ANALYSIS OF WETTING, FLOW AND END-USE PROPERTIES OF RESIN TRANSFER MOLDED NANOREINFORCED EPOXY-GLASS FIBER HYBRID COMPOSITES

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> > Ayça Ertekin

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ANALYSIS OF WETTING, FLOW AND END-USE PROPERTIES OF RESIN TRANSFER MOLDED NANOREINFORCED EPOXY-GLASS FIBER HYBRID COMPOSITES

Ayça Ertekin

Dissertation

Approved:

Accepted:

Advisor Dr. Sadhan C. Jana

Advisor Dr. Lloyd A. Goettler

Committee Member Dr. Kevin Cavicchi

Committee Member Dr. Richard R. Thomas

Committee Member Dr. Zhenhai Xia

Committee Member Dr. Wieslaw K. Binienda Department Chair Dr. Sadhan C. Jana

Dean of the College Dr. Stephen Cheng

Dean of the Graduate School Dr. George R. Newkome

Date

ABSTRACT

In this research, the usage of single wall carbon nanotubes (SWNTs) and nanoclays in the resin transfer molding (RTM) of biaxially stitched micro-fiber reinforced epoxy matrix composites was investigated to evaluate the role of nanoscale reinforcements on the wetting, flow and end-properties of composites through multi-scale effects. The study primarily focused on characterization of the state of dispersion and curing of nanoscale reinforced epoxy polymers, assessment of the relative importance of viscous forces over interfacial forces and the wettability of glass fabrics by the nanoscale reinforced epoxy polymers, analysis of complex flow of nanoreinforced epoxy systems through glass fiber porous media by several flow properties and evaluation of the properties of hybrid epoxyglass fiber composites enriched with nanoscale particles.

The presence of nanoreinforcements retarded the cure kinetics to some degree such that the activation energies increased with the nanoreinforcement content. Both the unsteady-state and steady-state relative tow permeabilities were observed to decrease as the nanoclay amount was increased. The presence of nanoclay was observed to reduce the *"tow wet-out"* with almost 50 % reduction in the steady-state tow permeability with the addition of 4 wt % nanoclay to the reactive epoxy. Contact angle measurements

indicated, approximately 21 % increase in the contact angle with the addition of 4 wt % nanoclay to epoxy.

It was found that beyond 0.3 wt % SWNT, RTM of epoxy-60 % biaxially stitchedglass fiber systems was not feasible. It was also observed that an addition of SWNT at only 10 % the level of nanoclay caused almost a 25 % increase in steady-state pressure level along with almost an 18 % decrease in permeability. It is believed that nanoreinforcements affected flow rate somewhat differently along the various fabric capillary paths and thereby leading to preferential flow paths in the mold cavity. It is proposed that nanoparticles, particularly at high weight percentages, agglomerate during flow inside the mold cavity and block some intra-tow regions and lead to instabilities in the flow resulting in anomalous pressure differentials at different regions of the flow and unusual permeability results.

While the use of nanoreinforcements reduced oxygen and moisture transport along with thermal expansion coefficient, the mechanical properties were found to decrease due to the several defects, such as voids and agglomerates introduced during RTM as a result of the differential micro- and macro-flows.

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CHAPTER I

INTRODUCTION

In this era of explosive advances in technology, there is a continuous demand for new, easy to manufacture and low-cost materials, meeting increasingly stringent conditions, as a result of the growth of economic and industrial activities. Recent progress in the field of nanotechnology has increased curiosity in novel composites reinforced with nanosized particles. These novel composites, called nanocomposites, have been found to exhibit markedly improved mechanical, thermal, optical and physicochemical properties as compared to the pristine polymers or conventional (microscale) composites. Such exciting features of nanocomposites include increased moduli, strength and heat resistance, decreased gas permeability and improved flammability. While most of the work to date in the literature has focused on nanocomposite synthesis and property evaluation, a full realization of these advantages critically relies on good dispersion of nanosized particles in the polymer, which is still one of the most important and not fully resolved issues in the manufacturing of nanocomposites.

Depending on how many dimensions of the dispersed particles are in the nanometer range, nanocomposites could be in various forms of which only two; *nanoclays* and

carbon nanotubes, were used in this study. The latter have been reported to possess remarkable thermal and electrical properties, exceptional stiffness and strength, extraordinary resilience and low density in many studies. As a result of their high aspect ratio, combined with high specific stiffness and strength, carbon nanotubes are also indicated as one of the most ideal candidates for reinforcing composites in many advanced technology applications, such as computing and data storage technology, electronics devices, sensors, nanoelectromechanical systems and tips in scanning probe microscopy for imaging.

As dispersion of nano-reinforcements is one of the key issues in the production of successful nanocomposite parts, the dispersions of nanoclay and nanotube reinforcements in epoxy polymers were assessed in the first stage of this research based on the interpretation of rheological, thermal, X-ray diffraction, and morphological characterizations of mixtures, cured under different conditions.

In the light of the results obtained from these dispersion studies, a novel combination of two different scale composites were next implemented in this research. For this purpose, *nanometer length scale* single walled carbon-nanotubes and nanoclays were combined with a *micro scale* (μ m) glass fibers via a conventional liquid composite molding (LCM) technique, resin transfer molding (RTM) to seek *synergistic* effects of nanoparticles on the polymeric flow and on the final properties of the hybrid composites. LCM processes, such as RTM, require the impregnation of a polymeric resin through a porous preform, generally composed of carbon, glass or Kevlar fibers. A curing reaction

is initiated usually after complete filling of the mold cavity. The finished product can then be removed from the mold. During the past two decades, numerous studies have been conducted on several aspects of RTM ranging from prediction and measurement of permeability, optimization of heat transfer, cure and analysis of mold filling to void formation. Currently, many research studies on RTM deal with the development of process models for computational simulation of the process. Traditionally, the LCM literature primarily focuses on single-scale micro-fibrous materials as reinforcing components. This research was initiated to fill a need in the LCM on the flow and enduse properties of multiscale polymer composites.

Unlike conventional RTM studies, analysis of flow through porous media in this proposed research required the flow, cure and surface wetting properties of *nanoparticle modified polymeric systems* as inputs to the RTM conducted under different processing conditions. The role of nanoparticles on the analysis of wet-out, flow and the final properties of the resultant multiscale polymer composites were primarily investigated in this study.

CHAPTER II

LITERATURE SURVEY

2.1 Layered Silicates

The silicates are one of the most attractive and complex classes of inorganic minerals. They belong to the general family of 2:1 layered silicates, also known as phyllosilicates. Their crystal structure is composed of layers, made up of two silica tetrahedra fused to an edge-shared octahedral sheet of either magnesia or alumina. Stacking up of the layers results in a regular van der Waals gap between the layers, named as interlayer or gallery. Isomorphic substitution within the layers generates negative charges that are normally counterbalanced by cations residing in the interlayer.¹⁻⁷

The most well known members of the phyllosilicates are clays, in which montmorillonite, hectorite, and saponite are the most commonly used layered silicates. The montmorillonite structure is given in Fig. 1^8 and its chemical formula is shown in Table 2.1.¹

Table 2.1 Chemical structure ^a of commonly used 2:1 phyllosilicates.¹

2:1 Phyllosilicate	General Formula
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$

^aM=Monovalent Cation; x=degree of isomorphous substitution (between 0.5 and 1.3)

Clays are generally formed as a result of four geological processes that are actually water-rock interaction processes: weathering; precipitation from concentrated solutions; burial diagenesis (chemical/thermal change) and hydrothermal alteration. Clays can be categorized by their swelling properties. The ones that can swell by absorbing water or other polar ions into their structure are named as smectites or "swelling clays". The others that cannot are called "non swelling clays". These concepts are reported in the literature. ⁹ Among many types of swelling clays, montmorillonite is one of the cheapest and most widely used layered silicate in polymeric nanocomposite systems. This is why it deserves special attention.

Montmorillonite is a crystalline, 2:1 layered clay mineral, a single layer of aluminum octahedral sheet sandwiched between two layers of silicon tetrahedral sheets, as shown in Figure 2.1.



Figure 2.1 Structure of 2:1 phyllosilicate Montmorillonite⁸

The surface area of the clay sheets is in the range of $750\text{-m}^2/\text{g}$. The thickness of silicate layers is generally around 1 nm while the lateral dimensions of the layers can range up to several microns. Hence, the aspect ratio of the layered silicates (ratio of length/thickness) is particularly high with values greater than 1000. The height of the gallery is generally reported, as 3-5 Å¹. Isomorphic substitution of Al³⁺ by Mg²⁺ and Fe²⁺ is very common in the octahedral aluminum layer, leading to a charge deficiency on the sheet surface. These negative charges are counterbalanced by alkali or alkaline earth cations located in the interlayer. In the nanotechnology nomenclature, the clay is generally characterized by a moderate negative surface charge, known as the cation exchange capacity, CEC and expressed in meq/100 g.

Table 2.2 Characteristic Features of Montmorillonite.¹⁻⁷

Physical Characteristics					
Transparency: translucent crystals and opaque masses					
Color: White, pink or gray with tints of green or yellow					
✤ Luster: Dull					
Classification					
• Chemistry: (Na, Ca)(Al, Mg) $_6(Si_4O_{10}) _3(OH) _6-nH_2O$					
 Class: Silicates 					
 Subclass: Phyllosilicates (sheets) 					
Group: the Clays and also the Montmorillonite/Smectite					
Crystallography					
 Crystal system: Monoclinic 					
Cell Dimensions: a: 5.17, b: 8.94 c: 9.95 Å					
Axial ratios: a: b: c: = 0.5782:1:1.1129					
◆ Crystal Habits: almost never observed in large individual					
crystals, generally found in compact lamellar masses					
Interactions					
 Ionic Interaction: Physical bonding 					
 Physical Interaction: Van der Waals 					
Not much covalent bonding with OH					
Mechanical Characteristics					
 Cleavage: Perfect in one direction, basal; not seen 					
in massive specimens					
 Hardness: 1-2 (can sometimes leave marks on paper) 					
Specific Gravity: 2.3-3					

The charge of layers is not locally constant but it varies from layer to layer. Hence, CEC must rather be considered as an average value over the whole crystal. The most significant characteristic features of Montmorillonite are also provided in Table 2.2. The intercalation of small molecules such as water between the layers is easy as the forces that hold the stacks are relatively weak.⁹ This is the most outstanding physical feature of this material. Clay's capability to swell and exchange its cations is actually very valuable especially in the case of polymer nanocomposite systems. This feature provides an opportunity for making the hydrophilic phyllosilicates more organophilic via the exchange of hydrated cations of the interlayer with cationic surfactants, such as alkylphosphonium or alkylammonium (onium) thus lowering the surface energy of clays and making them compatible with organic polymers. This phenomenon will be discussed in the next section.

2.2 Polymer Layered Silicate (PLS) Nanocomposites

In this section, the structure, synthesis, dynamic and static mechanical, thermal, and barrier properties of PLS nanocomposites will be summarized.

2.2.1. Structure of Polymer Layered Silicate Nanocomposites

Several review articles^{1-7, 10} in the PLS research have reported that three basic types of PLS nanocomposite structures can be obtained depending on the method of preparation and the nature of components (i.e., type of layered silicate, type of organic cations and type of polymer matrix) employed. These idealized structures are illustrated in Figure 2.2.

When a polymer is unable to intercalate between the silicate sheets, phase-separated composites, called *microcomposites*, are obtained. If a single or more than one extended polymer chain is intercalated between the silicate layers, *intercalated structures* are observed. In intercalated structures, a well ordered multilayer morphology of polymeric and inorganic layers is attained. If the silicate layers are completely and uniformly dispersed in a polymer matrix, forming a monolithic structure on the microscale, an *exfoliated (delamined) structure* is observed. It is also mentioned in several studies^{1-7, 10} that sometimes both intercalated and exfoliated structures can coexist in a polymer matrix, forming hybrid structures.



Figure 2.2 Schematic views of possible structures of PLS nanocomposites.¹

X-ray diffraction (XRD) and transmission electron microscopy (TEM) are the most commonly used characterization techniques listed in the literature for identifying the PLS structures. XRD technique can give reliable results only when the structure is intercalated, that is, when the structure allows the determination of interlayer spacing due to the presence of well-preserved, repetitive multilayer structure. The intercalation of the polymer chains generally increases the interlayer spacing as compared to the spacing of the organoclay used, causing a shift of the diffraction peak towards lower angle values. In the case of exfoliated structures, XRD diffractograms are deficient since there are no more diffraction peaks visible. This is usually explained either due to too large spacing between the layers or loss of ordering in the structure. Typical XRD diffractograms, depicted in Vaia and Giannelis' work¹¹ are also sketched in Figure 2.3.

TEM and AFM are the other most powerful techniques frequently used in characterizing nanoparticle dispersion. However, the former requires meticulous sample preparation and the latter needs correct etching or cutting line-free flat surfaces. The TEM micrographs obtained for intercalated and exfoliated structures are two ends of the spectrum of nanocomposite structures. When both intercalation and exfoliation prevail in a structure, this is observed as a broadening in the XRD diffractograms. However, wide angle X-ray diffraction (WAXD) technique can only provide reliable information for intercalated silicate nanocomposites, as it can be insufficient most of the time in differentiating exfoliated and delaminated structures from the disordered, agglomerated structures. Thus, TEM observations are essential to define the overall structure.



Figure 2.3 Schematic of powder X-ray diffraction spectra for various PLSN structures.

2.2.2. Synthesis of Polymer Layered Silicate Nanocomposites

Several strategies have been considered to prepare polymer-layered silicate nanocomposites. There are essentially four different processes to synthesize polymer-clay nanocomposites.¹

- Solution Approach
- In-situ Polymerization
- Melt Intercalation
- Sol-gel Technique (In-situ Formation or Template Synthesis)

In the solution method, as shown in Figures 2.4, a polar organic solvent is usually used for dissolving the clay in polymer. The diffusion of the polymer chains in between the clay layers is ensured via the entropy gained by the desorption of solvent molecules. After the precipitation of the mixture or evaporation of the solvent, the clay platelets reassemble, compressing the polymer to form, in the best case, an ordered multilayer structure.



Figure 2.4 Flowchart of the solution approach.

This technique is not an economical method for industrial applications since large amounts of solvent molecules must be used and desorbed from the clay to accommodate the incoming polymer chains. Nanocomposites based on high-density polyethylene, polyimide and untreated clay based nanocomposites have been synthesized by this method.¹²

In the in-situ polymerization technique, a monomer enters into a host compound (i.e., modified or natural layered silicates) containing interplanar spaces and then polymerized there generally with the aid of a curing agent or organic initiator, catalyst, heat or radiation, as depicted in Figure 2.5.



Figure 2.5 Flowchart of In-situ polymerization technique.

The polarity of the monomer molecules is the main driving force for the in-situ polymerization. During the absorption of monomer into the layered silicates, polar monomer molecules are attracted due to the high surface energy of the clay, thus they can diffuse between clay layers.¹² As the monomer commences to react with the curing agent, polymerization reaction is initiated. The overall polarity of the intercalated molecules drops off and as this mechanism occurs; organic molecules can finally exfoliate the clay. In-situ polymerization is the conventional process used to synthesize thermoset-clay nanocomposites. Nanocomposites based on epoxy, unsaturated polyester, polyurethane and polyethylene terephthalate have been synthesized by this method.¹² In this research, we also employ in-situ polymerization technique.

In the melt intercalation technique, layered silicates are mixed with polymer matrix, generally thermoplastic, in the molten state. This mixture is then annealed above the glass transition temperature at either static or flow conditions, thus forming a nanocomposite, as depicted in Figures 2.6. If clay layers are adequately compatible with the polymer, the polymer can crawl into the interlayer space and form either an exfoliated or an intercalated nanocomposite, depending on the degree of penetration.¹



Figure 2.6 Flowchart of Melt Intercalation technique.

The best advantage of this technique is that no solvent is required during the process. The anticipated driving force for the melt-intercalation is the enthalphic contribution of the polymer, layered silicate interactions during blending and annealing steps.¹² A wide variety of thermoplastics, ranging from strongly polar polyamide 6 to polystyrene have been intercalated between silicate layers via melt-intercalation.^{1, 4, 12, 13}

The sol-gel technique (in-situ formation or template synthesis) is a relatively new approach that is based on direct crystallization of clays by hydrothermal treatment of a gel containing organics and organometallics, including polymer. As precursor for the clay, silica sol, magnesium hydroxide sol and lithium fluoride are usually preferred. Sol-gel technique has been widely used for double-layer hydroxide-based nanocomposite synthesis but it has limited usage for layered silicate nanocomposites.¹ The nanocomposites, prepared by sol-gel technique, are then commonly based on the polymers reinforced by nanofillers, such as; zeolites and silica-titania oxides.⁴

2.2.3. Properties of Polymer Layered Silicate (PLS) Nanocomposites

This section is aimed to provide a fair discussion about the properties of polymer nanocomposites, especially the PLS nanocomposites. In the literature, numerous studies¹⁻^{7, 10} have indicated that polymer layered silicate nanocomposites demonstrate significant improvements as compared to virgin and unidirectional fiber-reinforced polymers, even at clay levels as low as 2-10 wt %. The basic improvements are listed as:

- lighter in weight than conventionally filled polymers because high degrees of stiffness and strength are observed with less high-density inorganic material;
- excellent flame retardancy;
- good optical properties;
- superior mechanical properties than virgin and unidirectional fiber-reinforced polymers;
- good ionic conductivity;
- outstanding diffusional barrier properties, such as permeability and solvent resistance without requiring a multipolymer layered design, allowing for recycling.

Mechanical Properties

Young's modulus of a PLS nanocomposite, which is considered as the stiffness of the material at the beginning of a tensile test, is observed to be strongly improved in comparison to its unfilled and microcomposite forms.

System	Wt % Clay	Tensile Strength	Tensile Modulus	Compressive Yield Strength	Compressive Yield Modulus
		(MPa)	(MPa)	(MPa)	(GPa)
Pure Epoxy	0	1.1	3.8	75	1.40
Epoxy-PCN ^a	5	1.5-3.5	6.0-9.5	79-81	1.5-1.56
Epoxy-PCN ^a	10	2.8-6.0	8.5-17	83-88	1.68-1.76

Table 2.3 Mechanical Properties of Epoxy and Epoxy-Clay Nanocomposites.¹⁰

^a Ranges in data occur because various premodified montmorillonites were used.

As seen in Table 2.3, Pinnavaia¹⁰ has reported that the epoxy-PLS nanocomposite systems are observed to have significant enhancements in their mechanical properties. Both the tensile strength and modulus of the epoxy-PCN (polymer clay nanolayer) nanocomposites increased substantially as compared to pure epoxy samples due to presence of exfoliation in the montmorillonite clay nanolayers. Considerable improvements in the mechanical properties are obtained even at clay loadings as low as 5 to 10 wt %. The findings of some other recent studies have also indicated that different types of functionality on the organocations that are used to modify the clay are observed to have profound effects on the degrees of exfoliation in the epoxy-PCN systems.

In addition, Pinnavaia *et al*¹⁰ have also indicated that the compressive yield strengths and moduli of the exfoliated epoxy-PLS systems were found to boost as a function of clay loading, while the intercalated nanocomposites were observed to display no enhancement. Dubois and Alexandre¹ reported that epoxy resins-based nanocomposites display a totally different behavior depending upon their glass transition temperature, located above or below the room temperature. Other researchers indicated that in high T_g epoxy thermosets,^{14, 15} neither intercalated nor exfoliated nanosilicates result in an increase of the tensile stress at break; they rather make the materials more brittle. This effect appears to be generally more pronounced for intercalated systems than for exfoliated ones.

In the study conducted by Velmurugan and Mohan,¹⁶ the researchers indicated that the usage of 10 wt % organoclay with an epoxy – aromatic amine system led to an
improvement in modulus of about there times that of neat epoxy while the tensile strength of all nanocomposites were determined to be lower than that of pure epoxy. The reduction in the tensile strength was deemed to the presence of voids, resulted from the hindrance of the complete degassing of highly viscous nanoclay reinforced epoxy systems.

Zhou *et al*¹⁷ reported that both flexural modulus and flexural strength of Bisphenol A epoxy–Montmorillonite clay nanocomposites, prepared by high intensity ultrasonication, improved up to 31.6 % and 27.1 % respectively as comparison to neat epoxy systems with an addition of 2 wt % clay. However, they also pointed out that further addition of clay up to 4 wt % reduced the improvements in the flexural properties.

Kotsilkova¹⁸ found out that the usage of solvent during processing of smectite/epoxy nanocomposites assisted the clay exfoliation such that solvent acted as a plasticizer for the epoxy resin and aided better delamination of the smectites in epoxy. He also claimed that usage of solvent gave rise to exfoliation of nanocomposites with small-scale heterogeneity and strong interfacial bonding, both of which in turn caused significant improvements in the strength and toughness of the epoxy nanocomposites.

Thermal Properties and Thermal Stability

Thermal stability and degradation behaviour of epoxy–clay nanocomposites is studied by several researchers.¹⁹⁻²¹ The studies conducted by Guo *et al*²² demonstrated that the thermal stability of Bisphenol A epoxy nanocomposites is influenced by the state of dispersion of organo-montmorillonites in epoxy eventhough they determined that all of the epoxy nanocomposites improved the thermal stability as comparison to the neat epoxy systems.

Sarathi *et al*²⁰ indicated that the thermal degradation of epoxy and epoxynanocomposites were detected by the gradual weight loss above 290 0 C. They also found out that the heat deflection temperature, the temperature at which a test coupon reaches a bending deflection of 0.25 mm, rose up to a critical percentage of nanoclay in epoxy, about 5 wt % above which it reaches a steady state.

Burnside and Giannelis²³ also investigated the thermal stability improvement of cross-linked poly (dimethylsiloxane) in which 10 wt. % of organomontmorillonite was exfoliated. Their thermogravimetric analysis (TGA) indicated a drastic shift of the weight loss at high temperatures, with stabilization as high as 140^oC at 50% weight loss. Diffusion of volatile decomposition products also declined owing to a decrease in permeability observed in exfoliated nanocomposites.

Daniel *et al*²⁴ determined that the coefficient of thermal expansion of (CTE) of epoxy-nanocomposites, 64 x 10^{-6} / 0 C, is 12 % lower than that of the neat epoxy, 73 x 10^{-6} / 0 C, with the addition of 3 wt % Nanomer I.28E, which is a octadecyl trimethyl ammonium modified clay. The lower CTE of epoxy-nanocomposites were ascribed to the fine dispersion of clay platelets in epoxy and the particle rigidity, both of which were considered to hinder the extension of polymer chains at high temperatures. The same

group of researchers also reported that CTE of nanocomposites could be affected by several factors, such as; lack of orientation of clay particles, insufficient adhesion at the clay-epoxy interface and inevitable aggregation of clay platelets at higher clay loadings.

Gas Barrier Properties

As indicated by Dubois and Alexandre,¹ the barrier properties of the nanocomposites are considerably improved as compared to that of pure or macroscopically filled polymers, even at high clay contents. The reason for the dramatic drop in permeability has been credited to the existence of well-dispersed silicate layers with a large aspect ratio, which forces the solutes to follow a tortuous path (see Figure 2.7), thereby increasing the effective path length for diffusion.



Figure 2.7 Proposed model for the torturous zigzag diffusion path in an exfoliated polymer–clay nanocomposite when used as a gas barrier.³

Nielsen reduced the tortuous path model into an equation for a two-dimensional case.²⁵ This model presumed perfect registry of the clay plates parallel to the surface of the film. Although this assumption was proved by TEM, it was only true at very low

loadings of clay (less than 1 wt %). At higher clay loadings the data diverged highly from this model.

Recently, Beall²⁶ has also proposed a modification in the simple tortuous path model that incorporates a constrained polymer and surface modifier region. According to this model, the observed permeabilities could be lower or higher than the ones predicted by simple tortuous path model based on the relative diffusion coefficients of the phases. The same model is also said to predict the difference in permeability of a given nanocomposite for different permeants. Nematic phases are observed to be dominant at or above 5 wt % clay loading in many polymers. Beall²⁶ also proposed that the aspect ratio of the mineral might not always correctly predict the permeability of a given polymer. His model assumed the presence of four distinct phases, i.e., the clay phase, a surface modified phase, a constrained polymer phase, and a polymer phase similar to pure polymer in a nanocomposite.

Water Absorption Properties

Apicella and co-workers²⁷ investigated water absorption properties of glassy epoxy resins. They proposed three absorption mechanisms, namely, the hydrogen bonding between water and polymer hydrophilic groups, bulk dissolution of water in the polymer network and the moisture absorption by the tiny pores on the sample surfaces which also determines the excess free volume of the glassy structure.

There are two common mechanistic approaches, generally used in the characterization of water absorption studies of epoxy, namely; free volume approach and interaction approach. While the former approach assumes the diffusion of water into epoxy resin and dwelling of water in the free volume of the polymer, the latter one proposes strong coupling of water molecules with certain hydrophilic groups such as hydroxyls or amines in epoxy resins. The free volume approach also assumes that bonding between epoxy resin network and water molecule is trivial.²⁸

Lucas and Zhou²⁹ studied the effects of water on the graphite/epoxy composites and found out that water sorption in the graphite/epoxy composites revealed both Fickian and non-Fickian diffusion behavior. Their study concluded that the non-Fickian behavior in the graphite/epoxy composites arose from chemical modification and physical damage to the epoxy resin. The diffusion data collected by Lucas and Zhou²⁹ also showed that the time for the onset of non-Fickian behavior was inversely proportional to the increase in the water exposure temperature.

Dynamic Mechanical Analysis (DMA) Properties

The response of a given material to a cyclic deformation (usually tension or threepoint flexion type deformation) as a function of the temperature can be observed via Dynamic mechanical analysis (DMA). DMA measurements are generally expressed by three major parameters: (i) the storage modulus E', i.e., the elastic response to the deformation; (ii) the loss modulus E'', i.e., the plastic response to the deformation and (iii) tan δ , that is, the E"/E' ratio, useful for detecting the incidence of molecular mobility transitions such as the glass transition temperature (T_g).

DMA studies performed on organoclays exfoliated within thermoset polymers show a remarkable improvement in the storage modulus, especially above T_g . Messersmith and Giannelis³⁰ illustrated that a 58 % increase in modulus for an epoxy matrix below T_g is caused by the dispersion of just 4 vol % montmorillonite as a result of formation of a well-ordered exfoliated nanocomposite (silicate layers separated by approximately 100 A). Their 40 0 C measurements revealed that the storage modulus, E', equals 2.44 and 1.55 GPa for the nanocomposite and the unfilled cross-linked matrix, respectively. However, the storage modulus value above T_g , e.g. at 150 0 C, improve to 50 and 11 MPa for the filled and unfilled epoxy, respectively. Some thermomechanical data for epoxy-PLS systems, gained from DMA measurements by several researchers^{10, 30} are provided in Table 2.4.

Reference	Wt % Clay	E' below Tg, % Higher Than Epoxy	E' above Tg, % Higher Than Epoxy
8	5	72	76
8	10	80	164
27	4	58	450

Table 2.4 Storage Modulus (E') Data for Epoxy-Clay PCNs.³¹

Note: Tg, the glass transition of epoxy is 82^{0} C

Giannelis and Messersmith³⁰ indicated that epoxy PLS nanocomposites display enhancements in glass transition temperature, dynamic behavior and a lowering of residual stress. Dubois and Alexandre¹, have reported that for exfoliated nanocomposites filled with layered silicates of high aspect ratio, the storage elastic modulus seems to be substantially improved at temperatures above T_g . This improvement is explained by the establishment of a three-dimensional network of interconnected long silicate layers, strengthening the material through mechanical percolation.

Jana and Park³² also investigated the dynamic mechanic properties and the mechanisms of exfoliation of several epoxy-nanoclay systems. Their study addressed the role of intra-gallery vs. extra-gallery polymerization rates, the use of polar solvents and the curing speed of epoxy in the extent of exfoliation. They indicated that the elastic forces, developed inside the clay galleries during curing stage were responsible for the exfoliation. Their experimental findings showed that complete exfoliation of clay layers was possible only when a fast increase in the storage modulus inside the clay galleries coexisted with a slow rise of complex viscosity outside the clay tactoids. These researchers also claimed that eventhough faster intragallery polymerization reactions promote complete exfoliation, they are not an absolute requirement to achieve full exfoliation. They also pointed out that complete epoxy-nanoclay exfoliation is possible if the ratio of shear modulus to complex viscosity is greater than or equal to 2 to 4 (1/s), such that the viscous forces caused by the extragallery epoxy are outbalanced by the elastic forces inside the galleries.

2.3 Carbon Nanotubes

Carbon nanotubes have been the focus of extensive research since their first examination almost a decade ago by Iijima.³³ They offer remarkable opportunities for the development of fundamentally new material systems, ranging from extraordinary mechanical properties where the strength, stiffness and resilience exceed any current material to unique electronic properties and a thermal conductivity higher than diamond. Nowadays, carbon nanotubes have a limited usage in the industrial markets due to their high cost of production. However, it's anticipated that they will find their way in numerous applications as new manufacturing techniques emerge on larger scale.

2.3.1 Structure and Morphology of Carbon Nanotubes

Carbon nanotubes are fullerene-based structures that can be imagined as a single sheet of graphite rolled into a cylinder of several microns in length and 1 nm. in diameter.³⁴ Fullerenes are geometric cage-like structures of carbon atoms that are made of pentagonal and hexagonal faces. The first closed, convex fullerene structure was C_{60} molecule, named after the architect R. Buckminster Fuller. That's why, the C_{60} molecule is also known as buckminsterfullerene and often referred as a bucky ball. As seen in Figure 2.8, in this closed cage of 60 carbon atoms, each side of a pentagon is adjacent to each side of a hexagon.^{34, 35} In the solid state, the C_{60} molecules form a crystalline structure and pack together in a face-centered cubic array.



Figure 2.8 Schematic diagram of the structure of a C₆₀ molecule.³⁶

A few years later, the discovery of fullerenes resulted in the synthesis of carbon nanotubes. Nanotubes are generally defined as long and slim fullerenes where the walls of the tubes have hexagonal graphitic structure. Carbon nanotubes can be visualized as a sheet of graphite that has been revolved into a tube. Unlike diamond, where a 3-D diamond cubic crystal structure permits each carbon atom to have four nearest neighbors arranged in a tetrahedron, graphite is formed as a 2-D sheet of carbon atoms located in a hexagonal array. In this case, each carbon atom has three nearest neighbors. 'Rolling' sheets of graphite into cylinders forms carbon nanotubes. The properties of nanotubes strongly rely on atomic arrangement, length, diameter and morphology of the nanotubes. Nanotubes can exist either in single-walled or in multi-walled form. Multi-walled carbon nanotubes (MWCNTs) are simply composed of concentric single-walled carbon nanotubes (SWCNTs). The atomic structure of nanotubes is generally expressed by means of tube chirality, or helicity, which is defined by the chiral vector, C_h , and the chiral angle, θ . The chiral vector, also named as the roll-up vector, is defined as follows:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

where the integers (n, m) are the number of steps along the zig-zag carbon bonds of the hexagonal lattice and a_1 and a_2 are the unit vectors. The chiral angle determines the amount of 'twist' in the tube.

Depending on how the planar graphite sheets are rolled and thereby the geometry of the carbon bonds around the circumference of the nanotube, different structural isomers of carbon nanotubes are possible. There are two basic atomic structures of carbon nanotubes forming at two limiting values of the chiral angle. These are named as zig-zag and armchair structures. The former is obtained when the chiral angle is at 0^0 and the latter is obtained when the chiral angle is at 30^0 , as shown in Figure 2.9. In other words, the two C–C bonds on opposite sides of each hexagon in the armchair structure are perpendicular to the tube axis while these bonds are parallel to the tube axis in the zig-zag arrangement.

All other conformations in which the C–C bonds lie at an angle to the tube axis are named as helical or chiral structures. In terms of the roll-up vector, the armchair nanotube is represented as (n, n) and the zig-zag nanotube is represented as (n, 0). The roll-up vector of the nanotube also denotes the nanotube diameter owing to the known value of the inter-atomic spacing between the carbon atoms.



Figure 2.9 Schematic views of the atomic structure of (a) zig-zag and (b) armchair nanotubes that can be capped by half a C_{60} molecule.^{35, 37}

Thostenson *et al*³⁵ indicated that the chirality of the carbon nanotube has an important effect on the material properties. Tube chirality is specifically known to have a strong impact on the electronic properties of carbon nanotubes. For instance, although graphite is generally regarded as a semi-metal, it has been proven that nanotubes can be either metallic or semiconducting, depending on tube chirality.³⁸

The morphology of carbon nanotubes can depend on several factors such as; their state deformation, defects and manufacturing techniques. For instance, when an armchair nanotube is stressed in its axial direction, the Stone-Wales transformation introduces a new defect in the nanotube structure, the heptagon. As it's mentioned at the beginning, fullerene structures are normally convex, closed cages consisting of hexagons and pentagons. As a result of the Stone-Wales transformation, heptagons allocate for concave regions in the nanotube. Hence, these heptagonal defects can give rise to many possible equilibrium shapes. That's why; most of the nanotubes are not straight cylinders with hemispherical caps.

The MWCNTs were the first to be discovered by Iijima.³³ They are basically concentric single walled tubes positioned around a common central hollow region with a constant separation between the layers close to the graphitic interlayer spacing of 0.34 nm. These concentric nanotubes are held together by secondary, van der Waals bonds. Each individual tube can be characterized by different chirality or helicity. In addition, these individual nanotubes can have a diameter, varying from 2 to 25 nm and a length of several microns.

Single walled carbon nanotubes (SWCNTs) were first synthesized in 1993 when it was observed that the addition of metals like cobalt to the graphite electrodes in the arc evaporation method gave rise to nanotubes with single layer walls.³⁷ A single walled nanotube can also be considered as a structure that is close to an ideal fullerene fiber and made of a single layer cylinder with a narrow diameter distribution ranging from 1 to 2 nm.

Another method of producing SWCNTs involves the laser-vaporization of graphite and results in a high yield of SWCNTs with uniform diameters. When produced in vapor phase, SWCNTs can self assemble into larger bundles, called ropes, composed of several nanotubes positioned in a one-dimensional triangular lattice.

It is noteworthy to emphasize that the discovery of SWCNTs has been very significant in that they are the most desired type of nanotubes for the fundamental researches on the structure/property relationships in carbon nanotubes as the intra-tube interactions in the case of MWCNTs further complicate the properties of carbon nanotubes.

2.3.2 Processing of Carbon Nanotubes

In the last few years, great effort has been dedicated to the development and enhancement of carbon nanotube synthesis techniques so as to attain high levels of yields and purity. The most common methods for producing single and multi-walled carbon nanotubes comprise arc-discharge^{33, 39}, chemical vapor deposition from hydrocarbons,⁴⁰⁻ ⁴² laser ablation⁴³ and gas-phase catalytic growth from carbon monoxide.⁴⁴

In the arc-discharge technique, two high-purity graphite rods as the anode and cathode are employed. During processing, the rods are exposed to a helium atmosphere and a voltage is applied until a stable arc is attained. The inert gas pressure, the current density, the cooling rate and the plasma stability between the two electrodes are the most critical process variables, which strongly rely on the size of the graphite rods. The quality, the alignment and the yield of the nanotubes also depend on the arc conditions. As the anode is consumed, a constant gap between the anode and cathode is preserved by altering the anode position. The material then deposits on the cathode to form a build-up of two different microstructures: an outer hard region and an inner core region. The outside shell contains nanotubes and nanoparticles fused together and is not of much use, while a highly porous network of randomly oriented nanotubes and other carbon particles forms the softer fibrous core.^{39,45-48} For the production of single walled carbon nanotubes, the electrodes are doped with a small amount of metallic catalyst particles.

Laser ablation technique was originally developed for the initial synthesis of fullerenes. The technique has been improved for making the production of single-walled nanotubes possible.^{43, 49, 50} In this technique, a laser is used to generate carbon plasma in a controlled inert atmosphere oven at temperatures around 1200 ^oC. For the production of single-walled nanotubes, the graphite target was doped with cobalt and nickel catalyst.⁴³ The condensed material is then collected on a water-cooled target. Advani *et al*³¹ has

indicated that a very high yield can be achieved by using two successive laser pulses generating 70 to 90 vol % SWCNTs organized in hexagonal ropes.

The major drawback of both the arc-discharge and the laser-ablation techniques is the limited amount of sample that they can produce depending on the size of the carbon source (the target in the case of laser ablation and the anode in the case of arc-discharge). Moreover, successive purification steps are essential to isolate the nanotubes from the undesirable by-products.

The gas-phase techniques such as; chemical vapor deposition (CVD), where nanotubes are formed by the decomposition of a carbon-containing gas were developed to overcome some of the limitations of arc-discharge and laser ablation techniques. The gas-phase techniques can also be pertinent to continuous processes since the carbon source is continually replaced by flowing gas. CVD is a universal technique used to transform gaseous molecules, called precursors, into a solid material in the form of slender films or powders. This technique basically involves a series of steps: vaporization of the precursor molecules into a reactor; diffusion and adsorption of the gaseous molecules on a substrate; decomposition and integration of the precursors into solid films and desorption of the reaction products into a gaseous phase. The synthesis of carbon nanotubes by CVD requires the catalytic decomposition of hydrocarbon gases (acetylene or benzene) over substrates: silica, carbon black or graphite covered by transition metals (Co, Fe, Ni) or mesoporous silica embedded with iron particles.⁵¹ CVD produces nanotubes that are not straight but curved and entangled in an assembly composed also of catalyst particles and

some other carbon products (soot, fibers) since the reactions are executed at lower temperatures than those of the carbon arc discharge technique.

Dai⁴³ described an experimental set up for CVD, similar to the one shown in Figure 2.10. He reported that CVD is a growth process entails heating of a catalyst material to sufficiently high temperatures in a tube furnace and flowing a hydrocarbon gas through reactor for a period of time.



Figure 2.10 Schematic experimental set-up for the CVD.³⁸

Advani *et al*³¹ indicated that it could be possible to produce large quantities of nanotubes with good uniformity of tube size by controlling the size of catalyst particles during CVD process. Furthermore, when mesoporous substrates, embedded with iron particles, is used in the CVD, aligned nanotubes can be obtained.

The gas-phase catalytic growth technique is a relatively recent synthesis technique employing the use of carbon monoxide as the carbon source in the production of SWCNTs. Nikolaev *et al*⁴⁴ reported that the highest yields and narrowest tubes of single walled nanotubes were obtained at the highest accessible temperature and pressure of 1200 0 C and 10 atm, respectively. In their study, SWCNTs were produced by flowing CO mixed with a small quantity of Fe(CO)₅ through a heated reactor. The products of Fe(CO)₅ thermal decomposition reacted to produce iron clusters in gas phase. These clusters acted as nuclei upon which SWCNTs nucleated and grew: solid carbon is produced by CO disproportionation (the Boudouard reaction):

$$CO + CO \rightarrow C(s) + CO_2$$

which took place catalytically on the surface of the iron particles. These particles also promoted the construction of the tube's characteristic graphitic carbon lattice. Unlike the other synthesis methods involving hydrocarbon feedstock, Nikolaev *et al*⁴⁴ indicated that this method led to almost no amorphous carbon overcoating on the nanotubes. Thus, they claimed that the process has more advantageous than the other SWCNT production methods such that it is a continuous-flow process rather than being a batch process and it can be scaled up to fabricate much larger quantities of SWCNTs.

2.3.3 Properties of Carbon Nanotubes

Carbon nanotubes exhibit remarkable material properties as a result of outstanding combination of their structure, topology and size. They are one of the stiffest and strongest materials found in nature due to their high aspect ratio (around 1000) and the inherent strength of the covalent carbon-carbon bond. While the lattice helicity and elasticity provide optimal electronic properties in carbon nanotubes, the graphitic nature of the nanotube lattice leads to high conductivity, inertness, high stiffness and strength. In particular, considerable challenges exist both in the modeling of the elastic and fracture behavior and in the micromechanical characterization of nanotubes at the nano-scale. Limitations on specimen size, insufficiency of test specimen preparation techniques, uncertainty in the data gained from indirect measurements, inadequacy of micromechanical characterization are the major difficulties in the characterization of nanotubes and their composites.

Numerous researchers⁵²⁻⁵⁷ have attempted to characterize the mechanical properties of carbon nanotubes directly. Treacy *et al*⁵² evaluated the elastic modulus of isolated multi-walled nanotubes by measuring the amplitude of their intrinsic thermal vibration in a transmission electron microscope. They obtained an average value of the elastic modulus as 1.8 TPa.

Salvetat and co-workers⁵⁴ measured the properties of SWCNT bundles with the AFM. They reported a significant decrease in the axial and shear moduli of the SWCNT as the diameter of the tube bundles increased. They concluded that this behavior is an indication of the slippage of the nanotubes within the bundle. Walters *et al*⁵⁵ further examined elastic strain of nanotube bundles by AFM. They calculated a yield strength of 45 ± 7 GPa for the nanotube ropes based on an assumed elastic modulus of 1.25 TPa and their experimental strain measurements. In fact, their calculated value for strength would be much lower if the elastic modulus of the nanotube bundle is dropped as a result of slipping within the bundle as suggested by Salvetat *et al*⁵⁴

Direct measurements of the stiffness and strength of individual, structurally isolated multi-wall carbon nanotubes via atomic force microscopy (AFM) were first performed by Wong *et al.*⁵¹ They measured bending force as a function of displacement. The average bending strength was determined as 14.2 ± 8 GPa while a value of 1.26 TPa was obtained for the elastic modulus.

The tensile loading of MWCNTs and SWCNT ropes was studied by Yu and coworkers.^{56, 57} They attached the nanotubes between two opposing AFM tips and loaded them under tension. For MWCNTs,⁵⁷ the failure of the outermost tube occurred followed by pullout of the inner nanotubes. Their measurements indicated that the experimentally calculated tensile strengths of the outermost layer varied from 11 to 63 GPa while the elastic modulus varied from 270 to 950 GPa. In their following research on single-walled nanotube ropes, Yu *et al*⁵⁷ calculated an average elastic moduli of 320 to 1470 GPa and tensile strength of 13 to 52 GPa, based on the assumption that only the outermost tubes assembled in the rope carried the load during the experiment.

2.4 Processing and Characterization of Carbon Nanotube Polymer Composites

In recent years, the addition of carbon nanotubes to polymers is found to have profound effects on the thermal stability, mechanical properties and electrical conductivity of the resulting composites. In the literature, the major uses of carbon nanotubes in polymers are indicated as conductive fillers in insulating polymer matrices to provide electrostatic discharge and electromagnetic radio frequency interference protection; polymeric modifiers for high temperature applications; doping of conjugated luminescent polymers to produce active materials for electronic applications and reinforcements for the polymer composite materials.³¹

The conventional polymer composites use continuous and short fibers as reinforcements. The use of continuous fiber advanced composites is limited to simple shape and limited production since the conventional polymer processing equipment cannot process the long continuous fibers. Conversely, it is also well known that the fiber aspect ratio represents the critical factor affecting the resultant structural properties of short-fiber composites in that composite strength and stiffness augment as the aspect ratio increases. On the other hand, percolation phenomenon is affected by the packing of short fibers in polymers such that the maximum packing decreases with an increase in aspect ratio,⁵⁸ which also indicates that short fiber composites may not be enough to produce very strong materials. Carbon nanotubes could overcome most of these problems thanks to their high aspect ratio (around 1000), small size and greater stiffness and strength than the corresponding macroscopic conventional composites. Moreover, they could also

provide considerable benefits in composite processing because of their capability to resist large strains.⁵⁹

The most critical issues in the processing of carbon nanotube polymer composites are uniform dispersion in the polymer, improved nanotube/matrix wetting and adhesion and alignment of the carbon nanotubes in the polymer matrix.³⁵

Shaffer and Windle⁶⁰ evaluated the tensile elastic modulus and damping properties of the carbon nanotube/polyvinyl-alcohol composite films as a function of nanotube loading and temperature in a dynamic mechanical thermal analyzer (DMTA). Their experimental results revealed a nanotube elastic modulus of 150 MPa, which was considered well below the values reported for isolated nanotubes. They reported that they did not thoroughly understand whether this result is an outcome of imperfections in the graphite layers of catalytically grown nanotubes used for their investigation or it is due to a difficulty in stress transfer.

Salvetat *et al*⁵⁴ indicated that the elastic properties of the nanotube-based composites are considerably affected by the slipping of nanotubes when they are assembled in ropes. Their study also showed that the aggregates of nanotube ropes efficiently reduced the aspect ratio (length/diameter) of the reinforcement though it was difficult to achieve a uniform dispersion of carbon nanotubes in the polymer matrix.

Winey *et al*⁶¹ observed significant improvements in flexural modulus (17 %) and strength (10 %) by the addition of solely 0.05 wt % nanotubes as a result of high shear mixing of SWNTs in a Bisphenol F epoxy resin and preheating of this mixture prior to the incorporation of an aromatic amine hardener. They claimed that covalent bonds between SWNTs and epoxy resin were formed during the preheating stage. They indicated that the load transfer between epoxy and the epoxy is facilitated by these covalent bonds. In addition, the increases in both flexural strength and modulus were mainly ascribed to two factors; good dispersion of SWNTs and grafting of epoxy resin to SWNTs via an esterification reaction. Their study also the increase in viscosity during preheating of epoxy/SWNT mixtures for solvent removal, plays a critical role in the processability of epoxy/SWNT mixtures particularly at higher SWNT loading levels.

Qian *et al*⁶² achieved a 25% increase in the tensile strength and between 36-42% increase in the elastic stiffness in the carbon-nanotube/polystyrene composites by the addition of only 1 wt. % carbon nanotubes to polystyrene matrix. They observed nanotube pull-out, nanotube fracture, as well as crack bridging by the nanotubes from the TEM examination of the fractured surfaces.

Pipes and Hubert⁶³ proposed two models for the prediction of the effective elastic mechanical properties of helical arrays of carbon nanotubes: a model employing the anisotropic elasticity theory for a layered cylinder with layers composed of discontinuous carbon nanotubes embedded in a polymeric matrix and a model using the traditional textile-mechanics analogy for helical yarns. They found out that the predictions for the

Young's modulus by the two theories are in excellent agreement when the shearing twist is prevented. Their results also revealed that the effective Poisson's ratio is a strong function of helical angle with maximum value corresponding to the zero twist case. In their following study, Pipes and Hubert⁶⁴ also aimed to predict effective thermal expansion coefficients of the same helical arrays of carbon nanotubes. They determined the effective axial, transverse and shearing thermal expansion coefficients of the arrays as a function of the number of layers, degree of twist, properties of the carbon nanotube and surrounding polymer matrix.

It is reported in many studies that a strong interfacial bonding is critical to take full advantage of the exceptional strength, stiffness and resilience of carbon nanotubes. Gong *et al*⁶⁵ studied surfactant-assisted processing of nanotube composites with a nonionic surfactant. Improved dispersion and interfacial bonding of the nanotubes in an epoxy matrix led to a 30% increase in elastic modulus with addition of only 1 wt.% nanotubes. They also hypothesized that surfactant can give rise to steric repulsive forces between carbon nanotubes that appear distributed and those aligned along one direction. Their SEM analysis results revealed many agglomerates of carbon nanotubes in the absence of surfactant in the epoxy polymers.

Lordi and Yao⁶⁶ studied the molecular mechanics of binding in nanotube-based composites with different polymeric matrix materials. To evaluate the binding energies and sliding frictional stresses between pristine carbon nanotubes and different polymers, they made force-field-based molecular-mechanics calculations. Their results pointed out

that a helical conformation of the polymer around the nanotube has profound effect in achieving a strong bond at the interface. They concluded that forced long-range ordering of the polymer and the molecular-level entanglement of the two phases are responsible for the strong bonding at the interface.

Many researchers investigated interfacial stress transfer efficiency so as to fully understand the mechanical behavior of nanotube-based composites since the interaction at the nanotube/matrix interface is critical. Wagner *et al*⁶⁷ studied on the stress-induced fragmentation of multi-walled carbon nanotube polymer films of approximately 200 mm thick. They explained that either process-induced stress resulting from curing of the polymer or tensile stress generated by polymer deformation and transmitted to the nanotube was leading to fragmentation. They determined the nanotube/polymer interfacial shear stress at the order of 500 MPa and higher based on the estimated values of nanotube axial elastic modulus and normal stress. Thostenson *et al*⁶⁷ was reliable, then such interfaces can sustain shear more than the matrix and the nanotubes themselves since this value is an order of magnitude higher than the stress-transfer capability of current advanced composites.

Stress transfer was also investigated by Raman spectroscopy. It is a common technique used to characterize carbon nanotubes and their composites. When a strain is applied to a material, a Raman peak shift is observed because of the changes in interatomic distances and the vibration frequencies of the normal modes. Cooper *et al*⁶⁸

spread an epoxy-resin/nanotube mixture to the surface of an epoxy beam and examined the composite samples after curing by Raman spectroscopy. They observed a shift in the G' Raman band (2610 cm⁻¹) to a lower wavenumber as a result of the stress transfer between the polymer and the nanotubes. This shift is attributed to the stress transfer by the nanotubes. Their results also showed that the effective modulus of single-walled nanotubes dispersed in a composite could be over 1 TPa and that of multi-walled nanotubes was about 0.3 TPa.

Ajayan *et al*⁶⁹ determined a nearly constant Raman peak value for the single-walled nanotube/epoxy composite samples tested in tension. This result is ascribed to the tube sliding within the nanotube bundles, thus, poor interfacial load transfer between the nanotubes. Schadler *et al*⁷⁰ tested multiwalled carbon nanotube/epoxy composites both in tension and compression and obtained similar results to those of Ajayan *et al*⁶⁹ The tensile modulus was determined to be less than the compressive modulus of the composites, and the Raman peak was observed to shift only in compression mode, demonstrating poor interfacial load transfer in tension.⁷⁰

In the literature, it is reported that the micromechanical characterization of the nanotube-based composites is difficult even with improved dispersion and adhesion when the distribution of the nanotubes is random. Hence, some alignment techniques have been investigated by X-ray diffraction and TEM. Jin and co-workers⁷¹ were able to align carbon nanotubes in nanotube composites by mechanical stretching of the composite

samples. They used X-ray diffraction to determine the orientation and degree of alignment. Their X-ray diffraction analysis indicated that:

- The degree of alignment is not affected by the thickness of the sample; that is, it did not change at a given stretching ratio.
- The percentage of aligned nanotubes raised with an increase in the stretching ratio
- Stretching of thick samples to the same maximum elongation value of the thin samples was more difficult since necking and fracture observed at lower strains.

Haggenmueller *et al*⁷² observed that well alignment in nanotube composites can also be achieved by melt spinning of single wall nanotubes in the fiber form.

2.5 Fundamentals of Resin Transfer Molding (RTM)

Liquid composite molding (LCM) consists of a range of composite manufacturing processes that have a common feature that requires the injection of a closed mold cavity preloaded with dry reinforcements. The most well known types of LCM comprise resin transfer molding (RTM), vacuum-assisted resin transfer molding (VARTM), structural-reaction injection molding (S-RIM), Seemann composite resin infusion molding process (SCRIMP) and injection compression molding (ICM).⁷³ Most of these LCM processes are capable of producing high quality; complex-shaped fiber reinforced polymeric products successfully. Thus, LCM processes can have a variety of application areas ranging from aerospace, automotive, marine to civil industries. Among these LCM techniques, Resin transfer molding (RTM) is a versatile process preferred for high

performance, high volume, low cost and net shape manufacturing of polymer composites, thus; gaining more attractiveness in the composites industry.

RTM can basically be divided into five steps. Initially, a fabric preform is formed by stacking up fabric layers. After the mold closure, a reactive resin system is injected into the mold cavity. A curing reaction is initiated, either during the mold filling or after the injection and impregnation. After the cure cycle of the molded part is completed, the product is removed from the mold.

Relatively low-pressure equipment for manufacturing is employed in RTM since the mold filling times are generally of the order of minutes. RTM owes its good reputation not only to its ability to form net shape products but also its flexibility in providing more opportunities to the designer in controlling the orientation of reinforcements, which in turn provides more opportunities in tailoring the properties of final products satisfying the requirements for the desired applications.⁷⁴

Although the concepts of RTM look like at first glance to be quite simple, successful results in RTM can only be achieved by the precise control and anticipation of numerous design criteria such as; process variables, material parameters, molding and tooling equipment selection, process modeling of mold filling and flow issues during impregnation. Thus, these issues will be introduced and discussed in the coming sections.

2.5.1 Process Technology

In this section, the basic components of RTM, i.e., resins, reinforcements and preforms, and molding and tooling equipments will be covered in detail.

Resins

A diversity of polymeric resin systems is utilized in LCM processes. The performance characteristics and application areas of resins commonly used in RTM are provided in Table 2.5.⁷⁵

The majority of RTM resins are generally chosen from thermoset resins, possessing relatively low viscosities, so as to decrease both the mold filling times and the required injection pressures during processing. The key characteristics pertinent to the selection of resin systems for RTM process comprise a low viscosity, long pot life, short gel-time at the curing temperature and low volatile levels. A long pot-life and low viscosity are essential for entire filling and impregnation of the preforms with little resistance or disturbance of material placement especially in the large, complex molds before gellation. A short gel-time at the cure temperature is important for efficient cycle times. Low outgassing and volatility capabilities aid minimization of voids in the parts.⁷⁶

Hansen⁷⁶ reported the major parameters determining the choice of appropriate resin systems for RTM as: viscosity, pot life, tensile modulus and elongation, glass transition temperature (T_g) and moisture absorbance. In Hansen's work, viscosity is indicated as the first critical parameter to decide when making a resin system selection for RTM. Most of

the time, the optimum viscosity range for RTM resins falls between 200 cps and 600 cps. The criterion for selecting a low viscosity resin is that the resin should wipe each filament as it flows through the mold so that it can find the path of least resistance leaving voids. The penetration of the fiber bundles cannot be fully achieved if a high viscosity resin system is used. Resin viscosity selection relies on a set of parameters: fiber volume fraction (porosity), the type of reinforcement (permeability) and the available output of the resin injection machine (flow rate and pressure). The second important parameter indicated in Hansen's study⁷⁶ is the resin pot life. It is defined as the time at which the resin viscosity reaches a certain viscosity level beyond which the resin cannot flow through the fibers in the mold.

The resin pot life has to be chosen based on the complexity of the parts. The same study also indicates that a resin tensile modulus of 400 ksi or higher is essential in RTM so as to prevent premature buckling and to support the reinforcements sufficiently. Similarly, the tensile elongation of a resin system, a measure of the brittleness of a resin system, has to be at least 3 to 5 % in RTM.

When deciding on the glass transition temperature (T_g) of a resin system for RTM, it should be kept in mind that the T_g must be proportionate with the performance requirements of the molded parts. In fact, the same study also mentions that it is preferable to select RTM resins with glass transition temperatures at least 50 ^oF higher than the service temperature.

Resin type	Applications	Typical neat resin properties
Polyester	Consumer products, tanks, pipes, pressure vessels, automotive structures	Tensile strength of 3.4 to 90 MPa; compressive strength of 90 to 210 MPa; up to 120°C continuous use; low viscosity; fast reaction; can be catalyzed; high shrinkage
Epoxy	Adhesives, tooling, electronics, aerospace and automotive structures	Tensile strength of 55 to 130 MPa; up to 175°C continuous use; high viscosity; fast reaction; can be catalyzed; intermediate reaction; low shrinkage; excellent chemical resistance
Vinyl ester	Consumer products, pipes, automotive structures, ducts, stacks, flooring, linings	Tensile strength of 60 to 90 MPa; elongation of 2-6%; up to 120°C continuous use; low viscosity; fast reaction; can be catalyzed; intermediate shrinkage
Polybutadiene	Resin modifiers, coatings, adhesives, potting compounds	Good chemical resistance; up to 120°C continuous use; high viscosity; fast reaction; can be catalyzed; low moisture pick-up
Polyimide	Primary and secondary aerospace structures in high-temperature areas, electronics	Tensile strength of 55 to 120 MPa; up to 315°C continuous use; high viscosity; slow reaction; can be catalyzed; reaction by-products; microcracking
Bismaleimide	Similar to polyimide	Similar to polyimide, except that continuous use only up to 230°C; no reaction by-product
Engineering-Grade Thermoplastics	Automotive and aerospace structures	High toughness; continuous use only up to 230°C; high processing temperatures and pressures; high viscosity

Table 2.5 Typical characteristics of resins used in RTM.⁷⁵

Among a variety of polymeric resins employed in LCM processes, epoxy resins, vinyl ester resins, phenolic resins and polyester resins are the most widely used. Each resin system has its distinctive chemistry and curing characteristics. Since epoxy resins are utilized in this research, they will be given special attention in the following section.

Epoxy Resin Systems

Epoxy resins are probably the most versatile and easy to use thermoset resins. The major application areas of epoxy resins comprise adhesives, bonding of laminated structures such as electronic circuit boards, complex shape casting of products, encapsulation, and high-performance fiber reinforced composites. They can be tailored to be compatible with a wide range of processing techniques, ranging from pultrusion or injection molding to solid tape laying or RTM. Depending on their formulation, their properties can vary from rubbery to rigid solids with a heat distortion temperature of up to 230 °C in their unreinforced form.⁷³ Nonetheless, they are usually less rigid than phenolic or polyester resins, but are more ductile and have a good chemical resistance. Epoxy resins are generally cured with anhydrides or diamines. Since diamines provide the best hot-wet characteristics to the epoxy resins, those systems are widely preferred in many applications. Most of the epoxies available on the market are characterized by the presence of epoxy groups, also called oxirane rings. These rings are located terminally, internally, or cyclically in a molecule. The most common oxirane ring is the terminal 1,2-epoxy found in a diglycidyl ether of bisphenol-A (DGEBA) resin, formed as a result of the reaction of bisphenol-A and epichlorohydrin, shown in Figure 2.11. The DGEBA type resins are the most frequently used epoxies in RTM applications. The molecular

weight of DGEBA resins are generally adjusted by altering the degree of polymerization, n, of the backbone, which varies from 0 for the low viscosity, low molecular weight resins, up to 10 for the more flexible cured thermosets. Increased heat resistances can also be achieved by augmenting the functionality of the resins. The most commonly used type of such resins is the 4-functional tetra-glycidyl methylene dianiline (TGMDA), shown in Figure 2.11.

Another type of epoxy resin is the Novolac, which has a higher molecular weight, functionality, and viscosity as compared to the other types. They are obtained as a consequence of the reaction of a novolac resin, either based on o-cresol or phenol, with epichlorohydrin. They usually have better heat and chemical resistance than bisphenol-A type resins. Cycloaliphatic, or peracid, resins are produced by peracetic epoxidation of cyclic olefins. They have the epoxide groups on a ring structure. These types of epoxies also have a low viscosity and reduced resin coloration. They tend to augment cross-link densities and possess superior weathering resistance.

Boogh and Mezzenga⁷⁷ reported that epoxy resins can be blended together or mixed with low viscosity reactive solvents, which are often mono or difunctional low molecular weight peracid epoxidized aliphatic molecules such as polybutadiene.

Epoxy resins are transformed into solids through thermosetting reactions using curatives. Epoxy is characterized by a high reactivity with numerous reactive groups such as anhydrides, amines, carboxylic acids, alcohols, and even epoxies. DIGLYCIDYL ETHER OF BISPHENOL-A



Figure 2.11 Chemical structures of diglycidyl ether of bisphenol-A (DGEBA), Novolac, tetraglycidyl ether methylene dianiline (TGMDA), cycloaliphatic epoxy monomers.⁷³

Figure 2.12 depicts the curing reactions between epoxy and amine curing agent. The curatives should be carefully chosen as a function of the process used and desired properties. Aliphatic and aromatic amines are the most commonly used curatives. Aliphatic amines, such as diethylene triamine (DETA) or iso-phorone diamine (IPD), enable epoxy resins to be cured at room temperature, but they are inclined to develop strong exotherms limiting the mass that can be polymerized. Their reactions also give rise to rather poor thermal and electrical properties.

Aromatic amines such as methylene dianiline (MDA), metaphenylene diamine (MPDA or Laromin-C) or diaminodiphenylsulfone (DDS) generally entail higher temperature curing reactions above 100 ^oC. The thermal resistance of the aromatic amine cured thermosets is usually very good. They are somewhat difficult to use since most of them are solid and thus, they should be melted and dissolved into the epoxy matrix.



Figure 2.12 Schematic of epoxy-amine curing reactions

Acid anhydride curatives, such as nadic methyl anhydride (NMA) or dodecenyl succinic anhydride (DDSA), are gaining much more popularity due to their effects in providing better thermal properties to the epoxies. They are very suitable for electrical applications due to their low polarity. These low viscosity curatives are less toxic than amines and are easy to employ. Nevertheless, they entail the addition of catalysts such as benzyl dimethylamine. Homopolymerization of epoxy resins can also be achieved by means of catalysts. The advantage of such cures is that they offer a long working life to the resin. However, they possess a drawback of producing strong exotherms during curing. Thermally activated Lewis acids such as boron trifluoride ethylamine complexes or piperidine are the most common catalysts, which require cure temperatures of generally above 100 ⁰C. Lately, new catalysts are produced for irradiation curing mechanisms induced by UV light or electron-beam irradiation.

Thermoset Curing

As mentioned above, thermoset resins consist of monomeric reactants that need to be polymerized during processing. Thus, chemical reactions take place during curing. Initiation reactions can be induced by various means depending on the chemical nature of the reactive site also named the reactive moiety, either by raising the temperature, or by the addition of a chemical co-reactant or a reaction initiator or by irradiation. Usually, a combination of energy input by external means and the use of a tailored co-reactant or initiator is employed. The higher temperatures or a higher energy input leads to faster cross-linking kinetics which generally follow a standard Arrhenius type relationship with temperature. All thermosetting reactions are exothermic, which might sometimes give rise to spontaneous combustion during curing due to the insulating nature of polymers.

Boogh and Mezzenga⁷⁷ indicated that chemical reactivity and the rheological behavior of the resin determine the processability of the resin. Among the many rheological parameters, initial resin viscosity is the most critical one in processing. The molecular weight, backbone rigidity, and degree of branching of the thermosets will all affect the viscosity of the initial resin. In general, the thermoset resin formulations utilized consist of several components. Furthermore, the quantity and rheological properties of any solvents or low molecular weight co-reactants used with the resin will strongly influence the resin's behavior during processing. As the temperature is increased by external heating or due to the exothermal reaction, the initial viscosity of the mixture decreases. As curing proceeds, the molecular weight of the resin rises, which in turn gives rise to an increase in viscosity. After a certain time, the resin starts to act like a gel. The gel time refers to a time limit for given processing conditions at which molding of the mixture is no longer possible due to the extreme increase in viscosity due to formation of an infinite molecular network. It can be determined by dielectric or rheological measurements, or more practically by means of a wooden probe. Thus, thermoset resins must be molded prior to the gelation time of the resin. Even though the gel point is considered as the degree of cure or curing advancement and a function of conversion, it's also influenced by the functionality of the resin depending on its functionality. The cure kinetics and temperature will directly effect the practical gel times. The events taking place during the resin cure can be plotted as a function of time
and processing conditions. Such types of processing windows are called timetemperature-transformation (TTT) diagrams.

Four main regions can be distinguished in a TTT diagram considering the curing temperature.⁷⁷ At temperatures below the glass transition of the monomer, Tg_0 , the system is always in the glassy state and the reaction remains in a low temperature diffusion controlled reactive state that can continue for months or years, thus explaining the long storage times of thermoset prepregs. In general, the temperature must be elevated to above Tg_0 so that the monomer can react at reasonable rates. When the temperature is kept in between the Tg₀ and the glass transition temperature, Tg_{GEL}, polymerization initiates, with the system being in the liquid state. Polymerization progresses until the vitrification curve is crossed, after which the polymer suddenly enters into the glassy state and thus polymerization enters into the diffusion controlled regime. When the temperature is maintained between Tg_{GEL} and $Tg \propto$, polymerization proceeds until the gel point is reached. At this stage, further processing of the thermoset cannot be possible, since the flow of the polymer is prevented by the infinite value of the steadystate viscosity as mentioned previously. Nonetheless, polymerization continues and the fluid polymer transforms into the glassy state as soon as the glass transition of the polymer reaches to the curing temperature. Finally, when polymerization is carried out at curing temperatures above the infinite glass transition temperature, that is, the glass transition of a fully cross linked polymer, the polymer crosses the gelation curve but never reaches the vitrification line. Hence, the thermoset resin always remains in the rubbery state during the overall curing process. Other time-temperature dependent relevant processes may also be included in the TTT diagrams, such as polymer degradation.

For practical and economical reasons, demolding at earlier stages is preferred to eliminate any risk of damaging expensive molding equipment. The curing can then be completed with a postcure, in most of the times. This entails that the part has to have sufficient strength not to deform upon demolding and that the remaining cure will not cause dimensional changes of the part. The postcure time is hard to determine and will strongly depend on the reaction scheme of the resin and its co-reactants, as well as on the part geometry. Even after postcuring, the full cure of the resin is often deliberately not completed. To cut down the process cycle time, the cure can be interrupted before the full conversion for economic reasons. Besides, the resin does not have to be cured at too high temperature unless a high Tg is required in service to minimize internal stresses or to maintain impact resistance. In fact, impact properties are inclined to decrease at the late stages of curing because of the boost of the molecular network rigidity. Care should also be taken that resin will not age during its service life and change its properties. For many resins, completion of curing at ambient conditions can require years.

Reinforcements and Preforms

The purpose of this section is to provide an insight about the properties, applications, the advantages and drawbacks of the textile materials used for preforms, with a special emphasis given on the ones employed in RTM. A proper choice of reinforcements and their conversion to the final preform shape is essential in the RTM process. Usually, the performance and cost requirements of the enduse application govern the selection of appropriate reinforcement materials. A variety of fiber types are utilized to manufacture LCM preforms. The most common ones are boron, aramid, ceramic, glass and carbon. The final properties of the composites are also predominantly controlled by the physical structure of the reinforcement materials i.e., base fiber material, sizing, and type of stitching or weaving.

Textile processes have been tailored to handle most of the fibers commonly used in structural composites. They assure a method of manufacturing integral, net shape structures, thus eliminating many machining and joining steps during the manufacturing, reducing material waste, and avoiding the possibility of debonding failures in service. Some textile technologies, particularly stitching and braiding, are already on the brink of creating cost-effective integral structures.⁷⁸

The major limitation in fiber selection is that most textile processes subject yarns to bending and abrasion. Machines have been customized to minimize the fiber damage, but it is still not possible to use exceptionally brittle or stiff fibers in many processes. Important properties of some popular fibers are provided in Table 2.6. The size of the yarn into which fibers are bundled is a significant parameter in textile composites. Yarn size is generally expressed as a filament count (the number of fibers, usually in thousands); or as a linear density, either the denier (the number of grams in 9000 m of yarn) or the yield (length per unit mass). Carbon fibers, which are often the most commonly preferred choices in high technology applications, possess high axial stiffness and strength because of the arrangement of carbon atoms in oriented graphitic sheets. On a coarser scale, typically ~ 1 mm., lots comprising $10^3 - 10^4$ fibers are bundled into yarns or tows. Within the finished composite, each carbon fiber tow acts as a highly anisotropic solid, with much higher stiffness and strength along its longitudinal axis than its transverse axis. Since tows are rarely packed in straight, parallel arrays, stresses and strains often induce strong deviations from tow to tow.

Name	Туре	E _A GPa	E _T GPa	G _A GPa	α _A μm/m- K	k _A W/m-K	σ ^A Ten MPa	σ ^A Comp MPa	hokg/m ³
P100	Pitch	772	7	22	-0.44	520	2440	700	2150
T300	PAN	231	14	22	-0.17	8.5	2970	2690	1770
AS4	PAN	248	13	21	-0.17	9.0	3490	2700	1800
IM6	PAN	276	12	19	-0.17	10.0	4500	2700	1770
IM7	PAN	276	12	19	-0.17	10.0	3940	2700	1740
S-2	Glass	90	90	36	0.5	9.0	2990	1570	2490
Kevlar49	Aramid	112	7	3	-1.50	0.04	3040	1050	1440

Table 2.6 The characteristic properties of commonly used fibers.⁷⁸

A – Axial, T – Transverse, σ^A – Axial Strength, k_A - Axial Thermal Conductivity

The majority of the preforms are manufactured using fabric reinforcements. Fabrics are laminate structures possessing fibers aligned in the in-plane directions. Cox and Flanagan⁷⁸ reported the most common textile forms available for high technology

applications. The classification into 2D and 3D composites is decided by whether the fiber preform can transport loads continuously in three or only two linearly independent directions.⁷⁸ A 2D-composite has discrete layers, which may be separated without breaking fibers. Tows can be oriented at different angles in 3-D space, allowing structural support in a multitude of directions. In modeling the macroscopic properties, Cox and Flanagan⁷⁸ named the textiles that behave similar to laminates in many ways, as "quasi-laminar." They indicated that all 2D and many 3D textiles can be considered to act as laminates, such that the majority of the fibers are arranged in-plane while only a moderate amount of through-thickness reinforcement is employed in the textile structure. Besides, they define "nonlaminar" textiles as the textile structures possessing fibers equally arranged along the three axes of a Cartesian system. Nonlaminar textiles are frequently employed in complex part geometries since they can resist considerable triaxial loads.

A large family of fabrics is produced either by weaving or stitching bundles, or "tows" of fibers together. The cross-section of these tows is usually elliptical. The crosssectional width and thickness of tows are of the order of millimeters. Another large group of preform fabrics comprises "chopped" and "continuous strand" random mats, which are typically made of low cost E-glass fibers are cheaper than woven and stitched fabrics, and are used for low-strength applications. These fabrics are manufactured by using small tows (approximately 100 fibers) and have a structure, which is more random in nature than woven or stitched fabrics. Random mats are typically isotropic in their structural and flow properties, while it is often not the case for the stitched or woven fabrics. Fiber tows can also be formed into 3-D shapes by means of braiding and weaving techniques.⁷³

Breitigam and Stark⁷⁵ have listed the advantages and disadvantages of some of the common RTM fibre reinforcement forms, as shown in Table 2.7.

Reinforcement Forms	Advantages/Disadvantages		
Continuous strand mat	Good formability, wash resistance, high bulk factor, high part fill-out, uses glass fibers		
Woven roving / fabric	High strength (biaxial), good formability		
Unidirectional roving / fabric	High strength (unidirectional), high stiffness, good formability		
Chopped-strand mat	Low formability, low wash resistance, low cost, high bulk factor, uses glass fibers		
Preforms	Highly complex forms possible, high initial cost, little forming / handling necessary		
Veils / surfacing mats	Good surface quality, wear resistance		

Table 2.7 Characteristics of RTM reinforcement forms.⁷⁵

The architectures of the most frequently employed textile preforms of LCM processes are provided in Figure 2.13.

In a review paper of the NASA textile composites research, Poe *et al*⁷⁹ have provided detailed discussions about the application of textile composites to primary structural components, test methods to measure material properties, mechanics methodologies to

forecast textile material response, experimental techniques to determine compaction and permeability behavior of textile preforms, and analytical methods to predict resin flow in textile preforms.



Figure 2.13 The architecture of major fabric types employed in LCM processes.^{73, 79}

Table 2.8 illustrates the application potentials of the most commonly used textile materials for the high technology applications. Each of these textile materials is certainly designed to satisfy specific needs. Among all of these textile forms, the ones which attracts the most interest are multiaxial warp knitting for large area coverage, triaxial braiding for complex structural shapes and stitching for improved damage tolerance.

Textile Type	Advantages	Limitations
Low Crimp Uniweave	High in-plane properties Good tailorability Highly automated perform fabrication process	Low transverse and out-of-plane properties Poor fabric stability Labor intensive ply lay-up
2-D Woven Fabric	Good in-plane properties Good drapability Highly automated perform fabrication process Integrally woven shapes possible Suited for large area coverage Extensive data base	Limited tailorability for off-axis properties Low out-of-plane properties
3-D Woven Fabric	Moderate in-plane and out-of-plane properties Automated preform fabrication process Limited woven shapes possible	Limited tailorability for the off-axis properties Poor drapability
2-D Braided Preform	Good balance in off-axis properties Automated preform fabrication process Well suited for complex curved shapes Good drapability	Size limitation due to machine availability Low out-of-plane properties
3-D Braided Preform	Good balance in in-plane & out-of-plane properties Well suited for complex shapes	Slow preform fabrication process Size limitation due to machine availability
MultiAxial Warp Knit	Good tailorability for balanced in-plane properties Highly automated perform fabrication process Multi-layer high throughput material suited for large area coverage	Low out-of-plane properties
Stitching	Good in-plane properties Highly automated process provides excellent damage tolerance and out-of-plane strength Excellent assembly aid	Small reduction in in-plane properties Poor accessibility to complex curved shapes

Table 2.8 Application potentials of textile-reinforcements for ancial structures.	Table 2.8 Applic	ation potentials of t	extile-reinforcements	for aircraft	structures. ⁷⁹
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Molding and Tooling

Resin transfer molding requires a matched mold set. Generally, RTM molds can be considered to possess five major parts: the injection port(s), the air vent(s), the guide pins, the mold cavity, and the gasket. The injection port(s) enable resin to access to the mold and the air vent(s) function as a means for removing volatiles and trapped air from the part. The guide pins ensure the proper alignment of the mold halves. The mold cavity imparts the desired shape to the part, while the gasket seals the mold and prevents leaking of the resin out of the mold.

Becker⁸⁰ indicated that the mold must preserve its dimensional stability such that it should stay within specified tolerances. It should also maintain its mechanical integrity under the temperature, chemical and pressure conditions, necessary to make the parts.

Breitigam and Stark⁷⁵ reported the typical materials employed in RTM tooling, as shown in Table 2.9. All of these material types can be used effectively in RTM so long as the appropriate tooling materials are chosen depending on the durability required to achieve the economically necessary product volume and the performance requirements of the part.

The process of injection and the applied injection pressure are one of the most prominent factors in the success of RTM parts such that they can have a harmful effects on the performance of the parts if the procedure leads to a considerable wash or an actual damage to the preform structure or/and material itself. The simplest way to guarantee complete wet-out of the preforms is to gate the mold successfully. The inlet port(s) should be correctly designed so that the resin system could wet all of the reinforcement. Dry spot regions can generally stem from bypassing a part of the reinforcement at the inlet of the mold, as the resin system will not flow backwards. By the same token, reasonable placement of the resin outlets is essential for successful bleeding of air from the mold so that the flow of resin takes place in such a way that air cannot be trapped in the mold.⁷⁶ Hence, a good design of the mold is critical for a successful part as indicated by many researchers.^{76, 80, 81} If the mold is not properly designed, then the resulting part will probably not have the desired mechanical properties. To illustrate, when the coefficient of thermal expansion of the mold material is different than that of the composite material, the mold and the composite part will expand or contract differently during the heating and cooling of the mold. Thus, the dimensions of the mold have to be adjusted to compensate with that of the composite part so that the dimensional tolerances of the part can be attained.⁷³

Cai,^{82, 83} Hansen⁷⁶ and Springer *et al*⁸⁴ proposed simple models for determining the locations of injection port(s) and vent(s). Hansen⁷⁶ found that resin is inclined to bypass some areas of reinforcement when the flow path of the resin is arranged in such a way that it flows into a configuration with increasing volume. This phenomenon is also a function of fiber volume fraction, resin flow rate and resin injection pressure. In the same paper, Hansen also concluded that when the gates are positioned in such a way that the flow of resin is symmetrical around the vent ports and the air volume left in the reinforcement decreases, a compression effect is induced. This effect will let the

remaining air sweep out of the part. Both Cai^{82, 83} and Hansen⁷⁶ pointed out the fact that the vent ports have to be positioned to draw the resin through the sections of the part that are difficult to wet out. They recommended that it is best to locate the vent ports at the stagnation points where the resin cannot flow by itself. This will both permit the pressure to build up in the mold and force the resin elsewhere in the part where pressure drop is higher. All venting ports should have the capability of being sealed after the bleeding operation is completed. This will lead to the resin to gel under pressure, thus restricting further the chances for the formation of voids in the finished part.

Tooling materials	Characteristics	Applications
Metals	Excellent mechanical strength, chemical resistance, durability, dimensional stability, surface finish, difficult to handle due to weight, expensive machining, requires durable mold	High volume, elevated temperatures (50 to 600°C)
Ceramics	Excellent mechanical and chemical properties, dimensional stability, problems with surface finish, cracking, low thermal conductivity, manufacturing to close tolerance specifications	Extremely high temperatures (Over 1000°C)
Composites	Easy to manufacture to tolerance specifications, low density, low processing cost, excellent chemical and mechanical properties, shorter life cycle than metals, difficult to maintain surface finish	Low to intermediate temperatures. (From room temperature to 180°C)

Table 2.9 Typical characteristics of RTM tooling materials.⁷⁵

Cai^{82, 83} and Hansen⁷⁶ have demonstrated that the inlet(s) and outlet(s) should be arranged in such a manner that possible shorter flow paths can be achieved. Furthermore, Cai^{82, 83} has emphasized that the resin flow direction should be arranged from larger sides

to smaller sides, or from outside perimeter to the inside, assuring a rapid reduction of the unoccupied volume. Cai's study has also indicated that line gates can ensure better results than the point gates. When a constant pressure boundary condition at the inlet is approached during a real RTM process, significant reductions in the mold filling times can be made possible with the aid of all of the above-mentioned arrangements.

2.5.2 Analysis of Mold Filling in RTM

A complete saturation of the preform during RTM is essential for successful manufacturing and final performance of the composite parts. Without any doubt, one of the most critical steps in the RTM process is the mold filling stage which depends on a variety of parameters, the most important ones being the part geometry, injection pressures or flow rates and location of the injection gates. During filling of a RTM mold, two issues require special attention: the resin should fill the entire preform and the mold filling should be accomplished in the shortest possible time.

Numerous simulations⁸²⁻⁸⁶ have been developed in the literature to model the flow of resin through fiber preforms. As the fluid advances in the mold, it exchanges heat with the fibers along its path. Middleton, *et al*⁸⁷ have developed an exact model for the mold filling stage comprising both the heat and force balance. They assumed that chemical reactions during flow could be neglected. The correlation between the fluid mechanics and heat transfer was found to be in the resin viscosity, since it is a function of temperature.

Fluid flow through a fibre packed mold can be thought of as equivalent to the flow through porous media or packed columns. Many investigators have agreed on the use of Darcy's law to describe mold filling phenomena during RTM. Thus, the simplest approach to the mold filling problems in RTM can be taken by considering the advancement of the resin being governed by Darcy's law, as follows:

$$q = \frac{Q}{A} = -\frac{K}{\mu} \cdot \nabla P \tag{2.1}$$

where q is the superficial velocity or the volume averaged "Darcy velocity" or the average flow rate (m/sec), Q is the total amount of the flow (m³/sec), A is the cross-sectional area (m²), K is the permeability tensor of the preform (m²), μ is the fluid viscosity (Pa.sec), ∇P is the pressure gradient or the pressure drop per unit length (Pa/m).

Darcy's law makes use of the following significant assumptions: impregnation or mold filling phase being represented by an incompressible fluid (i.e., constant density assumption); constant viscosity ($\mu = \mu_0$) during filling; no heat transfer by convection; negligible effects of lateral heat conduction during both impregnation and cure; same temperature of upper and lower mold halves; negligible inertial effects; uniform flow fronts and temperature through the laminate thickness during impregnation; constant mold temperature during impregnation and no curing reactions until complete impregnation of the preform by resin.

The Darcy relationship applies to Newtonian fluids. However, there are various forms of this equation applied for different types of fluid systems. For instance, Straus *et al*⁸⁵ presented the following analysis for rectilinear flow of an incompressible fluid, by making a generalization of Darcy's law.

$$\frac{\partial}{\partial x}h \cdot \overline{V_x} + \frac{\partial}{\partial y}h \cdot \overline{V_y} = 0$$
(2.2)

where h is the mold thickness, $\overline{V_x}$ and $\overline{V_y}$ are the gapwise average in-plane velocities, expressed as:

$$\overline{V_x} = \frac{1}{h} \cdot \int_0^h V_x \cdot dz \tag{2.3}$$

$$\overline{V_y} = \frac{1}{h} \cdot \int_0^h V_y \cdot dz$$
(2.4)

Most RTM processes cope with shell-like parts which have thickness dimension much smaller than the other dimensions. Hence, the flow can be modeled as twodimensional and the flow in thickness direction can be ignored. As a result, in most of the RTM studies, the relationship between pressure and flow rate is described by a two dimensional version of Darcy's law with anisotropic permeabilities.

Cai⁸³ proposed closed form solutions for RTM of several simple mold shapes such as rectangular, circular and trapezoidal geometries. In his simplified mold filling analysis models, he expressed the type of resin flow through a very simple one-dimensional composite structure of a long circular rod by following Darcy's law. This simple long

circular rod has the inlet and outlet at its two ends, as illustrated in Figure 2.14. He derived the continuity condition assuming no preform movement during the flow process.

$$q = \frac{dx}{dt} \tag{2.5}$$

where he presumed the inlet is at $x = x_0$ and the outlet is at $x = x_f$. Furthermore, he set the initial condition as x = 0 at t = 0 and the boundary condition at the inlet, $x_0 = 0$ being either a prescribed pressure p_0 , or a prescribed flow rate q_0 .



Figure 2.14 Simplified one-dimensional resin flow in RTM process.

In the real RTM applications, the resin viscosity, μ , is most of the times dependent on temperature, time and the degree of cure of the resin material and preform permeability could change at different positions of the mold or be time dependent if the resin flow

pushes the preform to move. For the simplification of his solutions, Cai⁸² assumed both viscosity and preform permeability are constant. This assumption could probably be reasonable if the resin is much longer than the pot-life the RTM process cycle time and if woven or braid preforms with high fibre volume fractions are employed. Thus, he derived the following solutions for the rectilinear flow conditions, as described in Figure 2.14, at different inlet boundary conditions:

Prescribed flow rate at the inlet: q_0 , at $x = x_0 = 0$. For this case, $p_0 = p_0$ (t), but p = p(x, t). Then, Equation (2.5) is used to determine the wet length, as:

$$x = q_0 . t$$
 (2.6)

It is known from Equation (2.1) that the pressure gradient is constant, leading to the pressure distribution be linear. Cai^{82} assumed a zero gage pressure at the flow front region, which in turn brought about the resultant pressure built-up at the inlet to be linearly proportional to the wet length (x) or mold filling time (t). Then, the inlet pressure is obtained as:

$$p_{o} = \frac{q_{0} \cdot \mu}{K} \cdot x = \frac{q_{0}^{2} \cdot \mu}{K} \cdot t$$
(2.7)

Then, as the wet length approaches the outlet position, x_f , the mold filling time (t_f) is derived as:

$$t_f = \frac{x_f}{q_0} \tag{2.8}$$

Prescribed pressure at the inlet: p_0 , at $x = x_0 = 0$. For this case, $q_0 = q_0$ (t) = q (t). Besides, Cai⁸² presumed the pressure gradient to be constant over the wet length (x) at a given time, giving rise to:

$$\frac{\partial \mathbf{P}}{\partial \mathbf{x}} = -\frac{\mathbf{p}_0}{\mathbf{x}} \tag{2.9}$$

Then, by substituting Equations (2.5) and (2.9) into Equation (2.1) and integrating, he obtained the average flow rate and the wet length equations, as follows:

$$\mathbf{x} = \sqrt{\frac{2 \cdot \mathbf{K} \cdot \mathbf{p}_0}{\mu}} \cdot \mathbf{t} \tag{2.10}$$

$$q = \sqrt{\frac{K \cdot p_0}{2 \cdot \mu \cdot t}}$$
(2.11)

The filling time in this case is found to be:

$$t_{f} = \frac{x_{f}^{2} \cdot \mu}{2 \cdot K \cdot p_{0}}$$
(2.12)

Guceri and Coulter⁸⁸ also investigated the 2-D RTM flow process and developed a computer simulation program, TGMOLD, that included all of the physics involved, such as heat transfer, resin flow and curing reactions. Their model was also based on the Darcy's law. They employed both flow rate and pressure inlet boundary conditions. They

transformed irregular mold shapes into rectangular computational domains by means of a boundary fitted coordinate system.

Molnar, Trevino and Lee⁸⁹ developed a model for controlling the RTM process parameters. Their results indicated that the pressure buildup increased with time during the mold filling process under a relatively constant flow rate inlet boundary condition.

Advani, et al^{90} and Wadsworth and Brosius⁹¹ reported in their studies that a precise control over narrow ranges of many of the process variables is essential for achieving high quality products in RTM. These variables basically comprise the proper choice of preheated resin systems, mold temperature, resin supply pressure and fiber volume fraction. All of these variables are found to be interdependent. Wadsworth and Brosius⁹¹ indicated that keeping the resin components at elevated temperatures is commonly preferred so that they can be easily pumped and mixed together. By the same token, it is usually desirable to maintain the mold at somewhat elevated temperature so that the resin viscosity can stay low enough during the mold filling. This will diminish the back pressure and improve wet-out of the preform. Furthermore, exclusive of the vinyl ester resins, aerospace resins in general entail the addition of heat to attain sufficient green strength for demolding. The drawback for this is that elevated temperatures also accelerate the curing reactions, leading to the build up of viscosity. Hence, the knowledge of resin rheology in RTM is essential when selecting the mold temperature. It should let the resin viscosity stay at a minimum value until the complete filling of the mold and then let the resin react sufficiently fast to minimize cure time. The ideal mold temperatures for

a resin vary with the part design, thanks to the differences in the mold filling time. Wadsworth and Brosius⁹¹ also pointed out that mold pressures during RTM, in most cases, should be kept as low as possible to reduce the clamping requirements. Moreover, a minimum back pressure should be retained so as to assure a consistent flow front and avoid encircling of air pockets. A proper choice of resin viscosity, vent sizing and fibre volume fraction can control back pressures. Selection of minimum pressure is crucial between the time of completion of mold filling and resin gelation. This ensures the success of RTM process based on the concept of low cost molds as well as good surface quality of the finished products. Besides, high injection pressure during the molding is apt to induce the movement of weakly bound reinforcements, a phenomenon known as *"fiber wash"*. The fiber volume fraction is indicated to have a two-folded effect on the mold filling time such that it acts both as a reservoir of heat and provides resistance to resin flow. The mold filling time for the bulk resin flow to penetrate the overall preform generally increases with an increase in the amount of fiber reinforcement.

2.5.3 Preform Permeability

Permeability measurements are essential to characterize the resistance of the fabrics to the flow. Permeability is primarily a function of fabric architecture, fiber volume fraction or porosity and shearing. In the literature, there have been many attempts to measure and anticipate the permeability of several fabrics since it is one of the most critical parameters in RTM.⁹²⁻¹⁰⁰

Trochu *et al*⁹² proposed a concurrent method for low-cost permeability estimation. The method employed a rectangular mold for the numerical determination of the principal permeabilities. Their method, called Concurrent Permeability Measurement Procedure (CPMP), enabled a simultaneous characterization of the permeability of fibrous materials by using all of the available experimental data. They also assessed and discussed the accuracy of CPMP by the introduction of two parameters, the maximum injection pressure and the minimum injected length, so as to control the consistency of their experimental set-up and the data processing procedure.

In most of the studies available in the literature,⁹⁵⁻¹⁰⁰ it is indicated that the greater the value of permeability, the faster the resin penetrates through the fibrous reinforcement. Moreover, permeability is thought as an intrinsic property of a fabric at a given fiber fraction. The permeability tensor reduces to a single scalar in the case of isotropic fabrics. The fiber mats are usually anisotropic since the fiber orientations may vary and the stacking sequence of the mats may alter. Hence, as it is stated in all of these studies that it is crucial to determine the principal permeabilities K_1 , K_2 , K_3 of the reinforcement, for the full characterization of reinforcement materials used in RTM.

Dave and Houle,⁹⁵ Lee, *et al*,^{96, 97} Peeters and Verheus¹⁰¹ and Advani and Bickerton¹⁰² have investigated a variety of permeability measurement techniques. Many of these studies have converged on the idea that the transverse permeability (K₃) could be neglected and the evaluation of only the in-plane permeabilities (K₁ and K₂) could be

sufficient in most of the RTM applications since the molded parts are generally, thin shells.

Advani and Sozer¹⁰³ indicated that the permeabilities at a certain positions in the mold might alter for many reasons. When the preform is positioned improperly in the mold, especially around the edges, the permeability will be higher around the edges than in the bulk and this will lead to a preferential path for the resin to flow faster around the edges, leading to "*racetracking effect*."^{100, 102, 104} If the mold has a compound curvature over which the preform is draped, the orientation of the fiber tows will modify again resulting in the alteration of permeability locally owing to the "*draping effect*."^{105, 106} The defects in the stitches of the preform or unequal compaction of the preforms could also bring about variations in the preform permeability.¹⁰⁶

Advani and Sozer¹⁰³ also reported that some of these factors affecting the permeability could be foreseen. Rangatnathan *et al*,¹⁰⁶ and Bickerton *et al*¹⁰² have shown that the variations in preform structure modify the flow resistance and thus result in disturbances in the way the mold fills. For low technology fabric styles, such as continuous strand random mat, considerable density variations might be seen throughout a single roll, and possibly from one side of the roll to the other. The LCM preforms could have complex geometries with a variety of fabric styles, varying volume fractions, and containing inserts. Steenkamer¹⁰⁷ indicated that both the production of a preform in a very repeatable manner and the prediction of permeability become more difficult as the complexity of the preform increase.

Luce *et.* al^{108} reported that "*nesting*" could be another cause of momentous variations in the preform permeability. The size and shape of flow channels between fiber tows will be influenced by the relative horizontal positioning of each fabric layer. This leads to significant changes in the permeability from part to part.

Lee, *et al*⁹⁴ reported that there exist two main methodologies for the measurement of in-plane permeabilities of woven cloths. Each used a different type of fluid flow model, namely rectilinear flow and radial flow. The permeability measurements, derived from the rectilinear flow, are mainly influenced by two factors: the side-edge effects and the assumption that the in-plane projection of flow front forms a straight line along the cavity width.

In general, the measurements of bulk permeability are carried out by conducting 1-D or 2-D experiments with the aid of either a constant pressure boundary condition or a constant flow rate boundary condition.¹⁰³ In the literature, various techniques for the measurement of permeability are employed either a simple radial or rectilinear flow in a fibrous medium using a non-reacting test liquid.

Tomlinson *et al*⁸⁵ conducted experiments of unidirectional flow inside a rectangular cavity and measured the preform permeabilities along the two principal directions. Their experimental set-up, used for the measurements of permeability was similar to the one schematically drawn in Figure 2.15. They utilized a gear pump for obtaining different flow rates during their experiments. The flow rate was measured by a graduated cylinder

over 30 seconds. The difference between two pressure transducers was then recorded for different flow rates as depicted in Figure 2.15.⁸⁵ Finally, they obtained the permeability values from the slopes of the plots of Q/h.w versus $\Delta P/\mu L$ values.



Figure 2.15 Schematic of the set-up used for in-plane permeability measurements.⁸⁵

Peterson and Robertson¹⁰⁹ have indicated that both the flow characteristics of the resin in RTM applications and reinforcement permeability are manipulated by a set of parameters including; fiber volume fraction, fiber diameter, roving geometry, fiber orientation, and pressure drop across the mold flow path.

Lee *et al*⁹⁶ characterized the fibrous reinforcement mats in RTM applications by measuring the mat permeability and compressibility. They used two or more different fiber types (random, bidirectional and unidirectional glass fiber mats) in the mat stack so

as to induce permeability, porosity and compressibility variations. Then, they measured the flow pressure and calculated the in-plane permeabilities of three different types of mats by observing the progress of the flow front of a nonreactive fluid in a clear acrylic mold. During their experiments, a hydraulic cylinder was loaded with DOP-oil (a nonreactive fluid) by means of a rotary pump and operated at a constant speed by the motion of an Instron machine. By altering the closing speed of the Instron crosshead, various fluid flow rates were obtained. A pressure transducer situated near the inlet was hooked up to a chart recorder. Then, the pressure measurements for K_x and K_y were made by positioning the fiberglass mats in the mold cavity without covering the inlet and outlet, thus permitting a unidirectional flow in the machine direction.

Furthermore, the fiber reinforcement mats were observed to exhibit viscoelastic compression behavior. This was attributed to the fact that, as the reinforcements were compressed to a given thickness, the pressure required to preserve that thickness decreased logarithmically to a pressure as much as 40% lower than the peak pressure attained at the instant compression. All of the plots of steady pressure versus porosity for three types of fibre mats clearly pointed out that as the compression pressure raises, the porosity of each of these mats declines. As a result, in-plane permeabilities were reported to reduce.

Yalvaç *et al*⁹³ and Wang *et al*⁹⁴ have found similar results for the effect of compressibility of the fibers on the permeability of fabric reinforcements. Both of these groups used the same type of measurement devices and non-reactive fluids, similar to the

ones used in the study of Lee *et al*⁹⁶ to measure the permeability variations in various types of fiber reinforcement materials. Likewise, the permeabilities of the reinforcements were determined from the changing slope of pressure differentials as a function of flow rate. The two research groups^{93, 94} have converged on the fact that as the pressure on the fiber reinforcements increases, the interstitial spaces become smaller, which augments the resistance to flow and thus declines the permeability.

Williams *et al*⁹⁹ pointed out that the distribution of porosity has a considerable effect on the permeability. Factors that can influence the distribution of porosity comprise fibre stiffness, number of fibres in the fibre bundles, degree of misalignment and the presence of sizing or any other textile aids used for bonding filaments together and facilitating movement. Williams *et al*⁹⁹ also explained the variations in the permeability of fibre reinforcements (*K*) as a function of fiber volume fraction and fiber diameter by means of the *Kozeny-Carman* equation:

$$K = \frac{d_f^2}{K_K} \cdot \left(\frac{\phi^3}{\left(1 - \phi\right)^2}\right)$$
(2.13)

where d_f is the diameter of the fibre, K_K is the *Kozeny-Carman* coefficient, and ϕ is the porosity.

The porosity is defined as the maximum volume of resin that a porous material can contain divided by the total volume, namely:

$$\phi = 1 - V_f \tag{2.14}$$

It was stated that the control of reinforcement permeability could be achieved by selecting proper type of reinforcement. In fact, permeability of the reinforcement was observed to be a strong function of fiber volume fraction and diameter.

By the same token, Gauvin *et al*¹⁰⁰ derived a more comprehensive equation for porosity. By this equation, porosity is also related to the fabric areal weight ξ , i.e., the mass of fabric per unit surface area, as follows:

$$\phi = 1 - \frac{n \cdot \xi}{t \cdot \rho_{solid}} \tag{2.15}$$

where t/n is the thickness of one ply, and ρ_{solid} represents density of the fibers. The values of ξ and ρ_{solid} are usually supplied by the manufacturer.

Yalvaç *et al*⁹³ measured the angle-averaged effective in-plane permeability in the principal directions of the 8-harness graphite fiber mat using the radial flow method. Their permeability was observed to be low at first and then greatly improved when the porosity surpassed the value of 0.45. A large scattering in the experimental data was noticed when the preform porosity exceeded the value of 0.45. This was attributed to two main reasons, namely; the woven structure and the low compressibility of the 8-harness graphite fiber mats. It was reported that⁹³ the 8-harness graphite fiber mat was easily

deformed thanks to its loose fiber structure and this resulted in large variations in the permeability, especially when the porosity was greater than 0.45.

Yalvaç *et al*⁹³ also underlined another important result indicating the in-plane permeability values decline as the number of fibre layers increases. This was ascribed to the fact that fibre cloth is effective in intermeshing together when compressed in the mould, which in turn, reduced the interlaminar pores introduced by each layer.

Wang *et al*⁹⁴ determined the permeability of the various fabric reinforcements with a very similar experimental set-up to that of Yalvaç *et al*⁹³ The pressure and flow rate relationship from both radial and unidirectional flow measurement methods was used to calculate the values of the permeability. They also estimated the edge flow effect by means of unidirectional flow measurement technique.

It is obvious from all of the available studies in the literature that the flow modeling, hence the mold filling stage in RTM process is extremely sensitive to the preform porosity and the resulting permeability.

2.5.4 Analysis of Resin Flow Phenomenon

In this section, some primary ideas and the governing equations of the resin flow in RTM will be discussed using the mass and momentum balance equations as well as the results from porous media literature. A special emphasis will be given on the studies of flow through woven fiber mats, since these fabrics are employed in this research. The optimization of the RTM process necessitates the derivations and applications of correct mathematical models and numerical simulations of the injection, mold filling and curing phases in RTM. The recent literature reveals the development of several simulations most of which, are solely based on isothermal filling flows, while the others incorporate heat transfer and chemical reactions.^{89, 110, 111} Even though the balance equations for the homogeneous flows are universally accepted, Tucker and Dessenberger¹¹² indicated that there is still no worldwide concurrence on the balance equations for porous media. All of the available simulations employ the theory of flow through porous media for the treatment of the flow phenomenon in RTM. Moreover, while the derivation strategies of the mathematical models and simulations could vary, all of them utilize the balance equations for mass, momentum and energy.

Several studies modeled the flow of resin through the fiber filled mold as a singlephase flow of a viscous liquid through a porous medium behind a progressing resin front. The preliminary assumption supporting this statement by several researchers is based on the fact that the medium behind the front is considered as *fully saturated*. Since the resin viscosities employed in RTM can be as low as 200 centipoise, the resin speed usually does notsurpass a few centimeters per second, causing the local Reynolds number to be much smaller than unity.

For this reason, the RTM flows can be first modeled by the macroscopic equation of continuity:¹¹²⁻¹¹⁴

$$\nabla \cdot \mathbf{v} = 0 \tag{2.16}$$

where \mathbf{v} is the phase averaged velocity, can be defined by the Darcy's law, as:

$$\mathbf{v} = -\frac{\mathbf{K}}{\mu} \nabla \cdot P \tag{2.17}$$

where K is the permeability of the medium in the form of a tensor, μ is the resin viscosity and *P* is the intrinsic phase averaged pressure. During the resin flow, the resin undergoes to exothermal chemical reactions as a result of curing. As this heat release will influence the flow through the temperature dependent viscosity, both energy and chemical species transport equations are also solved concurrently with the Eqns. 2.16 and 2.17.¹¹²

As emphasized in the previous section, the permeability K is the most significant material parameter in RTM due to its sensitivity to the fiber packing. Parseval *et al*¹¹⁵ measured permeability by substituting the measured pressure gradient and flow rates in Eqns. 2.16 and 2.17 through some transient mold filling experiments. In their flat rectangular mold experiments, Parseval *et al*¹¹⁵ recorded the change in inlet pressure as a function of time under constant flow rate conditions. They used two basic types of reinforcements: random and woven fiber mats (including the braided or stitched fiber mats) during the RTM experiments. The theoretical inlet pressure rises linearly with time as predicted by Eqns. 2.16 and 2.17. However, as illustrated in Figure 2.16, Parseval *et al* noticed that while the inlet pressure histories for the random mats were linear and can be

well predicted by Eqns. 2.16 and 2.17, the pressure histories for woven mats were nonlinear and yet can not be justified by these equations.



Figure 2.16 A schematic describing the inlet-pressure history during 1-D flow experiments, where a test liquid is injected at a constant rate from the left side of a flat rectangular mold.¹¹⁶

In the same study, Parseval *et al*¹¹⁵ also observed that an important region behind the flow front was partially saturated, as shown in Figure 2.17. This was in contradiction with the key assumption of fully saturated flow behind the front, assumed in Eqns. 2.16 and 2.17. For this reason, they developed a two-stage permeability model, in which the value of parameter rises as a function of distance from the resin front, and thus is capable of predicting the drooping pressure histories for woven mats successfully. However, this model has two drawbacks:

- The change of permeability behind the front was not explained since it is only a function of the geometry of fiber arrangement in a fibrous porous medium.
- It could not elucidate the partial saturation of fiber mats behind the front.

Pillai^{19, 21}later attempted to explain this inconsistency by means of the theory of twophase flow in porous media, but failed to predict the indispensable nonlinearity of the pressure histories for woven mats.



Figure 2.17 Appearance of an unsaturated flow region behind the flow-front during a point injection in a woven fiber mat. Regular pattern of dark and light spots in the unsaturated or partially saturated region is due to periodicity in the structure of the mat.¹¹⁶

Pillai¹¹⁶indicated that a new model that can allow for the structural differences between the random and woven fiber mats, and thus the resultant difference in microflow processes was required due to heterogeneous nature of the woven fiber mats. The woven fiber mats are woven out of fiber tows or bundles containing thousands of fibers. As it was illustrated in Figure 2.13, the woven fiber mats are locally heterogeneous owing to the existence of large gaps between the fiber tows. The random mats, on the other hand, are manufactured by a disorganized placement of fiber strands such that their packing in the molds enable a homogeneous porous medium. Pillai¹¹⁶ mentioned that the gaps between the fiber tows in woven fabrics could stay even after the fabrics are stacked and compressed in LCM molds. This is why when modeling the woven fiber mats, he classified the flow into two basic flow regions: the tow region with high flow resistance and the gap region with low flow resistance, laying next to each other. Pillai¹¹⁶ named the woven fiber mats as a *dual-scale* porous medium due to the two to three orders of magnitude difference between the widths of flow channels in the two regions, as depicted in Figure 2.18.

Pillai proposed a two-layer model elucidating the unexpected flow behavior in woven fiber mats, where the tow and gap regions alternate in the flow domain and are arranged in a line with the flow direction.^{19, 117} Pillai²⁸ assumed that the fluid pressure in the gaps surrounding the tows would force the fluid into tows as soon as the macroscopic flow-front exceeds a certain point. Advani and Pillai²⁸ indicated that the capillary suction pressure aided this movement of the fluid and microfront (i.e. liquid front in the tows). They developed a simple model via Darcy's law. As a result of a rigorous mass balance, their model led to the following equation of continuity:

$$\nabla \cdot \mathbf{v} = -S \tag{2.18}$$

where *S* is the sink function, defined as the rate of liquid absorption per unit volume in the dual-scale medium.



Figure 2.18 A dual-scale porous medium created by stacking woven fiber mats consists of two regions of different length scales: the characteristic width $l (\sim 10 \ \mu m)$ of flow channels within the fiber tows and the width $L (\sim 1 \ mm)$ of gaps surrounding the tows.¹¹⁶

Advani and Pillai²⁸ did not derive the momentum balance equation rigorously and used the one for the single scale medium in the form of Darcy's law in Eqn. 2.17. The application of this equation of continuity along with the Darcy's law in a rectangular mold filled with woven mats enabled them to successfully predict the drooping inlet pressure history. The same equations were also capable of elucidating the discrepancy in the inlet pressure histories for random and woven mats in the radial injection case.^{19, 118} Thus, the partial saturation behind the flow front was then explained via the degree of

impregnation of tows. Parnas and Phelan¹¹⁹ and Binetruy *et al*¹²⁰ also investigated the anomalous pressure drops and predicted void distributions in woven fiber mats by developing a similar model derived from the concept of dual-scale porous media.

In a following paper, Pillai¹¹⁶ made a rigorous analysis of the Eqns. 2.17 and 2.18 for isothermal flows in dual scale porous media and derived the governing equations of flow through woven mats, by means of the well-established volume averaging method as adapted to such media. The averaging theorems have been very widely used in the literature when deriving transport equations for single-phase flows in the single scale porous media.^{112-114, 121-124} They were then modified for the dual-scale fractured porous media applications.^{114, 125, 126} In the literature, the studies on the dual-scale media is usually limited to the transport equations for *saturated* (or single phase) flow and thus they can not be directly used to model the *unsaturated flow* in fiber mats owing to the concurrent flow of more than one phase (liquid, air) through such a medium.

Pillai¹¹⁶ used the volume averaging method to depict the flow of resin in the gaps between the fiber tows by deriving a set of the mass and momentum balance equations, applicable to model the unsaturated flow in woven fiber mats. For this purpose, he first showed the role of distribution of gaps in such media, which was missed earlier by the simpler models, by deriving the most general type of continuity equation (Eqn. 2.18) for a two-layer representation of the dual-scale porous media. He then derived the momentum balance equations for both saturated and unsaturated flows in such a medium by incorporating some additional terms that might be significant under certain circumstances.¹¹⁶

As it can be clearly seen from Figure 2.17, there exists an unsaturated region near the flow-front, indicating a two-phase flow in a dual-scale flow. Despite all the progresses in the field of flow through porous media, the multiphase flow phenomenon in porous media has not yet been fully understood. So as to successfully model the two-phase flow in the dual-scale porous media, a clear portrayal of the relevant flow regime is essential. Patel et. al.¹²⁷ conducted experiments on the flow of resin in a rectangular mold. Their results have shown that when the resin progress through the gaps faster than the wicking process inside the tows, the entrapment of air inside the tows is observed, as shown in Figure 2.19. Other studies¹²⁸⁻¹³⁰ indicated that smaller bubbles in the gap-flow could be seen as a result of the leakage of the air bubbles that are trapped inside the tows, through the skin of the tows. These air bubbles in the gap can move easily with the flowing liquid and don't influence the overall flow to a great extent due to two basic reasons: the viscosity of air is much smaller than that of the viscous resin and the air volume is less than 5% of the overall liquid volume.^{127, 129} Pillai¹¹⁶ pointed out that the influence of air bubbles on the hydraulic pressure build up in the gaps is trivial and thus could be ignored in the gap flow. However, it is also noteworthy to mention that the formation and the transport of air bubbles could be important in the tows due to its relation to the absorption of liquid by the tows, and its consequent effect on the magnitude of the sink term in Eqn. 2.18.



Figure 2.19: A schematic view depicting the inundation of gaps and tows in a dual-scale porous medium. Much faster movement of resin in the gaps than it is in the tows results in delayed impregnation of the tows, formation of the sink term in the equation of continuity (Eqn. 2.18), and possible formation of air bubbles.¹¹⁶

The fundamental idea of porous media theory is based on *local volume averaging* and the use of average quantities in the field equations. In the literature, many researchers^{19,}^{21, 28, 112-115, 117-122, 124, 131} utilized the single-phase flow in a single-scale porous medium for deriving the governing equations at the macroscopic level by means of the balance equations for several physical quantities at the microscopic level. In the case of the flow through a woven fabric, the medium is made of two phases, solid and liquid. The flow variables are averaged over an *averaging volume*, which should be much larger than the individual size of the pores and particles. This averaging volume is also called as the representative elementary volume (REV) by Bear.^{113, 132} The size of the REV must be
large enough to contain the representative amounts of both phases, but also small enough such that long-range variations don't lead to large fluctuations in the value of any averaged quantity. Pillai¹¹⁶ concluded that this could be guaranteed only when the REV is much larger than an individual pore or particle of the porous medium. Then, he defined the two "*phases*" in the dual-scale porous medium created by woven fiber mats as the *fiber tows* and *the surrounding gaps*. Pillai also assumed that unlike the solid phase in single-scale porous medium, the tows in the dual-scale porous medium contain fluid; solid and air phases while the gaps are utterly filled with the liquid phase. Figure 2.20 portrays an averaging volume for the dual-scale media. Based on the periodic nature of the woven fibrous media (see Figures 2.13 and 2.17), the size of *representative volume* was confined to a unit cell of such a periodic medium containing sufficient number of tows.

Tucker and Dessenberger¹¹² defined the terms "volume average" or "local volume average" or the "intrinsic phase average" as the average including only the points lying in a single phase but averaging over the entire averaging volume. Thus, the phase average of a physical quantity B in a dual-scale porous medium is defined as:

$$\langle B_g \rangle = \frac{1}{V} \int_{V_g} B_g \, dV \tag{2.19}$$

where V is the total volume of the averaging volume, the subscript g relates B with the liquid present in the gaps and V_g is the volume of gaps within the averaging volume.



Figure 2.20 An averaging volume used for averaging the flow variables in a dual-scale porous medium containing fiber tows. The dashed lines within the averaging volume stand for the gap region where "gap" average is calculated. S_{gt} represents the surface area of interface between the gaps and tows within the averaging volume. S_{gg} is the intersection area on the surface of spherical averaging volume as a result passing of gaps through the volume. n_{gt} and n_{gg} are unit normals to surfaces S_{gt} and S_{gt} respectively which point away from the gap region.¹¹⁶

Another important average in a single-scale porous medium is the so-called "gap average" or "intrinsic phase average" or "pore average". It is the average that considers only the points lying within a single phase and averages their values over just the volume occupied by that phase, as follows:

$$\langle B_g \rangle^g = \frac{1}{V_g} \int_{V_g} B_g \ dV \tag{2.20}$$

The two averages are associated to each other as:

$$\langle B_g \rangle = \epsilon_g \langle B_g \rangle^g \tag{2.21}$$

where $\varepsilon_g = V_g/V$ is the gap fraction. ε_g is also a measure of inter-tow distance in a fibrous dual-scale porous medium.¹¹⁶

Pillai derived the macroscopic balance equations for mass and momentum by using the termwise average of the corresponding microscopic balance equations. The volume average of a gradient and the volume average of a time derivative of various quantities are the most commonly employed averaging theorems.

The volume average of gradient of a scalar quantity B_g can be defined in terms of gradient of the volume average as:

$$\langle \nabla B_g \rangle = \nabla \langle B_g \rangle + \frac{1}{V} \int_{S_{gt}} B_g \mathbf{n}_{gt} dS$$
 (2.22)

where S_{gt} is the surface of the tow region inside the averaging volume as shown in Figure 2.20. \mathbf{n}_{gt} is the unit-normal vector on S_{gt} pointed from the gap (g) towards the tow (t) region inside the averaging volume. An analogous result developed for a vector or a second order tensor \mathbf{B}_g can be written as:

$$\langle \nabla \cdot \mathbf{B}_g \rangle = \nabla \cdot \langle \mathbf{B}_g \rangle + \frac{1}{V} \int_{S_{gt}} \mathbf{n}_{gt} \cdot \mathbf{B}_g dS$$
 (2.23)

The volume average of the time derivative of a scalar quantity is:

$$\left\langle \frac{\partial B_g}{\partial t} \right\rangle = \frac{\partial}{\partial t} \left\langle B_g \right\rangle - \frac{1}{V} \int_{S_{gt}} B_g \, \mathbf{u} \cdot \mathbf{n}_{gt} dS \tag{2.24}$$

where **u** is defined as the velocity of the gap-tow interface S_{gt} . The scalar B_g can also be replaced by a vector or a second order tensor B_g .

The averaging theorems have also been widely employed by some other researchers^{125, 126} for the modeling of the fluid transport in fractured rocks. Gray *et al*¹²² reported neat proofs of these averaging theorems. Unlike other proofs^{112-114, 124} which required the "other" phase to be impermeable, and demanded some special restrictions such as non-rotating averaging volume,¹¹² the proofs of Gray *et al*¹²² underlined that the equations are general enough to be used for the porous tows as the "other" phase in a dual-scale porous medium.

Tucker and Dessenberger¹¹² has provided comprehensive discussions, analysis and derivations on the governing equations for mass, momentum, energy and chemical reactions in RTM. For the fluid flowing through the gap region, the mass balance equation at each point is written as:

$$\frac{\partial \rho_g}{\partial t} + \nabla \cdot (\rho_g \mathbf{v}_g) = 0 \tag{2.25}$$

where \mathbf{v}_g and ρ_g are the velocity and density of fluid in the gap region. Applying volume averaging to the above relation, together with the assumption of incompressibility of the resin flow inside the gap region results in:

$$\langle \nabla \cdot \mathbf{v}_{g} \rangle = 0 \tag{2.26}$$

$$\nabla \cdot \langle \mathbf{v}_g \rangle = -\frac{1}{V} \int_{S_{gt}} \mathbf{v}_g \cdot \mathbf{n}_{gt} dS$$
(2.27)

Upon substituting the Eqn. 2.26 in Eqn. 2.23, one can obtain the above Eqn. 2.27. Pillai indicated that the rate of resin absorption by the tows per unit volume corresponds to the right hand side of the above equation. Thus, he referred this equation as the "sink" term S in the macroscopic equation of continuity. Then, with the use of this definition, Eqn. 2.27 is rewritten as:

$$\nabla \cdot \langle \mathbf{v}_{g} \rangle = -S \tag{2.28}$$

where

$$S = \frac{1}{V} \int_{S_{gt}} \mathbf{v}_g \cdot \mathbf{n}_{gt}$$
(2.29)

The Eqn. 2.28, the new continuity equation for a dual-scale porous medium, differs from the Eqn. 2.16, the previous mass balance equation for a single scale porous medium, in that it contains the non-zero term on the right hand side. The Eqn. 2.28 means that the gap flow impedes in the unsaturated region of the dual-scale medium as a consequence of the absorption of resin by the tows. Pillai¹¹⁶ revised Eqn. 2.28 in terms of the gap averages using Eqn. 2.21, as:

$$\nabla \cdot \langle \mathbf{v}_g \rangle^g = -S_g \tag{2.30}$$

where $S_g = \frac{1}{V_g} \int_{S_{gt}} v_g \cdot n_{gt}$ is the rate of liquid absorption per unit "gap" volume. (Note that $S_g = \frac{S}{\varepsilon_g}$.) It is intrinsically assumed in Eqn. 2.30 that the spatial variation of the gap fraction is absent i.e. $\nabla \varepsilon_g = 0$.

Pillai¹¹⁶ modeled the flow of resin through the woven fiber mats in LCM as a dualscale porous media where the gaps and fiber tows are treated as two different phases. The volume averaging techniques were adapted to derive the mass and momentum balance equations for the flow of resin in dual-scale porous media. During the derivation of the balance equations, some important terms such as the sink term S was evaluated. The advantage of treating the tows as a separate phase is that the S term which indicate the interaction of the gap flow with the flow inside the tows can easily be computed by using fluid velocity in area integrals over the gap-tow interface (Eqn. 2.29). According to the results of Pillai's work, the creation of a sink term, S, the rate of liquid absorption integrated over the gap-tow interface due to the delayed impregnation of fiber tows, in the equation of continuity (Eqn. 2.28) is the most significant mathematical effect of the dual-scale nature of a porous medium. Incorporation of non-zero S term in the continuity equation accounted for the drooping inlet pressure history for woven fiber mats.^{19, 117} The dynamic interaction of the gap flow with the tow walls acts together as the drag force during the averaging of the momentum balance equation.

Another important conclusion which can be drawn from Pillai's study is that the tow averaged fluid velocities "through" the tows are neglected and thus the mass and momentum averaging are limited only to the gap region since the resin velocities inside the tows is considered to be negligible as compared to the gap velocities. Moreover, Pillai¹¹⁶ assumed that the sizes of the averaging volumes for the two regions are not related in that the averaging volume for the tow region, treated as a single-scale porous medium, is taken as many orders smaller than the one for the gap region.

2.5.5 Analysis of Heat Transfer and Cure

To ensure complete curing of the resin, RTM molds are generally heated either during or after the mold-filling stage of the process. The temperature and the viscosity of the resin increases as a result of the heat transfer from the mold during RTM. Therefore, heating and injection designs should be carefully performed so that no premature cure takes place which otherwise will cause early gelation of resin. A bad design of the heating systems can also lead to uneven curing, which in turn causes uneven shrinkage and hence warpage of the composite parts. In addition to the heat transfer from the mold to the resin, there will be some extra heat generation as a result of the exothermic cure reactions during RTM. If the resin temperature surpasses a certain limit, polymer degradation could arise. Hence, in addition to the mathematical models for the mold filling, analytical models of heat transfer and resin curing are needed for ensuring a good design of the mold configuration (location of injection gates and vents) and heating system (location and temperature of heating elements).

Heat transfer in flow through porous media has been analyzed by numerous researchers.¹³³⁻¹³⁶ Even though many researchers have examined the role of heat transfer

during RTM processes by several different approaches, Advani *et al*¹³⁷ reported that there is no universal agreement exists on the analysis of the heat transfer in porous media. Similarly, Tucker¹³⁸ reported that coupled analytical models need to be built up by involving not only the flow mechanics, but also the resin rheology (η), heat transfer and cure kinetics (α and d α /dt), as depicted in Figure 2.21.

The available analytical models for heat transfer in LCM applications can be classified into two groups: (i) two-phase models and (ii) local equilibrium models. While the former models include the convective heat transfer between fibers and resin, the latter models ignore. The two-phase models require the heat transfer coefficient between the fiber and the resin which is measured experimentally.



Figure 2.21 A schematic indicating the interrelations among heat transfer, cure reactions and resin flow in RTM.

Experiments revealed that in many LCM processes with slow resin flow, the heat convection between the fiber and the resin is trivial as compared to the other terms of the heat transfer within the mold. Hence, the local equilibrium models, in which the temperature of the preform and the resin are assumed to be equal, are more preferable in many of the numerical simulations. Tucker and Dessenberger¹¹² reported the energy equation for the local equilibrium models, as follows:

$$\left[\left(1 - V_{f} \right) \rho_{r} c_{p_{r}} + V_{f} \rho_{f} c_{p_{f}} \right] \frac{\partial T}{\partial t} + \rho_{r} c_{p_{r}} u \cdot \nabla T =$$

$$\nabla \cdot \left[\left(k_{e} + K_{D} \right) \cdot \nabla T \right] + \left(1 - V_{f} \right) s + \mu u \cdot K^{-1} \cdot u$$
(2.31)

where V_f is the fiber volume fraction, s is the source term due to curing, t is the time, T is the temperature of resin and fabric preform, k_e is effective conductivity which is expressed in terms of fiber and resin thermal conductivities k_r and $k_f^{124} \rho$ is the density and c_p is the heat capacity and K_D is a heat dispersion coefficient. The subscripts r and f refer to the resin and fabric preform, respectively. Advani and Sozer¹⁰³ stated that dimensional analysis studies for mold-filling applications with a small Brinkman number indicates that the viscous dissipation can be neglected. Furthermore, Parnas *et al*¹¹⁹ indicated that the heat conduction in the plane directions and the heat convection in the transverse direction for thin shell-like domains, are also negligible. Nonetheless, both Tucker and Dessenberger,¹¹² and Advani *et al*¹³⁷ mentioned that heat dispersion in inplane directions may be significant. The heat dispersion term K_D is usually neglected in the many heat models¹³⁹ since it is hard to determine the heat dispersion term K_D .

first term on the left hand side of Eqn. 2.31 is written owing to the change in the internal energy of resin and preform, the second term is due to fluid convection in the in-plane directions. Even though the simplified mold-filling model is only two-dimensional, the energy equation is 3-D owing to the presence of the first term on the right hand side of Eqn. 2.31.

Eqn. 2.31 is a second order elliptic partial differential equation in spatial coordinates and first order in time. Boundary conditions on the entire spatial domain and an initial condition for temperature are needed to solve the Eqn. 2.31. While, some applications presumed constant mold temperature during the filling, Advani *et al*¹³⁷ and Advani and Simacek¹³⁹ stated that this is not a very realistic assumption and they proposed a quasisteady-state approach, yielding the following boundary condition:

$$\frac{\partial T}{\partial n} + C_{\rm bc}(T - T_{\infty}) = 0 \tag{2.32}$$

where they defined a boundary condition constant, C_{bc}, as follows:

$$C_{\rm bc} = \frac{1}{k} \frac{1}{1/h_{\rm h} + 1/h_{\rm m} + a/k_{\rm m}}$$
(2.33)

where h_h and h_m are the heat transfer coefficients between the heating fluid and the pipe, and between the mold and resin, respectively, a is the distance between the mold wall and the heating pipe, k_m is the thermal conductivity of the mold material, and T_{∞} is the temperature of the heating fluid. Advani also indicated that another boundary condition can be assigned at the injection gate where the temperature of the resin is usually fixed. Besides, an energy balance can also be carried out at the flow front for considering the convection into the unsaturated region.

Resin Cure Models

Many semi-empirical models prevail for resin cure reactions in RTM. The models proposed by Kamal *et al*¹⁴⁰ are the most commonly used ones for polyester and epoxy resin applications.

The heat generation term due to cure reactions, \dot{s} , appearing in Eqn. 2.31 was also modeled by Kamal *et al*¹⁴⁰⁻¹⁴² The model presumes that the specific energy generated during cure process is in proportion to the rate of the reaction, as follows:

$$s = R_{\alpha} E_{\alpha} \tag{2.34}$$

where R_{α} is the rate of reaction and E_{α} is the heat of reaction. R_{α} is a function of *T* and α which are the temperature and the degree of cure.

$$R_{\alpha} = \left(k_1 + k_2 \alpha^m \right) (1 - \alpha)^n \tag{2.35}$$

where

$$k_1 = A_1 \varepsilon^{E_1/RT} \tag{2.36a}$$

$$k_2 = A_2 \varepsilon^{E_2/RT}$$
(2.36b)
100

where *R* is the universal gas constant. The constants *m*, *n*, A_1 , A_2 , E_1 , and E_2 are material constants for the resin system and should be measured experimentally. Advani and Sozer¹⁰³ also reported a differential equation for the continuity of species, as follows:

$$\frac{\partial \alpha}{\partial t} + \bar{u}_x \frac{\partial \alpha}{\partial x} + \bar{u}_y \frac{\partial \alpha}{\partial y} = R_\alpha$$
(2.37)

The left hand side of Eqn. 2.37 stands for the total time derivative of α while the right-hand side refers to the source term due to the cure reactions.

2.6 Analysis of Rheology of Suspensions

Rheology is the science of deformation (a typical response of solids to an applied strain, elasticity) and flow (a typical response of a fluid to an applied shear, viscosity). The rheology of suspensions copes with how suspensions respond to an applied stress or strain. Masliyah and Liu defined *suspensions* as the dispersions of solids in fluids. Shenoy,¹⁴³ on the other hand, defined a *suspension* as a system in which denser particles, that are at least microscopically visible, are distributed in a less dense fluid and settling is hampered either by the viscosity of the fluid or by the impacts of its molecules on the particles. Suspension rheology doesn't normally correspond to the filled polymer rheology. In fact, it commonly discusses the rheological behavior of two phase systems in which one phase is solid particles; such as, fillers but the other phase is organic liquids or polymer solutions.¹⁴³

Suspensions exhibit quite different behaviors from simple Newtonian fluid flows and this give rise to complexities in their rheological behavior. When the dispersing medium is a Newtonian fluid or acts like a Newtonian one under a given spectrum of shear rates, then the suspension shows Newtonian behavior at low concentration of solids and non-Newtonian behavior at high concentrations. The two main rheological properties of suspensions are the yield stress and viscosity. Yield stress defines when a system is in a solid state and when it's in a fluid state while viscosity determines the ability to flow. The dynamic and transient measurements are also important for concentrated suspensions. Suspensions are often pseudoplastic: as the shear rate increases, the viscosity decreases. This is also known as shear thinning behavior. The viscosity of suspensions in Newtonian or non-Newtonian viscous fluids is described by a variety of theoretical and empirical relationships. The viscosity of both Newtonian and non-Newtonian suspensions is influenced by the characteristics of the solid phase such as shape, concentration and dimensions of the particles, size, distribution and the nature of the surface.¹⁴⁴

Dilute Suspensions

A large number of equations have been developed for estimating suspension viscosities. Most of these equations are empirical extensions of Einstein's equation. In each of these equations, the researchers attempted to describe the mutual relationships between the flow field and the particle motions. In very dilute suspensions, it is commonly assumed that particles never interact. Einstein¹⁴⁵ was the pioneer in the study of the viscosity of dilute suspensions of neutrally buoyant rigid spheres without Brownian motion in a Newtonian fluid. He developed the following relationship between the

relative viscosity of a suspension η_r and the volume fraction of the suspended particles, \emptyset :

$$\eta_r = 1 + \alpha_E \phi \tag{2.82}$$

where η_r is the ratio of the viscosity of the suspension η_s to the viscosity of suspending medium η_0 and α_E is Einstein's constant.¹⁴⁵ Einstein's constant, α_E , is equal to 2.5 when the suspended particles are neutrally buoyant, hard and spherical in shape, the particle motion is so slow that its kinetic energy can be neglected, there is no slip relative to the particle surface and the mean interparticle distance is large as compared to the mean particle size.

In the book written by Shenoy¹⁴³ Reiner and Kurgaev experimentally showed that $\alpha_{\rm E}$, becomes equal to 2.5 for filler concentrations of $\mathcal{O} = 0.003$ -0.05. The experimental studies conducted by Rutgers¹⁴⁶ showed that Eqn. 2.82 with $\alpha_{\rm E} = 2.5$ was valid for values up to $\mathcal{O} < 0.1$. Many researchers found a variety of $\alpha_{\rm E}$ values for different ranges of \mathcal{O} . Kambe¹⁴⁷ indicated that the lack of agreement among the experimental results of $\alpha_{\rm E}$ was due to the differences between the dimensions of the particles, the change in the velocity gradients for the experiments. Shenoy¹⁴³ reported that for solid spheres with large enough dimensions as compared to the molecular dimensions but small enough as compared to the characteristic length of the measuring instrument and for no slip at the sphere surface, the value of $\alpha_{\rm E} = 2.5$ is generally accepted although the values ranging from 1.5 to 5.5 have been suggested. Using a binomial expression, Ford¹⁴⁸ modified Einstein's Eqn. 2.82 into the following form:

$$\frac{1}{\eta_r} = 1 - \alpha_E \phi \tag{2.83}$$

where $1/\eta_r$ is defined as the fluidity and is equal to "0" when $\emptyset = 1/\alpha_E$. Experimental studies of Cengel *et al*¹⁴⁹ showed that Eqn. 2.83 can be valid for $\emptyset < 0.15$.

Even though there are a variety of opinions and equations available about the relationship between the relative viscosity of a suspension and the volumetric concentration of the spheres for dilute suspensions, Shenoy¹⁴³ reported that reasonable estimates can be obtained by Einstein's equation for $\emptyset < 0.1$ and by Ford's equation for $0.1 < \emptyset < 0.15$.

Concentrated Suspensions

The suspensions with $0.1 < O < O_m$ are generally considered as *concentrated* suspensions for which the equations of dilute suspensions don't apply. O_m is defined as the maximum attainable concentration and has the value of $O_m = 1 - \varepsilon$, where ε is the void fraction or porosity and defined as the ratio of the void volume to that total volume. McGeary¹⁵⁰ indicated that the value of O_m is theoretically 0.74 for equal spheres in compact hexagonal packing however in practice it is found more close to 0.637 for random hexagonal packing or 0.524 for cubic packing. As the filler concentration rises, several phenomena arise, such as:

- The interparticle attraction and repulsion forces become stronger owing to the electrostatic charges, which relies on the polarity of the medium,
- The rotation of the particles during the flow, in addition to the formation of doublets and their rotation during flow, induces extra dissipative effects which in turn cause an increase in the viscosity,
- The number of particles per unit volume which come in contact during the flow increases.

Unlike the dilute suspensions, the size of the filler affects the viscosity behavior of the concentrated suspensions considerably. De Brujin¹⁵¹ revealed that a concentrated suspension exhibits non-Newtonian behavior when the filler diameter is less than 10 μ m and its viscosity increases as the filler diameter declines. Clarke¹⁵² stated that for a filler diameter greater than 10 μ m, the viscosity of concentrated suspensions increases linearly with the diameter. For spherical particles, Shenoy¹⁴³ reported that as the sphere diameter increases, the lateral displacement of the particles towards the center of the tube increases. This results in an increase in the energy dissipated and thus causing a tendency for the viscosity of the suspension to increase with increasing diameter.

Since an increase in the concentration of the fillers can induce many-fold effects, several physical models have been proposed. However, Thomas¹⁵³ indicated that most of these models can be expressed by the nonlinear relationship between η_r and \emptyset in the following power series form:

$$\eta_r = 1 + \alpha_1 \cdot \phi + \alpha_2 \cdot \phi^2 \pm \alpha_3 \cdot \phi^3 \pm \cdots$$
 (2.84)

where α_1 is usually assumed to have a value of 2.5 as given by Einstein,¹⁴⁵ while the other coefficients α_2 , α_3 are assigned different values by different authors. The main disadvantage of this equation is that the termination of the series after \mathcal{O}^2 term causes an error of 10 % or more in the relative viscosity for $\mathcal{O} > 0.15$ -0.2. The validity of the series increases to $\mathcal{O} \approx 0.40$ upon the inclusion of \mathcal{O}^3 term. Nevertheless, the values of the coefficients of higher order terms are less precise since they should require more complex interactions than it is theoretically possible to treat. The literature is full of many other theoretical expressions for the explanation of the viscosity of suspensions as a function of filler concentration, \mathcal{O} .

Shenoy¹⁴³ indicated that for concentrated suspensions, it is essential to explain the hydrodynamic interaction of particles, particle rotation, particle collisions, doublet and higher order agglomerate formation and mechanical interference between particles as packed bed concentrations are approached.

2.7 Analysis of Fiber Wetting on the Impregnation Phenomenon during Resin Transfer Molding (RTM)

The incompatibility between surface properties of resins with those of reinforcements is one of the greatest concerns in Resin Transfer Molding applications. Such kind of incompatibilities might lead to micro-voids during the impregnation stage. These microvoids usually form inside the fiber tows where the pores of fabric are the smallest and thus, capillary wetting has uttermost importance. If such micro-voids prevail in large quantities in a composite part, deterioration of mechanical properties is inevitable. That's why, the proper match of the surface properties is one of the key issues to achieve successful wetting during Resin Transfer Molding. Usually, a low resin surface tension is necessary for good and fast fiber impregnation.

The analysis of wettability of the reactive thermoset systems is a scientific area which still needs to be further explored due to difficulties involved in the determination of surface tension while curing reactions take place.¹⁵⁴ A good wet-out is an essential, yet not an adequate condition for attaining good adhesion properties between the matrix and reinforcement systems in composites manufacturing, structural integrity and performance of the composites. Thus, a proper understanding of wetting of fibrous reinforcements through the evaluation of wicking phenomenon is essential via the measurement of surface tension and contact angle properties of the matrix systems. The analysis of flow through such porous structures is generally described by the Washburn Equation, Eqn. 2.85 which explains the dynamics of flow in single capillaries.

$$\cos\theta = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \cdot \sigma_L \cdot c}$$
(2.85)

where

$$c = \frac{1}{2} \cdot \pi^2 \cdot r^5 \cdot n_k^2 \tag{2.86}$$

 σ_L is liquid surface tension [mN/m], η is liquid viscosity [mPa.s], ρ is liquid density [g/cm³], θ is the contact angle between the liquid and the porous structure, c is a material constant pertinent to the porous architecture of the test material, r is the capillary radius, n_k is number of capillaries, m is weight of the liquid absorbed into the porous material [g] and t is time after the porous material and the test liquid are brought into contact [s].

The Washburn Equation is still one of the most commonly used approaches in evaluating the wetting characteristics of porous solids, including powders and fibrous materials.¹⁵⁵ Washburn theory¹⁵⁶ basically proposes that if a porous material is brought into contact with a liquid such that the material touches the liquid surface rather than being submerged into the liquid, there will be a climb of liquid into the pores of the test material as a result of capillary motion. Tucker and Dessenberger¹¹² proposed that it is also possible to gain vital information on the tow permeability of fabrics through a set of capillary rise measurements utilizing an equation, which is analogous to the Washburn equation, as follows:

$$\frac{d}{dt} \left(L^2(t) \right) = \frac{2 \cdot S_{zz} \cdot \gamma \cdot l_a}{\mu \cdot \varepsilon_f}$$
(2.87)

where, S_{zz} is tow permeability, ε_f is the porosity of the fabric, γ is the surface tension of the wetting material and l_a is the contact line length per unit area, which is also defined as the perimeter of each fiber per cross-sectional area of tow.

The full utilization of the Washburn equation requires determination of surface tension, γ , of the wetting material and the material constant, c, of the porous test material.

2.7.1. Determination of Surface Tension

Surface tension is measured as the force acting over the surface of a liquid per unit length of the surface perpendicular to that force. It is a material property of a liquid in contact with air making it act as though it was covered with a thin membrane under tension. While the interactions of the molecules within a liquid are even from all sides with respect to the neighboring molecules, the molecules at the surface are solely influenced by the ones, located right below them. This is why molecules in contact with air act differently and tend to contract to form the minimum possible area. The net effect of these interactions is the generation of excess free energy at the surface area. It is usually more common to quantify surface energy as surface tension which is force per unit length. In other words, surface tension is basically a measurement of cohesive energy attained at an interface.

There are several ways of measuring surface tension. The Du Nouy ring method is one of the most widespread ways of determining the surface tension. This method utilizes a platinum-iridium ring with a well defined geometry, a high precision balance and a mechanism to vertically move the sample liquid in a glass beaker. The ring hanging from the balance hook is first dipped into the liquid and then carefully pulled up the surface of the liquid. The force applied on the ring while the ring is pulled through the surface is continuously recorded by a micro balance. The surface tension is proportional to the maximum force acting on the ring from the liquid surface when it is pulled through the liquid surface.

As the original calculations employed by the Du Nouy ring technique are based on the theories which are developed for rings of infinite diameter, they don't account for the additional fluid volume that is raised as a result of the proximity of one side of the ring to the other. Thus, mathematical corrections should be made for the compensation of extra fluid after the Du Nouy ring measurements.

The second most commonly used technique to determine the surface tension of the liquids is the Wilhelmy Plate. This technique enables the determination of the weight of liquid absorbed by a plate when a plate is raised from the surface of a liquid. In this method, the plate should first be immersed into the liquid, second pulled out and finally lowered to the surface until its lower edge is just brought into contact with the surface. At that moment, the plate perimeter gets wetted by the fluid. This, in turn results in a rise in the total plate weight up to a peak point, proportional to the surface tension of the test fluid.

Another method which is quite commonly employed in the determination of surface tension is the Pendant Drop Technique. This method utilizes the shape of a drop of fluid hanging from a syringe tip for the calculation of surface tension of the liquid based on a balance of forces acting on the surface of the drop through the usage of the following equation:

$$\gamma = \Delta \rho \ g \ R_0^2 / \beta \tag{2.88}$$

where γ is the surface tension, $\Delta \rho$ is the difference in density between fluids at the interface, g is the gravitational constant, R₀ is the radius of drop curvature at its apex, β is a shape factor, which can be defined via the Young-Laplace equation expressed in the Figure 2.22.¹⁵⁷



Figure 2.22 A schematic depicting the calculation of the shape factor based on the Pendant Drop Technique.

2.7.2. Determination of Contact Angle

Contact Angle is the angle naturally formed when the liquid is placed on a solid surface. When the liquid does not spread, a drop forms a contact angle on the surface as depicted in Figure 2.23.



Figure 2.23 A schematic depicting the balance of forces on a liquid droplet based on Young's Equation.

One of the most fundamental equations used to determine the balance between the forces on the surface of a drop is Young's equation.¹⁵⁷

$$\sigma_s = \sigma_{sL} + \sigma_L \cos\theta \tag{2.89}$$

where, σ_L is the overall surface tension of the wetting liquid, σ_S is the overall surface tension of the solid, σ_{SL} is the interfacial tension between the solid and the liquid and θ is the contact angle between the liquid and the solid. The most common techniques, available for measuring contact angles are sessile drop, pendant drop, Wilhelmy plate and Washburn adsorption as described in the earlier sections.

CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

The Epon 828 aromatic epoxy resin system was chosen for this study due to its high utility in liquid composite molding applications. It is a diglycidyl ether of bisphenol A (DGEBA) with a viscosity of 11-15 Pa·s, an equivalent weight of 178-190 and a specific gravity of 1.15 at 25°C. It was supplied by Resolution Inc. through Miller Stephenson Chem. Inc. (Danbury, CT). The crosslinking of epoxy chains was accomplished with a polyoxypropylene aliphatic diamine curing agent, Jeffamine D-230, obtained from Huntsman Corp. (Houston, TX) with a nominal molecular weight of 225 g/g-mol and a viscosity of 9 cS at 25° C. The chemical formula of both Epon 828 and Jeffamine D-230 are illustrated in Figure 3.1.

The organoclay used in this study, Nanomer I.30E, an octadecyl ammonium ion modified montmorillonite with a density of 1.71 g/cm³ was supplied from the Nanocor Inc. The Nanomer I.30E nanoclay is reported to have 70-75 wt % montmorillonite and 25-30 wt % octadecylamine.



Epon 828: Diglycidyl ether of bisphenol A (DGEBA); n=0.1

H2NCH(CH3)CH2-[OCH2CH(CH3)-]NH2

Jeffamine®D-230; n=2.6

Figure 3.1 The chemical structures of epoxy and diamine systems used in this study.

The AP-grade single walled carbon nanotubes (SWCNTs) with a density of 1.3-1.4 g/cm³ were purchased from Carbolex Inc. (Lexington, KY). The nanotubes were indicated to have 10-30 % metal and carbon catalyst particles. These closed-ended SWCNTs were manufactured by the Arc Method. Carbolex Inc. reported that the AP-grade SWCNTs are usually produced in the form of "ropes" with a typical rope diameter of around 20 nm, an average carbon nanotube diameter of 1.4 nm and an average carbon nanotube length of 2–5 microns. No purifications or other alterations were made to the chemical structure of any of nanoreinforcements used in this study.

3.2 Molding Materials

The CD 185A biaxial stitched fabric was purchased from Owens Corning owing to its fast wet-out, good processing and end property features for resin transfer molding (RTM) experiments. This fabric was made of 0^0 and 90^0 tows perpendicular to each other with a fabric areal weight of 630 g/m². The tows were held together with a polyester knitting.

Owens Corning indicated that an amino silane sizing was applied the tows of this fabric to improve the fiber/matrix compatibility, processability, fiber strength, wetting and handleability. It is also reported by Owens Corning that the CD 185A fabric was made from SE 1200-675 yield (735 tex) rovings with 2000 filaments per tow and with a single filament diameter of 13 micron, specifically designed for epoxy resin systems.

In the design of RTM mold, two steel mold plates with 305 mm x 305 mm x 17.5 mm dimensions were machined to accommodate two 254 mm x 15.9 mm x 6.35 mm rectangular cartridge heaters of SR 15-10 model, purchased from Hotwatt Inc. The operating range of cartridge heaters was 10-180 watts. The GP-50 317-B-RB-CA/GZ model flush diaphragm pressure transducers with 0-150 psi operating range were positioned at four predetermined locations on the bottom mold plate. Detailed engineering drawings of the bottom and top mold plates are provided in Figures 3.2 and 3.3, respectively. A rectangular aluminum picture frame with 102 mm x 229 mm inside cavity dimensions and 2.5 mm nominal thickness was machined. This frame was sandwiched in between two steel mold plates during the resin transfer molding experiments. The picture frame was designed to have three vent channels with 5 mm width and 0.5 mm depth, equally spaced in the middle end of the frame, parallel to the upper mold plate. The two mold plates were held in place by steel bolts and dowels. The photographic illustrations of the mold plates and the picture frame are given in Figures 3.4 and 3.5, respectively.

Aside from building a RTM mold, an injection pump apparatus was also constructed to ensure constant flow rate measurements during RTM. This apparatus was designed to induce compression load on a piston firmly fitted in a cylindrical resin pot when used in conjunction with a Monsanto T-10 Tensile tensiometer machine which can normally work under tension load. Photographic view of the injection pump apparatus mounted on the Monsanto T-10 tensiometer is provided in Figure 3.6.

To ensure design validation, a PC-based data acquisition system with the LabVIEW[®] software was used to record the pressure sensor outputs and the thermocouple readings during the RTM experiments. A 16-channel rail block type data logger (TBX-68 from National Instruments) was used to gather the raw data from the pressure transducers and the thermocouples. The collected data was then sent to a precision board (NI-4351) for display on virtual instruments (VIs) and was concurrently recorded on a spreadsheet for easier analysis.



Figure 3.2 Engineering drawings of the bottom mold plate (a) top view (b) side view of the bottom plate-1 as seen from Y'Y' axis (c) side view of the bottom plate-2 as seen from Y'Y' axis.



Figure 3.3 Technical drawings of the top mold plate (a) top view, (b) side view of the top plate-1 as seen from Y'Y' axis (c) side view of the top plate-2 as seen from Y'Y' axis.



Figure 3.4 Photographic views of the steel mold plates (a) top mold plate and (b) bottom mold plate.



Figure 3.5 Photographic views of the aluminum picture frame (a) top view (b) vents.



Figure 3.6 Photographic view of the injection tool apparatus, mounted on the Monsanto T-10 Tensile tensiometer.

3.3 Procedures

In this section, the preparation of epoxy-nanoclay, epoxy-single wall carbon nanotube (SWNT) mixtures with and without curative and the procedures followed during the mold preparation, injection and curing stages of resin transfer molding (RTM) experiments will be described in detail.

3.3.1 Preparation of Nanoclay-Epoxy and SWNT-Epoxy Nanocomposites Prior to RTM

All materials were vacuum dried at 80°C for 12 hr. A calculated amount of nanoclay or nanotubes was first mixed with the epoxy at 80°C for 2 hr using a 700-watt, 1 HP high-shear mixing laboratory Omni GLH-115 model homogenizer from OMNI Inc., operating at 10,000 rpm.



Figure 3.7 Photographic illustrations of (a) Omni GLH-115 model homogenizer (b) MISONIX S-3000 sonicator.

The resultant mixture was then cooled down to 25°C and sonicated for 15 min. in an ice-bath by a MISONIX S-3000 sonicator with a 600-watt generator, 20 kHz convertor and ³/₄" tapped horn as illustrated in Figure 3.7. After the sonication, the mixture was cooled down to 25°C and degassed for 20 min. Then, a stochiometric amount of the Jeffamine D-230 curative was thoroughly mixed with epoxy at room temperature.

3.3.2 Resin Transfer Molding (RTM) Experiments

After all materials were thoroughly mixed as described in the previous section, the resultant mixture was poured into the cylindrical resin pot which was already mounted on the Monsanto T-10 tensiometer for the injection of mixture into the mold cavity. Prior to each RTM experiment, three different types of mold release agents were applied on the mold and the picture frame surfaces. The mold release agents were purchased from Zyvax Inc. At first, a small amount of water based surface cleaner, "Waterclean" was directly applied on both the mold surfaces and the picture frame. All surfaces were scrubbed using a wet paper towel before rinsing of all surfaces with a wet cloth. Rinsing was repeated until no residue was observed on the mold and picture frame surfaces. Once all surfaces were cleaned, a thin layer of solvent based mold release agent, "Sealer GP" was applied with a Bounty paper towel. Next, the surfaces were wiped by another dry paper towel before letting them dry. The "Sealer GP" was applied for 3 times by allowing a 15 min. waiting period in between each coating. After the application of third "Sealer GP" layer, 30 min. was allowed before the application of a thin coating of the final mold release agent, "Enviroshield" by a paper towel. The excess amount of mold release was wiped by another paper towel two minutes later. A second coating of Enviroshield was

applied after 15 minutes. The same procedure was repeated for the third coating application.

After waiting for another 30 minutes for complete drying of the mold and the picture frame surfaces, the mold cavity was preloaded with 5 or 6 plies of CD 185A biaxial stitched glass fabrics except for the neat resin experiments which were conducted without any fabric. The resin pot was connected to the mold through a transparent hose and three valves, one of which was located under the resin pot at the entrance of resin in to the hose while the other two valves were located at the entrance of the mold cavity. One of the two valves at the entrance of the mold cavity, the "air-vent valve" was located to ensure the removal of any entrapped gas during the injection and transfer of the resin mixture from the resin pot through the hose just prior to resin' s entrance into the mold cavity. It was thought that air bubbles which might have potentially formed during the transfer of resin mixture to the hose could be removed efficiently by opening this "*air-vent valve*" while keeping the other valve, "resin-inlet valve" at the entrance of mold cavity closed. After some air bubble containing resin mixture is collected in a beaker for 5 min., the remaining mixture was delivered into the mold cavity by opening of "resin-inlet valve" in front of the mold cavity. All resin transfer molding experiments were conducted at room temperature under constant flow rate condition by manually setting of the piston speed to either 2 mm/min or 4 mm/min on the Monsanto T-10 tensiometer instrument panel.

During the injection of resin mixture into the mold cavity, four pressure transducers and the mold temperature readings were continuously recorded via a LabVIEW data acquisition program. The injection of resin is continued for at least ten more minutes than the first observation of resin mixture exit at the end of the mold vents. Then, the piston motion is ceased manually by turning of the speed switch on the Monsanto T-10 tensiometer. Once the mold filling stage is successfully completed, the mold is heated to $80 \, {}^{0}$ C for 2 hours. Upon completion of the initial curing stage, the molded composite part is removed from the mold cavity. To ensure complete curing of the composites, the molded piece is post cured in a compression mold at 125 $\, {}^{0}$ C for 3 hours.

3.4 Characterization of Epoxy Nanocomposites Prior To Resin Transfer Molding

The dispersion of nanoclays and nanotubes and their resultant effects on the cure kinetics, viscosity, chemorheology and the wetting properties of epoxy polymers were evaluated through several experimental techniques. The basics and the procedures followed in each of these characterization techniques will be provided in this section.

3.4.1 Differential Scanning Calorimety (DSC) Measurements

DSC quantifies the amount of energy (heat) absorbed or released by a sample as it is heated, cooled or held at constant temperature. Isothermal curing of 8 to 10 mg samples of the epoxy-curative, epoxy-curative-clay and epoxy-curative-SWNT mixtures were conducted at 100°C for 1.5 hr under nitrogen environment in the differential scanning calorimeter, TA Instruments, Q 1000 Series DSC. The temperature of the liquid samples was raised from room temperature to the curing temperature at a rate of 50 °C/min at the beginning of each DSC experiment. The effects of presence of nanoclay and SWNT on
the degree of cure, rate of reaction and the heat of reaction curves were evaluated by this characterization technique.

3.4.2 Rheological Measurements

The influences of nanoclay and SWNT on the gelation time and on the rheological properties of epoxy-curative mixtures were investigated with a dynamic rheometer, RMS-800 Rheometrics Rheometer. This instrument is a mechanical spectrometer which is capable of subjecting either dynamic (sinusoidal) or steady (linear) shear strain deformation on a liquid sample and then measuring the resultant torque developed by the sample in response to the applied shear strain. During each experiment, the parallel plates were first preheated to the isothermal curing temperature, the plate spacing was set to zero and the liquid resin sample rapidly inserted after the plates are separated. The plates were then adjusted to a gap of approximately 0.1 mm. The chamber surrounding the plates was closed. The measurement was initiated when the chamber returned to the set temperature (2 min). All experiments were conducted with a pair of 25 mm parallel plate at 4 % strain and 4 rad/s frequency under oscillatory shear flow. The viscoelastic properties of the sample during the incipient stage of cure, including shear storage modulus, shear loss modulus and complex dynamic viscosity were monitored and recorded as a function of time at 100 °C, 120 °C and 140 °C.

3.4.3 Brookfield Viscosity Measurements

A Brookfield LV DV II + Pro Digital Viscometer was used to evaluate the effect of the amount of nanoparticles on the reactivity of epoxy-curative systems at room temperature. The use of "small sample adapter (SSA)" accessory in combination with disposable sample chambers and the Brookfield LV DV II + Pro Digital Viscometer made very precise and long viscosity measurements possible during the curing of thermoset systems.

The SSA accessory allowed conducting accurate viscosity measurements of very small sample volumes of 16 -18 mL at precise shear rates as depicted in Figure 3.8.



Figure 3.8 Photographic illustrations of Brookfield "small sample adapter" accessory used with (a) a standard sample chamber (b) a disposable sample chamber.

Brookfield Engineering Laboratories claimed that SSA accessory was designed to function similar to a "cone and plate rheometer" such that its well defined cylindrical sample chamber and spindle geometry allowed for more precise measurements of viscosity without any disturbance on the sample. Thus, a set of room temperature viscosity measurements of reactive nanoreinforced epoxy systems were conducted at 120 rpm using Brookfield LV DV II + Pro Digital Viscometer along with disposable sample containers, the "small sample adapter" accessory and the SC-25 Spindle.

3.4.4 Wide-Angle X-Ray Diffraction (WAXD) Measurements

The degree of clay separation and exfoliation was explored by Wide-angle X-ray diffraction measurements through which the effects of concentration and curing temperature on the distance between clay layers, (d_{001} -spacing) were investigated. The shifts in the (001) WAXD peak position are correlated to the increases in the clay d-spacing via Bragg's law.

WAXD experiments were performed on a Rigaku model X-ray diffractometer with a wavelength, λ of 1.54 Å (CuK α), a tube voltage of 50 kV and tube current of 150 mA. The scanning ranged from 2. θ values of 1.5° to 10° with a rate of 5°/min. The measurements were conducted for 35 min. periods on both liquid (uncured) and solid (cured) samples with and without the presence of nanoreinforcements. After mixing of all of the ingredients and cooling the mixture to the room temperature, small quantities of the liquid epoxy-clay mixture both with and without curative were contained in a rectangular sample holder covered with a special transparent 3M scotch-brite tape to prevent the liquid leakage during the measurements. This selected tape did not generate any diffraction peaks in the 2. θ range of 1.5° to 10°, as will be illustrated in the liquid

WAXD results in the next section. The solid samples used in the WAXD experiments were obtained by cutting small rectangular pieces from the cured epoxy-clay systems.

Nanoreinforcement orientation was believed to be random. The effects of clay and curative on the intercalation behaviour of liquid epoxy prepolymer during the incipient stage of curing were evaluated from the location of X-Ray diffraction peaks obtained via these measurements. The effect of clay content on the partial exfoliation behavior of solid epoxy samples cured at three different temperatures of 100 °C, 120 °C and 140 °C was also determined.

3.4.5 Determination of Wetting Properties via Wicking and Du Nouy Ring Experiments

A proper match of the surface properties of resins to those of reinforcements is one of the key concerns in achieving successful wetting during Resin Transfer Molding. Typically, a low resin surface tension is necessary for good and fast fiber impregnation.

A good wet-out is an essential yet an insufficient condition for obtaining good adhesion properties between the matrix and reinforcement systems in composites manufacturing and performance of the composites. Thus, an evaluation of wicking phenomenon via the measurement of surface tension and contact angle properties was crucial so as to ensure a proper understanding of wetting of fibrous reinforcements by different matrix systems. This would allow us to assess the effect of presence of nanoreinforcements in the epoxy matrix on the wetting and impregnation properties. The analysis of flow through such porous structures is generally described by the Washburn Equation¹⁵⁶which explains the dynamics of flow in single capillaries, as below:

$$\cos\theta = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \cdot \sigma_L \cdot c}$$

where σ_L is liquid surface tension [mN/m], η is liquid viscosity [mPa.sec], ρ is liquid density [g/cm³], θ is the contact angle between the liquid and the porous structure, m is weight of the liquid absorbed into the porous material [g], t is time after the porous material and the test liquid are brought into contact [sec] and c is a material constant pertinent to the porous architecture of the test material and it can also be expressed as a function of the capillary radius, r and the number of capillaries, n_k , as follows:

$$c=\frac{1}{2}\cdot\pi^2\cdot r^5\cdot n_k^2$$

The Washburn theory suggests that if a porous material is brought into contact with a liquid, there will be a climb of liquid into the pores of the test material as a result of capillary motion. This phenomenon is also called as "*wicking*". To evaluate the wetting properties of nanoclay enriched epoxy systems, an experimental set up was built as shown in the Figure 3.9. After a metallic wire attached to a 20 mm x 50 mm fiberglass sample was hung underneath an Ohaus Adventurer AR 1140 model high precision balance, the balance was tared.



Figure 3.9 The experimental set-up used for the Washburn Adsorption measurements.

The fiberglass sample was then brought into contact with epoxy mixture by carefully adjusting the level of a 100 mL beaker containing epoxy mixture with the aid of a laboratory jack. The change in the mass of fiberglass sample was continuously recorded as a function of time through a special RS-232 cable which is purchased from Ohaus and connected to both the balance and a computer with the transmission of the instant data readings through a COM1 serial port using a special software developed by ScaleSoft© Development Corp. (Alliance, OH). This data collector software was capable of collecting data at each five seconds for a desired period of time by setting the

communication and printing parameters of the Ohaus Adventurer balance to a baud rate of 2400, a data count of 7 and a stop bit of 2.

The "wicking" experiments were conducted with unreactive and reactive epoxy nanocomposite mixtures as well as silicon oil with 5 cSt viscosity purchased from Sigma Aldrich. The low viscosity silicon experiments were crucial to determine the material constant "c" of the glass fabrics by ensuring "complete wetting" of the fabric (i.e., *cos 0* = 1) using a liquid such as silicon oil with an already known surface tension so as to determine the effect of nanoclay concentration on the contact angle of various nanoreinforced epoxy systems.

The wetting behaviour of various nanoreinforced epoxy systems were further evaluated through an equation proposed by Tucker and Dessenberger¹¹²by determining the tow permeability of fabrics. This equation is analogous to the Washburn equation¹⁵⁶ and expressed as follows:

$$\frac{d}{dt} \left(L^2(t) \right) = \frac{2 \cdot S_{zz} \cdot \gamma \cdot l_a}{\mu \cdot \varepsilon_f}$$

where, S_{zz} is tow permeability, ε_f is the porosity of the fabric, γ is the surface tension of the wetting material and l_a is the contact line length per unit area, which is also defined as the perimeter of each fiber per cross-sectional area of tow. Du Nouy Ring measurements were next conducted to measure the surface tension of several unreactive and reactive epoxy nanocomposite mixtures using the same balance set-up which is used for the "wicking" measurements as depicted in Figure 3.10. The only difference between two set-up systems is that the Du Nouy Ring set up employed hanging of a platinum-iridium ring with a well defined geometry underneath the Ohaus Adventurer high precision balance instead of a piece of fabric.

The ring hanging from the balance hook was first dipped into the liquid. Then, the ring was carefully and very slowly pulled up the surface of the liquid by following the steps depicted in Figure 3.10. The force applied on the ring while the ring was pulled through the surface was continuously recorded through the same software via transmission of data from the high precision balance. The maximum force acting on the ring from the liquid surface was proportional to the surface tension when the ring was pulled through the liquid surface.



Figure 3.10 Schematic description of a Du Nouy ring measurement and the corresponding changes in the force needed to pull the ring from a liquid during an experiment.

As the original calculations employed by the Du Nouy ring technique were based on the theories which were developed for rings of infinite diameter, they didn't account for the additional fluid volume raised as a result of the proximity of one side of the ring to the other. Thus, mathematical corrections ought to be made for the compensation of extra fluid after completing the Du Nouy ring measurements. For this purpose, the Zuidema-Waters surface tension correction equation¹⁵⁸ was employed using the formula:

$$F = 0.7250 + \sqrt{\frac{0.01452 P}{C^2 (D-d)} + 0.04534 - \frac{1.679 r}{R}}$$

where *F* is the Zuidema-Waters surface tension correction factor (mN/m), *R* is the Du Nouy ring radius (cm), *P* is the apparent surface tension read by the balance (mN/m), *D* is the density of the test fluid (g/cm³), *d* is the upper phase, usually air (g/cm³), *C* is the circumference of the ring (cm), *r* is the inherent radius of the ring (cm), *K* is a parameter expressed as a function of *r* and *R* as K=0.04534-1.679r/R. The values of the constants *b* and *a* are 9.075 x 10⁻⁴ and 0.725, respectively.

3.4.6 Transmission Electron Microscopy (TEM)

TEM is a powerful microscopic technique which utilizes an electron beam and electrostatic and/or electromagnetic lenses which allows for the passage of monochromatic electrons through a very thin specimen in a presence of high vacuum. It is also one of the most powerful techniques frequently used in characterizing nanoparticle dispersion. While WAXS can only provide reliable information for intercalated silicate nanocomposites, it can be insufficient in differentiating exfoliated and delaminated structures from the disordered, agglomerated structures. That's why, TEM characterizations of the microstructure of the cured epoxy samples were essential. The samples for transmission electron microscopy were first sliced to 65-75 nm at room temperature using a Leica EM UC6 model ultramicrotome prior to examination in a FEI model TECNAI-12 transmission electron microscope.

3.4.7 Scanning Electron Microscopy (SEM)

SEM is one of the most heavily used microscopic techniques offering a great combination of higher magnification, larger depth of focus, better resolution and easy sample preparation in many research areas. It also allows for a large depth of field such that a larger area of a sample could be focused at one time. Some SEM instruments can have a magnification capacity of 15x to 600,000x and a resolution of 5 nanometers. Although the preparation of SEM samples is much easier than the TEM samples, most of the SEMs require samples to be conductive. If the sample isn't naturally conductive, then, it has to be coated with a very thin layer of conductive material such as Ag or Au in some high vacuum evaporation units or sputtering devices. SEM is considered to provide more precise information on the surface topology and morphology of the samples as comparison to TEM.

Prior to SEM examination of cured epoxy samples with various nanoreinforcement loadings, the samples were coated with Ag via the *Emitech K575x Turbo Sputter Coater*. The conductive specimens were then examined with an *SEM S-2150 Hitachi equipment*, operated at 20 kV.

3.5 Characterization of Epoxy Nanocomposites and Epoxy Fiberglass Nanocomposites after Resin Transfer Molding

The effects of nanoclays and carbon nanotubes on the *final properties* of the hybrid epoxy composites manufactured by resin transfer molding were assessed via several thermal, mechanical, microscopic and permeation analysis techniques as will be described in this section.

3.5.1 Thermogravimetric Analysis (TGA) Measurements

A thermogravimetric analyzer (TGA) quantifies weight changes in a material as a function of temperature (or time) under a controlled atmosphere. It is primarily employed to evaluate thermal stability and composition of materials. Thus, thermo-oxidative stability of epoxy composites with and without presence of nanoreinforcements was evaluated using a TA Instruments Q 500 TGA. Samples of 15-20 mg. were tested from 25 °C to 800 °C under an *air* atmosphere at a test scan rate of 10 °C /min according to the ASTM E 1131. The temperature at 5 % weight loss (T₁) and the temperature at the maximum rate of weight loss (T₂) were obtained from typical weight % change vs. temperature curves.

3.5.2 Thermomechanical Analysis (TMA) Measurements

Thermomechanical analysis (TMA) measurements of polymers detect changes in the physical properties resulted from changes in the free volume. Changes in free volume, V_f , can be monitored as a volumetric change in the polymer via the release or absorption of heat associated with that change; the increased flow; the loss of stiffness or the change in

relaxation time. Usually, unreinforced polymers exhibit a higher coefficient of linear thermal expansion above their glass transition temperature, T_g , than below it due to an increase in the segmental mobility of polymer chains in the amorphous regions of polymer.

The most commonly used and commercially available test fixtures for TMA are expansion, three-point bending or flexure, parallel plate and penetration probes. During a thermomechanical analysis, a sample is usually subjected to a small but constant load while its temperature is changed over a specific range. If the material tested in TMA is anisotropic, it will have different coefficient of thermal expansion at each direction in which the test is conducted. For instance, a glass fiber-epoxy composite will exhibit three distinct thermal expansions corresponding to the x, y, and z direction.

The coefficient of linear thermal expansion of 2.5 mm x 5 mm x 10 mm epoxy nanocomposites, epoxy-glass fiber composites and epoxy-nanoclay-glass fiber composites were determined by measurements conducted under 20 mN static force with the PerkinElmer Pyris Diamond TMA instrument. Each sample tested using expansion probe was first kept at -50 $^{\circ}$ C for 1 minute. Then, the sample was heated from -50 $^{\circ}$ C to 220 $^{\circ}$ C at 5 $^{\circ}$ C/min while the change in its probe position was recorded. The coefficient of linear thermal expansion (CTE) is later calculated from the ratio of the change in the length of a sample to the change in its temperature. All samples were tested in the 5 mm direction as the effect of nanoreinforcements on the CTE in that direction was expected to be more dominant than the one in the 10 mm direction.

3.5.3 Dynamic Mechanical Analysis (DMA) Measurements

Dynamic Mechanical Analysis (DMA) is another thermal characterization technique which provides information on the rheological properties of materials when they are subjected to usually a small, sinusoidal oscillating force as a function of temperature, frequency, stress, time, atmosphere or a combination of these parameters. Some of the key application areas where DMA is frequently employed are determination of glass transition and sub-transition temperatures, storage and loss modulus, softening temperatures, crosslink density, degree of crystallinity, creep and stress relaxation, impact resistance, compatibility of anisotropy or orientation, acoustical and vibrational damping, heat dissipation properties and aging effects.



Figure 3.11 A schematic illustrating the relationships between stress, strain and phase angle (δ) during a DMA measurements.

During a DMA test, the amplitudes of the stress and strain as well as the phase angle (δ) between them were measured as depicted in Figure 3.11. This is used to resolve the modulus into its in-phase - the storage modulus (E') - and an out-of-phase - the loss modulus (E'') components. The relationship between these components and the dynamic (or complex) modulus (E*) is depicted as follows:



The loss tangent (tan δ), i.e., the ratio E"/E', is also called as the damping factor and is an indication of the amount of mechanical energy dissipated as heat during a DMA loading/unloading cycle. While tan δ is zero for a perfectly elastic material, it is infinite for a perfectly viscous material.

A Pyris Diamond DMA instrument manufactured by Perkin Elmer was used for the measurements of 2.65 mm x 8 mm x 10 mm epoxy nanocomposite, epoxy-glass fiber composite and epoxy-nanoclay-glass fiber composite samples at a frequency of 1 Hz. in tensile mode with 3° C/min ramping rate from ambient temperature to 230 $^{\circ}$ C at a

sampling interval of 0.05 sec. N_2 flow rate set to 40 psi was circulated in the DMA furnace during the measurements.

3.5.4 Flexural Properties by Three Point Bending Tests

Flexure tests are often made on relatively flexible materials such as polymers, wood and composites. The flexural tests are conducted to evaluate the behavior of materials subjected to a simple beam loading. A flexure test causes tensile stress in the convex side of the specimen and compression stress in the concave side. This creates an area of shear stress along the midline. It is important to note that the shear stresses should be minimized as much as possible during a flexure test so that a test sample fails primarily due to tensile or compression stresses. This can be achieved by controlling the span to depth ratio; the length of the outer span divided by the height (depth) of the specimen. While an S/d ratio of 16 is acceptable for most materials, some materials require an S/d ratio of 32 or 64 to keep the shear stress low enough. There are two main test types; 3point flexure and 4-point flexure. In a 4-point test, the area of uniform stress exists between the inner span loading points (typically half the outer span length). In a 3-point test the area of uniform stress is quite small and concentrated under the center loading point.

An Instron 5580 Series Floor Model Universal Materials Test machine was employed to conduct flexure tests of 2.7 mm x 12.7 mm x 104 mm epoxy nanocomposite, epoxyglass fiber composite and epoxy-nanoclay-glass fiber composite samples with an S/d ratio of 32 at a test speed of 1.84 in/min using Bluehill® 2 Software according to the ASTM D 790-03.

3.5.5 Hygrothermal Measurements

Water absorption tests were conducted to determine the amount of water absorbed by the composites at ambient temperature conditions. This data was expected to shed a light on the effect of nanoreinforcements on the barrier performance of the materials in water or humid environments. The primary factors affecting water absorption include temperature, length of exposure, type of polymer and nanoreinforcements.

The edges of rectangular cut 2.65 mm x 20 mm x 50 mm epoxy nanocomposite, epoxy-glass fiber composite and epoxy-nanoclay-glass fiber composite samples are coated with molten wax so that any edge effects could be ignored during the water absorption tests and as such, a simple one dimensional diffusion model analysis could be employed to determine water diffusivity without introducing any significant error.

All composite samples were at first weighed at room temperature. The samples were then submerged in a distilled water containing beaker at ambient temperature conditions, often 24°C for a long period until the equilibrium water absorption was reached. Wet sample weight measurements were taken at periodic time intervals using a five digit precision Mettler Toledo balance after the specimens were removed from the beaker and dried with a paper towel.

3.5.6 Oxygen Permeability Measurements

Oxygen permeability of thin composite samples was measured via an 8001 Model Oxygen Permeation Analyzer manufactured by Illinois Instruments, Inc. (Johnsburg, IL).

A circular composite sample of 7 cm^2 was sandwiched between the two masking plates of 3 cm diameter and sealed with vacuum grease in the sample test chamber. Pure oxygen gas (99.9%) at 40 psi was sent into the upper half of the chamber while a nitrogen carrier gas at 40 psi was introduced through the lower half. Oxygen molecules diffusing through a sample into the lower chamber were carried by nitrogen gas to the sensor. This allowed for a direct measurement of the oxygen transmission rate (OTR) of the test sample. The tests were conducted at 0 % relative humidity under dry conditions.

3.5.7 Optical Microscopy (OM)

The optical microscopy is the simplest microscopic characterization technique utilizing lenses to bend the visible light waves instead of an electron beam such that these lenses are adjusted to magnify the images of small samples while providing the fastest information on a specimen. The biggest limitation of light microscope arises from the physics of visible light which has a magnification capacity ranging from 500x to 1000x and a resolution of 0.2 micrometers. Due to its practicality, optical microscopic pictures of the cross sectional cuts of some polished epoxy-glass fiber nanocomposite specimens were taken using a Leitz polarized optical microscope at 4X magnification to compare the void content of samples with different nanoclay loadings.

CHAPTER IV

CHARACTERIZATION OF THE STATE OF DISPERSION OF EPOXY NANOCOMPOSITES

In this chapter, the state of dispersion of nanoclay reinforced epoxy resins and single wall carbon nanotube (SWNT) reinforced epoxy resins as well as the subsequent effects of nanoscale reinforcements on crosslinking will be assessed by means of thermal (DSC), chemorheological (RMS-800), morphological (TEM and SEM) and wide angle X-ray diffraction (WAXD) techniques. TEM and WAXD results on the cured epoxy-clay samples reveal that highly intercalated (aggregated stacks of platelets) or partially exfoliated (individual platelets) epoxy nanocomposites could be attained depending upon cure conditions. The interrelationships between the intercalation and/or exfoliation of nanocomposites, crosslinking of thermoset systems under different cure conditions and their resultant effects on the rheological properties during the curing stage were investigated. The information gained through these characterization techniques will provide valuable insights into the processing windows of nanoclay or SWNT-reinforced, epoxy nanocomposites during RTM. Hence, a good understanding of these techniques was a prerequisite for the assessment of the eligibility of such nanoreinforced thermoset

polymers for RTM applications when they are expected not only to flow through porous fiberglass fabrics but also to provide sufficient wetting of reinforcements.

4.1 Cure Kinetics of Epoxy Nanocomposites

A good understanding of nanoreinforced thermoset curing mechanisms obtained via the control of several parameters such as curing temperature, curing time and nanoreinforcement type and content was the first stage for evaluating the roles of rate of cure and extent of cure on the state of dispersion of epoxy nanocomposites. The effects of different cure conditions on the degree of crosslinking, thereby the final cure state of the nanoreinforced epoxy systems, were explored prior to evaluating the interrelationships between the cure kinetics and the evolution of viscosity during curing via rheological measurements.

A set of isothermal calorimetric measurements were conducted on the reactive mixtures of several epoxy, epoxy-nanoclay and epoxy nanotube systems to determine the change in the heat flow during curing and the corresponding kinetic parameters affecting the degree of cure via the kinetic model developed by Kamal and co-workers.¹⁴¹ As the measured heat flow of both the neat epoxy and nanoreinforced epoxy systems stayed constant after 60 minutes of curing, isothermal DSC measurements were conducted for 90 minutes to ensure full curing. However, for improving the clarity of graphs, the DSC results were presented up to 60 minutes. Knowing that, in DSC measurements the heat flow is proportional to the change in extent of reaction, that is,

$$\frac{d\alpha}{dt} = \frac{1}{H_u} \left(\frac{dH}{dt}\right)_t$$

where H_u is the ultimate heat of reaction associated with complete conversion, α , is the extent of cure, $\alpha = \Delta H_t / H_u$, ΔH_t , is the heat released until time t determined by integration of the calorimetric signal (*dH/dt*) until the time t. After determining the integrals for each DSC experiment and determining the total heat of reaction of epoxy as 475.4 J/g, a graphical representation of all DSC measurements can be derived, as presented in Figure 4.1.



Figure 4.1 Evolution of the degree of cure of epoxy systems, as a function of clay and CNT content, (a) Neat Epoxy, (b) Epoxy-2 wt % clay, (c) Epoxy-4 wt % clay, (d) Epoxy-1 wt % CNT, (e) Epoxy-0.4 wt % CNT.

The DSC results indicate that the presence of organoclay up to 4 wt % decreased the overall cure state such that after 50 minutes of curing at 100°C, the 2 wt % nanoclay-epoxy system cures to 95 % while the presence of 4 wt % clay leads to 92 % extent of cure. To determine the effect of nanoreinforcement type, similar DSC experiments were conducted on both 0.4 wt % and 1 wt % CNT-epoxy systems. The results for CNT nanocomposites exhibited a larger decrease in cure extent than for the layered silicate systems, as plotted in Figure 4.1. It is believed that CNTs, having a higher total interfacial surface area than nanoclays, could induce more interaction with the epoxy, which, in turn, makes them a more severe barrier to mixing and diffusion. Due to their different curing mechanisms, a maximum extent of cure of only 82 % was attained in both cases of CNT nanocomposites at the end of the cure cycle.

The DSC results were also interpreted in terms of the evolution of rate of cure as a function of the degree of cure, at different nanoclay and nanotube loadings, as shown in Figures 4.2 and 4.3, respectively. At a given temperature, the rate of cure, α , increases initially with the degree of cure and attains a maximum at $\alpha = 0.025-0.029$ in the case of nanoclay-epoxy samples and at $\alpha = 0.065-0.15$ in the case of nanotube-epoxy samples, then gradually decreases, and finally tends to zero. These maximum points in the rates of cure, observed at some point other than the starting point, are deemed to result from either the autocatalytic nature of curing reactions or an artifact of the rapid heat-up cycle at the beginning of experiments.



Figure 4.2 Evolution of the reaction rate of cure with the degree of cure as a function of clay content, (a) Neat Epoxy, (b) Epoxy with 2 % clay, (c) Epoxy with 4 % clay.



Figure 4.3 Evolution of the reaction rate of cure with the degree of cure as a function of CNT content, (a) Neat Epoxy, (b) Epoxy with 1 % CNT, (c) Epoxy with 0.4 % CNT.

It is also believed that the remaining part of the curing of an epoxy-amine system after passing the maximum rate of cure is often diffusion-controlled; thus, the cure reaction rates reached a plateau before a full degree of cure was reached. Another interesting finding in the DSC results of epoxy-CNT systems in Figure 4.3 was observation of much broader and less pronounced peaks in the rate of cure curves in comparison to the ones obtained for the reactive nanoclay-epoxy and neat epoxy systems. This was attributed to possible differences in the cure effects of CNTs. Due to a combination of their superior thermal stability and very different geometry with extremely larger surface area and much higher aspect ratios than nanoclay reinforcements, CNTs might have acted as a heat sink, thus resulting in a much broader and less step rate of cure.

The retardation of cure rates with addition of nanoreinforcements at the same conversion level could arise from reduced mobility of the reacting molecules due to the nanoscale segregation effects. It is postulated that the physical hindrance of CNTs might be a major factor impairing the mobility of active groups in the epoxy and curing agent, thereby leading to a significantly lower degree of cure.

The study of cure kinetics by DSC can be compared to a realistic mathematical model describing the dependence of rate of cure on time and temperature. For this purpose, an additional evaluation of the DSC results was made using the Kamal kinetic model¹⁴⁰ for further analysis of the curing behavior of epoxy-nanoclay systems. The Kamal equation

is a very commonly employed equation describing the cure kinetics of epoxy and unsaturated polyester systems and is given as follows:

$$d\alpha/dt = (k_1 + k_2 \alpha^m)(1 - \alpha)^n$$

where the reaction constants, k_1 and k_2 are temperature-dependant parameters, given by Arrhenius expressions,

$$k_1 = k_0 \exp(-E_1/RT)$$
$$k_2 = k_0 \exp(-E_2/RT)$$

where k_0 is the pre-exponential factor, E_1 and E_2 are the activation energies, R is the universal gas constant and T is the absolute temperature in degrees Kelvin. The parameters, k_1 , k_2 , m and n were estimated without constraints by fitting the experimental data shown in Figure 4.2 using a nonlinear, least-squares regression analysis.

Comparisons of the experimental data with the predictions of the Kamal model are provided in Figure 4.4. A reasonable agreement between the experimental data and the Kamal equation has been obtained over a majority of the curing period. Yet, it is noteworthy to mention that the Kamal model is a generic, empirical model assuming an overall reaction order and fitting the entire experimental kinetic data to this model. It is believed that more complex mechanistic models might be needed for characterizing the "entire" curing period of such filled thermoset systems. This could require a thorough analysis of the mechanistic reactions involved during curing. As such an analysis would entail detailed measurements of the concentrations of reactants, intermediates and products, which go beyond the focus of this research, we instead applied the Kamal equation to the most representative portion of the curing curve. Thus, the initial part of each rate of cure vs. extent of cure curve was deliberately eliminated from the curve fitting in order to avoid the abnormalities resulting from the complex cure effects of the nanoreinforcements in that region of high cure rate.



Figure 4.4 Comparisons of experimental data with the predicted fits of Kamal equation. for the (a) neat epoxy and (b) nanoclay-epoxy systems isothermally cured at 100° C.

After gaining a good insight into the effects of different types and amounts of nanoreinforcement on the curing behavior of epoxy thermosets, our attention was focused on understanding the relationships between these cure kinetics and the chemoviscosity of the filled epoxy thermosets, as discussed in the next section.

4.2 Chemorheological Properties of Epoxy Nanocomposites

An understanding of the interactions between the cure kinetics and the viscosity of reactive thermoset systems along with their subsequent effects on the gelation and dispersion of nanoreinforcements was gained through detailed evaluation of rheological properties. To examine the effect of temperature on the chemorheological properties of the cure-activated, neat epoxy and nanoreinforced epoxy systems, oscillatory shear flow measurements were performed using an RMS-800 rheometer under isothermal curing conditions at 100°C, 120°C and 140°C. It is worthwhile to mention that the oscillatory shear flow measurements were intentionally preferred over those of steady shear during rheological characterization of reacting samples since the former can be applied to a material not only in the liquid state but also in the rubbery and perhaps even in glassy states. The effects of temperature and nanoreinforcement content on the evolution of storage modulus of both nanoclay and nanotube epoxy systems at 100°C and 120°C are illustrated in Figures 4.5 through 4.8.

The curing process of thermoset systems entails many stages proceeding from a reactive fluid to an elastomer (gelled polymer) and finally a crosslinked solid. During these stages, the reaction mechanisms change from kinetic to diffusion control. In the initial stage of cure reactions, the viscous character of the oligomeric epoxy is dominant. As the curing reactions progress, the molecular weight of oligomers increases. This leads to an increase in the dynamic loss modulus of the polymeric system while the storage modulus accelerates even more until it intersects and then surpasses the loss modulus.



Figure 4.5 Evolution of the dynamic storage modulus during curing of reactive mixtures of epoxy, epoxy-2 % clay and epoxy-4 % clay at 100⁰C.



Figure 4.6 Evolution of the dynamic storage modulus during curing of reactive mixtures of epoxy, epoxy-0.4 % CNT and epoxy-1 % CNT at 100^oC.



Figure 4.7 Evolution of the dynamic storage modulus during curing of reactive mixtures of epoxy, epoxy-2 % clay and epoxy-4 % clay at 120⁰C.



Figure 4.8 Evolution of the dynamic storage modulus during curing of reactive mixtures of epoxy, epoxy-0.4 % CNT and epoxy-1 % CNT at 120^oC.

After this stage of cure, the elastomeric character of the epoxy polymer becomes more prominent. It is apparent from Figures 4.5 through 4.8 that the elastomeric response of nanoclay reinforced epoxy mixtures was guite different than that of nanotube reinforced epoxy systems in that the latter exhibited much more stable elastic modulus development following the incipient stages of curing. This is attributed to probable differences in crosslink density due to the different natures of the nanoreinforcements. By the time the dynamic storage modulus of neat epoxy at 120°C started to increase at the end of 7.6 min. of cure, the addition of only 0.4 wt % CNT to the neat epoxy already resulted in about four orders of magnitude increase in the storage modulus. Another interesting observation is that the addition of 4 wt % clay to the neat epoxy at 120° C caused almost the same level of increase in the dynamic storage modulus of neat epoxy as was obtained by an addition of only 0.4 wt % CNT at the end of 7.6 min. of cure. Both systems led to almost four orders of magnitude of increase in the G' of neat epoxy. It must be noted that rheological measurements contain information on cure rate and extent in addition to time-dependent stress/strain relationships.

Comparisons of the isothermal dynamic complex viscosity, η^* , for various neat epoxy, nanoclay-epoxy, nanotube-epoxy systems at two temperatures as a function of the reaction time are also provided in Figures 4.9 and 4.10. At the beginning of the cure, the viscosity slowly increased with time. Then, at a certain point, a very rapid increase of the viscosity was observed, indicating gelation.



Figure 4.9 Comparisons of the dynamic complex viscosity during curing of reactive mixtures of epoxy, epoxy-2 % clay and epoxy-4 % clay at 100^oC.



Figure 4.10 Comparisons of the dynamic complex viscosity during curing of reactive mixtures of epoxy, epoxy-2 % clay and epoxy-4 % clay at 120^oC.



Figure 4.11 Comparisons of the dynamic complex viscosity during curing of reactive mixtures of epoxy, epoxy-2 % clay and epoxy-4 % clay at 140^oC.



Figure 4.12 Comparisons of the dynamic complex viscosity during curing of reactive mixtures of epoxy, epoxy-0.4 % CNT and epoxy-1 % CNT at 100^oC and 120^oC.



Figure 4.13 Evolution of the dynamic storage modulus during isothermal curing of epoxy, epoxy-CNT and epoxy-nanoclay mixtures at 100° C as a function of extent of cure.



Figure 4.14 Evolution of the dynamic complex viscosity during isothermal curing of epoxy, epoxy-CNT and epoxy-nanoclay mixtures at 100° C as a function of extent of cure.

A comparison of the results in Figure 4.10 with those in Figure 4.12 shows that, at the early stages of curing, the effect of nanotube concentration on viscosity of the epoxy system was much greater than that of the nanoclay, particularly at high temperatures. While the addition of 2 % clay to the neat epoxy at 120°C led to a 345 % increase in η^* as compared to the neat epoxy systems at the end of 6.6 min. of cure, the addition of only 0.4 % carbon nanotube resulted in a 15,000 % increase in η^* for the same time period. Figures 4.13 and 4.14 are plotted to elucidate substantial differences between the effect of extent of cure on the viscoelastic properties of epoxy-CNT systems and epoxy-nanoclay systems. Dynamic complex viscosity and storage modulus of these material systems obtained from Figure 4.13 and 4.14 at the intermediate ($\alpha = 0.5$) and later ($\alpha = 0.7$) stages of cure are also summarized in Table 4.1 to highlight the effect of different nanoreinforcement types on the viscoelastic properties as a function of the degree of cure. As is seen from Table 4.1, CNTs have a much more pronounced effect on both the storage modulus and dynamic viscosity than the nanoclays particularly for the more advanced cure state. This is explained by the fact that intensive particle-particle interactions and particle-matrix interactions in the case of CNT-epoxy nanocomposites could lead to superior structure development during curing due to their significantly higher aspect ratio and larger surface area than nanoclays. This would lead to a larger area of interfacial contact between particle and matrix/unit volume than for nanoclay.

Type of Reactive	$\alpha = 0.5$		$\alpha = 0.7$	
Material Systems	G', Pa	η^* , Pa.sec	G', Pa	η^* , Pa.sec
Epoxy	0.8	0.21	2.82	10.5
Epoxy-0.4% CNT	110	36.1	1.53E+05	3.88E+04
Epoxy-1% CNT	489	139	5.22E+04	1.96E+04
Epoxy-2% Clay	0.55	9.48	7.93	226
Epoxy-4% Clay	4.80	10	115	546

Table 4.1 Comparisons of the effect of extent of cure on the viscoelastic properties of epoxy nanocomposites cured at 100° C.

Gel times of the reacting systems were determined from the crossover time of the storage and loss modulus values. As expected, the gel time decreased with increasing temperature, as the rate of the crosslinking reaction increased with temperature. The effect of nanoreinforcement content on the gelation is depicted in Figure 4.15. The results are then further analyzed for various nanotube and nanoclay loadings, as shown in Figures 4.16 and 4.17, by comparing the activation energies obtained from the Arrhenius dependence of gel time as a function of temperature, according to:

$$(l/t_{gel}) = A \cdot exp(-E_A/R \cdot T)$$

where A is the pre-exponential factor in 1/min., E_A is the Arrhenius activation energy in J/mol, R is the gas constant 8.32 J/mol^{•0}K, and T is the temperature in degrees Kelvin.



% Nanoreinforcement

Figure 4.15 Effect of nanoreinforcement type, content and cure temperature on the gel-time measurements, (a) epoxy-clay mixtures at 100°C, (b) epoxy-clay mixtures at 120°C, (c) epoxy-clay mixtures at 140°C, (d) epoxy-CNT mixtures at 100°C, (e) epoxy-CNT mixtures at 120°C, (f) epoxy-CNT mixtures at 140°C.



Figure 4.16 Arrhenius plot for the early cure stage in epoxy systems with various nanoclay loadings, (a) Neat epoxy mixtures: $E_A = 35.38 \text{ kJ/mol}$, (b) Epoxy-2 % clay mixtures: $E_A = 42 \text{ kJ/mol}$, (c) Epoxy-4 % clay mixtures: $E_A = 44.38 \text{ kJ/mol}$.


Figure 4.17 Arrhenius plot for the early cure stage in epoxy systems with various CNT loadings, (a) Neat epoxy mixtures: $E_A = 35.38 \text{ kJ/mol}$, (b) Epoxy- 0.4 % CNT mixtures: $E_A = 62.21 \text{ kJ/mol}$, (c) Epoxy-1 % CNT mixtures: $E_A = 63.43 \text{ kJ/mol}$.

Rheological characterization reveals that the presence of nanoclay enhanced the cure kinetic dependence on temperature. Nonetheless, there was only a slight increase in the activation energy with a further increase in the nanoclay content. Simon¹⁶⁰ *et al* also reported similar results in that they observed a small change in the activation energies of various epoxy resin systems by the addition of up to 10 % organoclay. These findings are also in agreement with the work conducted by Krishnamoorti and Giannelis¹⁶¹ who stated that the activation energies of thermoplastic poly(ε -caprolactone) did not vary upon the incorporation of 1-10 % layered silicate. On the other hand, the activation energy was surprisingly found to increase up to 79 % upon addition of even such smaller amounts of CNTs in this research. Different reaction mechanisms in the presence of CNTs may be responsible for the higher activation energies, such as the dependence on reactant

diffusion through the nanoscale reinforcement network. This "physical segregation effect" by which dispersion of the nanoscale reinforcements separates the epoxy chains from the curative would lead to a much higher energy barrier that must be overcome by increasing the temperature to enhance molecular diffusion.

It is evident that the effects of both nanoclays and nanotubes on the relative change in gel time of epoxy systems were found to be larger at higher cure temperatures. However, larger absolute changes in gel time were observed for lower cure temperatures where cure times were also longer. Morphological properties of the epoxy nanocomposite systems were explored via wide angle X-Ray diffraction, SEM and TEM studies for further evaluation of dispersion.

4.3 Morphological Characterization of Epoxy Nanocomposites

The complexities involved during the course of thermoset cure reactions were expected to influence the exfoliation behavior of nanoclays in the epoxy matrix. As indicated in the studies of Pinnavaia and coworkers,^{162, 163} the exfoliation behavior of nanoclays in thermoset systems is governed by both thermodynamic and kinetic considerations. These principles, for example, would suggest that the heat of the intragallery polymerization released before the gel point could be larger than the van der Waals attractive energy between the interlayers, allowing complete exfoliation to take place.

During the curing of thermosets, a substantial increase in the viscosity of the system would restrict diffusion of reactants into the intragallery space, which in turn makes complete exfoliation of the clay tactoids more difficult to achieve. Important also is a balance in the relative cure rates in the intra- and intergallery regions. Wide angle X-Ray diffraction (WAXD) tests on both liquid "epoxy-clay" and "epoxy-clay-curative" mixtures were conducted to determine whether the intercalation process begins during the incipient stages of thermoset cure while still at room temperature or during later curing stages. Figure 4.18 summarizes the results of these experiments with and without the presence of curative. The value of θ is a measure of the intergallery d-spacing between nanoclay platelets in reciprocal space; therefore, a decrease in θ indicates a larger platelet spacing. As seen from the graphs, there is a decrease in $2 \cdot \theta$ values both with and without curative addition to the epoxy-clay mixture as compared to the characteristic peak position of neat clay $(2 \cdot \theta = 3.7^{\circ})$, indicating an expansion of the clay galleries. Contrary to expectations, the addition of curative caused a smaller increase in the clay gallery d-spacing than with no curative. One possible explanation is the collapse of the clay galleries as a result of faster curing of the epoxy outside of the clay galleries. Another possibility is that some outward migration of epoxy molecules from the clay galleries, subsequent to the addition of curative into the previously mixed epoxy-clay system, could reduce the gallery height over time. Either event could result in reduced swelling of the galleries after curative addition, thus causing the observed decrease in the gallery d-spacing. This interesting observation also led us to conclude that the expansion of clay galleries is taking place during curing.



Figure 4.18 Effects of curative and nanoclay on the intercalation behavior of liquid epoxy prepolymer during the incipient stages of curing.

To evaluate final clay d-spacings after complete curing, WAXD measurements were also carried out on the solid, cured samples. The results show that only under certain conditions are exfoliated or highly intercalated structures observed, depending on the clay content and cure temperature. Figures 4.19 and 4.20 present the effect of clay content on the intercalation / exfoliation behavior of epoxy cured at 120 °C and 140 °C, respectively. By the same token, effects of different cure temperature on the 4 wt % and 2 wt % clay reinforced epoxy systems are compared in Figures 4.21 and 4.22, respectively. These plots indicate that the neat clay peak at $2 \cdot \theta = 3.7$ ° is reduced to 2.5 ° and 1.98 ° when a 2 wt % clay nanocomposite is cured at 120 °C and 140 °C, respectively.



Figure 4.19 Effect of nanoclay content on the exfoliation behavior of epoxy cured at 120°C, as determined by WAXD.



Figure 4.20 Effect of nanoclay content on the exfoliation behavior of epoxy cured at 140°C, as determined by WAXD.



Figure 4.21 Effect of curing temperature on the exfoliation behavior of epoxy-4% nanoclay nanocomposites determined by WAXD.



Figure 4.22 Effect of curing temperature on the exfoliation behavior of epoxy-2% nanoclay nanocomposites determined by WAXD.

It is also noteworthy to mention that wider diffraction curves were obtained at higher clay concentration in higher temperature cures, indicating a higher state of intercalation leading to exfoliation of the nanoclays, as confirmed by TEM observations. However, as shown in Figure 4.23, contrary to the WAXD results obtained for 4 % clay-epoxy systems cured at 140 °C, TEM images of these nanocomposites revealed only partial exfoliation. This surprising result also confirmed that WAXD can be inadequate to differentiate fully exfoliated structures from otherwise disorganized structures and must be supported by TEM observations, as mentioned in the background section.





(a)

(b)



(c)

(d)

Figure 4.23 TEM images of various sections of an epoxy-4 wt % clay nanocomposite cured at 140 °C for 3 hr.; (a) highly intercalated clay structure, (b) mixed (mainly exfoliated and intercalated) clay structure, (c) exfoliated clay structure (d) low magnification image showing spatial distribution of highly intercalated clay structure.



Figure 4.24 TEM image of an epoxy-1 % CNT nanocomposite cured at room temperature.

Attempted TEM observations of CNT dispersion were considered not insightful since cylindrical CNT forms were not apparent, as shown in Figure 4.24. Despite the difficulties encountered during the TEM examinations of CNT-epoxy nanocomposites, based on the observation of tremendous increases in the dynamic complex viscosity of the epoxy-CNT samples and several supportive SEM images collected for these samples, it is deduced that the dispersion of CNTs in epoxy- CNT nanocomposites was excellent. Moreover, such an observed viscosity increase occurred at a reduced state of cure as physical segregation of curative moieties from the epoxy chains may have retarded the curing reaction due to the presence of a nanoscale reinforced structure. The reduced cures in both layered silicate-epoxy and CNT-epoxy nanocomposites are also supported by the DSC results as described in the earlier section.

SEM was also conducted on the nanocomposites to utilize the much larger depth of field than is possible by TEM. This also allowed for observation of larger sample areas. Representative SEM micrographs of the fractured surfaces of epoxy-clay and epoxy-CNT nanocomposites are presented in Figures 4.25 through 4.27. The fracture surfaces of epoxy-clay nanocomposites became rougher and flakier as the nanoclay loading was increased. This suggests that the dispersion of clay platelets was improved as evidenced by an increase in brittle fracture and indicative of a higher modulus with increased dispersion at higher clay loadings as supported by the absence of X-ray diffraction peaks for higher clay loaded epoxy nanocomposites.

In the case of epoxy-CNT nanocomposites, the fractured surfaces appeared to have a much larger degree of roughness which can be explained by the crack deflection and the continual crack propagation occurring on slightly different fracture planes. More curved patterns were observed throughout the whole crack surface. This is attributed to the resistance of strong SWNTs to breakage by fronts during crack propagation in the nanocomposites, which in turn forced the fronts to frequently change their propagation direction. Consequently, a fracture morphology with a great deal of highly curved patterns of crack propagation was revealed. These fractographs are also considered to be an indication of uniform dispersion.





Figure 4.25 SEM images of the fractured surfaces of epoxy-2 wt % clay nanocomposites cured at room temperature at high and low magnification.





Figure 4.26 SEM images of the fractured surfaces of epoxy-4 wt % clay nanocomposites cured at room temperature.



Figure 4.27 SEM images of the fractured surfaces of an epoxy-1 % SWNT nanocomposites cured at room temperature.

4.4 Summary

The relationships among the composition, cure, chemorheology and morphology of SWNT and layered silicate epoxy nanocomposites were examined. WAXD and TEM experiments on the cured epoxy-clay samples revealed that only under certain cure conditions are highly intercalated or partially exfoliated structures observed, depending on the changes in the clay content and usually at higher cure temperatures. Less swelling of the clay galleries in the presence of curative in the early stages of cure process is detected by a decrease in the gallery d-spacing as compared to the no-curative cases during WAXD measurements on the liquid samples. This is considered to be indicative of the expansion of clay galleries taking place during cure. It was found that the presence of nanoreinforcements retarded cure kinetics to some degree such that the activation energies increased with the nanoreinforcement content. The increases in the activation energies were observed to be more significant in the case of CNT reinforced epoxy systems. This phenomenon is explained by a "physical segregation effect" by which segregation of curative moieties from the epoxy chains due to the presence of nanoscale CNT structure is deemed responsible for the increases in the activation energies of the nanocomposites. It is postulated that the physical hindrance of CNTs plays a significant role in impairing the mobility of active groups in the epoxy and curing agent, thereby leading to a significantly lower degrees of cure. This hypothesis also supports the observed complexity in the chemorheological properties in the presence of nanoreinforcements through their effects on the gelation kinetics of the thermoset polymers.

CHAPTER V

ANALYSIS OF WETTABILITY OF BIAXIAL GLASS FABRICS WITH EPOXY NANOCOMPOSITES

In this chapter, the propensity of biaxially-stitched glass fabrics to be wetted by nanoclay-enriched, reactive epoxy mixtures will be explored through a set of contact angle and surface tension measurements. The objective of studying the wetting properties of such porous glass fabrics is to gain an understanding of the effects of curative and nanoclay particles on the control of wettability and to assess the feasibility of using such multicomponent, complex epoxy systems in the RTM applications. During the RTM of woven or stitched fabrics, the resin is basically forced to flow into two regions; the gaps among individual filaments in a tow and the gaps in between the fiber tows. Due to the two- to three-orders of magnitude difference in the widths of flow channels in between these two regions, non-uniform micro-flow and macro-flow fronts could result when the processing parameters such as injection pressure, flow rate and capillary forces are not properly controlled. Voids trapped during the mold-filling stage of the RTM are also believed to be the consequences of non-uniform micro- and macro-flows. Thus, the conditions controlling viscous and capillary flows in RTM should be examined to evaluate the fiber mat impregnation. For this purpose, the wetting effects of nanoclayreinforced epoxy systems are investigated with an emphasis on the changes in the axial resin impregnation rates and in the relative tow-permeability properties via Washburn-type capillary wicking experiments. As the wicking phenomenon is caused by surface forces, an evaluation of surface tension properties was essential. The relative magnitude and importance of the factors affecting the adsorption kinetics of these multicomponent, complex, reactive epoxy mixtures are also discussed.

5.1 Analysis of Capillary Wetting Phenomenon of Biaxial Glass Fabrics with Epoxy Nanocomposites via Capillary Flow and Du Nouy Ring Experiments

The Washburn theory proposes that if a porous material is brought into contact with a liquid, there will be a flow of liquid into the pores of the test material as a result of capillary forces. This phenomenon is also known as *"wicking"*. Knowing that a good wetting is a critical condition for obtaining good adhesion properties between the matrix and reinforcement systems during RTM, an evaluation of the wicking phenomenon via the measurements of axial resin impregnation rates, contact angle and surface tension properties was essential. These capillary measurements allowed us to assess the effect of nanoreinforcements in an epoxy matrix on the wetting and impregnation properties of biaxially stitched glass fabrics.

For this purpose, an experimental set-up comprising a high precision Ohaus Adventurer AR 1140 microbalance, a laboratory jack, a 100 mL glass beaker full of test fluid and a computer utilizing a special software developed for the instant data collection was built as illustrated in Figure 3.9 earlier. Samples of biaxially-stitched, rectangular glass fabrics were prepared with dimensions of 0.52 mm × 20 mm × 50 mm. The samples were suspended from the microbalance such that the 20 mm edge was parallel with the wetting liquid surface. The wetting liquids were epoxy-curative and epoxy-curative-nanoclay mixtures. Data collection was initiated and the wetting liquid was raised just high enough to contact the edge of the glass fabric. Data collection was terminated when the wetting rate ceased to change with time. Representative results of these measurements are presented in the form of weight gain as a function of square root of time from Figures 5.1 through 5.3 to facilitate the calculations of " m^2/t " to be used in the Washburn Equation¹⁵⁶ which can be expressed in the form of:

$$\cos\theta = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \cdot \sigma_L \cdot c}$$

where σ_L is liquid surface tension [mN/m], η is liquid viscosity [mPa.sec], ρ is liquid density [g/cm³], θ is the contact angle between the liquid and the porous fabric, m is weight of the liquid absorbed into the porous material [g], t is time after the porous fabric and the test liquid are brought into contact [sec] and c is a material constant pertinent to the porous architecture of the test material and it can also be expressed as a function of the capillary radius, r and the number of capillaries, n_k , as follows:

$$c = \frac{1}{2} \cdot \pi^2 \cdot r^5 \cdot n_k^2$$

The value of c is known also as the hydraulic constant. As direct measurement of the volume or the height of liquid uptake by the glass fabric is much more difficult than the direct measurement of the mass uptake, the capillary measurements were conducted based on the changes in weight gain. The negative weight gain readings observed at the initial part of the wicking curves are due to the buoyancy effect such that a negative force is applied to the glass fabric as it penetrates the liquid interface. Figure 5.1 through 5.3 also reveal that there are mainly two regimes during which the impregnation rates of viscous epoxy mixtures are substantially different.

To ensure correct analysis and comparisons of the observed impregnation rates in different epoxy-nanoclay systems, the raw data readings of fluid mass uptake as a function of square root of time are recast into fluid impregnation or spreading height as a function of time. The instantaneous impregnation or spreading height values are calculated by dividing the raw data readings of fluid mass uptake to the experimentally determined density of each material system and to the constant cross-sectional area of 10.4 mm² of glass fabric sample. Comparisons of the spreading heights of epoxy mixtures at different nanoclay loadings are illustrated in Figure 5.4. A careful observation of Figure 5.4 indicates that the impregnation of viscous epoxy mixtures appears to occur too fast at the beginning of wicking experiments such that the epoxy-curative mixture could penetrate into the glass fabric at 2.06 mm/sec while the epoxy-4 % nanoclay-curative mixture could spread at 1.22 mm/sec. These initial impregnation rates are considered unusually high and are unreasonable considering the material properties. This abnormality is attributed to the "edge" effects.



Figure 5.1 Adsorption of epoxy-curative mixtures into the biaxiallystitched glass fabrics during the room temperature wicking experiments.



Figure 5.2 Adsorption of epoxy-2 wt % clay-curative mixtures into the biaxiallystitched glass fabrics during the room temperature wicking experiments.



Figure 5.3 Adsorption of epoxy-4 wt % clay-curative mixtures into the biaxiallystitched glass fabrics during the room temperature wicking experiments.

The edge of the glass fabric contacting with the wetting liquid first is much more "jagged" and irregular than the remaining portion of the fabric. Undoubtedly, it has a much more "open" structure resulting in a larger effective capillary radius (hydrodynamic volume). According to the Washburn equation, the wetting rate, *inter alia*, is directly proportional to the capillary radius. Another source of error could arise from the motion of fibers at the beginning of capillary measurements. Although it was assumed that the fibers remained immobile during impregnation, this assumption may be questionable as surface tension forces may induce fiber motion at the beginning of the measurements. Hence, the initial part of the wicking experiments is considered as unsteady-state and is not representative of the tow internal structure or capillarity.

The impregnation height and spreading rate appeared to reach steady-state at the end of approximately 3 minutes. Figure 5.4 also indicates that the impregnation height of glass fabric sample with the epoxy-4 wt % nanoclay-curative mixture is observed to be approximately 44 % less than that is obtained by an epoxy-curative mixture after 5 minutes. Although the times required to reach the steady-state conditions in the nanoclay containing epoxy mixtures didn't appear to follow a trend at the beginning of wicking experiments, calculation of the rates of impregnation, dh/dt, eliminated this apparent conflict and showed a decreasing trend as the nanoclay content is increased. A comparison of the impregnation rates of wetting with and without presence of nanoclay is presented in Figure 5.5. The impregnation rates calculated for the steady-state regimes of wicking experiments will also be used later to correlate the effect of nanoclay on capillary flow so as to explain the implications on the limiting nanoclay content in RTM, in the next section. The decrease in the impregnation rate with an increase in nanoclay content is attributed to the curing reaction promoting to higher contact angle, higher surface tension and higher viscosity conditions as the cure rate progresses. In addition, the effect of presence of nanoclay on resin viscosity has to be considered. Moreover, decreases in spreading rates with time are explained by the viscous drag effects since more fluid has to be dragged along as time passes.

For a complete analysis of capillary flow of reactive epoxy nanoclay mixtures through the porous, biaxial glass fabric structures using the Washburn Equation, room temperature density, surface tension and viscosity measurements of epoxy-curative and epoxy-nanoclay-curative mixtures were essential.



Figure 5.4 Comparisons of the impregnation heights of epoxy mixtures at different nanoclay loadings into the biaxially-stitched glass fabrics (a) data collected during the entire wicking experiments (b) data collected during the initial part of wicking experiments.



Figure 5.5 Comparison of the impregnation rates of reactive epoxy mixtures with and without nanoclay into the biaxially-stitched glass fabrics during the steady-state regime of wicking experiments.

Moreover, the material constant "c" had to be determined via additional wicking experiments conducted with a Dow Corning 200® poly(dimethylsiloxane) 5 cSt fluid which was known to have a surface tension of 19.7 mN/m, a specific gravity of 0.915, a viscosity of 4.57×10^{-4} Pa.sec and a contact angle of $\theta = 0^0$ (cos $\theta = 1$) on the glass fabrics. Using a wetting fluid with a contact angle of 0° ensured that the Washburn equation could be solved for "c" alone. Upon substitution of all of these constants along with the experimentally determined " m^2/t " slope of 1.66×10^{-4} into the Washburn equation, the material constant, *c*, of the biaxially-stitched glass fabrics was determined as 4.60×10^{-7} cm⁵. The results of silicon oil capillary flow measurements are also provided in Figure 5.6.



Figure 5.6 Adsorption of the Dow Corning 200® poly(dimethylsiloxane) 5 cSt silicon oil fluid into the biaxially stitched glass fabrics for determination of the material constant, "c".

The experimental density measurements of all reactive and non-reactive epoxy and epoxy-nanoclay mixtures were conducted by first pouring 3 mL of each test fluid into a tared 4 mL graduated cylinder and then weighing the mixture in the graduated cylinder with a high precision balance. The densities calculated by the division of measured weight to 3 mL sample volume are summarized in Table 5.1. The density measurements could not be performed with a pycnometer due to the difficulty of cleaning highly viscous, reactive epoxy mixtures. Density measurements were repeated at least five times for each material system to estimate errors due to meniscus readings. Differences in the densities of these material systems were observed to be very small. This was attributed to the small differences in the nanoclay loadings and probable experimental errors during

meniscus readings. The data shown in Table 5.1 indicate that differences in measured densities are not significant statistically.

Material Systems	Density, g/cm ³
Epoxy	1.092 ± 0.0056
Epoxy-2% Clay	1.097 ± 0.0006
Epoxy-4% Clay	1.094 ± 0.0053
Epoxy-Cur.	1.027 ± 0.0024
Epoxy-2% Clay-Cur	1.064 ± 0.0027
Epoxy-4% Clay-Cur	1.066 ± 0.0026

Table 5.1 Summary of the density measurements of epoxy mixtures.

All viscosity measurements were conducted with a SC-25 spindle at 120 rpm using the "small sample adapter" accessory of the Brookfield LV DV II + Pro Digital Viscometer. The results of room temperature viscosity measurements of reactive nanoreinforced epoxy systems are presented in Figure 5.7.

Considering that the mold filling stage of RTM experiments usually takes less than 10 minutes, the averages of initial viscosity data collected only in the first 15 minutes of these measurements were used in the Washburn equation calculations.



Figure 5.7 Comparisons of room temperature viscosity measurements of reactive epoxy-nanoclay mixtures at different nanoclay loadings.

Representative results of the Du Nouy Ring experiments, conducted to measure the surface tensions of both unreactive and reactive epoxy-nanoclay mixtures are summarized in Table 5.2. The spreading pressure¹⁶⁴ is defined as the difference between liquid-vapor surface tensions of pure liquid and a mixture in a general sense and epoxy and amine/epoxy mixtures in the current work. These results serve to emphasize the relative importance of the competition between the chemical reactions of amine in the bulk of the epoxy resin mixtures and the diffusion of amine molecules to the epoxy liquid/air interface.

Material Systems	Surface Tension,	Spreading Pressure, π ,	
	min/m	mN/m	
Epoxy	50.9	50.9	
Curative	31.4	-	
Epoxy-2% Clay	45.8	5.03	
Epoxy-4% Clay	45.8	5.05	
Epoxy-Cur.	38.4	12.5	
Epoxy-2% Clay-Cur	38.9	12.0	
Epoxy-4% Clay-Cur	43.4	7.50	

Table 5.2 Comparisons of the effects of nanoclay and curative on the surface tension and the spreading pressure of epoxy mixtures.

In composites manufacturing, as a low surface tension of the matrix is considered as the driving force for good wetting and impregnation of fabrics, anything that reduces the intermolecular forces at the surface is important since it will also reduce the interfacial tension of the matrix. Hence, both the epoxy/air and the epoxy/glass fiber interfacial tensions are critical factors in determining the rate of migration of epoxy mixtures into the porous glass fabrics.

In the case of the epoxy-curative mixture employed in this research, the amine molecules absorbed at the epoxy/air interface are deemed to lower the overall surface tension of epoxy mixtures as the measured surface tension of the Jeffamine D230 diamine curative is much smaller than that of neat epoxy. The diamine curing agent is expected to act as a surfactant such that it caused a 25 % reduction in the surface tension of epoxy during the incipient stages of cure.

The surface tension of epoxy-nanoclay mixtures, without any curative, is observed to be only about 10 % lower than that of neat epoxy. This is attributed to the probable interactions/reactions of the "octadecylamine" surfactant, a mono-amine which constitutes 25-30 % of the montmorillonite Nanocor I30.E nanoclay, with the epoxy molecules. The octadecylamine surfactant on the surface of the nanoclay particles is used as a compatibilizer and to prevent aggregation. Beyond 2 wt % nanoclay, no further decrease in surface tension of the epoxy mixture was observed. This indicates that any octadecylamine, released from the nanoclay, has reached a saturation concentration at the epoxy/air interface.

Another interesting result of these Du Nouy Ring measurements was that the addition of only 2 wt % nanoclay to the epoxy-curative mixtures did not change the surface tension while that of 4 wt % nanoclay led to a 12 % increase in the surface tension. This was explained by a reduction in the surface excess of amine in the higher nanoclay loading levels. In fact, it is very well-known that most minerals, such as nanoclays, have negative zeta potentials due to the presence of ionizable groups¹⁶⁵ such as Si-OH \leftrightarrow Si-O⁺ + H⁺. In a solvent-borne or nonaqueous system, the dielectric constant of the solvent is much lower than water. As a consequence, the Si-OH groups may not be ionized and are relatively acidic. Therefore, they could react (moderately acidic silanol/relatively basic amine) with the curing agent in the following acid/base reaction on one extreme or simply form a hydrogen bonded complex on the other:

$$\text{Si} = OH + H_2 N$$
 $NH_2 = Si = O^{-} H_3 N^{+} NH_2$

The consumption of the curative in such a reaction would have a very negative ΔG driving force and could reduce surface excess of the amine substantially. The surface of montmorillonite clay also contains silanol groups¹⁶⁶ and octadecylamine compatibilizer interacts with the clay surface in a manner similar to that illustrated above. Chemistry such as this is the basis for the use of compatibilizers and coupling agents.^{167, 168} In essence, there is a competition of octadecylamine compatibilizer and amine curative for the clay and resin/air interfaces. Ultimately, thermodynamics will determine the partitioning coefficients. Larger amounts of nanoclay could sequester larger quantities of amine curative and result in less amine to be able to reach to the surface at the same levels of added curative. Remembering the fact that nanoparticles have a large surface area/mass, they must be capable of sequestering large amounts of surface active material; particularly, if the surface active material can participate in a reaction such as that shown above. Such events could change the effective level of curative and alter the cure state. Hence, a reduction in the surface excess of amine would lead to higher surface tension in the case of epoxy-4 wt % clay-curative mixtures.

The studies conducted by Foister¹⁶⁴ indicated that the spreading pressure, π , could also be considered as an indicative of relative measure of surface concentration of amine. The results of spreading pressures calculated for the reactive and unreactive epoxynanoclay mixtures employed in our research are tabulated in Table 5.2. The fact that spreading pressure, π , decreased with the addition of nanoclay indicated that the surface activity of amine molecules decreased in the presence of nanoclay. More pronounced effects are observed when both nanoclay and curative are present in the epoxy at the same time as illustrated in Figure 5.8. It is postulated that the mono-amine surfactant coming from nanoclay is changing the reaction stoichiometry of the epoxy/amine reaction, particularly at higher addition levels of nanoclay.



Figure 5.8 Effect of nanoclay surfactant and curative on the surface adsorption of amine at the epoxy-air interface.

Although the curative is assumed to be present at the initially added stochiometric level to the epoxy, the reaction equilibrium in the epoxy-nanoclay-curative mixtures will be affected from a mixture of mono-amine and diamine molecules in the epoxy as the mono-amine surfactant of nanoclay was displaced by the curative and released to react with epoxy. This hypothesis is also supported by the reductions in the extent of cure and the rate of cure at the higher nanoclay loadings as confirmed by the DSC results given in the previous chapter.

Contact angles of reactive epoxy-nanoclay mixtures against glass fabric were calculated upon substitution of all of these experimental results for density, viscosity, surface tension of each material system and the material constant, "c" of 4.60×10^{-7} cm⁵ into the Washburn equation. The results are presented in Figure 5.9.



Figure 5.9 Effect of nanoclay on the contact angle of reactive epoxy-nanoclay mixtures.

The results of contact angle calculations indicated that, while the addition of 4 wt % nanoclay to the epoxy caused approximately a 21 % increase in the contact angle, a 13.5 % increase was observed in the case of epoxy-2 wt % nanoclay-curative mixtures. A contact angle is an indicator of the degree of affinity of a fluid for a substrate. In the

present case, the affinity of nanoclay reinforced reactive epoxy mixtures for the glass fabric has to be considered. It is concluded that, as the difference between the surface energy of the glass fabric reinforcement and that of epoxy-nanoclay-curative mixtures become smaller with an increase in the nanoclay content, it becomes much more difficult for the adhesive forces of the epoxy mixture to overcome the cohesive forces. Thus, the "wet out" or spreading of reactive epoxy-nanoclay mixtures on the glass fabrics becomes more difficult; leading to contact angles approaching 90⁰ as the nanoclay amount is increased.

5.2 Implications on the Limiting Nanoclay Content in RTM Capillary Wetting and *"Relative Tow Permeability"*

In this section, the capillary flow of reactive epoxy-nanoclay mixtures in the biaxial glass fabrics will be assessed from the point of view of the factors affecting the tow permeability and the limitations on the maximum amount of nanoclay that can be used in RTM. As a good impregnation of the fabrics is a prerequisite for the success of RTM, an evaluation of the degree of tow impregnation in the presence of nanoclay particles was crucial. For this purpose, the relative tow permeabilities of the biaxially-stitched glass fabrics were determined by an equation proposed by Tucker and Dessenberger¹¹². This equation is analogous to the Washburn equation and expressed as:

$$\frac{d}{dt} \left(L^2(t) \right) = \frac{2 \cdot S_{zz} \cdot \gamma \cdot l_a}{\mu \cdot \varepsilon_f}$$

where, S_{zz} is the tow permeability, ε_f is the porosity of the fabric, γ is the surface tension of the wetting material and l_a is the contact line length per unit area of the fabric, which is also defined as the perimeter of each fiber per cross-sectional area of tow.

As the experimental measurement of l_a was considered very difficult, the "relative" tow permeabilities were calculated using the raw data from capillary wetting experiments with surface tension and viscosity values of corresponding material systems. As the initial part of capillary flow experiments are believed to represent an "unsteady-state", the relative tow permeabilities of biaxially-stitched glass fabrics were determined for both the "unsteady-state" and the "steady-state" regimes of the experiments. The results are provided in Table 5.3.

Table 5.3 Comparisons of the relative tow permeability and the rate of fluid absorption determined for both unsteady-state and steady-state regimes of wicking experiments.

Reactive Material Systems	$\left(W/\sqrt{t}\right)^{2}_{State}^{Unsteady},$ g^{2}/sec	$\left(W/\sqrt{t}\right)^{2}_{Steady}_{State},$ g ² /sec	$(S_{zz})^{Unsteady}_{State}$	$(S_{zz})_{Steady}_{State}$
Epoxy	1.82 x 10 ⁻²	1.23 x 10 ⁻⁶	1	1
Epoxy-2% Clay	$1.32 \ge 10^{-2}$	7.25 x 10 ⁻⁷	0.88	0.71
Epoxy-4% Clay	1.20×10^{-2}	5.72×10^{-7}	0.76	0.53

Both the unsteady-state and steady-state relative tow permeabilities are observed to decrease as the nanoclay amount is increased. Thus, the presence of nanoclay is believed

to reduce the "*tow wet-out*" with almost 50 % reduction in the steady-state tow permeability in the case of 4 % nanoclay addition to the reactive epoxy.

The capillary number, $Ca = \eta \cdot v / \gamma$, is a measure of the ratio of viscous-to-capillary forces, where η is viscosity, v is velocity and γ is surface tension. The results of wicking experiments are also interpreted to correlate the effect of impregnation or spreading rates, dh/dt, evaluated during steady-state regime of experiments on the capillary flow in the presence of nanoclay. Capillary numbers for reactive epoxy-nanoclay systems are calculated from data obtained during steady-state capillary wetting measurements discussed earlier. Capillary wetting experiments were conducted under axial impregnation conditions and without the influence of the RTM mold. The capillary numbers evaluated under these conditions should give a reasonable estimate of flow parameters due to the fabric alone. The results are provided in Table 5.4 while their relationship to viscosity and surface tension are illustrated in Figure 5.11.

Reactive Material Systems	dh/dt, m/sec	η / γ, Pa.sec/(N/m)	Ca
Epoxy	1.20 x 10 ⁻⁶	16.92	2.03 x 10 ⁻⁵
Epoxy-2% Clay	8.36 x 10 ⁻⁷	20.30	1.70 x 10 ⁻⁵
Epoxy-4% Clay	7.78 x 10 ⁻⁷	19.36	1.51 x 10 ⁻⁵

Table 5.4 Comparisons of the effect of spreading rate and nanoclay amount on the capillary flow in the steady-state regime of wicking experiments.



Figure 5.11 Effect of nanoclay on the capillary flow as a function of (a) viscosity and (b) surface tension of the reactive epoxy-nanoclay mixtures during resin impregnation.

Since the capillary number $\propto \eta/\gamma$, the relative change of these two quantities will determine the value. The capillary wetting experiments, shown in Figure 5.5, show that steady-state wetting is achieved over a timescale of t > 200 seconds. The surface tension data, illustrated in Figure 5.11 (b), indicated a substantial increase of epoxy-curative surface tension with the addition of clay; such that the increase in surface tension was larger than the increase in viscosity, thus, the capillary number was reduced. The Washburn equation suggests that the capillary wetting rate, dh/dt $\propto \gamma/\eta$ and, as a consequence, an increase in this ratio will result in a smaller rate and this is, indeed, observed by the values shown in Table 5.4. A capillary number < 1 indicated that surface tension was the dominant factor, under the current set of conditions, in the fluid flow inside the fabric.

Several researchers^{127,169,170} reported that capillary forces have a substantial influence on the uniformity of the micro- and macro-flows that exists in RTM. Voids trapped during the mold-filling stage of the RTM are also believed to be the consequences of non-uniform micro- and macro-flows. The micro-flows in between the filaments in a tow are driven by both capillary forces and injection pressure while the macro-flows in between the fiber tows are driven mainly by injection pressure. Wicking flows in the fiber tows are usually observed at low-filling velocities when the micro-flow in the fiber tows preceded the macro-flow due to the capillary effects. In such cases, macro-voids may be trapped in between the fiber tows. Thus, there is a critical capillary number range below which severe void problems are observed in RTM. While studies conducted by $Chang^{169}$ reported a critical capillary value of 2.5 x 10⁻³, Young¹⁷⁰ indicated a critical
capillary number range of 1 x 10^{-4} - 2 x 10^{-4} . In any event, a Ca << 1 indicates that capillarity dominates over inertia in governing fluid dynamics. Considering the fact that capillary numbers of the reactive epoxy-nanoclay mixtures are found to be as low as 1.51 x 10^{-5} , the formation of macro-voids in the epoxy-nanoclay composites are expected. Indeed, several optical micrographs taken from the cross-sectional areas of RTM molded composites supported this expectation and will be discussed in the future chapters.

5.3 Summary

Whether a reactive epoxy-nanoclay system impregnates a porous glass fabric effectively depends on its viscosity, surface tension and contact angle characteristics. These also enable the liquid to wet the fabric. The effect of surface concentration of amine molecules on the reduction of surface tension of epoxy mixtures was evaluated by the changes in the spreading pressures of these mixtures. It is hypothesized that the mono-amine surfactant coming from nanoclay is changing the reaction stoichiometry of the epoxy-curative reaction, particularly at higher addition levels of nanoclay. Thus, it is believed that the diamine curative is interacting with the nanoclay. These observations are also supported by the DSC results as both cure rates and extent of cure are found to decrease at the increased levels of added clay. The percentage increase in the viscosity of the nanoclay reinforced reactive systems at high clay loadings is observed to be smaller than the percentage increase in the surface tension of the same material systems. This situation resulted in lower capillary numbers than the critical capillary numbers usually seen in RTM applications. The results served to emphasize the relative importance of capillary effects and viscosity during the impregnation of nanoreinforced epoxy systems.

CHAPTER VI

ANALYSIS OF RESIN TRANSFER MOLDING OF EPOXY-GLASS FIBER HYBRID COMPOSITES ENRICHED WITH NANOSCALE PARTICLES

In this chapter, resin transfer molding (RTM) of epoxy nanocomposite-impregnated, biaxially-stitched glass fabrics will be analyzed with an emphasis on the differences in the pressure profiles and flow permeability. Implications on instabilities in flow patterns in the presence of nanoscale reinforced epoxy resins will be discussed based on evaluation of flow properties and observations of many RTM experiments conducted under different processing conditions. The relationship between experimental observations and the effect of complex flows through dual-scale media will be discussed.

6.1 Analysis of the Resin Transfer Molding of Nanoclay or Nanotube-Enriched Epoxy-Glass Fiber Hybrid Composites

The effects of nanoclay and single wall carbon nanotube (SWNT) on the flow behaviour during RTM of biaxially-stitched glass fabrics will primarily be evaluated based on the observed variations in the pressure profiles. All RTM experiments were conducted by epoxy-curative, epoxy-nanoclay-curative and epoxy-SWNT-curative test liquids injected at a constant flow rate from one side of the thin mold cavity filled with biaxial glass fabrics. For this purpose, a 2.5 mm thick aluminum picture frame (Figure 3.5) sandwiched between two steel mold plates was employed so that one-dimensional linear flow conditions could be assumed for the simplification of mold flow analysis.

Pressures measured by four pressure transducers positioned at predetermined locations on the bottom mold plate (Figure 3.2) were used to calculate the pressure gradients along the length of the mold. Comparisons of the pressure profiles measured at different flow rates, nanoreinforcement levels and numbers of layers of fabric will be discussed to explain the complex flow phenomena observed in the presence of nanoreinforcements. The RTM molding of epoxy-curative mixtures without fabric and/or nanoreinforcement served as base experiments.



Figure 6.1 Experimental pressure histories measured during RTM of epoxy-curative mixture without fabric or nanoreinforcement.

for evaluation of responses of pressure transducers inside the mold cavity and to check the isotropic flow condition without fabric or any nanoreinforcement. As can be seen from Figure 6.1, all the pressure transducer readings track each other closely. This indicates that isotropic flow conditions, with constant flow velocity and negligible pressure drop in the absence of fabric, prevailed in the mold cavity. The simultaneous response and coincidental pressure readings at steady-state flow suggest that viscosity changes of the epoxy-curative mixture were not important over the timescale of the moldfilling experiments. Careful examination of the steady-state region (\sim 125 – 400 s) reveals a slight increase of pressure with time. This could be attributed to a small increase in viscosity due to curing; however, the viscosity build over the timescale of mold filling is slight (see, Figure 5.7). It is more likely that the steady-state pressure increase is due to a continued displacement of air from the fabric as the epoxy-curative mixture saturates the fabric. This experiment also served to verify the proper functioning of the pressure transducers.

RTM experiments of epoxy-curative, 60 % V_f biaxial glass fabric system were conducted at 2 mm/min (7.9 cm³/min) constant injection flow rate. The pressure profiles recorded during the mold filling stage of this experiment indicated a pressure differential based on the velocity gradient as the flow front progressed along the longer axis of the mold, as shown in Figure 6.2. While the transducer closest to the resin inlet port, PT-1, reached the highest steady state pressure due to the longer flow path from PT-1 to the mold exit, the other transducers followed a systematic order when reaching their corresponding steady state values. The difference in pressure transducer responses between Figures 6.1 (neither fabric nor reinforcement) and 6.2 (fabric without reinforcement) clearly demonstrates that the fabric imposes a resistance to flow. This is discussed in detail in Chapter V. The flow through and around the fabric proceeds at different velocities. Furthermore, the flow through the fabric is anisotropic due to the biaxial orientation of the tow as was also demonstrated in Chapter V. As a consequence, a very complex flow field will be established during RTM mold filling.

Another important difference exists between pressure transducer responses as illustrated in Figures 6.1 and 6.2. With neither fabric nor nanoreinforcement, there is no time lapse between PT-1 and PT-4 initial responses. In the presence of fabric and without nanoreinforcement, the time difference between PT-1 and PT-4 initial transducer responses is approximately 200 seconds. An RTM mold filling experiment was performed with the top metal plate replaced by glass so that a movie could be recorded. On a gross scale, the mold appeared visually to be filled after approximately 270 seconds. It is concluded, therefore, that the pressure transducers show the appropriate responses with time and correlate with RTM flow.

To determine the effect of nanoclay on the flow behavior of reactive epoxy systems during RTM of high fiber containing (i.e., 60 % V_f fiber mat volume fraction) systems, 2 wt % of nanoclay-epoxy-curative mixtures were prepared and injected into the mold cavity at 2 mm/min piston speed.



Figure 6.2 Experimental pressure histories measured during RTM of epoxy-curative-no nanoreinforcement with 60 % glass fabric at 2 mm/min piston speed.



Figure 6.3 Experimental pressure histories measured during RTM of epoxy-curative-2 wt % nanoclay with 60 % glass fabric at 2 mm/min piston speed.



Figure 6.4 Experimental pressure histories measured during RTM of epoxy-curative-4 wt % nanoclay with 60 % glass fabric at 2 mm/min piston speed.

The results of this experiment showed that the qualitative responses of pressure transducers were similar to those with no nanoclay containing reactive epoxy mixtures such that all transducers followed the correct temporal order when reaching steady state values as plotted in Figure 6.3. As expected, higher steady-state pressure values were observed with the incorporation of clay into the reactive epoxy systems. Irregularities in the pressure transducer-1 profile at the 2.3×10^5 Pa and 3.8×10^5 Pa level were observed. These irregularities might be due to void formation and transformation during the mold-filling stage of the nanoclay-reinforced, reactive epoxy systems.

The effect of nanoclay content on the flow behavior of reactive epoxy systems was also examined via the RTM experiment performed by addition of 4 wt % nanoclay into the reactive epoxy systems with 6 layers of glass fabrics at the same piston speed of 2 mm/min. The pressure profiles of this experiment provided in Figure 6.4 also indicate similar features to the results of 2 wt % nanoclay experiments. Steady-state pressure levels further increased as the amount of clay was doubled. Nevertheless, the observation of slightly higher steady-state pressure readings for transducer # 4 over transducer # 3 was unusual and might have resulted from preferential, complex flow patterns and probably, capillary fingering during mold filling of such higher viscosity reactive material systems. In addition, the nanoclay particles could be of such a size and state of aggregation that they could become trapped while passing through the fabric and, more specifically, between individual fibers in the tow as it will be discussed later in this chapter. Capillary fingering is a phenomenon associated with anisotropic flow through multi-scale, porous media.^{127, 170}

To assess the effect of flow rate on flow behavior during RTM of nanoclaycontaining reactive epoxy systems, a set of experiments without nanoclay, 2 wt % and 4 wt % nanoclay were conducted at the same fiber volume fraction level with 6 layers of glass fabrics at a piston speed of 4 mm/min (0.264 cm³/sec). The pressure profile histories of each of these experiments are illustrated in Figures 6.5 to 6.7. The steadystate pressure level reached by the reactive epoxy systems without any nanoclay run at 4 mm/min, shown in Figure 6.5, looked similar to the same system run at 2 mm/min, plotted in Figure 6.2. Comparison of Figure 6.6 with Figure 6.7 indicates an increase in the steady-state pressure levels at the higher nanoclay loading level as also seen in the case of lower flow rate experiments run with the same material systems.



Figure 6.5 Experimental pressure histories measured during RTM of epoxy-curative-no nanoreinforcement with 60 % glass fabric at 4 mm/min piston speed.



Figure 6.6 Experimental pressure histories measured during RTM of epoxy-curative-2 wt % nanoclay with 60 % glass fabric at 4 mm/min piston speed.



Figure 6.7 Experimental pressure histories measured during RTM of epoxycurative-4 wt % nanoclay with 60 % glass fabric at 4 mm/min piston speed.

To evaluate the effect of fiber volume fraction on the flow of nanoclay-containing reactive epoxy systems, RTM experiments with 0, 2 and 4 wt % nanoclay in the reactive epoxy systems were run with 5 layers of biaxial glass fiber (50 % fiber volume fraction) at 2 mm/min piston speed.

Representative results of these RTM experiments for 0 wt % and 4 wt % nanoclay systems are plotted in Figures 6.8 and 6.9. Comparison of the pressure profiles collected for 50 % V_f biaxial-glass fabric-no nanoclay containing epoxy systems shown in Figure 6.8 with those of 60 % V_f biaxial-glass fabric-no nanoclay systems plotted in Figure 6.2 indicated approximately an 85 % increase in the steady-state pressure values with only 20

% increase in the V_f of fabrics while all other RTM process parameters and epoxy mixtures were kept the same. This was attributed to the higher flow resistances attained at higher levels of fiber loading. Figures 6.8 and 6.9 also show that, with an increase in the nanoclay content, steady-state pressure levels of 50 % V_f biaxial-glass fabric-containing epoxy systems are observed to increase. This observation was in accordance with the trends observed for the 60 % biaxial-glass fabric-containing epoxy systems as discussed earlier.

To examine the effect of different types of nanoreinforcement on the flow behaviour of epoxy systems, RTM experiments of SWNT-reactive epoxy mixtures were conducted at 0.1 wt %, 0.2 wt% and 0.3 wt % SWNT levels with the presence of 6 layers of biaxial glass fabric (60 % fiber volume fraction) at 4 mm/min injection speed. Representative pressure profile histories of these RTM experiments for 0.2 wt % and 0.3 wt % SWNT-containing epoxy systems are plotted in Figures 6.10 and 6.11. Both of these figures indicate a common feature in that the steady-state pressure levels recorded by transducer # 4 of both systems exceeded the steady-state pressure levels attained by transducers closer to the resin inlet.



Figure 6.8 Experimental pressure histories measured during RTM of epoxy-curativeno nanoreinforcement with 50 % glass fabric at 2 mm/min piston speed.



Figure 6.9 Experimental pressure histories measured during RTM of epoxy-curative-4 wt % nanoclay with 50 % glass fabric at 2 mm/min piston speed.



Figure 6.10 Experimental pressure histories measured during RTM of epoxy-curative-0.2 wt % SWNT with 60 % glass fabric at 4 mm/min piston speed.



Figure 6.11 Experimental pressure histories measured during RTM of epoxy-curative-0.3 wt % SWNT with 60 % glass fabric at 4 mm/min piston speed.

It is believed that both of these transducer readings may not be reliable when characterizing the flow behavior or evaluating any flow properties of these systems. The validity of maximum steady-state pressures recorded by all transducers during RTM of 0.3 wt % SWNT enriched epoxy systems is somewhat questionable as very high steady-state pressure readings are very near to the maximum operation limit of the pressure transducers. Despite this uncertainty in the absolute values of the steady-state pressures collected during RTM of 0.3 wt % SWNT and considering that usage of only 0.2 wt % SWNT could lead to significant steady-state pressure levels of 7.5x10⁵ Pa, an expectation of higher steady-state pressure levels with the incorporation of 0.3 wt % SWNT-loaded systems. Hence, the results of 0.3 wt % SWNT containing epoxy systems served to indicate an upper bound in the amount of SWNTs that can be feasible for RTM of epoxy-SWNT-60 % biaxially-stitched glass fiber systems.

Comparisons of Figures 6.6 with 6.10 signified another interesting result in that addition of SWNTs to epoxy at a nanoclay weight percentage of only 0.1 gave rise to an almost 25 % higher steady-state pressure level during the mold filling stage of RTM. This is attributed to the differences in flow front velocity and profile resulting from the different particle geometry and viscosity levels of two different types of nanoreinforcements.

Ambient temperature viscosity measurements of reactive SWNT-epoxy systems were conducted with the Brookfield LV DV II + Pro Digital Viscometer under the same conditions used for the measurements of reactive, nanoclay-epoxy systems described in Chapter 5. Comparison of the effects of nanoreinforcement type and amount on viscosity behavior of SWNT- or nanoclay-epoxy-curative mixtures are plotted in Figure 6.12. Viscosity data were recorded within 15 minutes of mixing. The relative effects of viscosity with weight percentage reinforcement are substantial. The SWNTs yield much larger viscosities at a given loading. This can be attributed to the state of aggregation or dispersion and the large aspect ratio of SWNTs ("needles") versus clay (platelets).



Figure 6.12 Comparison of the effects of nanoreinforcement type and amount on the room temperature viscosity of SWNT or nanoclay reinforced reactive epoxy mixtures.

6.2 Implications on the Processability of Nanoreinforced Epoxy Resins via RTM and *"Saturated Bulk Flow Permeability"*

In this section, the flow of reactive epoxy-nanoclay and epoxy-nanotube mixtures during RTM through biaxially-stitched glass fabrics will be further characterized by comparing the effects of several process parameters, such as flow rate, volume fraction of glass fabrics, and amount and type of nanoreinforcements on flow properties. A particular emphasis will be placed on discrepancies in the saturated bulk flow permeabilities of nanoreinforced epoxy resin systems. Probable mechanisms which could affect the complex flow behavior in the presence of nanoreinforcements will also be discussed.

Traditionally, the most commonly accepted equation for describing one-dimensional steady-state flow through RTM molds is Darcy's law:⁸⁷

$$u = \frac{Q}{A} = \frac{K_{sat}}{\eta} \cdot \frac{\Delta P}{L}$$

where *u* is the superficial velocity or the volume-averaged "Darcy velocity" or the average flow rate (m/sec), K_{sat} is the saturated flow permeability of the preform (m²), η is the fluid viscosity (Pa· sec), *Q* is the total flow rate (m³/sec), *A* is the cross-sectional area of flow (m²), and ΔP is the imposed pressure gradient or the pressure drop per unit flow length, *L*, (Pa/m).

Darcy's law has several limitations and is based on a set of assumptions: the impregnation or mold filling phase being represented by an incompressible fluid (i.e., constant density assumption); constant viscosity ($\mu = \mu_0$) during filling; no heat transfer by convection; negligible effects of lateral heat conduction during both impregnation and cure; same temperature of upper and lower mold halves; negligible inertial effects; uniform flow fronts and temperature throughout the laminate thickness during impregnation; constant mold temperature during impregnation and negligible curing reactions until complete impregnation of the preform by resin.

Despite its limitations, Darcy's law is frequently employed in RTM applications. Thus, the bulk flow properties of epoxy-nanoreinforced material systems, such as ΔP and the saturated flow permeabilities of the biaxially-stitched fabrics were evaluated using this equation. For this purpose, pressures measured by transducers positioned at predetermined locations in the bottom mold plate (see Figure 3.2) were used to compute the pressure gradients along the length of the mold. The effects of fiber volume fraction and nanoclay concentration on the pressure gradients measured between the transducers # 2 and # 3 during the RTM of epoxy-nanoclay mixtures are shown in Figure 6.13.



Figure 6.13 Effects of fiber volume fraction and nanoclay concentration on the pressure gradients developed during RTM of epoxy-nanoclay mixtures with 50 V_f % and 60 V_f % glass fabric at 2 mm/min piston speed.



Figure 6.14 Effects of injection flow rate and nanoclay concentration on the pressure gradients developed during RTM of epoxy-nanoclay mixtures with 60 V_f % glass fabric.

Although higher pressure gradients observed at higher fiber volume fractions of glass fabrics were anticipated, the reduction of pressure gradients with an addition of more clay at the same fiber volume fraction loadings were surprising owing to the higher viscosities of high nanoclay loaded epoxy systems. The effects of flow rate and nanoclay concentration on the pressure drop of epoxy-nanoclay mixtures during RTM with 6 layers of glass fabric are illustrated in Figure 6.14. These results indicate that the effect of flow rates employed in this research on the pressure gradients during RTM of nanoclay-epoxy systems was found to be insignificant.

Another important bulk flow property which is examined to provide valuable information on the resistance of the fiber preforms to the flow of nanoreinforced-epoxy systems is the permeability of the fabrics. For this purpose, Darcy's law was employed for the calculations of saturated mat permeability. The permeability results for all molding conditions are summarized in Table 6.1. Comparison of the saturated flow permeability data for epoxy-nanoclay-60 % V_f systems shows a significant increase in the permeability as the flow rate increases. This finding is also in agreement with the recently reported research results of Daniel and Kim¹⁷¹ who claimed that the saturated permeability depends not only on the preform structure but also on the flow rate and resin properties. Daniel and Kim¹⁷¹ attributed this flow rate dependence of permeability to the changes in the nature of the flow. They have argued that permeability can vary in certain preform structures owing to variations in the slip flow conditions in that flow resistance can change depending on the Reynolds number and the interaction between wetting fluid and the mold wall affecting the slip conditions on the wall.

Molding Materials	Injection Speed, mm/min	ΔP ₍₂₋₃₎ , Pa	K ₍₂₋₃₎ , m ²
Epoxy-6 ply-0 % Clay	2	1.08×10^5	$1.7 \text{ x} 10^{-10}$
Epoxy-6 ply-2 % Clay	2	8.70×10^4	$2.5 \text{ x} 10^{-10}$
Epoxy-6 ply-4 % Clay	2	$6.09 \text{x} 10^4$	$3.9 \text{ x} 10^{-10}$
Epoxy-6 ply-0 % Clay	4	$9.70 ext{ x10}^4$	3.8×10^{-10}
Epoxy-6 ply-2 % Clay	4	$8.71 \text{ x} 10^4$	5.1 x10 ⁻¹⁰
Epoxy-6 ply-4 % Clay	4	$6.60 ext{ x10}^4$	$7.2 \text{ x} 10^{-10}$
Epoxy-5 ply-0 % Clay	2	$6.05 \text{ x} 10^4$	$3.0 \text{ x} 10^{-10}$
Epoxy-5 ply-2 % Clay	2	$2.50 ext{ x10}^4$	8.8×10^{-10}
Epoxy-5 ply-4 % Clay	2	$1.60 \text{ x} 10^4$	$1.5 \text{ x} 10^{-10}$
Epoxy-6 ply-0.1 % SWNT	4	$3.38 ext{ x10}^4$	1.6 x10 ⁻⁹
Epoxy-6 ply-0.2 % SWNT	4	$1.47 \text{ x} 10^4$	$4.2 \text{ x} 10^{-10}$
Epoxy-6 ply-0.3 % SWNT	4	$4.1 \text{ x} 10^4$	1.6 x10 ⁻⁹

Table 6.1 Summary of saturated permeability results for all RTM conditions.

To highlight the combined effects of injection flow rate, nanoclay loading and fiber volume fraction during the RTM of epoxy-nanoclay-fiberglass hybrid composites, regression analysis results of saturated mat permeability are also presented in Figure 6.15. Contrary to our expectations, the saturated flow permeabilities of nearly all nanoreinforced-epoxy moldings are observed to increase as the concentration of nanoclay/nanotube is increased. These unusual permeability results may be attributed to variations in the local flow front velocities leading to instabilities in the flow through porous media for these complex epoxy-nanoreinforced resin systems. In this regard, some experimental evidence supporting such anomalies in the flow behaviour and thereby in the flow properties will be discussed next.



Figure 6.15 Effects of injection flow rate, nanoclay loading and fiber volume fraction on mat permeability for epoxy-nanoclay-fiberglass hybrid composites.

Figure 6.16 illustrates the multiple length scales in a typical composite. This TEM image¹⁷²demonstrates a dual-scale porous medium consisting primarily of two regions of different length scales: one with a characteristic width *l* of approximately 10 μm within the fiber tows and the other one with a characteristic width *L* of approximately 1 mm in the gaps between the fiber tows. Several researchers^{127, 169, 170, 173} investigated factors causing the variations in impregnation speed within and between these fiber tow regions during RTM. Lee *et al*¹²⁷ reported that fingering took place at the flow front due to the differences in the permeabilities inside the fiber tows and between the gaps of the fiber tows during RTM of unidirectional, stitched fiberglass mats. Their studies showed that the extent of fingering relied on the relative magnitudes of the capillary and the hydrodynamic pressures.

Advani *et al*¹⁷³ and Young¹⁷⁰ also presented similar results suggesting that differences in flow front velocities and the flow patterns are directly related to the degree of interactions between micro- and macro-scale flows. Figure 6.17 illustrates a schematic diagram of these two types of flows.



Figure 6.16 A TEM image showing the multiple length scales of flow; intra-tow regions (the gaps between fibers) and inter-tow regions (the gaps between tows) in composites.¹⁷²



High Filling Velocity

Figure 6.17 Schematic diagram describing the micro- and macro-flows which could be effective depending on different flow front velocities developed during RTM.

Patel *et al*¹²⁷ suggested that wicking flows inside fiber tows were dominant at low filling velocities. This would, in turn, lead to micro-flows preceding macro-flows owing to capillary forces. That is, the flow front would be dominant in the intra-tow region. Conversely, macro-flows pass ahead of micro-flows as viscous forces become larger than capillary forces at high filling velocities. Hence, any factors increasing disparities between the micro- and macro-flows could give rise to instabilities in flow patterns and

create voids. These factors need to be considered for successful impregnation and wetting of dual scale porous fabrics during RTM. Such instabilities would automatically be reflected in flow properties, such as permeability, and lead to anomalous results.

With these considerations in mind, it is believed that observation of flow patterns during RTM of epoxy-biaxial glass fabrics with and without nanoclay would provide valuable information. For this purpose, RTM experiments of 4 wt % nanoclay- and without nanoclay- mixtures were conducted with 50 V_f % biaxial-glass fabrics by replacing the steel top-mold plate with a thick glass plate while the flow front was recorded with a video camera. As can be seen from Figure 6.18, while the flow front of the no-nanoclay-containing epoxy mixture exhibited an almost "*plug-flow*" characteristic, the flow front of the 4 wt % nanoclay-containing system looked quite different and nonlinear suggesting non-uniform, preferential flow patterns due to the presence of nanoclay. These visual observations are believed to suggest variations in the local flow velocities arising from differences in the micro- and macro-flows in the presence of nanoscale reinforcements.



(b)

Figure 6.18 Comparisons of the flow patterns observed in the RTM of (a) epoxy-50 % glass fiber-without nanoclay and (b) epoxy-50 % glass fiber-4 % nanoclay composites.

Considering the dual-scale nature of glass fabrics, it is further postulated that instabilities in flow behavior could result from partial blockage or clogging of gaps between tow fibers in the presence of partially-intercalated nanoreinforced-epoxy resin systems. To investigate the possibility of this hypothesis, calculations were made assuming traditional hexagonal, close-packing of fibers as shown in Figure 6.19.

Knowing that the approximate diameter of the fibers employed in this research was 13 μm , calculations were conducted over a wide range of fiber volume fractions to evaluate the available gap distance, (s-D) at various glass fiber loadings.



Figure 6.19 Schematic views describing the calculation of the available gaps in between filaments of a tow in a hexagonally close-packed fabric.



Figure 6.20 Variations of the available gaps between hexagonally, close-packed filaments of 13 μ m diameter as a function of the fiber volume fraction.

The results of these calculations, plotted in Figure 6.20, indicate that, while the available gap distances are about 4.5 μm at the 50 % glass fiber loading level, the available gap distances were reduced to 3 μm at the 60 % glass fiber loading levels.

After gaining an insight on the available gap spaces between tow fibers, experimental evidence which could suggest clogging effects of nanoclay agglomerates was investigated by TEM examination. Representative TEM micrographs taken from different regions of epoxy-4 % nanoclay reinforced resin systems are presented in Figure 6.21. The dimensions of the nanoclay agglomerates marked in the first micrograph are found to be approximately $1.35 \ \mu m \times 1 \ \mu m$ and $1 \ \mu m \times 1 \ \mu m$. Both are smaller than the theoretically available gap distances. The dimensions of the clay tactoids in the second micrograph are determined as 7.4 $\mu m \times 3.7 \ \mu m$ indicating a possibility for clogging of some of the available gaps in between fibers by larger size clay agglomerates. As the sample sizes examined with TEM are always very small, many TEM observations from various sections would be needed to quantitatively evaluate the degree of clogging in the intratow regions of the fabrics.



Figure 6.21 Low magnification TEM images taken from two different regions of epoxy - 4 wt % clay nanocomposites showing spatial distribution of some highly intercalated nanoclay structures.

Considering that shear rates available in traditional RTM applications are usually low, it is hypothesized that, particularly at high weight percentage addition levels, nanoparticles could agglomerate during flow inside the mold cavity while entering a constrained area loaded with high volume fraction levels of glass fabrics. These aggregates would, in turn, block some intra-tow regions and lead to instabilities in the flow resulting in anomalous pressure differentials at different regions of the flow and unusual permeability results. It is also believed that nanoclay or nanotubes affect the flow rate somewhat differently along the various fabric capillary paths and give rise to preferential flow paths throughout the mold cavity.

6.3 Summary

The movement of nanoreinforced epoxy systems through the dual scale porous structure of the biaxially-stitched glass fabrics was analyzed based on experimental observations of flow and an evaluation of properties, such as pressure differentials and saturated permeabilities. Possible mechanisms explaining the instabilities of flow behavior were explored. It was found that beyond 0.3 wt % SWNT, RTM of epoxy-60 % biaxially stitched-glass fiber systems was not feasible. It was also observed that an addition of SWNT at only 10 % the level of nanoclay gave rise to almost a 25 % increase in steady-state pressure levels along with almost an 18 % decrease in permeability. This observation signifies the superior reinforcing effects of SWNTs over nanoclays due to their different geometry (much higher aspect ratio) and interactions with epoxy and fabrics. The permeability of the fabrics both with and without nanoclay is observed to

significantly increase when higher flow rates are employed. The saturated flow permeabilities of virtually all nanoreinforced-epoxy moldings are observed to increase as the concentration of nanoclay/nanotube is increased. These unusual permeability results are attributed to the variations in the local flow front velocities leading to instabilities in the flow through porous media in the presence of complex epoxy-nanoreinforced resin systems. Possible mechanisms leading to unusual permeability results were investigated. It is believed that visual observations of flow fronts with and without nanoclay indicated variations in local flow velocities arising from differences in the micro- and macro-flows in the presence of nanoscale reinforcements. Based on theoretical calculations and TEM micrographs, it is also surmised that nanoparticles, particularly at high weight percentages, could agglomerate during flow inside the mold cavity. These aggregates would, in turn, block some intra-tow regions and lead to instabilities in the flow resulting in anomalous pressure differentials at different regions of the flow and unusual permeability results. Thus, nanoreinforcements could be affecting the flow rate somewhat differently along the various fabric capillary paths and thereby giving rise to preferential flow paths throughout the mold cavity.

CHAPTER VII

PROPERTIES OF RESIN TRANSFER MOLDED EPOXY GLASS FIBER HYBRID COMPOSITES ENRICHED WITH NANOSCALE PARTICLES

This chapter reports the mechanical, thermal, morphological, water absorption and oxygen permeation properties of resin transfer molded epoxy-nanoclay and epoxy-SWNT impregnated, biaxial-glass fabric hybrid composites and evaluates the potential improvements in such composites through multi-scale reinforcement arising from incorporation of nanoparticles into the epoxy resin.

7.1 Mechanical Properties

The mechanical performance of all composites was assessed by flexural three-point bending and dynamic mechanical analysis (DMA) tests. While the former technique is chosen to provide information on the improvement of static mechanical properties due to the presence of nanoreinforcements, the latter technique was employed to evaluate the tensile properties of the composites under dynamic loading conditions over a range of temperatures. The flexural tests were conducted following the ASTM D 790. The results of flexural three-point bending measurements are summarized in Table 7.1. The results revealed that, while the sole incorporation of nanoclay to the neat epoxy resulted in a 12-17 % increase in the flexural modulus, its addition along with glass fabric had usually either no effect or caused a reduction in the flexural modulus of hybrid composites as compared to that of epoxy-glass fiber composites without nanoclay. This pointed to the possibility of void formation. Thus, the void contents of all composites were investigated using ASTM 2734-94. Calculations of the void content of the composites required determination of both theoretical and experimental densities. The results for both densities and the void contents of the composites are also provided in Table 7.1.

Table 7.1 Effects of nanoclay, SWNT and glass fiber on the flexural properties and the void content of epoxy-nanocomposites, epoxy-glass fiber-nanotube and epoxy-glass fiber-nanoclay hybrid composites

Material Systems	$E_{\rm Flexural},$ GPa	ρ Theoretical, g/cm ³	$\rho_{\text{Experimental}}, g/\text{cm}^3$	Void Content, %
Ероху	3.3 ± 0.04	1.14	1.14	-
Epoxy-2 % Clay	3.7 ± 0.05	1.148	1.14	0.7 ± 2
Epoxy-4 % Clay	3.9 ± 0.05	1.155	1.14	1.3 ± 2
Epoxy-50 % GF	33 ± 1.0	1.840	1.77	3.80 ± 2
Epoxy-50 % GF-2 % Clay	34 ± 0.1	1.850	1.75	5.40 ± 2
Epoxy-50 % GF-4 % Clay	29 ± 0.4	1.850	1.69	8.65 ± 2
Epoxy-60 % GF	39 ± 2.5	1.986	1.86	6.34 ± 2
Epoxy-60 % GF-2 % Clay	35 ± 2.0	1.989	1.89	4.98 ± 2
Epoxy-60 % GF-4 % Clay	40 ± 2.0	1.992	1.90	4.62 ± 2
Epoxy-60 % GF-0.1 % CNT	42 ± 2.0	1.986	1.87	5.84 ± 2
Epoxy-60 % GF-0.2 % CNT	38 ± 3.0	1.986	1.88	5.34 ± 2
Epoxy-60 % GF-0.3 % CNT	27 ± 2.0	1.986	1.88	5.34 ± 2

Theoretical densities are calculated based on the density of each component, supplied from manufacturers, and the weight percentage of each component employed with our experiments. The experimental densities are determined using the measured weights and volumes of well-defined, rectangular shaped and smooth samples cut from each composite. The void content of the composites was then calculated based on the following formula:

% Void Content = ((
$$\rho_{\text{Theoretical}} - \rho_{\text{Experimental}}) / \rho_{\text{Theoretical}} \times 100$$

It is believed that the absolute values of calculated void contents for the 60 % glass fiber-containing nanoreinforced composites may not be reflecting the true void content due to experimental errors encountered during the experimental density measurements. At such low weight percentage additions of nanoclay and nanotubes, the differences in the theoretical densities of SWNT- and nanoclay-containing hybrid composites are negligible. Furthermore, it is quite possible to obtain very close experimental density values for each of these composite systems as a result of probable errors made during volume measurements of the samples. The higher void contents produced at higher nanoclay loading levels are also supported by optical microscopy examinations which will be presented in the next section.

The incorporation of SWNTs to the epoxy-glass fiber systems gave rise to a more severe reduction in the flexural modulus than is caused by nanoclay. It is postulated that the interactions of nanotube-epoxy, nanotube-nanotube and nanotube-glass fiber systems were not favorable thermodynamically, thus leading to lack of adhesion and bonding of epoxy to the glass fabrics. It is believed that although the interaction effects might have had some contribution to the reductions in the mechanical properties of the composites, the major contribution was coming from the voids.

The decrease in flexural properties of hybrid composites at higher nanoclay or SWNT loading levels is also supported by similar trends observed in the dynamic tensile storage modulus properties. Dynamic mechanical measurements on all composites are presented in Table 7.2 along with the corresponding glass transition temperature of each composite system.

Material Systems	E', at 30 ⁰ C, GPa	$T_{g}(^{0}C)$
Ероху	1.03	100
Epoxy-2 % Clay	1.07	94
Epoxy-4 % Clay	1.11	100
Epoxy-0.1 % CNT	1.61	101
Epoxy-0.2 % CNT	1.14	99
Epoxy-0.3 % CNT	1.04	95
Epoxy-50 % GF	2.64	108
Epoxy-50 % GF-2 % Clay	2.22	101
Epoxy-50 % GF-4 % Clay	2.29	107
Epoxy-60 % GF	3.22	134
Epoxy-60 % GF-2 % Clay	2.44	102
Epoxy-60 % GF-4 % Clay	2.91	113
Epoxy-60 % GF-0.1 % CNT	2.87	107
Epoxy-60 % GF-0.2 % CNT	2.27	124
Epoxy-60 % GF-0.3 % CNT	2.35	118

Table 7.2 Effects of nanoclay, SWNT and glass fiber on the dynamic tensile storage modulus and the glass transition temperature of epoxy-nanocomposites, epoxy-glass fiber-nanotube and epoxy-glass fiber-nanoclay hybrid composites.

The results reveal that the effect of SWNTs or nanoclays on the glass transition temperature is almost negligible compared to the effect of glass fiber content. It is surprizing to observe that microscale glass fibers have such an appreciable effect on a purely matrix dependant property like T_g . Hence, we have no explanation for these unusual trends observed in T_g measurements at the moment.

The results indicate that, whenever nanoclay or SWNT and glass fiber coexist in the composites, the dynamic storage modulus is observed to decline. Another notable observation gained from the DMA results was that, while the nanoclay addition to epoxy in the absence of glass fabrics always led to an increase in the dynamic storage modulus, the incorporation of SWNT without any glass fabrics resulted in a decrease of the dynamic storage modulus. This could be due to poor load transfer and interfacial bonding between the nanotubes in the ropes and between the nanotubes and epoxy matrix. Another possibility could be the breakage of the SWNT ropes into small pieces during the high shear and ultrasonic mixing stage. Similar reasons could also be valid for the observed reduction in the dynamic storage modulus of hybrid SWNT-glass fiber composites in addition to the possibility of poor load transfer and interfacial bonding between the nanotubes and the glass fabric.

7.2 Morphological Observations

The optical micrographs taken from the cross-sections of both hybrid composites and composites without nanoreinforcements were compared qualitatively for evidence of higher void content with the incorporation of nanoclay. Due to the dark black color of hybrid composites containing SWNTs, the optical microscopy examinations were limited to only epoxy-glass fiber-nanoclay systems. Representative optical micrographs are provided in Figures 7.1. These micrographs clearly illustrated that the size and the number of voids dramatically increased with the incorporation of nanoclay. However, these observations may not be directly correlated to the amount of change in the flexural or dynamic storage modulus data presented in the previous section as there are not statistically enough microscopic examinations to represent the overall structure of the hybrid composites. Therefore, these observations can only prove the presence of voids that would explain the decreased flexural and storage moduli.

Some possible reasons for void formation may be partial evaporation of mold release agent, mechanical entrapment of air already present in the mold and volatilization of any dissolved gases during curing. Various process parameters, such as molding temperature, pressure during curing, injection flow rate, pressure, resin characteristics (viscosity, surface tension, etc.), reinforcement properties (surface treatment of nanoclay and the type, orientation and the surface treatment of the glass fibers, etc.) influence void formation.


(a)



(b)

Figure 7.1 Comparisons of void level between (a) epoxy-50 % glass fiber composites with no nanoclay and (b) epoxy-50 % glass fiber- 4 % nanoclay hybrid composites.



(a)



(b)

Figure 7.2 Comparisons of void level between (a) epoxy-60 % glass fiber-2 % nanoclay hybrid composites and (b) epoxy-60 % glass fiber-4 % nanoclay hybrid composites.

As discussed in Chapter 5, low values of the capillary number, Ca, along with higher contact angles between the nanoreinforced epoxy resin and glass fabrics with the incorporation of clay and SWNTs are deemed to promote differences between the permeabilities internal to the fiber tows and those between the fiber tows. This would, in turn, result in preferential flows in the intra-tow and inter-tow regions, thereby leading to void trapping in the glass fabrics. In addition, inhomogeneities, such as stitches, impede the pathway of voids and prevent them from being swept away by the liquid flow.

7.3 Thermal Stability

Thermal-oxidative stability of the epoxy-nanoclay-glass fiber and epoxy-SWNT-glass fiber hybrid composites as well as the epoxy-nanoclay and epoxy-SWNT composites was determined by thermogravimetric analysis (TGA). The samples were tested from 25 °C to 800 °C under an *air* atmosphere at a test scan rate of 10 °C /min. The temperature at 5 % weight loss (T_1) and the temperature at the maximum rate of weight loss (T_2) were obtained from typical weight % change vs. temperature curves. The results of all TGA measurements are summarized in Table 7.3.

Material Systems	$T_1 (^{0}C)$	$T_2 (^{0}C)$
Ероху	350	378
Epoxy-2 % Clay	339	367
Epoxy-4 % Clay	331	368
Epoxy-0.1 % CNT	350	375
Epoxy-0.2 % CNT	354	376
Epoxy-0.3 % CNT	345	368
Epoxy-50 % GF	358	376
Epoxy-50 % GF-2 % Clay	354	368
Epoxy-50 % GF-4 % Clay	349	369
Epoxy-60 % GF	367	377
Epoxy-60 % GF-2 % Clay	357	373
Epoxy-60 % GF-4 % Clay	360	374
Epoxy-60 % GF-0.1 % CNT	361	373
Epoxy-60 % GF-0.2 % CNT	352	372
Epoxy-60 % GF-0.3 % CNT	360	371

Table 7.3 Effects of nanoclay, SWNT and glass fiber on the thermal-oxidative stability of epoxy-nanocomposites, epoxy-glass fiber-nanotube and epoxy-glass fiber-nanoclay hybrid composites.

The TGA results revealed that there was a decline in the thermal stability of epoxynanoclay composites as comparison to pristine epoxy while the thermal stability was not affected by such small addition levels of SWNTs up to 0.3 wt %. The reduction in the thermal stability of epoxy-clay composites was unexpected. This could be related to several factors, such as the decomposition of clay surfactant, a fraction of excess (unexchanged) surfactant on the clay surface and the clay itself, which can catalyze the degradation of the epoxy matrix. In contrast, decomposition temperatures of nanoclayglass fiber composites do not appear to reflect the presence of the nanoreinforcement. This could be due the much larger volume fraction of glass fiber compared to nanoreinforcement. The dimensional stability of the epoxy-nanoclay-glass fiber and epoxy-SWNT-glass fiber hybrid composites as well as the epoxy-nanoclay and epoxy-SWNT composites was determined by thermomechanical analysis (TMA). The results of TMA measurements are summarized in Table 7.4.

Table 7.4 Effects of nanoclay, SWNT, glass fiber reinforcement on the longitudinal (//) and transverse (⊥) coefficient of thermal expansion (CTE) of epoxy-nanocomposites and epoxy-glass fiber-nanotube and epoxy-glass fiber-nanoclay hybrid composites

Material Systems	$CTE_{\perp}, 1/^{0}C$	CTE // , 1/ ⁰ C
Ероху	6.42 x 10 ⁻⁵	6.07×10^{-2}
Epoxy-2% Clay	6.20 x 10 ⁻⁵	-
Epoxy-4% Clay	6.16 x 10 ⁻⁵	-
Epoxy - 50 % GF	0.78 x 10 ⁻⁵	1.20 x 10 ⁻²
Epoxy - 50 % GF - 2 % Clay	1.73 x 10 ⁻⁵	6.88 x 10 ⁻³
Epoxy - 50 % GF - 4 % Clay	1.39 x 10 ⁻⁵	7.99 x 10 ⁻³
Epoxy – 0.1 % SWNT	6.65 x 10 ⁻⁵	-
Epoxy – 60 % GF- 0.1 % SWNT	1.08 x 10 ⁻⁵	-
Epoxy – 0.2 % SWNT	6.45 x 10 ⁻⁵	-
Epoxy – 0.3 % SWNT	6.39 x 10 ⁻⁵	-

The results indicate that the effect of glass fibers on the thermal expansion properties is much superior to those of nanoclays and SWNTs both in longitudinal and transverse directions as witnessed by smaller values of CTE_{\perp} and CTE_{\parallel} . Nanoclay was found to induce more pronounced effects on the coefficient of thermal expansion (CTE) of hybrid composites in the transverse direction than in the longitudinal fiber direction. This was supported by the results of the epoxy - 50 % glass fiber-clay hybrid composites such that the addition of 4 wt % nanoclay to the epoxy-50 % glass fiber was observed to yield 2.3 times more reduction in the CTE in the transverse direction than it did in the longitudinal direction. It is believed that the reductions in the CTE of epoxy-glass fiber systems with the presence of clay might also be related to the increase in the void content.

Another interesting finding which is noteworthy to mention is that, although the addition of nanoclay without any glass fibers resulted in a 3 - 4 % reduction in the CTE of neat epoxy in the transverse direction, the effect of SWNT on the CTE was not noticeable up to a 0.3 wt % SWNT loading level. Perhaps the interaction of SWNTs with the adhering epoxy polymers may not have been sufficient below a certain threshold concentration level to affect the thermal expansion. As a result, SWNTs below 0.3 wt % were not able to contribute to the expansion. It is important to note that the volume fraction of nanoparticles is much lower (by nearly two orders of magnitude) than that of glass fabric; therefore, mechanical properties would be expected to be dominated by the latter.

7.4 Barrier Properties

Layered silicates with large aspect ratios, such as nanoclay, can reduce permeability to dissolved liquid or gas transport, particularly when well-dispersed. The presence of nanoclay would cause a significant increase in the effective diffusion path length, leading to appreciable reductions in both oxygen permeability and water diffusivity. Figure 7.3 illustrates that up to 86 % and 97 % reduction in the oxygen permeability of epoxynanoclay composites was possible with the incorporation of 2 wt % and 4 wt % nanoclay, respectively.



Figure 7.3 Oxygen permeability properties of epoxy-nanoclay composites.

The observed reductions in the oxygen permeability rates of epoxy-nanoclay composites are attributed to the increased diffusional path length of gas molecules in the presence of nanoclay.

By the same token, water absorption properties of all composites were found to agree qualitatively with oxygen permeability results such that both the maximum water gain percentage at saturation and the diffusivity coefficient were observed to decline as the nanoclay and SWNT loadings are increased, even in the presence of glass fiber. The effects of nanoclay and SWNTs on room temperature water absorption properties of epoxy-nanoclay-60 % glass fiber hybrid composites are illustrated in Figures 7.4 and 7.5, respectively. Water absorption was determined as an increase in the weight percent of a sample according to the following formula:

$$M\% = \frac{(W - W_d)}{W_d} \times 100\%$$

where *W* is the wet sample weight, W_d is the dry sample weight and *M*% is the % water absorption. The water diffusivity coefficient, *D*, was determined from the initial slope of the water gain percentage M_t vs. \sqrt{t} curve [1], using the following formula:

$$D = \frac{\pi}{16} \left(\frac{h}{M_{\rm m}}\right)^2 \left(\frac{M_{t2} - M_{t1}}{\sqrt{t_2} - \sqrt{t_1}}\right)^2$$

where *h* is the thickness of the specimen, *t* is exposure time and M_m is the maximum water gain at saturation, M_{t1} is the wet sample weight at $t = t_1$ and M_{t2} is the wet sample weight at $t = t_2$.



Figure 7.4 Effect of nanoclay loading on the room temperature water absorption properties of epoxy-nanoclay-60 V_f % glass fiber hybrid composites.



Figure 7.5 Effect of SWNT loading on the room temperature water absorption properties of epoxy-SWNT-60 V_f % glass fiber hybrid composites.

The results of both the maximum water gain percentage at saturation and the diffusivity coefficient are presented in Table 7.5. It is noteworthy to mention that, while the addition of 0.2 wt % SWNT and 0.3 wt % SWNT are observed to cause virtually the same effect on the maximum water gain at the saturation level of epoxy-60 % glass fiber-SWNT hybrid composites, the addition of 0.3 wt % SWNT is determined to bring about twice as much improvement in the diffusivity coefficient as is possible by that of 0.2 wt % SWNT.

Material Systems	Max. Water Gain at Saturation, %	Diffusivity, mm ² /sec
Ероху	0.86	2.43 x 10 ⁻⁷
Epoxy - 60 % GF	0.38	2.35 x 10 ⁻⁷
Epoxy - 60 % GF - 2 % Clay	0.20	2.29 x 10 ⁻⁷
Epoxy - 60 % GF - 4 % Clay	0.16	1.96 x 10 ⁻⁷
Epoxy - 60 % GF - 0.1 % SWNT	0.09	2.29 x 10 ⁻⁷
Epoxy - 60 % GF - 0.2 % SWNT	0.06	1.98 x 10 ⁻⁷
Epoxy - 60 % GF - 0.3 % SWNT	0.06	1.54 x 10 ⁻⁷

Table 7.5 Summary of Room Temperature Water Absorption Properties of Epoxy-Nanoclay- and Epoxy-SWNT-Glass Fiber Hybrid Composites

The superior maximum water gain properties of nanoclay to those of SWNT are attributed to the fact that clay is considered as a better sequestering agent for water than SWNTs. Another interesting observation is that, while the addition of SWNTs to epoxy at a nanoclay weight percentage of only 0.1 gave rise to almost 6.5 times improvement in the diffusivity coefficient of epoxy-60 % glass fiber composites its effect on the reduction of maximum water gain was found to be 1.85 times as great as the effect of nanoclay.

The comparisons of the effect of nanoclay and SWNT on the water diffusivity of epoxy-60 % glass fiber-SWNT and epoxy-60 % glass fiber-nanoclay hybrid composites are depicted in Figure 7.6.



Figure 7.6 Comparisons of the effect of nanoclay and SWNT on the water diffusivity of epoxy-60 % glass fiber-SWNT and epoxy-60 % glass fiber-nanoclay hybrid composites.

7.5 Summary

In this chapter, mechanical, thermal, morphological and barrier properties of resin transfer molded epoxy-nanoclay and epoxy-SWNT impregnated biaxial-glass fabric hybrid composites are examined to evaluate the potential benefits and disadvantages of the use of SWNTs and nanoclays in micro-scale glass fiber reinforced epoxy thermoset

composites. The benefits of added nanoreinforcements include a reduction on oxygen and moisture transport along with a reduction in the coefficient of thermal expansion. A noticeable disadvantage discovered in this work, is a reduction of mechanical properties in the form of G' and sometimes observed for the flexural moduli of nanoreinforced systems compared to the native epoxy. It is believe that the reduction of mechanical properties in the presence of nanoreinforced materials is due to the occurrence of voids that may be the result of several factors including differential micro- and macro-flows during RTM.

CHAPTER VIII

CONCLUSIONS

In this research, the usage of single wall carbon nanotubes (SWNTs) and nanoclays in the resin transfer molding (RTM) of biaxially stitched micro-fiber reinforced epoxy matrix composites was investigated to evaluate the role of nanoscale reinforcements on the wetting, flow and end-properties of composites through multi-scale effects. The study has shown that resin transfer molding of epoxy resins enriched with nanoreinforcements could be successfully carried out. The major findings of this research are listed as:

- The presence of nanoreinforcements retarded the cure kinetics such that the activation energies increased with the nanoreinforcement content.
- The presence of biaxially stitched glass fabric reinforcement along with the nanoclay and SWNT reinforcements induced substantial flow gradients during RTM filling.
 - The biaxial nature of the glass fabric reinforcement provided pathways for a variety of capillary flows within the intra- and inter-tow regions.

- Visual observation of flow fronts with and without nanoclay indicated variations in local flow velocities arising from differences in the microand macro-flows in the presence of nanoscale reinforcements.
- Nanoparticles, particularly at high weight percentages, agglomerate during flow inside the mold cavity and block some intra-tow regions and lead to instabilities in the flow resulting in anomalous pressure differentials at different flow regions.
- This was observed by considerable pressure development during RTM filling.
- o "Fingering" flow was observed.
- RTM of epoxy-60 V_f % biaxially stitched-glass fiber systems beyond 0.3 wt% SWNT was not feasible.
- Impregnation rate of biaxially stitched glass fabrics was examined by capillary wetting measurements.
 - Unsteady-state and steady-state relative tow permeabilities decreased as the nanoclay amount is increased. The presence of nanoclay decreased the *"tow wet-out"* with almost 50 % reduction in the steady-state tow permeability along with a 21 % increase in the contact angle upon addition of 4 wt % nanoclay to the reactive epoxy.
 - Nanoclay particles lowered the impregnation rate.

- The presence of nanoparticle reinforcement in epoxy-glass fabric composites was found to:
 - Decrease or have no effect on thermal properties compared to epoxy-glass fabric composites
 - Glass transition temperatures
 - Decomposition temperatures
 - Decrease mechanical properties due to several defects, such as voids and agglomerates, introduced during RTM.
 - Increase barrier properties substantially:
 - Water/moisture absorption decreased
 - Oxygen permeability decreased

CHAPTER IX

SUMMARY

In this research, the usage of single wall carbon nanotubes (SWNTs) and nanoclays in the resin transfer molding (RTM) of biaxially-stitched micro-fiber reinforced epoxy matrix composites was investigated to evaluate the role of nanoscale reinforcements on the wetting, flow and end-properties of composites through multi-scale effects. The study primarily focused on characterization of the state of dispersion and curing of nanoscale reinforced epoxy polymers, assessment of the relative importance of viscous and interfacial forces and the wettability of glass fabrics by the nanoscale reinforced epoxy polymers, analysis of the complex flow of nanoreinforced epoxy systems through glass fiber porous media by several properties such as relative-tow permeability and saturated mat permeability and evaluation of the properties of hybrid epoxy-glass fiber composites enriched with nanoscale particles.

Chemorheological, cure and morphological examinations of SWNT and layered silicate epoxy nanocomposites indicated that highly intercalated or partially exfoliated nanoreinforced-epoxy systems could only be observed under certain processing conditions, usually with low nanoreinforcement loading levels and at higher cure temperatures. Less swelling of the clay galleries in pristine epoxy than in the presence of epoxy-curative mixtures during the incipient stages of curing reactions is considered to be an indicator of the expansion of clay galleries taking place during cure. It was found that the presence of nanoreinforcements retarded the cure kinetics to some degree such that the activation energies increased with the nanoreinforcement content. The increases in the activation energies were observed to be more significant in the case of SWNT reinforced epoxy systems. This phenomenon is explained by a "physical segregation effect" by which segregation of curative moieties from the epoxy chains due to the presence of nanoscale SWNT structure is considered to be responsible for the increases in the activation energies of the nanocomposites. It is postulated that the physical hindrance of SWNTs played a significant role in impairing the mobility of active groups in the epoxy and curing agent, thereby leading to a significantly lower degrees of cure.

The relative importance of viscous forces over interfacial forces and the wettability of the glass fiber fabrics with the nanoscale reinforced epoxy polymers was assessed by the impregnation rate and distance as well as measurements of viscosity, surface tension and contact angle. The effect of surface concentration of amine molecules on the reduction of surface tension of epoxy mixtures was evaluated by the changes in the spreading pressures of these mixtures. It is hypothesized that the mono-amine surfactant coming from nanoclay could change the reaction stoichiometry of the epoxy-curative reaction, particularly at higher addition levels of nanoclay. Thus, it is believed that the diamine curative is interacting with the nanoclay. These observations are also supported by the DSC results as both cure rates and extent of cure are found to decrease at the increased levels of added clay. The observation of smaller percentage increase in the viscosity of the nanoclay reinforced reactive systems at high clay loadings than the percentage increase in the surface tension of the same material systems gave rise to lower capillary numbers than the critical capillary numbers usually seen in RTM applications. The impregnation rates calculated for the steady-state regimes of wicking experiments are used correlate the effect of nanoclay on capillary flow. Observed decreases in the impregnation rates with an increase in nanoclay content are attributed to the curing reactions promoting a higher contact angle, higher surface tension and higher viscosity as the cure rate progresses. Decreases in the spreading rates with time are explained by the viscous drag effects since more fluid has to be dragged along as time passes. Both the unsteady-state and steady-state relative tow permeabilities are observed to decrease as the nanoclay amount is increased. Thus, the presence of nanoclay is believed to reduce the "tow wet-out" with almost 50 % reduction in the steady-state tow permeability in the case of 4 % nanoclay addition to the reactive epoxy. The results of contact angle measurements indicated approximately a 21 % increase in the contact angle with the addition of 4 wt % nanoclay to the epoxy. The results serve to emphasize the relative importance of capillary effects and viscosity during the impregnation of nanoreinforced epoxy systems.

Possible mechanisms explaining the instabilities of flow behavior of nanoreinforced epoxy systems through the dual scale porous structure of the biaxially-stitched glass fabrics were explored. It was found that beyond 0.3 wt % SWNT, RTM of epoxy-60 % biaxially stitched-glass fiber systems was not feasible. It was also observed that an

addition of SWNT at only 10 % the level of nanoclay gave rise to almost a 25 % increase in steady-state pressure levels along with almost an 18 % decrease in permeability. This observation signifies the superior reinforcing effects of SWNTs over nanoclays due to their different geometry (much higher aspect ratio), extent of dispersion and interactions with epoxy and fabrics. The permeability of the fabrics both with and without nanoclay is observed to significantly increase when higher flow rates are employed. The saturated flow permeabilities of virtually all nanoreinforced-epoxy moldings are observed to increase as the concentration of nanoclay/nanotube is increased. These unusual permeability results are attributed to variations in the local flow front velocities leading to instabilities in the flow through porous glass fabrics in these complex epoxynanoreinforced resin systems. Visual observations of flow fronts with and without nanoclay indicated variations in local flow velocities arising from differences in the micro- and macro-flows in the presence of nanoscale reinforcements. Through theoretical calculations based on hexagonal packing of fibers and TEM micrographs, it is also surmised that nanoparticles, particularly at high weight percentages, could agglomerate during their flow inside the mold cavity. These aggregates would, in turn, block some intra-tow regions and lead to instabilities in the flow resulting in anomalous pressure differentials at different regions of the flow and unusual permeability results. Thus, it is believed that nanoreinforcements could be affecting the flow rate somewhat differently along the various fabric capillary paths and thereby giving rise to preferential flow paths throughout the mold cavity.

The potential benefits and disadvantages of the use of SWNTs and nanoclays in micro-scale glass fiber reinforced epoxy thermoset composites are also evaluated by examination of mechanical, thermal, morphological and barrier properties of resin transfer molded epoxy-nanoclay and epoxy-SWNT impregnated biaxial-glass fabric hybrid composites. The benefits of added nanoreinforcements comprise a reduction in oxygen and moisture transport along with a reduction in the coefficient of thermal expansion. A noticeable disadvantage discovered during this research is, however, the reduction of mechanical properties in terms of both dynamic storage modulus and flexural moduli of nanoreinforced systems in comparison to the pristine epoxy systems. It is believed that the reduction of mechanical properties in the presence of nanoreinforced systems arise from defects, such as voids and agglomerates introduced during RTM as a result of several factors including differential micro- and macro-flows.

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