

EFFECTS OF DISPERSION TECHNIQUES ON FLAMMABILITY  
AND MECHANICAL PROPERTIES OF  
PHENOLIC/E-GLASS NANOCOMPOSITES

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## **ABSTRACT**

### **EFFECTS OF DISPERSION TECHNIQUES ON FLAMMABILITY AND MECHANICAL PROPERTIES OF PHENOLIC/E-GLASS NANOCOMPOSITES**

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**SUPERVISING PROFESSOR: JITENDRA S. TATE**

Nanomaterials are currently the most researched materials in the scientific world. The term “nanotechnology” or “nanotech” (NT) refers to the ability to measure, manipulate, and organize matter at nano scale (Kobayasi, 2007, p. 13). It influences many aspects of our life, such as social, cultural, and economic. There are more than a thousand NT consumer products on the market and this number is constantly growing (Nanotechnology Consumer Products Inventory, 2009). Manufacturers use the term “nano” in products’ names to increase sales, while these products have no connection to NT. These products are widely known, such as the Indian car Tata Nano or the music player iPod Nano. It shows that the word “nano” and NT in general

has a psychological effect and is a new marketing tool to promote new products. However, products made of the true nanomaterials are rare on the market.

Nanomaterials have unique properties and, if properly used, can improve properties of existing products. Nevertheless, there are many unsolved problems while using nanomaterials including safety, handling, processing, and disposal. Also, nanomaterials cannot be used “as-is.”

The easiest way to use them is as a one of the constituents in other traditional materials such as composite materials, and then it becomes a “nanocomposite.” Nanomaterials blended into polymers can be called “polymer nanocomposite” or simply “nanopolymers.” Fiber reinforced polymer nanocomposites consist of fiber reinforcement and a nanomodified polymer matrix. Nanomodification of polymer matrices using the right kind of nanoparticle in the right percentage, leads to multifunctional composites that enhances two or more properties, such as mechanical, thermal, chemical, and barrier. The major challenge in property enhancement is uniform dispersion of nanoparticles in the polymer matrix. Popular methods used for dispersing nanoparticles into liquid thermoset resins are mechanical stirring, high shear mixing, centrifugal mixing, and sonication.

E-glass/phenolic composites have gained popularity due to their excellent fire, smoke, and toxicity (FST) properties. In this research water-based phenolic resin was modified using low-cost montmorillonite nanoclay (Cloisite<sup>®</sup> Na<sup>+</sup>) to improve flammability properties. Two different dispersion techniques, high-shear mixing and planetary centrifugal mixing, were used to blend nanoclay into phenolic resin, followed by low-cost vacuum assisted resin transfer molding (VARTM) to manufacture glass-reinforced nanocomposites. The loading of nanoclay included 2.5, 5.0, and 7.5 wt.% in both techniques. The degree of dispersion was analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Mass loss

calorimeter tests were conducted at a heat flux of 35 kW/m<sup>2</sup>. Mechanical properties such as flexural strength, interlaminar shear strength (ILSS), and compressive strength were evaluated. It is observed that 7.5wt.% loading of Cloisite<sup>®</sup> Na<sup>+</sup> improves flammability properties in both dispersion techniques. Planetary centrifugal mixing techniques did not fully exfoliate nanoclay particles; however it did not adversely affect mechanical properties but still provided near equivalent flammability performance as that of high shear mixing. It can be concluded that cost-effective centrifugal mixing can be used in manufacturing nanocomposites to enhance flammability property without sacrificing mechanical properties.

**Key Words:** Nanocomposite, nanoclay, phenolic, mechanical properties, flammability properties, and dispersion

## **I. INTRODUCTION**

Fiber reinforced (FR) polymer nanocomposites typically consist of carbon or glass fiber, and a nanomodified polymer matrix. Using the right kind of nanoparticles to modify polymer matrices with the right percentage can lead to multifunctional composites. The major challenge in property enhancement is uniform dispersion of nanoparticles in polymer matrix (Ray & Okamoto, 2003). This study attempts to evaluate effects of dispersion techniques and the quality of dispersion of nanoclay in phenolic resin, and the flammability and mechanical properties of FR polymer nanocomposites.

### **Background Information**

#### **Reinforcement Materials**

Reinforcement for composites varies depending on their intended usage; it can be fibers, whiskers, or particles. Fibers are the most common on the market. Especially long fibers are now being sometimes referred to as a new class of solid materials, other reinforcements are also used but due to fibers' distinct properties, they are preferred in the industries. Fibers have one very long axis with significantly higher strength in the longer direction. They are available in many diameters and lengths including continuous that can be

used as is, or chopped to desired shape (Strong, 2008). The list of fiber types includes E-glass, S-glass, carbon and aramid. Their properties are shown in Table 1.

**Table 1: Properties of Typical Fibers (Strong, 2008)**

Fiber Type	<i>Diameter</i> ( $\mu\text{m}$ )	<i>Density</i> ( $\text{g/cm}^3$ )	<i>Tensile Strength</i> ( $\text{MPa}$ )	<i>Tensile Modulus</i> ( $\text{GPa}$ )	<i>Elongation at break</i> (%)
E-glass	8-14	2.5	3447	69	4.9
S-glass	10	2.5	4585	83	5.7
Carbon	7	1.8	4137	228	1.6
Aramid	12	1.45	3660	83	30

### **Carbon fiber**

Carbon fiber is a very strong, light, and expensive material commonly used in making of composites. It has very thin fibers with diameters ranging from 5 to 10  $\mu\text{m}$  and consists of carbon atoms, which are bonded together in microscopic crystals that are typically aligned to the long axis of the fiber which makes it strong. Several thousand fibers are twisted together to form a yarn, which could be used directly or woven into a fabric. Carbon fiber could also be made into weave patterns and its combination with matrix form composite materials. Carbon fiber has been studied to be ideal in many applications due to its high strength-to-weight ratio (high specific strength), and also has a lower density than steel. Processing temperature in making carbon fibers play a major role in determining carbon properties, heating carbon in the range of 1500 – 2000°C exhibits highest tensile strength while carbon heated from 2500 - 3000°C exhibits a higher modulus of elasticity, often called as graphite fibers (Strong, 2008).



## **Glass fiber**

Glass fibers are made from raw materials like silica sand, limestone, boric acid and other ingredients. It is usually formed from extruding thin strand of silica-based, or other formulation glass, into many fibers with small diameters. The most commonly type of fiber glass used in industry is E-glass, others like A-glass, C-glass, D-glass, R-glass and S-glass are also being used due to their various distinct properties. Nevertheless, E-glass still makes up most of the fiberglass production in the world. Its specific components may differ slightly in percentage, but usually fall within a particular range. The letter “E” in E-glass is used because the glass fiber was originally made for electrical applications. The letter “S” is used in S-glass because it has a high-strength formulation for use when tensile strength is the most important property desired, while C-glass was developed to resist attack from chemicals, mostly acids which destroy E-glass. A-glass was formed with alkaline lime glass with little, or no, boron oxide. R-glass is a high mechanical requirement glass made of alumino silicate without magnesium oxide and calcium oxide.

Pure silica is a major component used in making glass fiber. It requires a high temperature to work with which constitute a drawback for flexibility in manufacturing temperature. Impurities can be introduced into the constituents by the addition of other materials in order to lower the working temperature. It also imparts other properties to the glass that may be advantageous in different applications. In addition, most glass fibers are rarely water soluble and depend on pH, in most cases the chloride ion will attack E-glass surfaces.

Glass fiber has high ratio of surface area to weight and the larger its surface area, the more susceptible it becomes to chemical attack. Glass fiber has a widely applications in

making of components where high strength-weight, excellent molded surfaces, dimensional stability, high dielectric strength, and parts consolidation are important (Strong, 2008).

Although, glass fibers' optimal usage in corrosion-resistant and electrical products depends on the suitability as well as performance strength of the matrix used in conjunction with the glass fiber. Glass fibers are fragile and could easily abrade when processing. This could cause a major problem during weaving. In order to avoid loss of strength, which depends on surface defects that might occur during handling, a temporary sizing is applied. Sizing is the process of applying chemicals to the fiber strands in order to protect the fibers during handling and also holds the individual filaments together. In most cases the size is removed after weaving, and finish is applied. Finish is usually added to fiber to enhance its compatibility with the matrix (Strong, 2008).

### **Reinforcement Forms**

Fibers are available in many oriented forms such as chopped strand mat (CSM), woven fabrics, braided, stitched and knitted fabrics.

#### **Roving**

Roving is the simplest and most common form of glass. Roving is bundle of few thousand monofilaments and this term is used in glass industry. It can be chopped, woven or processed and also used in creating secondary fiber forms for composite manufacturing. It is supplied by weight with specific filament diameter.

## **Mats**

Mats are generally non-woven fabrics derived from fibers and are held together by a chemical binder. Chopped mats consist of randomly distributed fibers with a cut length of 38 mm to 63.5 mm (McConnell, 2010). They are isotropic because of the random nature of the fibers and possess equal strength in all directions. The chemical binder does not give much concern since it dissolves in styrene (a material contained in polyester and vinyl ester resins). Chopped-strand mats (CSM) conform easily to complex shapes, by providing low-cost plastic reinforcement, chopped-strand mats are primarily used in hand lay-up, continuous laminating, and some closed molding applications.

Stronger than chopped-strand, continuous-strand mats are formed by swirling continuous strands of fiber onto a moving belt, and finished with a chemical binder to hold fibers in place. A non-dense fiber arrangement accepts a high ratio of resin to fiber, which results in a thick, smooth, resin-rich finish. It is usually used in non-critical applications, as most applications of composites are non-critical (McConnell, 2010).

## **Woven Fabrics**

Woven fabrics are usually made on looms with different weaves and widths. They are bi-directional and provide high strength in yarn direction, but the tensile strength is always compromised because fibers are crimped as they pass over and under one another during the weaving process. Weaving is commonly used in applications that require thick reinforcement, especially in hand lay-up and vacuum assisted resin transfer molding (VARTM). Several different weaves are used for bi-directional fabrics. In a plain weave, each yarn or roving alternately crosses over and under each warp fiber. Harness satin and basket weaves, in

which the yarn or roving crosses over and under multiple warp fibers at a time, are more pliable and conform easily to curved surfaces. Due to its relatively coarse weave, woven roving wets quickly; it is relatively inexpensive and results in a thick fabric used for heavy reinforcement, especially in hand lay-up operations (Tate, Kelkar, & Whitcomb, 2006).

### **Braided Fabrics**

Braided fabrics are a continuous weave process that has at least one of its axial yarns not crimped in the weaving process. This is commonly done by intertwining three or more yarns and not twisting any two yarns around each other. This ingenious process gives braided fabrics vastly improved strength and greater strength-to-weight ratio than woven fabrics. The quasi-isotropic formation within a single layer tends to eliminate the problem associated with layering multiple fabrics with other formations and it also reduces delamination which is the cause of most failures in composite. Braids are widely used in the industry because of the possibility of maximizing properties in all directions of a part (Strong, 2008).

### **Knitted fabrics**

Knitted fabrics are formed by simply placing yarns atop one another in practically any arrangement and binding them together. Orienting all strands in one direction, for example, results in a fabric with greater flexibility. Placing the yarns on top, rather than over and under each other, makes greater use of their inherent strength. Since they have no crimped fibers, knitted fabrics are more pliable than woven. Due to the wide variety of yarn orientations and fabric weights, knitted fabrics are tailored to individual customer

requirements. They are much more elastic and are not available in lightweights (Strong, 2008).

### Different weave types

Figure 1 displays some of the common types of weaves available. The fabric or long direction is commonly called warp direction, while the cross or width direction is called the fill or weft direction.

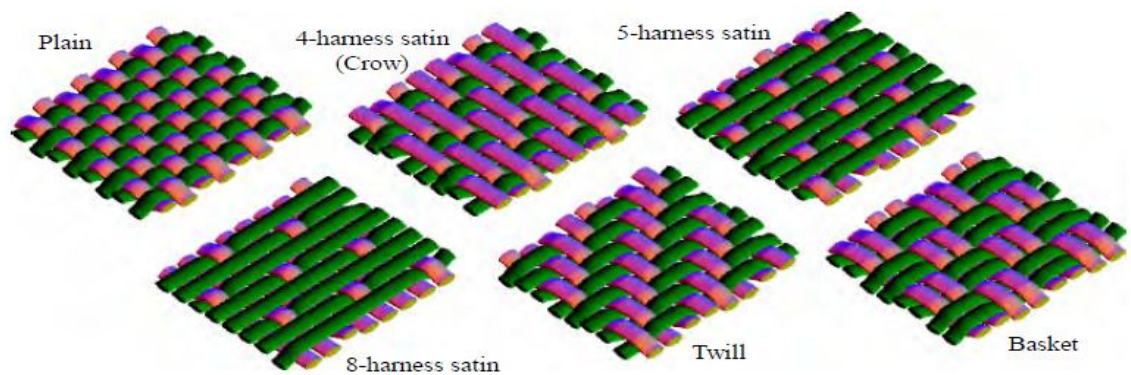


Figure 1: Different weave patterns: plain, twill, satin and basket (Tang & Whitcomb, 1999)

The plain weave is the simplest of the weave patterns, the warp and weft are aligned, and are made by interlacing yarns in an alternating over-and-under pattern. There is usually one warp fiber for one fill fiber. It has a peculiar checker board like appearance. This pattern gives uniform strength in both directions when yarn size and count are similar in warp and fill. The weave is considered stiff and stable, which is usually left quite open for good resin penetration and air removal (Zac-Williams, 2006).

In the crowfoot satin weave, one warp yarn is taken over three and then under one fill yarn. This produces a weave with improved unidirectional quality with more strength in the

fiber directions than with plain weave. The fabric is more pliable and can comply with complex contours and spherical shapes (Strong, 2008).

The long-shaft or 8-harness satin weave typically has one warp yarn weaving over seven fill yarns then under one fill yarn. It has a high degree of drape and stretch in all directions. This weave is less stable and open than most weaves, therefore, it requires a vacuum for resin impregnation and air removal. It is widely used in applications that need complex shape formation and contoured surfaces. 5-harness satin weave follows the same pattern (McConnell, 2010).

The basket weave is similar to the plain weave except that two warp yarns are woven as one over and under two fill yarns. It is less stable than the plain weave and has similar usages but it drapes on mild contours. Twill is formed with a diagonal parallel pattern, which is made by passing the weft yarn over one or more warp yarns. It usually has some form of offset between rows to create the characteristic diagonal pattern, and drapes because of this pattern. Twill fabrics usually have front and back sides unlike the plain weave in which both sides are the same. Twill recovers better from wrinkles than plain weave fabrics. It requires vacuum for good resin impregnation and air removal (McConnell, 2010).

## **Resins**

Resins are one of the most important components of polymer matrix composites. While the loads are essentially carried by fibers, modulus and failure strain depends on resin/matrix adhesion in the performance of composites. It also determines the type of fabrication process, service temperature, and flammability and corrosion resistance of the composite. Thermosets and thermoplastics are commonly used matrix systems.

Thermoplastic resins become soft when heated, may be shaped or molded while in a heated semi-fluid state, and become rigid when cooled. Thermoset resins are usually liquids or low melting point solids in their initial form. When used in making finished goods, these thermosetting resins could be cured at room temperature or under high heat depending on the desired properties. Unlike thermoplastic resins, once cured, solid thermoset resins cannot be converted back into their original liquid state. Cured thermosets will not melt and flow, but will soften when heated (and lose hardness), and once formed, they cannot be reshaped. Heat distortion temperature (HDT) and the glass transition temperature ( $T_g$ ) are used to measure the softening of a cured resin. Both test methods (HDT and  $T_g$ ) measure the approximate temperature where the cured resin will soften significantly to yield (bend or sag) under load (MDA Composites, 2009).

**Table 2: Properties of Typical Polymer Matrix Materials (Callister, 2007)**

Resin	Liquid Density (g/ml)	Tensile Strength (MPa)	Tensile Modulus (GPa)	CTE ( $10^{-6}/^{\circ}\text{C}$ )	GT $T_g$ ( $^{\circ}\text{C}$ )
Phenolic <sup>1</sup>	1.22	34.5-62.1	2.76-4.8	122	160
Polyester <sup>2</sup>	1.1-1.5	5.8-13	0.46-0.51	33-110	50-110
Vinyl Ester <sup>3</sup>	1.23	12.5	1.5	212-514	220
Epoxy <sup>4</sup>	1.20	60-75	2.7-3.2	59-212	140-176

<sup>1</sup>Phenolic Resin: Cellobond J2027L, Hexion Specialty Chemicals.

<sup>2</sup>Unsaturated Polyester: AROPOL 724IT15, Ashland Specialty Chemicals, Inc.

<sup>3</sup>Vinyl ester: Derkane Momentum 510-A40, Ashland Specialty Chemicals, Inc.

<sup>4</sup>Epoxy: Epikote RIM 135, Hexion Specialty Chemicals.

Thermosetting resins have a number of advantages, unlike thermoplastics, they retain their strength and shape even when heated. This makes thermosetting resins well suited to the

production of permanent components and large, solid shapes. Additionally, these components have excellent strength attributes (despite being brittle), they will not become weaker when the temperature increases (Thomasnet, 2008). The most common thermosetting resins used in the composites industry are unsaturated polyesters, epoxies, vinyl esters, polyurethanes, and phenolics.

### **Nanocomposites**

Nanocomposite refers to a composite material in which one of the components is nanomaterial. There are two types of nanomaterials: synthesized nanomaterials and natural. Some are synthesized nanomaterials, such as carbon nanotubes (CNT) or Carbon Nano Fibers (CNF) (Yeh, Tai, & Lin, 2009). They are referred as “engineering nanomaterials.” Some nanomaterials have been always existed in nature and are referred to as “natural nanomaterials” or “industrial nanomaterials.” Organic nanoclays from Southern Clay Products, Inc. are examples of natural nanomaterials. These materials have been around for a long time but were not studied and used until recent years. During the last decades, technological development allowed study and characterization of many nanomaterials. Nanomaterials have unique properties, and are materials in the purest form. They have large surface-area-to-volume ratio because of their size (Thostenson, Li, & Chou, 2005).

However, these materials and other nanoparticles cannot be used as structural elements. Therefore, they should be used as part in composite materials. These materials are called nanocomposites and can be fiber reinforced. Nanocomposites have been extensively investigated in recent years and found to have superior properties over conventional composites, and are already being used in production. Nanoclays manufactured by Southern



Clay Products are used as additives to polymers. The major challenge in property enhancement is uniform dispersion of nanoparticles in polymer matrix. These can be achieved in different ways. The popular methods used for dispersing nanoparticles in liquid thermoset resins are mechanical stirring, high shear mixing, centrifugal mixing, and sonication. On the other hand, introduction of nanoparticles to composites increases manufacturing cost and raises safety issues. As a result, usage of nanocomposites is limited to specific applications.

### **Phenolic Resins**

Phenolic resins exhibit excellent dimensional stability and excellent chemical and corrosion resistance. The major contribution of phenolic resins as a matrix in fiber reinforced composites is its fire, smoke, and toxicity (FST) characteristics (Botcher & Pilato, 1997). There are numerous applications that require excellent FST characteristics such as aircraft interiors, tunnel materials, offshore oilfield grating and deluge pipe, and fire safe components. Pilato *et al.* have provided an excellent review on phenolic and related resins and their nanomodification into FRP (Fiber reinforced plastics) systems (Pilato, Koo, Wissler, & Lao, 2008). The introduction of a nanophase within a polymeric system has been shown to substantially improve the overall physical and mechanical properties of the resulting nanomodified polymers (Koo, 2006).

The use of nanomodified phenolic resins as matrix into fiber reinforced composites is in its early stages. Koo *et al.* has investigated nanomodified (clay, POSS, and CNF) phenolic resole resin into carbon fiber-reinforced composites for ablative applications. They have

reported that nanomodification lowers ablation rate and also lowers backside temperature rise for rocket ablative materials (Bray, Beall, & Stretz, 2004).

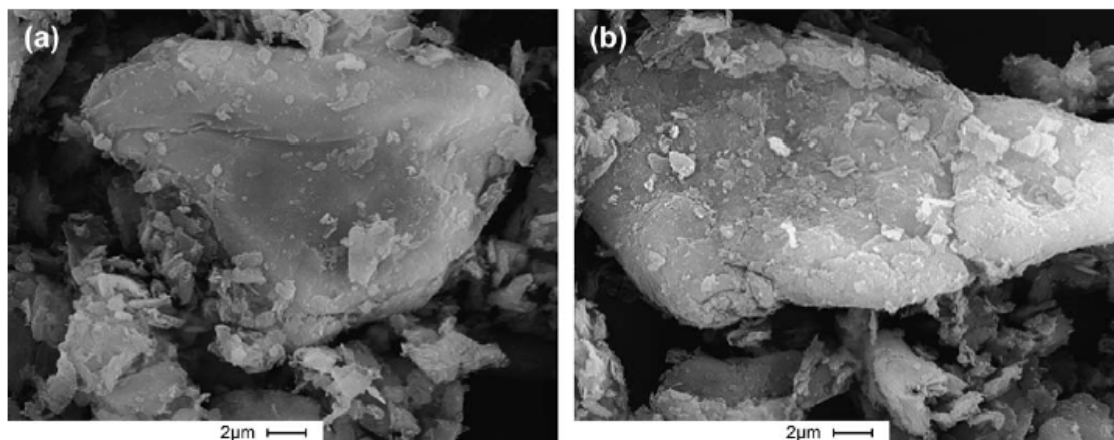
### **Montmorillonite (MMT) Organoclay**

Nanoclay is the most widely investigated nanoparticle in a variety of different polymer matrices for a wide spectrum of applications (Botcher & Pilato, 1997) and (Pilato, Koo, Wissler, & Lao, 2008). The origin of natural clay (bentonite) is in-situ alteration of volcanic ash and hydrothermal alteration of volcanic ash. Bentonite contains mainly montmorillonite but also can contain illite, kaolinite, quartz, zeolite, and carbonates. The starting materials of Southern Clay Products (SCP) are volcanic eruptions in the Pacific Ocean and western United States.

The chemical structure of MMT clays is layered sheets consisting of tetrahedral silicate layers and the octahedral alumina layer. The chemical formula of the MMT clay is  $\text{Na}_{1/3}(\text{Al}_{5/3}\text{Mg}_{1/3})\text{Si}_4\text{O}_{10}(\text{OH})_2$ . In the natural state  $\text{Na}^+$  cation resides on the MMT clay surface. Layered silicates are hydrophilic materials hence they must be made hydrophobic to become compatible with most polymers that are hydrophobic polymers. There are several types of clay surface treatments performed such as quaternary ammonium salts and alkyl imidazoles. Cloisite<sup>®</sup>  $\text{Na}^+$  (Figure 2) was used in this research. It is natural montmorillonite. It is used as additive to improve various physical properties such as heat deflection temperature (HDT), coefficient of linear thermal expansion (CTE), and barrier properties.

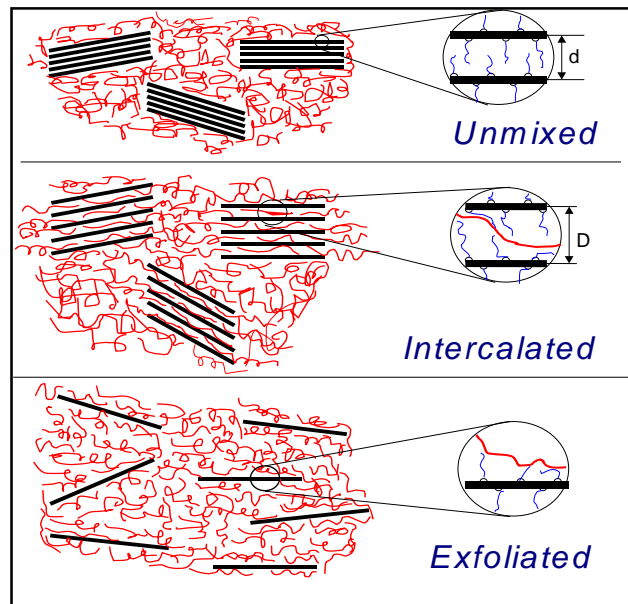
Achieving exfoliation of montmorillonite in various polymers is a function of the surface treatment of MMT clays and the mixing efficiency of the dispersing apparatus (Varley, Groth, & Leong, 2008). For Cloisite<sup>®</sup>  $\text{Na}^+$ , SCP recommends that it be dissolved in

either, water using high-shear mixing or to add directly into a water-soluble aqueous polymer solution. This research uses water-based phenolic resin. Cloisite<sup>®</sup> Na<sup>+</sup> was added into phenolic resin and stirred well. Later high-shear mixing was used to achieve intercalation or exfoliation.



**Figure 2:** SEM images of (a) Cloisite Na<sup>+</sup> and (b) processed Cloisite Na<sup>+</sup> (Horsch, Serhatkulu, Gulari, & M., 2006)

As shown in Figure 3, polymer-clay nanocomposites can be classified morphologically into unmixed, intercalated, and exfoliated states depending on dispersion of the nanoclays. The most desirable morphological state for polymer-clay nanocomposites is exfoliation, followed by intercalation. The challenge of processing nanoclay is dispersing the 8-μm particles into millions of platelets using proper processing techniques and conditions. Transmission electron microscopy (TEM) is the most useful technique to determine the dispersion of the nanoparticles in the polymer matrix (Krishnamoorti, 2001) (Pinnavaia, 2000).



**Figure 3: Three steps of dispersion of nanoclay (Koo, 2006)**

Exfoliation of nanoparticles within polymer matrix is vital for major improvements in properties. High-shear mixing is time-consuming and expensive method to achieve exfoliation of nanoclays. This research indicates that intercalation state can be achieved by using inexpensive dispersing technique, planetary centrifugal mixing.

### **Composites Manufacturing**

Weight reduction offered by composite laminates over metals has made composite parts attractive in many applications. Advanced composites are composites made by optimizing the relationship of mechanical properties and weight, or optimizing thermal performance and weight while engineering composites are composites made for superior properties but focus on cost reduction. There are many methods used in making engineering and advanced composites such as wet lay-up, prepreg method, autoclave processing, filament winding, Resin Transfer Molding (RTM), and Vacuum Assisted Resin Transfer Molding

(VARTM). In the following section, a brief description of these methods, their advantages and disadvantages are explained.

### **Wet lay-up Method**

It is a method that involves laying of reinforcement into the mold followed by applying the resin system. The wet composite is usually rolled by hand for even distribution of the resin and air pockets removal. Another layer of reinforcement is placed on top of the wet composite and resin poured into it. This same process is repeated until the desired thickness is achieved; the composite is then allowed to dry through curing. Wet lay-up is a simple method which does not require any special handling of wet fabrics, it allows the resin to be applied only in the mold which helps in maintaining a neat working environment. Variations in resin viscosity affect the curing process and also cause problems in creating good wet-out of reinforcement. A mold release is usually applied to the mold thereby preventing the composite from sticking and allows for easy removal of the composite from the mold (Strong, 2008).

### **Prepreg Method**

Prepreg method can be viewed to a great extent as an extension of the wet lay-up method. The fibers are usually arranged in a unidirectional tape or a woven fabric, it is impregnated with partially cured resin and stored in a way to avoid complete cure of the resin. Prepregs are made in different rolls which could later be put or cut to fit into mold depending on its desired usage. It is usually stacked up in layers until the desired thickness is achieved. Prepregs are always made to be moldable so that complex shapes can be produced.

Prepregs usually have a limited shelf-life because its resins have already been initiated when the prepreg is made. The shelf-life is usually several days to weeks and stored at room temperature, but shelf life can be extended by storing the prepreg in the freezer. It is a common practice to record the time out of the freezer in order to determine the remaining shelf life. If prepregs are not stored well, they turn out dry and rigid which are difficult to use. Although this method is slow and labor intensive, it offers better part definition, higher fiber content and better consolidation than wet lay-up (Strong, 2008).

### **Autoclave Processing**

This is the most common method used for curing thermoset prepregs (composite world, 2010). It involves applying high pressure and heat to the part through the autoclave atmosphere. The autoclave consists of a vessel that can be pressurized internally up to 5 bar (~ 75 psi), before its contents are heated. The vessel is used for component curing and is usually large, to accommodate large components. They are pressurized with gas, usually nitrogen that is circulated through the heaters to maintain a uniform temperature throughout the vessel. Attaining proper airflow is essential in achieving uniform temperature in the vessel. Heat enters through the end side of the autoclave and circulates the entire area of the vessel through a series of ducts and fans. This whole unit of the part in this case; composite is kept in a vacuum bag to maintain vacuum pressure on the laminate. The outer membrane is pressed against the laminate by atmospheric pressure. The part is then placed in the autoclave where the bagged molding may be reconnected with the evacuation system to maintain the vacuum. The autoclave is pressurized which augments the consolidated pressure. The temperature of the autoclave is reduced when the resin is adequately cured. The major

advantage of the autoclave is the manufacturing of composites with high fiber volume fraction and uniform thickness of the structure. However, the high cost of equipment is a huge set back as well as stringent pressure code regulations in using autoclave processing (Strong, 2008).

### **Pultrusion**

This is a continuous molding process that combines fiber reinforcements and thermosetting resin. It is widely used in making composite parts that have a constant cross-section profile which is also automated. It is a process by which reinforcements are positioned in a specific location using shapers to form a profile. It involves passing of reinforcement through a resin bath where it is thoroughly coated with the resin before passing through a heated metal pultrusion die (McConnell, 2010).

The dimension and shape of the die usually define the finished shape of the part being fabricated. Heat is transferred by temperature control to the die which cures the combination of the reinforcement and the resin passing through it, and heat energy transferred changes the resin from liquid to solid. Solid laminates emerges from the pultrusion die having the exact shape of the die cavity; the laminates usually solidifies when cooled and continuously pulled through pultrusion machine by tandem pullers between the die exit and cut to the desired length.

However, the initial capital investment on pultrusion is exceedingly high than most other manufacturing processes which limits its common application but has low cost to high volume production that justifies its usage in the industry (Strong, 2008).

### **Filament Winding**

This is a process of winding resin-impregnated fiber on a mandrel surface in a precise pattern. It is usually done by rotating the mandrel while a delivery head precisely position fiber on the mandrel surface to form the part. Successive layers could be added using the same or different winding angles until the required thickness is achieved.

Filament winding machines operate on the principles of controlling machine motion through various axes. The basic motions are the spindle or mandrel rotational axis, the horizontal carriage motion, and the cross or radial carriage motion axis. The mandrel or the application head can rotate to give the fiber coverage over the mandrel and transverses longitudinally giving the coverage.

In addition, filament winding does not use prepreg materials but incorporates the impregnation of the fiber tows as part of the filament winding process. The use of more than one type of reinforcement material may have some advantages in terms of cost and product performance like a vessel wound with carbon fiber for strength and modulus, and then over wound with aramid to protect the vessel from impact damage when in use.

Defining the relative speed of the mandrel and the head are important in successful filament winding. The two motions determine the wrapping angles and the overlap as well as the mechanical properties of the part (Strong, 2008).

### **Resin Transfer Molding (RTM)**

This is a process that involves placement of reinforcement materials between two matching mold surfaces. These matching mold surfaces are commonly called male and female molds, and are usually closed in molding processes, and a low-viscosity resin system



is injected into the mold cavity through one or series of ports under moderate pressure. A vacuum is usually used in enhancing the flow of the resin and reducing void formation.

Design of the mold is the most critical factor in proper resin transfer. The mold is usually fabricated and ensures that resin reaches all areas with the same concentration. RTM molds are usually made of composite materials but other materials may also be used; very large and complex shapes can be made efficiently and inexpensively. Molds are vented in such a way that air is pushed out of the mold by the resin but the vent is too shallow to allow passage of resin outside. It is arguably one of the widely used manufacturing processes in making composite laminates but control of resin uniformity is always difficult, radii and ends are usually resin rich (Strong, 2008).

### **Vacuum Assisted Resin Transfer Molding (VARTM)**

VARTM is an adaptation of the RTM process and is very cost-effective in making large structures such as boat hulls. In this process, tooling costs are cut in half because one-sided tools such as open molds are used to make the part. In this infusion process, fibers are placed in a one-sided mold and a cover – either rigid or flexible – is placed over the top to form a vacuum-tight seal. A vacuum procedure is used to draw the resin into the structure through various types of ports. This process has several advantages compared to the wet lay-up process used in manufacturing boat hulls. Because VARTM is a closed mold process, styrene emissions are close to zero. Moreover, a high fiber volume fraction (70%) is achieved by this process, and therefore, high structural performance is obtained for the part (Mazumdar, 2002).

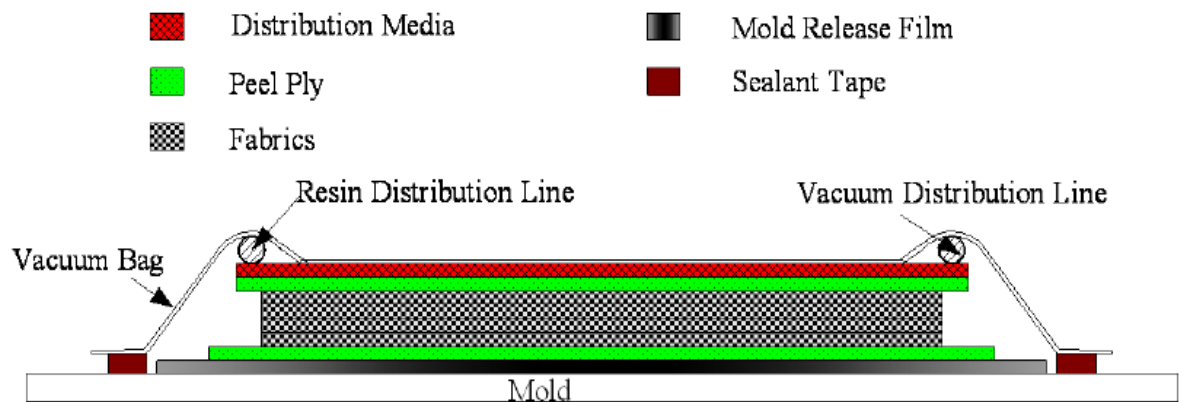
Distribution media aids the proper distribution of the resin over the reinforcement while peel ply which is usually used in covering both top and bottom of the stacked fabrics helps in easy removal of the composite part from the mold. This method also allows visual monitoring of the resin amongst other things while impregnating and defects could be easily spotted.

Generally, VARTM is an attractive and affordable method of fabricating composite laminates and lends itself to the production of large scale and high quality parts provided the resin system has low viscosity in the range of 100 to 1000 cP for proper wet out of the fabrics. During VARTM, dry fabric is placed into a tool and vacuum bagged in conjunction with the resin distribution line, the vacuum distribution line, and the distribution media. A low viscosity resin is drawn into the fabric through the aid of a vacuum. Resin distribution media ensures resin infiltration in the through-the-thickness direction. The key to successful resin infiltration of the fabric is the design and placement of the resin distribution media which allows complete wet-out of the fabric and eliminates voids and dry spots. Properly designed and properly placed resin distribution media eliminate race tracking and resin leakage around the fabric (Seemann W. H., 1990) (Seemann W. H., 1994). The schematic for the fabrication is shown in Figure 4.

Although autoclave and RTM processes are the most widely used in aerospace and other industries due to their regular high fiber volume fractions and uniform thickness of the composite structures but autoclave is expensive and VARTM process has various advantages; the process is relatively low cost for low volume production, and tools used are relatively simple and inexpensive. It can be used to make large and complex parts such as turbine blades, with their high fiber volume fraction, on-site manufacturing and repair is

possible. Styrene emission is major concern in open molding processes when using unsaturated polyester and vinyl ester resins. VARTM is a closed molding process and has less environmental concerns.

For example, most wind turbine blades are extremely long which could cost a fortune in transferring them to turbine farms, but VARTM process could be set up on the farm manufacturing and repairing blades and returning them to active service with very little down time. The above process was used in manufacturing composite panels in this research. The VARTM process is explained in detail in the next section.



**Figure 4: Schematic for VARTM**

### Objectives

In this research two different mixing techniques are compared. High-shear (HS) is the superior method of uniformly dispersing and exfoliating nanoclay. In contrast, planetary centrifugal (PC) mixing is a good method for dispersion, but will not provide exfoliation, since it provides only little or no shearing forces. Therefore, we expect to see mixture of

exfoliated and intercalated nanoclay after HS mixing and mostly intercalated nanoclay after PC mixing.

According to researches, nanoclays improve fire properties of polymers (Schartel, et al., 2010) (Choi & Chung, 2003) (Bahramian & Kokabi, 2009) . We expect that nanomodifications of phenolic resin will improve fire properties of composites regardless of mixing techniques. Nanoclays do not burn under fire; they create a ceramic-like protective layer which protects the polymer. Thus, the greater concentration of nanoclay in the polymer, the better the fire performance should be observed.

On the other hand, nanomodifications can hinder mechanical properties if large unmixed particles are presented in polymers. These particles work as imperfections or voids in composites and create stress concentration points. In contrast, fully exfoliated nanoclay should improve mechanical properties by providing better fiber-matrix adhesion. Quality of dispersion and loading of nanoclay will have dominant effect on mechanical and flammability properties.

It is expected that PC technique would give intercalated state of nanoclay and would improve flammability properties without sacrificing mechanical properties. If the expected outcome and our hypothesis are proved, the study will be very applicable and useful for industrialization of nanocomposites. We believe that there is no need for high cost and complicated mixing techniques if the major goal is to improve fire properties without knocking off mechanical properties. Thus, manufacturers will be able to use simpler and cheaper mixing technique for successful manufacturing of fire-safe nanocomposites.

## II. MANUFACTURING AND PERFORMANCE EVALUATION

### Material System

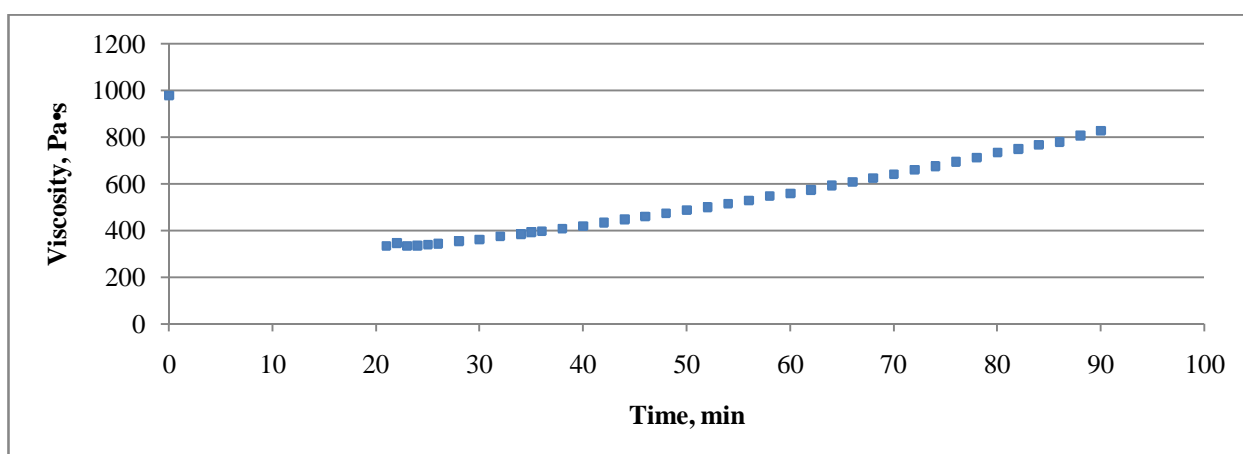
Water-based liquid resole phenolic resin, Cellobond<sup>®</sup> J-2027L, was used with acid catalyst, Phencat<sup>®</sup> 382 (both were supplied by Hexion Inc.). The resin was modified with montmorillonite nanoclay, Cloisite<sup>®</sup> Na<sup>+</sup>, which was supplied by Southern Clay Products, Inc. Nanoclay was blended with phenolic resin in 0.0, 2.5, 5.0, and 7.5 wt.% loadings. Further phenolic resin was reinforced with E-glass woven roving fabrics, Rovcloth<sup>®</sup> 1854, which was supplied by Fiberglass Industries. Sizing used on this fabric is compatible with acid catalyzed phenolic resin. Fiber reinforced (FR) nanocomposites were manufactured using VARTM process. Table 3 shows the experimental design of the study. It is 2-by- 3 design with a control group, which generates a total of seven groups.

**Table 3: Experimental Design**

Mixing Technique	0.0 % (Control)	2.5 %	5.0 %	7.5 %
High Shear	0	1.1	1.2	1.3
Planetary Centrifugal	0	2.1	2.2	2.3

### **Viscosity Study of Phenolic Resin**

The viscosity of the resin is crucial for VARTM process. Ideally, viscosity should be in the range of 100 to 1000 cP for proper impregnation of fabric in polymer resin. Once catalyst is mixed with resin, exothermic reaction begins. In this cross-linking reaction viscosity of the resin increases and eventually resin stops flowing, it gels. Thus gel time is time available for processing of composites. As per manufacturer's data, 5wt% of acid catalyst Phencat<sup>®</sup> 382 should provide 50 minutes of gel time in standard conditions. Gel time was re-evaluated in-house using rotational viscometer (HAAKE 7R+ with spindle R2). The resin and catalyst were mixed under a fume hood, degassed for 4 min at vacuum of 47 kPa, and then heated to 35°C in standard conditions. In VARTM process, resin was heated at 35°C, therefore, gel time study was also performed by heating resin at 35°C. Figure 5 displays time vs. viscosity graph. Viscosity increased with respect to time. At 90 minutes, viscosity was well-below 900 cP so test was stopped. The processing window of this resin system is sufficient to use the VARTM process to manufacture composites.



**Figure 5: Gel time study: viscosity vs. time for catalyzed phenolic resin**



**Figure 6: Rotational viscometer during experiment**

It is known fact that as loading of nanoparticles is increased the viscosity of polymer resin increases rapidly. Increase in viscosity poses difficulties in VARTM processing. High viscosity resin would not flow through fabric. In such situation viscosity is decreased by heating the resin or adding solvent. Both these solutions increase processing cost. Fortunately, the viscosity was not an issue with his type of nanoclay at these loadings. The VARTM process was successfully carried on for all of the test panels.

### **Thermal Curing Study**

According to the manufacturer, the thermal curing occurs after 80°C. Thus, the temperature of the resin should also be monitored and controlled during mixing process.

This study was performed to investigate the behavior of resin under high heat. Resin was heated with no catalyst on a heated plate until the cross linking of the resin occurred. The heater was set on the maximum heat setting and a small amount of resin (100 mL) was

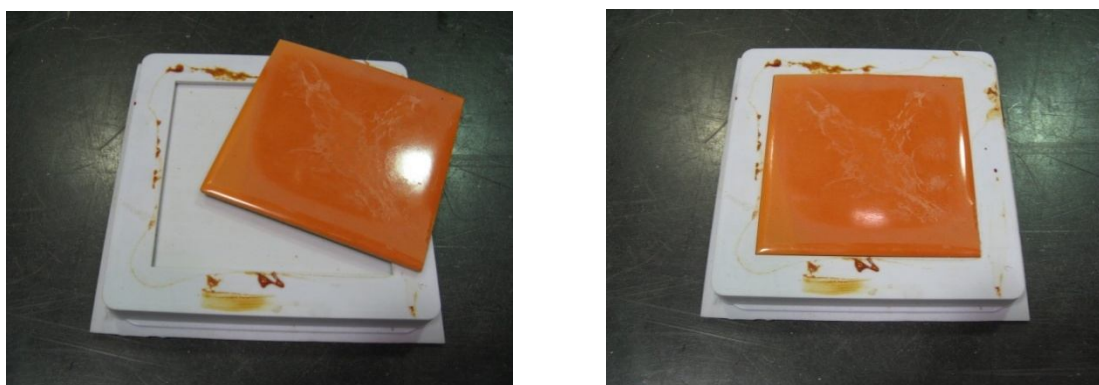
placed into a glass beaker. The study confirmed that the resin does not cure until 30 minutes even under rapid heating. Thermal curing began about 35 minutes (Figure 7). Therefore, it was decided to limit mixing time in high shear mixing to 25 minutes as a safety precaution.



**Figure 7: Thermal cure of phenolic resin occurs after 35 min of rapid heating**

### **Neat Resin Coupons: Manufacturing**

Neat resin coupons (11 cm x 11 cm) were cast using silicone molds as shown in Figure 8. The molds were kept in the oven at 80°C for 3 hours. These specimens were used for initial screening on mass loss calorimeter and for dispersion analysis. Few small specimens were cast for TEM analysis. TEM was used to evaluate the degree of dispersion of nanoclay in the resin.



**Figure 8: Silicone molds used to cast neat resin coupons for initial screening and for TEM analysis**



### **Initial Screening: Mass Loss on Resin Coupons**

The standard mass loss testing was performed according to ASTM E2102. A Mass Loss Calorimeter was calibrated to flux of  $35 \text{ kW/m}^2$ . The neat resin specimen (0.0 wt %) exploded at surface on 55<sup>th</sup> sec of the experiment as shown in Figure 9. It was dangerous and unsafe to proceed with testing. Also, the results of mass loss data were useless since material was losing mass due to explosion and not burn. The phenolic resin used in this research is water-based. This explosion was probably due to residue water remained in the specimen. It was attempted to modify procedure: the specimens were further cured at  $80^\circ\text{C}$  for 6 hours. This would remove all moisture from material. The test was repeated, but still neat resin coupons exploded. Therefore, it was decided to carry mass loss tests on reinforced composites and skip initial screening.



**Figure 9: Mass loss calorimeter test on neat resin coupon**

## **Nanomodifications of Phenolic Resin**

### **Blending of Nanoclay using High Shear Mixer**

High shear (HS) mixer was the first of two techniques used for blending nanoclay into phenolic resin. HS mixing is a very effective technique to disperse solid nanoparticles in liquid polymer resins. Koo and coworkers have successfully used high-shear mixing techniques to incorporate carbon nanotubes, layered silicates, nanosilicas, carbon nanofibers, and POSS to form polymer nanostructured materials in several of their research programs (Koo, 2006). Layered silicates, carbon nanofibers, and POSS were incorporated separately into resole phenolic using high-shear, non-sparking paint mixing equipment to form different polymer nanocomposites (Patton, Pittman, Wang, Hill, & Day, 2002) (Koo, Pilato, & Wissler, 2007). Previous study indicates that, shear rate is in the order of 45,000 to 110,000 s<sup>-1</sup> provides good mixing in terms of intercalation and exfoliation of nanoclays (Cheng, 2006).

HS Mixer (IKA® Labor Pilot 2000/4) with a DR module was used in this research. This mixer was previously used for successful dispersion and exfoliation of nanoclays in phenolic resin (Tate, Kabakov, Koo, & Lao, 2009). It has three generators (stator and rotor together are known as generator), two medium and one fine. The motor speed is controlled using digital controller by changing motor frequencies. Shaft speed depends on the belt drive that connects motor and shaft. As per manufacturer's data, the radial (grinding) gap between stator and rotor is fixed to 0.2 mm. The diameter of rotor (D) was 57mm. Shaft speed determines the shear rate. Table 4 shows relationships between motor and shaft speed; circumferential speed and shear rate. Previous study indicates that, shear rate is in the order of 45,000 to 110,000 s<sup>-1</sup> provides good mixing in terms of intercalation and exfoliation of

nanoclays (Koo, 2006). It was found that there is no recirculation that occurs if the frequency of the motor is set lower than 35 Hz.

**Table 4: High Shear Mixer's Shear Rates**

<i>Motor Freq.</i> (Hz)	<i>Motor Speed</i> (RPM)	<i>Shaft speed</i> (n) (RPM)	<i>Circumferential speed</i> ( $\pi Dn$ ) (m/s)	<i>Shear rate</i> (circumferential speed/ grinding gap) ( $s^{-1}$ )
0	0	0	0.000	0
10	600	1221	3.645	18223
20	1200	2536	7.570	37849
24	1440	3057	9.126	45632
30	1800	3848	11.486	57429
<b>40</b>	<b>2400</b>	<b>5153</b>	<b>15.381</b>	<b>76906</b>
50	3000	6455	19.268	96338
60	3600	7768	23.187	115935

In this research, 25-minute mixing at 40 Hz frequency was used which provided a shear rate of about  $76,906 s^{-1}$ . Cooling jackets on mixing chamber and hopper were used to avoid thermal curing of resin. Only the resin - without a catalyst - was mixed with nanoclay in the high shear mixer. Phenolic resin was mixed in batches with nanoclay in three different proportions: 2.5, 5.0, and 7.5% by weight.

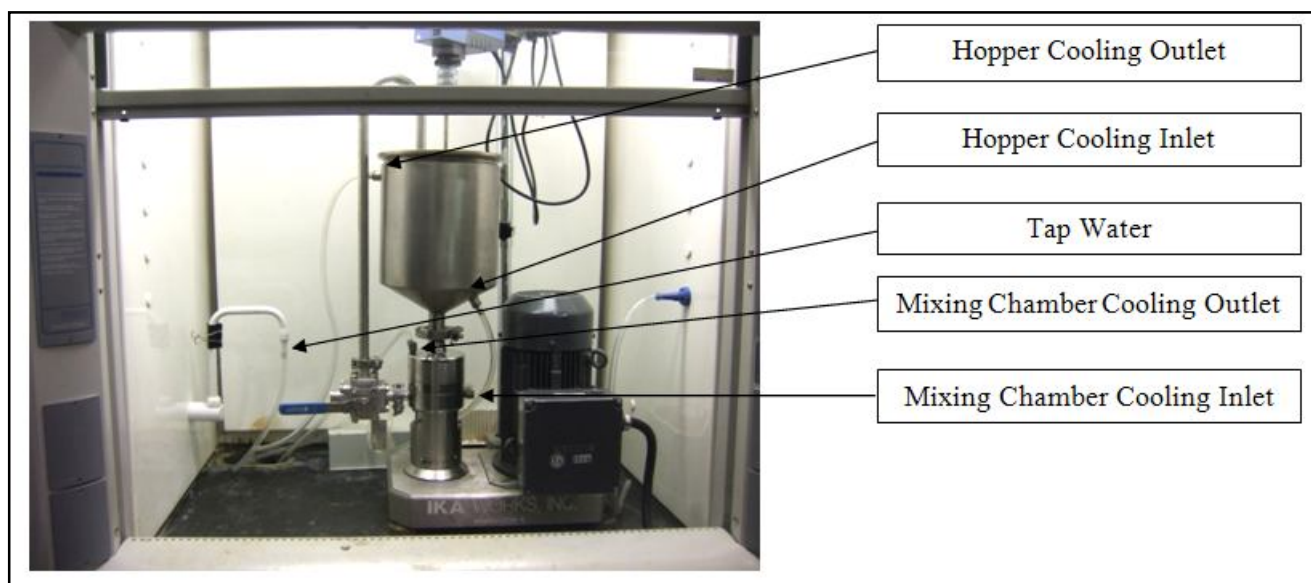
High shear mixer was used for blending nanoclay into phenolic resin. Only the resin (no catalyst) was mixed with nanoclay in the high shear mixer. The first batch of resin with 2.5 wt% of nanoclay was mixed for 50 min at 50 Hz frequency that gave shear rate of  $96,338 sec^{-1}$ . Since Cellobond<sup>®</sup> J2027L is a resole resin; it can cure simply by heating. During the mixing in the high shear mixer, temperature of the resin rose to approximately 90°C and thermal curing occurred. Resin was solidified in the various parts of mixer such as stator, rotor, and pipes. The arrangement of setup is displayed in Figure 10. Therefore, high shear

viscosity parameters needed to be modified. The thermal curing study was performed in order to modify the high shear mixing procedure as explained in the next section.



**Figure 10: High shear mixer without cooling jackets**

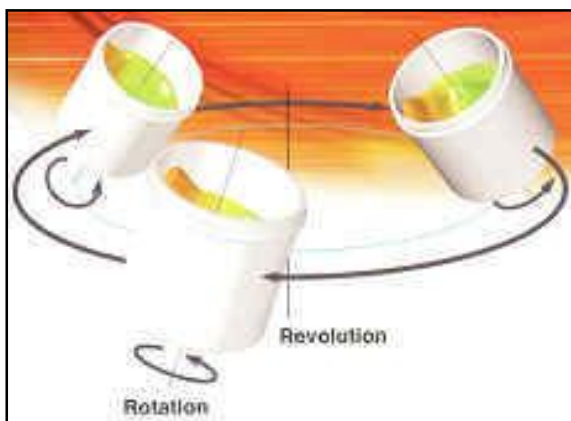
In the modified procedure, the water cooling system was used both on the mixing chamber and on hopper. Figure 11 display cooling lines on high shear mixer. The motor frequency and mixing time were reduced to 40 Hz and 25 min, respectively. The temperature of the resin and the mixing chamber was constantly monitored with IR thermometer. The temperature was maintained below 50°C.



**Figure 11: High shear mixer after modifications with cooling jackets on mixing chamber and hopper**

### **Blending of Nanoclay using Planetary Centrifugal Mixing**

Planetary Centrifugal (PC) mixing was the second mixing techniques used in this study. ARV-310 mixer manufactured by THINKY<sup>®</sup> was used. The speed of revolution can be adjusted in a range of 200-2000 RPM. The maximum centrifugal power is 400G at 2,000 RPM. The ratio of the revolution to the rotation of the cup holder is fixed at a 2:1. The mixer can also apply vacuum while mixing. It can be programmed to a minimum of 0.67 kPa vacuum pressure. Figure 12 shows the operational principle of the mixer.



**Figure 12: The material container rotates and revolves in air or vacuum pressure at high speed. The centrifugal power reaches to 400G force at highest speed (Courtesy of THINKY®)**

PC mixers are simple in use. It provides uniform stirring during rotation and revolution, concurrent defoaming and deaeration. These abilities are very critical for manufacturing of FR polymer nanocomposites because it allows to eliminate voids and to produce quality materials. The mixer was used to mix nanoclay with uncatalyzed resin and later to mix resin with catalyst.

PC mixers can successfully disperse nanoclay in polymer resin but should not be able to exfoliate platelets of nanoclay because it provides only a small amount of shearing force. The nanoclay was not expected to be exfoliated in this study. The nanoclay was used in the same weigh percentage as was with high shear mixer. Phenolic resin was mixed in batches with nanoclay in 3 different loadings: 2.5, 5.0, and 7.5% by weight. Because of mixer's limitations only up to 150 mL of resin could be mixed at a time. The resin was mixed in batches right before VARTM process. Nanoclay was added to uncatalyzed resin in a container and placed in the mixing chamber. Table 5 shows the details of the mixing procedure. Since the resin is water-based, vacuum pressure was kept above water vapor pressure. It should be noted that temperature of resin rises to about 35°C after 2 min of mixing.

**Table 5: Mixing Procedure for Mixing Nanoclay with Phenolic Resin Using Planetary Centrifugal Mixer**

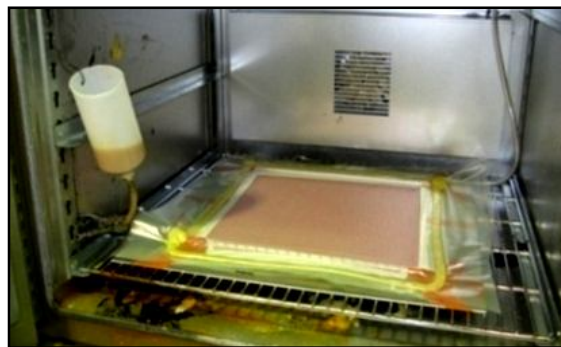
	<i>Speed</i>	<i>Pressure</i>	<i>Time</i>
Premixing (Step 1)	750 RPM	55 kPa	10 sec
Final Mixing (Step 2)	2,000 RPM	55 kPa	2 min

The mixer was also used to mix resin with acid catalyst for all nanocomposites.

Nanomodified resin was mixed with 5.75% by weight (5% by volume) catalyst and mixed in mixer for about 30 seconds at 2000 RPM and 55 kPa.

### **VARTM Process: Nanocomposites Manufacturing**

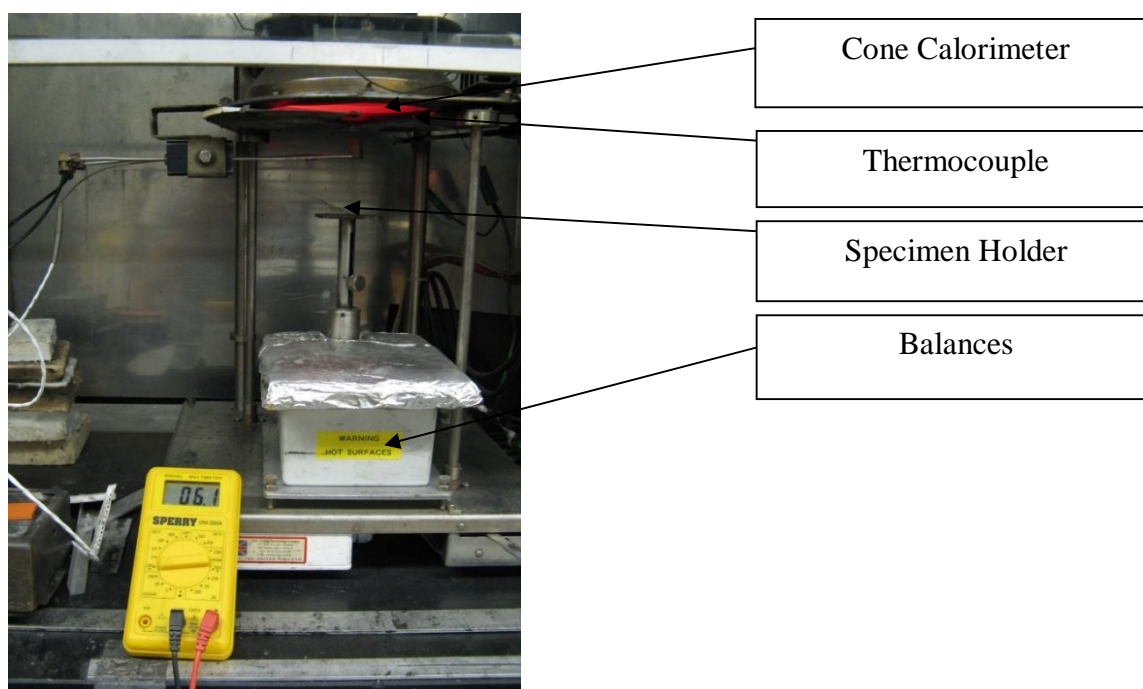
All composites panels were manufactured using Vacuum Assisted Resin Transfer Molding (VARTM) process. The resin was mixed at room temperature with catalyst in planetary centrifugal mixer with vacuum of 55 kPa and infused at RT under 50 kPa. After full infusion, composites were heated to 70°C for 1 hour and kept under vacuum for 6 hours. Composites were demolded after 12-16 hours. The edges of panel were trimmed and panel was post cured at 80°C for 3 hours. Panels were visually inspected for any defects such as dry spots, discoloration, and surface voids. Fiber volume fraction of these panels was measured using density method and found to be  $0.45 \pm 0.05$ .



**Figure 13: VARTM process setup inside an oven before impregnation**

### Mass Loss Calorimeter Tests on Nano-modified Phenolic / E-Glass Composites

Fire Testing Technology (FTT) Mass Loss Calorimeter was used to evaluate flammability properties of nanocomposites (Figure 14). FTT Mass Loss Calorimeter is an inexpensive stand alone instrument that enables mass loss rates to be determined at any heat flux in the range of the cone calorimeter model of ISO 5660.



**Figure 14: Mass loss calorimeter setup**

Mass loss testing was performed according to ASTM E2102 with flux of  $35 \text{ kW/m}^2$ . The heat flux was calibrated with a fluxmeter. The fluxmeter resistance which corresponds to this flux was  $6.1 \text{ m}\Omega$ . On the day of the testing, this heat flux corresponded to  $550^\circ \text{C}$ . According to the standard, the exposed surface's area should be square of  $100 \text{ cm}^2$ . The specimen holder had a top cover with standard open area. The specimens were held  $25 \text{ mm}$  below base of the cone. The temperature of the cone remained constant and was controlled by a digital controller and thermocouples. The data was manually collected every 10 seconds. Four



specimens were tested for control panel (control panels contain no nanoparticles) and for PC panels. Only one specimen was tested in HS categories (Figure 15). Right after the test, it was noted that materials burn differently depending on loading of nanoparticles (Figure 16).

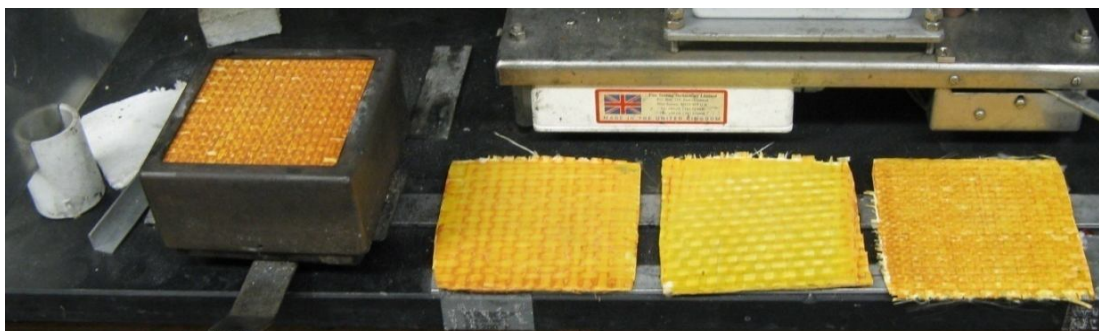


Figure 15: Composite specimens before testing with 0, 2.5, 5, and 7.5wt% nanoclay loading (left to right)



Figure 16: Composite specimens after testing at 0, 2.5, 5, and 7.5wt% nanoclay loading (left to right)

### Mechanical Testing

Universal testing system MTS 810 was used to perform, collect, and analyze mechanical tests. Specimens were cut using abrasive cutting water jet to avoid delaminations and for consistency of geometries. Nanocomposites were tested according to following ASTM standards. All tests were conducted in the displacement control mode with a rate specified in the appropriate ASTM standard. Table 6 shows number of specimens in each category. All the tests were performed according to the ASTM standards discussed below.

**Table 6: Number of Test Samples in Each Category**

Mixing Technique Loading	N/A 0%	<i>High Shear</i>			<i>Planetary Centrifugal</i>		
		2.5%	5.0%	7.5%	2.5%	5.0%	7.5%
Flexure	5	5	6	6	6	6	6
Short Beam	5	6	5	5	5	5	5
Compression	6	4	6	4	6	4	4
Tension	6	2	0	0	6	5	5
Mass Loss Calorimeter	4	1	1	1	4	4	4

Note: N/A – Not Applicable

Flexure tests were performed according to ASTM D 790 titled “Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials” to evaluate flexural strength and flexural modulus. Flexural properties are dependent on both fiber reinforcement and matrix.

Short Beam tests were performed according to ASTM D 2344 titled “Standard Test Method for Short-Beam strength of Polymer Matrix Composite Materials and their Laminates” to evaluate interlaminar shear strength (ILSS). ILSS is major of fiber/matrix adhesion and matrix dominant property. Low ILSS leads to poor bond between two layers, delamination, and splitting of laminates. This test was chosen to evaluate effect of nanomodification on interlaminar shear properties.

Compression tests were performed according to ASTM D 6641/D 6641M titled ‘Standard Test Method for Determining the Compressive Properties of Polymer Matrix Composite Laminates Using a Combined Loading Compression (CLC) Test Fixture.’ This test method determines the compressive strength and modulus properties of polymer matrix composite materials.

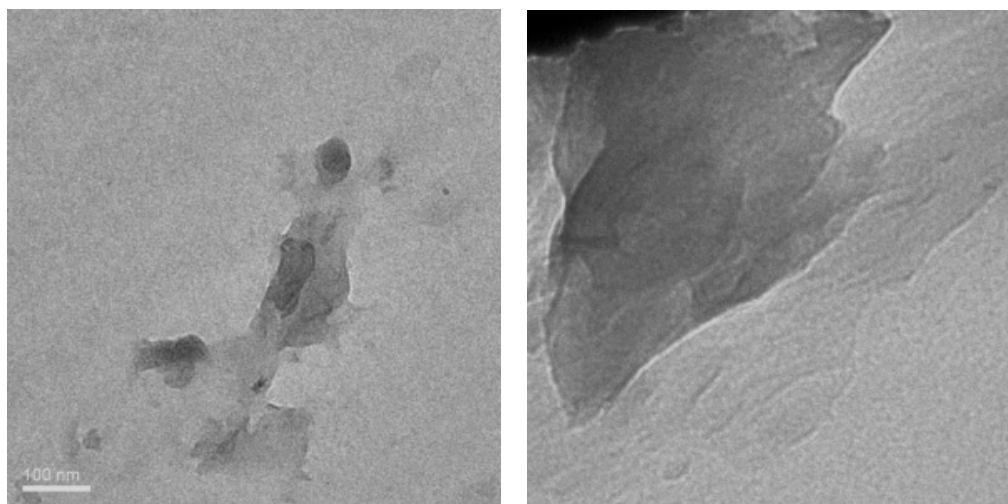
Static tensile tests were performed according to ASTM D3039 titled “Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.” The in-plane tensile properties (viz.,) ultimate tensile strength (UTS or,  $S_u$ ), strain at UTS, and longitudinal tensile

modulus were evaluated. The axial strain was measured by an extensometer. Tensile strength is fiber dominant property but matrix materials do have effect on tensile modulus and failure strain.

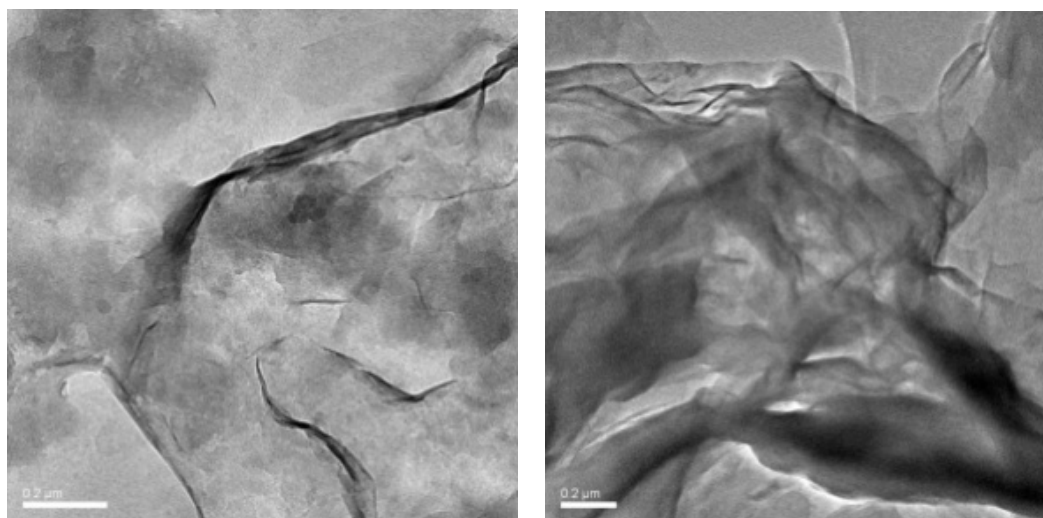
### III. RESULTS AND DISCUSSION

#### **TEM Analysis: Exfoliation of Nanoclay after High Shear Mixing**

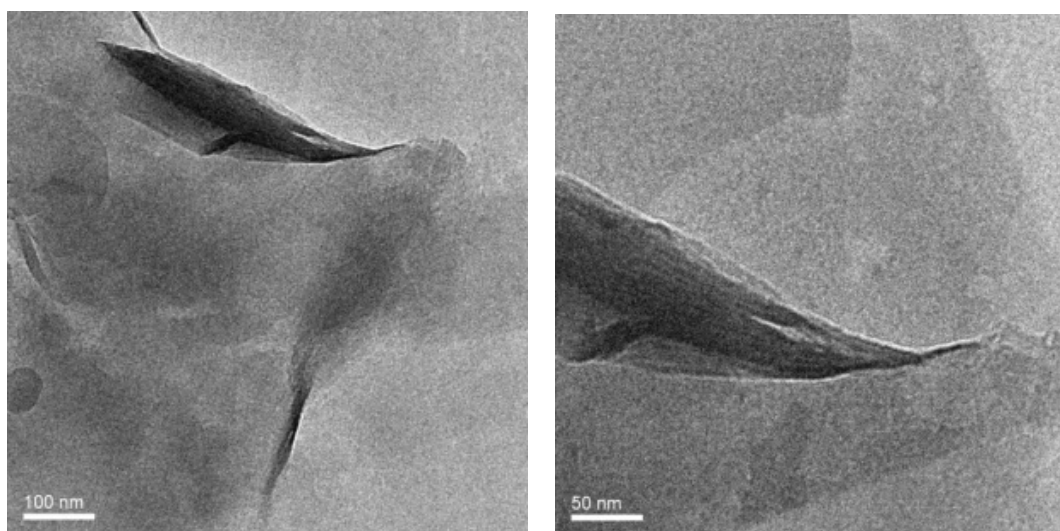
Figures 17, 18, 19 display TEM images for high shear mixing of 2.5, 5, and 7.5 wt.% loadings, respectively. TEM confirmed a good degree of exfoliation and dispersion of nanoclay for all the coupons (Tate, Kabakov, Koo, & Lao, 2009). Based on TEM analyses, the best nanoclay dispersion (mixture of interrelated and exfoliated states) in the phenolic resin was observed in the 5wt% loading. For 7.5wt% loadings, stacks of nanoclays were observed in the TEMs with unit bars of 100 and 50nm. It would be considered that nanoclays are in an intercalated state in the phenolic resin.



**Figure 17: TEM images of 2.5 wt.% loading of nanoclay after high shear mixing. Image is 800X800 nm**



**Figure 18: TEM images of 5.0 wt.% loading of nanoclay after high shear mixing. Image is 1600X1600 nm**



**Figure 19: TEM images of 7.5 wt.% loading of nanoclay after high shear mixing. Left image is 800X800 nm; right image is 400X400 nm**

### **SEM/EDS Analysis of Dispersion and Exfoliation**

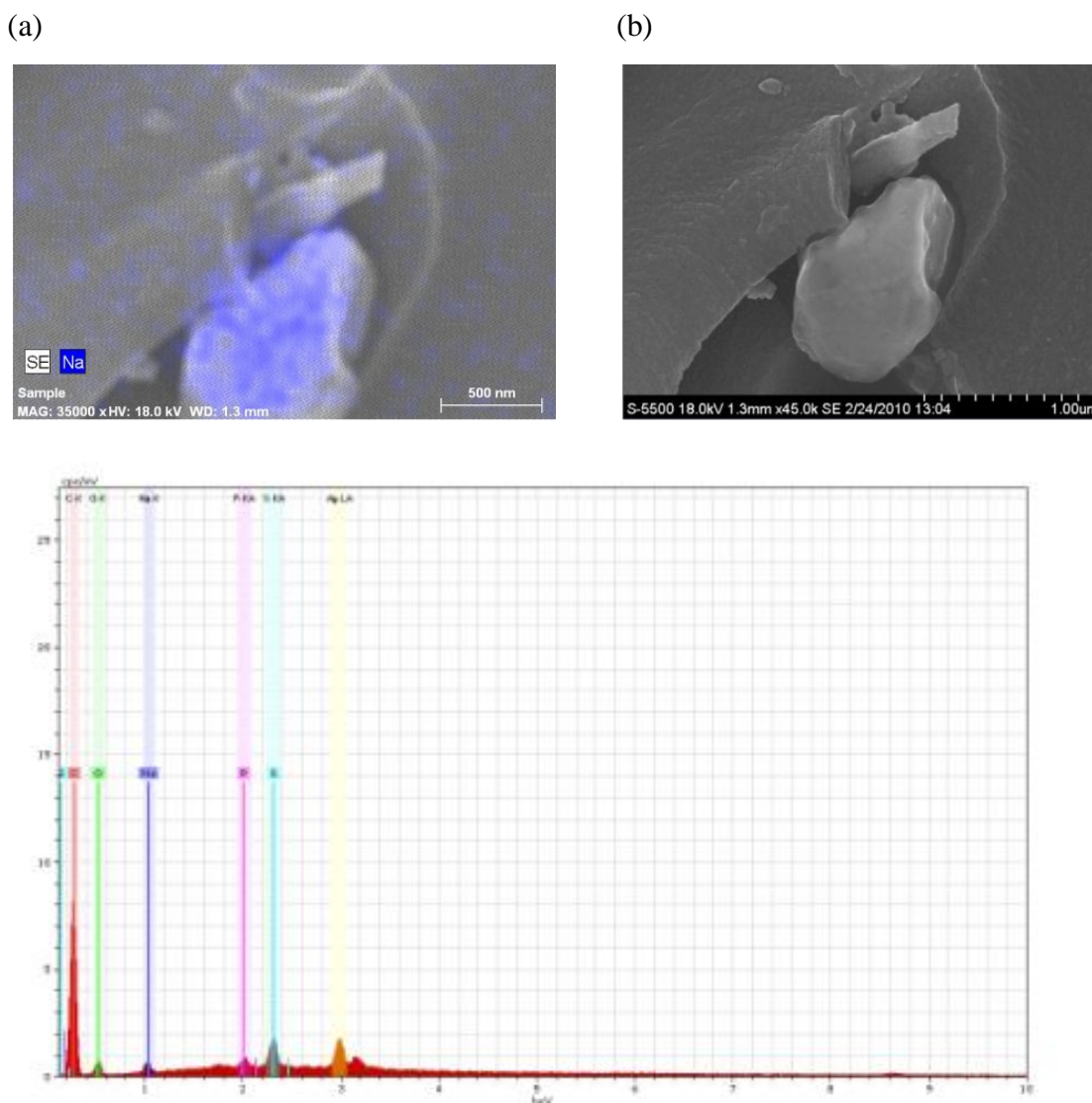
SEM was used to understand the morphology of nanoclay after different processes. Small samples of nanomodified resin were fully cured and SEM/EDM analysis was

conducted at the Faulkner Nano Science and Technology (NST) facility of the University of Texas at Austin. Hitachi S-5000 SEM was used to analyze dispersion of nanoclay in phenolic resin. This SEM has a resolution of 0.4 nm at 30 kV (Hitachi High Technology Europe, 2010). The purpose of this analysis was to compare dispersion of nanoclay using different mixing techniques.

A sample of resin was randomly selected. Samples with flat surfaces were selected for analysis and attached to standard specimen holder of Hitachi S-5000. Specimens were coated with silver in physical deposition chamber for 20 seconds. Then, they were analyzed in SEM at beam voltage of 30 kV. This instrument also performs energy-dispersive X-ray spectroscopy (EDS).

Nanomodified polymers were inspected in order to evaluate the degree of dispersion of nanoclay. HS and PC samples were compared and was concluded that both mixing techniques uniformly disperse clay, but the HS method provides better exfoliation.

In order to understand morphology of nanoclay, some of the areas were analyzed with energy-dispersive X-ray spectroscopy. Figure 20 shows typical nanoclay particle in an intercalated state and its spectroscopy. This particle is sodium rich – blue on the image. This confirms that the particle is most likely nanoclay. The smallest dimension of this particle is about 500 nm. Similar particles were found in all nanomodified polymers. The larger particles appear to consist of many tightly bound tactoids, which align to form ellipsoidal shaped agglomerations (Figure 21 and Figure 22).

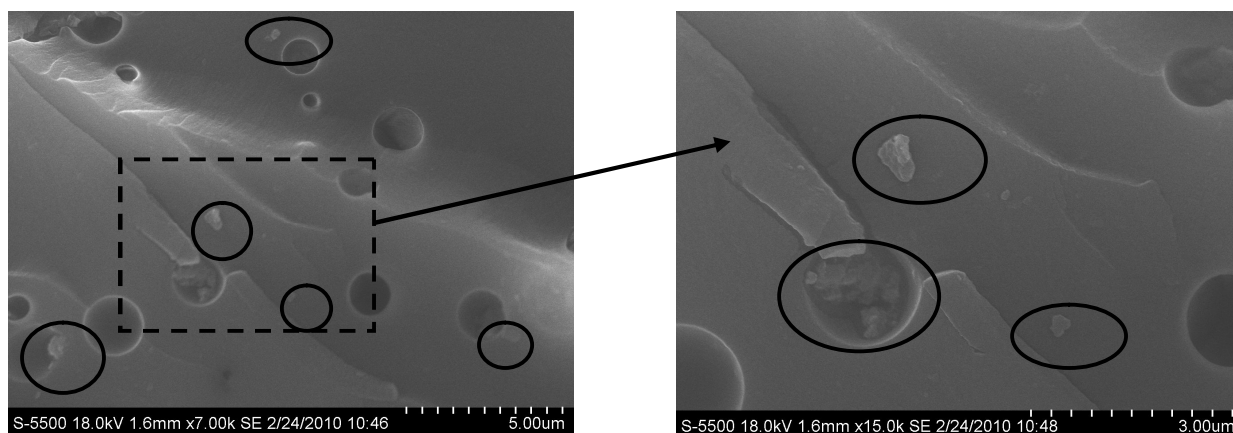


**Figure 20: (a) Sodium (Na) presence (blue) at area of interest confirms that the particle is Cloisite® Na<sup>+</sup> nanoclay; (b) SEM image of a particle**

### **Dispersion after High Shear Mixing**

HS is superior mixing method for platy nanoclays. In this research after 25 min of mixing at shear rate of  $77,000 \text{ s}^{-1}$ , the nanoclay were observed in mix of intercalated and exfoliated state and were uniformly dispersed in the matrix. Particles of small size were

found in different parts of material as shown in Figure 21. As per manufacturer, the particle size of Cloisite Na<sup>+</sup> varies 6 to 13  $\mu\text{m}$  in dry state (Appendix A). The size of nanoclay particles varies 50 to 500 nm in SEM micrograph as shown on the right of the image. It can be concluded that HS has achieved mix of intercalated and exfoliated state of nanoclay.



**Figure 21: SEM image of 5% nanoclay loading using high shear techniques**

### **Dispersion after Planetary Centrifugal Mixing**

PC mixing techniques worked well as predicted. Nanoclay was not exfoliated and was found in large sizes in different areas of polymer. SEM images of polymer after 2 minutes of centrifugal mixing at 400 G are shown in Figure 22. In microscopic level nanoclays are typically stacks of hundreds of platelets and size is in the range of 500 to 1000 nm. This indicates that only intercalated state has been achieved in PC technique. High shear forces are required to separate these platelets. However, low shear can be achieved using zirconium balls.



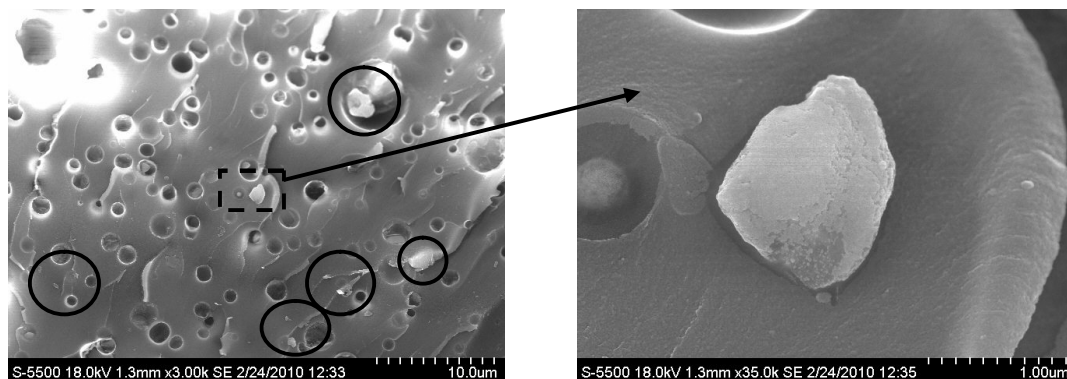


Figure 22: SEM image of 5% nanoclay loading using planetary centrifugal mixing

### **Mass Loss Calorimetry: Mass Remaining Analysis**

Effects of increasing nanoclay concentration on the flammability properties (percent mass remaining) are shown in Figure 23. Higher loading of nanoclay demonstrates higher mass remaining after being exposed to  $35 \text{ kW/m}^2$  heat flux for 10 min. Higher the mass remaining after 10 minutes of exposure, better are fire properties. These parameters of experiment were selected based on recommendation from ASTM E2102. Similar test results and trend were observed for HS and PC specimens. For HS composites mass remainder was 1.5% and 2.9% higher than control composites for 5.0wt% and 7.5wt% loading of nanoclay, respectively. For PC composites mass remainder was 0.6% and 1.5% higher than control composites for 5.0wt% and 7.5wt% loading of nanoclay, respectively. However, with 2.5 wt% loading of nanoclay mass remainder lowered compared to with both HS and PC techniques. The possible explanation is quality of composite panels. In 2.5 wt% HS composites, the nanoclay was mostly in intercalated state whereas for 5wt% and 7.5wt% nanoclay was mix of intercalated and exfoliated state. The quality of dispersion might be cause of drop in mass remainder for HS composites. In PC techniques mostly intercalated

state of nanoclay has been achieved. Secondly this technique might not provide good distributive dispersion of nanoclay within polymer matrix domain. Therefore at 2.5wt% performance might have drooped. Higher loadings provided more amount of nanoclay which might have led to property improvement.

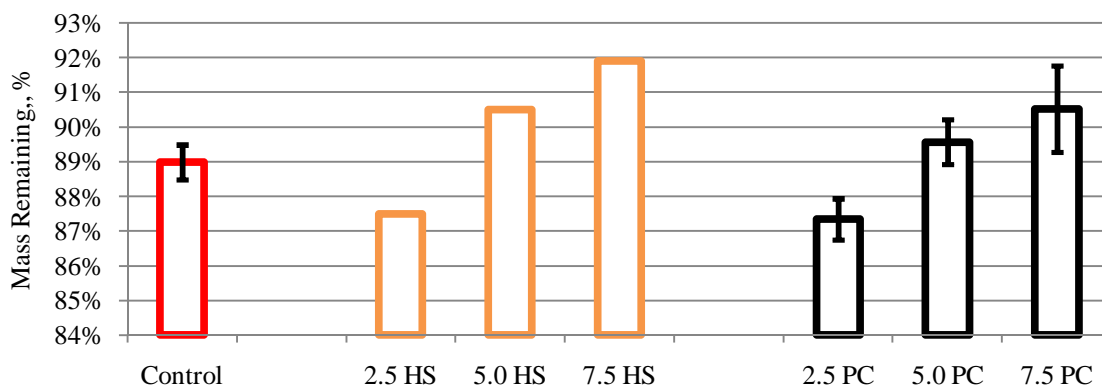


Figure 23: Percentage mass remaining after 10 min under 35 kW/m<sup>2</sup> heat flux

### Mass Remaining: High Shear Mixing

Figure 24 displays percentage mass loss with respect to time. It is observed that, 7.5wt% loaded specimen loses less mass which would exhibit better flammability properties. Mass loss calorimeter tests were used for initial screening.

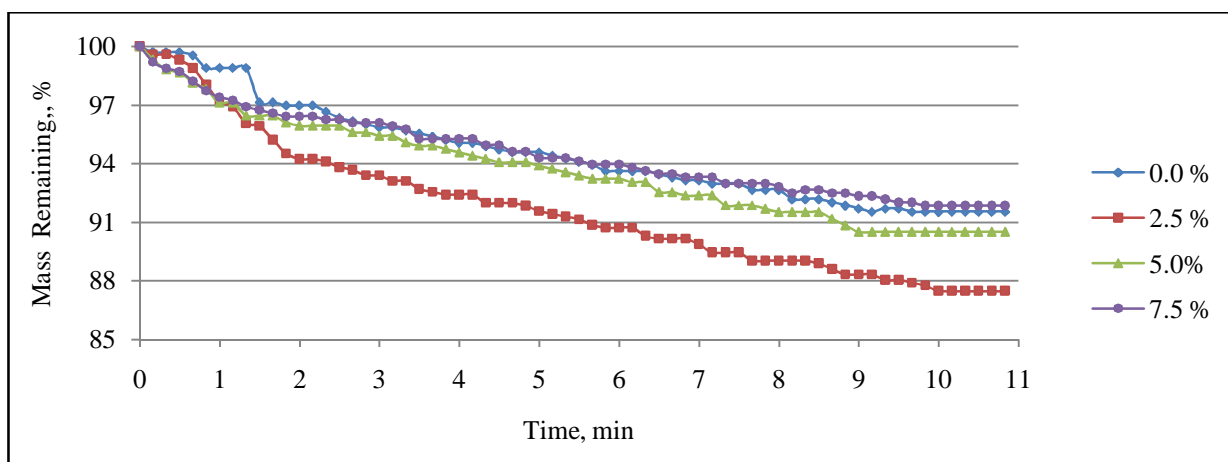
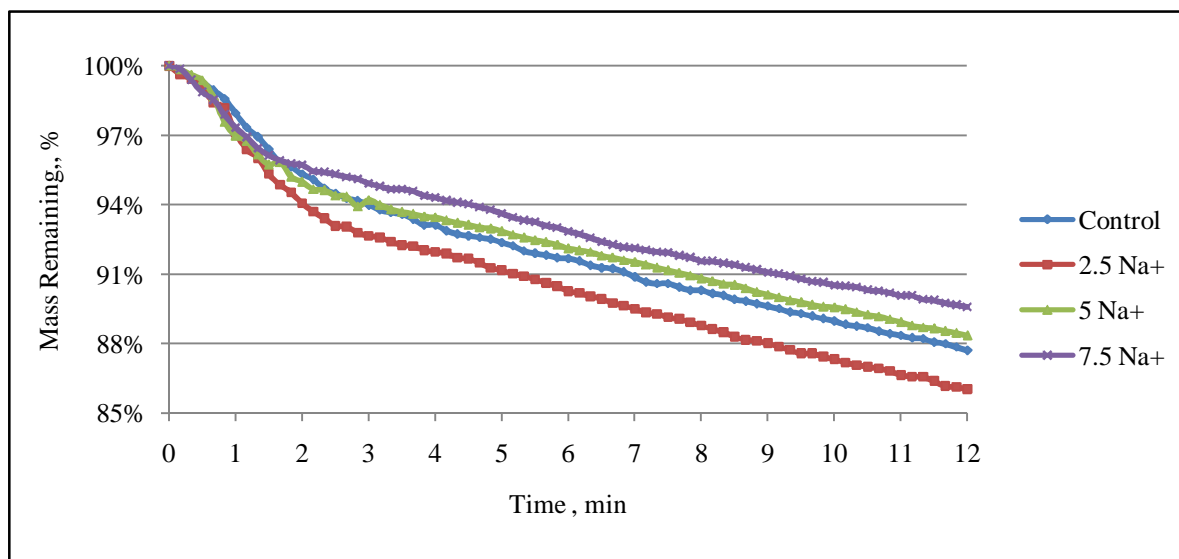


Figure 24: Mass loss calorimetry results for high shear specimens

### Mass Remaining: Planetary Centrifugal Mixing



**Figure 25: Mass loss calorimetry results for centrifugal planetary mixer**

Fiber reinforced composites manufactured with phenolic resin prepared by using PC mixer performed slightly worse than high-shear composites (Figure 25). The best result was obtained by composites with 7.5 wt% HS composites.. The 7.5 wt% PC composites were second best after HS 7.5wt% and better than HS 5.0 wt% composites It is recommended that wt% of nanoclay should be increased further to understand optimum level of loadings. However there would be two concerns with higher wt% loading of nanoclay: increase in viscosity of resin that would make VARTM processing difficult and decline in mechanical properties as more locations of intercalated nanoclays would provide more stress riser locations.

**Table 7: % mass remaining at 10 minutes of Mass Loss Test at 35 kW/m<sup>2</sup>**

	0 wt%	2.5 wt%	5 wt%	7.5 wt%
High Shear	89.0% (0.5)*	87.5% (N/A**)	90.5% (N/A)	91.9% (N/A)
Planetary Centrifugal	89.0% (0.5)	87.3% (0.6)	89.6% (0.6)	90.5% (1.2)

Note: \*standard deviation; \*\*N/A – not available

### **Mechanical Testing**

Composites were characterized in order to understand effect of dispersion on mechanical performance. All test panels were manufactured using the same procedure. Panels and test specimens were visually inspected for voids and dry fabric. Fiber volume fraction of specimens was measured in order to confirm quality of panel. Fiber volume fraction was in range of  $0.49 \pm 0.05$ . According to statistical analysis (shown in the later part of the thesis), mechanical properties did not change. It means that nanomodifications do not degrade these properties.

### **Flexural Test**

Flexural test is a key parameter in evaluating performance of matrix (resin). Flexural strength, strain, and modulus are matrix dependent properties. The following figures show results of the tests (Figure 26). The standard specimen size of 100 mm X 13 mm was used. Loading span was set to 80 mm and the loading rate to 2.0 mm/min. At 95% confidence level, there is no strong statistical difference between mean values of flexural strength and strains. Only flexural modulus significantly varies between categories. Control panel had the lowest flexural modulus. That means that nanoclay makes material stiffer compare to the base material.

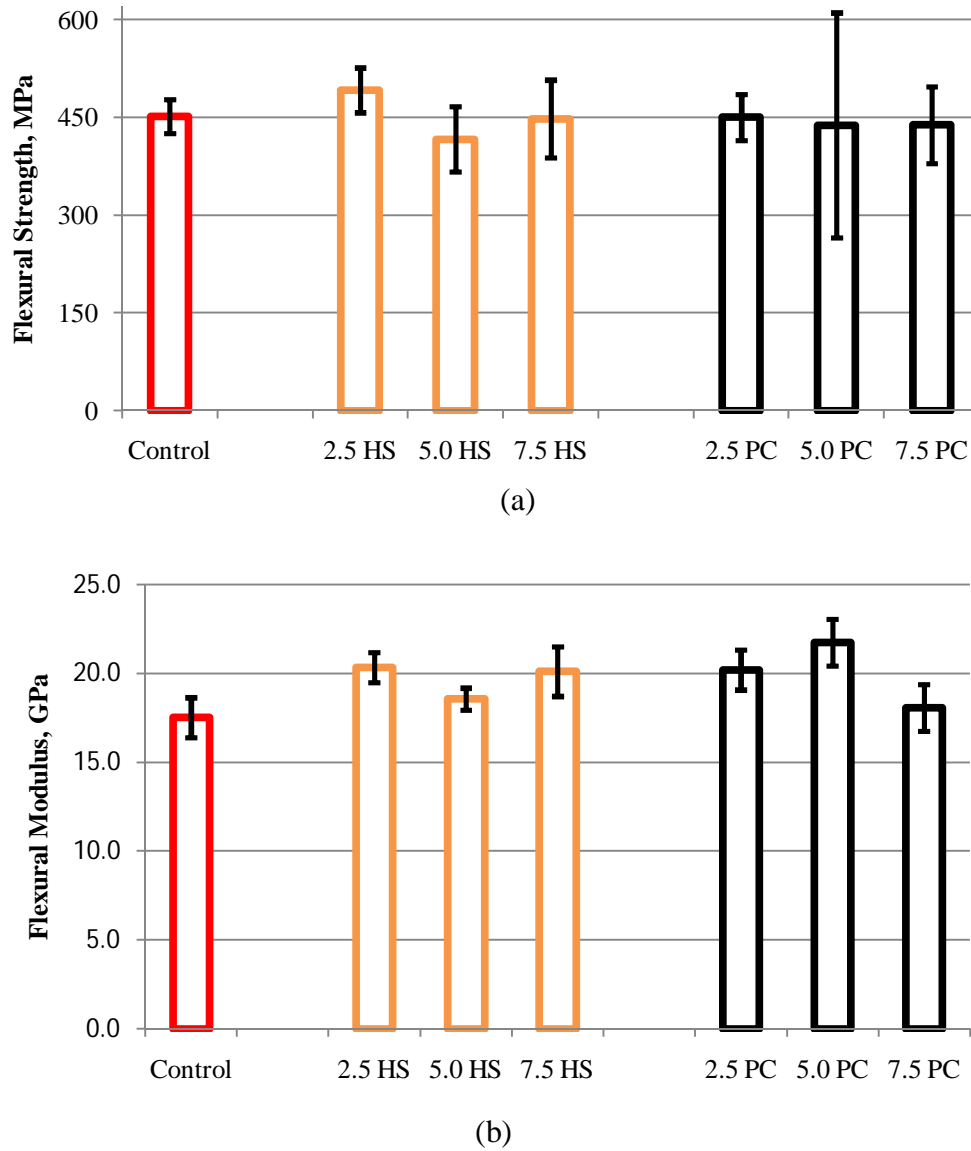


Figure 26: Flexure test results: (a) Flexural strength, MPa; (b) Flexural modulus, MPa

### Compression Test

Compression properties are matrix dominated properties. The test was conducted on MTS 810 universal material testing system with compression fixture. Standard specimen size for this fixture is 140 mm by 12 mm according to ASTM D6641. Gage length was kept the same for all specimens at about 13 mm and the loading rate of 1.3 mm/min was applied. The

test results can be found in Figure 27. Nanocomposites with 2.5% loading prepared by PC had the highest compression strength. This composite showed 22% improvement compare to the base material.

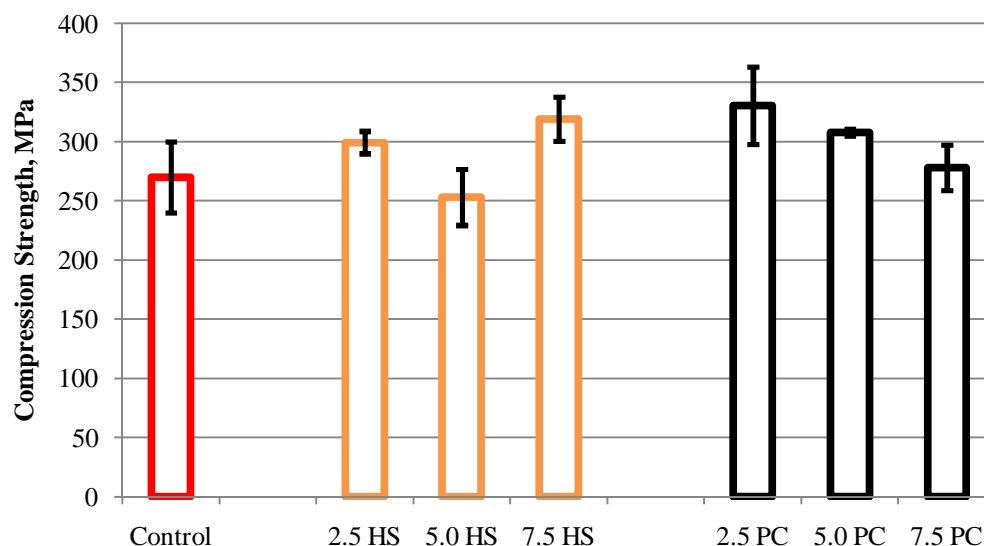


Figure 27: Compression test results: Compression strength, MPa

### Interlaminar Shear Strength

The short-beam shear test is used to determine inter laminar shear strength (ILSS) which is indicator of the fiber/matrix adhesion in the composite materials. The most important aspects of the tests for these materials view shear as a peel phenomenon (shearing along an adhesive plane). Short beam shear test is used as a quality control test of the lamination process and related matrix-dominated properties of the composite. The specimen span-to-thickness ratio is constrained to 4:1, forcing the shear stress to attain failure levels before tension and compression stresses reach their ultimate values (Strong, 2008). This test is similar to the flexure testing except that the sample-to-thickness ratio is much less and is

approximately 4:1. These tests were performed according to ASTM D 2344/D 2344M. The results are shown in Figure 28. Nanocomposites with 7.5% loading prepared by HS had almost same ILSS as that of control while 2.5% PC composite had slightly better properties.

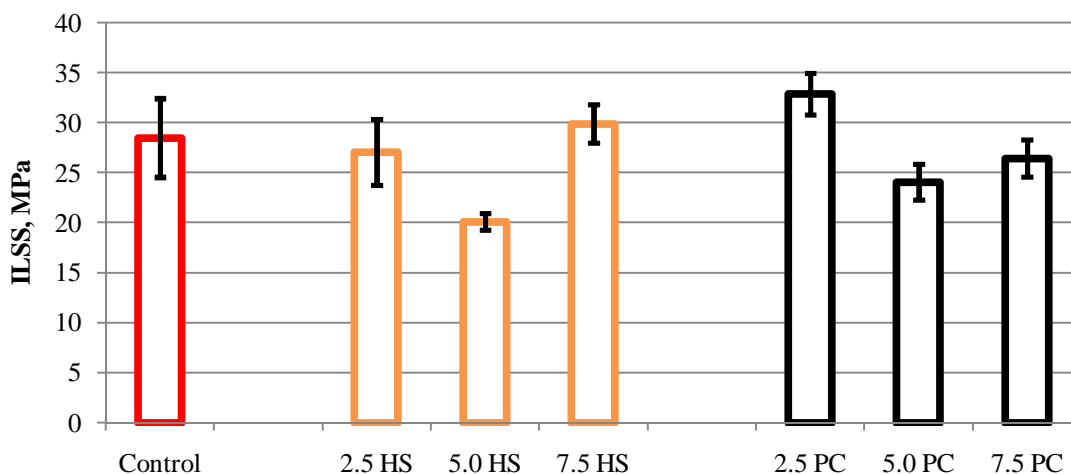
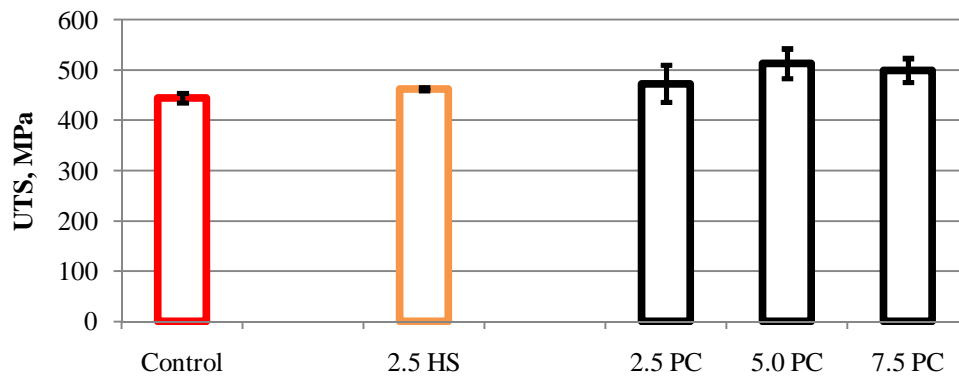


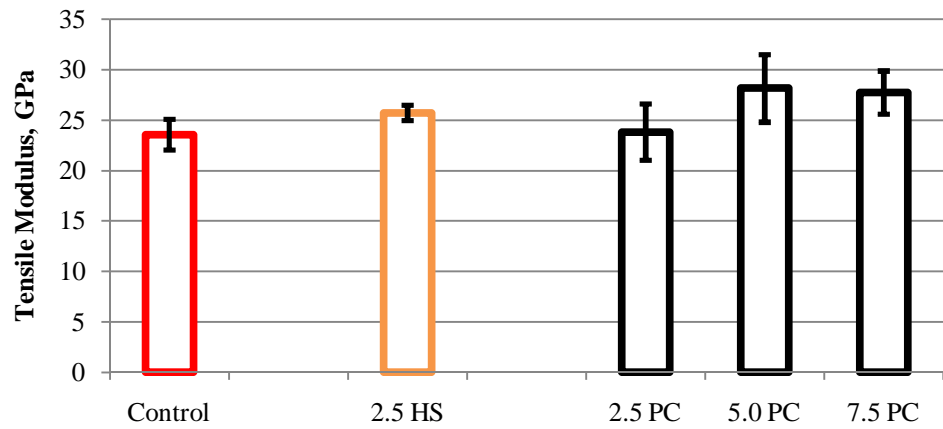
Figure 28: Short beam test results: ILSS, MPa

### Tension Test

Tensile properties are reinforcement (fibers) dominated properties. Because all of the composites used the same woven rowing E-glass and the same orientation of fibers, significant differences in the results were not expected. According to ASTM D3039, standard size specimens of 250 mm by 25 mm were cut along 0° fiber orientation. Then, the specimens were inspected. Finally plastic tabs were adhesively bonded and specimens were tested. Only samples in a few categories were tested and the results are shown in Figure 29: Tension test results: (a) Ultimate Tensile Strength (UTS), MPa; (b) Tensile modulus, GPa. **Error! Reference source not found..** All of the test specimens failed in DGM (Delamination at Gage area on the Middle) mode. Delamination occurs before other failures. This indicates that the phenolic resin has low percent of elongation.



(a)



(b)

**Figure 29: Tension test results: (a) Ultimate Tensile Strength (UTS), MPa; (b) Tensile modulus, GPa**



**Table 8: Mechanical properties of HS Composites**

	0 wt%	2.5 wt%	5 wt%	7.5 wt%
Tensile strength, MPa	444.29 (9.65)*	462.08 (3.15)	N/A**	N/A
Tensile modulus, GPa	23.54 (1.52)	25.69 (0.77)	N/A	N/A
Flexural strength, MPa	451.20 (25.93)	491.79 (34.37)	416.34 (49.97)	447.63 (59.65)
Flexural modulus, GPa	17.51 (1.13)	20.32 (0.85)	18.55 (0.62)	20.11 (1.40)
Compressive strength, MPa	270.03 (29.97)	299.44 (9.49)	253.08 (23.75)	319.23 (18.76)

Note: \*standard deviation; \*\*N/A – not available

**Table 9: Mechanical properties of PC Composites**

	0 wt%	2.5 wt%	5 wt%	7.5 wt%
Tensile strength, MPa	444.29 (9.65)*	472.95 (36.97)	512.74 (29.73)	499.76 (23.79)
Tensile modulus, GPa	23.54 (1.52)	23.79 (2.80)	28.13 (3.35)	27.73 (2.13)
Flexural strength, MPa	451.20 (25.93)	450.02 (35.22)	437.74 (172.68)	385.79 (58.97)
Flexural modulus, GPa	17.51 (1.13)	20.19 (1.12)	21.74 (1.31)	21.05 (1.074)
Compressive strength, MPa	270.03 (29.97)	330.48 (32.77)	307.96 (2.90)	278.12 (19.20)

Note: \*standard deviation

### **Analysis of Variance**

The major objective of this research was to improve flammability properties in cost-effective way without deteriorating mechanical properties. PC mixing is an economical method, while HS is more labor intensive. In order to evaluate significance of the result, one-way analysis of variance (ANOVA) was performed at 95% confidence level (alpha 0.05) using Palisade Stat Tools application for Microsoft Excel. ANOVA was performed for

different combinations of test groups in order to better compare and understand the effects of mixing techniques and nanoclay concentration of mechanical properties. Differences between the mean values are statistically significant if p-value is below 0.05. P-values were collected and analyzed. Table 10 shows p-values for different properties and test groups. *PC* group represent three different loadings mixed using planetary centrifugal mixer. *HS* group consists of three loading mixed using high shear mixer. *Control* group is the base material without nanomodifications. *All* represents results from the entire experiment, while *n* is the total sample size.

**Table 10: p-Values from ANOVA for Different Groups**

	<i>n</i>	<i>All</i>	<i>PC and Control</i>	<i>HS and Control</i>	<i>PC and HS</i>
Flexural Strength	40	<b>0.4805</b>	<b>0.6201</b>	<b>0.0942</b>	<b>0.4480</b>
Flexural Modulus	40	0.0000	0.0001	0.0010	0.0009
Mass Remainder	15	NA	0.009	NA	NA

**Note: In bold are p-value that are above or close to 0.05 significance level (n – total sample size, NA – not available)**

Statistical analysis confirms that there are no significant differences between PC and HS results for flexural strength (p-Value higher than 0.05). Flexural strength, one of the most important matrix dominated properties, is statistically has no difference between control material and nanomodified material. Most of the differences between mean values are insignificant which means neither there is improvement nor loss in mechanical properties.

On the other hand, PC composites performed significantly better in mass loss test compare to control material. The p-value calculated was only 0.009 (at alpha 0.05).

## VI. CONCLUSIONS

Glass-reinforced phenolic nanocomposites were successfully manufactured using low- cost VARTM process. Two different dispersion techniques were employed to uniformly disperse nanoclay. Mass loss tests showed that nanoclay addition improves flammability properties considerably at 5.0 and 7.5 wt.% loading. The major goal of the study was to provide cost-effective method to manufacture nanocomposites that would improve flammability properties without much sacrifice in mechanical properties. It is believed that nanocomposites are the future of composites industry. Some nanocomposites have been already used in mass production. Some of the challenges that manufacturers face in the production of nanocomposites are expensive processing methods, high capital cost, quality control, environmental and safety issues. Implementing cost-effective and high-efficiency processing methods would be a key in bringing lab-based technologies into commercialization.

Nanoclays are cheaper nanoparticles but are difficult to disperse uniformly in polymer matrix. Exfoliation of nanoclays is critical because relatively large stacks of nanoclays can become stress concentration points. Under mechanical loading micro cracks can be initiated at these locations that will eventually propagate leading to premature failure. It is difficult to achieve fully exfoliation state. Most of the mixing techniques would provide a combination of exfoliation and intercalation. This research indicates that for improvement

of flammability property intercalation state is adequate. In this study, it is observed that high-shear mixing is better technique to achieve exfoliation of Cloisite<sup>®</sup> Na<sup>+</sup> nanoclay in phenolic resin whereas planetary centrifugal mixing provided mostly intercalation state of nanoclay. Using both techniques, significant improvement in flammability properties with addition of 7.5wt% of nanoclay was achieved. This improvement in flammability property does not deteriorate other mechanical properties such as tension, flexure, compression, and ILSS.

High shear mixer, IKA<sup>®</sup> Labor Pilot 2000/4 with DR module, used in this study is one of the most advanced models available on the market. It has very high shear rate. However, this equipment is highly labor-intensive. There are difficulties in cleaning the equipment associated with waste of material. High shear generates heat which can be a problem with certain types of resins.

It can be concluded that cost-effective planetary centrifugal mixing can be used in manufacturing nanocomposites if flammability property enhancement is a primary concern. Planetary centrifugal mixer, such as ARV-310 by THINKY, can be used to successfully disperse nanoclays in phenolic resin and improve flammability properties. We have demonstrated this mixing method is significantly easier and faster than high shear method to disperse nanoclays in a phenolic resin.

## APPENDIX A: TECHNICAL DATA SHEETS

SOUTHERN CLAY PRODUCTS / A SUBSIDIARY OF ROCKWOOD SPECIALTIES, INC.

### PRODUCT BULLETIN/Cloisite®



Southern Clay Products, Inc.  
1212 Church Street  
Gonzales, TX 78629  
Phone: 800-324-2891  
Fax: 830-672-1903  
www.scprod.com

### Cloisite® Na<sup>+</sup>

#### Typical Physical Properties Bulletin

**Description:**

Cloisite® Na<sup>+</sup> is a natural montmorillonite.

**Designed Used:**

Cloisite® Na<sup>+</sup> is an additive for plastics to improve various plastic physical properties, such as reinforcement, HDT, CLTE and barrier.

**Typical Properties:**

Treatment/Properties:	Organic Modifier	Modifier Concentration	% Moisture	% Weight Loss on Ignition
Cloisite® Na <sup>+</sup>	None	None	4-9%	7%

Typical Dry Particle Sizes: (microns, by volume)

10% less than:	50% less than:	90% less than:
2µm	6µm	13µm

Color: Off White

Density:

Loose Bulk, lbs/ft <sup>3</sup>	Packed Bulk, lbs/ft <sup>3</sup>	Density, g/cc
12.45	20.95	2.86



X Ray Results:  $d_{001} = 11.7\text{\AA}$

For additional information or technical assistance contact Southern Clay Products, Inc.  
toll free at 800-324-2891.

Disclaimer of Warranty: The information presented herein is believed to be accurate but is not to be taken as a warranty, guarantee, or representation for which we assume legal responsibility. This information does not grant permission, license, or any rights or recommendations to practice any form of proprietary intellectual property without obtaining the appropriate license or grant from the property owner. The information is offered solely for your consideration, investigation and verification, but you must determine the suitability of the product for your specific application. The purchaser assumes all risk of use of handling the material, including but not limited to transferring the material within purchaser's facilities, using the material in applications specified by the purchaser and handling any product which includes the material, whether or not in accordance with any statements made herein.



**Product Data Sheet**  
 Revised 11/16/2007  
 SAP Product Code #: 332371, 353909

## CELLOBOND® J2027L

### Phenolic Liquid Resole – Composites & Laminates

#### Description

J2027L is a low viscosity unmodified liquid phenolic resole resin.

#### Application

Cellobond® phenolic resins are used to impregnate fibre reinforcements in the manufacture of structural and decorative composites for the mass transit, marine, offshore and construction industries.

#### Benefits

J2027L has been designed to have a low viscosity to facilitate the manufacture of composites primarily by RTM and VARI automated processes where a high degree of fire safety, excellent mechanical properties or resistance to high temperatures is required.

#### Typical Properties

Properties	Test Method	Unit	Value
Viscosity, Brookfield	IR-111	cps	270-500
Specific Gravity	IR-026		1.220-1.240
Free Formaldehyde	IR-076	%	0.0-1.0
pH @ 25°C	IR-034		7.3-7.8
Pot Life	IR-148	min	3.6-7.2
Water, Karl Fisher	IR-046	%	10.0-15.5
Free Phenol	IR-050	%	8.0-11.0

#### Packaging

J2027L is supplied in standard drums containing approximately 500 lbs net or drums containing 227 kgs net.

#### Storage

The resin should be usable for a minimum of 2 months if stored in sealed containers at less than 25°C.

All information, recommendations and suggestions offered by Hexion Specialty Chemicals, Inc. orally, in written form or otherwise ("information"), is provided to the best of our knowledge, it may however not be regarded as legally binding. Hexion Specialty Chemicals excludes any and all liability resulting from the use of information. Nothing herein waives or amends Hexion Specialty Chemicals' Conditions of Sale. Our support does not release the customer from the obligation to conduct its own review of the information and in particular of our product data sheets, safety data sheets and our technical information bulletins. The customer needs to test our products for its own risk and exposure to determine suitability for use. Experimental samples are for laboratory use only. The customer must further observe any and all patents and applicable laws and regulations. This publication does not represent a license, nor does it intend to infringe or encourage infringement of any existing patent.



## Rovcloth® Super 317

## Rovcloth® Super 317

Rovcloth® Woven Roving is a woven fabric consisting of single end glass rovings. FGI's Super 317 sizing allows for ease of handling, fast wet out and compatibility with Polyester, Vinyl Ester, Epoxy, and Polyurethane resins. Rovcloth comes in a variety of weights, weave patterns and widths to suit any application.

### Product Data

	1854	2254	2454	2977 Twill	3273
Nominal Weight oz./sq. yd.	17.2	22.0	23.3	27.4	31.7
Warp	5.0/in.	5.0/in.	5.0/in.	7.0/in.	7.0/in.
Percent of Weight	59%	58%	55%	33%	56%
Fil	3.5/in.	3.6/in.	4.1/in.	7.2/in.	2.7/in.
Percent of Weight	41%	42%	45%	67%	44%
Nominal Thickness	.030 in.	.035 in.	.040 in.	.040 in.	.060 in.
Roll Length Yards	134	100	100	49	100
Roll Length Meters	122.5	91.4	91.4	44.8	91.4
Weight per Inch of Width	4.1 lbs.	3.9 lbs.	4.1 lbs.	2.3 lbs.	5.6 lbs.

\* Optional styles available upon request — Special pricing may be applicable.

### Packaging Data

Standard widths include 6", 8", 10", 12", 36", 50" and 60". Optional widths from 4" to 129" and optional roll lengths are available upon request. Special pricing may be applicable. All edges contain a glass locking leno.

All rolls individually stretch wrapped and palletized according to size and weight, stacking varies from 1 to 3 layers. Widths 12" and less will be boxed for shipment.



### Typical Test Data

Properties	1854, 2454		
	0° (ksi)	90° (ksi)	Modulus (msi)
Tensile	32.00	27.50	2.15
Compressive	27.50	27.50	2.30
Flexural	40.00	40.00	2.00
Glass Content by Weight	50%	50%	50%

The information herein is to assist customers in determining whether our products are suitable for their applications. Nothing herein shall constitute a warranty, expressed or implied. Relative values shown are accurate to the best of our knowledge.

Rev. 02 03/09/05

### Fiber Glass Industries, Inc.

69 Edison Street  
Amsterdam, NY 12010  
Tel. (518) 842-4000 • Fax (518) 842-4408  
[www.fiberglassindustries.com](http://www.fiberglassindustries.com)



18 oz. Basket Weave



29 oz. Twill Weave



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## VITA

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