LOW COST MANUFACTURING AND PERFORMANCE EVALUATION OF SOY-BASED POLYURETHANE/E-GLASS COMPOSITES

THESIS

Presented to the Graduate Council of
Texas State University-San Marcos
in Partial Fulfillment of
the Requirements

for the Degree of

Master of SCIENCE

by

Srujan kumar Konga

San Marcos, Texas
December, 2008

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Committee Members Approved:

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Jitendra S. Tate, Chair

_____

Andy H. Batey

_____

Bahram Asiabanpour

Approved:

_____

J. Michael Willoughby
Dean of Graduate College

To my parents,

inspired,

and inspiring.

ACKNOWLEDGEMENTS

Several people have been instrumental in shaping this thesis. One such dignitary is my advisor Prof. Jitendra S. Tate, without whose support this thesis could not have been completed. I would like to immensely thank him, for his support and encouragement, which was always there when I needed it. He helped me to build on my technical, writing and research skills. On the personal side, he did not hesitate to invite his students to become an extended part of his family. It has been a rewarding experience to work with him and his research group. I would like to express my deepest thanks to my committee members, Prof. Andy H. Batey and Prof. Bahram Asiabanpour for guiding and helping me in every aspect of my thesis.

I would like to express my gratitude to Prof. Jesus Jimenez, Prof. John Massingill, Pulin Patel, Jesse Hancock, Shane Arabie, Ray Cook, Gus Cantu, Jason Wagner, Dima and Temi for helping in my thesis.

I cannot end without thanking my family, on whose constant encouragement and love I have relied throughout my time at Texas State University-San Marcos. I thank my parents, for their absolute confidence in me. It is to them that I dedicate this work. Finally I would like to thank God almighty, for this blessed opportunity.

This manuscript was submitted on November 20, 2008.

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ABSTRACT

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by

Srujan kumar Konga, B.A.

Texas State University-San Marcos
December 2008

SUPERVISING PROFESSOR: JITENDRA S. TATE

'Presently, there is a renewed interest in developing materials and products based on bio-based and renewable resources' (Pollock, 2004). The principal drivers for this interest include environmental regulatory and economic factors. Glass reinforced composites are very popular in construction and in the boat building industry because of their low cost material and low manufacturing cost. The popular thermoset resins in such applications are unsaturated polyester and vinyl ester, which contain styrene. Recently,

the Environmental Protection Agency has applied stringent regulations on releasing of styrene (considered a volatile organic compound-VOC) for open-molding composite processes such as hand layup and spray layup. Therefore, there is great interest among composite manufacturers to use styrene-free resins and low-cost closed molding processes.

There is a significant interest in the use of soybean oil as a component in printing inks, as plasticizer, and as stabilizer in the manufacture of plastic parts, because of its environmentally friendly, biodegradable, and non-corrosive properties (Amendment, 2006). Two-part thermoset polyurethane (PU) contains polyol and isocynate. In the proposed research, soy-based polyol will be used to formulate PU resin. Further, this PU resin will be used to produce E-glass reinforced composites using a low-cost Vacuum Assisted Resin Transfer Molding (VARTM) process. VARTM has been established as a low-cost closed molding process having capability to produce large and complex parts. The literature indicates that mechanical properties of PU composites are comparable to vinyl ester composites and superior to unsaturated polyester composites (Sherman, 2004; Tate, Massingill, Patel, Rikka, and Arabie, 2007). Another major advantage is that PU does not contain styrene. Thus, E-glass reinforced PU composites would provide a viable alternative to polyester and vinyl ester composites. The overall objective of this research is to manufacture PU composites using a low-cost VARTM process, and to carry out a detailed mechanical characterization. Mechanical characterization includes tension, compression, shear, flexure and inter laminar shear strength tests.

Three different polyurethane/E-glass composites were manufactured using soy-based polyol. Those are ‘lab prepared’ (N type composites), ‘Vikol-1’ (P type

composites), and ‘Soypolyol DB-5’(S-type composites). The ‘Lab prepared’ polyol was made in IEIS (Institute of Environmental and Industry Science) in the Center for Coatings and Bio-Based Technology (CCBT) lab at Texas State University-San Marcos under supervision of Dr. Massingill. Arkema, Inc. supplied ‘Vikol-1,’ and ‘Soypolyol DB-5’ polyols, which are development grade materials. ‘Soypolyol® DB-5’ is a modified polyol that has shown considerable improvement in fiber/matrix adhesion in coating applications (Massingill, 1991; Mannari and Massingill, 2006). This research explores whether there is any advantage in using modified ‘Soypolyol® DB-5’ in bulk form in composites. ‘Derakane Momentum 510-A40’ is a very popular vinyl ester resin made by Ashland Chemicals, Inc. (originally developed by Dow Chemical Company). It is used extensively in FRP (Fiber Reinforced Plastics) ductwork, stacks, stack liner applications, and in the handling of mixtures of air and hot gases or potentially flammable liquids. Vinyl ester/E-glass composites (VW type composites) were prepared to compare their properties with soy-based polyurethane composites.

The VARTM process was successfully implemented to manufacture PU/E-glass and vinyl ester/E-glass composites. When compared to other composites, VW type composites have significantly higher compressive strength, flexural strength, and flexural modulus.

Statistically, there is no difference in P-type and S-type composites in terms of compressive strength and flexural strength. But also P-type composites have significantly superior Inter laminar shear strength among all composites.

CHAPTER 1

INTRODUCTION

1.1 Overview of Composites

A composite material is made of two or more chemically different materials with a distinct interface between them. The individual constituents maintain their own properties. However, the combination of materials develops a material that has properties and characteristics different than those of the original constituents. The properties of the composite material depend on the properties and geometry of the constituent materials and the distribution of the phases.

Composites are becoming popular in industry due to their high specific strength and high specific modulus. They possess improved corrosion and wear resistance, as well as low thermal conductivity, and increased fatigue life. The endurance limit of toughened composites can be much higher than for steel and aluminum. Composites also have certain disadvantages: they are expensive, and there is a lack of high productivity manufacturing methods and clear-cut design rules. Composites have an enormous number of applications in the aerospace, automotive, construction, sports and medical industries. (Kelkar, Tate and Bolick, 2003).

Constituent materials in the composite are fibers and matrix. Fibers are major load carrying components. Matrix transfers stresses between the fibers, provides a barrier

against adverse environments, protects the surface from abrasion and provides lateral support. The different fibers used are glass, carbon, aramid, boron and alumina (Kelkar, Tate and Bolick, 2003). There are mainly four different types of composite materials depending upon the matrix used. They are Polymer Matrix Composite (PMC), Metal Matrix Composite (MMC), Ceramic Matrix Composite (CMC) and Carbon/Carbon Composites. PMCs are suitable for relatively low temperature applications. Polymer Matrix Composites (PMC), very often referred to as Fiber Reinforced Plastics (FRP), consist of fiber reinforcement (E-glass, S2-glass, carbon) and polymer matrix (polyester, vinyl ester, polyurethane, and epoxies). In this research, E-glass woven roving fabric is used in conjunction with polyurethane resin to manufacture composites using a low-cost Vacuum Assisted Resin Transfer Molding (VARTM) process.

1.2 Constituent Materials in PMC

Matrix and reinforcement are constituent materials in polymer matrix composites. Polymer matrix can be thermoplastics or thermosets, although thermoset matrices dominate the composite market. Reinforcement is in the form of fiber. Again, there are varieties of fiber materials available. The following sections explain matrix and fibers.

1.2.1 Matrix

Polymer matrices are also called as resins. Resin plays a very important role in polymer matrix composites. The loads are mainly carried by fibers but modulus, failure strain, and resin/matrix adhesion play a dominant role in the performance of composites. Resin also determines the type of fabrication process, the service temperature, the flammability and the corrosion resistance of the composite. Secondly, it protects the

reinforcement from adverse environmental effects. Polymer resins are of two kinds: thermosets and thermoplastics.

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, on the other hand, are usually liquids or low melting point solids in their initial form. When used to produce finished goods, these thermosetting resins are "cured" by the use of a catalyst, by heat, or a combination of the two. Once cured, solid thermoset resins cannot be converted back into their original liquid form. Unlike thermoplastic resins, 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 (Tg) are used to measure the softening of a cured resin. Both test methods (HDT and Tg) measure the approximate temperature where the cured resin will soften significantly to yield (bend or sag) under load (American Composites Manufacturers Association [ACMA], 2004).

Thermosetting plastics, however, have a number of advantages. Unlike thermoplastics, they retain their strength and shape even when heated. This makes thermosetting plastics well suited to the production of permanent components and large, solid shapes. Additionally, these components have excellent strength attributes (although they are brittle), and 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. Table 1.1 provides properties of popular thermoset resins. Polyurethane resin has two components: polyol and isocynate. By varying the mix ratio of these components,

polyurethane can be made flexible, semi-rigid, and rigid. Full density, non-foam, two-part, thermoset polyurethane resin is used in this research. In the present research, the polyol component is made from soybean oil. Polyol and isocynate are mixed on a 1:1 equivalent basis. This ratio makes polyurethane non-foam and rigid.

Table 1.1 Properties of Typical Polymer Matrix Materials (Daniel and Ishai, 1994)

Matrix type	Density, g/cc	Tensile strength, ksi	Tensile modulus, Msi	Coefficient of thermal expansion, 10^{-6} /°F	Glass transition temperature, T_g , °F
Unsaturated polyester	1.1-1.5	5.8-13	0.46-0.51	33-110	50-110
Vinyl ester	1.23	12.5	1.5	212-514	220
Epoxy	1.27	10	0.62	25	200

Vinyl ester: Derkane Momentum 510-A40, Ashland, Inc.
Epoxy: Hercules 3501-6, Hexcel, Inc.

1.2.2 Fibers

Fibers are materials that have one very long axis compared to the others. The fibers may be aramid, carbon or graphite, glass, ceramic, quartz, natural materials (hemp, flax, kenaf, etc.), and many other things. E-glass is a popular fiber made primarily of silica oxide, along with oxides of aluminum, boron, calcium and other compounds. Named for its good electrical resistance, E-glass is strong, yet low in cost and accounts for over 90% of all glass fiber reinforcements, especially in aircraft radomes, antennae and applications where radio-signal transparency is desired. E-glass is also used extensively in computer circuit boards where stiffness and electrical resistance are required (Composites One, 2005). E-glass composites are also extensively used in the marine, sports, transportation, military, and construction industries. Table 1.2 lists properties of major fibers in polymer matrix composites.

Table 1.2 Properties of Typical Fibers (Strong, 1989)

Fiber type	Diameter, micron	Density, g/cc	Tensile strength, ksi	Tensile modulus, Msi	Elongation at break, %
E-glass	8-14	2.5	500	10	4.9
S-glass	10	2.5	665	12	5.7
Carbon (standard modulus)	7	1.8	600	33	1.6
Aramid (Kevlar 49)	12	1.45	550	19	30

Each type of fiber has its own unique properties that make it suitable for different uses. These fibers are normally treated with sizing and coupling agents. These treatments reduce the effects of fiber-fiber abrasion, which can significantly degrade the mechanical strength of the individual fibers. Fibers are available in many diameters and lengths. Fibers are available in many different forms, such as chopped fibers, prepregs, and textile fabrics. Prepregs contains all fibers oriented in one direction. Prepreg is fiber reinforcement preimpregnated with a polymer resin that is only partially cured (cross linked). Prepregs need to be stored at 32 ºF, otherwise, the polymer resin gets cured at room temperature. These prepregs are then laid in layers to obtain the required thickness and shape. Then it is post cured i.e. the process of keeping composites at a high temperature for a specific amount of time, so that entire resin cross-links. Textile fabrics include woven, braided, stitched, and knitted fabrics.

The types of composites in common use are uni-directional, multidirectional, and woven composites. Uni-directional and multidirectional composites are formed by laying all prepreg layers oriented in one direction and in different directions, respectively. Uni-directional and multidirectional composites have good in-plane properties. Woven

composites are being seriously considered for primary structural applications, where out-of-plane properties are also important, so that the structure can take up the secondary loads due to load eccentricities, local buckling, etc. In general, woven composites offer better dimensional stability over a large range of temperatures: better out-of-plane properties, better impact resistance, subtle conformability and deep draw moldability/shapability. Orthogonal woven fabrics are formed by interlacing two sets of yarn at right angles to each other (Naik, 1994). The Warp yarn runs parallel to the length of the fabric and the fill yarns run perpendicular to it. Two dimensional types of orthogonal weaves are plain weave, twill weave and satin weave. They exhibit good dimensional stability in warp and fill directions and offer highest cover or yarn packing density. Figures.1.1 through 1.4 displays different forms of textile fabric. E-glass woven roving which is shown in Figure 1.4 (b) fabric was used in this research.

E-Glass woven roving fabrics were used in this research. Woven roving fabric looks similar to plain woven, the only difference being rovings are not tightly woven. The diameter of individual glass filament (very often also referred as fiber) is approximately 8-14 micron. The bundle of fibers is called as tow. In the case of glass fibers, the tow is called as roving. Tows are designated as 3K, 6K, and 12K containing 3000, 6000, and 12000 filaments, respectively. In woven roving fabrics tows run 0 and 90 degrees to each other. These directions are called machine (0^o) and weft (90^o). Fibers have significantly more strength in the long direction (0^o) than in the other directions.

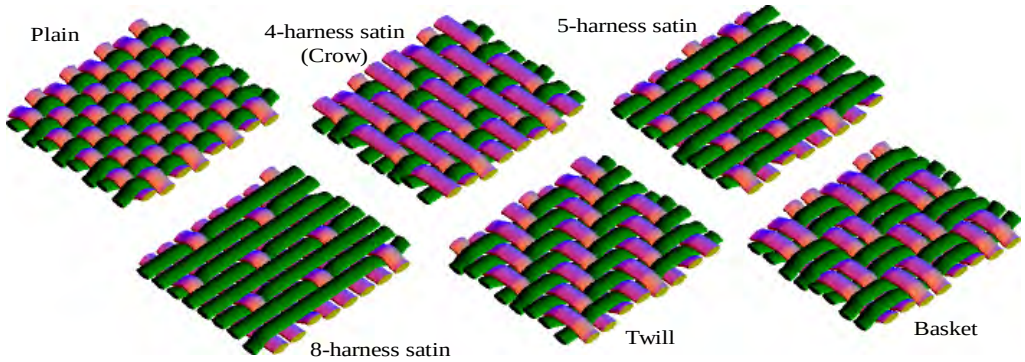


Figure 1.1 Different Weave Patterns: Plain, Twill, Satin and Basket (Whitcomb and Tang, 1999)

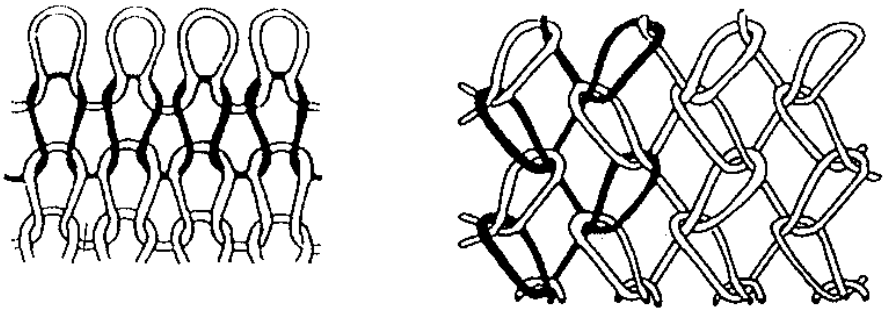


Figure 1.2 Knitted Tows

Figure 1.3 Biaxial Braid sleevings (Tate, 2004)

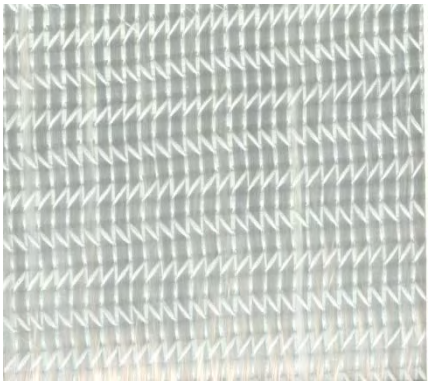


Figure 1.4 (a) Stitched E-glass fabric

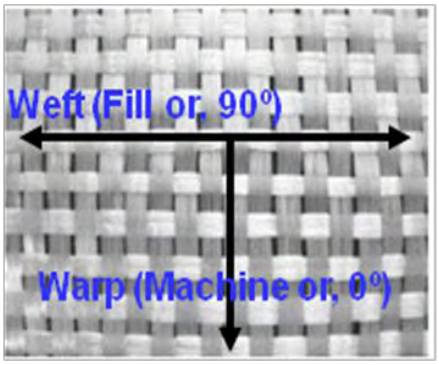


Figure 1.4 (b) E-glass woven roving

1.3 Polyurethane

A polyurethane, commonly abbreviated PU (or PUR), is any polymer consisting of a chain of organic units joined by urethane links. Polyurethane polymers are formed by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two alcohol groups in the presence of a catalyst.

Polyurethanes (PU) are thermo set products, which are the addition of polyisocyanates and polyols. PU composites provide an alternative to unsaturated polyester and vinyl ester composites, which are under environmental, pressure because of

styrene releases. Because of stringent EPA regulations (Amendment, 2006) on styrene emissions, composite manufacturers are interested in using styrene-free resin systems such as non-foam and full-density polyurethanes (PU).

Polyurethane is an ideal matrix for composites because of excellent flow characteristics and the ability to be formulated with a high range of hardness values and densities. In addition, polyurethanes can be processed at low pressures and temperatures in low-cost molds. They cure rapidly and adhere reliably to many materials, including glass, metal, and plastic. They can be processed by a variety of methods, from casting or spraying to reaction injection molding.

Polyurethane is one of the most useful three-dimensional polymers due to its unique features. It can be produced in the form of sheets, foams, adhesives, etc. PU is a tough polymer useful in coatings, structural foams, and composites. Polyurethanes (PU) have found extensive applications in industry mainly because they exhibit excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance, and a wide range of mechanical strengths. Two-component Polyurethane (2K-PU) systems are especially attractive since they offer flexibility in formulation, which enables customizing for demanding end-use requirements. In this research, the polyol component in PU formulation is made from soybean oil.

Polyurethane formulations cover an extremely wide range of stiffness, hardness, and densities. The success of polyurethane is due to its ability to be produced in various forms from flexible to rigid structures (Saunders and Frisch, 1962; Szycher, 1999).

Today, polyurethanes are finding a growing interest for applications as composites due to the increasing demand for lightweight, durable and cost effective compounds for sectors such as the automotive market (Dwan'Isa, Mohanty, Misra, Drzal, and Kazemizadeh, 2004).

1.3.1 Advantage of PU Composites

Superior Mechanical Properties: Composites manufactured from PU resins have superior tensile strength, impact resistance, and abrasion resistance compared with composites based on unsaturated polyester and vinyl ester resins (Connolly et al., 2005 and 2006).

Fast curing time: PU composites are also said to be attractive for their processing advantages. Curing times are much faster than for polyester spray-up—about 20 min versus 2 to 4 hr in non-automotive applications (Sherman, 2006).

No Styrene. They contain no styrene and therefore do not generate large amounts of VOCs (volatile organic compounds).

Secondary operations: The superior toughness of PU composites pays off in secondary operations such as drilling, machining, and assembling. Machined and punched edges exhibit little or no micro-cracking compared with traditional thermoset composites (Sherman, 2006).

1.3.2 Limitations of PU Composites

MDI Emissions: PU contains diphenylmethane-diisocyanate (MDI), which is a regulated material. However, Bayer sources report that MDI emissions from PU composite processing should usually be negligible, due to the low vapor pressure of MDI.

This conclusion seems to be supported by the results of industry emissions tests (Sherman, 2006).

Reaction Speed: The fast reactivity of PU makes it a good candidate for open-mold processes, such as spray-up of tubs, provided the appropriate engineering controls are in place for MDI. There is a downside to the fast reaction speed of polyurethanes. Current technology of PU resins have maximum open times of about 30 minutes, and their use to *manufacture prepregs* is limited (Connolly et al., 2005).

1.4 Soy-based polyurethane

Bio-based resources have played a major role throughout human history because they are environmental friendly and can be available from the natural resources. Bio-based composite materials are the innovative class of materials being developed today. They consist of environmentally friendly resins and natural fibers. Bio-based composite materials are a revolutionary idea with many potential benefits, because they are made from renewable agricultural resources like soybeans and corn. By using bio-based products, the user is avoiding reliance on petroleum resources.

A recent study indicates that soy-based polyols have 25% lower total environmental impact compared to petroleum based polyols and that use of soy polyols will result in reductions in net CO_2 contributions to global warming, smog formation, ecological toxicity, and fossil fuel depletion (Pollock, 2004). The polyol component in PU formulation in this research is made from soybean oil. The polyisocynate component is petroleum based.

Soy-based polyol has been used mainly in coating, adhesive, sealant, and foam applications. Very few attempts have been made to use it in reinforced composites. Bio-

based polyurethane from soybean oil derived polyol and diisocyanate on reinforcement with glass fibers enables a significant improvement in the mechanical properties of the base resin significantly. Thermogravimetric analysis (TGA) shows the improved thermal stability of the biobased polyurethane on reinforcement with glass fiber (Dwan'Isa, Mohanty, Misra, and Drzal, 2004).

1.5 Vacuum Assisted Resin Transfer Molding (VARTM)

Vacuum-assisted resin transfer molding or resin vacuum infusion process is a low-cost composite manufacturing process. VARTM has many advantages over the traditional resin transfer molding such as lower tooling cost and room temperature processing. This process has been employed to manufacture many large components ranging from turbine blades and boats to rail cars and bridge decks (Dong, 2008)

In VARTM the dry fabric is placed into the mold and vacuum bagged in conjunction with distribution media, resin line, and vacuum line. A low-viscosity (100 to 1000 cP) resin is drawn into the fabric through the aid of a vacuum. Distribution media consists of a plastics mesh that aids in uniform distribution of resin in the mold. The driving force in VARTM is the pressure differential between resin at atmospheric pressure and the vacuum in the mold. VARTM process is explained in detail in Chapter 2.

1.6 Objectives of Research

E-glass/unsaturated polyester and E-glass/vinyl-ester composites are extensively used in marine, sports, transportation, military, and construction industry. Both unsaturated polyester and vinyl ester contain styrene. Currently the Environmental Protection Agency has applied stringent regulations on release of styrene (considered a

volatile organic compound-VOC) for open-molding composite processes. Therefore, there is great interest amongst composite manufacturers to use styrene-free resins and low-cost closed molding processes. VARTM has been established as a low-cost closed molding process. The literature indicates that mechanical properties of PU composites are comparable to vinyl ester composites and superior to unsaturated polyester composites (Sherman, 2006; Tate et al., 2007). Thus, E-glass reinforced PU composites would provide a viable alternative to polyester and vinyl ester composites. The proposed research would carry out detailed mechanical characterization of soy-based PU/E-glass composites. This mechanical characterization would include tension, compression, shear, flexure, and inter-laminar shear strength tests.

In the beginning, soy-based polyol was made in a Chemistry lab by Dr. Massingill's research team as explained in the reference (Mannari and Massingill, 2006). This polyol is named as 'lab prepared' and its glass composites are named as 'N-type.' Improving fiber/matrix adhesion can enhance mechanical performance of composites. Poor fiber/matrix adhesion results in low compressive, flexural, and shear strengths. All fiber-manufacturers provide chemical treatment on fibers which provides better fiber/matrix adhesion. Fiber/matrix adhesion can be further improved by modifying the resin itself. It has been proved by researchers that epoxy phosphate ester polyols improve adhesion epoxy coatings to metal by a factor of ten (Massingill, 1991). Massingill also observed adhesion improvement to glass. The improvement in adhesion to metal and glass results from the reaction of phosphate with metal or glass to form a chemical bond. The phosphate group did not interfere with the cure of PU coatings (Mannari and Massingill, 2006). Commercially, Arkema supplies soy oil phosphate ester polyol under

the name 'Soypolyol® DB-5.' Glass composites of 'Soypolyol® DB-5' are named as S-type. Properties of lab prepared PU composites and 'Soypolyol® DB-5' composites are compared. Both 'lab prepared' and 'Soypolyol® DB-5' polyols are viscous and impose limitations on VARTM processing. Arkema, Inc. also makes low-viscosity non-modified soy-based polyol under name Vikol®-1. Glass composites of Vikol®-1 are named as 'P-type.' Finally, glass composites are also made from traditional vinyl ester manufactured by Ashland, Inc. under name 'Derakane Momentum 510-A40.' These composites are named as 'VW-type.' The comparison of mechanical properties of all N-type, P-type, S-type and VW-type composites is presented. Fabric used was Rovcloth® 1854 E-glass woven roving fabric supplied by Fiberglass Industries, Inc. (Refer Figure 1.4(b)).

The specific objectives of this research are as follows:

1. To develop a low cost VARTM process that can handle viscous PU resins.
2. To fabricate soy-based PU/E-glass and vinyl ester/E-glass composites using low cost VARTM process.
3. To evaluate the mechanical properties of composites.
4. To compare the performance of these composites under mechanical loading.

Chapter 2 provides details on VARTM manufacturing.

CHAPTER 2

MANUFACTURING

2.1 Composite manufacturing methods

There are various methods that are used to manufacture the composite laminates. These methods include wet lay-up, prepreg method, autoclave processing, filament winding, pultrusion, Resin Transfer Molding (RTM), and Vacuum Assisted Resin Transfer Molding (VARTM). The brief description of these methods is given in the following section. This section also presents merits and demerits of these methods. In addition, this section explains VARTM process in detail.

2.1.1 Wet lay-up method

'This is one of the oldest methods that involve laying the dry reinforcement (most often a fabric or a mat) into the mold and applying the resin. The wet composite is rolled by hand to evenly distribute the resin and thereby removes the air pockets. Another layer of reinforcement is laid on top, after which more catalyzed resin is poured, brushed, or sprayed over the reinforcement. This sequence is repeated until the desired thickness is reached. The layered structure is then allowed to harden (cure). This method is conceptually simple, does not require special handling of wet fabrics, and allows the resin to be applied only in the mold, thus helping to maintain a neat surrounding area. However, it is very difficult to maintain product uniformity. Voids are a common

problem. Mechanical properties are low compared to other composite manufacturing methods' (Strong, 1989).

2.1.2 Prepreg method

'This can be viewed as an extension of the wet lay-up method. The fabrics are usually a uni-directional tape or a woven fabric, impregnated with initiated resin, partially cured and then rolled up for shipment. However the prepreg method requires vacuum bagging and is often autoclaved. The resin distribution in the prepreg method is usually very even and is controlled during tape manufacture. However this method is slow and labor-intensive compared to the automated methods and has a potential high rejection rate because of faulty bagging procedures' (Strong, 1989).

2.1.3 Autoclave processing

'The autoclave consists of a vessel (as shown in Figure 2.1) that can be pressurized internally up to 5 bar (~ 75 psi), and then the contents are heated. The vessel must be sufficiently 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. The basic feedstock for the process is preimpregnated warp sheets or prepreg. A raw laminate along with a bleeder pack is placed under a nonstick gas permeable film, and then that is followed by a breather pack. This whole unit 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 whole unit 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 main aim of this process is to manufacture the laminate with uniform thickness and to ensure minimum porosity. The major difficulty in the autoclave process is the high capitalization cost and the stringent pressure code regulations' (Strong, 1989).

Front view

Side view

Figure 2.1 Autoclave Processing

(Courtesy: NC A&T State University, Greensboro, NC 27411)

2.1.4 Filament winding

'A continuous tape of fibers impregnated with resin is wrapped over a mandrel to form a part (as shown in Figure 2.2). Successive layers are added at the same or different winding angles until the required thickness is attained. The mandrel or the application head can rotate to give the fiber coverage over the mandrel. Cylindrical parts can be manufactured with the filament winding procedure. The pressure vessels, fuel and water tanks for storage and transportation, and pipes can be manufactured by this method. Use of pressure during the cure is another method of making non-cylindrical parts. The process can be used to make parts with strength in several directions. This process can

easily manufacture parts with high-pressure ratings. The difficulty of this process is programming the winding' (Strong, 1989).

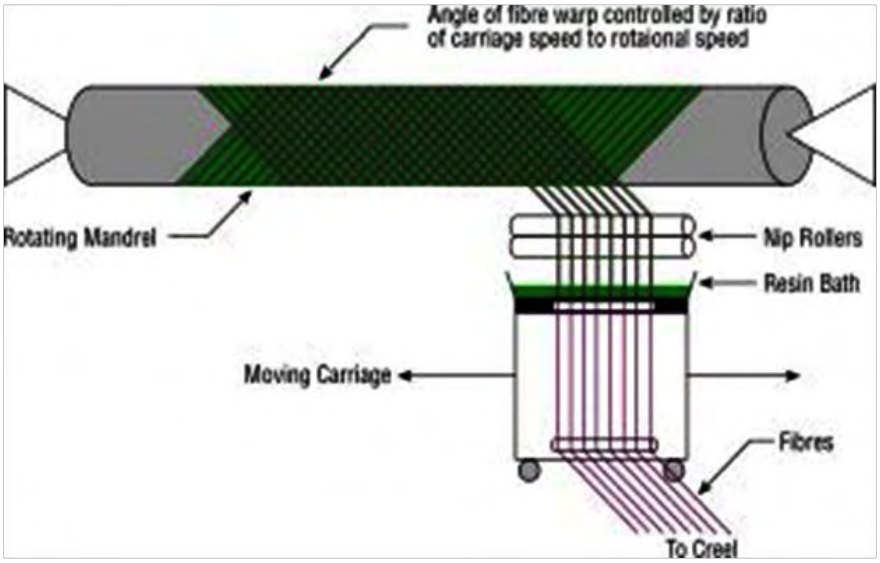


Figure 2.2 Filament Winding

(http://www.seecom.org.uk/education.asp?sequence=57)

2.1.5 Pultrusion

'Continuous reinforcement fibers are impregnated with resin and passed through a die (as shown in Figure 2.3). Then the part is cured and available for use. As this is a continuous process, the production rate is very high. The cross section of the part has to be constant for using this process, but the thickness of the part produced can be varied by having movable dies. The part usually gels in the die itself and then is fully cured when the part travels through a curing oven. The main advantage of this process is the high usage of fabrication material. However the problem can come when the resin or fibers accumulate and build up at the die opening and the equipment can jam. Voids can also result if the dies are run with too much opening for the fiber volume' (Strong, 1989).

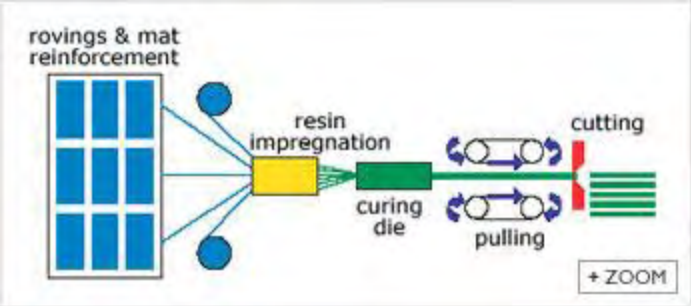


Figure 2.3 Pultrusion

(http://www.ocvreinforcements.com/processes/pultrusion/pultrusion.aspx)

2.1.6 Resin Transfer Molding (RTM)

'In this process, a mold is loaded with the reinforcement material and then closed. The resin is injected into it. The mold with the preform is often put under a vacuum so that the vacuum removes all the entrapped air in the preform and speeds up the RTM process. Typically, the resin is injected at the center of the top surface of the mold and the flow of resin occurs radially outwards untill it reaches the vent lines (as shown in Figure 2.4). In this process the flow of the resin occurs in the plane as well as in the transverse direction of the preform. The fiber architecture, permeability of the perform, and fabric crimps has an influence on the wetting of the fabric' (Strong, 1989).

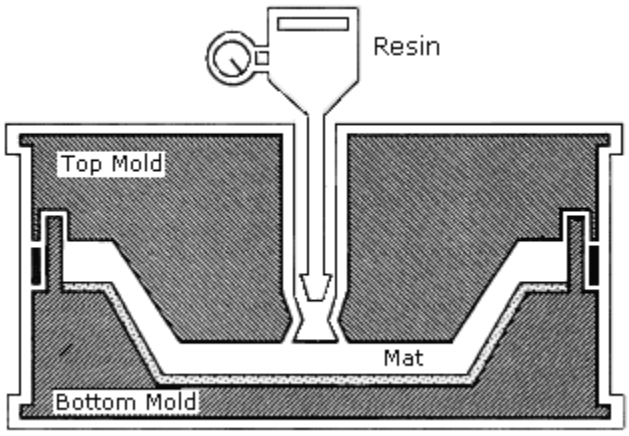


Figure 2.4 Resin Transfer Molding
(http://www.osha.gov/dts/osta/otm/otm_iii/otm_iii_1.html)

2.1.7 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 in the part (Mazumdar, 2002).

This process was used in manufacturing composite panels in this research. VARTM process is explained in detail in next section.

2.2 Vacuum Assisted Resin Transfer Molding process (VARTM)

Usually, Resin Transfer Molding (RTM), hand-layup and Vacuum Assisted Resin Transfer Molding process (VARTM) are widely used as low cost manufacturing processes. VARTM offers many advantages over the traditional resin transfer molding such as lower tooling cost, room temperature processing. As we discussed earlier in Section 2.1.1, the hand layup process is labor intensive and because of its open mold nature it produces the styrene emissions.

Vacuum Assisted Resin Transfer Molding (VARTM) is an attractive and affordable method of fabricating composite products. It can produce high-quality large-scale components. The major requirement of a resin system for VARTM is that viscosity

should be in the range of 100 to 1000 cP for the resin to flow throughout the fabric (Steven, 2001). The viscosity plays the major role in the VARTM process.

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 (Seeman, 1990 and 1994). The schematic for the fabrication is shown in Figure 2.5.

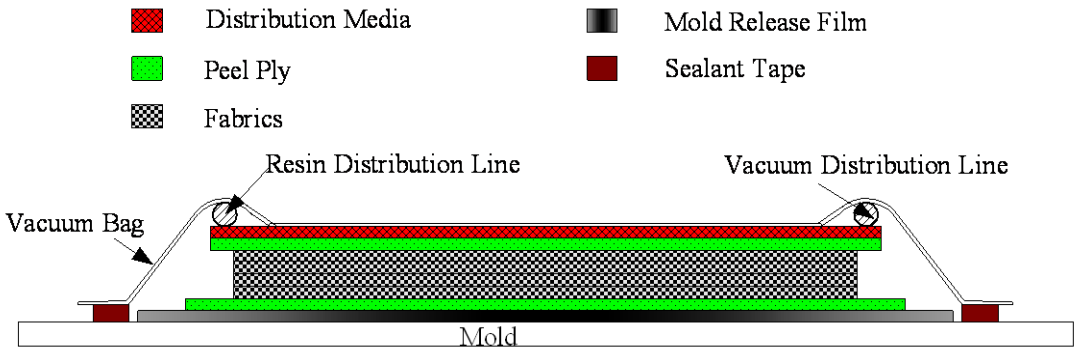


Figure 2.5. Schematic for VARTM (Tate, 2004)

The parameters of the VARTM process are currently designed by a trial-and-error method. Therefore, a series of experiments are required to design a suitable distribution media and to determine the proper location of the resin line and the vacuum line.

2.3 Material System:

Four different resin systems were used in this research:

1. Polyurethane: ‘lab-prepared’ polyol mixed with polyisocynate
2. Polyurthane: ‘Vikol®-1’ polyol mixed with polyisocynate
3. Polyurthane: ‘Soypolyol® DB-5’ polyol mixed with polyisocynate
4. ‘Derkane Momentum® 510-A40’ vinyl ester

All above mentioned polyols were mixed with Desmodur® Z4470 BA, aliphatic polyisocynate in 1:1 equivalent basis to formulate polyurethane (PU) resin. Desmodur® Z4470 BA is trade name of Bayer, Inc. Dibutyltin dilaurate (DBTL) was used as catalyst. For room temperature processing, tertiary butyl acetate was added as a solvent by 3-7 wt%. This solvent drops the viscosity of polyol in the range of 1000 cP.

Derkane® Momentum 510-A40 was mixed with MEKP (Methyl ethyl ketone peroxide) as catalyst and CoNaP6% (Cobalt naphathanate) as retardant in specified proportion

Fabric used was Rovcloth® 1854 E-glass woven roving fabric supplied by Fiberglass Industries, Inc. (Refer to Figure 1.4(b)).

2.4 Properties of Polyol

Table 2.1 lists oxirane number, hydroxyl value, acid value, room temperature viscosity, molecular weight (GPC), and polydispersity of these polyols. Molecular weights were evaluated by using GPC technique. Figures 2.6, 2.7 and 2.8 shows GPC analysis on ‘lab prepared,’ ‘Vikol-1,’ and ‘Soypolyol DB-5’ polyols. Room temperature viscosities of ‘lab prepared’ and ‘Soypolyol® DB-5’ were higher than the typical requirements of VARTM process.

Table 2.1. Properties of Polyols

Sr. No.	Property	Lab-prepared	Soypolyol DB-5	Vikol-1
1	Oxirane Number, % (ASTM D 1652-97)	0.082	0.07	0.21
2	Hydroxyl value, mg KOH/g (ASTM D 1957-86)	154	287	158
3	Acid value, mg KOH/g (ASTM D 1639-90)	8.5	56.8	0.35
4	Viscosity at RT, cP	20,970	121,800	1102
5	Molecular weight, Mw	27549	6193	6126
6	Polydispersity	1.177	5.997	5.807
7	Liquid density, g/mL	1.07	1.07	1.04

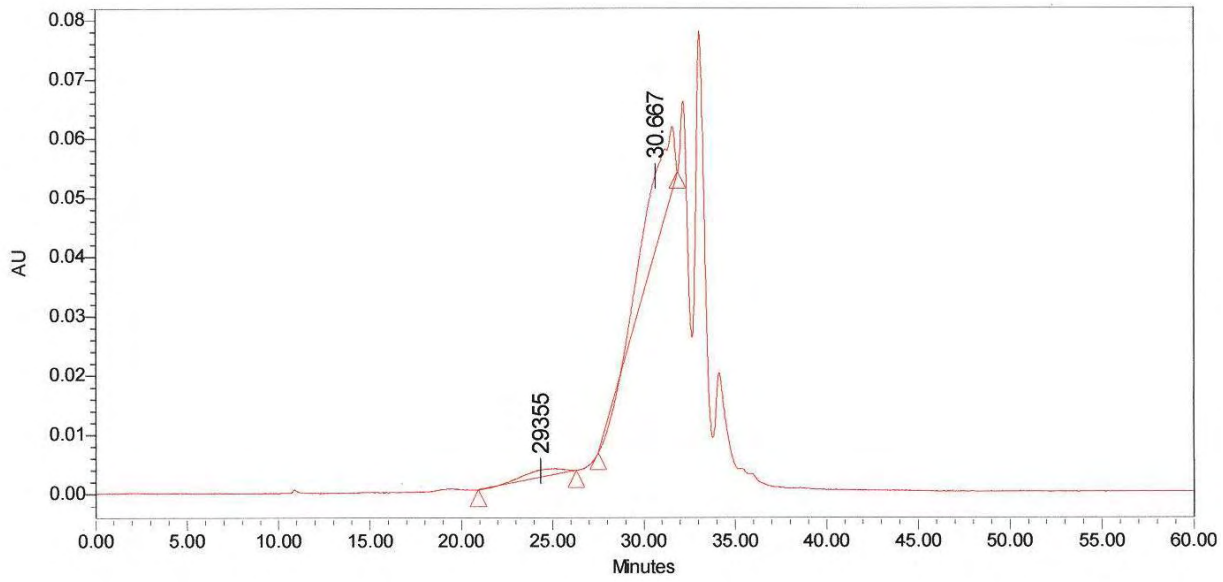


Figure 2.6 Molecular weight of Lab-prepared' Polyol

Table 2.2 GPC Results of 'Lab-prepared' Polyol

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		27549	32450	29355	37982	43610		1.177889		
2										

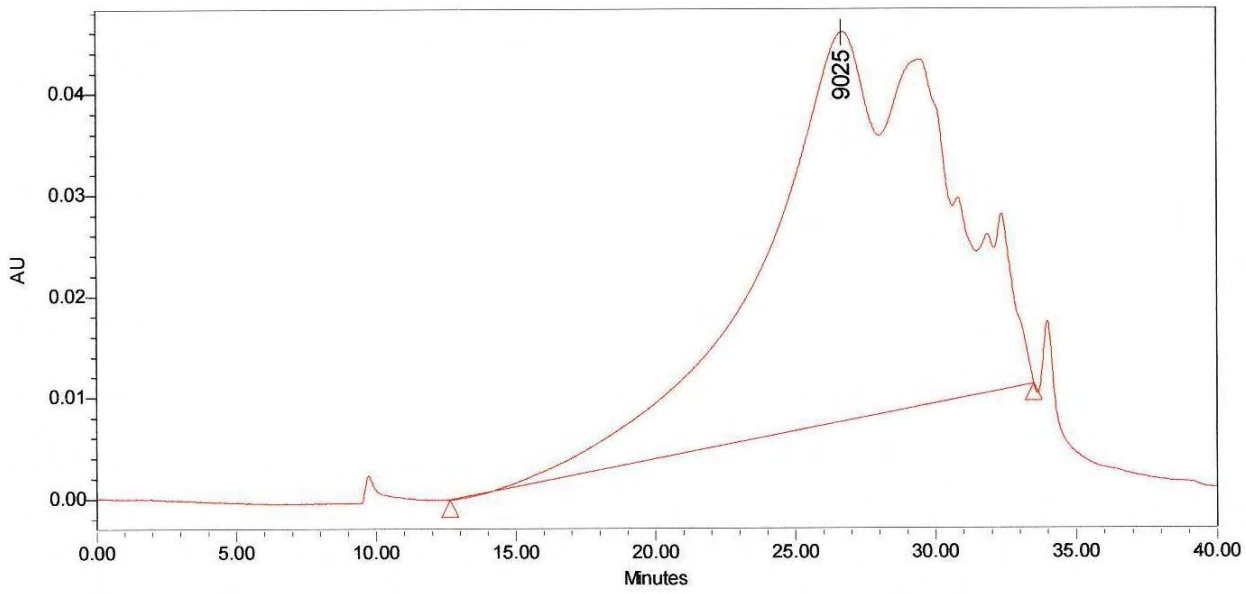


Figure 2.7 Molecular weight of 'Vikol-1' Polyol

Table 2.3 GPC Results of Vikol-1' Polyol

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		6126	35579	9025	175401	324938		5.807895		

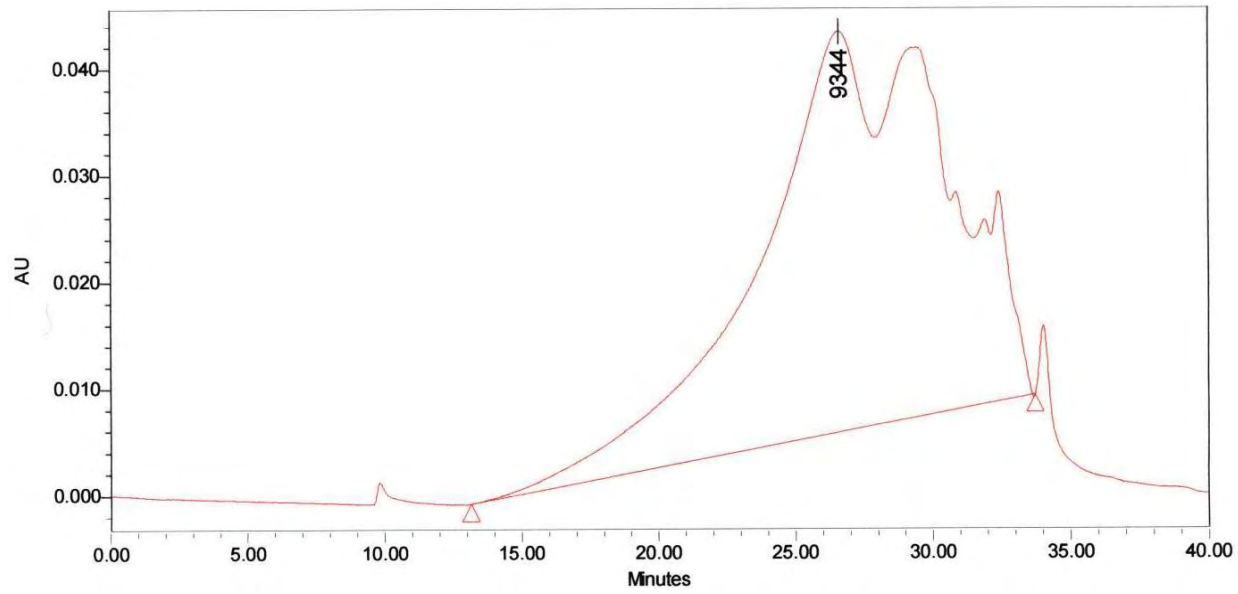


Figure 2.8 Molecular weight of 'Soypolyol DB-5' Polyol

Table 2.4 GPC Results of 'Soypolyol DB-5' Polyol

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		6193	37146	9344	178780	326696		5.997631		

2.5 Viscosity study

As discussed early in section 2.2, for VARTM process typically resin viscosity should be 100 to 1000 cP for complete wet-out of fabric. The viscosity of 'lab prepared' polyol was 20970 cP and 'Soypolyol® DB-5' was 121,800 cP. Viscosity vs temperature study (Refer Figure 2.6 and 2.8) was performed on these polyols to evaluate the temperature corresponding to viscosity around 1000 cP. Brookfield CAP 2000+ Viscometer was used to measure change in viscosity with respect to temperature and time (Refer to Figure 2.7). The spindle No. 3 was used with spindle speed of 25 rpm for 'lab prepared' polyol. The spindle No. 6 was used with spindle speed of 50 rpm for 'Soypolyol® DB-5' polyol. It is observed that viscosity of 'lab prepared' polyol was 840 cP at 140 ºF and viscosity of 'Soypolyl® DB-5' was 1375 cP at 167 ºF.

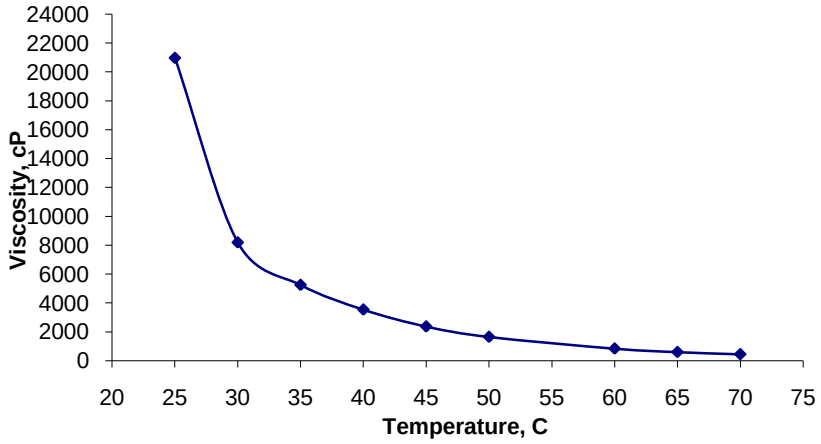
Gel time study was performed on formulated PU resin. A total of 100g formulated PU resin was prepared and temperature was increased to 140 ºF for 'lab prepared' and 167 ºF for 'Soypolyol® DB-5.' The viscous flow of the resin was monitored every three minutes with gentle mechanical stirring. The resin was unable to flow after a certain amount of time and mechanical stirring was not possible. This particular time was approximately 15 minutes for 'lab prepared' and 12 minutes for 'Soypolyol® DB-5' was recorded and referred to as gel time.

Table 2.5 Viscosity vs Temperature for 'Lab-prepared Polyol'

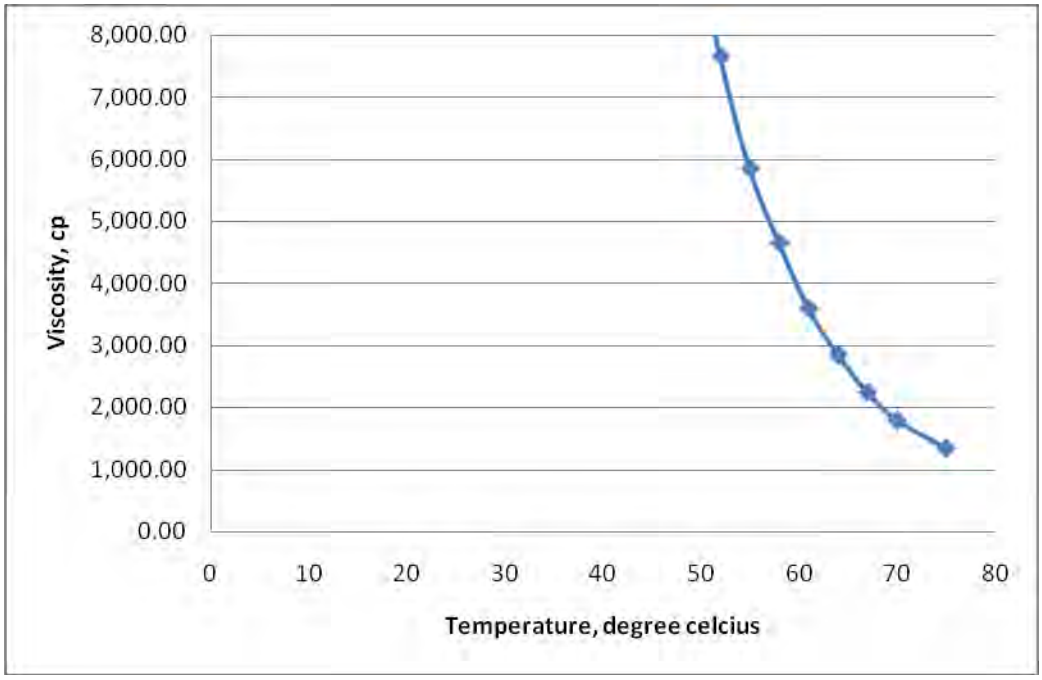
Temperature, ºF	Viscosity, cP
77	20970
86	8190
95	5250
104	3540
113	2370
122	1650
140	840

Table 2.6 Viscosity vs Temperature for 'Soypolyol DB-5'

Temperature °F	Viscosity (cP)
77	121800
82.4	84000
87.8	59550
93.2	42750
98.6	30900
104	22800
109.4	17100
114.8	12900
120.2	9900
125.6	7650
131	5850
136.4	4650
141.8	3600
147.2	2850
152.6	2250
158	1800
167	1350



(a) 'lab prepared' polyol



(b) 'Soypolyol® DB-5' polyol

Figure 2.9 Viscosity vs. Temperature study on (a) 'Lab prepared' Polyol and (b) Soypolyol® DB-5' Polyol

Figure 2.10 Brookfield Viscometer

2.6 VARTM of Viscous Resins

The room temperature viscosity of vinyl ester and Vikol®-1 polyol have viscosity values within the range of 100-1000 cP which is suitable for VARTM. But the viscosity of lab prepared polyol and Soypolyol was 20970 cP and 121,800 cP, respectively. There are two methods of dealing with high viscosity resins: first is to use solvent to decrease the viscosity and second is by heating the resin such that its viscosity drops in workable range. There are advantages and disadvantages for both the methods. The advantage of adding solvent is that processing can be performed at room temperature. The major drawback of adding solvent is that changes occur in the mechanical properties due to the presence of remainder solvent in composites. Heating of the resin adds manufacturing cost and also drops gel time dramatically. However, there is no sacrifice on mechanical properties. At 140ºF, 'lab prepared' resin becomes unable to flow in VARTM mold in about 15 minutes (Tate et al., 2007). The solvent was used for all composite panels prepared in this research.

Heating of the resin was investigated only for ‘Soypolyol® DB-5’ for comparison purposes. It was observed that ‘lab-prepared’ polyol needs to be heated to 140 ºF to get viscosity of 840 cP and ‘Soypolyol DB-5’ needs to be heated to 167 ºF to get viscosity of 1350 cP.

2.7 Room Temperature VARTM **(**Tate, 2004)

Typically, the VARTM process at room temperature involves the following steps

1. Mold Preparation and Vacuum Bagging
2. Formulation and Degassing of Resin
3. Resin Impregnation and Curing

2.7.1 Mold Preparation and Vacuum Bagging

In VARTM, there is a typical sequence of vacuum bagging. The sequence of lay-up from bottom to top is mold, mold surface protection film, bottom release fabric (also called bottom peel ply), fabrics, top release fabric (also called top peel ply), resin distribution media, vacuum and resin distribution lines, and vacuum bag. The vacuum bag is sealed using sealant tape. This procedure is depicted in Figures 2.11 and 2.12.

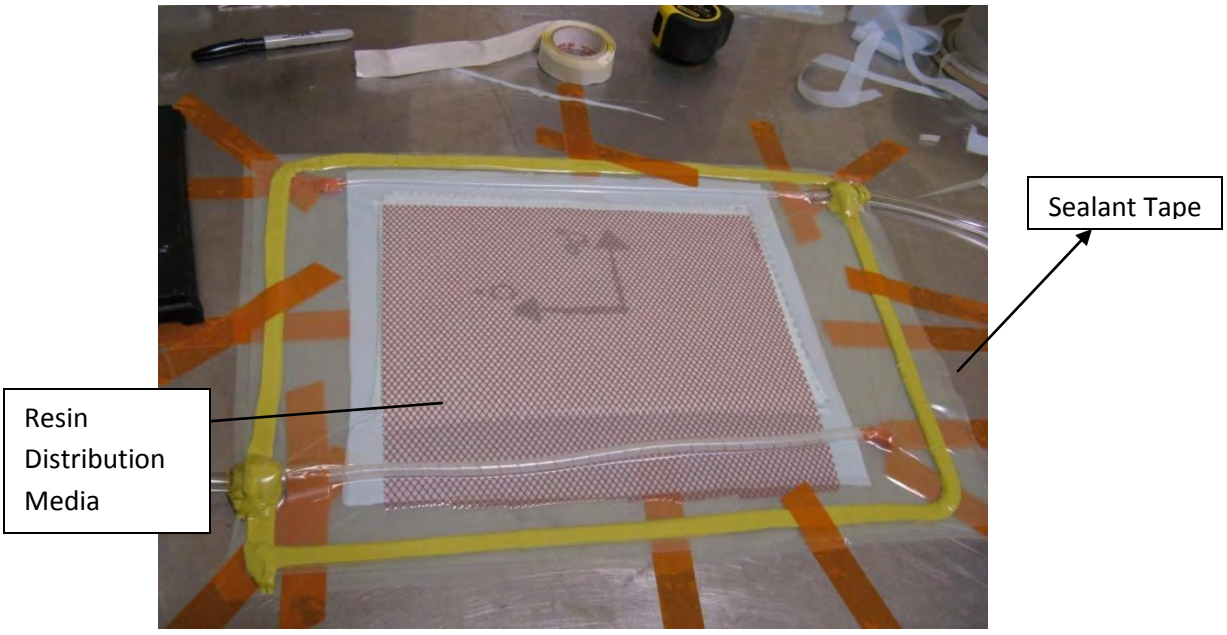


Figure 2.11 Room Temperature VARTM Setup: Vacuum bagging

Figure 2.12 Resin Flow in VARTM Process

The purpose of each of these items is as follows:

1. Mold: The flat plate mold used for the fabrication is a Polycarbonate one.

2. Bottom Peel Ply: This is a porous nylon fabric, which leaves an impression on the part suitable for secondary adhesive bonding (like tabbing) without further surface preparation. Its use is optional.

3. Fabric Lay-up: The fabric used is the E-glass woven roving fabrics (Rovcloth® 1854) manufactured by Fiberglass Industries, Inc. The composites panels of 12" x 8"with 8 layers of E-glass woven roving were produced in this research.

4. Top Peel Ply: This is the same material as the bottom release fabric. It is laid on top of the braided fabrics to facilitate the flow of resin through it. It also leaves an impression on the part suitable for secondary bonding without further surface preparation.

5. Distribution Media: The distribution media is polyethylene mesh laid on top of the top release fabric. This helps maintain an even distribution of resin and facilitates the flow of resin through the thickness of the panel.

The use of distribution media is a patented technology termed as SCRIMP (Seemann Composite Resin Infusion Manufacturing Process) that was invented by W. H. Seemann. Seemann also patented different patterns of distribution media and the placement technique for these patterns (Seemann, 1990 and 1994). Distribution media control the flow of resin through the thickness. Resin flows quickly through the media and then remains in the mesh pockets. It then travels through the thickness.

6. Resin and Vacuum Distribution Lines: Spirally cut HDPE (High Density Polyethylene) tubes are used for this purpose. These lines are laid above the distribution media at two sides of the fabric lay-up and can run along its length or along its width. One end of the resin line is closed, and the other end is connected to the resin supply

through the flow control device (if used). The vacuum line is closed at one end and connected to the vacuum pump through the vacuum gage.

7. Breather: The breather material acts as a distributor medium for the air and escaping volatiles and gases. It is placed over the resin distribution media and the resin and vacuum lines. It also acts as a buffer between the vacuum bag wrinkles and the part surface. It is a highly porous material composed mostly of fiberglass, polyester felt, and cotton. The use of a breather is optional. It was not used in the present research.

8. Vacuum Bag: This is made from 25 μm nylon film. The film is placed completely over the mold area and sealed firmly using a special sealant tape. The sealant seals the vacuum bag and helps maintain a uniform vacuum throughout the molding process.

The other equipment used in the processing are a vacuum pump, flow control devices (optional), a vacuum gage, a degassing chamber, a temperature and humidity gage, and a stop watch. Flow control devices like valves, clamps, and peristaltic pumps are used with certain material systems. These devices deliver a controlled amount of resin according to the unit time in the mold. Thus, the resin has a chance to flow through the thickness and complete wet-out of the fabrics is ensured. A peristaltic pump delivers a fixed amount of resin in the mold per unit of time. The quantity of resin (e.g., cm^3/min) is dependent on the pump speed. The pump speed is selected according to the fabric-resin system and the thickness of the panel.

Once the fabrics and other relevant materials are laid over in the required sequence, the entire mold is sealed with sealant and a vacuum bag. The vacuum pump is then used to maintain the lowest possible vacuum pressure throughout the process. The

care should be taken that vapor pressure of ingredients should not exceed in the mold. Polyisocynate contains n-butyl acetate as solvent for which vapor pressure is 29.14" of Hg. Solvent used was t-butyl acetate for which vapor pressure is 28.35" Hg. Vinyl ester contains styrene which has vapor pressure of 29.53" Hg. Bag leaks are the most common problems that occur in VARTM. One of the reasons for leaks is a damaged vacuum bag. A vacuum bag is typically made of nylon film. The moisture level in the surrounding environment affects the nylon film. Dry and brittle film can cause cracking when handled frequently. Another common reason for bag leak is foreign material entrapped between the vacuum bag and the sealant tape. Once the leaks have been removed and the vacuum bag is completely sealed, the vacuum pump remains running for at least 1 to 2 hours to achieve a good vacuum in the bag. The typical vacuum achieved is in the order of 28" of Hg for polyurethane and 29" of Hg for vinyl ester. The vacuum pump is then shut off, and the vacuum line is clamped. If the bag remains tight and holds almost the same vacuum after 1 to 2 hours, the mold is ready for resin impregnation.

The vacuum plays a vital role in the VARTM process. The pressure differential between the atmosphere and the vacuum provides the driving force for infusing the resin into the mold. The vacuum also removes all of the air from the mold before and during the introduction of resin.

2.7.2 Formulation and Degassing of Resin

The following table provides formulation details for polyurethane resins. The amount of aliphatic polyisocynate (Desmodur® Z4470BA) depends on hydroxyl value of polyol.

Table 2.7 Formulation of Polyurethane Resin System

	Lab prepared	Soypolyol	Vikol-1
Polyol, g	41.94	27.9	41.32
Aliphatic polyisocynate, g	58.06	71.97	58.67
DBTL, g	0.201	0.134	0.210
Solvent, g	3	7	N/A

The following table provides formulation for Derkane® Momentum 510-A40, vinyl ester resin.

Table 2.8 Formulation of Vinyl ester Resin System.

Ingredient	Quantity
Resin, g	100
MEKP, g	1
CoNap6%, g	0.2

After the formulation of the resin, degassing is the important step because the resin had to be free from entrapped air and/or gases that could cause voids in the composite panels. After the mixing of all the ingredients, the resin container was kept in the degassing chamber for about 2-3 minutes to maintain a vacuum of approximately 28” of Hg (Refer to Figure 2.13). The vacuum in the chamber removed all the entrapped air and/or gases out of the resin. This was a crucial step in the VARTM process and had to be performed very carefully to ensure high quality composite panels. Degassing resin for too short a period of time could not ensure complete removal of the entrapped air and/or gases. If the resin was degassed for too long a period of time, some of the ingredients (mainly styrene) in the resin could evaporate during processing. This would change the final formulation of resin and also create voids. Five to ten minutes is the sufficient amount of time to remove all the entrapped air and/or gases.

Figure 2.13 Vacuum Degassing Chamber

2.7.3 Resin Impregnation and Curing

The resin impregnation process was the same for all types of resins used in this research. The resin was poured in the container that connects to the resin line in Figure 2.12. The resin was allowed to flow in the mold until the whole panel was soaked. There was no need to use a flow control device with this design. The driving force created by the vacuum alone was sufficient for complete wet-out of the fabric. Properly designed and properly placed resin distribution media eliminate race tracking and resin leakage around the fabric (Seeman, 1990 and 1994). Figure 2.12 displays the resin impregnation set-up. Panels remained in the mold for 24 hr at room temperature for curing, which is termed as the 'Green Cure.' Panels were removed from mold and were post cured. This post cure cycle was different for PU and vinyl ester.

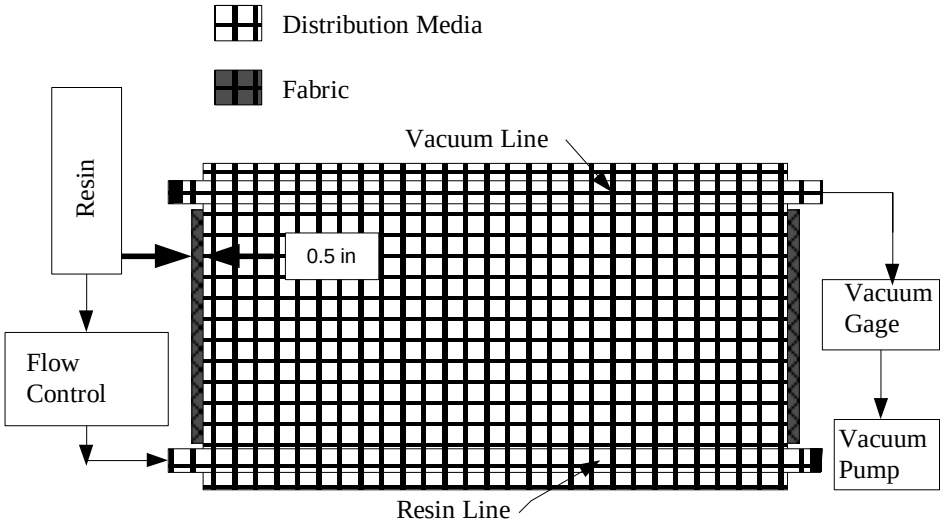


Figure 2.14 Schematic Diagram of VARTM

Post-cure is the final and most important step in composites processing. Although the degree of cure increases with time at room temperature, post-curing at elevated temperatures accelerates the process and achieves an ultimate heat distortion temperature and optimal mechanical properties. Generally, manufacturer of the resin recommends the post-cure cycle according to the type of curing agent in the resin system. Lab prepared polyol, Vikol®-1, and Soypolyol®-DB5 polyols were developmental grade materials; therefore, definite post cure cycle was not available. Secondly, post curing on PU depends on type of polyisocynate used. Desmodur® Z4470BA is popular aliphatic polyisocynate in coating applications. In coating applications, researchers have recommended 7-days at room temperature as post cure cycle (Guo et al., 2006). Cure temperature of thermoset polymers is close to glass transition temperature (Tg). DMA studies showed that Tg of N and S-type polyurethanes is around 284ºF (Tate, 2007). The post cure cycle used for N, P, and S-type composites was 7-days at room temperature

followed by 250ºF for 3 hours. Later heating at 250ºF for 3 hours was just to ensure complete curing. This cure cycle is time consuming and expensive. When this technology is deployed to industry, composite manufacturers would not prefer such a long post cure cycle. Author felt need for researching on accelerated cure cycle and still achieving optimal properties. Derkane® Momentum 510-A40, viyl ester composites were cured at 175ºF for 6 hours as per recommendations of manufacturer.

2.8 High Temperature Processing of VARTM (HVARTM)

As we discussed earlier in section 2.6, HVARTM is another way of producing the composite materials by heating the high viscosity resins such that its viscosity drops in workable range. This method was used only for 'Soypolyol® DB-5' resin. The HVARTM was done using the similar steps that are used in the room temperature processing of VARTM. The mold used was polycarbonate plate. This procedure is depicted in Figures 2.15, 2.16, and 2.17.

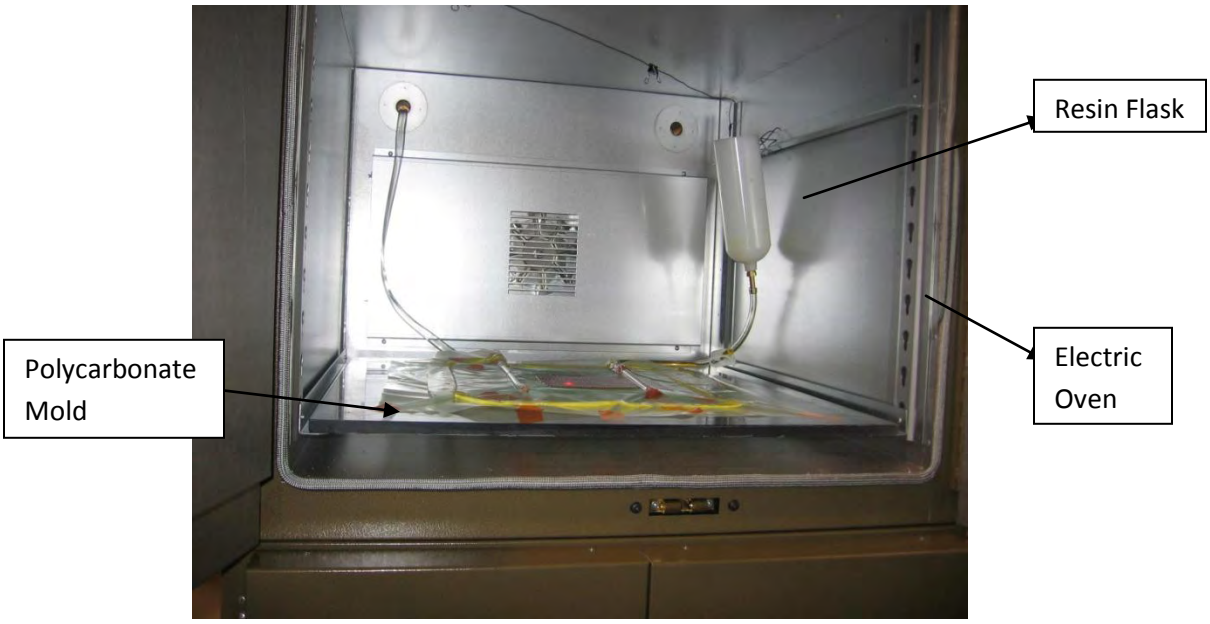


Figure 2.15 HVARTM Setup View 1

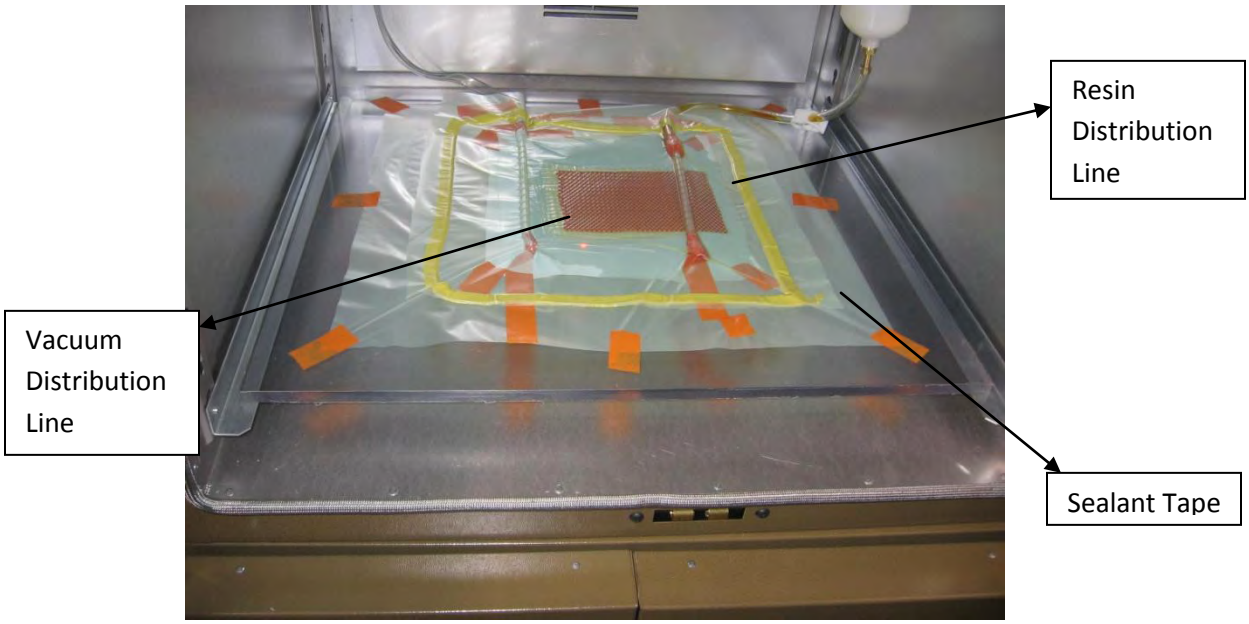


Figure 2.16 HVARTM Setup View 2

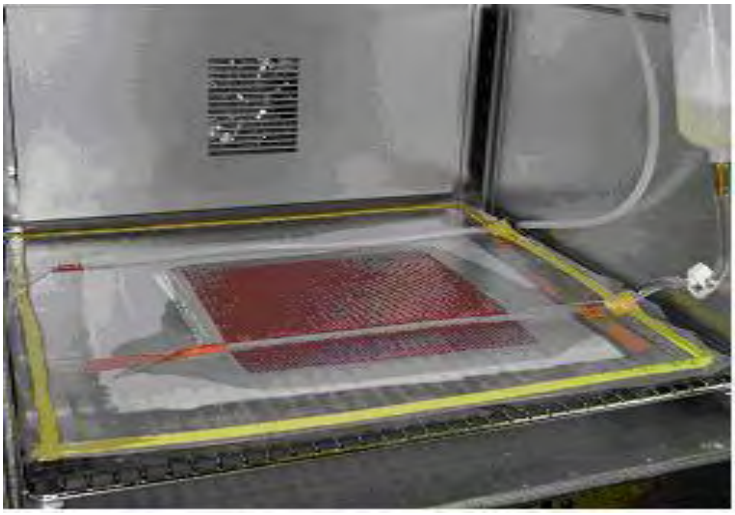


Figure 2.17 HVARTM Fully Impregnated Panel

Once the fabrics and other relevant materials were laid over in the required sequence, the entire mold was sealed with high temperature sealant and a vacuum bag. Then this entire setup was kept in the oven at 167 ºF for 1-2 hours. Another major change was, no solvent was added in PU formulation. Thermal heat would drop viscosity of polyol in workable range of VARTM. Composite panels were kept in the mold for 24

hours in the mold. The panels were removed from the mold and post curing was performed. The post cure cycle was same as that of room temperature processing: 7-days at room temperature, and 250 ºF for 3 hours.

2.9 Overall Fiber Volume Fraction

It is very important to evaluate the overall fiber volume fraction ($V_f^{Overall}$) in the composite panels after manufacturing. Since the fibers are the main load carrying elements in the composites, their percentage has a direct effect on mechanical properties of the composites. Various methods are available to determine the overall fiber volume fraction in composite panels:

1. Ignition Method (ASTM 2584-68)
2. Areal Weight Method (ASTM D792-86)
3. Density Method

2.9.1. Ignition Method

The resin is burned off in a high temperature oven. The ash is rinsed from the remaining fiber (using acetone or alcohol) and the fiber is dried and weighed. The volume of the fiber is calculated by dividing the mass of the fiber by the density of the fiber material. This method cannot be used with carbon fiber because carbon oxidizes at elevated temperatures.

2.9.2 Areal Weight Method

The fiber volume fraction is determined from the areal weight of the reinforcing fabric and the volume of the composite using the following relationship.

$$V_f^{\text{Overall}} = \frac{(V)_{\text{Fiber}}}{(V)_{\text{Composite}}} = \frac{(n * W * A)/\rho_f}{A * t} = \frac{n * W}{t * \rho_f} \quad \text{where}$$

$(V)_{\text{Fiber}}$ = Volume of the fiber material in the specimen

$(V)_{\text{Composite}}$ = Volume of the composite specimen

n = Number of layers or plies in the composite specimen

W = Areal weight of the fabric

A = Cross-sectional area of the composite specimen

t = Thickness of the composite specimen

ρ_f = Mass density of fiber material

2.9.3 Density Method

The fiber volume fraction is determined from the densities of the composite assuming that voids are negligible (Daniel and Ishai, 1994). The density of PU composite, post cured resin, and glass fibers are found by using the techniques explained by ASTM D792-86. The expression for fiber volume fraction based on the density of the composite is:

$$V_f^{\text{Overall}} = \frac{\rho_c - \rho_m}{\rho_f - \rho_m} \quad \text{Where}$$

ρ_f, ρ_m, ρ_c = Densities of fiber, matrix and composite.

This method is easy to implement and therefore was used to calculate the overall fiber volume fraction of the PU composites manufactured in the present research.

Typically, fiber volume fraction of each test specimen was evaluated. The density of E-glass fiber is 2.5 g/cm^3. In general, the composite panels manufactured by the VARTM process provide a fiber volume fraction of 0.5. For Tension specimens, the overall fiber volume fractions for N-type, P-type, S-type, and VW-type was 0.53, 0.58, 0.49, and 0.45, respectively. For flexural, compression, shear, and short-beam tests specimens overall fiber volume fractions for N-type, P-type, S-type, and VW-type were 0.53, 0.55, 0.41, and 0.45, respectively.

2.10 Discussion

The driving force in VARTM is pressure differential between resin entering at atmospheric pressure and vacuum in the mold. The VARTM process requires viscosity of resin in the range of 100-1000 cP. Low-cost VARTM was successfully implemented to manufacture PU/E-glass and vinyl ester/E-glass composites. The following are some of the observations made:

a. Good quality panels can be obtained at room temperature with the addition of solvent in case of N type and S type composites. The viscosity of resin used in P and VW type was in the range of 100-1000 cP. Quality panels were produced without solvent in case of P and VW type composites.
b. The complete wet-out of the fabric is achieved by placing the resin distribution media and the vacuum line in a specific way as shown in Figure 2.14.
c. A flow control device like the peristaltic pump is not required for polyurethane and vinyl ester resin systems.

d. The experimental study indicated that the overall fiber volume fraction of composites manufactured by VARTM yielded a 50% fiber volume.

Chapter 3 explains the performance of various types of composites under mechanical loading.

CHAPTER 3

PERFORMANCE EVALUATION

3.1 Introduction

Chapter 2 discussed the low-cost VARTM manufacturing process for soy-based composites in detail. The anisotrophy and inhomogeniety of composites materials make the characterization of their engineering properties a complex issue. The mechanical properties of composites are determined by specially designed test methods as per ASTM standards. Secondly, the damage mechanism of composites is highly complex and may be in one or more forms such as fiber/debonding, matrix cracking, delaminations, and fiber breakage. Some of these damage mechanisms may interact simultaneously. Therefore, interpretation of test results is a crucial issue. This chapter discusses the performance evaluation of the soy-based polyurethane/E-glass and vinyl ester/E-glass composites under mechanical loadings. All the mechanical tests were performed according to the ASTM standards discussed below.

3.2 Mechanical Testing

As per the American Standard for Testing Material (ASTM) there are specific standards related to composites. All mechanical tests pertaining to this research were performed on MTS servo hydraulic test system (shown in Figure 3.1). The loading capacity of the load frame was 110 kN. This machine was capable of conducting tensile, compression, flexural, v-notch rail shear, fracture toughness, and fatigue tests. It was

controlled by “Multi Purpose Testware (MPT)” software developed by the MTS Corporation.

Figure 3.1 MTS servo hydraulic test system

3.2.1 Static Tensile Test

Static tensile tests were performed according to ASTM D3039/D3039M titled ‘Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.’ This test method determines the in-plane tensile properties of polymer matrix composite materials reinforced by high-modulus fibers. The shape of the specimen is rectangular as shown in Figure 3.2. The specimen should be tabbed at the ends to ensure failure occurs in gage area. Tabs are made of glass/polyester composite and are glued to specimen using high-strength 2-part epoxy adhesive DP-460 (manufactured by 3M, Inc.). Tabs strengthen the specimen at ends to ensure that failure doesn’t occur in grip area. The in-plane tensile properties, such as ultimate tensile strength (UTS or, S_u), strain at UTS, and longitudinal

tensile modulus were evaluated. The axial strain was measured by an extensometer. All static tensile tests were conducted in the displacement control mode with a cross head rate of 0.05 in/min.

In this test method a flat strip of material having a constant rectangular cross section was mounted in the hydraulic grips and loaded in tension while recording the load, displacement and time. The ultimate tensile strength of the material can be determined from the maximum load carried before failure. After the collection of data the stress vs. strain graph was plotted from which the ultimate tensile strength (UTS or, S_u), strain at UTS, longitudinal tensile modulus were determined for that particular material.

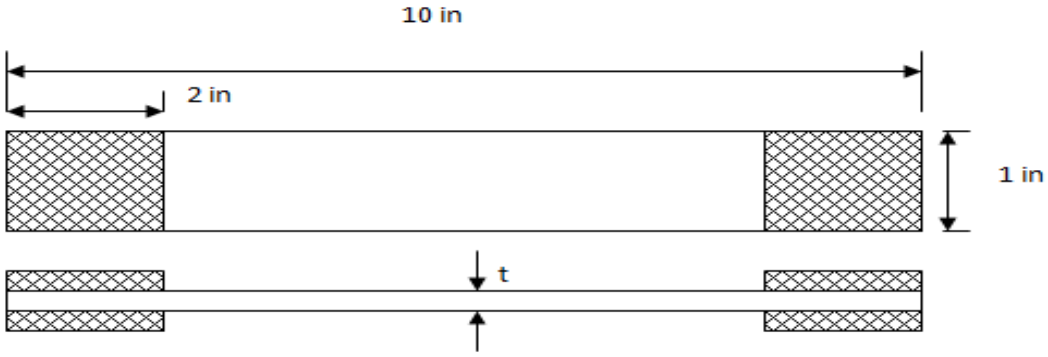


Figure 3.2 Tensile Tests Specimen

3.2.2 Compression Test

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.

In this test method CLC test fixture can be used to test the untabbed, straight sided composite specimen of rectangular cross section. The typical specimen dimensions are 5.5 in. long and 0.5 in. wide as shown in Figure 3.3. The unsupported gage length of 0.5 in. was maintained. The specimen is loaded with a loading rate of 0.05 in. /min. while recording the load and displacement. CLC fixture is shown in Figure 3.4. After the collection of data the load vs. displacement was plotted from which the ultimate compressive strength (UCS) was evaluated.

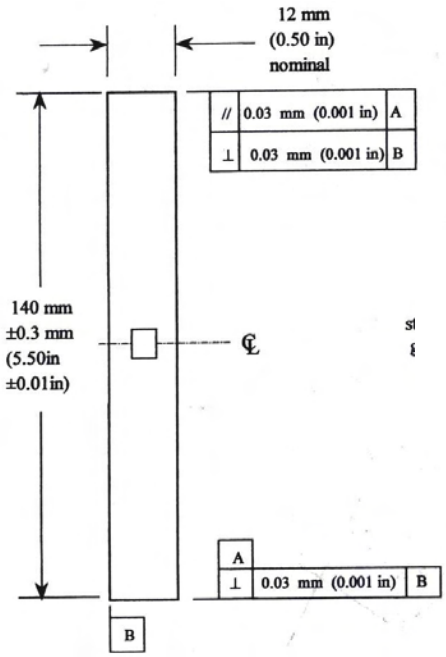


Figure 3.3 Compression Tests Specimen (ASTM D 6641/D 6641 M)

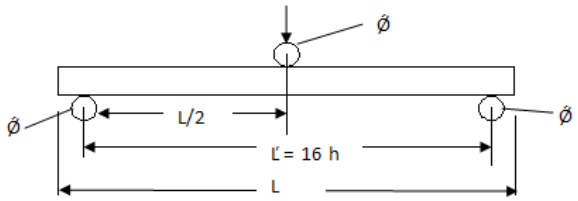
Figure 3.4 Combined Loading Compression (CLC) Test Fixture

3.2.3 Flexure Test

Flexure tests were performed according to ASTM D 790-92 titled 'Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials.' These test methods determine the flexural properties of unreinforced and reinforced plastics, including high-modulus composites and electrical insulating materials in the form of rectangular bars molded directly or cut from sheets, plates, or molded shapes.

Specimens were loaded under 3-point loading as shown in Figure 3.6. The ratio of loading span to depth of specimen was 16. As per thickness of the specimen, loading span was 3 in. and width was 0.5 in. The specimen rests on two supports and was loaded by means of a loading nose midway between the supports. The proportions of specimen geometry are shown in Figure 3.5. The specimen was loaded at a rate of crosshead

movement of 0.05 in/min., while recording load and the displacement. From the load and displacement data we can find the flexural strength and flexural modulus of the composite materials.



Where h=thickness, Specimen Length =L, Span Length (L^1) =16h, width=b

Figure 3.5 Flexure Test Specimen Loading

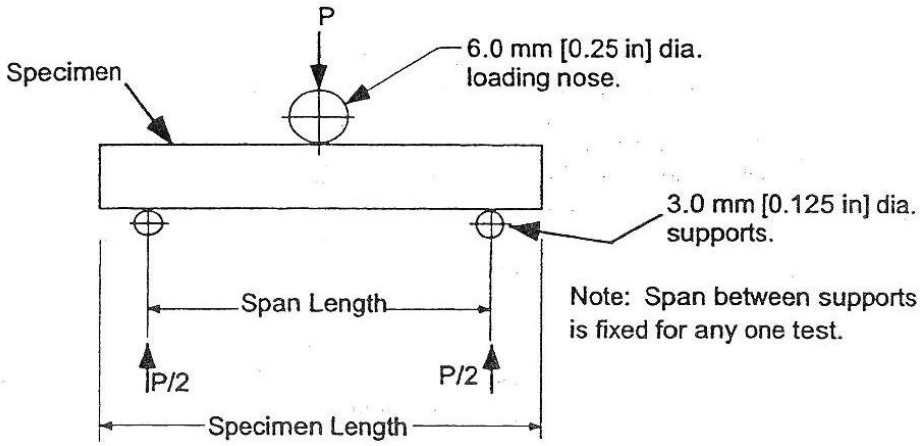
Figure 3.6 Flexure Test Specimen and Fixture

3.2.4 Inter laminar Shear Strength-ILSS Test (Short-Beam Test)

Short Beam tests were performed according to ASTM D 2344/D 2344M titled ‘Standard Test Method for Short-Beam strength of Polymer Matrix Composite Materials

and their Laminates.' This test method determines the short-beam strength of high-modulus fiber-reinforced composite materials. The specimen is a short beam machined from a flat laminate up to 0.25 in. thickness. The beam is loaded in three-point bending.

The size of the specimen depends on the thickness of the specimen. The proportions of specimen geometry are shown in Figure 3.7. The specimen is loaded at a rate of crosshead movement of 0.05 in./min. while recording load and the displacement. From the load and displacement data we can find the short-beam shear strength which is also referred to as inter-laminar shear strength (ILSS). The specimen geometry is shown in Figure 3.7 and related fixture is displayed in Figure 3.8.



Where h=thickness, Specimen Length (L)= 6h, Span Length (L^1) =4h, width (b) =2h

Figure 3.7 Short Beam Specimen Loading (ASTM D 2344/D 2344M)

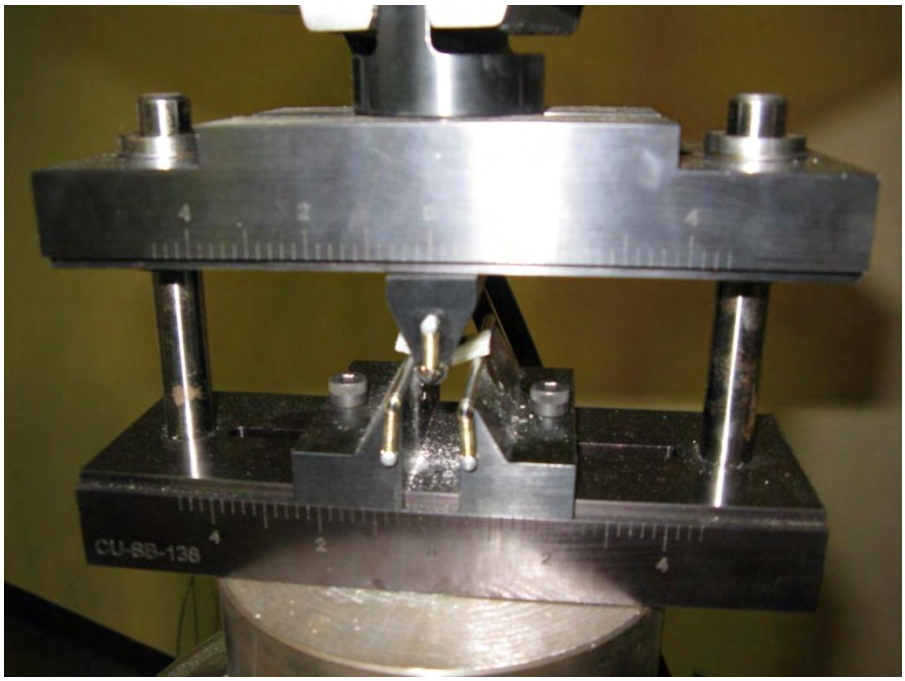


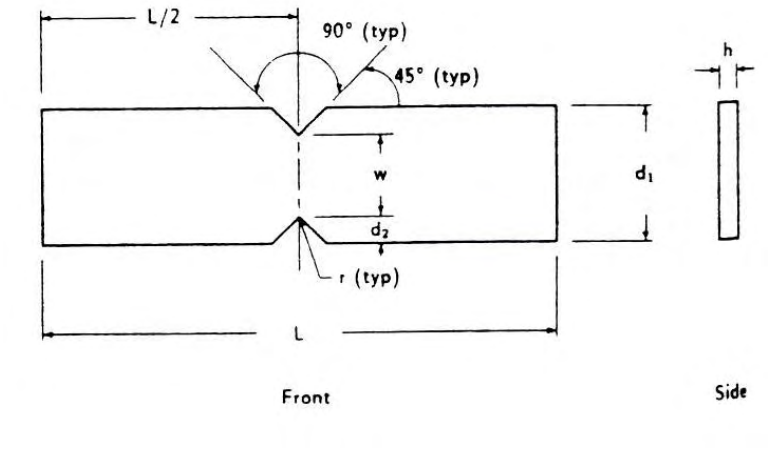
Figure 3.8 Short Beam Test Fixture Loaded with VW-type Specimen

3.2.5 V-Notch Beam Test (ASTM D 5379/D 5379M-98)

V-Notch Beam tests were performed according to ASTM D 5379/D 5379M-98 titled ‘Standard Test Method for Shear Properties of Composite Materials by V-Notched Beam Method.’This method determines the shear properties of high-modulus fiber-reinforced composite materials.

The specimen in the form of a flat rectangle with symmetrical centrally located V-notches is clamped as shown in the Figure 3.10. The two halves of the fixture are compressed by a testing machine while monitoring load. The relative displacement between the two fixture halves loads the notched specimen. The notches influence the shear strain along the loading direction, making the distribution more uniform than would be seen without the notches. A standard head displacement rate of 0.05 in./min. was used. Load should be applied to the specimen until it fails. The load and displacement data was

recorded. From the load and displacement data shear strength of the composite specimen was evaluated. Figure 3.9 shows the test specimen geometry in inches and Figure 3.10 displays the test fixture.



d_1=0.75 in., d_2=0.15 in., h= as required, L= 3 in., r= 0.05 in., w= 0.45 in.

Figure 3.9 V-Notch Beam Test specimen (ASTM D 5379/D 5379M-98)

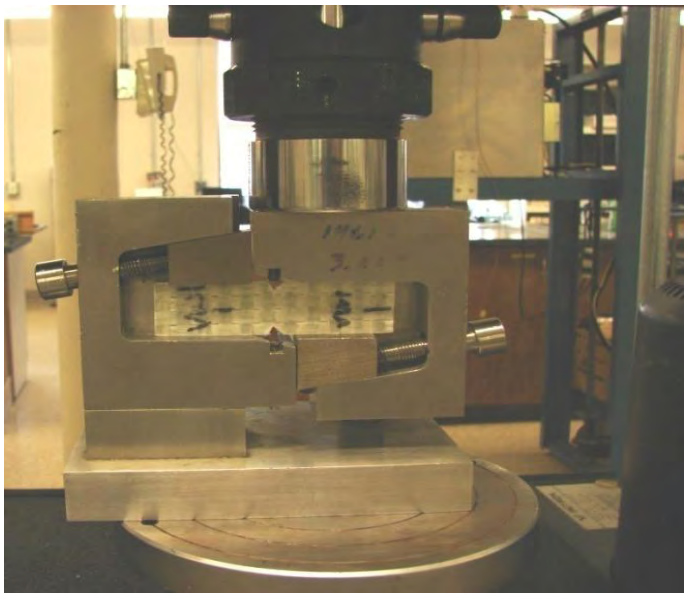


Figure 3.10 V-Notch Beam Fixture Loaded with VW-type Specimen (ASTM D 5379/D 5379M-98)

The different specimen geometries for different mechanical testing as per the ASTM Standard are shown in the Table 3.1.

Table 3.1 Summary of Test Specimen Geometry

Specimen	Width (in.)	Length (in.)
Tension Test (ASTM D3039)	1	10
Compression Test (ASTM D 6641)	0.5	5.5
Flexure Test (ASTM D 790)	0.5	4
Short Beam Strength Test (ASTM D 2344)	2t	6t
V-Notch Beam Test (ASTM D 5379)	0.75	3

The thicknesses of various composites varied from 0.129 in. to 0.192 in.

The specimens which met the requirements of the related ASTM standards were selected. As per ASTM thickness variation should be $\leq \pm 4\%$ and width variation should be $\leq \pm 1\%$. A sufficient number of specimens need to be tested for statistical analysis. As per the ASTM Standard the minimum number of specimens for the testing should be five. Since the manufacturing of composites involves the high cost materials, preparation of specimens (cutting, tabbing) takes a considerable amount of time and effort. Only the minimum numbers of specimens necessary for statistical considerations were used.

3.3 Mechanical Test Results

All the specimens tested in this section were manufactured at room temperature. The cure cycle used was 24 hours at room temperature in the mold, demolding, 7-days at room temperature, and 250 °F for 3 hours. For tension specimens, the overall fiber

volume fractions for N-type, P-type, S-type, and VW-type was 0.53, 0.58, 0.49, and 0.45, respectively. All tension test specimens were cut from the same panel. For flexural, compression, shear, and short-beam tests specimens were cut from the same panels. The overall fiber volume fractions for N-type, P-type, S-type, and VW-type were 0.53, 0.55, 0.41, and 0.45, respectively.

3.3.1 Tensile Testing and Their Results

These tensile tests were performed according to ASTM D3039/D3039M titled 'Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.' The tension test coupons were cut according to the tension specimen geometry mentioned in Table 3.1. After cutting of the test specimens, the density of each specimen was measured to compute overall fiber volume fraction. When tabbing is done, the test specimen thickness and width were measured. The specimens that meet ASTM requirement were selected. Then the specimen is placed in the testing machine such that the fixture grips hold the specimen parallel and tight. The extensometer was kept in the mid-section of the test specimen to determine the corresponding strain values.

The tensile stress is the highest engineering stress that develops in the material before rupture. The tensile stress, also known as the ultimate tensile strength (UTS), can be determined manually by dividing the maximum load by the un-deformed area of the specimen. The equation below shows the UTS, which is the maximum stress

$$\sigma_{max} = \frac{P_{max}}{A_o}$$

where $P_{max.}$ = maximum load, A_o = un-deformed cross-sectional area.

The chord modulus of elasticity in tension is computed within strain range of 0.001 in./in. to 0.003 in./in absolute strains.

$$E^{chord} = \frac{\Delta\sigma}{\Delta\varepsilon}$$

The failure modes of tensile specimens were noted as per the ASTM standard (Refer to Figure 3.11). Figure 3.12 gives typical stress-strain graph for the N-type composite. As per ASTM standard, the slope of the initial linear portion of the stress-strain graph is termed as chord modulus and is reported. Figure 3.13 shows the stress-strain data and corresponding value of chord modulus. Figure 3.14 and 3.15 shows failed specimens of P, S, and VW-type. VW-type specimens showed excessive delamination. Tension test results are tabulated in the Table 3.2.

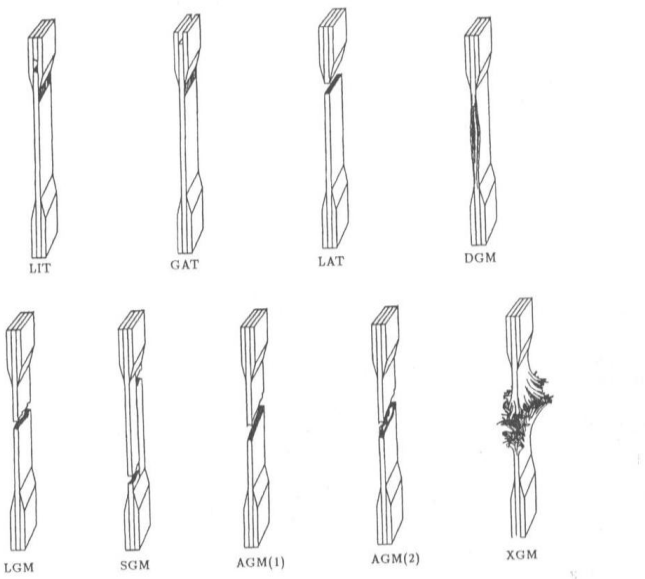


Figure 3.11 Typical Tensile Test Failure Modes (ASTM D3039)

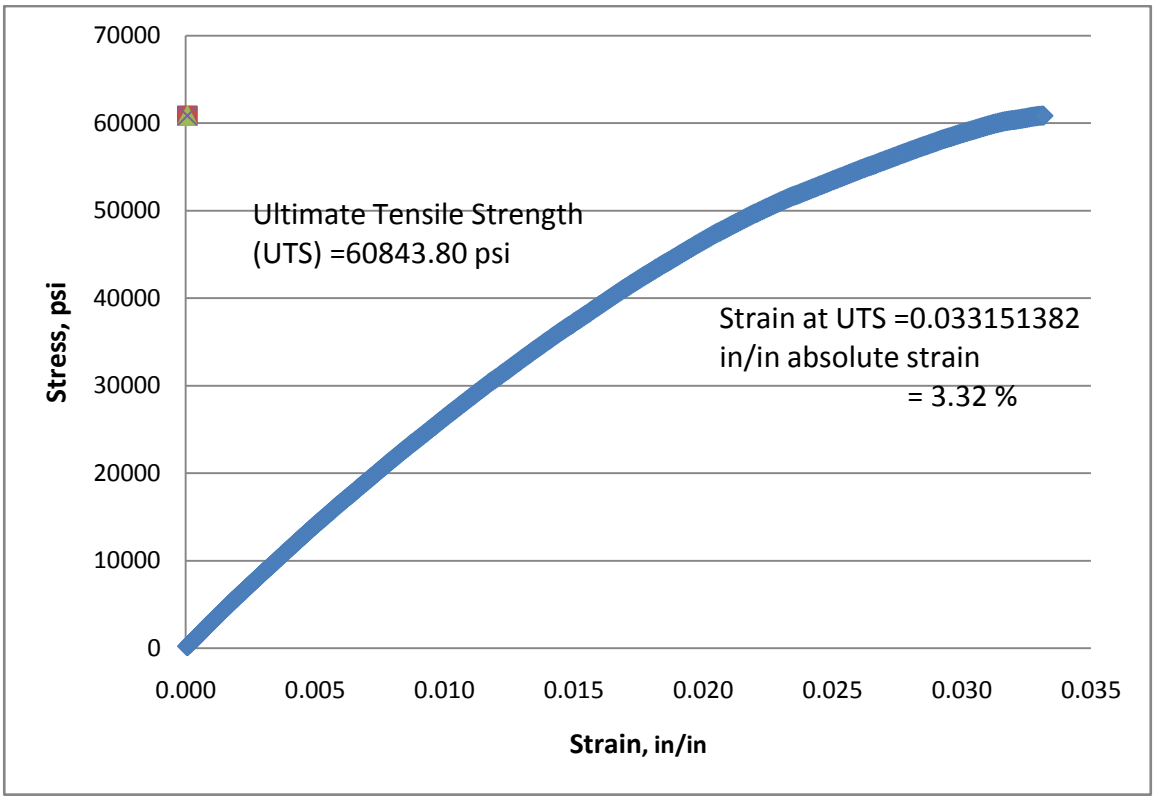


Figure 3.12 Typical Stress-Strain Graph of N-Type Composite

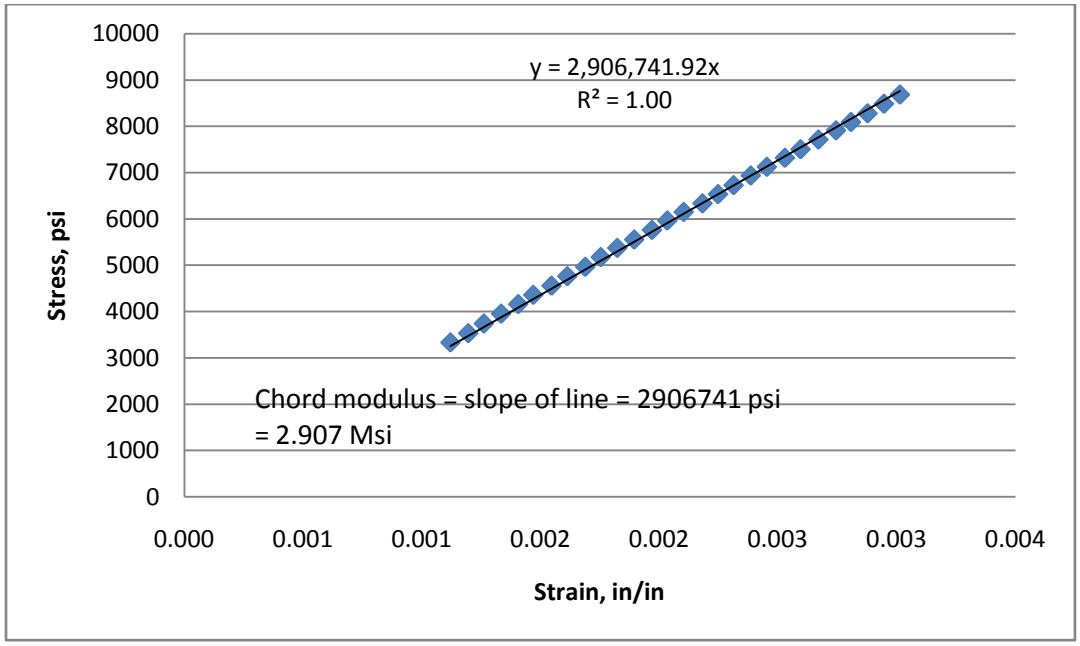


Figure 3.13 Slope of Stress-Strain curve between 0.001 to 0.003 Strains is Chord Modulus

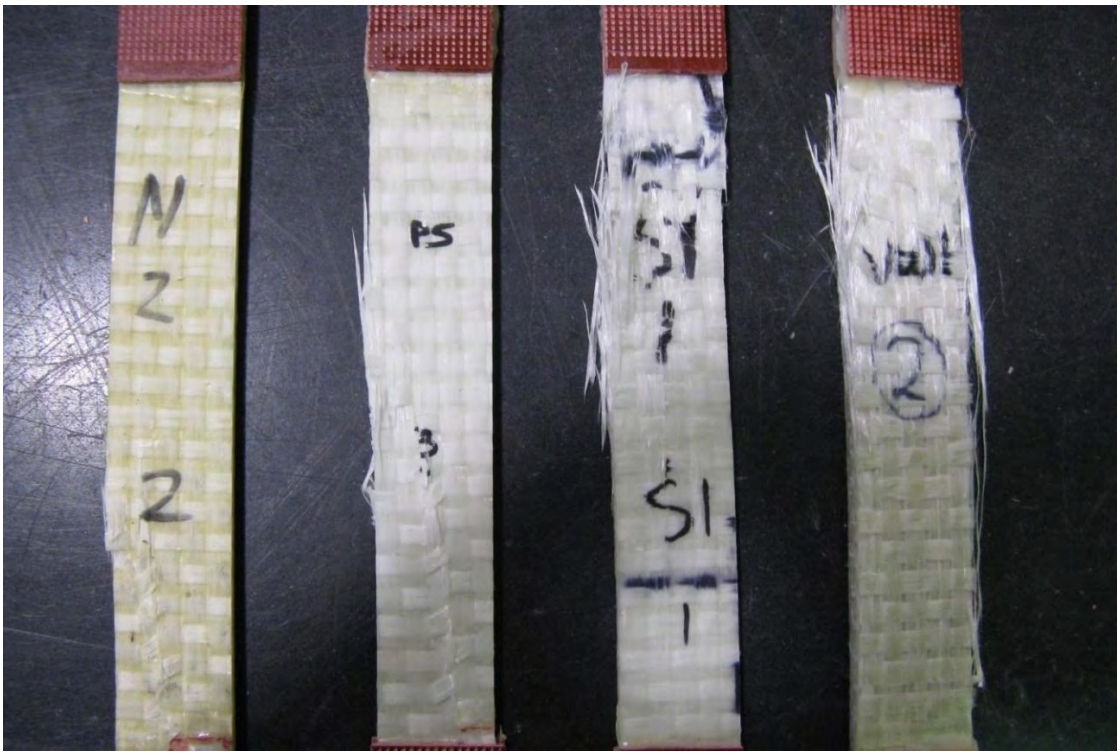


Figure 3.14 Failed Tension Specimens N, P, S, VW Types (Front view)

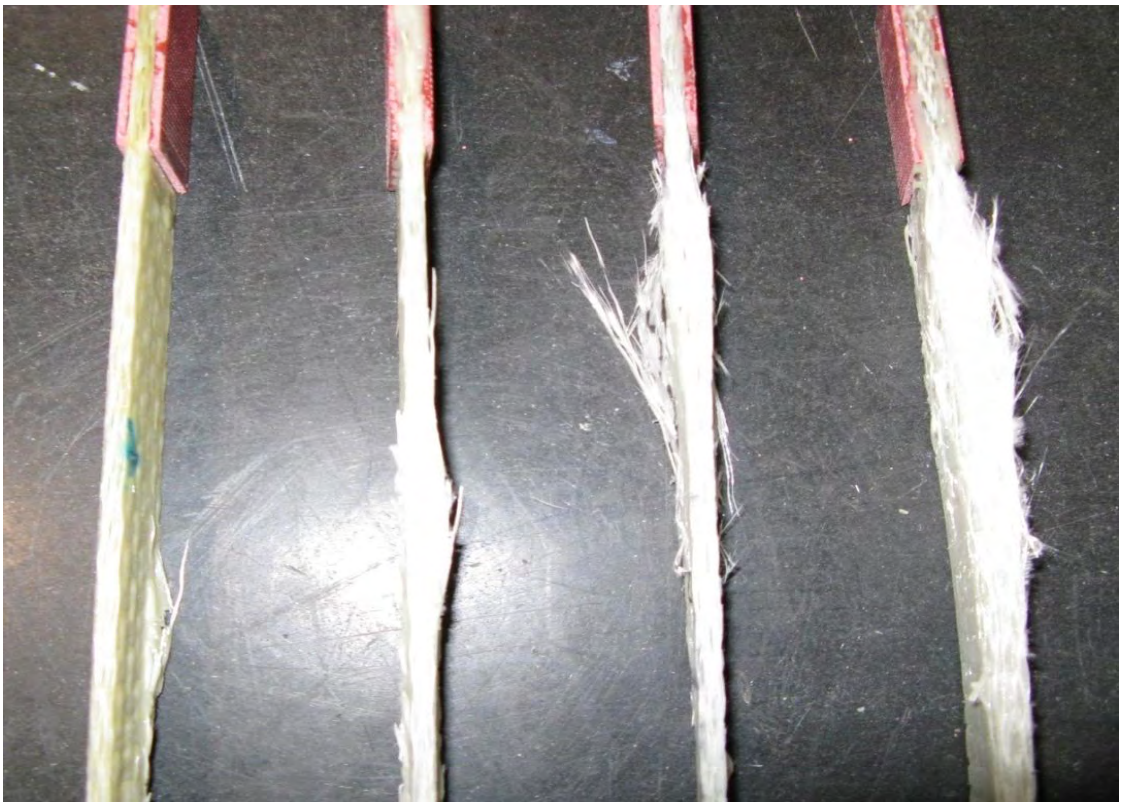


Figure 3.15 Failed Tension Specimens N, P, S, VW Types (Side view)

Table 3.2 Tension Test Results

Property		N-Type	P-Type	S-Type	VW-Type
Ultimate Tensile Strength, UTS	**Average, ksi**	54.26	71.56	71.68	53.99
	σ , ksi	6.68	0.77	2.32	1.20
	COV, %	12.33	1.07	3.24	3.70
Tensile Modulus, E	**Average, Msi**	2.80	3.47	3.33	2.22
	σ , Msi	0.23	0.26	0.06	0.23
	COV, %	8.07	7.60	1.93	10.59
Failure Strain, Є	**Average, %**	3.80	2.55	2.53	3.32
	σ , %	0.45	0.37	0.30	0.13
	COV, %	11.95	14.40	11.83	4.07

σ -Standard Deviation; COV- coefficient of variance, %

3.3.2 Compression Testing and Their Results

"The main function of the compression test is to detect the presence of delaminations. Compressive force yields information about the strength and stiffness of a columnar sample supported on its sides to prevent buckling when it is pressed on its ends. The compressive properties can be quite different from the tensile properties because of the difference in the ability of the composite to support a columnar load versus a pulling load. The fibers, in particular, have a tendency to buckle within the composite, especially when voids are present, and this greatly diminishes the compressive properties" (Strong, 1989).

The compression tests utilize the same testing equipment as the tensile tests but the crosshead is run in the opposite direction. These Compression tests were performed

according to ASTM D 6641/D 6641M. The compression loading on the specimen can be shear loading or end loading as shown in Figure 3.16 (Wilson and Carlson, 1997). The failure modes of compression test specimens are shown in Figure 3.17 (Wilson and Carlson, 1997). The fixture used in this ASTM standard applies combined loading i.e. shear and end loading. The compression test coupons were cut according to the compression specimen geometry mentioned in table 3.1. After cutting of the test specimens the density of each specimen was measured to compute overall fiber volume fraction.

The test specimen thickness and width were measured. The specimens that meet ASTM requirement were selected. The specimen was then tightened in CLC fixture. The torque wrench was used for the purpose with torque value of 20 lb-in. The fixture was placed in the testing machine. Compression tests were conducted in the displacement control mode with a cross head rate of 0.05 in. /min. The gage length of each specimen between two fixtures halves was maintained 0.5 in. The load and displacement data was collected.

This data was used to calculate the compressive stress using corresponding areas. Stress is calculate by using the formula, $\text{Stress} = \frac{P}{A_o}$, where P =load, A_o = original cross-sectional area. Stress corresponding to first peak was reported as ultimate compressive strength. Figure 3.18 shows typical load-displacement curve for S-type material. Compressive test results are tabulated in the Table 3.3.

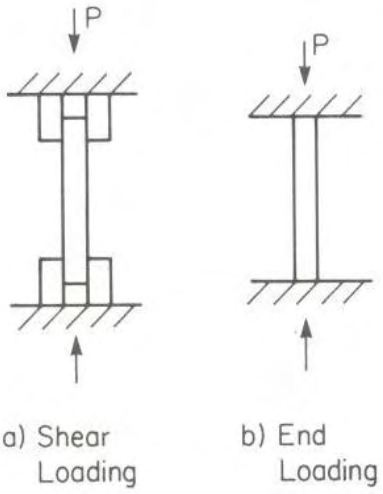


Figure 3.16 Compression Test Methods (Wilson and Carlson, 1997)

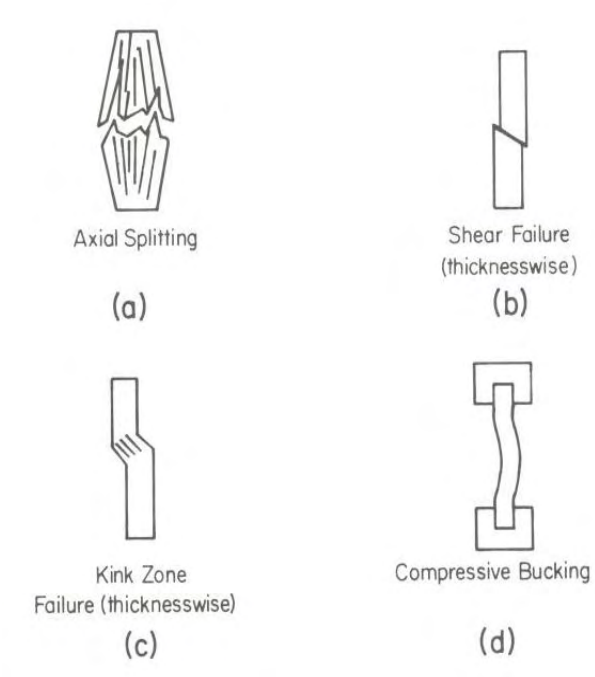


Figure 3.17 Typical Failure Modes of Compression Specimens (Wilson and Carlson, 1997)

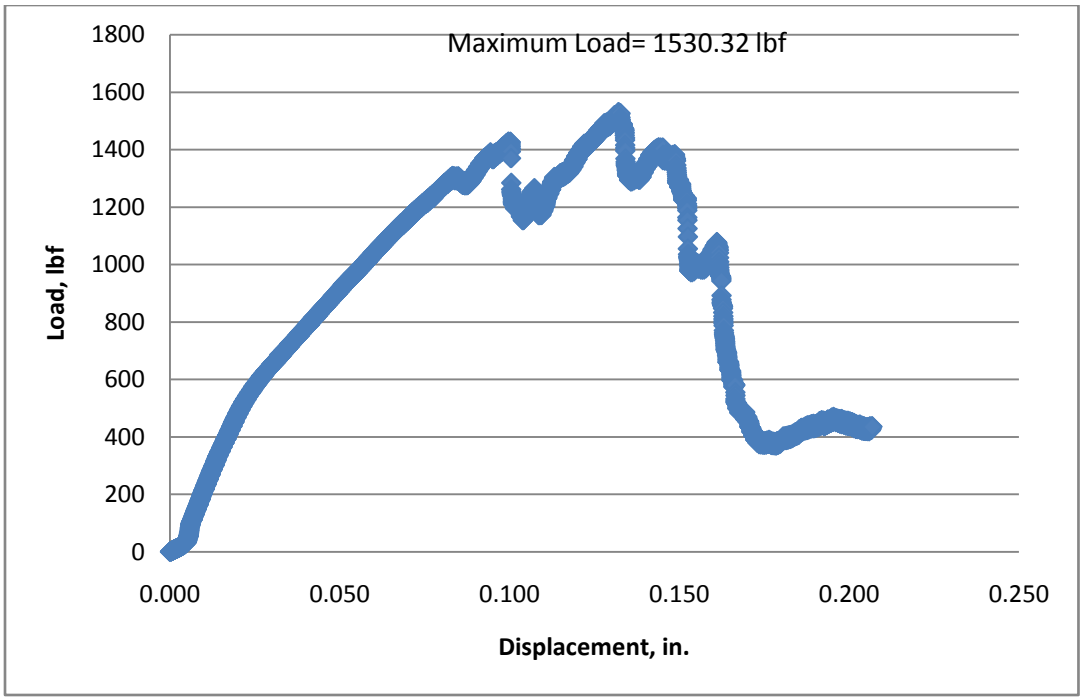


Figure 3.18 Typical load-displacement curve of S-type composite

(a) P-type **(b) S-type** **(c) VW-type**

Figure 3.19 Typical Failure Modes of Compression Specimens: Axial splitting

Table 3.3 Compression Test Results

Property		P-Type	S-Type	VW-Type
Ultimate Compressive Strength, UCS	**Average, ksi**	13.47	16.19	41.58
	σ , ksi	1.46	1.99	3.12
	COV, %	10.84	12.30	7.49

σ -Standard Deviation; COV- coefficient of variance, %

It is important to inspect tested specimen and noting type and location of failure. For valid tests, final failure of specimen should occur within the gage section. Figure 3.19 displays failure of P, S, and VW types composites. The failure mode in compression may be axial splitting, through-thickness shear, kink zone, and compression buckling as shown in Figure 3.17 (Wilson and Carlson, 1997). Compression buckling is invalidating failure. It is evident from Figure 3.19 that all compression specimens have failed in axial splitting.

Load-displacement curve shows multiple peaks in load data. First peak is used for computation of compressive strength. The first peak indicates major damage in the specimen.

3.3.3 Flexure Testing and Their Results

The main use of the Flexure test is as a quality control test and for determining resistance of composite laminates to environmental factors. During the test, the top of the sample under the loading force is in compression and the bottom opposite the loading

force is in tension (Strong, 1989). Depending on span-to-thickness ratio and strengths in tension/compression/shear, the beam may fail in tension at bottom or compression at top or in shear. Failures in shear requires very short span (span-to-thickness ratio 4:1) and failure in tension and compression occurs for longer spans (span-to-thickness ratio 16:1 and above). Flexural tests in this research are conducted with span-to-thickness ratio 16:1.

In flexure test load is applied out-of-plane that imposes both compression and tensile stresses. These flexure tests were performed according to ASTM D 790-92. The flexure test coupons were cut according to the specimen geometry mentioned in table 3.1. After cutting of the test specimens the density of each specimen was measured to compute overall fiber volume fraction. The test specimen thickness and width were measured. The specimens that meet ASTM requirement were selected. The specimen is placed in the testing machine such that the loading nose and two support cylinders were parallel and straight as shown in the Figure 3.6.

The specimen is loaded at a rate of crosshead movement of 0.05 in/min. The load and displacement data was recorded. The load and displacement data was used to calculate the flexural strength, maximum strain and flexural modulus.

Flexural strength is calculated by using the formula, $\sigma_{fs} = \frac{1.5.Fmax.L}{b.d}$ where, F_{max}.= Maximum load, L= Loading span of the specimen, b= width of the specimen, d= thickness of the specimen.

Maximum strain is calculated by using the formula, $\epsilon = \frac{(6 * D * d)}{L^2}$, Where D = maximum deflection, d= Thickness, L= Loading span length

Flexural modulus is calculated by using formula, $E_{fs} = \frac{(m.L^3)}{(4.b.d^3)}$, where m slope of initial linear portion on load-deflection curve, L= Length of the specimen, b= width of the specimen, d= thickness of the specimen.

The Load-Displacement graph is shown in the Figure 3.20 for VW-type of material. The slope (m) of initial linear portion is shown in Figure 3.21. Failure of P, S, and VW type composites is shown in Figure 3.22. Flexural test results are tabulated in the Table 3.4.

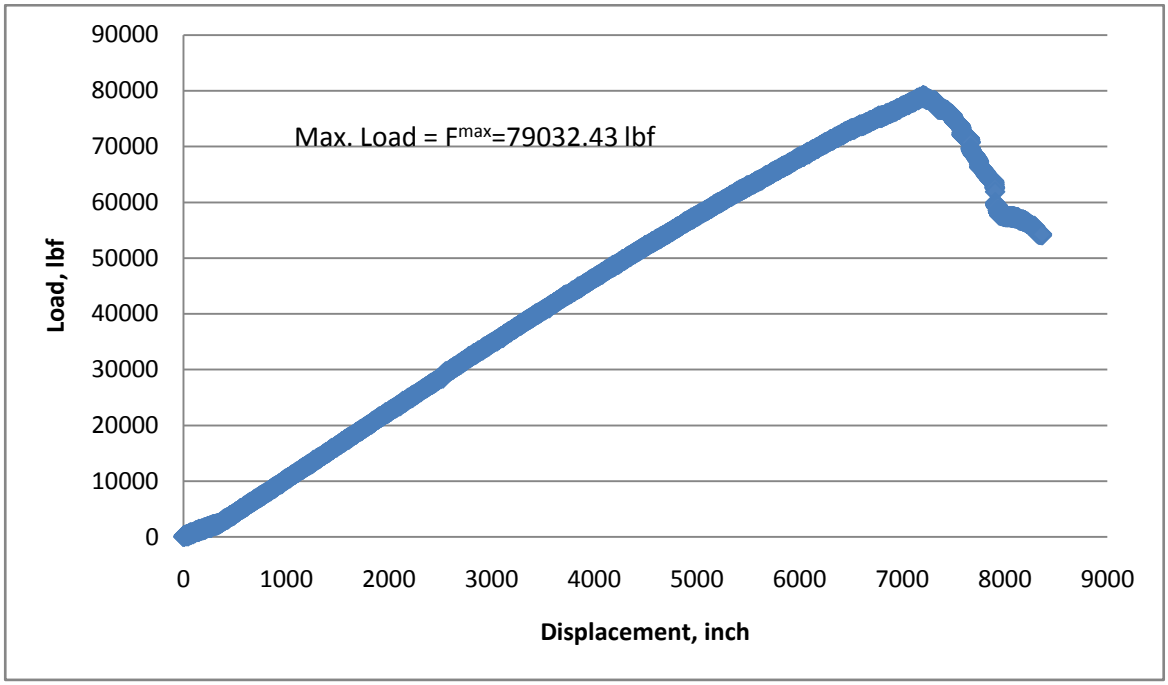


Figure 3.20 Load-Displacement Graph of VW-Type

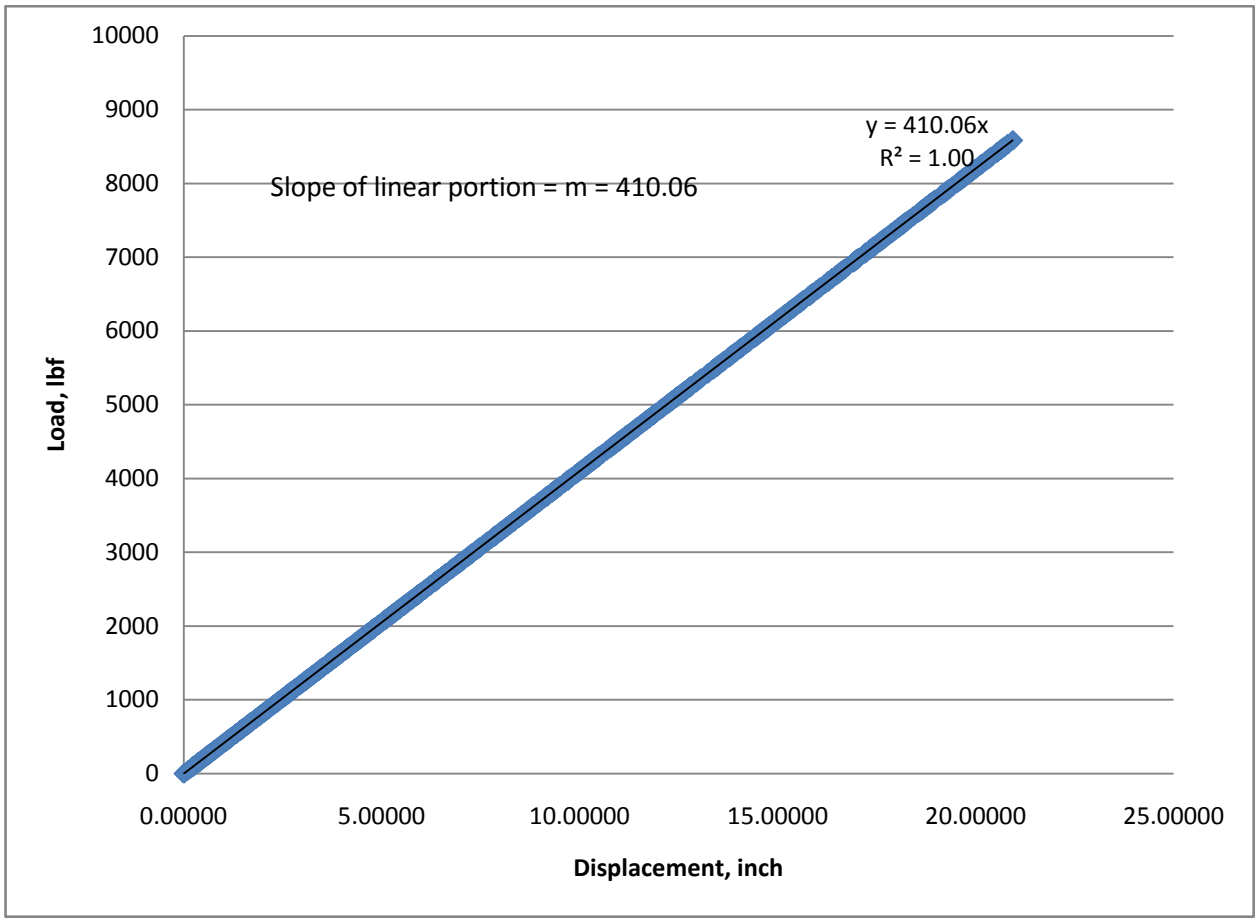


Figure 3.21 Slope of Initial linear portion of Load-Deflection Curve

(a) **(b)** **(c)**

Figure 3.22 Failure of P, S, VW types

(a) P type – Failure in compression at top (b) S- Failure in compression at top (c) VW- Failure in tension at bottom

Table 3.4 Flexure Test Results

Property		N-type	P-Type	S-Type	VW-Type
Flexural Strength, Fs	**Average, ksi**	44.63	25.13	33.96	64.992
	σ , ksi	4.99	3.83	5.34	8.53
	COV, %	11.19	15.26	15.72	13.12
Flexural Modulus, E	**Average, Msi**	2.59	2.36	2.39	2.83
	σ ,Msi	0.08	0.36	0.11	0.25
	COV, %	3.09	15.47	4.67	8.84
Maximum Strain, €	**Average, %**	--	1.27	2.38	2.63
	σ , %	--	0.07	0.82	0.47
	COV, %	--	5.66	34.6	17.967

σ -Standard Deviation; COV- coefficient of variance, %

3.3.4 Inter laminar Shear Strength (ILSS) Testing and Their Results

The short-beam shear test (also called as inter laminar shear strength-ILSS) is used to determine the fiber/matrix adhesion of the composite materials. The most important 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, 1989)

This ILSS (Short Beam) testing is similar to the flexure testing except that the sample-to-thickness ratio is much less-approximately 4:1, for ILSS. These Short Beam tests were performed according to ASTM D 2344/D 2344M. The Short-Beam test

coupons were cut according to the Short-Beam specimen geometry mentioned in table 3.1. After cutting of the test specimens the density of each specimen was measured to compute overall fiber volume fraction. The test specimen thickness and width were measured. The specimens that meet ASTM requirement were selected. The beam is loaded in three-point bending as shown in the Figure 3.7.

The specimen is loaded at a rate of crosshead movement of 0.05 in. /min. From the load and displacement data we can find the Short Beam strength of the composite materials was determined. The Load-Displacement graph is shown in the Figure 3.23 for N-type of material. These Short-Beam strength test results were tabulated in the Table 3.5.

Short Beam strength is calculated by using the formula, Short Beam strength (ILSS), $F^{sbs}=\frac{(0.75 * Pm)}{(b * h)}$, where Pm= Maximum load observed during the test, b= specimen width, h=specimen thickness.

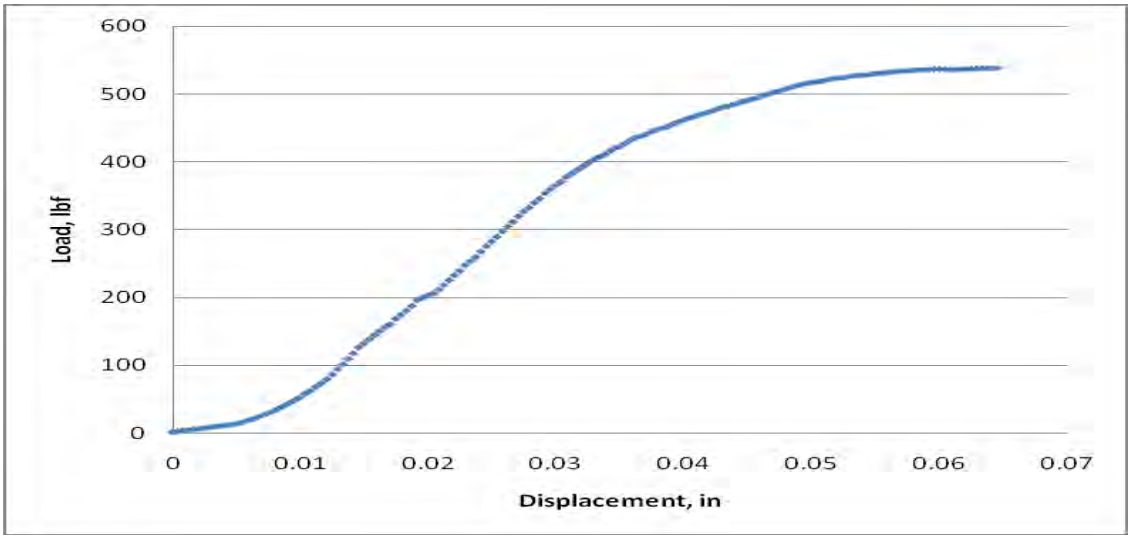


Figure 3.23 Load-Displacement Graph of N-Type

Table 3.5 ILSS Test results

Property		N-type	P-Type	S-Type	VW-Type
Inter laminar Shear Strength (ILSS) (ksi)	**Average, ksi**	2.88	7.06	5.6	5.38
	σ, ksi	0.06	2.64	0.77	0.28
	COV, %	2.31	37.37	13.75	5.23

σ -Standard Deviation; COV- coefficient of variance, %

3.3.5 V-Notch Beam Testing and Their Results

The v-notch shear test was investigated as a mean for determining the in-plane shear strength. This test was used to evaluate in-plane shear properties in this research. ASTM D2344 was used to determine out-of-plane shear strength.

These V-Notch Beam tests were performed according to ASTM D 5379/D 5379M-98. The V-Notch Beam test coupons were cut according to the specimen geometry mentioned in Table 3.1. After cutting of the test specimens the density of each specimen was measured to compute overall fiber volume fraction. The test specimen thickness and width were measured. The specimens that meet ASTM requirement were selected. The testing of these specimens was done by the Intertek, Inc.and the fixture is shown in the Figure 3.10. A standard head displacement rate of 0.05 in./min. was used. Load was applied to the specimen until it fails.

The shear strength is calculated by using the formula Shear Strength, $F^u = \frac{Fmax.}{A}$ where Fmax.= Maximum load, A= Area of cross section. These shear strength test results were tabulated in the Table 3.6.

Table 3.6 V-Notch Rail Shear Test results

Property		N-Type	P-Type	S-Type	VW-Type
Shear Strength (ksi)	**Average, ksi**	4.34	4.57	4.41	3.40
	σ , ksi	0.26	0.15	0.48	0.42
	COV, %	5.98	3.36	10.87	12.32

σ -Standard Deviation; COV- coefficient of variance, %

3.4 Mechanical Properties Comparison: Mfg I cycle I

Table 3.7 lists average mechanical properties of all composites for comparison purposes.

Table 3.7 Average Mechanical Properties

Property	N-Type	P-type	S-type	VW-type
Tensile strength, ksi	54.26	71.56	71.68	53.99
Tensile Modulus, Msi	2.80	3.47	3.33	2.22
Compressive strength, ksi	------	13.47	16.2	41.58
Flexure strength, ksi	44.63	25.13	33.96	64.99
Flexure Modulus, Msi	2.59	2.36	2.39	2.83
ILSS, ksi	2.88	7.06	5.59	5.38
Shear strength, ksi	4.34	4.57	4.41	3.40

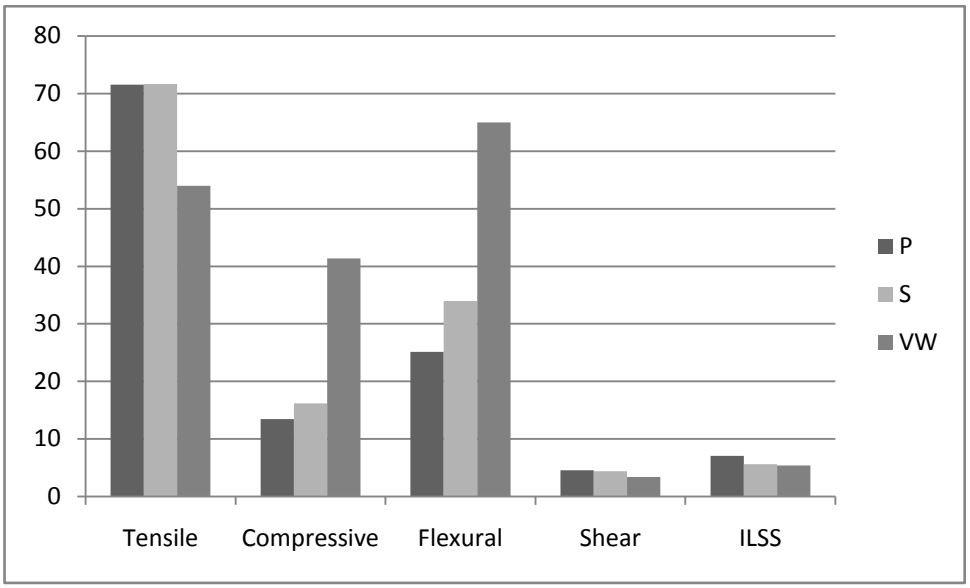


Figure 3.24 Different Strengths of P, S, and VW Type Composites

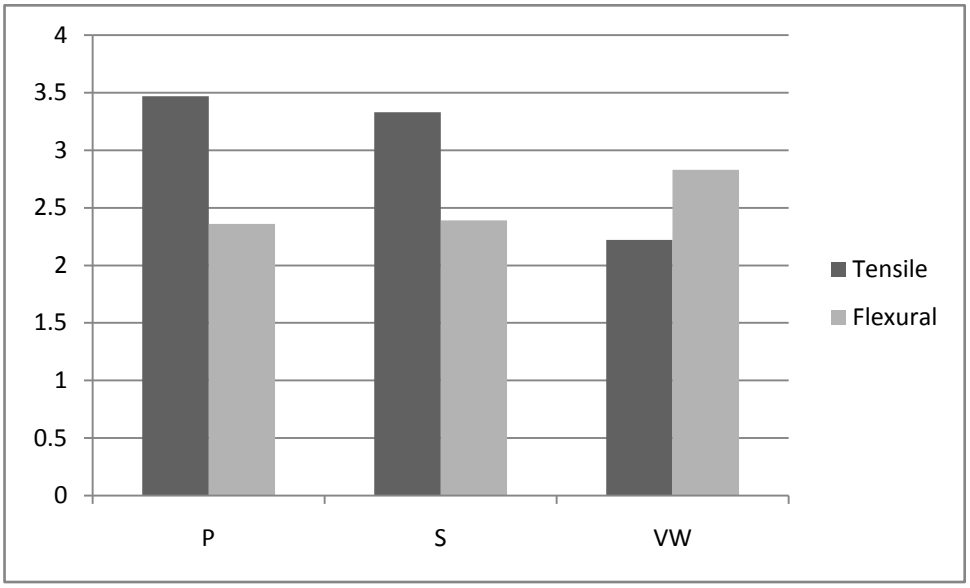


Figure 3.25 Tensile and Flexural Modulus of P, S, and VW Type Composites

3.5 Statistical Analysis

The test results reported in section 3.4 were analyzed in order to determine which resin had the better mechanical properties. This statistical analysis was done using Analysis of Variance (ANOVA).

3.5.1 ANOVA

Composite materials consist of reinforcement in the form of fibers and matrix material in the form of a binder. Fibers are the major load carrying elements and dominate the mechanical properties. Although the loads are mainly carried by fibers, modulus, failure strain, and resin/matrix adhesion play a dominant role in the performance of composites. There were 4 different resins used to make composites in this research. Three different polyurethanes were formulated using 3 different soy-based polyols namely, ‘lab prepared’, ‘Vikol-1’ and ‘Soypolyol DB-5’. These composites are designated as N, P, and S, respectively. Vinyl ester/E-glass composites are designated as VW. Soypolyol DB-5 or S-type composites used resin which was intentionally modified to improve fiber/matrix adhesion. The fiber/matrix adhesion is reflected in interlaminar shear strength (ILSS). Flexural and compressive properties are also affected by performance of the matrix material. ANOVA was performed on the compressive, flexural, and interlaminar shear strengths (ILSS) of the P, S, and VW type composites. Table 3.8 shows the Compressive, Flexural, and Interlaminar Shear Strengths obtained from all specimens.

Table 3.8 Compressive, Flexural, and Interlaminar Shear Strengths of P, S, and VW type composites

Type	Specimen	Compressive strength, ksi	Flexural strength, ksi	ILSS, ksi
Vikol-1(P-Type)	P-1	15.15	27.22	7.02
	P-2	12.51	28.73	8.92
	P-3	14.13	24.71	9.7
	P-4	14.1	26.2	7.8
	P-5	11.48	18.79	
	N	5	5	4
	Mean	13.4740	25.1300	8.3600
	Std. Deviation	1.46087	3.83552	1.18580
Soypolyol DB-5 (S-Type)	S-1	18.49	38.66	5.5
	S-2	16.68	39.09	4.7
	S-3	13.17	30.83	5.2
	S-4	17.1	34.69	5.8
	S-5	15.55	26.53	
	N	5	5	4
	Mean	16.1980	33.9600	5.3000
	Std. Deviation	1.99298	5.33717	0.46904
Vinyl ester (VW-Type)	VW-1	41.8	63.1	5.5
	VW-2	37.86	58.06	5.6
	VW-3	42.59	79.55	5.1
	VW-4	39.6	64.45	5.65
	VW-5	46.06	59.8	
	N	5	5	4
	Mean	41.5820	64.9920	5.4625
	Std. Deviation	3.11840	8.52670	0.24958

Where N= Number of specimen

The following are the results of the ANOVA.

3.5.2 One-way ANOVA: Compressive Strength versus Resin Types (P, S, and VW)

The Homogenity of variance assumption was confirmed for compressive strength using Levene's statistic, which resulted in a value of 0.999 (P<0.397).

Table 3.9 shows the results of the ANOVA for compressive strength. Clearly, resin type had significant impact on the compressive strength (P<0.0001) of the specimen. The Student-Newman-Keuls procedure was used to perform pair-wise comparisons among the means of the three resin groups. Vinyl ester (VW-Type) proved to exhibit significantly superior compressive strength (P<0.01) when compared with either Vikol-1 (P-Type) or Soypolyol DB-5 (S-Type), but there was no significant difference found between the mean compressive strengths of Vikol-1 (P-Type) and Soypolyol DB-5 (S-Type).

Table 3.9 Univariate Analysis of Variance for Compressive Strength

	Sum of Squares	**Df**	**Mean Square**	**F**	**Significance**
Resin Type	2403.045	2	1201.523	227.697	0.0001
Error	63.322	12	5.277		
Total	2466.368	14			

Table 3.10 Student Newman Keuls Test for Compressive Strength

Type	N	Homogeneous Subsets for Alpha=0.01	
		1	2
Vikol-1(P-Type)	5	13.4740	
Soypolyol DB-5 (S-Type)	5	16.1980	
Vinyl ester (VW-Type)	5		41.5820
Significance		0.085	1.000

3.5.3 One-way ANOVA: Flexure Strength versus Resin Types (P, S, and VW)

The Homogenity of variance assumption was confirmed for Flexure Strength using Levene's statistic, which resulted in a value of 0.867 (P<0.445).

Table 3.11 shows the results of the ANOVA for Flexure Strength. Clearly, resin type had significant impact on the Flexure Strength (P<0.0001) of the specimen. The Student-Newman-Keuls procedure was used to perform pair-wise comparisons among the means of the three resin groups. Vinyl ester (VW-Type) proved to exhibit significantly superior Flexure Strength (P<0.01) when compared with either Vikol-1 (P-Type) or Soypolyol DB-5 (S-Type), but there was no significant difference found between the mean Flexure Strengths of Vikol-1 (P-Type) and Soypolyol DB-5 (S-Type).

Table 3.11 Univariate Analysis of Variance for Flexure Strength

	Sum of Squares	Df	Mean Square	F	Significance
Resin Type	4383.222	2	2191.611	56.728	0.0001
Error	463.605	12	38.634		
Total	4846.826	14			

Table 3.12 Student Newman Keuls Test for Flexure Strength

Type	N	Homogeneous Subsets for Alpha=0.01	
		1	2
Vikol-1(P-Type)	5	25.1300	
Soypolyol DB-5 (S-Type)	5	33.9600	
Vinyl ester (VW-Type)	5		64.9920
Significance		0.044	1.000

3.5.4 One-way ANOVA: ILSS versus Resin Types (P, S, and VW)

In the case of the ILSS data, Levene's Statistic revealed that a violation of the Homogenity of Variance assumption had occurred which resulted in a value of 7.048 ($P<0.014$), however, because the cell sizes were equal (i.e., number of specimens in each type are equal), this result does not pose a serious threat to the analytical conclusions.

Table 3.13 shows the results of the ANOVA for ILSS. Clearly, resin type had significant impact on the ILSS ($P<0.0001$) of the specimen. The Student-Newman-Keuls procedure was used to perform pair-wise comparisons among the means of the three resin groups. Vikol-1 (P-Type) proved to exhibit significantly superior ILSS ($P<0.01$) when compared with either Soypolyol DB-5 (S-Type) or Vinyl ester (VW-Type), but there was no significant difference found between the mean ILSS of Soypolyol DB-5 (S-Type) and Vinyl ester (VW-Type).

Table 3.13 Univariate Analysis of Variance for ILSS

	Sum of Squares	Df	Mean Square	F	Significance
Resin Type	23.714	2	11.857	21.068	0.0001
Error	5.065	9	0.563		
Total	28.779	11			

Table 3.14 Student Newman Keuls Test for ILSS

Type	N	Homogeneous Subsets for Alpha=0.01	
		1	2
Soypolyol DB-5 (S-Type)	4	5.3000	
Vinyl ester (VW-Type)	4	5.4625	
Vikol-1(P-Type)	4		8.3600
Significance		0.766	1.000

Chapter 4 provides conclusions of this research.

CHAPTER 4

CONCLUSIONS

Recently, the Environmental Protection Agency has applied stringent regulations on releasing of styrene (considered a volatile organic compound-VOC) for open-molding composite processes such as hand layup and spray layup. Therefore, there is great interest among composite manufacturers to use styrene-free polyurethane resin and low-cost closed molding processes such as vacuum assisted resin transfer molding (VARTM). In this research, polyurethane/E-glass composites were manufactured using a VARTM process and extensive mechanical testing was performed. Polyurethane has two major components 'polyol' and 'polyisocynate'. The 'polyol' component in this research was made from soybean oil. A recent study indicates that soy-based polyols have 25% lower total environmental impact compared to petroleum based polyols and that use of soy polyols will result in reductions in net CO_2 contributions to global warming, smog formation, ecological toxicity, and fossil fuel depletion (Pollock, 2004).

The performance of polyurethane/E-glass and vinyl ester/E-glass composites were compared under mechanical loading such as tensile, compressive, shear, flexure, and interlaminar shear strength. Three different polyurethanes were formulated using 3 different soy-based polyols namely, 'lab prepared', 'Vikol-1' and 'Soypolyol DB-5'. These composites are designated as N, P, and S, respectively. Vinyl ester/E-glass

composites are designated as VW. The following are specific conclusions based on average mechanical properties:

a. Tensile strength is a fiber-dominant property. The variation in tensile strength was mainly due to variation in fiber volume fraction.

b. Tensile modulus is affected by the matrix material. Vikol-1, or P-type composites were superior amongst all composites and showed 4% improvement compared to Soypolyol DB-5 S-type composites.

c. In-plane shear strength of Vikol-1 P type composites is superior amongst all composites. P type composites showed 3.6% improvement compared to Soypolyol DB-5 S type composites.

d. Flexural modulus of Vinyl ester/E-glass, or VW type composites was superior compared to both Vikol-1 P type, and Soypolyol DB-5 S type composites.

One of the objectives of this research was to identify superior polyurethane in terms of mechanical performance. Compressive strength and interlaminar shear strength (ILSS) are matrix-dominant properties. Flexural strength is also highly affected by matrix properties. Analysis of variance (ANOVA) was performed on compressive strength, interlaminar shear strength (ILSS), and flexural strength. The following are the conclusions derived from the ANOVA:

a. Vinyl ester (VW-Type) proved to exhibit significantly superior compressive strength ($P<0.01$) when compared with either Vikol-1 (P-Type) or Soypolyol DB-5

(S-Type), but there was no significant difference found between the mean compressive strengths of Vikol-1 (P-Type) and Soypolyol DB-5 (S-Type).

b. Vikol-1(P-Type) proved to exhibit significantly superior ILSS ($P<0.01$) when compared with either Soypolyol DB-5 (S-Type) or Vinyl ester (VW-Type), but there was no significant difference found between the mean ILSS of Soypolyol DB-5 (S-Type) and Vinyl ester (VW-Type).
c. Vinyl ester (VW-Type) proved to exhibit significantly superior Flexure Strength ($P<0.01$) when compared with either Vikol-1 (P-Type) or Soypolyol DB-5 (S-Type), but there was no significant difference found between the mean Flexure Strengths of Vikol-1 (P-Type) and Soypolyol DB-5 (S-Type).

Overall, Vinyl ester VW-type composites are superior in compressive strength, flexural strength, and flexural modulus amongst all composites. Vikol-1 P-type composites are superior in interlaminar shear strength (ILSS) amongst all composites. Vikol-1 P-type, and Soypolyol DB-5 S-type composites have comparable compressive strength and flexural strength. One major advantage of Vikol-1 (P-type) is its low viscosity (1050 cP) at room temperature. It is beneficial in room temperature VARTM processing. This research concludes that, Vikol-1 (P-type) should be the material of choice for further development.

Improving fiber/matrix adhesion can enhance mechanical performance of composites. All fiber-manufacturers provide chemical treatment on fibers which provides better fiber/matrix adhesion. These chemicals are called as coupling agents. These

chemicals should be compatible with resin. The fabric used in this research Rovcloth 1854 has been treated by coupling agent that is compatible with polyester, vinyl ester, epoxy, phenolic, and polyurethane. Fiber/matrix adhesion can be further improved by modifying the resin itself. It has been proved by researchers that soy oil phosphate ester polyol (SOPEP) improves adhesion to metals and glass in coating applications (Massingill, 1991; Mannari and Massingill, 2006). Commercially, Arkema supplied soy oil phosphate ester polyol under the name 'Soypolyol® DB-5' for this research. The property improvement at molecular-level (as is the case in coatings), may not reflect at bulk level (as is the case in composites). This research explored whether there is any improvement in fiber/matrix adhesion by using modified 'Soypolyol® DB-5' in bulk form in composites. ILSS of S-type composites (that used 'Soypolyol® DB-5') was much lower than P-type composites (that used non-modified 'Vikol-1'). The possible reasons are: difference in molecular-level and bulk level properties, and non-compatibility of 'Soypolyol® DB-5' with coupling agent used on fibers. Secondly, modified 'Soypolyol® DB-5' polyol and non-modified 'Vikol-1' polyol have different chemical properties such as hydroxyl number, oxirane value, and molecular weight. It is not apple to apple comparison. For true comparison, both these polyols should have equivalent chemical properties such as hydroxyl number, oxirane value, and molecular weight. Then both these polyols need to be used to manufacture composites using untreated glass fabric. There is need of further investigation.

But, commercial development of polyols is governed by market needs such as low-viscosity resin for low-cost VARTM processing and compatibility with glass fabric that

is already available on the market. This research studied advantages and disadvantages of these commercial polyols in terms of processing and mechanical performance.

The present research has also laid the foundation for the following studies:

a. Literature review indicates that, the addition of nano-silica or natural nanotubes in polyurethane resin enhances mechanical properties of composites. When nano-particles are added in resin, viscosity of resin increases dramatically. Low viscosity resins are preferred for nano-modification. This research proves that low-viscosity resin used in Vikol-1 P-type composites should be the choice for nano-modification. Secondly, P-type composites have comparable mechanical properties as compared with that of Soypolyol DB-5 S-type.

b. There is always suspicion that solvent remainder affects the mechanical properties of composites. The performance of composites manufactured with solvent and by heating of the resin should be compared for matrix-dominant properties such as compressive strength and interlaminar shear strength (ILSS).

c. This research used developmental grade materials that were successful in coating applications. The cure cycle used was very time-consuming (i.e. 24 hours in the mold). Curing was then followed by demolding, keeping at room temperature for 7-days, and heating at 250^{o}F for 3 hours. There is a need to identify an accelerated cure cycle.

d. There are many possible reasons why Soypoly DB-5 didn’t improve ILSS which is indicator of fiber/matrix adhesion. There is need to develop non-modified

polyol that has equivalent chemical properties as that of Soypolyol DB-5. Then both the polyols should be used to manufacture composites using untreated glass fabric. This apple to apple comparison would clarify whether there is any improvement in fiber/matrix adhesion by using Soypolyol DB-5.

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VITA

Srujan kumar Konga was born in Andhra Pradesh, India on August 11, 1983, the son of Bhaskar rao Konga and Uma devi Konga. After graduating from high school in 2000 at LLHS Warangal, AP, India, he studied at Kakatiya Institute of Technology and Science, and obtained a degree of Bachelor of Science in Mechanical Engineering in May 2005. In January 2007, he joined the M.S.T program in Industrial Technology at Texas State University-San Marcos.

Permanent Address: 327 W Woods Street
Apt # 707
San Marcos, Texas 78666

This thesis was typed by Srujan kumar Konga.