic forces, mechanical mixing, or a high-shear device. An initiator or curing agent is then added to the system and in-situ polymerization takes place. With the subsequent polymer chain growth, the space between nanoparticles can be further expanded. This process will result in a nanocomposite.
2.5 Properties

Nanoparticles are added to polymer materials and FRPC to obtain improved overall properties (i.e., mechanical, thermal and electrical properties). These properties depend on nanoparticle type as well as level of dispersion and nanoparticle loading. In general, the high aspect ratio of the nanoparticles results in stronger interfacial interactions between matrix and the nanoparticles yielding improved properties.

2.5.1 Mechanical Properties

Several studies have been conducted into the influence of nanoparticles on the mechanical properties of polymer resins as well as conventional composites. The most common mechanical properties measured are tensile strength and modulus, flexural strength and modulus, interlaminar shear strength, as well as fatigue life.

2.5.1.1 Interlaminar Shear Strength

Studies conducted on the influence of nanoparticles have shown an increase in mechanical properties such as fracture toughness and interlaminar shear strength (ILSS). One study produced nanotube/epoxy composites which exhibited a significant increase in fracture toughness, as well as an enhancement of stiffness already at low nanotube contents. Later on, the influence of CNTs on the ILSS of a glass-fiber-reinforced
composite (GFRP) was studied and reported an increase of 19% in interlaminar shear strength with a weigh fraction as low 0.3 wt.% of amino-functionalized double wall CNTs (DWCNT-NH₂) in the epoxy matrix as seen in Figure 7.

Figure 7. Interlaminar shear strength (ILSS) of the nano-reinforced Glass Fiber Reinforced Polymer (GFRPs) (EP-epoxy, CB-carbon black and DWCNT-double wall carbon nanotubes) (Gojny, 2005)
2.5.1.2 Flexural Strength and Modulus

CNTs have shown to have a significant effect on the mechanical behavior of epoxy/CNT nanocomposites. A recent study showed that the modulus of the nanophased epoxy increased continuously with higher CNT content. The modulus improved by 11.7% with an addition of 0.4 wt% of CNTs. However the system with 0.3 wt.% infusion is the best with a 28.3% flexural strength enhancement. The flexural strength begins to degrade with 0.4 wt%, although the gain in modulus is maintained. See Figure 8 and Figure 9.

Figure 8. Stress-strain curves for epoxy and CNT/epoxy (Zhou Y. P., 2008)
Figure 9. Effect of CNT content on strength and modulus of neat and nanophased epoxy

(Zhou Y. P., 2008)
2.5.1.3 Tensile Strength and Modulus

Other studies have conducted analyses of the effect of CNFs on the tensile strength and modulus of epoxy resins. To identify optimal loading of CNFs, the weight fraction of CNFs in epoxy was varied from 0 to 3%. Tensile tests on neat and nanophased epoxy were performed according to ASTM standard D638-89. Figure 10 shows the tensile stress-strain curves of epoxy with different CNFs contents. The average strength and modulus obtained from these test are listed in Table 1 and also plotted in Figure 10.

The relationship between modulus, strength, and CNFs weight fraction was plotted in Figure 11.
Figure 11. Effect of CNF content on tensile strength and modulus of epoxy (Zhou Y. P., 2008)

Table 1. Tensile properties of CNF-modified epoxy (Zhou Y. P., 2008)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>σf (MPa)</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>58.78 ± 2.65</td>
<td>2.78 ± 0.16</td>
<td>55.5</td>
<td>-0.0471</td>
</tr>
<tr>
<td>1 wt.% CNF</td>
<td>64.84 ± 2.27</td>
<td>2.87 ± 0.21</td>
<td>68.3</td>
<td>-0.0676</td>
</tr>
<tr>
<td>2 wt.% CNF</td>
<td>68.98 ± 2.35</td>
<td>3.17 ± 0.15</td>
<td>115.6</td>
<td>-0.0981</td>
</tr>
<tr>
<td>3 wt.% CNF</td>
<td>63.96 ± 3.03</td>
<td>3.32 ± 0.19</td>
<td>103.6</td>
<td>-0.104</td>
</tr>
</tbody>
</table>
2.5.1.4 Fatigue Life

The fatigue performance is important for applications where cyclical stress will be a factor. A study was conducted on the fatigue performance of epoxy/CNFs nanocomposites. In this study, stress-controlled tension-tension fatigue test were performed at 21.5°C. The ratio of the minimum cyclic stress and the maximum cyclic stress, i.e., the R-ratio, was 0.1. A cyclic frequency of 1 Hz was used to reduce the possibility of thermal failure. Figure 12 shows the fatigue S-N curves of the neat and nanophased epoxy at ambient temperature. As seen in Figure 12, the fatigue life of the nanophased epoxy was significantly higher than that of the neat epoxy. Based on the experimental data, the following equation was established for the S-N curves:

\[
\sigma = \sigma_f (N_f)^b
\]

The values of the fatigue strength coefficient \(\sigma_f\) and fatigue strength exponent \(b\) with different CNFs content are listed in Table 1. Figure 13 shows the fatigue life versus CNF weight fraction at different cycling stress levels. 2 wt% CNF/epoxy exhibited the largest fatigue performance.
Figure 12. S-N curves of epoxy and nanocomposite (Zhou Y. P., 2008)

Figure 13. Effect of CNF contents on fatigue life of neat and nanophased epoxy (Zhou Y. P., 2008)
2.5.1.5 Fracture Toughness

In this same study, the fracture toughness of neat and nanophased epoxy were determined using single edge notch tensile (SENT) specimens. Each SENT specimen was first cycled 100 times between 4 and 40% of the peak load at 1 Hz and then statistically tested in tension. Figure 14 shows the load-displacement diagrams obtained in static tensile testing of SENT specimens. The critical stress intensity factor ($K_{IC}$) was calculated using the peak load. The $K_{IC}$ values are plotted in Figure 15 as a function of CNFs weight fraction. It shows that the addition of CNFs up to 2 wt% increased $K_{IC}$; however, at the higher CNFs content, the $K_{IC}$ started to decrease.

Figure 14. Load-displacement curves in fracture test (Zhou Y. P., 2008)
Figure 15. Effect of CNF content on fracture toughness of neat and nanophased epoxy (Zhou Y. P., 2008)
2.5.1.6 Conductive Properties

A study conducted by Finegan and Tibberrs (Tibberrs, 2001) reported extensive conductivity measurements for vapor grown carbon nanofibers (VGCNF), polypropylene and nylon composites. They found a percolation threshold around 3 vol% (6 wt%) and were able to reach resistivity values as low as 0.15 $\Omega$ cm at about 20 vol% fiber loading. Later work demonstrated that by processing the fibers at higher temperature and with higher care as to avoid fiber breakage, the percolation threshold was lowered to 1 wt% of fibers as shown in Figure 16.
Figure 16. Resistivity of some polypropylene/VGCNF composites. Approximate resistivity values required for static discharge, electrostatic painting and radio frequency interference shielding indicated. Data from three different types of fibers are plotted and compared to a simple superposition model for graphitized or as grown fibers (Tibberrs, 2001)
Fiber reinforced polymer nanocomposites are three phase composites comprised by long fiber reinforcements such as glass fiber or carbon fiber, nano-reinforcements such as CNFs or CNTs, and a polymer matrix. These hybrid composite materials provide the optimal combination of properties by combining the strength of conventional composite materials with the multifunctionality of nanocomposites.

3.1 Flexural Strength and Modulus

A study by Zhou Y. P. incorporated CNFs into carbon fiber/epoxy composites by premixing CNF into the epoxy matrix, and then infusing the resin into carbon fiber performs. The cured composites where then tested for flexural properties. Flexural stress-strain curves of neat and nanophased composites are shown in Figure 17. The curves reveal that by infusing 2 wt% CNF in the epoxy matrix, strength and failure strain were significantly improved. As shown in Table 2, the nanophased system showed approximately 22.3% increase in flexural strength, 7.9 % increase in failure strain with respect to the neat system and no change in flexural modulus.
Figure 17. Flexural stress-strain curves (Zhou Y. P., 2008)

Table 2. Flexural properties of neat and nanophased carbon/epoxy and carbon/CNF/epoxy composites (Zhou Y. P., 2008)

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td>48.9 (±5.1%)</td>
<td>49.4 (±6.2%)</td>
</tr>
<tr>
<td>Gain in modulus</td>
<td>–</td>
<td>2.0%</td>
</tr>
<tr>
<td>Failure strain (%)</td>
<td>1.17 (±2.6%)</td>
<td>1.27 (±2.4%)</td>
</tr>
<tr>
<td>Gain in failure strain</td>
<td>–</td>
<td>7.9%</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>488 (±3.1%)</td>
<td>597 (±3.5%)</td>
</tr>
<tr>
<td>Gain in strength</td>
<td>–</td>
<td>22.3%</td>
</tr>
</tbody>
</table>
3.2 Tensile Strength and Modulus

This same study performed an analysis on the tensile strength and modulus of the carbon/epoxy and the nanophased carbon/CNF/epoxy composites. The tensile stress-strain curves and the tensile properties of neat and nanophased laminates are shown in Figure 18 and Table 3. Infusing 2 wt% CNFs in epoxy resin produced 11% enhancement in ultimate tensile strength (UTS), 4.1% enhancement in failure strain, and no changes in modulus. A possible reason for the observed mechanical properties of the carbon fabric reinforced laminate infused with CNFs. The CNFs increase the strength and modulus of the epoxy matrix, as was observed in section 2.5.1.3. The modulus of the composite laminate was not affected by CNFs, since modulus is dominated by the carbon fibers present in the laminate. However, the presence of CNF increased crack propagation resistance by the bridging effect, which improves strength.
Figure 18. Tensile stress-strain curves (Zhou Y. P., 2008)

Table 3. Tensile properties of neat and nanophased carbon/epoxy composites (Zhou Y. P., 2008)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td>45.2 (±1.6%)</td>
<td>46.1 (±2.5%)</td>
</tr>
<tr>
<td>Gain in modulus</td>
<td>–</td>
<td>2.2%</td>
</tr>
<tr>
<td>Failure strain (%)</td>
<td>1.45 (±4.5%)</td>
<td>1.51 (±5.2%)</td>
</tr>
<tr>
<td>Gain in failure strain</td>
<td>–</td>
<td>4.1%</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>556 (±2.4%)</td>
<td>617 (±3.6%)</td>
</tr>
<tr>
<td>Gain in strength</td>
<td>–</td>
<td>11.0%</td>
</tr>
</tbody>
</table>

Table 3. Tensile properties of neat and nanophased carbon/epoxy composites (Zhou Y. P., 2008)
3.3  Fatigue Life

Stress-controlled tension-tension fatigue test were performed at 21.5°C. The ratio of the minimum cyclic stress and the maximum cyclic stress, i.e., the R-ratio, was 0.1. A cyclic frequency of 2 Hz was used to reduce the possibility of thermal failure. Figure 19 shows the fatigue S-N curves of the neat and nanophased carbon fabric reinforced epoxy. The fatigue S-N curve of the nanocomposite was significantly higher than that of the neat carbon/epoxy composite.

Figure 19. S-N curves of neat and nanophased composite (Zhou Y. P., 2008)
Works Cited


Chapter 2: Analysis of the Effect of Nanoparticles on Mold Filling in a Vacuum Assisted Resin Transfer Molding System

1 Introduction

Seeman composite resin infusion molding process (SCRIMP) is a vacuum assisted resin transfer molding (VARTM) technique, for manufacturing large composite parts. It is more cost effective than prepreg/autoclave process and more environmentally friendly than hand lay-up or spray-up processes. Although its origin can be traced back to early 1950s [1], SCRIMP and similar processes were developed primarily in the 1980s. As SCRIMP is used to manufacture very large parts, the manufacturing time is a key factor. Thus, the mold filling time becomes extremely crucial for the applicability and economics of the process. In this context, several related issues of the process, such as resin flow [2–4] and preform compaction [5,6], have been investigated in the past. Detailed permeability and compressibility measurements have been carried out in our laboratory [7–9]. Several numerical and computer simulation methods of flow in VARTM have also been studied [10,11]. All these studies focused on a system consisting of two main components, namely the continuous fiber reinforcement (glass or carbon fibers) and a resin matrix.
This article deals with a new type of hybrid composite consisting of both long fibers and nanofibers as the reinforcing components of the resin matrix. These hybrid composites combine the advantages of both the long fibers and the nanofibers to produce a superior composite. Some property studies have already been done [12–14]. However, there have been no comprehensive mold filling studies of these hybrid composites. The addition of nanofibers drastically changes the flow characteristics of the resin inside the mold. This work studies the mold filling behavior based on this three component system and uses a simplified model to calculate the mold filling time corresponding to nanofiber loading.

2 Experimental

An unsaturated polyester resin (Aropol Q6585, Ashland Chemical) was used in this study. It contains 35 styrene and 65 wt% unsaturated polyester prepolymer. The prepolymer is a step growth polymerization product of 1:1 maleic anhydride and propylene glycol with an average molecular weight of 1560 g/mole. Styrene from Aldrich was used as the cross-linking monomer. All the samples were formulated with extra styrene to provide a ratio of styrene C=C to unsaturated polyester C=C bonds equal to 2. A single component initiator, methyl ethyl ketone peroxide solution (MEKP, Aldrich), was used. Cobalt octate (CoOct, Pfaltz and Bauer) was used as the promoter. The amount of MEKP and CoOct added into the UP resin was 1.5 wt% and 0.5 wt% respectively.
Benzoquinone (BQ, Aldrich) was the inhibitor used to control the curing process. The viscosity of the resin feed mixture is about 0.035 Pa s at 25°C.

The long fiber reinforcement used in this study is a stitched unidirectional glass fiber (GF) mat, QM6408 from Brunswick Technologies. The nanoparticle reinforcement used is Pyrograf®-III carbon nanofiber (CNF, PR19-LHT LD) from Applied Sciences Inc. The CNFs have an average diameter of about 150nm and an average length of 20 µm.

The CNFs were pre-bound onto the GF mats (23x16.5 cm) using a spray process. It involved mixing CNFs and unsaturated polyester prepolymer in a 1:1 ratio and making a 2% solution of this mixture in acetone. This solution was sonicated using a Branson Digital sonifier S-450D for 30 min and then sprayed onto both sides of the GF mats. The GF mats were placed in a fume hood for solvent evaporation until the weight of the fiber mats did not decrease with time. The amount of CNFs on the GF mats was determined by the weight differences of the fiber mats before and after the spraying. SCRIMP was used to impregnate the GF preforms. Three layers of the GF mats were used in each composite sample. They were placed on a glass plate (30.5x30.5 cm) and the inlet and outlet were prepared using standard LDPE tubing along with an extended spiral for letting the resin flow through. The schematic of the system set-up is shown in Figure 20. Mold filling experiments were carried out with 0, 3.5, and 5 wt% CNF loading respectively, at room temperature (all wt% are with respect to the cured composite sample). Flow visualization was done using a digital video camcorder. After mold filling, the samples were cured at
room temperature for 12 h and were post cured in a mechanical convection oven at 150°C for 2 h.

Flexural properties were tested with an Instron 5848 Testing Machine according to ASTM D790-03. The support span of 3-point bending tests was 25.4 mm. Five specimens were tested for each composite sample.

![Figure 20. Schematic of experimental set-up for VARTM](image)

Figure 20. Schematic of experimental set-up for VARTM
2.1 Mold Filling Analysis

Flow in SCRIMP can be modeled as viscous flow through porous media. The thermosetting fluids used in the composite manufacturing are considered as Newtonian fluids, i.e., their viscosity is independent of the velocity of the flow. When the flow rate of the resin is not too high, Darcy’s law holds for the flow through porous media [16]:

\[ Q = \frac{kA\Delta P}{\mu\Delta L} \]  

(1)

where \( Q \) is the volumetric flow rate (m\(^3\)/s), \( \mu \) is the fluid viscosity (Pa·s), \( A \) is the cross sectional area of the composite sample (m\(^2\)), \( \Delta P/\Delta L \) is the pressure drop per unit length (Pa/m), and \( k \) is the permeability of the porous medium (m\(^2\)). The introduction of an additional reinforcing agent may affect the resin viscosity \( \mu \), the reinforcement permeability \( k \), or both these factors. It has been shown that the addition of carbon nanofibers into the resin matrix increases the resin viscosity by several orders of magnitude at low to medium shear rates [17]. Therefore, this increases the mold filling time drastically and may lead to processing problems like premature cure, filtering of nanofibers by long GF mats, resulting in a non-uniform distribution of the nanofibers in the composite and incomplete saturation of the reinforcement.
Figure 21. Composite samples prepared by the pre-mix and pre-bind methods

Figure 21 shows the difference in the composite samples obtained by the pre-mix method and by the pre-bind method. A non-uniform distribution of nanofibers in the composite can be clearly seen in the sample obtained by the pre-mix method. Two hybrid composite samples with equal amounts of nanofibers (3.5% wt) were prepared using the two methods. The one prepared with the pre-mix method took 15 times longer to fill the mold when compared to the sample prepared by the pre-bind method. This difference is because the new pre-bind technique presented in this study mainly affects the permeability of the fiber preform, while the pre-mix method affects the resin viscosity. As the thickness of the GF reinforcement is small in our experiments, the flow can be considered as one-dimensional. For a one-dimensional flow, Equation (2) can be used to calculate the permeability of the GF reinforcement.

\[ t = \frac{\mu \phi}{2k\Delta P} s^2 \quad \ldots \ldots (2) \]
Here, $s$ is the distance from the inlet to the flow front (obtained from observing the flow), $t$ is the corresponding time, and $\phi$ is the porosity of the reinforcement medium, given by Equation (3):

$$\phi = 1 - \frac{n \xi}{d \rho_f} \ldots \ldots (3)$$

where $n$ is the number of reinforcement layers inside the mold (three in this study), $\xi$ is the surface density of the unidirectional GF mat (0.27 kg/m$^2$), $d$ is the thickness of the fiber stack, and $\rho_f$ is the density of the GF (for E-glass, $\rho_f = 2560$ kg/m$^3$). The porosity value turns out to be 0.71 for the stack of three GF mats without CNFs. The porosity value changed as CNFs were sprayed onto the GF mats because the nanofibers occupy the pore gaps in the long GF mats. This in turn affects the permeability and the mold filling time.

Based on Equation (2), the permeability can be calculated by plotting $t$ vs. $s^2$. The slope of the curve is inversely proportional to the permeability of the GF mat. For predicting the changed porosity of the GF mats after spraying CNFs, the following equations are used:

$$\phi = \frac{V_p}{V_t} \ldots \ldots (4)$$

where $V_p$ is the pore volume and $V_t$ is the total volume of the cured composite. $V_p$ is given by

$$V_p = V_t - (V_f + V_{cnf}) \ldots \ldots (5)$$
where $V_f$ is the volume occupied by the GF reinforcement and $V_{cnf}$ is the volume occupied by CNFs.

By simple calculation, the weight increase required after spraying of the GF mats to achieve a particular value of CNF loading can be obtained. This can then be used in Equations (4) and (5) to calculate the porosity. In this way, the porosity value of the reinforcement for a specific CNF loading can be determined. After the permeability of the system is calculated, Equation (2) can be used to determine the mold filling time. The mold filling data was also fit to conventional mold filling models like the simple capillary model and the Kozeny–Carman model [15]. The simple capillary model considers the porous media as a bundle of capillaries and generally takes the form

$$S = \frac{\phi^3}{\tau^2 A_v^2} \ldots \ldots (6)$$

where $S$ is the permeability, $\phi$ is the porosity $\tau$ is the tortuosity, and $A_v$ is the surface area per unit volume. The Kozeny–Carman model is given by:

$$S = \frac{\phi^3}{CA_v^2(1 - \phi)^2} \ldots \ldots (6)$$

where $C$ is a constant. Figure 22 shows the fit of experimental mold filling data fit to these two models.
Figure 3 shows the distribution of pre-bind CNFs on the fiber mats for a 5% CNF loading. Figure 4 shows the plot of flow front length vs. filling time for the samples with various CNF loadings. From the data, it can be seen that there is a significant effect of nanofibers on the mold filling time. While a 0% CNF loading has a filling time of 45 s, the filling time of 3.5% CNF and 5% CNF samples is much longer. This can be attributed to the fact that CNFs fill in the pore gaps within the long fiber mats and reduce the pore volume within the sample. This, in turn, increases the mold filling time as the resin has to flow through smaller gaps.

Figure 5 is a plot of filling time vs. square of flow length, which is used to determine the permeability of the reinforcement. It can be noticed that as the CNF loading increases, the slope of the curve increases. Based on Equation (2), the permeability $k$ and the porosity $\phi$ are the variables for the slope change if the resin viscosity $\mu$ and the pressure difference $\Delta P$ are unchanged in the three experiments. The porosity $\phi$ can be calculated by Equations (4) and (5). By substituting it into Equation (2), the value of permeability can be determined. All results are shown in Table 4. The porosity decreases slightly with the increase of the CNF loading in the samples, but the permeability reduces significantly.

Figure 6 shows the comparison of the calculated and experimental flow front positions for the three experimental samples. It can be seen that for 0% CNF sample,
there is a very good agreement between the calculated and experimental flow front data. On the other hand, we can see that for 3.5 and 5% CNF loading samples, there is a slight difference between the experimental and calculated flow front. The flow front is slightly slower in the experimental data towards the end of the mold (latter stages of mold filling). This can be attributed to the increase of resin viscosity when nanofibers are dispersed in polymer resin during mold filling [17]. As the resin fills the mold, the binder, the UP resin in this study, slowly dissolves in the UP/styrene resin feed and some CNFs diffuse from the GF surface into the resin. This may greatly increase the resin viscosity, and hence the advance of the flow front becomes slower. However, choosing different binders could change this behavior. CNFs will reinforce the whole composite better if they are well dispersed in the resin phase than when they stick to the long GF surface. An optimum choice of binder would ensure constant viscosity of the polymer resin throughout the mold filling process. The binder should dissolve in the resin after the mold filling process to release the nanofibers into the resin phase.
Figure 22. SEM image of 5wt% CNFs pre-binding on GF mat

Figure 23. Comparison of mold filling profile with various CNF contents
Figure 24. Filling time vs. (flow length)$^2$ plots for permeability calculation

<table>
<thead>
<tr>
<th>CNF content (wt%)</th>
<th>0</th>
<th>3.5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability (m$^2$)</td>
<td>$1.42 \times 10^{-10}$</td>
<td>$4.67 \times 10^{-11}$</td>
<td>$1.92 \times 10^{-11}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.710</td>
<td>0.671</td>
<td>0.659</td>
</tr>
</tbody>
</table>

Table 4. Permeability and porosity values of reinforcement with various CNF loadings
Figure 25. Experimental and calculated flow length of various CNF loadings: (a) 0, (b) 3.5, and (c) 5 wt%.
Figure 26. Flexural properties of UP-CNFGF hybrid composites: (a) flexural strength; (b) flexural modulus. (all samples tested in transverse direction to long fiber longitudinal axis)

Figure 27. Mold filling data fit to the simple capillary
Figure 28. Mold filling data fit to the Kozeny-Carman model

Figure 29. SEM images of the cured composite sample: (a) CNFs at the fracture surface of the tested composite sample; (b) glass fiber, CNFs, and resin at the interface of the phases
Though the introduction of nanofibers in the composite system does change the flow characteristics of the resin through the reinforcement, it does not necessitate the need to develop an entirely new set of working models to predict the flow behavior. This is seen from the fact that the mold filling data of this hybrid composite system fits conventional models like the simple capillary model (Figure 27) and the Kozeny Carman model (Figure 9) pretty well.

The flexural properties of 0, 1 and 3.5wt% CNF hybrid composites were measured. All samples with GFs were tested in the transverse direction (90°) in order to reduce the effects of long fibers and emphasize the reinforcement of nanofibers. As shown in Figure 26, the addition of CNFs in UP-GF composites can improve both flexural strength and modulus. For example, the flexural strength and modulus of UP-GF composites increased 66 and 20% with 3.5wt% CNFs respectively. The reason is that CNFs with a high aspect ratio can prevent crack generation and crack propagation in the polymer matrix between long fibers. It can also be seen that the composites manufactured by the pre-bind method have higher flexural strength and modulus when compared with those obtained by the pre-mix method. This can be attributed to the fact that the pre-bind method enables a more uniform distribution of the carbon nanofibers in the composite than the pre-mix method. Figure 29(a) shows the CNFs at the fracture surface of the tested UP/Glass fiber/CNF composite. Energy dissipation by CNF pull out is evident in this micrograph. Figure 29(b) shows the three phases namely, the long glass fiber, CNF and the resin at the interface region. As can be seen, a significant amount of CNFs are
covered by the UP resin, proving our hypothesis that the CNFs pre-bound on the glass fibers will eventually move into the resin phase after the resin infusion. This results in a significant reinforcement of the weak resin phase. The CNFs with a high aspect ratio can prevent crack generation and propagation in the polymer matrix between long fibers.

However, with an even higher increase (e.g., 5 wt%) in the CNF loading (not shown in Figure 26), the flexural properties decrease slightly. This can be due to the formation of carbon nanofiber micro aggregates in various regions of the polymer matrix, which act as areas of weakness. Better nanofiber dispersion and spraying methods are needed for higher particle loading.

4 Conclusions

Mold filling experiments for hybrid long fiber and nanofiber composites were conducted and the effect of the CNF phase on the fill time was studied. The presence of CNFs on the GF mats decreases the porosity and permeability, and thus increases the mold filling time. But this increase is not as substantial as the one when the nanofibers are premixed into the resin instead of being pre-bound onto the reinforcement. A simplified model was used to predict the filling time for 0, 3.5, and 5wt% CNF loading.
References


Chapter 3: Preparation and Properties of Nanoparticles and Long Fibers
Reinforced Thermoset Composites

1. Introduction

Fiber reinforced plastics (FRPs) are the most widely used composites. In general, fibers are the principal load-carrying members, while the surrounding matrix keeps the fibers in the desired location and orientation, acting as a load transfer medium and protecting fibers from environmental damage. Fiber-reinforced composites have low specific gravity, a high strength-to-weight ratio, and a high modulus-to-weight ratio.\(^{[1-2]}\)

Polymer/nanoparticle composites have been extensively studied since the 1990s.\(^{[3-8]}\) Because of the nanoscale dispersion and the high aspect ratios of the nanoparticles, polymer nanocomposites exhibit light weight, dimensional stability, heat and flame resistance, barrier properties, and improved modulus and strength with far less reinforcement loading than conventional composite counterparts.\(^{[9-10]}\)

Although fiber-reinforced plastics have good in-plane mechanical properties that are determined by the long fibers, the properties in the transverse and the thickness directions defined by the characteristics of the matrix resin are much weaker. Under tension, compression, shear, or impact, failure of the polymer matrix may take place.\(^{[2]}\) While
nanoparticles may reinforce the polymer matrix, the loading of nanoparticles in polymer nanocomposites often cannot reach a high level (<10 wt.%) due to the dispersion difficulty. Thus, mechanical properties of polymer nanocomposites are relatively low compared with those of highly loaded FRPs (>50 wt.%).

In this work, we try to combine the advantages of both FRP and polymer nanocomposites to produce a superior composite — long fibers and nanoparticles reinforced polymer composites. Continuous fibers can provide good mechanical properties to the composites, while nanoparticles may strengthen the matrix between the long fibers in order to reduce the matrix failure in the composites and extend the longevity of the composites.

To succeed in producing these new composites, two questions need to be answered: How to well disperse nanoparticles into FRPs? Can the resin processability be maintained with the presence of nanoparticles? Pre-mixing nanoparticles into polymer resins is a common approach to make nanoparticles reinforced polymer-long fiber composites.\textsuperscript{[11-14]} However, well-dispersed nanoparticles may greatly increase the resin viscosity\textsuperscript{[15-16]} and cause difficulties during composite processing. To solve these problems, we designed a new method to pre-bind nanoparticles onto the long fibers instead of mixing them with the polymer resin. Systematic experiments were carried out using these two approaches to compare the nanoparticle dispersion and the composite properties.
Experimental

An unsaturated polyester (UP) resin, Aropol Q6585, provided by Ashland Chemical was used in this study, which contains 35 wt.% styrene and 65 wt.% unsaturated polyester prepolymer. The prepolymer is a step-growth polymerization product of 1:1 maleic anhydride and propylene glycol, with an average molecular weight of 1560 g mole$^{-1}$. Styrene from Aldrich was used as the crosslinking monomer. All of the tested samples were formulated with extra styrene to provide a ratio of styrene C=C double bond to unsaturated polyester C=C double bond equal to 2. A single component initiator, methyl ethyl ketone peroxide solution (MEKP, Aldrich), was used in this study, which contains 32% peroxide. Cobalt octoate (CoOct, Pfaltz & Bauer) was employed as the promoter to decompose the initiator at low temperatures. The amount of MEKP and CoOct added into the UP resin was 1.5 wt.% and 0.5 wt.% respectively. The inhibitor, 300 ppm benzoquinone (BQ, Aldrich), was used to control the curing process.

The carbon nanofiber (CNF) used in this study was Pyrograf®-III (PR19-LHT), which is a type of vapor grown carbon nanofiber from Applied Sciences Inc. The length of CNFs is about 30-100 $\mu$m and the diameter is 100-200 nm.

A stitched unidirectional glass fiber (GF) mat, QM6408 from Brunswick Technologies, was used as the long fiber reinforcement in this study.
For comparison, UP-CNF nanocomposites were prepared. A desired amount of CNFs were added into the UP/styrene solution, and the mixture was sonicated for 1 h. The promoter CoOct, inhibitor BQ, and initiator MEKP were added into the system after ultrasonication. The mixture was degassed in a vacuum chamber for 10 min, and then cured in a silicone rubber mold at room temperature (~25 °C) for 12 h, and post-cured at 150 °C for an additional 2 h.

UP-CNF-GF composites were prepared in two different methods. (1) Pre-mixing approach: The resin mixture was prepared the same way as in UP-CNF nanocomposites. The GF mats were used without further treatment. (2) Pre-binding approach: The neat UP resin was used in this method. The GF mats were treated using the following procedure: 5 g CNFs and 5 g Q6585 prepolymer (binder) were dissolved in 490 g acetone to prepare a 1 wt.% CNF solution. The solution was sonicated for 2 h, and then was sprayed onto both sides of the GF mats. The GF mats were placed in a fume hood for solvent evaporation until the weight of the fiber mats did not decrease with time. The amount of CNFs was determined by the weight difference of the fiber mat before and after spraying.

Vacuum assisted resin transfer molding (VARTM) was used to impregnate the GF preforms, as shown in Figure 30. Three layers of GF mats with pre-bound CNFs were sealed in a vacuum bag. Each layer was 240 mm in length and 160 mm in width. The inlet was inserted into a resin tank, and the outlet was connected to a vacuum pump. Before mold filling, a vacuum was applied to force the bag to press tightly against the fiber stack. The neat UP resin or UP-CNF mixture was degassed in a vacuum chamber
for 10 min, and then was introduced into the fiber preforms. After the mold was fully filled, the inlet and outlet pipes were clamped to maintain the vacuum pressure in the system. The samples were cured at room temperature (≈25 °C) for 12 h, and post-cured at 150 °C for an additional 2 h. The GF content in the composites was controlled at 48-51 wt.%.

Thermal mechanical analysis (TMA) was performed on a TA 2940 thermal mechanical analyzer to measure the glass transition temperature and thermal expansion coefficients. The heating rate was 5 °C/min. For each sample, three specimens were tested.

Flexural properties were tested with an Instron 5848 Testing Machine according to ASTM D790-03. The support span of 3-point bending tests was 25.4 mm. Five specimens were tested for each composite sample.

Scanning electron microscopy (SEM) was carried out on a Hitachi S-4300 scanning electron microscope. The sample was coated with a thin layer of gold.
3 Results and Discussion

Figure 31 shows the flexural properties of UP-CNFR nanocomposites. It is obvious that a small amount of CNFs can improve both flexural strength and modulus of the UP resin. With the addition of 3.5 wt.% CNFs, the flexural strength and modulus increased about 103% and 11%, respectively. This is attributed to the high aspect ratio of the CNFs, which can make the UP resin much stronger. Because the UP resin used in this study is very brittle, the improvement of flexural modulus is not as great as that of flexural strength.

The thermal properties of UP-CNFR nanocomposites were also improved. As shown in Table 5, the glass transition temperature ($T_g$) of the UP resin rose and the thermal expansion coefficients declined with the increase of the CNF content in the composites. Well-dispersed CNFs have a large surface area and strong interactions with polymer molecules, which may restrict the movement of polymer chains and lead to higher transition temperatures and lower thermal expansion coefficients.

In Figure 32, the appearances of 3.5 wt.% CNF pre-mixing and pre-binding samples are shown respectively. For the CNF pre-mixing sample in Figure 32(a), it was found that CNFs concentrated near the resin inlet, and very few could reach the outlet because of the filter effect of the GF mats. The CNFs also increased the resin viscosity obviously and caused the slow flow during the mold filling, which may result in more CNFs to be filtered out. On the other hand, our new approach can avoid such drawbacks. First, the pre-bound CNFs did not cause any viscosity increase of the UP resin. Second, when the
UP resin flowed into the mold, the binder would dissolve and the pre-bound CNFs could release into the resin gradually. This does not require the CNFs to flow through the fiber mats from the inlet to the outlet, and thus prevents the CNFs from being filtered. Moreover, CNFs are hydrophobic particles because of their surface characteristics. After the binder dissolves, the pre-bound CNFs prefer to diffuse from the hydrophilic GF surface to the hydrophobic polymer resin. Therefore, the CNF pre-binding sample shown in Figure 32(b) indicates a uniform distribution of CNFs. The SEM picture of pre-bound CNFs on the GF mat is shown in Figure 33.

The flexural properties of UP-CNFGF composites prepared by both methods are compared in Figure 34. All samples with GFs were tested in the transverse direction (90°) in order to reduce the effects of long fibers and emphasize the reinforcement of nanofibers. For 1.0 wt.% and 3.5 wt.% CNF samples, the flexural properties of the CNF pre-mixing samples are much lower than those of the CNF pre-binding composites, essentially the same as the sample without any CNFs. This is due to the filter effect of long fibers, which cause very few nanoparticles in the composite samples. For the CNF pre-binding samples, the improvement of flexural properties results from the reinforcement of the UP matrix with nanoparticles. The CNFs with a high aspect ratio can prevent crack generation and crack propagation in the polymer matrix between long fibers.
Table 5. Thermal properties of UP-CNF Nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>$\alpha_1$ (μm/m°C) (50-125 °C, below Tg)</th>
<th>$\alpha_2$ (μm/m°C) (175-250 °C, above Tg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP Resin</td>
<td>140.0 ± 3.7</td>
<td>98.0 ± 0.8</td>
<td>153.8 ± 2.6</td>
</tr>
<tr>
<td>UP + 1.5 wt.% CNF</td>
<td>148.2 ± 0.7</td>
<td>93.9 ± 0.9</td>
<td>152.4 ± 1.0</td>
</tr>
<tr>
<td>UP + 3.5 wt.% CNF</td>
<td>151.6 ± 7.0</td>
<td>90.0 ± 1.1</td>
<td>150.3 ± 4.7</td>
</tr>
</tbody>
</table>

Figure 30. Schematic of experimental set-up for VARTM
Figure 31. Flexural properties of UP-CNF nanocomposites: (a) flexural strength; (b) flexural modulus

Figure 32. Pictures of UP-CNF-GF hybrid composites: (a) 3.5 wt% CNF pre-mixing sample; (b) 3.5 wt% CNF pre-binding sample (resin flow is left to right)
Figure 33. SEM image of CNFs pre-bonded on glass fibers
4 Conclusions

CNF reinforced UP and UP-GF composites have been prepared. The addition of CNFs can improve both thermal and mechanical properties of the UP resin. Compared with the pre-mixing approach, our new pre-binding method can reduce the filter effect of long fibers on CNFs and prepare the composites with better distribution of nanoparticles, resulting in better mechanical properties. This study also proves that the incorporation of nanoparticles into the polymer matrix is a promising way to improve the properties of FRPs in the transverse and/or thickness direction.

References


Chapter 4: Improving the Thermal Conductivity of Epoxy Hybrid nanocomposites for Aerospace Applications

1 Introduction

Thermal management of aerospace structures is very important for many applications including space platforms, re entry vehicles, propulsion systems, electronics, and high energy systems. Thermal conductivity is also increasingly desired in specific parts of the airplane fuselage and engine. Next generation aerospace structures could potentially use more thermally conductive materials to judiciously direct heat flow in satellites, thermal protection systems, near-propulsion structures, electronic boxes, directed energy systems, radiators and their accompanying thermal interfaces[1]. The inherent poor thermal conductivity of polymer composites, which are the most widely used materials in aerospace structures due to their high strength to weight ratio is a significant drawback in such kind of applications. Several studies have been done to study mechanisms of improving thermal conductivity of polymers by using various micro and nanoparticulate fillers[2-5]. Current thermally conductive polymeric materials use particles like silver, alumina or silica which require 50-70 vol% of filler to achieve reasonable thermal conductivity values. A number of nanomaterials have been explored as candidates for improving the thermal conductivity of polymer composites and carbon
nanotubes (CNTs) have emerged as an efficient filler due to their excellent thermal conductivity (~3000 W/m-K along the tube axis) and high aspect ratio[6, 7]. However, the exorbitant cost of CNTs is prohibitive for large scale applications, even in the aerospace industry.

In the present work, it is shown that Carbon nanofibers (CNFs) which are much cheaper, compared to CNTs can be used as effective thermal conductive reinforcement to significantly increase the thermal conductivity of an epoxy matrix. Other types of nanoparticles like silver oxide, MWNTs and synthetic diamond were also studied for their effectiveness in increasing the thermal transport properties of the epoxy/carbon fiber composites.

1.1 Thermal Conductivity

It is defined as the quantity of heat, $Q$, transmitted in time $t$ through a thickness $L$, in a direction normal to a surface of area $A$, due to a temperature difference $\Delta T$, under steady state conditions and when the heat transfer is dependent only on the temperature gradient, i.e. thermal conductivity = heat flow rate $\times$ distance / (area $\times$ temperature difference)

$$k = \frac{Q}{t} \times \frac{L}{A \times \Delta T}$$
1.2 Thermal Resistance

The R value of a material is the inverse of the thermal conductivity (k) multiplied by the thickness (d) of the insulator. The SI units of resistance value are K·m²/W)

\[ R = \frac{d}{k} \]

Conductance is defined as the inverse of Resistance. It gives the true conductive property of a material, irrespective of its thickness. As the thickness of the samples is not an accurately controlled variable in a soft molding process like SCRIMP, conductance was used to compare the various conductivity results.

2 Experimental

EPON 862, an aerospace epoxy resin obtained from Hexion was used as the polymer matrix. Unidirectional carbon fiber mats were used as the continuous fiber reinforcement. Carbon nanofibers (PR 19 LHT LD and PR 24 LHT HHT), obtained from Applied Sciences Inc, Multiwalled Carbon nanotubes (MWNTs), Silver oxide from Fisher and synthetic diamond obtained from Diamond Innovations Inc were used as the thermally conductive reinforcing agents. The Epoxy/carbon fiber/nanoparticle composites were prepared in the following way: A 1 wt% nanoparticle-Acetone mixture was
prepared and ultrasonicated using a Branson digital sonifier at an amplitude of 50% for about 45 minutes. This helped in the dispersion of the nanoparticles, which otherwise form aggregates. The sonicated mixture was sprayed onto the carbon fiber mats (3’ x 4’) using an air compressor based sprayer. The resultant structure of the particles on the fiber mats was investigated using a Scanning Electron microscope (SEM).

The sprayed fiber mats (7 mats per each composite sample) were placed in the mold and vacuum assisted resin transfer molding of EPON 862 was carried out. The mold was maintained at a temperature of 70 degrees centigrade in order to reduce the viscosity of the epoxy resin and make the mold filling easier. Some pictures of the SCRIMP mold and the composite samples in the mold are shown in Figure 35. Once the epoxy resin saturated the reinforcement completely, the samples were cured at a temperature of 70 degrees centigrade for about 12 hours and then post cured in a convection oven at 121 degrees centigrade for 1 hour and 177 degrees centigrade for two and a half hours. Then, the samples were de-molded, and their thermal conductivity was measured using a Lasercomp parallel plate heat flow meter.

3 Results and Discussion

The results clearly showed that adding carbon nanofibers improved the thermal conductivity of the composite. There was a threshold limit above which there was a significant increase in the thermal conductivity. Adding 3.6% by volume of non heat
treated carbon nanofibers produced a significant increase (77%) in the $k$ value of the composite, but the actual conductance did not increase much because of the increase in the sample thickness. Adding about 4.5% of carbon nanofibers by volume increased the $k$ value by about 110% and the actual conductance value by about 24%. On the other hand, the addition of silver oxide particles did not provide much improvement in the thermal conductivity of the composite.

Silver oxide by itself is highly conductive thermally, but the addition of silver oxide to the composite did not help in increasing the thermal conductivity of the composite. This can be explained from the SEM micrograph of silver oxide on carbon fiber mats (Figure 40(b)). There is no continuous contact between the silver oxide particles and the polymer filled in the gaps between the particles acted as an insulator. The addition of silver oxide particles created more void spaces in between the long fiber mats, which in turn resulted in more polymer being filled in the composite sample. This explains why the conductivity of this sample is even lower than that of the pure composite sample. However, the composite sample having a combination of silver oxide and carbon nanofibers showed a 49% increase in the $k$ value and a 6% increase in the actual heat conductance value. The carbon nanofibers act as bridges between individual silver oxide particles and therefore increase the overall conductivity in this case. The results are shown in Figures 36(a) and 36(b).

The improvement in thermal conductivity of the composites containing untreated CNF and silver oxide was promising, but not high enough. Highly Heat treated carbon nanofibers (PR 24 LHT HHT) were used as the nano reinforcement in our next series of
experiments and this improved the thermal conductivity of the epoxy/carbon fiber composite significantly. These nanofibers are heat treated at 1800 degrees centigrade under inert atmosphere. Figures 37(a) and 37(b) show the results obtained using HHT carbon nanofibers. A sample containing 4.0 wt% of the HHT CNFs had a 200% increase in the thermal conductivity value k, while a sample with about 7.6 wt% of the HHT CNFs had a 272% increase in the thermal conductivity. There was a 237% increase in the actual heat conductance of both the samples. This can be explained by the fact that the sample containing the higher content of CNFs was also slightly thicker. This difference is due to the fact that vacuum de-bulking used in SCRIMP (soft mold process), cannot control the thickness accurately. Figures 38(a) and 38(b) show the effect of synthetic diamond (particle size ~ 0.1-0.2 micron) on the thermal conductivity of the composite. A 143% increase in the thermal conductivity k was noted when the sample had about 12.6 wt% of synthetic diamond particles. A sample containing a mixture of diamond and HHT CNFs (4.0 wt% diamond + 4.0 wt% HHT CNF) showed a 166% increase in the thermal conductivity. This is because the relatively long nanofibers (about 20 microns in length) act as bridges between individual diamond particles and thus improve the overall conductivity. The improvement in the actual heat conductance of both the samples was around 124%. The sample containing the mixture of diamond and CNF was slightly thicker than the sample containing only diamond. Therefore, even though it had a higher thermal conductivity value, it had about the same heat conductance.

The increase in thickness of the composite samples was a major hurdle faced in this study. We have designed a hardened steel mold for making samples for thermal
conductivity studies in the future in order to maintain uniform thickness. This will be used in future work. A temporary solution to the problem was used in the present work. A couple of steel plates were used to apply pressure on the samples in order to prevent increase in thickness. Two flat steel plates were used to apply high clamping pressure on the fiber mats and the SCRIMP process was carried out according to the usual procedure. Three types of nanoparticles were used, namely, HHT CNFs, nanographite, and MWNTs.

The improvement in the thermal conductivity was promising, but not as dramatic as expected. A comprehensive result chart for all the carbon nanoparticles is shown in Figure 40. All the nanoparticle loadings here are represented in wt %. This is calculated as the amount of nanoparticles in the composite in grams/total weight of the cured composite in grams. In both the figures, the last 3 bars are the results obtained with the improvised pressure de-bulking.
Figure 35. SCRIMP setup for Epoxy resin – Three carbon fiber/epoxy composite panels being prepared simultaneously.
Figure 36. (a) Effect of carbon nanofibers and silver oxide on the thermal conductivity of epoxy/carbon fiber composites. (b) Effect of carbon nanofibers and silver oxide on the conductance of epoxy/carbon fiber composites
Figure 37. (a) Effect of heat treated carbon nanofibers on the thermal conductivity of epoxy/carbon fiber composites. (b) Effect of heat treated carbon nanofibers on the conductance of epoxy/carbon fiber composites.
Figure 38. (a) Effect of synthetic diamond and heat treated carbon nanofibers on the thermal conductivity of epoxy/carbon fiber composites (b) Effect of synthetic diamond and heat treated carbon nanofibers on the conductance of epoxy/carbon fiber composites.
Figure 39. (a) SEM of heat treated carbon nanofibers on continuous carbon fiber (b) SEM of Silver oxide particles on continuous carbon fiber mats
Figure 40. Effect of various carbon based nanoparticles on the conductivity and conductance of epoxy/carbon fiber composites
Figure 40. Continued

![Graph showing actual heat conductance](image)

- Pure sample
- 4 wt% MWNT
- 9 wt% MWNT
- HHT CNF 4.0 wt%
- HHT CNF 7.6 wt%
- 5.7 wt% HHT CNF
- 7.9 wt% nanographite
- 6.5 wt% MWNT

(b)
4 Conclusions

It was concluded that adding heat treated CNFs to the composite increases the thermal conductivity of the composite significantly. Adding synthetic diamond also improves the thermal conductivity significantly, apart from the fact that diamond can bring in additional functionality like tremendous wear resistance to the composite. However, adding the relatively large silver oxide powder doesn’t provide any significant improvement at all. Overall, HHT CNFs and MWNTs were found to be the most effective reinforcement for improving the overall heat conductance. Surface modification of the carbon nanofibers to make them even more polymer compatible and attachable to other thermally conductive particles will be studied. Vacuum de-bulking that takes place during SCRIMP is responsible for the higher thickness of samples with higher loading of nanoparticles. This in turn reduces the overall heat conductance. A temporary solution was sought to maintain the thickness of the samples during the SCRIMP process. This yielded good results, but not a very dramatic improvement. Therefore high pressure compression de-bulking in the new rigid mold will be done in the future to maintain the thickness. This is expected to increase the overall heat conductance significantly.
References


Chapter 5: Novel Methods of Incorporating Nanoparticles into Fiber Preforms

Introduction

Although fiber-reinforced plastics have good in-plane mechanical properties that are determined by the fiber reinforcement, the properties in the transverse direction defined by the characteristics of the matrix resin are much weaker. Under tension, compression, shear, or impact, failure of the polymer matrix may take place.\[2\] While nanoparticles may reinforce the polymer matrix, the loading of nanoparticles in polymer nanocomposites often cannot reach a high level (<10 wt.% due to the dispersion difficulty. Thus, mechanical properties of polymer nanocomposites are relatively low compared with those of highly loaded FRPs (>50 wt.%).

In this work, it is the goal to combine the advantages of both FRP and polymer nanocomposites to produce a superior composite: long fibers and nanoparticle reinforced polymer composites. Continuous fibers can provide good mechanical properties to the composites, while nanoparticles may strengthen the matrix between the long fibers in order to reduce the matrix failure in the composites and extend the longevity of the composites.
To succeed in producing these new composites, two questions need to be answered: How to well disperse nanoparticles into the FRP? Can the resin processability be maintained with the presence of nanoparticles? Pre-mixing nanoparticles into polymer resins is a common approach to make nanoparticles reinforced polymer-long fiber composites.\cite{11-14} However, well-dispersed nanoparticles may greatly increase the resin viscosity\cite{15-16} and cause difficulties during composite processing. To solve these problems, a new method to pre-bind nanoparticles onto the long fibers was designed instead of pre-mixing them with the polymer resin. Systematic experiments were carried out using these two approaches to compare the nanoparticle dispersion and the composite properties.

2 Experimental

The composite panels were prepared using two different methods. (1) Nanoparticle deposition via spray gun: The GF mats were treated with a solution of CNF dispersed to a 0.2% by weight ratio in acetone; the solution was sonicated for 30 min, and then sprayed onto both sides of each GF mat. The GF mats were then placed in a fume hood for solvent evaporation until the weight of the fiber mats did not decrease with time. The amount of CNF was determined by the weight difference of the GF mat before and after spraying. (2) Nanoparticle incorporation via cross-flow assisted spraying: The GF mats were prepared in the same manner as method (1), with the addition of an apparatus that forced a cross-flow of air through the fiber mats in the direction of the sprayed
solution, aiding in the incorporation of the CNF into the GF mat itself, as shown in Figure 41. Samples were prepared using different surface areas to control the rate of airflow per unit area to optimize the incorporation of CNF as observed in Table 6.

Vacuum assisted resin transfer molding (VARTM) was used to impregnate the GF performs, as shown in Figure 42. Seven layers of GF mats with pre-incorporated CNF were sealed in a vacuum bag. The inlet tube was clamped and the outlet tube was connected to a resin trap which was connected to a vacuum pump. Before mold filling, a vacuum was applied to evacuate the mold and achieve a vacuum pressure of 30 mm Hg. The VE resin was degassed in a vacuum chamber for 10 min, and then was introduced into the fiber performs. After the mold was fully filled, the inlet and outlet pipes were clamped to maintain vacuum pressure in the mold. All samples were cured at room temperature (~25°C) for 12 hr, and post-cured at 100 °C for an additional 2.5 hr.

Flexural properties were measured using an Instron 5581 Testing System according to ASTM D790-03. The support span for the 3-point bending tests was 50.8 mm. For each sample, a minim of 6 specimens were tested.

Scanning electron microscopy (SEM) was carried out on a Hitachi s-4300 model SEM. The samples prepared for SEM were coated with a thin layer of gold to achieve a high image resolution.
2.1 Materials

A Vinyl Ester (VE) resin, DERAKANE 601-200, provided by Ashland Chemical. Cobalt Naphthenate (1 %) was used as the promoter. Diethyl Acetoacetamide (DEAA) was used as the accelerator. 2-4-Pentanedione (2,4-P) was used as the retarder. t-Butyl Catechol (TBC) was used as the inhibitor. Methyl Ethyl Ketone Peroxide (MEKP) was used as the initiator under the trade name Norac HDP. The nanoparticle selected for this study was carbon nanofiber (CNF) Pyrograf®-III (PR 24-XT-LHT-OX). This particular nanoparticle is a type of vapor grown CNF from Applied Sciences Inc. The length of the CNF is in the range of 15 to 20 μm, with an average diameter of 150 nm.

The long fiber reinforcement used is a stitched ±45° glass fiber (GF) mat, named WindStrand™, a high performance reinforcement designed for wind energy applications produced by Owens Corning. The specific GF reinforcement used has a fiber diameter of 12 μm and has a bulk density of 2.567 gr/cm³.
Figure 41. Schematic representation of cross-flow assisted spraying

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dimensions (in)</th>
<th>Sprayed Side(s)</th>
<th>CNF (% Loading)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4x4</td>
<td>Single</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>5x5</td>
<td>Single</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>6x6</td>
<td>Single</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>8.5x7.5</td>
<td>Single</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>7x7</td>
<td>Double</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 6. Specifics for cross-flow assisted spraying samples
3 Results and Discussion

Referring to Figure 43 and Figure 44, it can be observed that there is a significant difference amongst the flexural strength values for the two different methods. The tendency of the flexural strength improvement between the two different methods is actually opposite from each other as observed in Figure 45 and Figure 46. This opposite tendency can actually be explained due to the fundamental difference between the two methods: method (1) deposits a layer of CNF that accumulates to form an interwoven spider-web like structure on the surface of the fiber perform, causing individual CNF to
stay lodged within the network, sometimes creating micro aggregates, and preventing them from reinforcing the polymer matrix, resulting in a resin rich area that consequently reduces the composite’s overall strength. Method (2), on the other hand, incorporates the CNF into the fiber perform itself, without causing an increase in thickness to the fiber perform, as the individual CNF are rapidly forced into the GF upon contact, preventing the formation of an interweaved network.

In order to interpret the results in Figures 43, 44, 45 and 46, it is important to mention that mechanical property reinforcement by the CNF is a function of dispersion; therefore it is important to analyze the dispersion of the CNF not just on the fiber perform, but most importantly in the actual post-cured composite. The location of the dispersed CNF is also a crucial factor in determining the degree of mechanical reinforcement, as the target area for reinforcement is the polymer matrix between GF tows. As can be observed in Figure 47, Figure 48 and Figure 49, the pure VE sample is used for comparison to the samples prepared by method (1), which can be observed in Figure 50, and method (2), which can be observed in Figure 51.

The pure VE sample displays good adhesion between the polymer matrix and the GF reinforcement, giving it high mechanical properties as is.

The sample prepared by method (1) does not display much presence of CNF amongst the polymer matrix; therefore the CNF might have formed micro-aggregates which would explain the decrease in flexural strength.
The samples prepared by method (2) display excellent presence of CNF both inside and around the GF tow as well as in the polymer matrix, evidence of proper dispersion.

Figure 43. Flexural strength of the composite samples
Figure 44. Flexural strength improvement of the composite samples
Figure 45. Flexural modulus of the composite samples
Figure 46. Flexural modulus improvement of the composite samples
Figure 47. SEM image of the Pure VE sample cross-section (50 µm scale bar)

Figure 48. SEM image of the Pure VE sample cross-section (10 µm scale bar)
Figure 49. SEM image of the Pure VE sample cross-section (5 µm scale bar)

Figure 50. SEM image of a method (1) sample cross-section (5 µm scale bar)
CNF reinforced GF-VE composites have been prepared. Two methods of incorporating nanoparticles into the GF-VE composites are described. The resulting incorporation of nanoparticles is discussed with the help of electron microscopy. Method (2) has been proven to achieve good mechanical property improvements of the VE-GF composite.
References


Chapter 6: Conclusions and Future Work

6.1 Conclusion

Mold filling experiments for hybrid long fiber and nanofiber composites were conducted and the effect of the CNF phase on the fill time was studied. The presence of CNFs on the GF mats decreases the porosity and permeability, and thus increases the mold filling time. But this increase is not as substantial as the one when the nanofibers are premixed into the resin instead of being pre-bound onto the reinforcement. A simplified model was used to predict the filling time for 0, 3.5, and 5wt% CNF loading.

CNF reinforced UP and UP-GF composites have been prepared. The addition of CNFs can improve both thermal and mechanical properties of the UP resin. Compared with the pre-mixing approach, our new pre-binding method can reduce the filter effect of long fibers on CNFs and prepare the composites with better distribution of nanoparticles, resulting in better mechanical properties. This study also proves that the incorporation of nanoparticles into the polymer matrix is a promising way to improve the properties of FRPs in the transverse and/or thickness direction.
It was concluded that adding heat treated CNFs to the composite increases the thermal conductivity of the composite significantly. Adding synthetic diamond also improves the thermal conductivity significantly, apart from the fact that diamond can bring in additional functionality like tremendous wear resistance to the composite. However, adding the relatively large silver oxide powder doesn’t provide any significant improvement at all. Overall, HHT CNFs and MWNTs were found to be the most effective reinforcement for improving the overall heat conductance. Surface modification of the carbon nanofibers to make them even more polymer compatible and attachable to other thermally conductive particles will be studied. Vacuum de-bulking that takes place during SCRIMP is responsible for the higher thickness of samples with higher loading of nanoparticles. This in turn reduces the overall heat conductance. A temporary solution was sought to maintain the thickness of the samples during the SCRIMP process. This yielded good results, but not a very dramatic improvement. Therefore high pressure compression de-bulking in the new rigid mold will be done in the future to maintain the thickness. This is expected to increase the overall heat conductance significantly.

CNF reinforced GF-VE composites have been prepared. Two methods of incorporating nanoparticles into the GF-VE composites are described. The resulting incorporation of nanoparticles is discussed with the help of electron microscopy. Method (2) has been proven to achieve good mechanical property improvements of the VE-GF composite.
6.2 Future Work

It is planned to further investigate surface modification of nanoparticles in order to further improve the physical properties of fiber reinforced polymer nanocomposites. A continuous process is to be developed and studied. With a continuous nanoparticle incorporation set-up, a relationship will be developed between processing parameters and relative improvement in mechanical properties.

Multifunctional nanoparticle films will be studied as an option of nanoparticle incorporation into composite materials. Optimal processing for the films will be investigated. These nanoparticle films will be developed to increase mechanical properties, thermal conductivity, electrical conductivity, as well as abrasion resistance. Other desired properties as EMI shielding will also be investigated.

Overall mechanical performance of the composite materials will be studied at elevated temperature to determine the temperature dependant improvement of nanoparticles on these materials.
Bibliography


110


