EFFECTS OF TOUGHENED MATRIX RESINS ON COMPOSITE MATERIALS FOR WIND TURBINE BLADES

by

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Different resins with a potential for use in wind turbine blades have been studied. The main consideration in the resin selection has been to increase the structural integrity such as delamination resistance in blades while maintaining or improving other mechanical properties. A second concern was to increase the temperature and moisture resistance relative to the baseline orthophtalic polyester resin. The resins included in the study are also appropriate for the wind turbine blade application in terms of cost and have a sufficiently low viscosity to allow processing by resin transfer molding. Resins included unsaturated polyesters, vinylesters, epoxies, and a urethane. Neat resin properties evaluated include stress-strain and heat deflection temperature. Composite properties evaluated include Modes I and II delamination resistance (G_{IC} and G_{IIC}), transverse tension of $[0/\underline{+}45/0]_s$, $[0]_6$ and $[\underline{+}45]_3$ laminates, 0^o compression of $[0/\underline{+}45/0]_s$ laminates and skin-stiffened substructural tests. Moisture effects on neat resins, $[0/\underline{+}45/0]_s$ and $[0]_6$ laminates have been briefly explored. Composite properties are also compared relative to resin cost, and processing observations are given for each resin.

The results are presented relative to those for the baseline low cost unsaturated orthophthalic polyester resin system. Significant improvements are shown for some vinyl ester and epoxy resins in terms of delamination resistance, structural integrity, transverse strength, and moisture and temperature resistance. While some of the tougher resins show significantly lower resin modulus, heat resistance, and laminate compressive strength, several of the resins perform as well as the baseline system in terms of these properties. Composite property dependence on neat resin properties is generally consistent with theoretical expectations. The best performing vinyl esters cost moderately more than the baseline polyester, while the best epoxies are significantly more costly; the epoxies are also more difficult to process.

CHAPTER 1

INTRODUCTION

This thesis presents the results of a study of matrix resins for use in wind turbine blades constructed from glass fiber reinforced plastic composite materials. Wind turbines must perform for 20 to 30 years in a variety of climates. The cost of the blades is a major component to the cost of wind generated energy. The blade materials consist of fibrous glass reinforcement fabrics with a polymer resin matrix as the continuous phase, surrounding each fiber. While many manufacturing methods are available for composite materials, most blades use either hand lay-up or resin transfer molding (RTM). This limits the type of resin to thermosets, which have a sufficiently low viscosity for these manufacturing methods. A database has been developed at MSU [1] using a common orthophthalic polyester resin matrix for most of the materials. The purpose of this study was to seek resins which would provide improved structural integrity (primarily delamination resistance) while maintaining other properties similar to the baseline polyester resin. Improved temperature and moisture resistance and reasonable cost were major objectives.

The approach taken was to select several potential resins which were suitable for RTM manufacturing (thermosets with low viscosity). The resins included polyesters, epoxies, vinyl esters and a urethane. Of these, the first three classes of resins are currently used in wind turbine blade manufacture, and the urethanes are an extreme case of high toughness. Composite laminates with a common glass fabric reinforcement and ply configuration including plies with fibers oriented at 0^o and $\underline{+}45^o$ were prepared by RTM and machined into test specimens. The mechanical tests chosen for evaluation are of importance in blade performance and are also sensitive to the matrix. Tests included the following: compressive loading parallel to the main reinforcing fibers (0°), tension perpendicular to the main reinforcing fibers (90°) and at $\underline{+}45^o$, interlaminar fracture toughness (G_{IC} and G_{IIC}), and neat resin tension. Performance in a typical substructure geometry, a T-stiffener section, was also evaluated.

A major concern driving test selection was that, as resins are modified to increase toughness, stiffness (elastic modulus) tends to decrease, which has led to decreases in compression strength in other studies [2]. Softening of the matrix at elevated temperatures and high moisture contents tends to exacerbate this problem.

The various resins included in this study are thought to represent a meaningful selection of relatively low cost resins suitable for RTM processing, which could reasonably be expected to perform well under typical wind turbine blade use conditions.

CHAPTER 2

BACKGROUND

Polymer Matrix Selection

The Matrix of a composite works as a binder transferring the loads through the fiber network. It maintains the fiber orientation and protects the fibers from environmental effects, redistributing the load to surrounding fibers when and individual fiber breaks. Important considerations when selecting a resin candidate are the stiffness (elastic modulus) and the yield and ultimate strength and toughness properties. Other factors such as thermal properties, processability, cost, availability, and health concerns are also of a great importance [3].

The resin must be compatible with the processing method. Resin transfer molding (RTM) is the main process of concern in this study. This process involves a two-part mold, with a fiber preform placed into the mold and the mold then closed. The resin is then pumped under low pressure through injection ports into the mold, filling the mold and completely wetting out the reinforcement. Both the mold and resin can be heated depending on the type of resin. Currently, the aerospace industry is a major user of RTM components, and the automotive industry has made limited use of RTM for decades [4]. Infrastructure, sports and military are industries where RTM is also gaining popularity.

The advantages of RTM relative to hand layup are improved quality, higher production rates, reduced labor, and lower volatiles emissions; the main disadvantages are higher equipment costs and the need for low viscosity resins.

The application of composite materials to primary structure to reduce structural weight is forcing structural designers and materials engineers to look for new, toughened resin systems. Thermosets, elastomers, and thermoplastics are the three main polymer categories. Thermoset polymers dominate as matrices in structural composite applications for reasons of good mechanical and thermal properties, good bonding to reinforcement, low cost, low viscosity and ease of processing. Thermoplastics are raising interest for their advantages in areas such as: toughness, potential processing advantages, recyclability and low volatile emissions; their high viscosity and poor bonding to reinforcement are disadvantages [5]. Tough resins are generally formulated by adding elastomeric or thermoplastic compounds to the more brittle thermoset resin base. Elastomers generally have too low of an elastic modulus to serve as a matrix for rigid structural composites.

The selection of a resin involves several factors. Chemical characteristics such as resin viscosity, glass transition temperature, gel time, cure cycle, injection pressure, thermal stability, shelf life, environmental resistance, and volatile emissions during processing, are some of the parameters that need to be considered in order to determine operating and processing conditions for a specific resin. Mechanical properties such as strength and elastic modulus in certain directions, interlaminar fracture toughness, and environmental resistance are major composite properties to which the matrix must contribute [5].

The most common thermoset resins used as composite matrices are unsaturated polyesters, epoxies, and vinyl esters. These resins offer good processability for liquid processing techniques such as RTM. The nature of the RTM process and the requirements of the wind turbine blade applications demand that the resin system should meet the target requirements shown in Table 2.1. Of these, the resin modulus is important in maintaining composite compressive strength, particularly under hot, wet conditions.

Table 2.1 Preferred resin characteristics.

Low cost
Resin elastic modulus of 2.75 GPa or higher
Resin viscosity from 100 to 500 cps
Glass transition temperature of 70 C or higher
Low moisture absorption
Gel time of at least 20 minutes
Room temperature cure preferable
Tough resin preferable

Currently, unsaturated polyester resins are the most common systems used in composites by the wind industry for the manufacture of blades. They are the most affordable, are easily processed, and possess adequate mechanical properties. However, most polyesters are brittle resins and have a low temperature resistance and significant moisture sensitivity. Vinyl esters are a chemical mixture of unsaturated polyesters and epoxy resins. The result is a resin that has mechanical, thermal and chemical properties similar to epoxies, with the ease of processing and high rate of crosslinking of unsaturated polyesters [5]. Vinyl ester resins are also stiff and brittle, but tougher than polyesters due to the presence of the epoxy backbone [6]. Epoxy resins are widely used for high performance composites, especially in aerospace, military and sports industries [7]. Epoxy resins generally offer an increase on mechanical properties compared with polyesters and vinyl esters, but at a higher cost [3]. Another disadvantage of epoxies is their relatively high water absorption rate when compared to vinyl esters [8]. The nature of curing for thermosets is explained in the following section. Details of each of the mayor thermoset resin materials are described later.

Polymer Overview

A polymer is a long molecule containing atoms held together by primary covalent bonds along the molecule; secondary bonds act between molecules [7]. The secondary bonds are an order of magnitude weaker than the covalent bonds. In general, thermoplastic polymers consist of separate molecules held together by secondary bonds. Thermoset polymers, when cured, form a three-dimensional network of covalent bonded segments, with secondary bonds acting between adjacent segments between the crosslinks [9].

Thermoplastics can be separated into two subgroups, semi-crystalline and non-crystalline (amorphous). Thermoplastics are linear or branched polymers which melt upon heating when the thermal energy is adequate to overcome secondary bonds. When melted, thermoplastics have relatively high viscosity which restricts available processing methods. Thermosets are cross-linked network polymers which are amorphous and can not be melted once the network is formed during curing. Thermosets have a relatively low viscosity prior to curing, which provides for convenient processing with adhesives and composites. They are also very reactive prior to curing, which allows for good bonding to reinforcement [10]. Curing occurs after the product is in its final form.

In amorphous polymers, molecules can slip relative to each other without breaking covalent bonds. Chain slippage provides high strain to failure, toughness and damage tolerance. Semi-crystalline polymers have increased strength and temperature-environmental resistance compared with amorphous thermoplastics. In thermosets, cross-linking is the process in which covalent bonds are formed between molecules through a chemical reaction creating a giant three dimensional network. The polymer chains between crosslinks are now not as free to slip relative to each other, and thermosets have improved elastic modulus, creep resistance and thermal/environmental resistance relative to thermoplastics, but at the expense of relatively brittle behavior [11].

When crosslinks are formed in thermosets, the liquid polymer starts losing its ability to flow since the molecules can no longer slip past one another. Curing is the process of extending polymer chain length and crosslinking chains together into a network. The molecular weight increases with the growth of the chain and then chains are linked together into a network of nearly infinite molecular weight. Curing is evident when there is a sudden change of the resin from a liquid to visco-elastic mass called a gel [12]. From a processing point of view, gelation is a critical factor because the polymer does not flow and is no longer processable beyond this point. The mechanism of curing differs for each polymer group, as discussed later.

Fiber reinforcements used in this research project are E-glass fibers manufactured by Alpha Owens Corning. The fibers are coated with silane, a coupling agent. The reason for coating the fibers is to improve the fiber/matrix interfacial strength and moisture resistance through both physical and chemical bonds, and to protect the fiber surface from abrasion during handling conditions. The chemical structure of silane is represented by R' - Si(OR03), in which the functional group R' must be compatible with the matrix resin in order to be effective. The silane film reacts with the resin to form a chemical coupling between fibers and matrix [10]. Compatibility of the coupling agent with different resin systems is generally provided in the company data sheets for a specific fabric. The product is coded as PVE, if the coupling agent is compatible with polyesters, vinyl esters and epoxy resins, as was the reinforcement used in this study.

Curing parameters and chemical agents which cross-link a resin are different for each specific type of resin. A system which only needs a catalyst to start the curing process is said to be promoted. A system which needs chemical compounds in order for the catalyst to start the cross-linking reaction of a resin is called an un-promoted system. Epoxy resins are usually obtained in a two or three part system which reacts when mixed together at the proper temperature. The reason suppliers often provide unpromoted resins to users is because the amount of promoter added to a resin will directly affect the processing time and shelf life. The Dow Chemical Company for example, provides tables for Derakane vinyl ester products that enable the user to achieve different gel times depending on the type of catalyst [13].

Properties of Polymers

Thermal Properties

A major concern in the application of composite materials is with the elevated temperature properties and the maximum use temperature; these properties are dictated by the polymer matrix. The glass transition temperature (T_g) is defined as the temperature at which mobility between molecules and segments in amorphous regions is possible. Above this temperature the polymer is rubbery; below it, the polymer is rigid. A partially crystalline polymer retains some rigidity up to the melt temperature, T_m, which is higher than T_g, even though the amorphous part of the material is soft and rubbery. The glass transition temperature is the point where there is adequate thermal energy to overcome secondary bonds; thus, segments of chains are then free to move, restrained at points of crosslinking (thermosets), chain entanglement (amorphous thermoplastics) or crystallites (semicrystalline thermoplastics). The polymer softens significantly as T_g is approached. The maximum use temperature for an amorphous polymer used as a composite matrix is usually below T_g [9].

The specific heat capacity of a polymer is higher when the molecules are free to move, so it decreases with decreased cross-linking, and increases with temperature increases, as T_g is approached. A differential scanning calorimeter (DSC) apparatus represents one way to measure T_g trough heat capacity change. The DSC measures the difference in enthalpy and weight between a sample and a reference material, both subjected to a controlled temperature program [9]. Measurement of T_g for the thermosets used in this study proved difficult, particularly when wet.

Another method to estimate the temperature at which a polymer softens is called the heat deflection temperature (HDT) [12]. This technique determines the temperature when bending deflection at a constant stress increases rapidly. Details are described later.

Tension and Compression

Tension and compression tests are used to determine the yield and ultimate strengths and ductility of a material. For a composite material, the stress-strain response is a function of the matrix and fiber properties. For a unidirectional composite, the slope of the stress-strain curve (Figure 2.1), the longitudinal elastic modulus, E_{11},can be accurately predicted by the rule of mixtures:

$$E_{11} = V_f \cdot E_f + V_m \cdot E_m \qquad (2.1)$$

where:

E_f = fiber modulus

E_m= matrix modulus

V_f= fiber volume fraction.

V_m= (1- V_f) if no porosity is present.

In the transverse direction, perpendicular to the fiber axis, the modulus E_{22} is approximated by Halpin-Tsai relationship [14],

$$E_{22} = E_m \cdot (1+\zeta \cdot \eta \cdot V_f)/(1-\eta \cdot V_f) \qquad (2.2)$$

where:

$$\eta = (E_{12f}/E_m - 1)/(E_{12f}/E_m - \zeta)$$

$$E_{12f} = E_f/2 \cdot (1+\upsilon)$$

and

ν = Poissons ratio

E_{12f} = shear of modulus fiber

ζ = curve fitting factor given as 2 for E_{22} [14]

η= curve fitting factor

In polymer matrix composites, the transverse modulus is dominated by the matrix modulus, while the longitudinal modulus is dominated by the fiber modulus. The stress-strain curve for unidirectional materials is usually approximately linear to failure. The tensile strength in the longitudinal direction occurs approximately when the strain in the fiber reaches a value close to the fiber ultimate strain. The transverse strength (and shear strength) are matrix dominated, with the mode of failure being a crack growing parallel to the fibers in the matrix and fiber/matrix interface. The limiting value for the transverse tensile strength is the matrix ultimate strength. For brittle resins and/or poorly bonded fibers, the transverse strength will be lower than the matrix strength [15]. The compressive strength of unidirectional composites in the longitudinal direction is also a matrix dominated property for most glass fiber composites [15]. Failure occurs when the fibers locally buckle or kink in the matrix; the matrix provides lateral resistance against buckling. The compressive strength can be approximated by:

$$\sigma = G_m / 2(1 + v_f) \quad (2.3)$$

where:

$$G_m = E_m / 2(1 + v)$$

σ = predicted compressive strength

G_m = shear modulus of resin

ν = poisons ratio of resin

E_m = tensile modulus resin

This formula assumes perfect fiber alignment and tends to significantly overestimate the compressive strength [14]. Most composites are used with layers in various directions. The ply layup used for multidirectional laminates in this thesis was mostly [0/±45/0]s, where S indicates symmetry about the mid-thickness; thus, this is an eight ply laminate. This laminate was tested in both the 0^o and the 90^o directions. The stress-strain curve for a multidirectional laminate is a function of the stress-strain behavior of each ply, transformed to the overall laminate coordinates. Stress-strain response is usually predicted by a laminated plate theory based software program [12]. A typical stress-strain curve for a multidirectional laminate in tension would then include nonlinear responses where off-axis plies cracked, with the ultimate strength dominated by 0^o layers if there are any present (Figure 2.1).

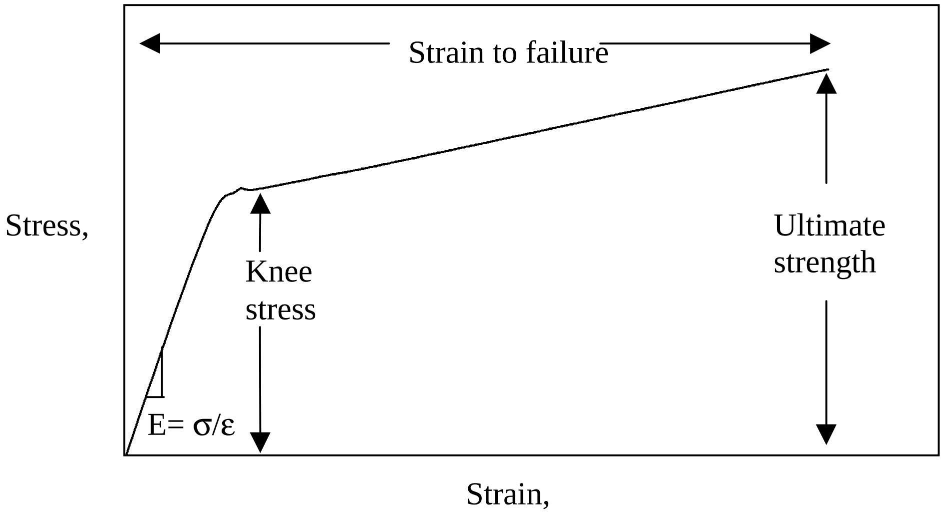


Figure 2.1 Laminate stress – strain curve.

If there are no 0^o fibers present in the direction considered, then the knee strength is the most important value for design. It gives the designer an estimate of how much elastic elongation the material can tolerate prior to significant matrix cracking. The stress at which the knee strain occurs is called the 0.2 % offset knee stress, calculated by drawing a parallel line (that has an origin at 0.2 % strain) to the linear portion of the stress-strain curve until it intersects the curve (Figure 2.2) [16]. This is similar to the usual method used to define the yield stress in metals and polymers. The neat matrix yield stress was calculated in this manner in this study.

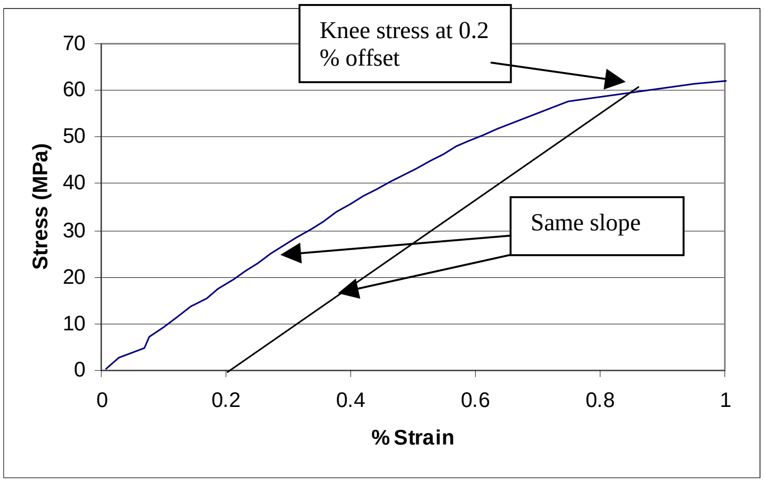


Figure 2.2 Knee stress at 0.2 % strain.

Polymer Chemistry

Polyester Resins

Polyester resins are formed by reacting a diacid and a dialcohol by condensation polymerization to form an ester. Orthophthalic polyesters are prepared by combining phthalic anhydride with either maleic anhydride or fumaric acid. A combination using isophthalic acid or terephthalic acid results in an isophthalic polyester, which has better thermal stability, chemical resistance and mechanical properties than orthophthalic polyester, but also a higher cost. The number of repeating units for a typical polyester is in the range 10 to 100. Because double carbon-carbon bonds are called unsaturated bonds, the thermoset polyesters containing these bonds are called unsaturated polyesters [17]. After the polymerization is done and depending in the number of units, a highly viscous liquid may result. For further processing, polyesters are dissolved in low molecular weight monomers such as styrene (the most widely used), also known as solvents. Unsaturated polyesters usually contain 35-50 percent monomer by weight.

Polyesters are cured by using organic peroxides as initiators, such as methyl ethyl ketone peroxide (MEKP) or benzoyl peroxide (BPO). The initiator reacts with the carbon-carbon double bond forming a new bond and another free radical on the carbon (Figure 2.3). This new radical reacts with another carbon-carbon double bond to form a new bond and another free radical. Typical concentrations of initiators is one to two percent. Higher or lower concentrations of initiator will result incomplete cross linking with inferior properties. Cross-linking takes place when carbon-carbon double bonds from separate molecules are linked together, creating a giant three dimensional molecule, increasing the molecular weight of the polymer. Monomers also take part in the crosslinking reaction since they contain active carbon-carbon double bonds and they serve as bridges between polyester molecule chains. One disadvantage of the solvents is that they are volatile and their vapors are deposited in the environment when processing. One advantage of polyester is that crosslinking does not generate by-products; this makes them easy to mold (this is true for epoxies and vinyl esters as well) [5].

The mobility of molecules decreases as molecular weight increases and the viscosity is increased; the reaction stops when free radicals are prevented from finding new double bonds. An increase in temperature during the curing process will allow increased mobility and the creation of more free-radicals. Post cure is a process that increases T_g in a resin because it allows the completion of crosslinking by eliminating reactive sites. Often the highest temperature reached by a room-temperature crosslinking polyester (with exothermic curing) will become its T_g [7].

Mechanical properties of cured polyester resins are affected by the monomer type and amount, acids, and curing temperatures. Orthophthalic polyesters are the least costly form of unsaturated polyesters but they have limited mechanical properties and sensitivity to environmental conditions. Isophthalic polyesters are more costly but they show higher tensile and flexural properties due to the higher molecular weight and more linear chains [3]. The reaction between a polyester resin and a free radical (provided by the catalyst) is shown on Figure 2.3.

Vinyl Ester Resins

Vinyl ester resins are obtained by reacting and unsaturated acid with an epoxy. The reaction of methacrylic acid and bisphenol A (BPA) epoxy resin dissolved in styrene monomer is the most common version of vinyl esters [18]. An advantage of vinyl esters is that the cross-linking reaction is identical to the free radical crosslinking of unsaturated polyesters. A structure of BPA vinyl ester is shown on Figure 2.4. The crosslinking density of BPA vinyl esters decreases as the molecular weight of the epoxy increases because the methacrylate sites of crosslinking are at the ends of the molecular chain. Novolac epoxy vinyl ester resins offer an increased number of crosslinking sites along the backbone which raises the final T_g of the resin and the temperature resistance. The crosslinking reaction of vinyl esters is identical to the free radical crosslinking of unsaturated polyesters; it also uses similar initiators and inhibitors. The double carbon-carbon bond is located at the end of the units only (Figure 2.4). MEKP, BPO and Trigonox are common catalysts for vinyl esters, used in ranges from 1 to 2% volume. Trigonox catalyst is known for its non-foaming character with vinyl esters. Cobalt Naphthalene is a promoter and is usually added to the resin from 0.2 to 0.4% by weight.

Vinyl esters are well known for resistance to environmental conditions because their high reactivity achieves complete curing easier and faster than for polyesters. Vinyl esters have higher elongation to break than polyesters, which also makes them tougher. The chemical resistance of vinyl esters is generally greater than for polyesters because of the influence of the methyl group [5].

Epoxy Resins

Epoxy resins are generally formed by the three membered epoxy group ring. The most common type of epoxy used is known as the diglycidyl ether of bisphenol A (DGEBA) (Figure 2.5). Epoxy groups could be located in different locations other than the ends [17]. At least two epoxy groups have to be on the polymer molecule for crosslinking. Epoxies usually have high viscosities at room temperature, therefore dilutents that also contain epoxide groups are used to lower the viscosity.

Hardeners are used to crosslink epoxies. Amine hardeners are the most common; hardener should be added in amounts such that the number of epoxide groups is equivalent to the number of crosslinking sites provided by the hardener [5]. If the hardener is added in the right amounts, a well crosslinked structure with the maximum properties will result. Some epoxies are formulated to crosslink at room temperature, but most epoxies used in composite applications require an increased temperature to initiate the crosslinking [3]. Physical and mechanical properties are also improved by increasing the molecular weight when curing. As for polyester resins, no condensation by-products are formed during epoxy curing reactions.

The toughness of epoxies depends on the length of the polymer chain between epoxy groups. Longer chains (higher molecular weight) will result in tougher polymers. One disadvantage of long chains is that there are less crosslinks per unit length (lower crosslink density), which results in less stiff and less strong materials, with lower modulus and heat resistance. Rubber polymers are added to epoxy resins to increase toughness.

Epoxies are usually more expensive than unsaturated polyesters, but have important advantages. Epoxies are stronger, stiffer, tougher, more durable, more solvent resistant and have a higher maximum operating temperature than polyester thermosets [5].

Polyurethane Resins

Polyurethane resins can be either thermoset or thermoplastic. Polyurethanes are formed by reacting two monomers, each having at least two reactive groups. Polyol and isocyanate monomers are generally liquids that are combined to form the polyurethane. A typical polyurethane molecule can be seen on Figure 2.6. Polyurethanes are very versatile polymers. The role of the polyol in polyurethane chemistry is like the role of the epoxy molecule in epoxy chemistry. The isocyanate role in polyurethanes is like the hardener in epoxy chemistry. Polyols have OH groups on the ends of the branches. Polyurethanes have superior toughness and elongation to failure, therefore they are used by the automotive industry, for example, to manufacture car bumpers [19]. Mechanical properties of polyurethanes will depend in the type of monomer used. Ether based polyurethanes have the highest mechanical properties, and they are also known for their short and fast solidification times, which makes them suitable for processing methods with faster injection time such as reaction injection molding (RIM) as compared with RTM [17]. There are semi-rigid and rigid polyurethanes. A low glass transition temperature caused by the flexible polyol chains is a characteristic of semi-rigid polyurethanes which results in good flexibility. Rigid polyurethanes can be used at temperatures up to 150 °C due to the cross-link structure of the matrix material [3].

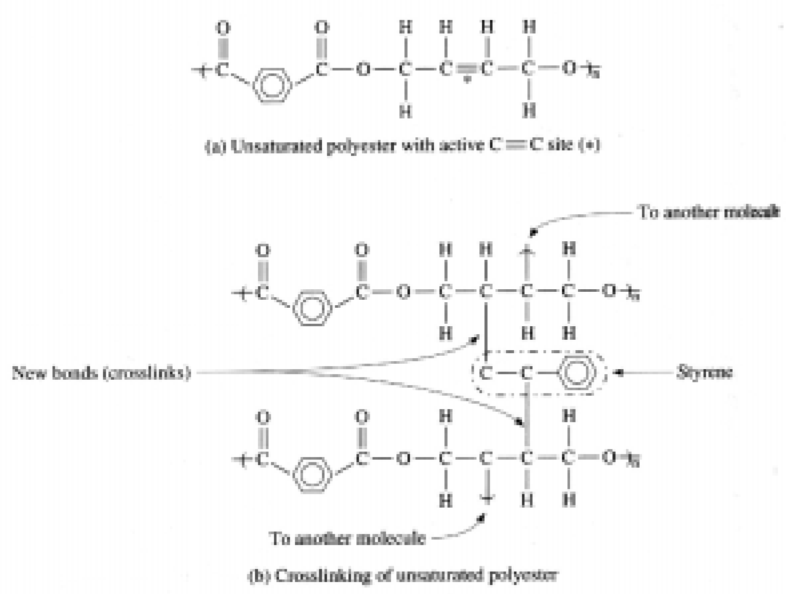


Figure 2.3 Unsaturated polyester showing (a) reactive carbon-carbon double bond and (b) crosslinking reaction (from reference 17).

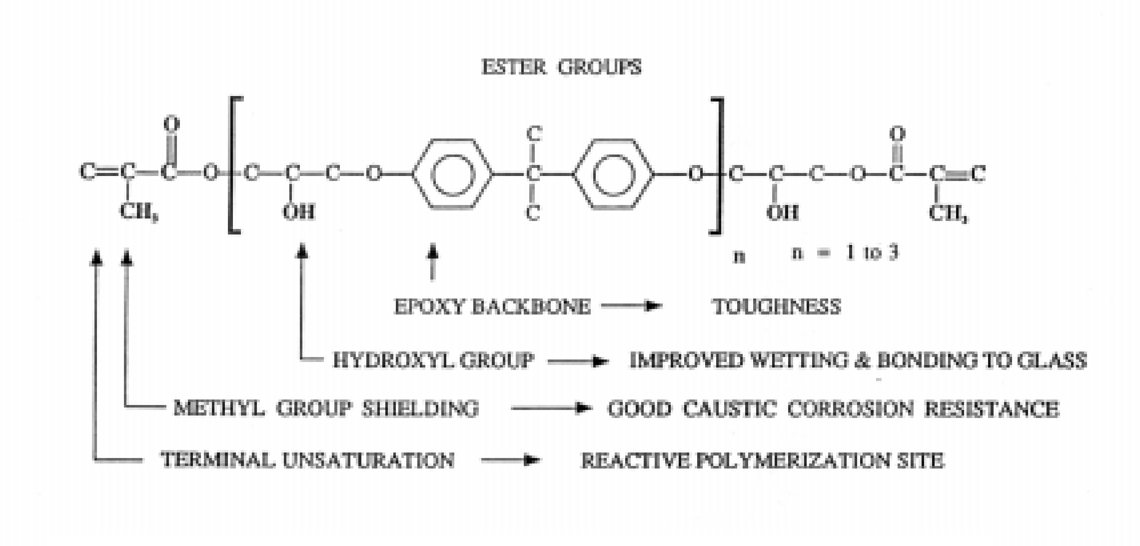


Figure 2.4 Bysphenol A vinyl ester (from reference 18).

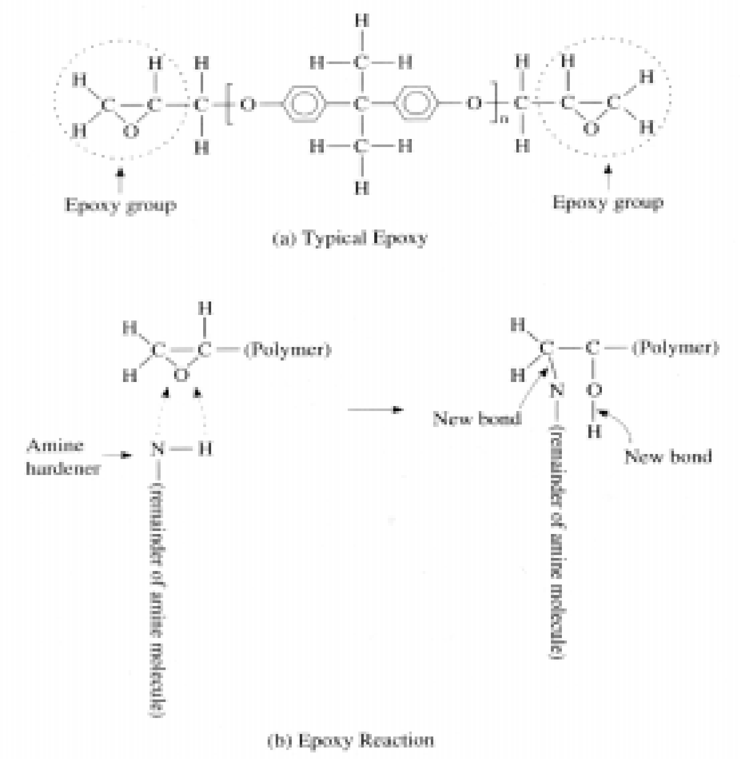
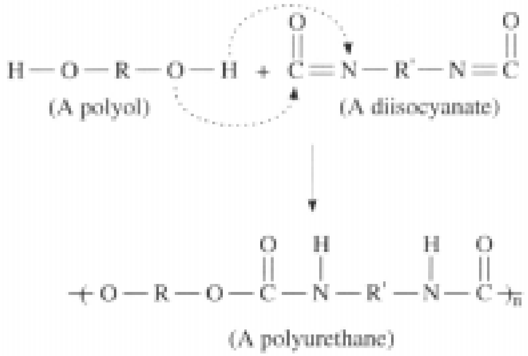


Figure 2.5 (a) Typical epoxy and (b) epoxy reaction (from reference 17).



Note: R is usually a multifunctional polyether or polyester but can also be a small organic group.

R' is usually a large aromatic group

Figure 2.6 Polyurethane reaction (from reference 17).

Resin Toughness in the Composite

The primary factor determining composite delamination resistance is the toughness of the resin matrix. A test method used to characterize the resistance of a composite to the initiation or growth of interlaminar cracks is the double cantilever beam (DCB) discussed in the following section (Figure 2.8) [20]. The toughness of a resin system is not always translated into the composite due to fiber nesting, bridging, pull out and breakage that can produce an increase in the apparent interlaminar G_{IC} of a composite (Figure 2.7), while poor fiber matrix bonding may increase or decrease composite toughness. Its has been observed that toughened matrices restrict the crack tip deformation zones affecting the determination of G_{IC} [2].

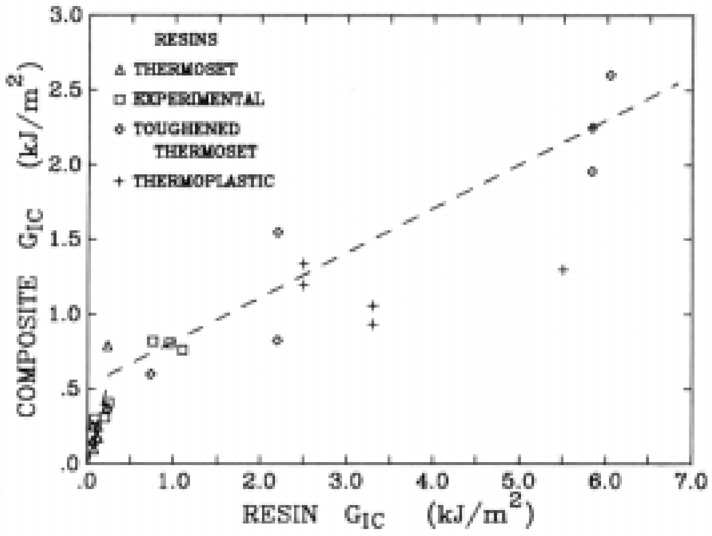


Figure 2.7. Composite interlaminar strain energy release rates for steady crack growth as a function of the neat resin G_{IC} for different resins systems from reference 7.

DCB and ENF Test Methods

Fracture mechanics treats crack-dominated failure modes. In composites fracture mechanics is applied primarily to delamination between plies. There are three different modes in which delamination takes places in a composite under different loading conditions: opening (I), shearing (II) and tearing (III) [21]. For a fracture to occur, a crack has to be initiated and then propagated. In fracture mechanics terms, initial crack growth occurs when the energy release rate G equals the crack resistance of the material [22]. Initiation fracture toughness in mode I, (G_{IC}), is a material property used in materials selection and design. The most widely used method to test mode I delamination is the double cantilever beam (DCB) test described in the ASTM D 5528 [23,25]. Geometry and loading for this test can be seen in Figure 2.8. End notched flexure (ENF) is a test method developed to test mode II delamination and is explained in detail in Chapter 3.

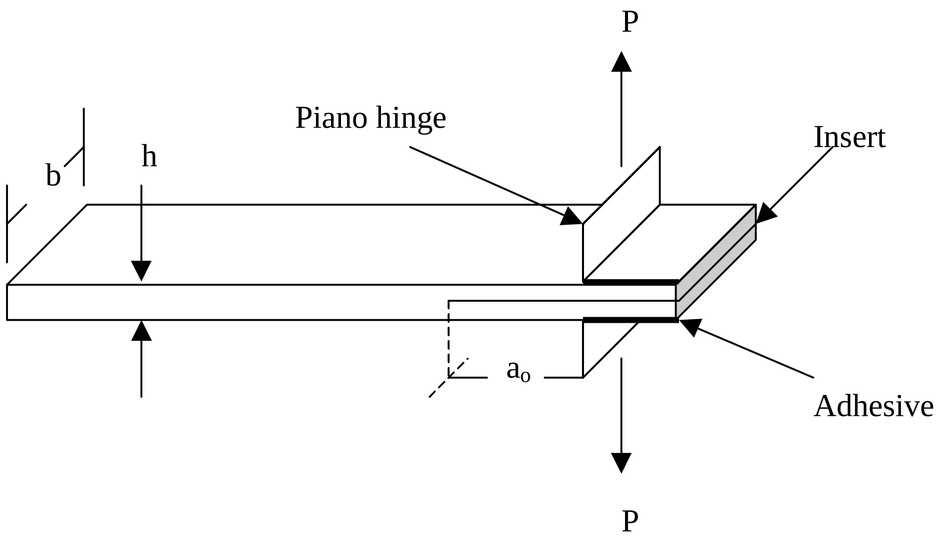


Figure 2. 8 Geometry and loading for a DCB specimen.

Skin Stiffener Structure

Skin stiffener structures are used in wind turbine blades to transfer shear loads and increase bucking resistance. Delamination is a failure mode and a major concern in this type of structure [24]. The flange is bonded to the skin by the matrix (Figure 2.9); therefore, it is important to study delamination effects when using different resins. Initial damage load, maximum loads and displacements are recorded as shown in Figure 2.10.

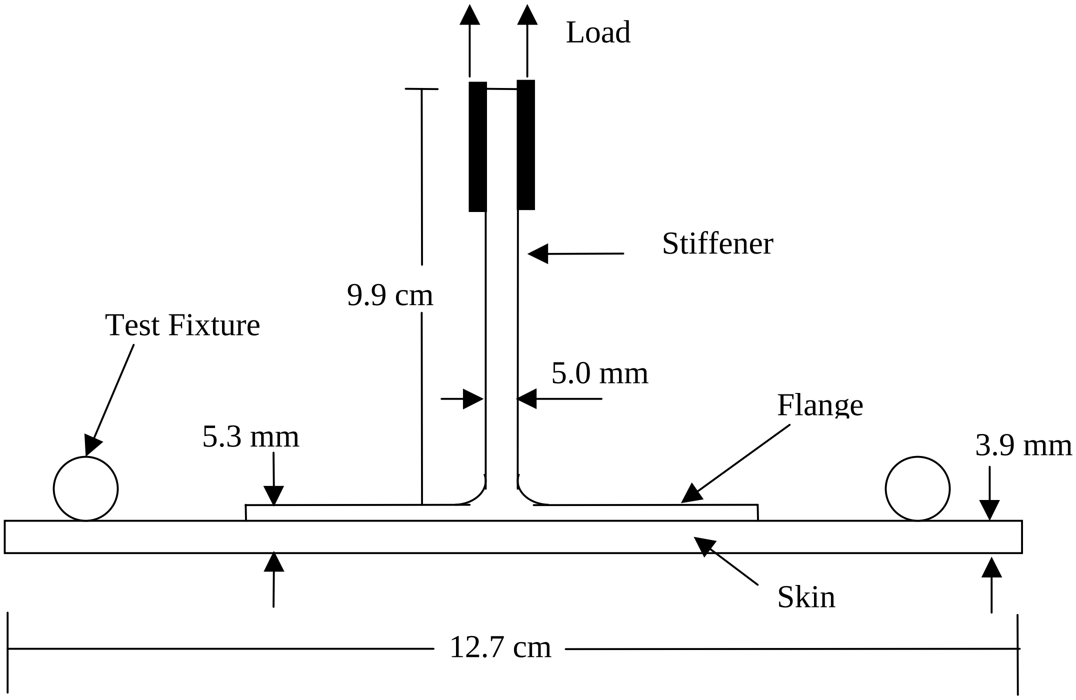


Figure 2.9 Loading and approximate dimensions for skin-stiffener T-specimens.

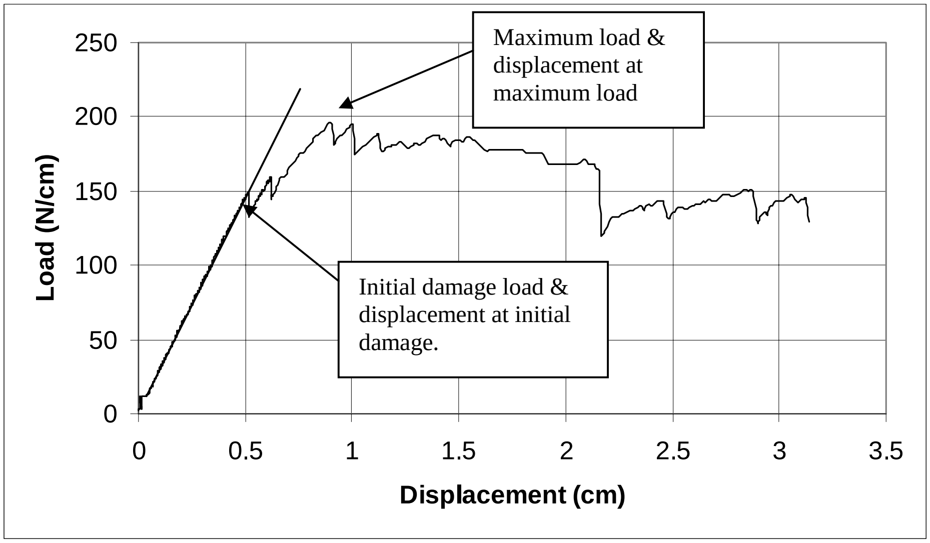


Figure 2.10 Typical load-displacement curve for a skin-stiffener specimen.

CHAPTER 3

EXPERIMENTAL METHODS

Polymer Resin Systems

Thermoset resins including polyesters, vinyl esters, epoxies and one urethane were investigated. The polyester CoRezyn 63-AX-051 manufactured by Interplastics Corp, is an unsaturated orthophthalic polyester resin, has been used by industry to manufacture wind turbine blades and is the resin used for most of the DOE/MSU Database [1]. The CoRezyn polyester has been extensively researched and therefore is considered as the baseline polyester to compare with other systems.

Two other polyester systems were studied briefly, a PET-Polyester P460 from Alpha Owens Corning and an unsaturated polyester Arotran Q 6038 from Ashland Chemicals. The Arotran polyester was selected because of its intensive use in the automotive industry on applications such as body panels for the Chrysler Viper. The three polyesters were catalyzed using 2% by volume Methyl Ethyl Ketone Peroxide (MEKP). Gel times for polyester resins were on the order of 30 to 40 minutes, with 6 to 15 hours cure time. Finished parts were postcured by in an oven for two hours at 60 °C.

Vinyl esters are gaining acceptance in wind blade manufacture and in several other composite materials uses primarily due to improved properties and lower viscosities and ease of manufacturing. Four vinyl esters where studied. The first two were obtained from TECTRA Inc.: Swancorp 980 which is an elastomer-modified vinyl ester diluted in styrene monomer, and Swancorp 901, which is an epoxy-novolac based vinyl ester diluted in styrene monomer. Two additional vinyl ester resins were obtained from Dow Chemical, Derakane 411C-50 and Derakane 8084 (rubber modified), which were both epoxy vinyl ester based systems. These resins were unpromoted as received (except the second batch of Derakane 8084). Cobalt Naphthenate-6% (CoNap) was used to promote them using the amounts shown in Table 3.1. Trigonox 239A was the catalyst used to cure vinyl ester resins since it did not cause foaming of this type of resin as did MEKP. Table 3.1 shows the amount of promoter and catalyst used in each vinylester resin [13]. Formulations were mixed by volume and estimated for a 20 °C processing temperature. All plates were postcured for two hours at 60 °C.

Table 3.1 Catalysts, promoters and curing conditions for vinyl ester resins.

Vinyl Ester Resins (Mixed by volume)	Gel Time 20-40 Minutes	Demold Time	Mold Release
Swancorp 901, 50-50% Blend Swancorp 901 & 980, and Derakane 411c-50	2.0% Trigonox 239A 0.3% CoNap	10 to 14 hrs 10 to 14 hrs	A 1380
Derakane 8084 Swancorp 980	2.0% Trigonox 239A 0.5% CoNap	8 to 12 hrs	A 1380

The epoxy resins used were: System 41, a two part epoxy system referred as an RTM laminating resin from System Three. The other two epoxies were obtained from Applied Poleramic Inc. Both resins were two phase - acrylate modified epoxies. Epoxy SC-12 is a three part system while epoxy SC-14 is two part. Table 3.2 shows mixing ratios and curing cycles for the epoxy resins used. SC-12 and SC-14 cannot be demolded or un-clamped until the cure cycle is completed.

Table 3.2 Mix ratios and cure conditions for epoxy resins.

Epoxy Resins	Mix ratio by weight (A:B:C)	Cure Cycle	Post Cure Cycle	Mold Release
System 41	4,1	12 hr at 20 °C	2 hrs at 60 °C	A1380
SC-12	100,80,20	1 hr at 60 °C	2 hr at 90 °C	Monocoat E-91
SC-14	100,35	3 hr at 60 °C	5 hr at 100 °C	Monocoat E-91

The urethane was a liquid polyurethane plastic formula Poly 15-D65 from Polyteck Development Co. The mixing ratio for this resin was one part of part A to one part of part B. The injection time for this resin is 20 minutes and a de-mold time of 16 hours. Finished parts were postcured for 2 hours at 60 °C.

Test Methods

Three specimens of each resin type were tested in most cases. Average values and standard deviations calculated. If less than three specimens were tested, no standard deviation was calculated.

Delamination Tests

Composite delamination tests were run in Mode I with DCB specimens and Mode II with ENF specimens as described earlier. For the Mode I DCB tests, specimens are prepared with an even number of unidirectional plies, with delamination occurring in the zero direction [26]. A Fluoro-Peel teflon release film (30 μm thick) which does not bond to the resin (in this case) is placed at the mid-thickness of the laminate when it is fabricated, to function as a crack starter. Hinges are attached to the specimen as a means of transferring load. Modified beam theory (MBT) is used to calculate the Mode I critical strain energy release rate:

$$G_{IC} = (3 \cdot P_c \cdot \delta)/(2 \cdot b \cdot a) \qquad (3.1)$$

where:

P_c= critical load at the onset of nonlinearity (shown on Figure 3.2)

δ= load point displacement at P_c

b= specimen width

a = crack length measured from hinges

Mode II delamination resistance, also known as the forward shear delamination resistance (G_{IIC}) is generally measured using the end notch flexure (ENF) specimen [27]. The specimen is manufactured with a crack starter and the test consists of a three point bending load. Specimen dimensions and loading geometry are shown on Figure 3.1. Unstable crack growth is generated when the maximum load is applied to a ENF specimen. The mode II fracture energy was determined from the following equation used by Mandell and Tsai [28]:

$$G_{IIC} = (9 \cdot a^2 \cdot P^2)/(16 \cdot E \cdot W^2 \cdot h^3) \qquad (3.2)$$

Where:

P = maximum load for crack extension

a = crack length measur4ed from the outer pin

E = longitudinal elastic modulus

W= specimen width

h= half thickness of the specimen

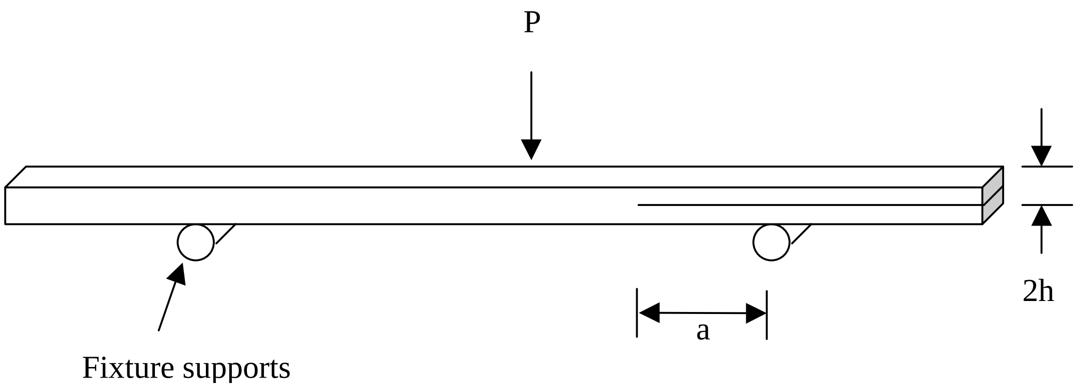


Figure 3.1 Geometry and loading for ENF

Equation 3.1 was used to calculate the strain energy release rates for Mode I using the different resin systems. The critical load used in the MBT equation was taken from onset of non-linearity in the load displacement plot shown in FIG. 3.2. For some resins, there was a linear load displacement response until the crack was propagated. For other resins, the load displacement curve was nonlinear and the crack extension point was taken as the onset of non-linearity (Figure 3.2).

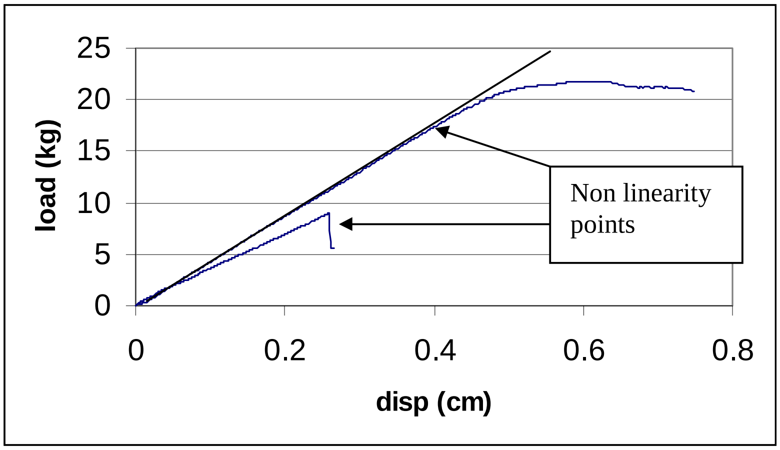


Figure 3.2 Load-displacement plot for a DCB test.

During the ENF testing, the load was increased on the specimen until it experienced a sudden and unstable crack growth. The value of the energy release rate for Mode II (G_{IIC}) was then estimated using this value of maximum load. Specimens were pre-cracked in Mode I using the criteria suggested Carlsson and Gillespie [22] to generate unstable crack growth. For stable crack growth, the critical load can be used to generate a more conservative G_{IIC} value [29]. The longitudinal modulus E was calculated for each resin using the correlation for different fiber contents given by Mandell and Samborsky [1]:

$$(E_L / E_{L*}) = (1/32.71)(3.1+65.8V_f) \qquad (3.3)$$

This equation adjusts approximately linearly the longitudinal modulus E_L with fiber volume fraction V_F, where E_L* indicates the property at the 45% fiber volume with a lay-up of $[0]_6$ in Table 9a of reference [1]. This equation was developed for the polyester matrix, and will not be accurate for low modulus matrices.

Skin Stiffener Test

The test geometry and loading conditions were given in Figure 2.9. The T-Specimens were tested under a tensile load in the same manner as described by Haugen [24]. The initial damage load and displacement at initial damage are recorded as the onset of non-linearity on a load-displacement plot. The maximum load and displacement at maximum load may be reached before the specimen fails (Fig 2.10), with the load decreasing as damage accumulates at higher displacement. Molding and ply configurations for skin, flange and web are discussed later.

Heat Deflection Temperature

A rectangular neat resin specimen is subjected to a three point bending load while immersed in a heat transfer medium (Figure 3.3) [30]. The temperature is raised at uniform rates, between 0.2 to 2 °C/min. The temperature of the medium is measured when the test bar has deflected 0.25mm. The deflection versus temperature is plotted for each specimen as shown in Figure 3.4. The plots were initially adjusted to a zero displacement due to the negative displacement caused by the initial deflection of the test coupon under load. The result of this test is called the deflection temperature under flexural load [30]. The load is calculated as follows:

$$P = (2 \cdot S \cdot b \cdot d^2) / 3 \cdot L \qquad (3.6)$$

Where: P = load

S = maximum stress in the specimen of 1820 KPa

b = width of specimen

d = depth of specimen

L = span between supports

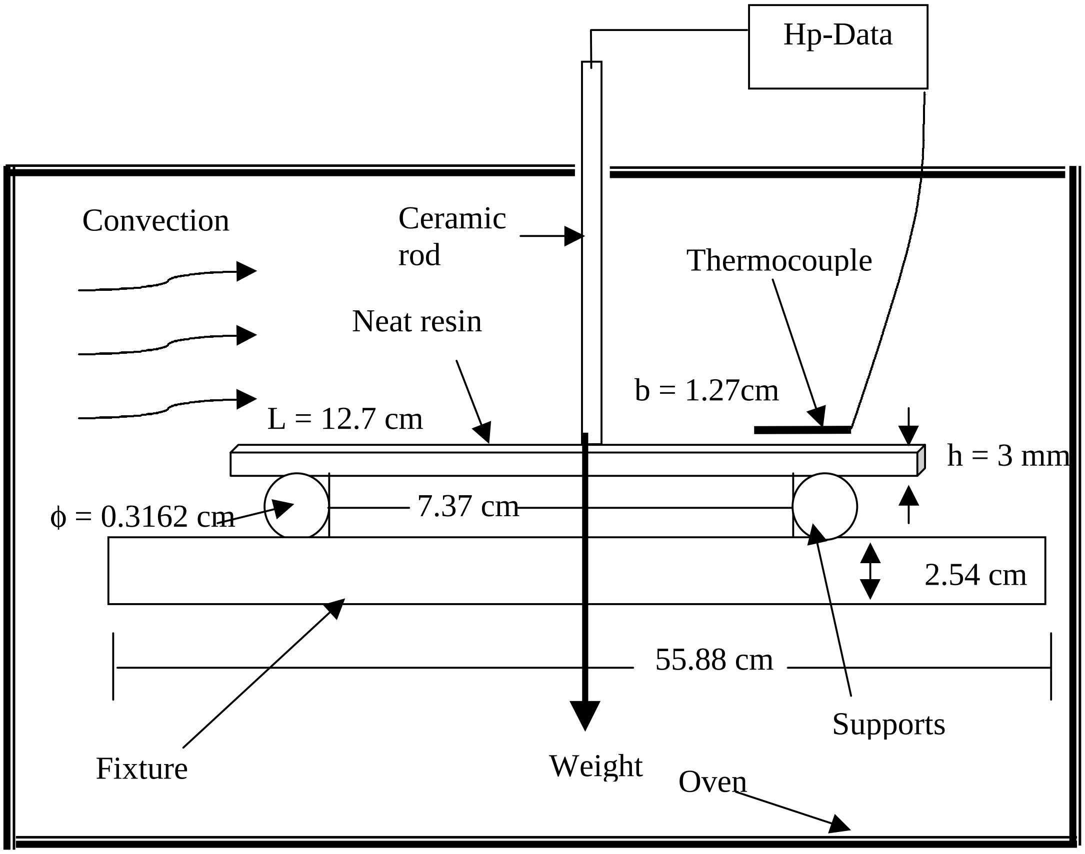


Figure 3.3. Schematic of heat deflection test

A convective Lindberg Blue oven Model MO1450 C was adapted by Samborsky perform the HDT Test following the ASTM D648 standard [30]. Figure 3.3 shows the settings for the test. A ceramic displacement rod and a type K thermocouple were attached to an HP Data Acquisition System (Model HP 34970A) to record displacement and temperature. The ceramic rod was chosen because of its well known low coefficient of thermal expansion. The thermocouple was supported on the fixture touching the specimen on one side and did not interfere with the deflection. The constant heating rate selected and used for all resins was 0.3 °C/min. The tests were run until a mid-span deflection of at least one millimeter took place (Figure 3.4)

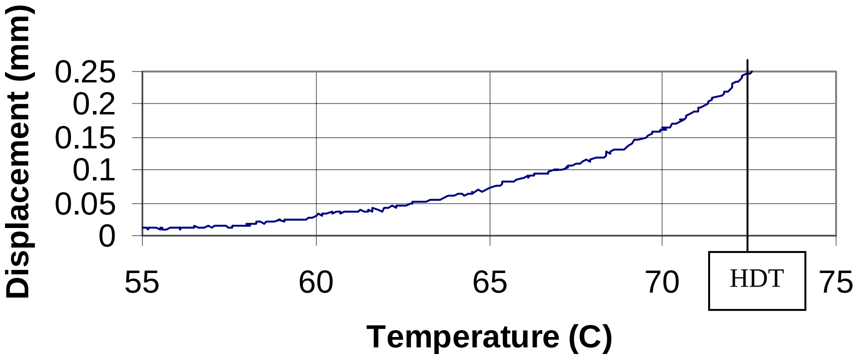


Figure 3.4 Displacement – temperature curve for a HDT test.

Manufacturing Process

All the materials except stiffeners were manufactured as flat plates at Montana State University – Bozeman by resin transfer molding. Three different molds were used depending on the specimen type and size. For DCB, ENF, tensile and compressive specimens, rectangular flat plates with dimensions of 42 x 14 cm were cured using an aluminum mold labeled as Mold A. This mold was also used to cure pure resin plates for tensile specimens for each resin, as well as heat deflection temperature (HDT) specimens. Mold A was placed vertically when injecting pure resin, letting the resin flow from the one end to the bottom in order to let the let air bubbles in the resin rise to the surface. The bottom port was closed off, using one of the two top ports to inject the resin and the other as a vent port.

The second mold (Mold B) also called the T-Mold was used to manufacture skin-stiffener T – specimens. This mold was designed by Haugen [24]. Mold B had dimensions of 16 x 46 cm for the skin and 10 x 46 cm for the flange. The resin was injected using a peristaltic pump from Cole Parmer Co (Model 7553) with Mold A and Mold B. Once the fibers were wetted out by the resin the vent ports were closed off and the resin cured inside the mold for a period of time different for each resin. The injection pressures for the three molds were less than 150 KPa and adjusted depending on the fiber content and lay-up.

Specimen Preparation and Testing Equipment

Composite test specimens consisted of either unidirectional $[0]_6$ or [0/±45/0]s configurations. Reinforcements were primarily unidirectional E-Glass stitched fabric Knytex D155 and double bias (+45/-45) DB120. After postcuring, test specimens were machined with a water cooled diamond blade saw. The lay-ups, fiber volume (V_f) content, and average thickness for the different specimens are shown in Table 3.3. Ply configurations for T - specimens are shown in Table 3.4

Table 3.3 Lay-ups, fiber volumes and thickness for different tests.

Specimen Type	Lay-up	Type of Fabric	V_f	Average thickness (mm)
DCB	$[0]_6$	D155	40	3.4
ENF	$[0]_6$	D155	40	3.4
Transverse Tension	[90/±45/90]s	D155/DB120	37	3.0
Compression	[0/±45/0]s	D155/DB120	37	3.0

V_f = Fiber volume (%)

Table 3.4 Ply configuration and average thickness for skin-stiffener specimens.

Region	Ply configuration	Average thickness (mm)
Skin	[+45/-45/0_2/+45/-45]s	4.3
Flange	[+45/-45/0_2/+45/-45]	1.5
Web	[+45/-45/0_2/+45/-45]s	4.5
Interface	(45/-45)	
Skin + flange		6.0

The majority of the test specimens (except T-Specimens) had a rectangular flat shape. Selected tensile and compressive specimens were soaked in water for 330 hours at 50 °C as pure resin and composite samples. Dimensions for tensile and compressive specimens and for water absorption tests are shown on Table 3.5.

Table 3.5 Dimensions for tensile, compressive and water absorption specimens.

Specimen Type	Dimensions (cm).
Tensile Specimens	15.24 x 2.54
Compressive Specimens	12.7 x 2.54
Specimens For Water Absorption	5.08 x 1.27

DCB and ENF delamination specimens had a an average length of 17 cm and a width of 2.54 cm. These specimens where manufactured with a Fluoro-Peel Teflon release film that was inserted at the mid-plane of the laminate to serve as a crack initiation site according to ASTM 5528 [23]. Removable pin hinges (N121-606:V508) were bonded to the end of each DCB sample on both sides using and adhesive Hysol EA 9302.2NA. DCB and ENF specimens can be seen at Figure 3.5

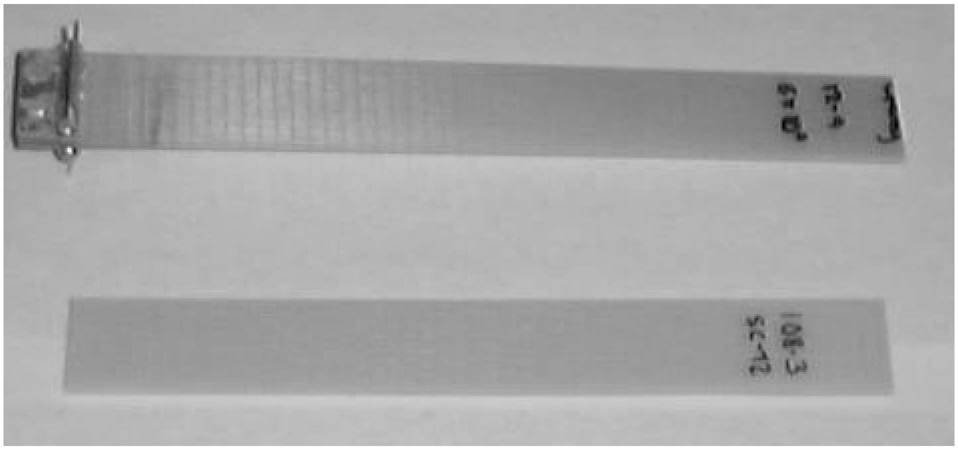


Figure 3.5 DCB and ENF specimens.

An Instron 8562 servo electric testing machine was used to perform all the static tests including tension, compression, T-Pull off, DCB and ENF. For all tests a load cell calibrated to its respective ASTM standard was used. Tensile tests on composite and pure resin specimens were performed by attaching an extensometer (Class B2) to the specimen using rubber bands. The fixture shown in Figure 3.6 was used to apply compressive loads on ENF bending specimens and tensile loads on T-Specimens. Table 3.6 shows displacement rates used for the different tests.

Table 3.6 Test rates for different tests.

Test type	Test rate (cm/min)
DCB	0.01
ENF	0.64
Tensile test in resin	0.51
Tensile test in composite	0.38
T-Pull off test	0.64
Compression Test	76

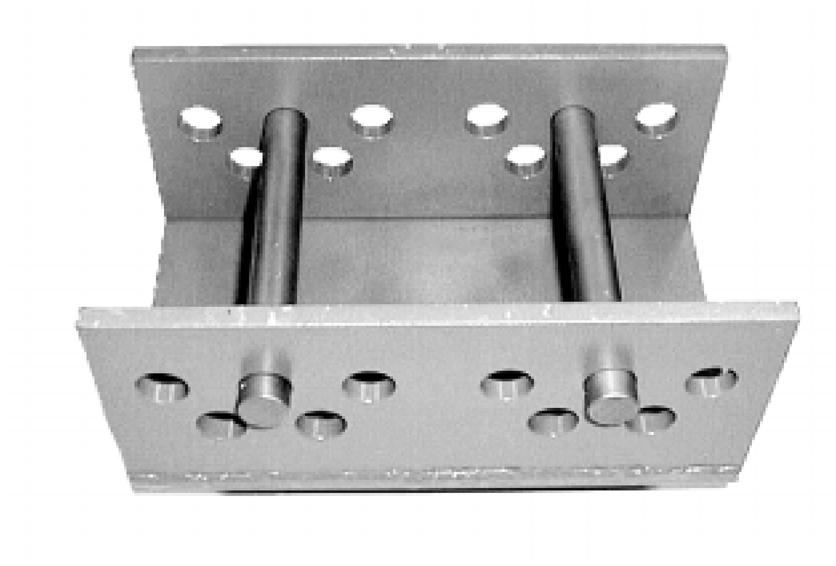


Figure 3.6 Test fixture used for ENF and T-Specimens

Test for DCB and ENF Specimens

Three sets of tests were performed on DCB specimens (see Appendix B). On the first set of DCB tests as recommended by the ASTM 5528 standard [23], specimens were not pre-cracked in order to obtain an initiation value of G_{IC} free from any fiber bridging across the crack front for all the different resins. The values for G_{IC} considered to be the initiation values were then obtained from the second test performed on each specimen (after 1 to 3 mm of crack growth), which is equivalent to pre-cracking a specimen. Davies and Benzeggagh [21] recommend pre-cracking the specimens, considering that G_{IC} values are more accurate when fiber bridging occurs. The second set of tests was performed on a 50-50% blend of Swancorp vinylester resins between a rubber modified vinyl ester Swancorp 980 and a plane vinyl ester Swancorp 901 to study the effects on the fracture toughness when blending compatible resins. Pure resin tensile modulus was also measured on the Swancorp blend.

A separate set of tests was performed for DCB specimens manufactured with the unidirectional UC1018/V experimental fabrics. These fabrics have bonded unidirectional fiberglass on one side and a thin veil on the other side, which holds the fibers. Two different types of veils were used, polyester and glass veil. Lay-up configurations are shown on Table 3.7. The UC1018/V, D155 and DB120 fibers can be seen in Figure 3.7. The motivation of this test was to study the changes in the delamination toughness when using different fiber reinforcements, using polyester resin CoRezyn 63-AX-051.

Table 3.7 Geometry and lay-ups for DCB specimens using UC1018/V fabrics.

Veil Type	Placement at the mid-plane	Lay-up
Polyester Veil	Veil-Veil	$[0]_6$
Glass Veil	Veil-Veil	$[0]_6$
Polyester Veil	Glass-Glass	$[0]_6$

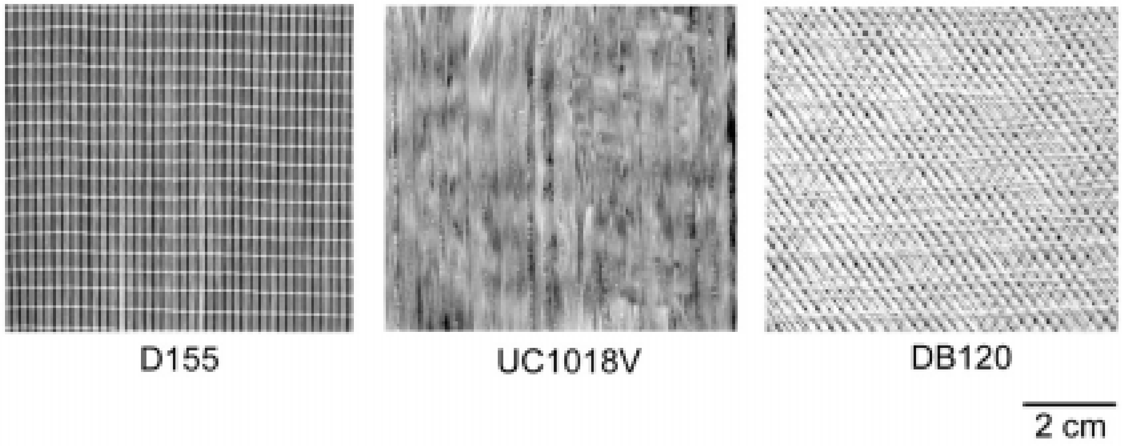


Figure 3.7 Different fabrics used.

CHAPTER 4

RESULTS AND DISCUSSION

Introduction

This chapter presents the results of this study, first considering the neat resin behavior and heat deflection temperature, followed by composite interlaminar fracture toughness, T-stiffener pull-off, transverse tensile strength, compressive strength and moisture effects. The resin systems are then compared in terms of cost versus overall performance and processing characteristics. Complete details for each test can be found in the Appendix.

Neat Resin Properties

Tensile Stress-Strain Curves

Results for tensile modulus, yield stress, ultimate tensile strength (UTS) and strain to failure for different resins are shown in Table 4.1. Tensile stress - strain curves for various neat resins are given in Figure 4.1.

Table 4.1 Tensile test results for neat resin.

Resin	UTS MPa	Yield strength MPa	Modulus, E GPa	Failure % strain
CoRezyn 63-AX-051	54.07 (4.64)*	45.19 (2.47)	3.18 (0.12)	2 (0.31)
Swancorp 980 (batch a)	25.65 (0.29)	20.56 (0.48)	1.63 (0.02)	29.51 (15.05)
Derakane 411C-50	57.68 (0.78)	50.39 (2.49)	3.21 (0.04)	2.06 (0.06)
Derakane 8084	72.57 (2.73)	55.16 (2.39)	3.25 (0.15)	2.97 (0.31)
System 41	52.61 (1.08)	52.61 (1.08)	3.57 (0.06)	1.60 (0.05)
Epoxy SC-12	44.34 (3.06)	**	3.48 (0.04)	1.38 (0.12)
Epoxy SC-14	68.31 (2.68)	48.50 (1.33)	2.80 (0.03)	3.31 (0.27)

* (Std. Deviation)

**No clear yield stress prior to fracture

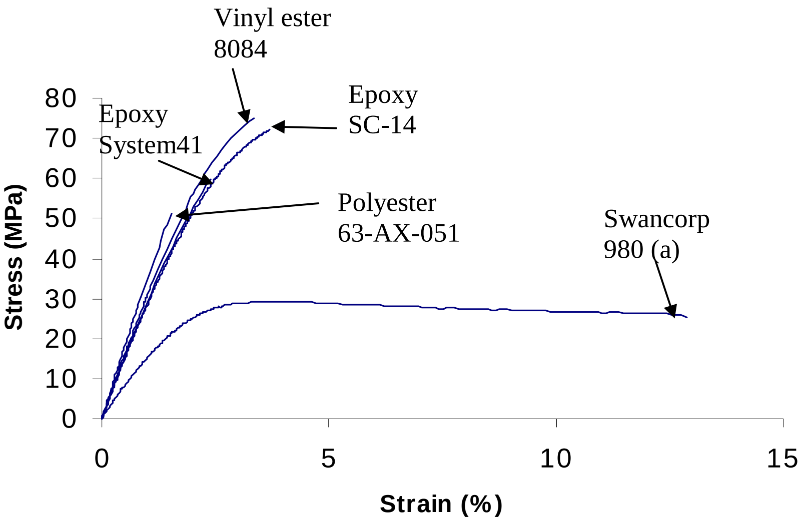


Figure 4.1 Stress-strain curves for tensile tests of neat resins.

The tensile modulus and ultimate tensile strength are similar for the majority of the resins except for the Swancorp 980, which is lower. Toughened resins (excluding epoxy SC-12), such as Derakane 8084, Epoxy SC-14 and Swancorp 980 (a) tend to have a higher ultimate strength and strain to failure compared to the untoughened base resins. Epoxy System 41 has the highest resin modulus. It is shown later that higher resin modulus is associated with lower interlaminar toughness, but higher composite compressive strength. Swancorp 980 (a) had the highest strain to failure, showing a ductile behavior, but a lower E than the 2.25 GPa target given earlier for wind turbine blades. The rubbery urethane was not tested as a neat resin because of its foaming character. It is evident form later composites data that it has a very low modulus but high strain to failure.

Heat Deflection Temperature

Results for heat deflection temperature (HDT) can be seen in Table 4.2. Standard deviations for an average of 3 specimens are included. Heat deflection temperatures were around 20 ^{o}C lower than the glass transition temperatures (T_g) listed by the manufacturer of the resins. This is commonly expected because the heat deflection temperature test applies a load to force a deflection in the specimen, while the T_g test only applies heat to the specimen. The cure and postcure cycles are directly related to the heat deflection temperature of a cured resin (discussed earlier). SC-12 and SC-14 were postcured at higher temperatures, as shown on Table 3.2, and their HDT temperatures were higher than the rest of the resins that were postcured at 60 °C. Derakane vinyl ester resins generated more exothermic heat while curing (room temperature processing) and had higher HDT temperatures than the Swancorp vinyl ester resins. Results for CoRezyn 63-AX-051 are similar to the epoxy System 41 and the vinyl ester Swancorp 980 batch (b). Good consistency of results was observed in most resins. The manufacture's T_g for the urethane resin was not provided.

Table 4.2 Heat deflection temperatures for different resins.

Resin	Value listed by Manufacturer °C	Average HDT °C	Standard Deviation	Specimens tested
Polyester 63-AX-051	68 (HDT)	55	0.94	3
Vinyl ester 980 batch (b)	82 (T_g)	60	1.73	3
Vinyl ester 411C-50	82 (HDT)	78	3.69	3
Vinyl ester 8084	77 (HDT)	75	1.38	3
Epoxy System 41	51 (HDT)	56	3.64	3
Epoxy SC-12	125 (T_g)	95	1.22	3
Epoxy SC-14	103 (T_g)	83	1.9	3

If 70 °C is taken as a target T_g for wind turbine blades, as discussed earlier, then the acceptable resins were the vinyl esters Derakane 411C-50 and 8084, and the Epoxies SC-12 and SC-14. These tests were run at ambient moisture content, and the HDT would be lower at higher moisture contents.

Composite Properties

Interlaminar Fracture Toughness

Modified beam theory (Equation 3.1) was used to obtain the results for G_{IC} on composite specimens. The first set of DCB tests included ten different matrices. All the tests were performed with the same unidirectional lay-up of $[0]_6$ using D155 fabrics with the crack growing in the 0^o direction. Three values of G_{IC} are recorded for each resin system. Each test corresponds to a loading on a specimen. The first test performed on each specimen, denoted test (a), is run without pre-cracking the specimens; this provides a G_{IC} initiation value at the artificial crack tip as recommended by the ASTM 5528 [23]. The results of test (a) are usually affected by a resin rich area inevitably formed in front of starter film as reported by Davies and Benzeggagh [21]. The second test performed on each specimen, denoted test (b), involves propagation of the crack previously generated by test (a). Test (b) therefore, uses a sharp crack with a tip position 2 to 4 mm beyond the original teflon strip (see Appendix). The value from test (b) is affected by slight fiber bridging but it provides useful information on the delamination resistance for short cracks. G_{IC} values for test (b) are usually higher than values for test (a) due to the fiber bridging phenomenon. The third G_{IC} value listed in some cases, the overall G_{IC}, is the average G_{IC} value of the all the tests performed on each specimen (Appendix), covering a range of crack lengths up to 15 mm. The energy release rate for Mode II, G_{IIC}, was determined on the same DCB specimens used to determine G_{IC} after cracks were grown in Mode I. The hinges were removed from the DCB specimens and the cracks propagated as discussed previously. At least two DCB and ENF specimens were tested for each matrix system, usually taken from a single molding.

Polyester Resins. Three different polyester resins were tested and results for G_{IC} test(a), G_{IC} test(b) and G_{IIC} are shown on Table 4.3. The values obtained for G_{IC} test(a) are very similar for the three matrices. The PET P460 modified polyester did not show an increase in fracture toughness as expected [31], but it showed an increase of the G_{IC} value obtained with test (b). The PET P460 showed the maximum G_{IIC} for polyesters, twice as high as for the CoRezyn 63-AX-051. The maximum loads for the CoRezyn 63-AX-051 and the PET-Polyester were relatively low, between 1.5 to 4 kilograms while other systems reached 20 kilograms (see Appendix). The maximum load depended directly on the initial crack length [29]. Arotran Q6038 had the highest G_{IC} value for test (b) but the lowest G_{IIC} value of all resins. This system was not processed to manufacture specimens for other types of test due to its high reactivity and smoke generation while curing.

Table 4.3. G_{IC} and G_{IIC} for polyester resins.

Resin	G_{IC} (a) initial J/m^2	G_{IC} (b) J/m^2	G_{IIC} J/m^2	Specimens tested
CoRezyn 63-AX-051	153 (10)*	159 (29)	977 (229)	4 for G_{IC} 3 for G_{IIC}
PET P460	144 (50)	219 (59)	1866 (197)	5 for G_{IC} 4 for G_{IIC}
Arotran Q6038	153	309	305	1 for G_{IC} 1 for G_{IIC}

*(Std. Deviation)

<u>Vinyl Ester Resins.</u> Three vinyl ester resins were tested. Two rubber modified versions: Swancorp 980 and Derakane 8084, and one non-toughened vinyl ester, Derakane 411C-50. Results for G_{IC} test(a), G_{IC} test(b) and G_{IIC} are shown in Table 4.4 for the different vinyl ester resins. Toughness was measured on two different batches of Swancorp toughened resins, Swancorp 980 (a) and Swancorp 980 (b). Differences between G_{IC} values for the two batches of resin are discussed later. Swancorp 980 (a) had the second highest G_{IC} value after the polyurethane (discussed later).

Table 4.4. G_{IC} and G_{IIC} for vinyl ester resins

Resin	G_{IC} (a) initial J/m^2	G_{IC} (b) J/m^2	G_{IIC} J/m^2	Specimens tested
Swancorp 980 (batch a)	1441 (313)*	1840 (161)	3116 (812)	4 for G_{IC} 3 for G_{IIC}
Derakane 8084	344 (7)	595 (133)	2638 (567)	3 for G_{IC} 4 for G_{IIC}
Derakane 411C-50	234	396	2557	2 for G_{IC} 2 for G_{IIC}

*(Std. Deviation)

Swancorp 980 (a) had a superior toughness compared to the other vinyl ester resins. Its G_{IC} value in test (a) is 6.1 times higher than for vinyl ester 411C-50 and 4.1 times higher than for the rubber modified Derakane 8084. The toughened vinyl ester Derakane 8084 showed an increase in the resin toughness compared to the Derakane 411C-50, but not very significant in test (a). Figure 4.2 shows mode I and mode II delamination in Swancorp 980 (a) and Epoxy SC-14 specimens. Loose fibers indicating fiber bridging can be seen on the Swancorp 980 resin. This resin had slow, stable crack growth in both modes while Derakane resins had a similar behavior to polyester resins, fast and unstable cracks in modes I and II.

Epoxy Resins. Epoxy System 41 is a non-toughened epoxy resin while epoxies SC-12 and SC-14 are acrylate-modified systems. SC-14 had the highest G_{IC} value for epoxies, 2.9 times higher than system 41, and four times higher than the baseline polyester, when comparing test (a) G_{IC} values. However, System 41 had the highest G_{IIC} value of all resins (Figure 4.4). One System 41 specimen failed in compression during

ENF testing (Appendix). Epoxy SC-14 is a tough system, but it has a high viscosity and a heated mold is required in order to cure it, which makes it hard to process (see Processing Observations). Epoxy SC-12 has similar G_{IC} and G_{IIC} values to Derakane 411C-50. System 41 is relatively tough, brittle, low HDT and moderately expensive for an untoughened epoxy. Fiber bridging was not as evident for epoxies as it was for polyesters and vinyl esters (Figure 4.2).

Table 4.5 G_{IC} and G_{IIC} values for epoxy resins.

Resin	G_{IC} (a) initial J/m^2	G_{IC} (b) J/m^2	G_{IIC} J/m^2	Specimens Tested
System 41	219 (22)*	231 (38)	3776	3 for G_{IC} 2 for G_{IIC}
SC-14	638 (58)	638 (157)	3223 (520)	3 for G_{IC} 3 for G_{IIC}
SC-12	347	427	2530	2 for G_{IC} 2 for G_{IIC}

*(Std. Deviation)

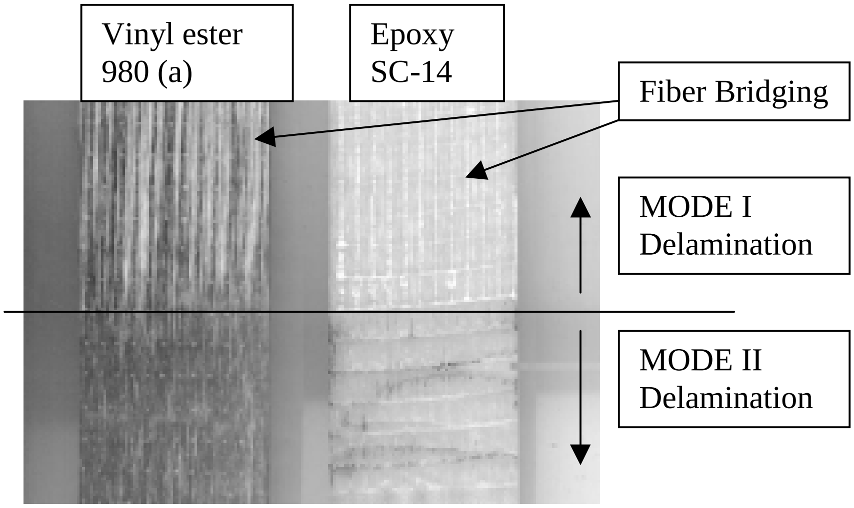


Figure 4.2 Modes I and II for Toughened Resins.

Polyurethane Resin. The thermoset polyurethane is a very ductile, rubbery resin with a very high toughness and low T_g. It behaves similarly to a thermoplastic resin because it has the ability to stretch without breaking [17]. The polyurethane resin was difficult to test in mode one due to its high content of porosity formed while curing. The crack front was difficult to locate since the marker ink used for this was absorbed by the pores. Additionally, only one specimen was tested in mode I because the other two specimens lost their hinges during DCB testing. The specimens failed in compression when doing ENF testing and no crack growth was generated in mode II. A lower bound G_{IIC} value for this resin was calculated using the maximum load that caused the compression failure using the initial crack length; no crack growth was generated (Table 4.6)

Table 4.6 G_{IC} and G_{IIC} values for polyurethane resin.

Resin	G_{IC} (a) initial J/m^2	G_{IC} (b) J/m^2	G_{IIC} J/m^2	Specimens tested
Poly 15-D65	2663	2752	3145*	2 for G_{IC} 1 for G_{IIC}

* Did not fail in mode II; lower bound.

Overall Toughness Comparison. The polyurethane composite resin had the highest value for G_{IC} (Figure 4.3). The rubber modified vinyl ester resin Swancorp 980 batch (a) had the second highest value of G_{IC}. It is shown in Figure 4.3 that Derakane 411C-50 has the highest G_{IC} for neat resins and similar toughness values to Epoxy SC-12. G_{IIC} values are compared in Figure 4.4 for the resin systems studied. Epoxy System 41 had the highest G_{IIC} followed by Epoxy SC-12. PET P460 resin had the lowest performance for toughened resins, but higher performance than for non-toughened polyesters.

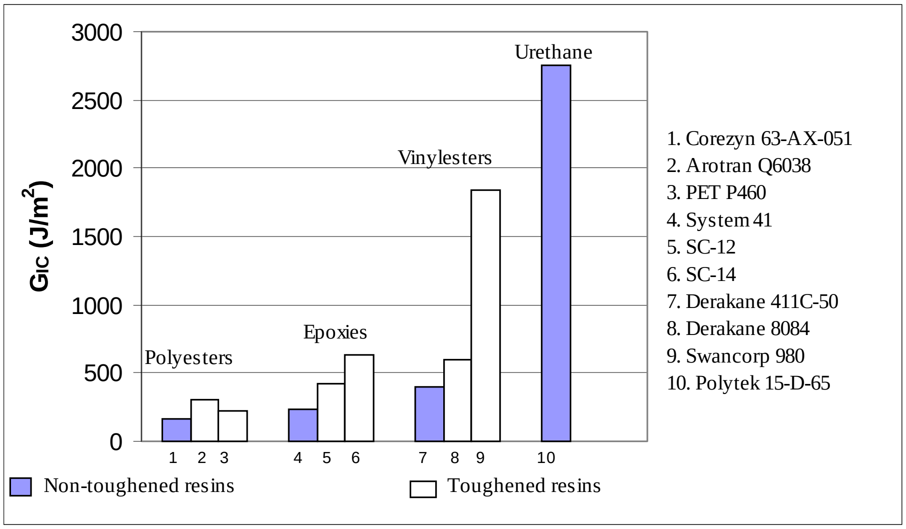


Figure 4.3 Comparison of G_{IC} test (b) results for different resin systems.

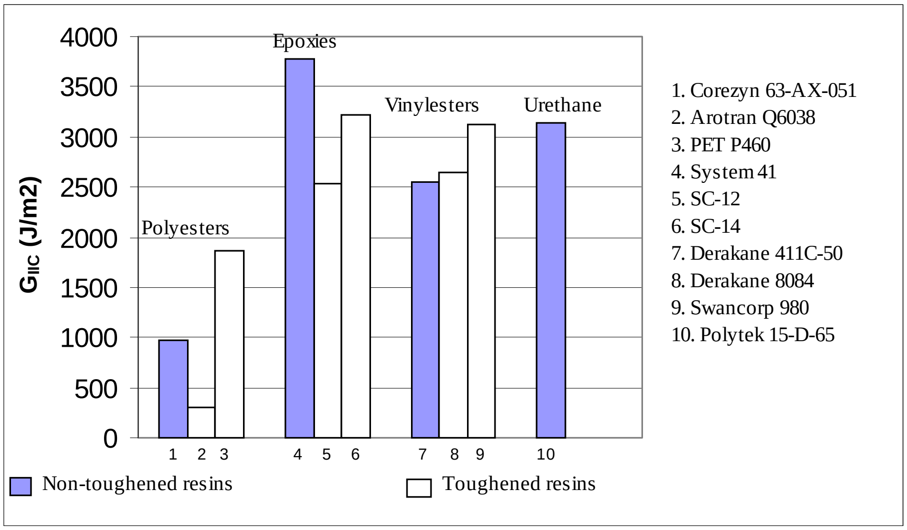


Figure 4.4 Comparison of G_{IIC} results for different resin systems.

Blended Resins. The first batch of vinyl ester resin Swancorp 980 (denoted as Swancorp 980 (a)) was tested for toughness and resin tensile modulus. A value of 1840 (J/m^2) for G_{IC} test (b) and 1.61 GPa for resin modulus was obtained for this first batch. Wind turbine blades require resin systems with a resin tensile modulus of at least 2.75 GPa. Turbine blades may not require the high toughness of the Swancorp 980, which made this system an extremely tough resin candidate but with low modulus. TECTRA Inc., manufacturer of the Swancorp vinyl ester series, suggested blending the Swancorp 980 resin with a compatible system, Swancorp 901, a non-toughened vinyl ester resin, as an alternative to increase the resin modulus relative to Swancorp 980 while providing a moderate toughness. The motivation for this blend was to study the effects of toughness and resin modulus when blending compatible resins. The amount of rubber in a toughened resin is related to the toughness of the system [25]. Toughness can be decreased and the resin modulus increased by diluting the amount of rubber in such resin, by mixing it with a non-toughened resin [31].

A second batch of resins was received, Swancorp 980 (b) and Swancorp 901. They were blended and cured as described in Table 3.1. G_{IC} and tensile modulus results for the resin blend are shown in Table 4.7 . It is shown in this Table that Swancorp 980 (b) resin had a much lower G_{IC} value and a higher resin tensile modulus than the initial Swancorp 980 (a). Swancorp 901 had only a slightly higher resin modulus than 980 (b), therefore the modulus did not change much for the blend. Modulus changes could probably be better observed if 980 batch (b) was similar to (a). The cause of the difference between batches received is unknown. Toughness changed as expected for the blends [32]. Difficulties with consistency of the Swancorp vinyl ester resins led to a focus on Derakane vinyl esters.

Table 4.7 Comparison of G_{IC} and E Modulus for different Swancorp resins and blend.

Resin	Neat resin E Modulus GPa	G_{IC} (b) J/m^2	Overall G_{IC} J/m^2	Specimens tested
Swancorp 980 (a)	1.63 (0.02)*	1840 (161)	1923 (94)	4
Swancorp 980 (b)	3.05 (0.04)	852 (215)	809 (104)	3
Swancorp 980 (b) & 901	2.76 (0.06)	569 (23)	635 (46)	3
Swancorp 901	3.37 (0.07)	208 (20)	289 (24)	3

*(Std. Deviation)

Effects of Fabric Architecture on G_{IC}.Most G_{IC} values were determined using the D155 stitched unidirectional fabric, but several tests were also run for comparison in a bonded unidirectional fabric with a thin veil backing. G_{IC} values were determined for the UC1018/V bonded fabrics (Appendix) to be greater placing the fabrics back to back (veil to veil) at the mid-plane in the DCB specimens as shown in Figure 4.5.

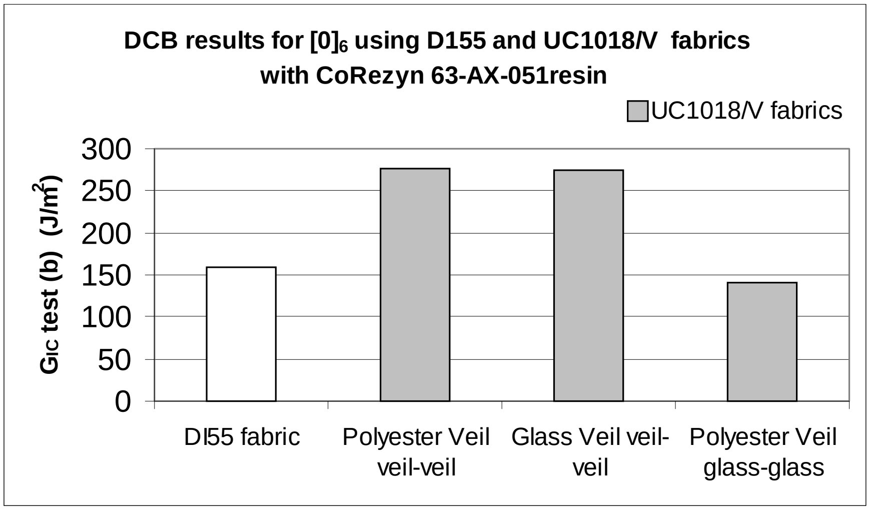


Figure 4.5 Comparison of G_{IC} test (b) values using different fabrics.

Baseline D155 fabrics had similar G_{IC} values to UC1018/V fabrics when the fibers were arranged glass to glass at the mid-plane. Overall, fabric type had little effect on G_{IC} for this limited comparison.

Results for T-Stiffener Specimens

The T-Stiffener pull off test gives a measure of structural integrity in a delamination sensitive geometry (Figure 2.9) [24]. Two non-toughened resin systems and five toughened systems were compared. Maximum load, initial damage load and the displacement at the maximum load are shown on Table 4.8. Displacement at initial damage load and thickness of skin plus the thickness of flange are given in the Appendix. Typical load - displacement curves are compared in Figure 4.6.

Table 4.8 Results for T-Stiffener Pull off Tests.

Resin	Initial Damage Load N/cm	Maximum Load N/cm	Displacement at maximum Load cm	Specimens tested
CoRezyn 63-AX-051	87 (5.57)*	135 (6.03)	0.68 (0.06)	3
PET-P460	120	164	0.84	1
Swancorp 980 (batch a)	119 (9.29)	182 (6.03)	1.35 (0.18)	4
Derakane 8084	144	194	0.90	2
System 41	168	209	0.67	2
SC-14	132	192	1.91	2
Poly 15-D65	141	262	1.16	1

*(Std. Deviation)

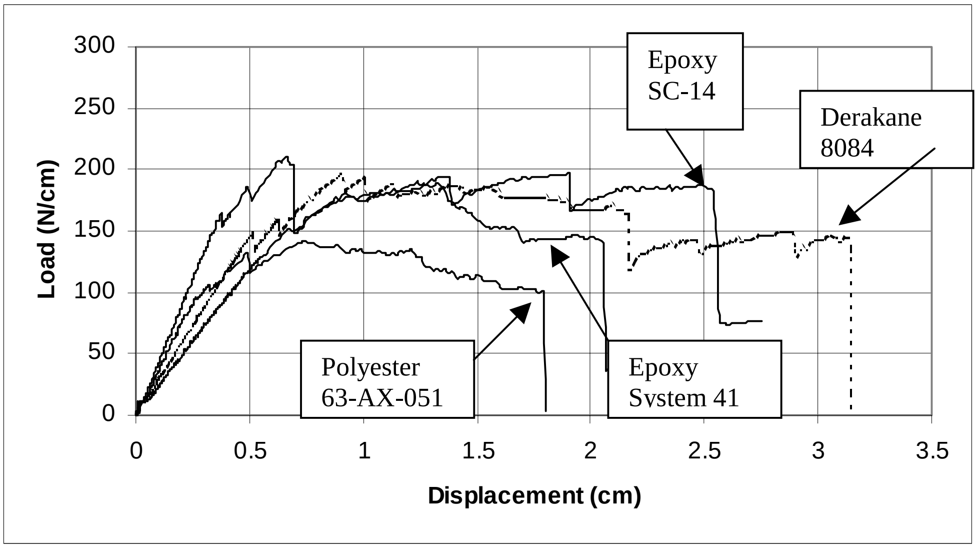


Figure 4.6 Load – displacement curves for T-Specimens

Polyester resin 63-AX-051 and the toughened PET P460 had the lowest maximum loads and low ultimate displacements. The polyurethane Poly15-D65 in fact had the highest maximum load but its ultimate displacement was similar to the polyester resins. Initial damage load and displacement at initial damage are recorded at the onset of non-linearity on the load displacement curve for a T-Pull of test (Figure 2.10). Delamination growth as crack propagation in the specimen can be seen when the initial damage load is reached. One of the reasons for recording this load is to compare resin effects when a wind turbine blade is going to develop cracks and delamination in skin stiffened regions. System 41 had the highest initial load of all resins.

The specimens differed significantly in thickness for various resins. Thinner specimens fail at lower loads and higher displacements for the same toughness (Appendix). A combination of high maximum load and high displacement at maximum load provide the toughest system. Delamination failure could be seen for polyester resins, epoxy System 41 and vinyl ester resin Derakane 8084. The difference between them is that CoRezyn 63-AX-051 and Derakane 8084 experienced a total delamination between skin and flange. System 41 and PET P460 resins also experienced delamination but the flange was still attached to the skin after the composite failure. System 41 and a Derakane 8084 specimens can be seen in Figure 4.7.

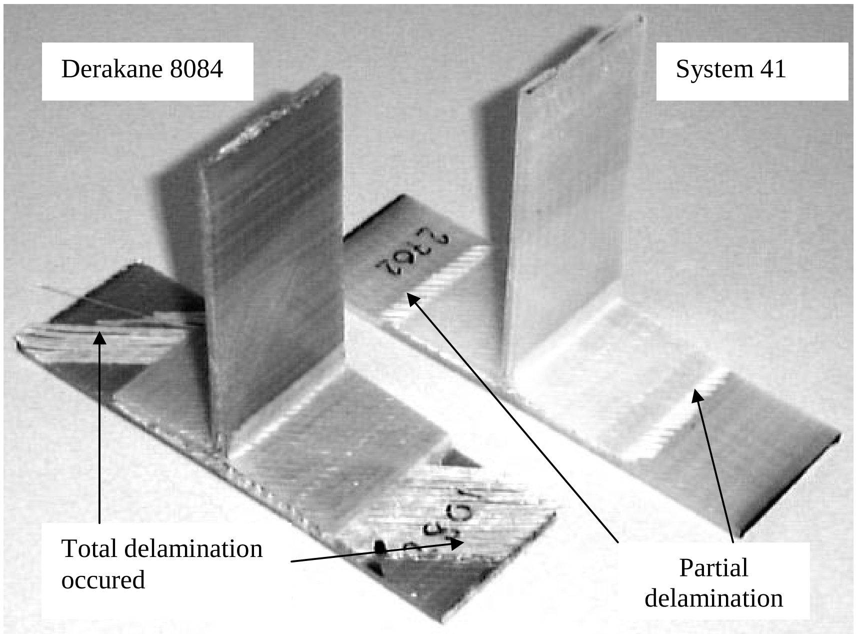


Figure 4.7 Derakane 8084 and System 41 T-Specimens.

The toughened resins epoxy SC-14, vinyl ester Swancorp 980 (a), and the polyurethane Poly 15-D65 experienced a compression failure prior to delamination. These systems experienced no delamination between skin and flange. Swancorp 980 and SC-14 resins behave similarly in the way that noisy cracks were formed on the web region, but the polyurethane cracks were not heard due to its rubbery state and high damping. Shown in Figure 4.8 is an SC-14 T specimen, which shows the failure line at the bottom of the skin generated by the compression failure.

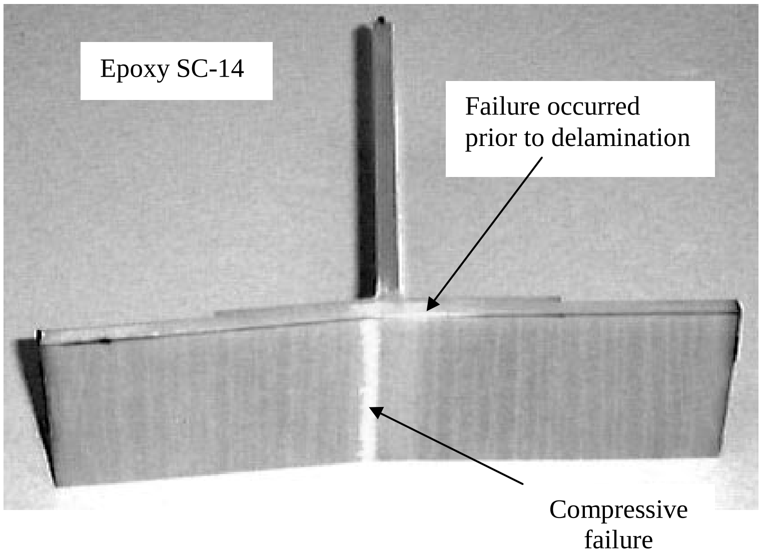


Figure 4.8 Epoxy SC-14 T-Specimen.

Figure 4.9 shows a comparison between maximum load for T-specimens and G_{IIC}. Mode II energy release values and maximum load for T-Specimens correlate for the different resins as shown on Figure 4.9. This is probably due to the nature of the loads during ENF and T-Pull off testing. Pull-off testing is a mixed mode (between modes I and II) dominated test [24]. The high performance of the non-toughened epoxy System 41 for mode II and T-Pull off tests is again evident.

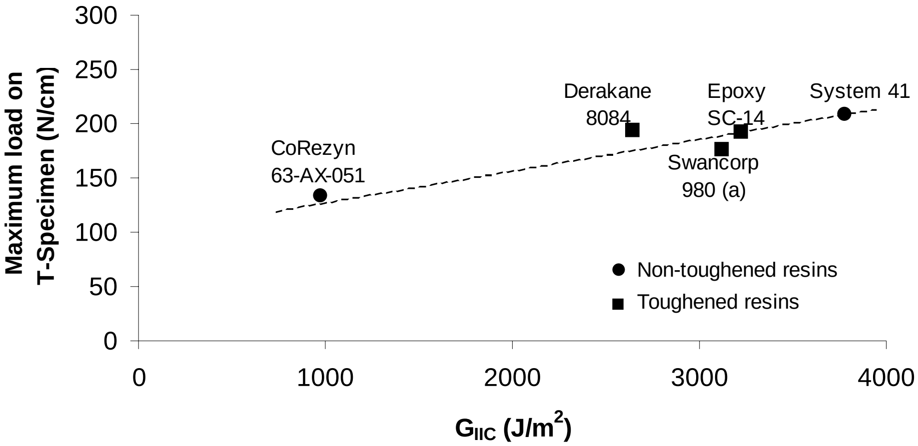


Figure 4.9 Comparison between Maximum load for Stiffener Pull off Tests and G_{IIC}.

Transverse Strength

The ultimate transverse strength (UTS) of a composite is dominated by the resin matrix. A layup of [0/±45/0]s was used with D155/DB120 fabrics. Tests were conducted by loading in the 90° direction, so that the dominant ply stresses were transverse tension in the 0 ° plies and shear and transverse tension dominated in the ±45 plies [24]. Results for different resins are shown in Table 4.9. Tensile results for Derakane vinyl ester resins using different fiber contents are shown in Table 4.10. Stress – strain diagrams for the resins studied can be seen in the Appendix. Figure 4.10 gives a typical stress-strain curves for different materials.

Table 4.9 Tensile results for [0/±45/0]s composite using different resins. Three specimens were tested for each resin. V_f is the fiber volume in %.

Resin	UTS MPa	Knee stress MPa	Tensile E GPa	Maximum % strain
CoRezyn 63-AX-051 37% V_f	73.75 (4.06)	29.47 (0.61)	10.42 (0.23)	2.97 (0.52)
Swancorp 980 (batch a) 36% V_f	107.40 (2.12)	52.10 (2.72)	6.91 (0.19)	3.81 (0.07)
Poly 15-D65 39% V_f	107.80 (13.03	38.47 (1.02)	5.56 (0.07)	4.54 (0.79)
System 41 42% V_f	113.70 (6.00)	60.47 (0.33)	11.63 (0.11)	3.39 (0.32)
SC-14 38% V_f	111.28 (6.91)	60.53 (0.97)	9.41 (0.07)	3.80 (0.67)

*(Std. Deviation)

Table 4.10 Tensile results for [0/±45/0]s composite using Derakane vinyl ester resins. Three specimens were tested for each fiber volume (V_f).

Resin	UTS MPa	Knee stress MPa	Tensile E GPa	Maximum % strain
Derakane 411C-50 39% V_f	56.32 (1.17)	36.20 (0.57)	9.31 (0.09)	4.44 (0.37)
Derakane 411C-50 35% V_f	59.11 (0.56)	46.37 (2.25)	8.22 (0.20)	3.94 (0.32)
Derakane 8084 39% V_f	65.09 (1.66)	43.50 (1.19)	9.11 (0.41)	4.49 (0.43)
Derakane 8084 35% V_f	62.97 (0.24)	44.16 (0.78)	8.35 (0.21)	4.10 (0.29)

*(Std. Deviation)

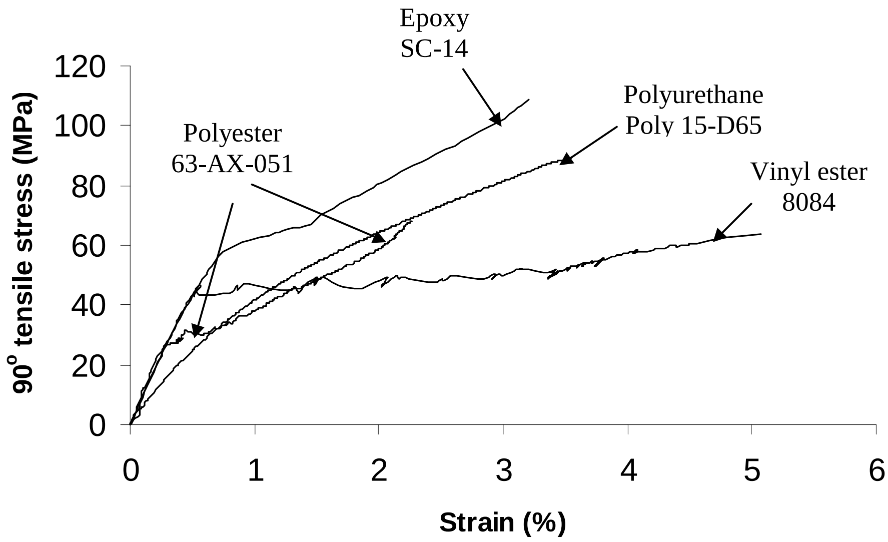


Figure 4.10 Stress-strain diagram for [0/±45/0]s composite with different resins.

Knee stresses were determined by a 0.2% strain offset technique described earlier. Knee stress is a more meaningful value than the ultimate tensile stress for a composite with no 0^o fibers. The knee stress occurs when the composite starts to matrix crack, while the UTS is recorded when the composite has failed. With no 0^o fibers, the knee stress is the limiting practical value for design [34]. Epoxy resins, System 41 and SC-14 had the highest knee stresses, twice as high as the Polyester 63-AX-051 which had the lowest knee stress of all the resins tested. Toughened vinyl esters Derakane 8084 and Swancorp 980 (a) had the second highest knee stresses. The polyurethane Poly 15-D65 had similar knee stresses to the untoughened Derakane 411C-50, apparently due to the low yield stress of the rubbery urethane matrix.

Toughened materials and the non toughened Derakane 411C-50 had higher tensile strain to failure than the CoRezyn. The polyurethane Poly 15-D65 had the highest transverse ultimate strength. The results show that toughened resins are more likely to have a lower transverse modulus but a higher UTS. Non-toughened and stiff resins such as CoRezyn 63-AX-051 and System 41 had higher transverse modulus than toughened thermosets. Epoxy SC-14 had the highest transverse modulus for a toughened resin. Most toughened resins show higher UTS than their non toughened base resin. High performance was observed in epoxy resins, with high transverse modulus, knee stresses and UTS. Delamination was observed on several sites in Polyester 63-AX-051 specimens, and some delamination was observed in Derakane 8084 and Epoxy SC-14 around the failure crack (Figure 4.11).

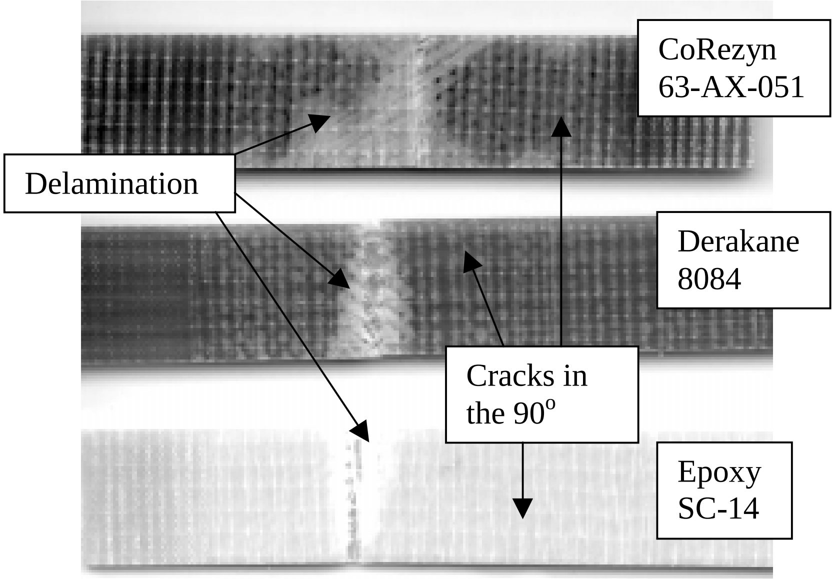


Figure 4.11 Tension specimens tested in the 90° direction.

Transverse tests on unidirectional $[0]_6$ and $(+45/-45)_3$ were carried out by Samborsky [35]. The transverse modulus for unidirectional specimens was predicted earlier in Equation 2.2. Experimental and predicted results can be seen on Figure 4.12.

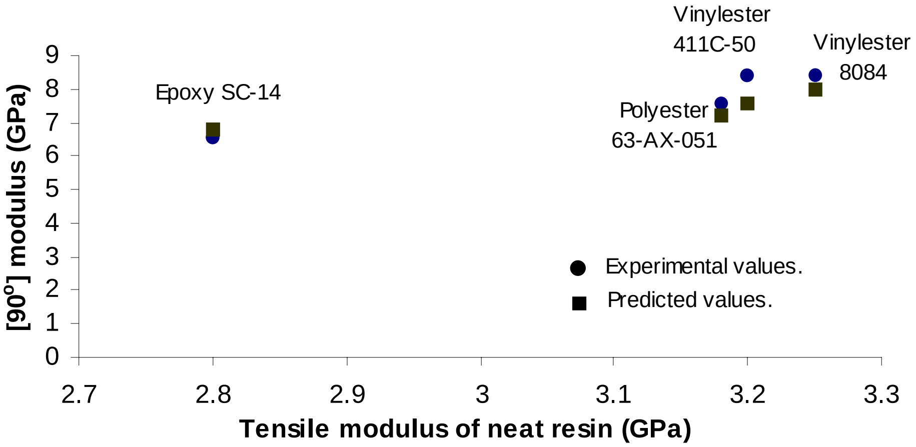


Figure 4.12 Experimental vs. predicted 90° Modulus for $[0]_6$ composite.

Predicted results were found using Equations 2.3. Good agreement with the experimental values can be seen. This indicates that, as predicted, the neat resin modulus dominates the composite transverse modulus.

A layup of $[0]_6$ was tested for resins: polyester 63-AX-051, vinyl esters 411C-50 and 8084 and epoxy Sc-14, while a layup of $[\underline{+}45]_3$ was tested on polyester 63-AX-051 and vinyl ester 8084 [35]. Tests were conducted by loading in tension transverse to the fibers in the 90° specimens, and the results are compared to the $[0/\underline{+}45/0]$s test results. Results and comparisons for the 90° tensile modulus and the 90° knee stress are shown on Figures 4.13 and 4.14 respectively.

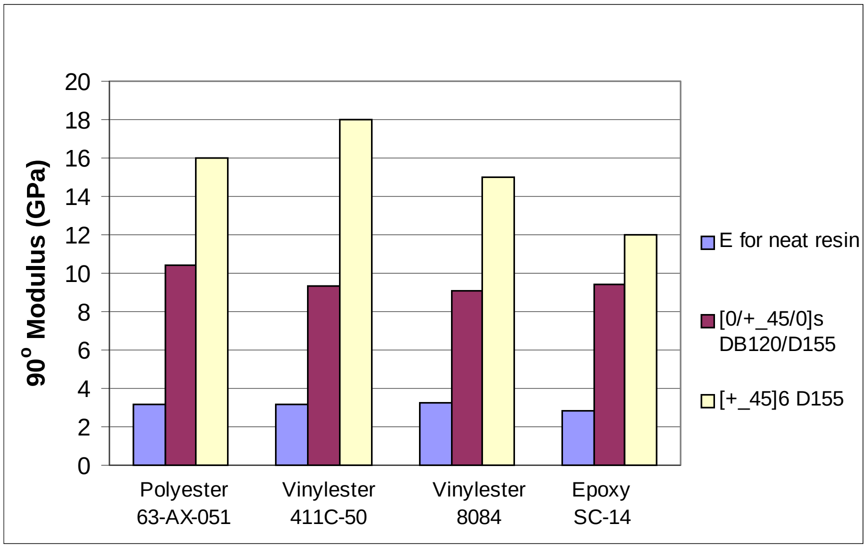


Figure 4.13 Modulus E, for neat resin and composites tested at 90° in tension.

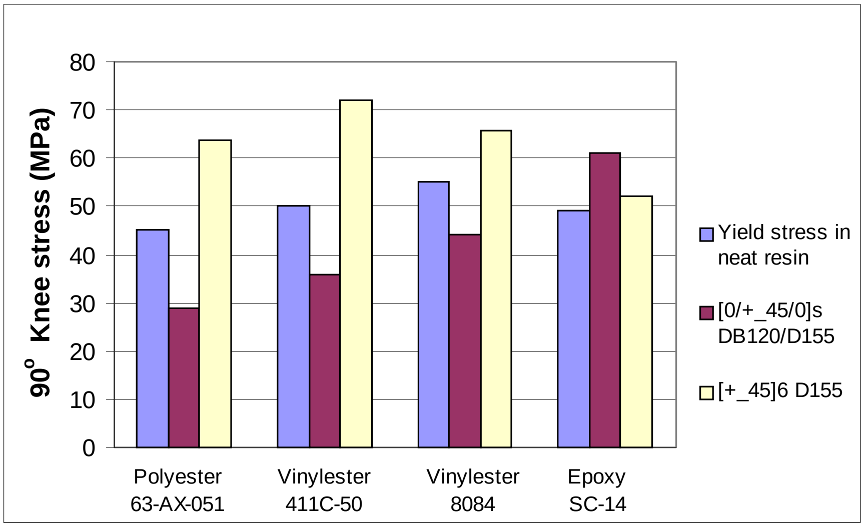


Figure 4.14 Knee stress for neat resin and composites tested at 90° in tension.

Similar moduli for the neat resin are observed in the four systems. Polyester had the highest transverse modulus for the [0/±45/0]s layup. Derakanes 411C-50, 8084 and the epoxy SC-14 showed similar transverse modulus with a [0/±45/0]s layup. Vinyl ester

411C-50 had the highest transverse modulus for a $(\pm45)_3$ layup, followed by the CoRezyn 63-AX-051. The epoxy SC-14 had the lowest transverse modulus for a $(\pm45)_3$ layup.

Derakane 8084 had the highest yield stress values for a neat resin, while epoxy SC-14 had the highest value for knee stress in [0/±45/0]s layups. The polyester had the lowest knee stresses for neat resin and for [0/±45/0]s composites. Derakane 411C-50 had the highest knee stresses and resin modulus for the $(\pm45)_3$ laminates.

Compressive Strength

Compressive strength in the 0^o direction is a critical property for wind turbine blades and is also a matrix dominated property [15]. Compressive strength results for the [0/±45/0]s composite loaded in the 0^o direction are compared with 90^o tensile knee stress and neat resin modulus for different resins in Table 4.11 and for different fiber volumes (V_f) using Derakane vinyl ester resins in Table 4.12.

Table 4.11 Results for [0/±45/0]s composite using different resins. Three specimens were tested for each type of resin.

Resin	Compressive 0^o Strength MPa	Tensile 90^o knee stress MPa	Neat resin E GPa
CoRezyn 63-AX-051 36% V_f	517.39 (29.24)*	29.47 (0.61)	3.18 (0.12)
Swancorp 980 (batch a) 36% V_f	420.37 (25.17)	52.10 (2.72)	1.63 (0.02)
Poly 15-D65 39% V_f	378.93 (24.25)	38.47 (1.02)	
System 41 39% V_f	567.80 (44.85)	60.47 (0.33)	3.57 (0.06)
SC-14 37% V_f	531.64 (10.71)	60.53 (0.97)	2.80 (0.03)

*(Std. Deviation)

Table 4.12 Results for [0/±45/0]s composite using Derakane vinyl ester resins. Three specimens were tested for different fiber volumes (V_f).

Resin	Compressive Strength MPa	Tensile 90° Knee stress MPa	Neat resin E GPa
Derakane 411C-50	451.36	36.20	3.21
39% V_f	(16.17)	(0.57)	(0.04)
Derakane 411C-50	572.39	46.37	
35% V_f	(21.19)	(2.25)	
Derakane 8084	461.60	43.50	3.25
39% V_f	(11.92)	(1.19)	(0.15)
Derakane 8084	541.45	44.16	
35% V_f	(39.21)	(0.78)	

As predicted by Eq. (2.3), higher neat resin modulus correlates with higher compressive strength. Rubbery polyurethane and Swancorp 980 (a) showed the lowest compressive strengths. The Derakane resins processed in different molds with different fiber contents show significant differences in compressive strength which are not understood at this time. The higher values at 35% fiber are probably more representative, with some unknown problem evident in the 39% tests. Compressive strength should not be that sensitive to fiber content [14]. The matrix plays an important role in compressive failure. As discussed earlier, a compressive load can not be supported by the fibers themselves. Figure 4.15 Compares experimental compressive strength with predictions from Eq. 2.3. In both results, experimental and predicted, it was found that increases in modulus of the resin corresponded to increases in compressive strength of the composite. Predicted values were a factor of 3.5 higher than the experimental results. This model, which assumes perfectly straight fibers is expected to provide a high estimate of compressive strength by a factor of 2 to 4 [14]. Since the prediction does not include ± 45 layers, it is expected to be further increased relative to the laminate tested.

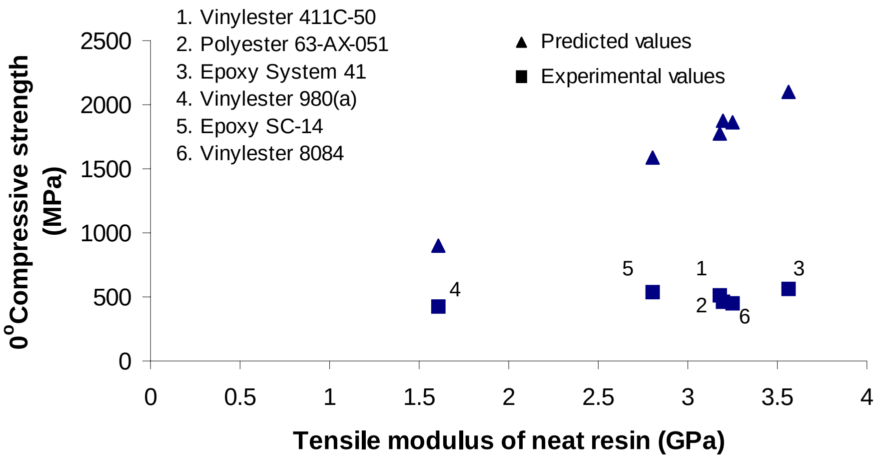


Figure 4.15 Experimental values for [0/+45/0]s versus predicted compressive strength for the 0° layers alone.

Toughness vs. Other Mechanical Properties

It is accepted that the toughening of a resin usually degrades its yield strength, modulus and T_g [5,7,20,26]. It is shown in Figure 4.16 that increases in G_{IC} of a resin are associated with decreases in the composite transverse modulus, which is dominated by matrix modulus. Figures 4.17 compares G_{IC} test (b) values and 0° compressive strength of [0/+45/0]s laminates. Again reflecting matrix modulus effects, increases in G_{IC} for the tested thermoset resins correlate to moderate decreases in compressive strength. Current results indicate that interlaminar fracture toughness increases at the expense of some mechanical properties. However, as noted earlier, the 90° tensile knee stress is generally increased by toughening the resin. Finally, the main reason for toughening the resin is to increase the structural integrity, and T-section pull off tests in Figure 4.9 demonstrate a significant improvement for toughened resins with the exception of untoughened System

41, which inherently has a high G_{IIC}.

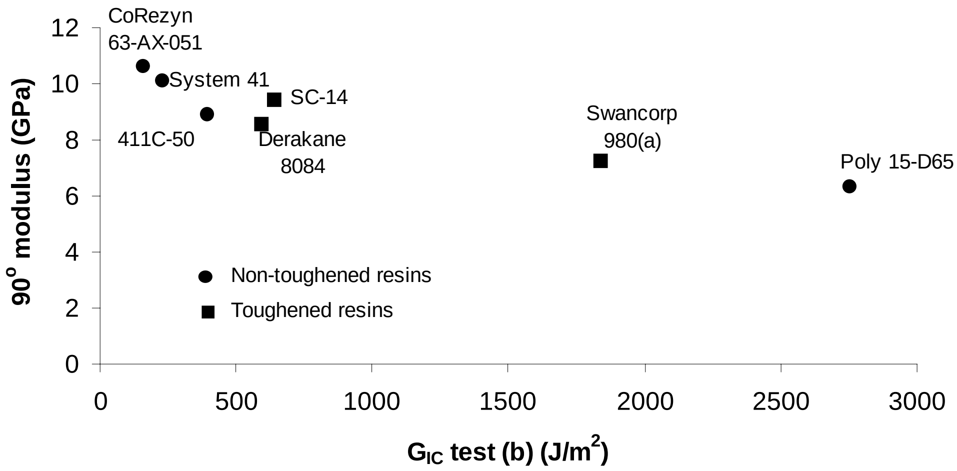


Figure 4.16 90° Modulus vs. G_{IC} for [0/±45/0]s composite.

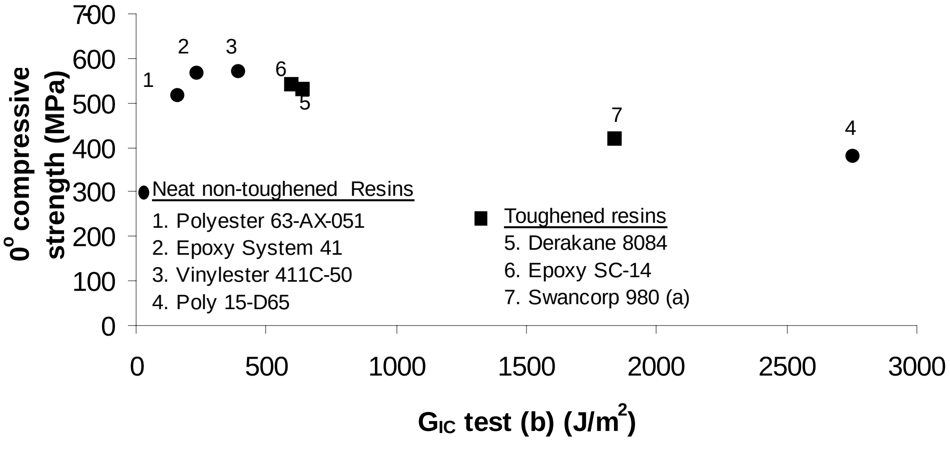


Figure 4.17 0° Compressive strength vs. G_{IC} for [0/±45/0]s composite.

Moisture Effects on Mechanical Properties

Earlier results showed that the toughened vinyl esters decrease slightly in heat deflection temperature relative to untoughened vinyl esters. [0/±45/0]s composite specimens were also soaked in water for 330 hours at a temperature of 50 °C and tested at 20°C while still wet. . Transverse tension and 0° compression tests were performed on specimens before and after water exposure. Results for 90° modulus, 90° tension, 0°compression and 90° knee stress are shown in Figures 4.18, to 4.21 respectively. Polyester resin CoRezyn 63-AX-051 had a decrease of 15 % in its 90° modulus and 0°compressive strength, while the 90° tensile strength was unaffected (it should be noted that longer term conditioning has produced more significant reductions for this resin [35]). Swancorp 980 (a) resin was less moisture sensitive, with decreases of around 5 % in its 90° modulus and tensile strength; its 0°compressive strength was unaffected.

The polyurethane Poly 15-D65 was the most moisture sensitive resin. It had a decrease of almost 50% in its 90° modulus while its 90° tensile and 0° compressive strengths decreased 26 and 29%, respectively. T_g for Poly 15-D65 (and most urethanes) is below 0 °C, which reduces the performance at room and elevated temperatures. For the epoxy System 41, the 90° modulus and 90° tension strength values decreased 12%, while 0°compressive strength decreased 5%.

The polyurethane resin mechanical properties decreased almost 10 times more than did those of the vinyl ester resin. Overall, Swancorp 980 is the least moisture sensitive resin. Epoxy and polyester resins behave similarly. Their mechanical properties were decreased three times more than for the Swancorp 980, when subjected to moist conditions. (More extensive hot/wet results for many of the resins tested in this study can be found in Reference [13]). Knee stresses were not significantly reduced for most resins, except for the Poly 15-D65, which had a reduction of around a 30% in the knee stress after water absorption.

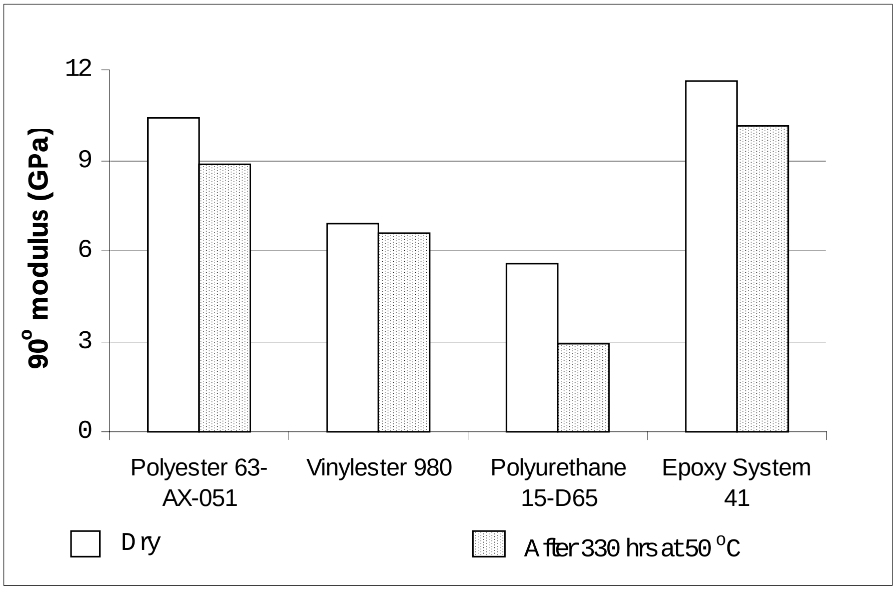


Figure 4.18 90° Modulus for wet and dry [0/±45/0]s composite tested at room temperature.

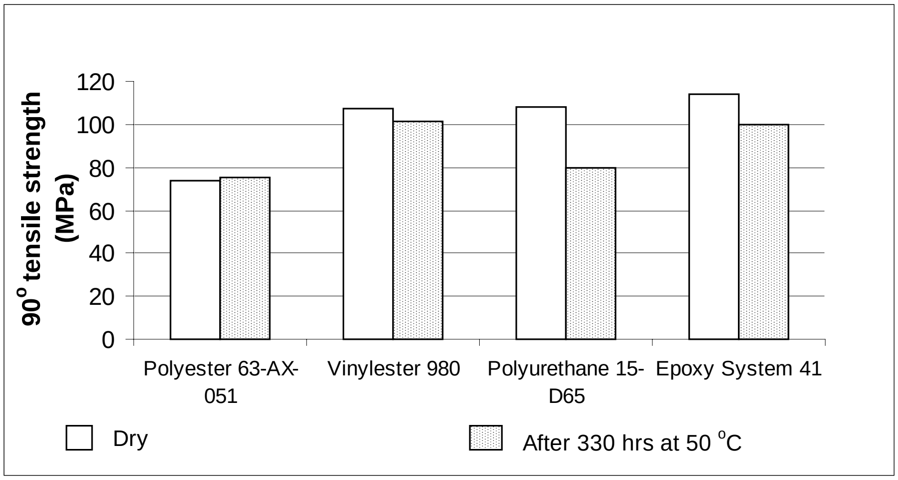


Figure 4.19 90° tensile strength for wet and dry [0/±45/0]s composite tested at room temperature.

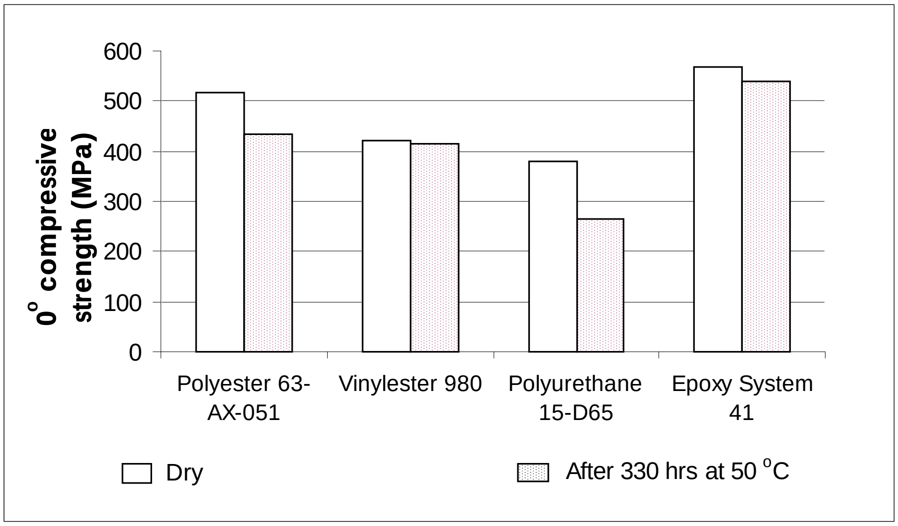


Figure 4.20 0° Compressive strength for wet and dry [0/±45/0]s composite tested at room temperature.

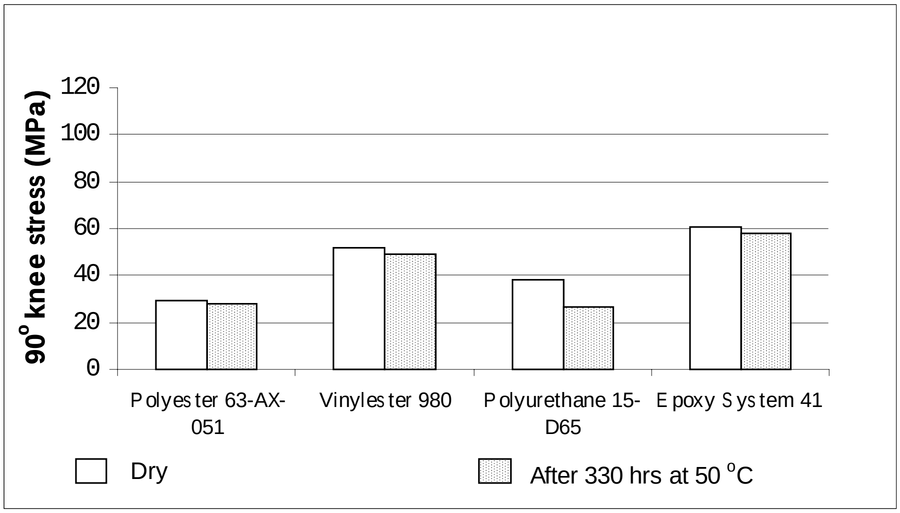


Figure 4.21 90° Knee stress for wet and dry [0/±45/0]s composite tested at room temperature.

Water Absorption

Water absorption was measured on cured pure resin specimens and composite. Results for water absorption of pure resin and composite for specimens soaked for 300 hours at 50 °C are shown on Table 4.13. Vinyl ester resins absorbed less water for neat resin and composites, followed by the polyester resin. Derakane 8084 absorbed 25 % less water for neat resin and 13 % less for the composite than did polyester. Swancorp 980 absorbed 64 % less water for neat resin and 56% less for the composite than the polyester.

Table 4.13 Water absorption (% weight gain) for and average of 3 specimens of neat resin and [0/±45/0]s composite specimens.

Resin	Neat resin (% weight gain)	Composite (% weight gain)
Polyester		
CoRezyn 63-AX-051	1.41	0.47
Vinyl esters		
Derakane 411C-50	0.84	*0.35
Derakane 8084	1.06	*0.41
Swancorp 980	0.51	0.21
Epoxies		
System 41	2.51	0.83
**SC-14	1.85	1.22
Polyurethane		
Poly 15-D65	2.25	0.87

(*) Tests performed by Li [13] on $[0]_6$ composite specimens.

Epoxy resin System 41 absorbed the highest amount of water for neat resin, 77% more water than for the polyester, and Epoxy SC-14 absorbed the most water for a composite, 159 % more water than for the polyester. Polyurethane 15-D65 resin is also very moisture sensitive, it absorbed 60% more water for the neat resin and 85% more water for the composite than did the polyester. The polyurethane resin absorbed similar amounts of water to the epoxy resins, but its mechanical properties were decreased much more after water absorption, apparently due to low T_g values.

Resin Pricing and Overall Comparisons

Resin Pricing

Prices of resins vary greatly and a comparison is given here for vendor quotes for 40,000 lb lots in Spring, 1999. Price comparison between different polyester, vinyl ester and epoxy resins is shown in Figure 4.22. Polyester resins have the lowest prices of the resins used, while vinyl ester and the urethane prices are in between epoxies and polyester resins. Epoxy resins had similar prices and also the highest prices of all the resins tested. System Three and Applied Poleramic companies use non-toughened epoxies from Dow Chemical and Shell as the resin base for their products. Additives to increase mechanical properties are included in the resin which increases the price of the epoxy base resin from average prices of 1.75 $/lb to an average of 2.8 $/lb. Different prices can be seen for the non toughened Derakane resin 411C-50 and the rubber modified Derakane 8084, the second one being more expensive because of its additive content to increase toughness performance.

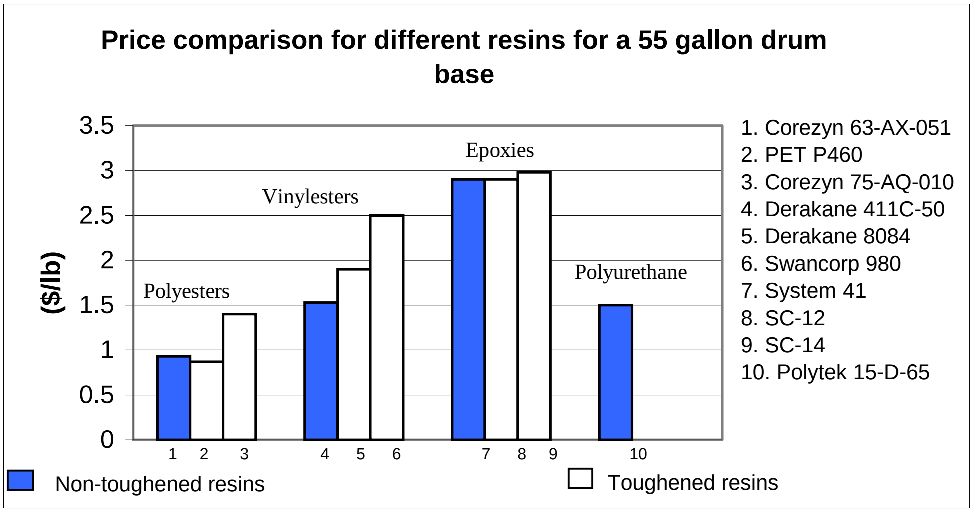


Figure 4.22 Resin prices for a 40,000 lbs estimation.

Overall Comparisons

Figures 4.23 to 4.26 show prices and mechanical property comparisons of the baseline polyester CoRezyn 63-AX-051 with the other polyesters, vinyl esters, epoxies and polyurethanes, respectively. Price and results for each mechanical test were divided by the CoRezyn values in order to compare them. It is shown on Figure 4.23 that the other two polyester resins had higher G_{IC} values than the base polyester. G_{IIC} values were almost twice as high for the PET P460 but the Arotran Q6038 G_{IIC} values were almost four times lower than for the baseline polyester resin. Derakane vinyl ester 411C-50 has a higher cost compared to polyester prices. It costs 50 cents per pound more than the CoRezyn but it was twice as tough in both delamination modes. Derakane 8084 costs one dollar per pound more than the polyester but is almost four times tougher. Swancorp 980 rubber modified vinyl ester resin is more than 2.5 times more costly than CoRezyn but is also more than 11 times tougher. Its G_{IIC} values were not very high compared to the Derakane values but at least 3 times higher than the CoRezyn. (Figure 4.24)

Epoxy resin results compared with CoRezyn are displayed on Figure 4.25. Prices for epoxy resins were almost three times higher than the CoRezyn. System 41 epoxy resin did not show a significant increase in G_{IC} compared with the CoRezyn but its G_{IIC} value and T-pull off resistance were the highest of all resins. Epoxy SC-14 had the highest G_{IC} value for epoxy resins, four times higher than for the CoRezyn. System 41 and SC-14 epoxies had similar compressive strengths with a higher knee stresses than the CoRezyn.

The CoRezyn polyester has a low toughness compared to the other resins tested, but it offered similar compressive strength to most resins at a very reasonable price. The polyurethane Poly 15-D65 had a superior toughness compared with all resins used at a relatively low price with a G_{IC} value seventeen times greater than the CoRezyn, but its 0° compressive strength and 90° composite modulus were the lowest of all resins (Figure 4.15). Its G_{IIC} value could not be determined because the specimen failed in compression, and the value given in the results is an estimate of G_{IIC} using the maximum compressive load. The urethane has too low of a compressive strength for use in wind turbine blades (Figure 4.26).

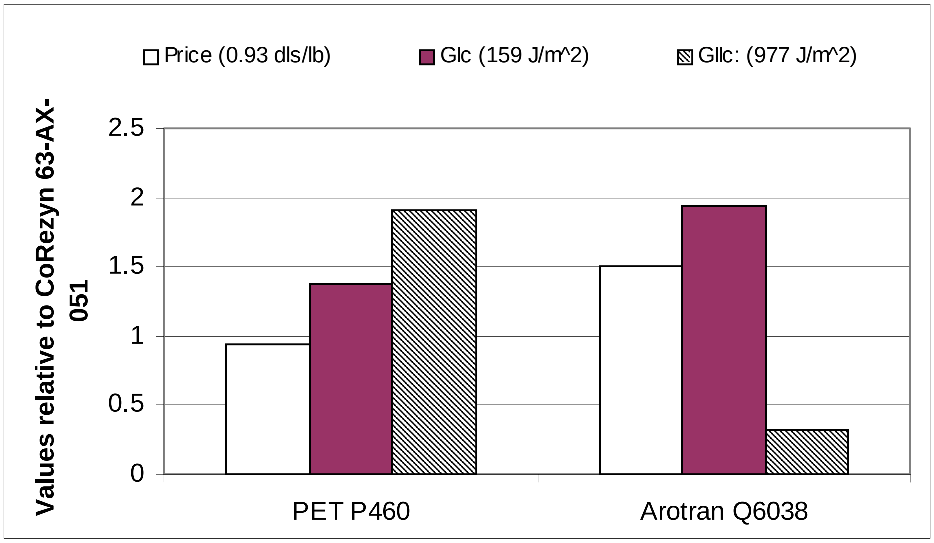


Figure 4.23 Comparison between polyester resins studied and the CoRezyn 63-AX-051 whose values are in ( ).

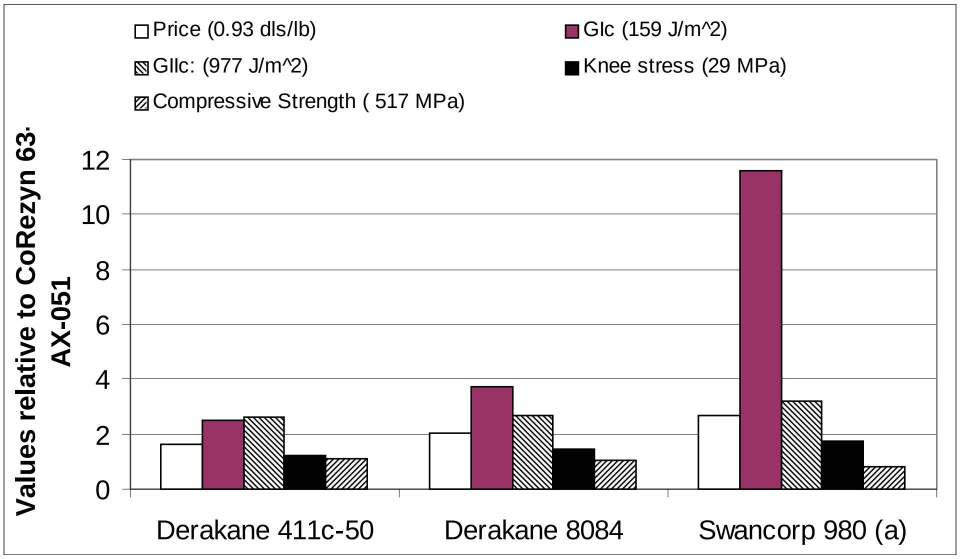


Figure 4.24 Comparison between vinyl ester resins studied and the CoRezyn 63-AX-051, whose values are in ( ). Derakane compressive strength are for the 35 % fiber batch.

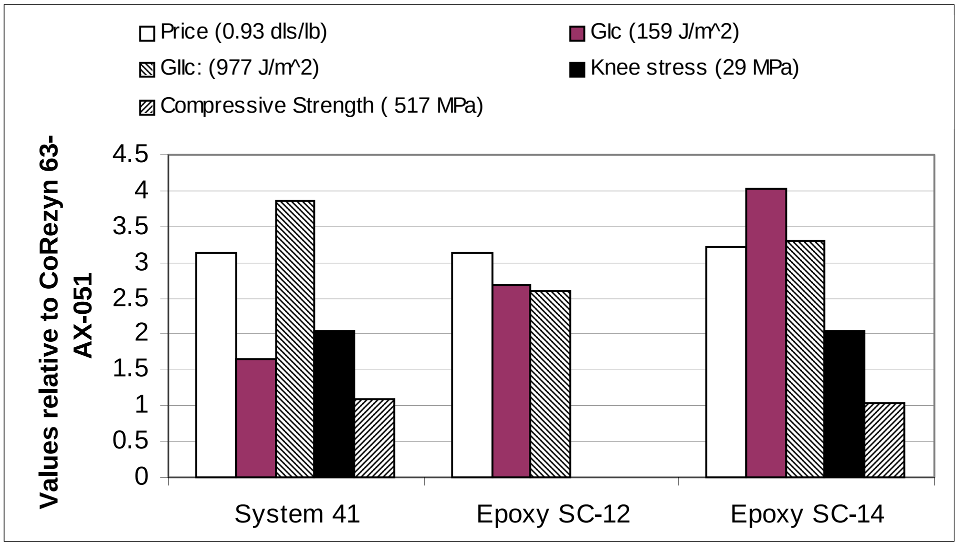


Figure 4.25 Comparison between epoxy resins studied and the CoRezyn 63-AX-051 whose values are in ( ).

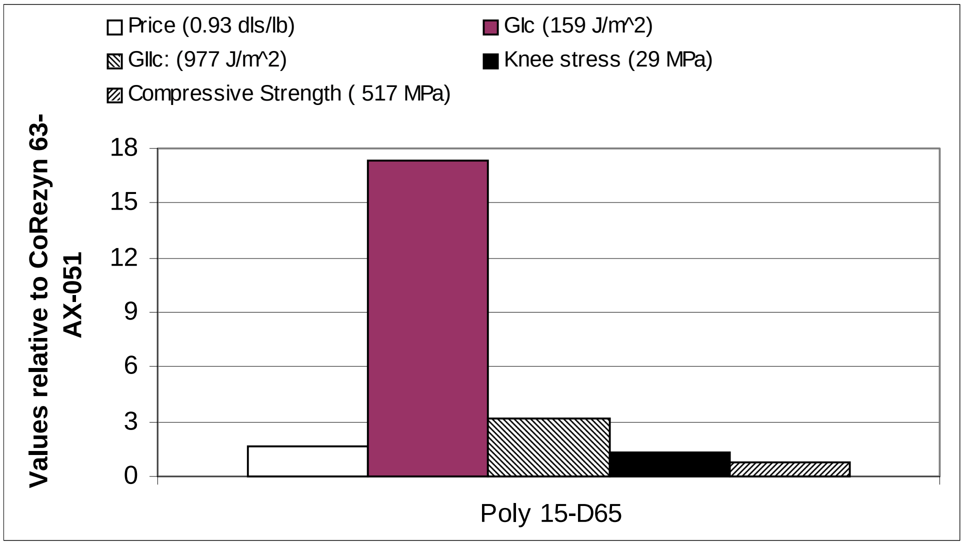


Figure 4.26 Comparison between urethane resin studied and the CoRezyn 63-AX-051 whose values are in ( ).

Processing Observations

The polyester and vinyl ester resins tested had similar low viscosities (100 to 200 cp) which made them relatively easy to process by RTM and to wet out fibers by injecting at moderate speeds. The epoxy resins had higher viscosities, on the order of 500 cp, which requires lower speed injection to decrease the probability of void formation and fiber wash out. The polyurethane resin had the lowest viscosity (50 to 80 cp), which made it easy to inject, but a disadvantage was that it developed porosity while curing. Anti-porosity forming agents are available for Poly 15 polyurethane series, which were not used because they can potentially accelerate the already rapid curing process and reduce the available injection time. For this study, most of vinyl ester resins needed to be promoted as discussed in Chapter 3 which is not very convenient since the user is exposed to promoter chemicals. These can be supplied in promoted form if required as was one Derakane 8084 batch. It is important to add the proper amount of promoter, CoNap, according to the amount of Trigonox catalyst to be used (Table 3.1). If this is not followed, improper curing may result.

Vinyl ester resins, especially Swancorp 980, shrink more than any other resin cured. Molded parts such as flat plates experienced a slight deflection, therefore it is recommended to de-mold them before applying heat to post-cure them. Combined stresses generated on the mold glass plate by the shrinkage and thermal expansion coefficient differences relative to the glass represent a potential risk of breaking the mold glass (this is a special problem for the molds used in this study). Toughened epoxy resins required the most time to cure. System 41 required from 15 to 20 hours to cure but Epoxy resins SC-12 and SC-14 required at least 3 days at room temperature to start gelling. For these two epoxies the better way to cure them was by heating from 3 to 4 hours at 60 °C to accelerate the curing process. Higher temperatures will degrade gaskets and cause thermal expansion problems. Once heat is applied to the resin, the plate can then be demolded and postcured following the resin curing cycles (Chapter 3). It is recommended to apply mold release agent on the rubber gaskets used for SC-12 and SC-14 epoxies since they bond to the gasket when curing. Mold release agents for each resin work better when applied six hours or more in advance of molding.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Several potential wind turbine blade resins differing in properties and cost have been evaluated in terms of their effects on composite laminate delamination resistance, matrix dominated mechanical properties, integrity of skin/stiffener substructure, environmental resistance and processing characteristics. Relative to the baseline polyester resin, most resins showed improved delamination resistance and transverse composite strength properties, while maintaining the desired level of compression strength and modulus. Several resins also showed improved temperature and moisture resistance. Two of the toughest resins, a toughened vinyl ester and a urethane, did not have the requisite modulus and temperature resistance for the wind turbine blade application. However, several resins did provide significantly improved properties over the baseline polyester at moderate increases in cost.

In general, the orthophthalic polyesters showed lower cost, the lowest toughness and structural integrity, and low temperature resistance with significant moisture sensitivity. The primary mechanical properties of the polyesters were adequate for wind turbine blades at moderate temperatures. The vinyl esters provided significant improvements in toughness, increased temperature and moisture resistance and adequate strength and modulus properties, thus providing a compromise in properties and cost. Epoxy resins showed the best strength and toughness properties and improved temperature resistance, but were sensitive to moisture and had the highest costs and processing difficulties. The urethane was very tough, but did not have adequate modulus, temperature or moisture resistance.

The effects of changes in matrix stress-strain properties on composite properties followed expected trends. More ductile resins provided greater delamination resistance and structural integrity in the composites. Reductions in matrix modulus resulted in reduced composite modulus in the transverse direction as well as reduced compressive strength in the fiber direction. Resins with the greatest ductility also showed significant reductions in modulus and temperature resistance, including cases where relatively brittle base resins were modified to increase toughness. Modified resins were also more costly than unmodified resins. Resin moisture sensitivity correlated with composite moisture sensitivity. Non-toughened vinyl ester and epoxy resins showed significant improvements in mode II toughness over the baseline polyester, which also improved the structural integrity of skin-stiffened sections.

In terms of the best way to screen matrix materials, the results of this study lead to several conclusions. If the neat resin can be tested, the stress-strain, heat deflection temperature, and moisture sensitivity data correlate well with the various composite properties determined in this study, as noted in each section. Critical composite tests are G_{IC} and G_{IIC} and compressive strength. The structural integrity of the stiffened skin section correlated well with G_{IIC}. Knee stress in an off-axis tension test is a good indicator of matrix modulus (if not available) and general off-axis, matrix dominated tensile strength properties (which depend on matrix strength, ductility, and bonding to fibers). Off-axis tests such as ±45° are more convenient to run than are 90° tests on unidirectional materials.

Specific conclusions for each type of resin are as follows:

1. Polyester Resins. The baseline resin, CoRezyn 63-AX-051, was brittle, resulting in poor delamination resistance, low transverse knee stress, and poor structural integrity. However, its elastic modulus was high enough to provide adequate compressive strength. The temperature resistance was not sufficient for many applications and it was moisture sensitive. Relative to the baseline resin, the polyester PET P460 showed slight increases in mode I toughness, and greater increases in mode II toughness and skin-stiffener maximum loads at a lower price than the CoRezyn. The polyester Arotran Q6038 showed significant increases in mode I, toughness but its mode II toughness was much lower than the baseline polyester. Other disadvantages of the Arotran Q6038 where it higher cost and its high exothermic reaction while curing, which caused some processing difficulties.
2. Vinyl ester Resins. Swancorp and Derakane vinyl ester resins showed improvements in toughness, especially the toughened versions. Swancorp 980 batch (a) had a much higher toughness in mode I and the highest tensile knee stress for vinyl ester resins, but a lower modulus than is acceptable for wind turbine blades. This resin also showed significantly different results for mode I toughness and resin

modulus in a later batch (b). Resin toughness was increased in the brittle Swancorp 901 base resin by mixing it with the 980 batch (b) resin with minor changes in resin modulus. For Derakane resins, the 8084 showed a higher value for mode I toughness than the 411C-50, but they had similar modulus, mode II toughness, knee stress and compressive strength values, all higher than the baseline polyester. Costs for Derakane resins were moderately higher than for the baseline polyester. It is not clear whether the added cost of 8084 over 411C-50 is warranted considering the small improvement in properties. Some tests including skin-stiffener integrity were not run for the 411C-50. All vinyl ester resins showed a good resistance to moisture effects, with the Swancorp 980 the least moisture sensitive. Their room temperature mechanical properties remained almost constant after water absorption for 330 hours at 50^{o}C. Heat deflection temperature was improved for Derakane resins over the baseline polyester.

3. Epoxy Resins. Non toughened System 41 showed a stiff but brittle behavior. Its mode I toughness value was not significantly higher than for the baseline polyester, but it had the highest mode II toughness and initial damage load in skin-stiffener tests of all the resins tested. Its tensile knee stress and compressive strength were similar to those for the toughened SC-14 resin, which had a much higher mode I toughness. The toughened SC-12 resin had lower mode I and II toughness values than SC-14 resin, similar to the non-toughened 411C-50 vinyl ester, but significantly higher than the baseline polyester. Batch SC epoxy resins showed a stiff and tough behavior. Epoxy resin System 41 absorbed the most percent weight of water, but its

mechanical properties were not substantially reduced after water exposure as they were for other resins. Epoxy SC-14 had the highest water absorption value for composites.

4. Polyurethane. The polyurethane Poly 15-D65 showed a very ductile behavior. It had the highest mode I toughness and maximum load for skin-stiffener specimens, but the lowest composite modulus and compressive strength. Its price is significantly higher than for the polyester, and it was the most environmentally sensitive resin. Its mechanical properties were greatly reduced after water exposure. This resin is not appropriate for wind turbine blades.

Recommendations

Polyester resins are commonly less costly, so it is recommended to seek other toughened unsaturated orthophthalic polyesters with increased moisture and temperature resistance at moderate cost and to study isophthalic polyesters which are known for increased mechanical, thermal, and environmental properties. Other non-toughened vinyl ester resins and blends of Derakanes 411C-50 and 8084 should also be considered due to their reasonable cost, good properties and low environmental sensitivity. It is also recommended to explore neat epoxy resins with lower prices and no additives included to compare their mechanical performance with the baseline polyester. Thermoplastic resins might be added to the list if manufacturing methods which allow high resin viscosity are considered. The comparison of different resins in this study might be affected by the general purpose coupling agent used with the reinforcement. Specific coupling agents for, say, vinyl ester resins might provide improved transverse strength and structural integrity.

Resins which have received favorable ratings in the screening tests used in this study should be subjected to more intensive testing. The vinyl esters such as Derakane 411C-50 and 8084 appear to be strong candidates for wind turbine blades. They should be tested more intensively, including elevated temperature testing, fatigue under various loading conditions, and performance in substructural elements like beams as well as small blades. Only then can the full potential as a replacement for the baseline polyester be judged. It is possible that improved properties could reduce blade weight, more than offsetting the increased resin costs.

REFERENCES CITED

1. Mandell, J.F., Samborsky, D.D., "DOE/MSU Composite Material Fatigue Database: Test Methods, Materials, and Analysis," Sandia National Laboratories Contractor Report, SAND97-3002. December 1997.

2. Hunston, D.L., Johnston, N.J., "Matrix Resin Effects in Composite Delamination: Mode I Fracture Aspects," *Toughened Composites, ASTM STP 937, American Society for Testing and Materials,* Philadelphia, 1987, pp. 74-114.

3. Volume II, "Engineered Plastics," *ASM International, Engineered Materials Handbook,* November 1988, pp. 240-292.

4. Valenti M "Resin transfer molding speeds composite making", *Mechanical Engineering - CIME,* November 1992, Vol. 114, No. 11, pp. 46-49.

5. Astrom, B.T., "Manufacturing of Polymer Composites," *Department of Aeronautics, Royal Insitute of Technology,* Chapman & Hall, 1997, pp. 1-175.

6. White, D.W., Puckett, P.M., "Resin Systems and Applications for Resin Transfer Molding" *The Dow Chemical company U.S.A, Freeport, Texas,* pp. 1-5.

7. Kinloch, A.J., Young, R.J. "Fracture Behaviour of Polymers," *Elsevier Applied Science Publishers,* 1988, pp. 1-181.

8. Li, M., "Environmental Effects on Composites Materials," Master's Thesis in Chemical Engineering, Montana State University-Bozeman, to be published.

9. Turi, E.A. "Thermal Characterization of Polymeric Materials," *Corporate Research and Development, Allied Corporation,* Academic Press, New York, 1981, pp. 92-563.

10. Mallick, P.K., "Fiber Reinforced Composites: Materials, Manufacturing, and Design," Department of Mechanical Engineering, University of Michigan-Dearborn, Michigan, Marcel Dekker Inc., New York, 1988.

11. Hong, X.C., Wing., Y.M., "The Effects of Particle Bulk Modulus on Toughening Mechanisms in Rubber-Modified Polymers," *Polymer Engineering and Science,* October 1998, Vol. 38 I10, pp. 1763-1769.

12. "Tutorial on Polymer Composite Molding," *Developed by The Intelligent Systems Lab under the Technology Reinvestment Program,* http://islnotes.cps.msu.edu/trp/index.html, Michigan State University, 1999.

13. “Fabricating Tips: Derakane Epoxy Vinyl Ester Resins” *Dow Plastics, a business group of The Dow Chemical Company* , Form No. 125-00082-196 SMG, Revised Edition October 1994, pp.16-25.

14. Swanson, S.R. “Introduction to Design and Analysis with Advance Composite Materials,” *Department of Mechanical Engineering, University of Utah, Salt Lake,* Prentice Hall, Ed., 1997, pp. 29-101.

15. Agarwal, B.D., Broutman, L.J.,“Analysis and Performance of Fiber Composites,” *Second Edition, Wiley Interscience*, 1990, pp. 55-113.

16. Hanks, R.W., “Materials Engineering Science: An Introduction,” *Brigham Young University,* Harcourt, Brace & World, Inc. 1970, pp. 3-14.

17. Strong, B.A., “Plastics: Materials and Processing,” *Brigham Young University,* Prentice Hall Ed., 1996, pp.211-235.

18. Blankenship, L.T., White, M.N., Puckett, P.M., “Vinyl Ester Resins: For Composites,” *Dow Chemical U.S.A, Freeport, Texas,* pp. 1-36.

19. Huang, D.D. “Applying fracture Mechanics to material selection,” *Plastics Engineering, 1996 Society of Plastics Engineers Inc.,* June 1996, Vol. 52, No. 6, pp. 37-40.

20. “Fracture toughness” *Guidelines for Characterization of Structural Materials,* Military Hand Book 17-1, Section 6.7.7.

21. Davies, P., Benzeggagh, M.L., “Chapter 3, Interlaminar Mode-I Fracture testing,” *Application of Fracture Mechanics to Composite Materials,* K. Friedrich, Ed., 1989, pp.81-112.

22. Aliff, N., Carlsson, L.A., Gillespie, J.W.,“Mode I, Mode II, and Mixed Mode Interlaminar Fracture of Woven Fabric Carbon/Epoxy,” *Composite Materials: Testing and Design, Thirteen Volume,* ASTM STP 1242, S.J. Hooper, Ed., American Society for Testing and Materials, 1997, pp. 82-106.

23. “Standard test Method for Mode I Interlaminar Fracture toughness of Unidirectional fiber-Reinforced Polymer Matrix composites, D5528 – 94a”, *1997 Annual Book of ASTM Standards,* Vol. 15.03, 1997, pp. 271-279.

24. Haugen, D.J. “Fracture of Skin-Stiffener Intersections in Composite Wind Turbine Blade Structures,” Master’s Thesis in Mechanical Engineering, Montana State University-Bozeman, August 1998.

25. Hunston D.L., “Characterization of Interlaminar Crack Growth in Composites with the Double Cantilever Beam Specimen,” *National Bureau of Standard, Polymers Division,* Washington, D.C., 1985, pp. 2-28.

26. Bradley, W.L., “Chapter 5, Relationship of Matrix Toughness to Interlaminar Fracture Toughness,” *Application of Fracture Mechanics to Composite Materials,* K. Friedrich, Ed., 1989. pp. 159-187.

27. Russell, A.J., Street, K.N., “Factors affecting the Interlaminar Fracture Energy of Graphite/Epoxy Laminates,” *Progress in Science and Engineering of Composites,* ed. Hayashi, T, Kawata, K., and Umekawa, S., ICCM IV, Tokyo, 1982, pp. 27.

28. Mandell, J.F., Tsai, J.Y., “Effects of Porosity on Delamination of Resin Matrix Composites,” *Department of Materials Science and Engineering, Massachusetts Institute of Technology,* Massachusetts 02139, April, 1990, pp. 8-10.

29. Scott, M.E., “Effects of Ply Drops on the Fatigue Resistance of Composite Materials and Structures,” *Master’s Thesis in Chemical Engineering, Montana State University-Bozeman,* August 1997.

30. “Standard test Method for Deflection Temperature of Plastics Under Flexural Load, D 648 – 82”, *ASTM Standards and Literature References for Composites Materials,* First Edition 1987, pp. 272-278.

31. Ullett, J.S., Chartoff, R.P. “Toughening of Unsaturated Polyester and Vinyl Ester Resins With Liquid Rubbers,” *The Center for Basic and Applied Polymer Research, University of Dayton. Dayton, Ohio.* Polymer Engineering Science, July 1995, Vol. 35, No. 13, pp. 1086-1096.

32. Babbington, D., Barron, J., Enos, J., Ramsey, R., Preuss, W., “Evolution of RTM with Vinyl Ester Resins,” *How to Apply Advanced Composites Technology, Fourth Annual Conference on Advanced Composites,* Dearborn, Michigan, ASM International, September 1988, pp. 269-280.

33. Flinn, R.A., Trojan, P.K., “Engineering Materials and Their Applications,” *Third edition, Hughton Mifflin,* 1986, pp.61-103.

34. Krock, R.H., Broutman, L.J., “Principles of Composites and Composite Reinforcement,” *Addison-Wesley Series in Metalurgy and Materials,* Addison Wesley, 1967, pp. 365-371.

35. Samborsky, D., Master Thesis in Civil Engineering at Montana State University-Bozeman, to be published in December 1999.

APPENDIX

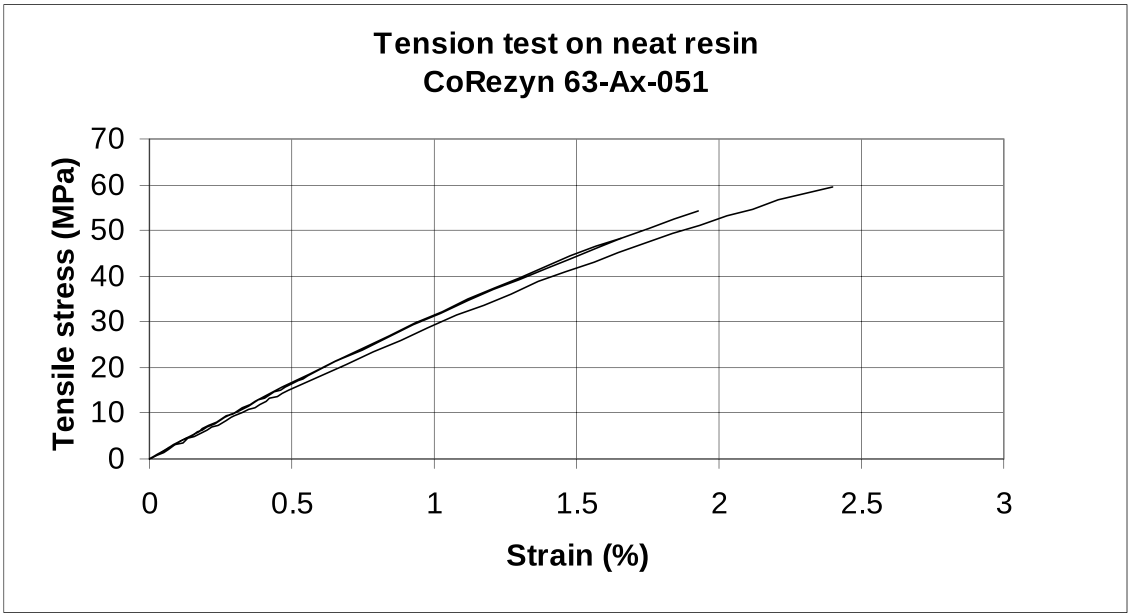
Individual Test Results

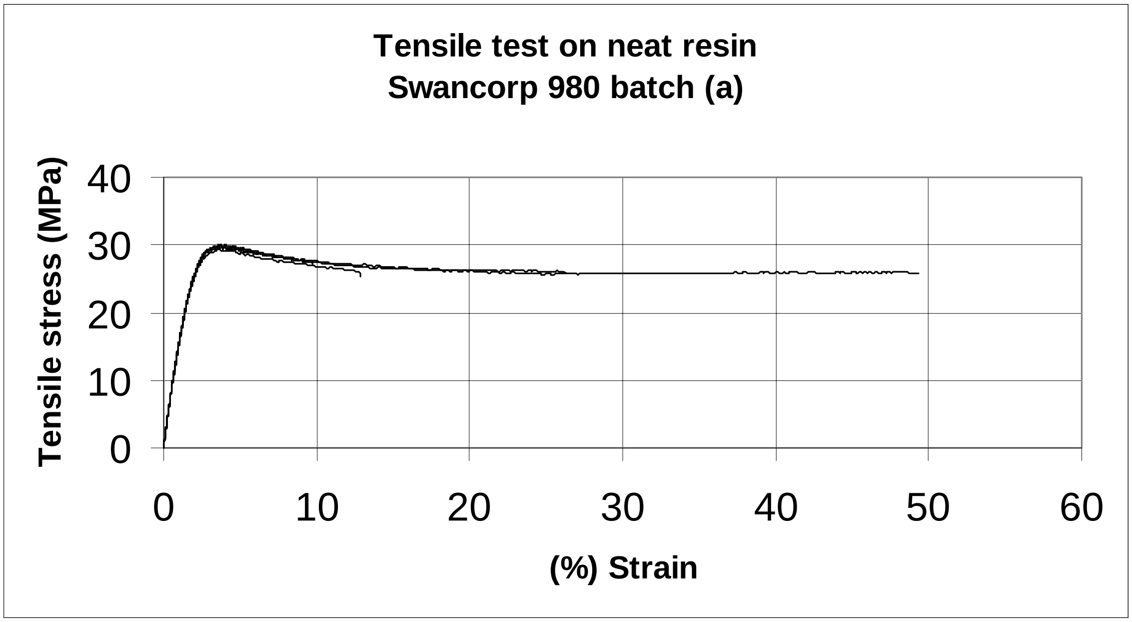
Tensile test results for neat resin.

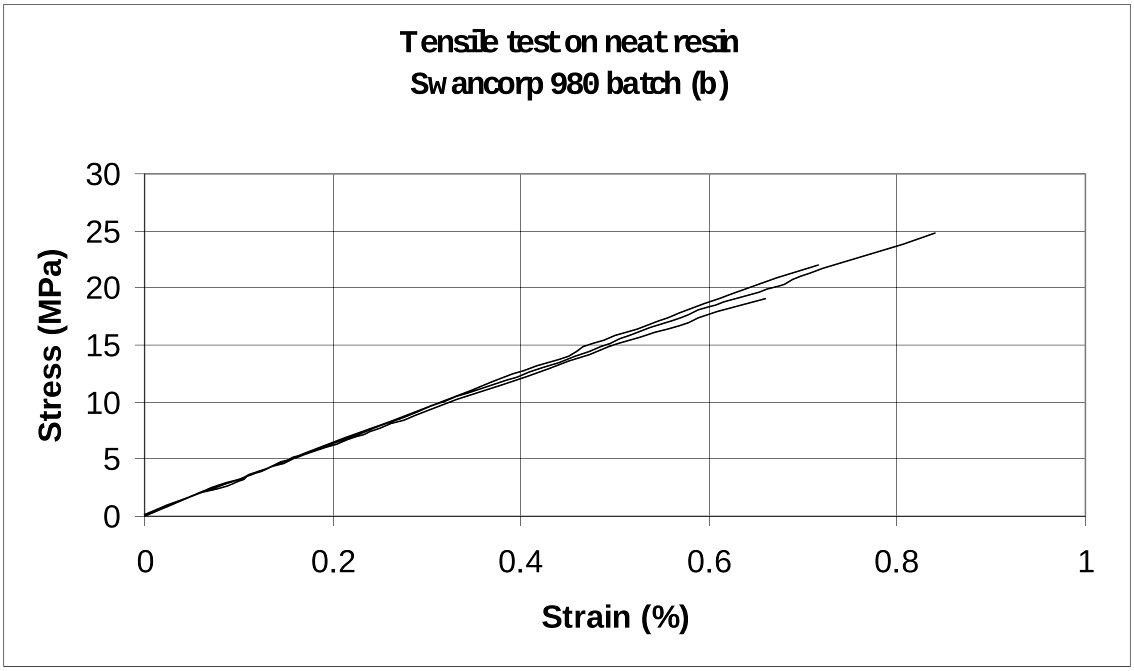
CoRezyn 63-AX-051	UTS (MPa)	Yield strength (MPa)	Tensile E (GPa)	Maximum % strain	thickness (mm)
poly-1	59.63	47.36	3.01	2.4	2.87
poly-2	48.26	41.73	3.25	1.66	2.84
poly-3	54.31	46.48	3.29	1.93	2.83
Average	**54.07**	**45.19**	**3.18**	**2.00**	**2.85**
Std dev	**4.64**	**2.47**	**0.12**		
Swancorp 980 (batch a)					
M031	25.23	19.96	1.60	12.88	2.71
M032	25.86	21.13	1.64	26.32	2.63
M033	25.85	20.6	1.65	49.33	2.67
Average	**25.65**	**20.56**	**1.63**	**29.51**	**2.67**
Std dev	**0.29**	**0.48**	**0.02**		
Swancorp 980 (batch b)					
980-1	22.04		3.10	0.716	3.09
980-2	19.13		2.99	0.66	3.14
980-3	24.79		3.06	0.84	3.12
Average	**21.99**		**3.05**	**0.74**	**3.11**
Std dev	**2.31**		**0.04**		
Swancorp 901					
901-1	46.91		3.27	1.52	3.18
901-2	35.15		3.40	1.08	3.18
901-3	46.32		3.43	1.46	3.20
Average	**42.79**		**3.37**	**1.35**	**3.19**
Std dev	**5.41**		**0.07**		
Swancorp 901 & 980 (batch b)					
100-1	63.89	40.89	2.68	4.52	3.37
100-2	65.44	38.73	2.81	4.65	3.30
100-3	65.08	44.39	2.80	4.16	3.31
Average	**64.80**	**41.34**	**2.76**	**4.44**	**3.33**
Std dev	**0.66**	**2.33**	**0.06**		

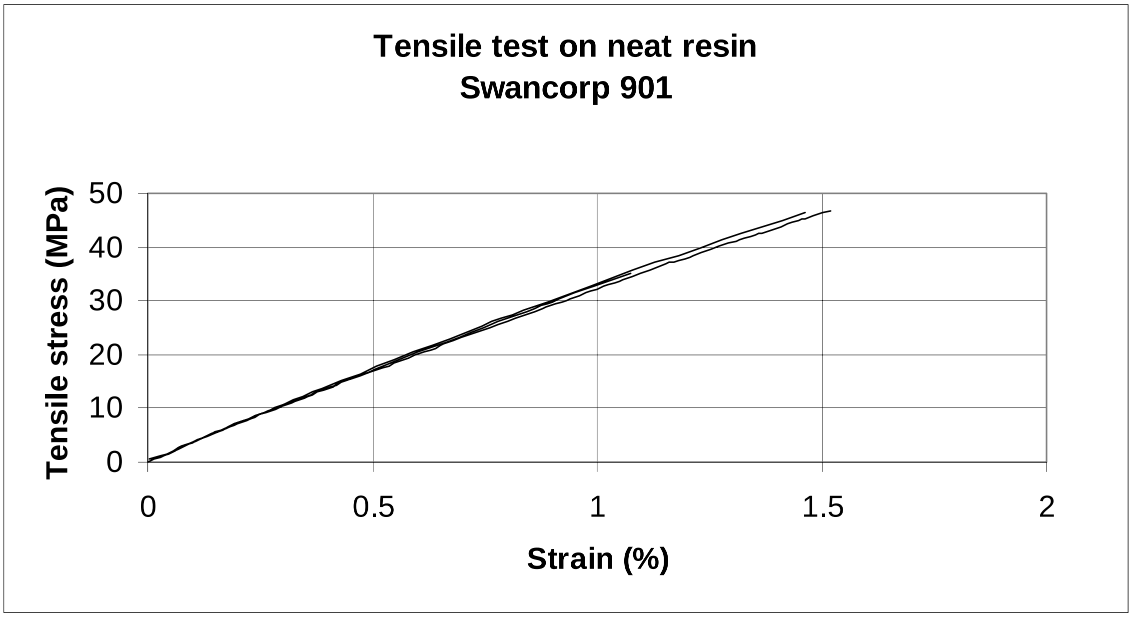
	UTS (MPa)	Yield strength (MPa)	Tensile E (GPa)	Maximum % strain	thickness (mm)
Derakane 411C-50					
411C-1	57.2	47.13	3.26	2.02	3.23
411C-2	58.79	53.17	3.16	2.14	3.21
411C-3	57.06	50.88	3.21	2.02	3.23
Average	**57.68**	**50.39**	**3.21**	**2.06**	**3.22**
Std dev	**0.78**	**2.49**	**0.04**		
Derakane 8084					
8084-1	75.11	58.35	3.04	3.36	3.32
8084-2	73.81	54.53	3.33	2.95	3.35
8084-3	68.79	52.61	3.38	2.6	3.40
Average	**72.57**	**55.16**	**3.25**	**2.97**	**3.36**
Std dev	**2.73**	**2.39**	**0.15**		
System 41					
sys3-1	51.11	51.11	3.59	1.54	2.77
sys3-2	53.1	53.1	3.63	1.58	2.77
sys3-3	53.62	53.62	3.49	1.67	2.79
Average	**52.61**	**52.61**	**3.57**	**1.60**	**2.78**
Std dev	**1.08**	**1.08**	**0.06**		
SC-12					
sc12-1	41.12		3.48	1.26	3.38
sc12-2	48.46		3.43	1.55	3.33
sc12-3	43.44		3.52	1.32	3.35
Average	**44.34**		**3.48**	**1.38**	**3.35**
Std dev	**3.06**		**0.04**		
SC-14					
sc14-1	72.1	50.06	2.83	3.68	3.36
sc14-2	66.27	46.81	2.76	3.15	3.37
sc14-3	66.57	48.62	2.82	3.09	3.36
Average	**68.31**	**48.50**	**2.80**	**3.31**	**3.36**
Std dev	**2.68**	**1.33**	**0.03**		

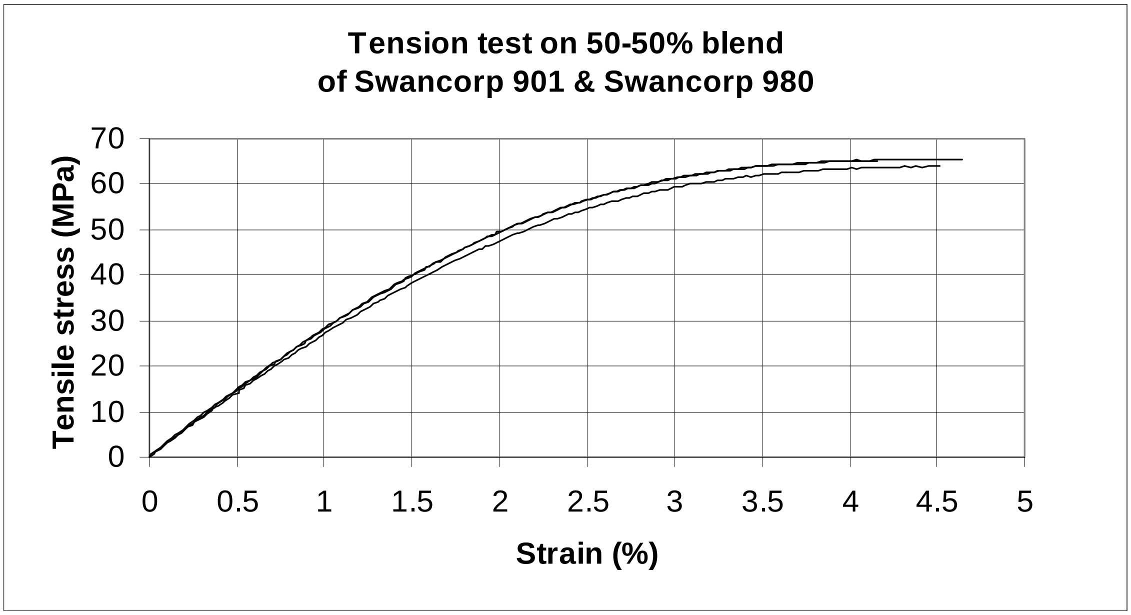
Stress-strain diagrams for tensile tests on neat resin (3 specimens).

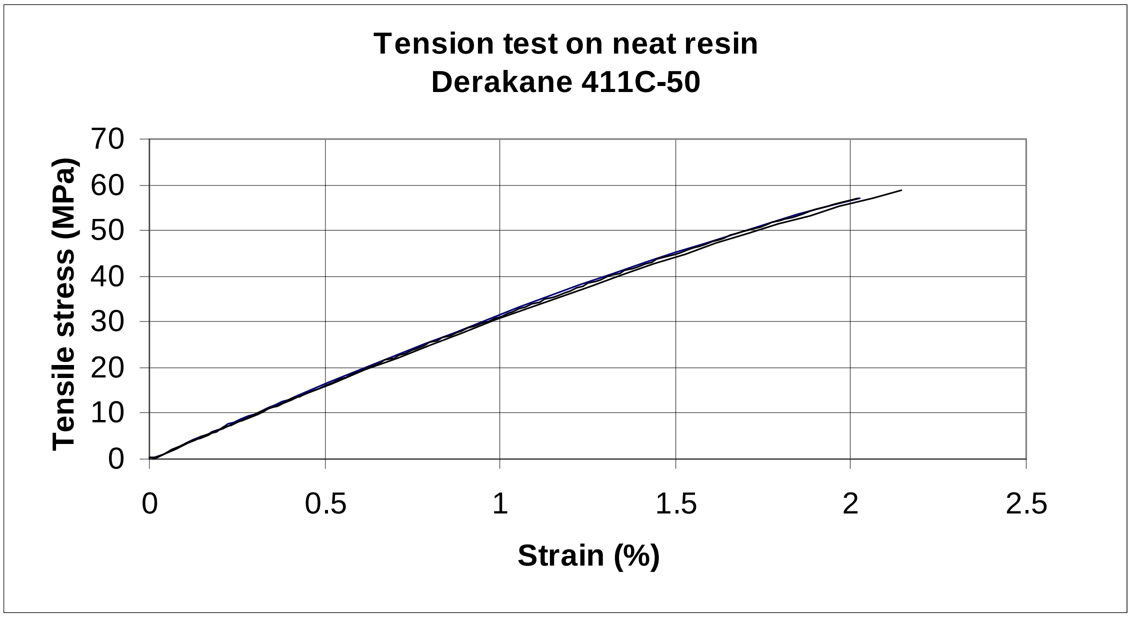


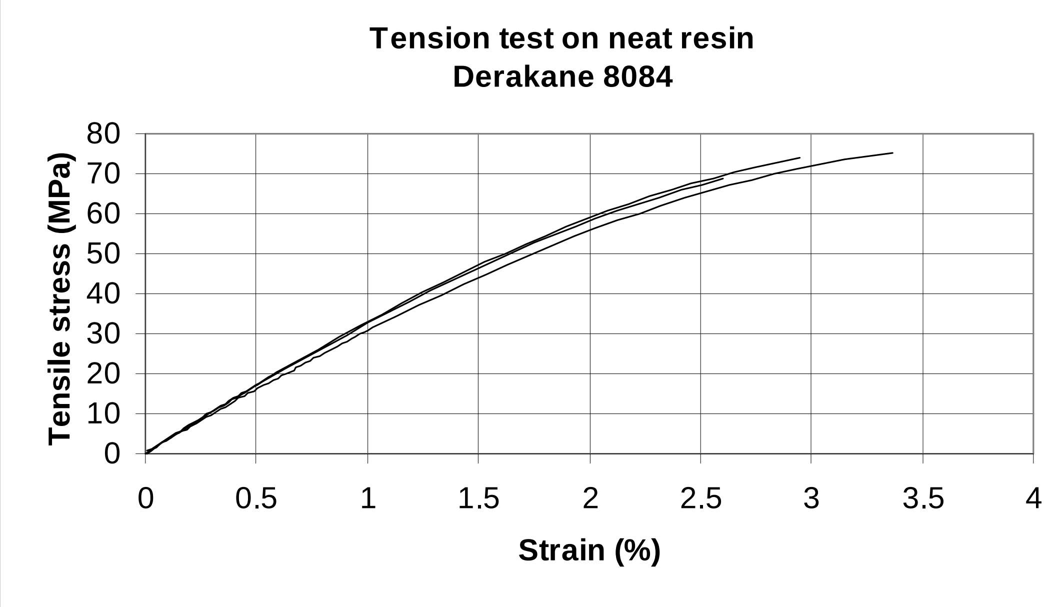


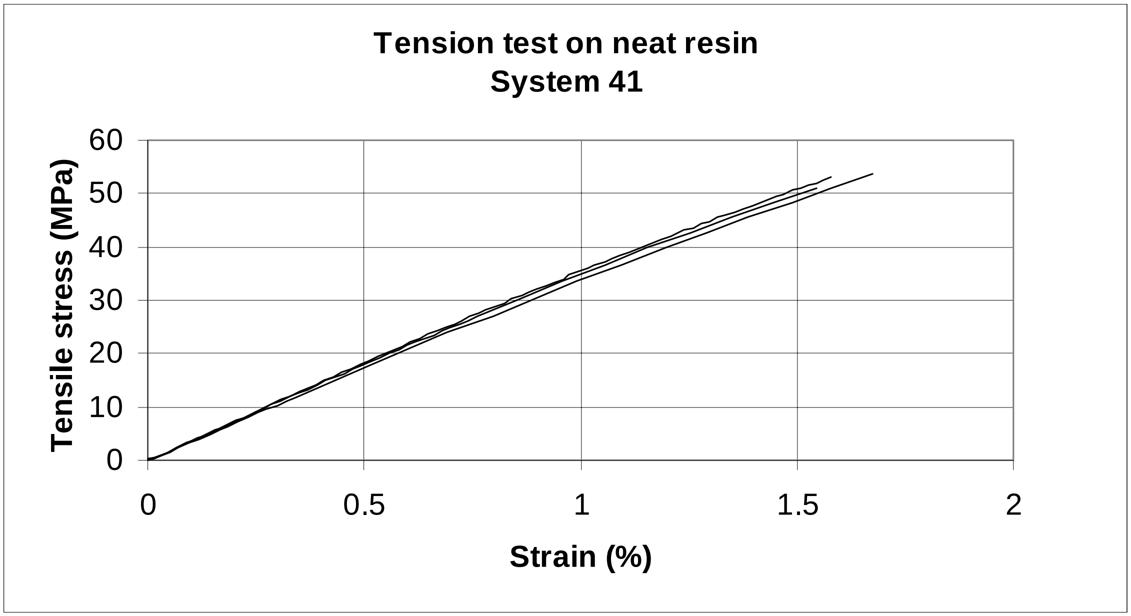

Tensile test on neat resin
Swancorp 980 batch (b)
Stress (MPa)
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
Strain (%)

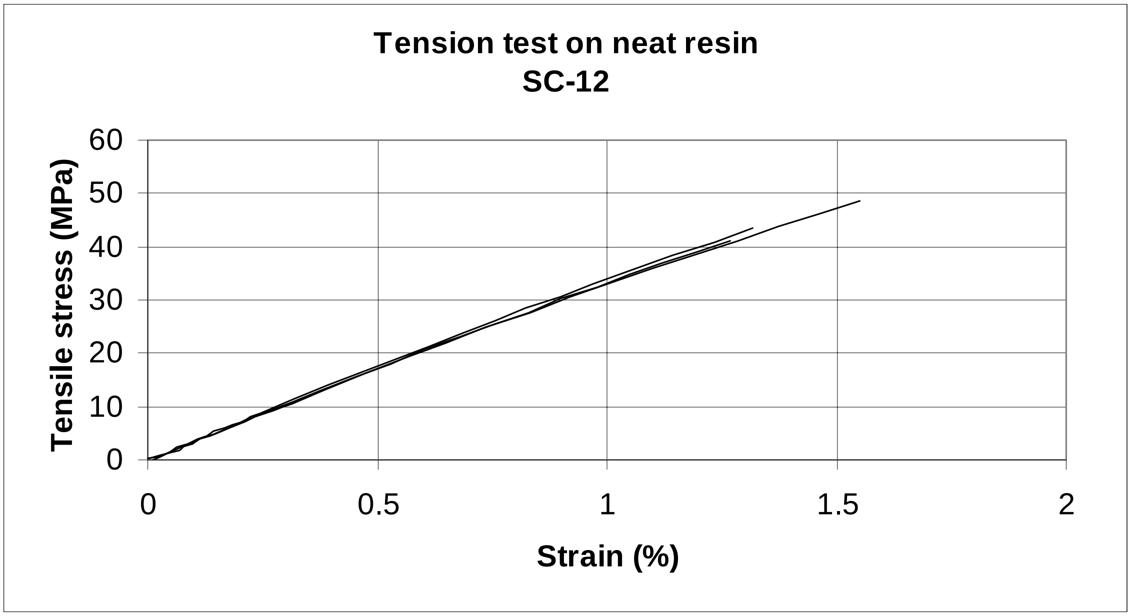

Tensile test on neat resin
Swancorp 901
Tensile stress (MPa)
50
40
30
20
10
0
0
0.5
1
1.5
2
Strain (%)

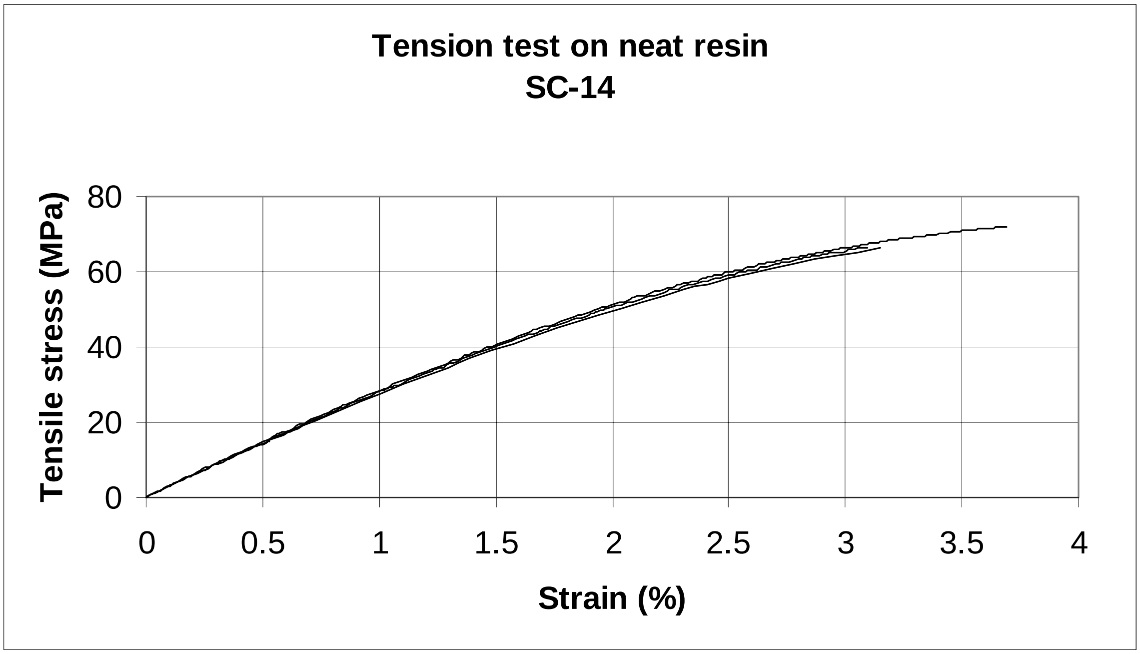

Tension test on 50-50% blend
of Swancorp 901 & Swancorp 980
Tensile stress (MPa)
70
60
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Strain (%)


Tension test on neat resin
Derakane 411C-50
Tensile stress (MPa)
70
60
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
Strain (%)


Tension test on neat resin
Derakane 8084
Tensile stress (MPa)
0
10
20
30
40
50
60
70
80
0
0.5
1
1.5
2
2.5
3
3.5
4
Strain (%)


Tension test on neat resin
System 41
Tensile stress (MPa)
0
10
20
30
40
50
60
0
0.5
1
1.5
2
Strain (%)


Tension test on neat resin
SC-12
Tensile stress (MPa)
60
50
40
30
20
10
0
0
0.5
1
1.5
2
Strain (%)


Tension test on neat resin
SC-14
Tensile stress (MPa)
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
4
Strain (%)

Results for heat deflection temperature (HDT) tests on neat resin.

CoRezyn 63-AX-051	**HDT (°C)**	**thickness (mm)**	**load (gr)**
poly-1	53.60		
poly-2	55.34		
poly-3	55.08		
Average	**54.67**	**2.85**	**592**
Std dev	**0.94**		
Swancorp 980 batch (b)			
980-1	57.42		
980-2	60.13		
980-3	60.63		
Average	**59.39**	**3.11**	**638**
Std dev	**1.73**		
Derakane 411C-50			
411c-1	73.5	3.38	
411c-2	80.157	3.41	
411c-3	79.59	3.33	
Average	**77.75**	**3.37**	**682**
Std dev	**3.69**		
Derakane 8084			
8084-1	72.60		
8084-2	74.70		
8084-3	75.20		
Average	**74.17**	**3.36**	**683**
Std dev	**1.38**		
System 41			
sys3-1	59.38		
sys3-2	52.90		
sys3-3	53.28		
Average	**55.19**	**2.78**	**581**
Std dev	**3.64**		

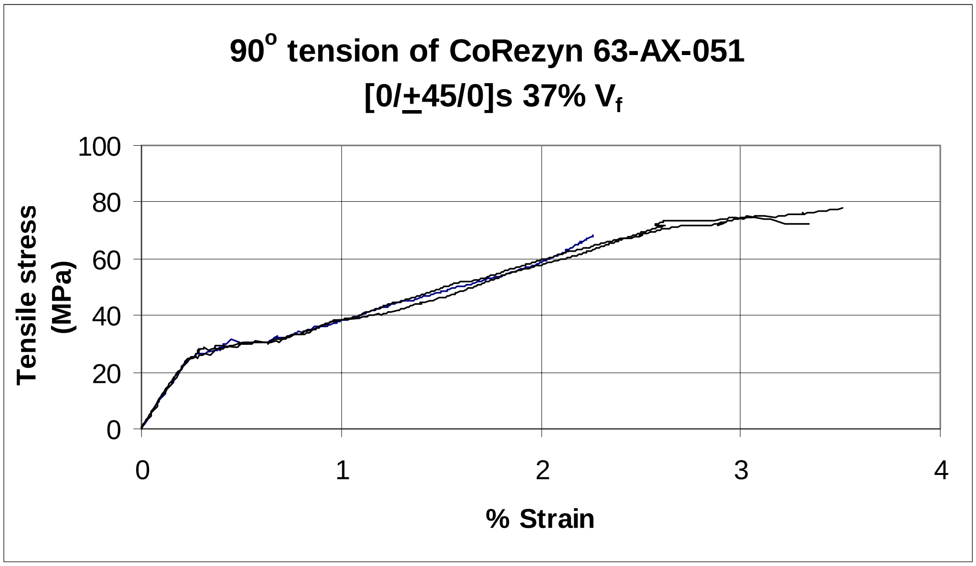
SC-12	**HDT (°C)**	**thickness (mm)**	**load (gr)**
sc12-1	92.74	3.40	
sc12-1	94.75	3.40	
sc12-1	94.95	3.40	
Average	**94.15**	**3.40**	**703**
Std dev	**1.22**		
SC-14			
sc14-1	80.49	3.37	
sc14-2	82.69	3.40	
sc14-3	84.28	3.42	
Average	**82.49**	**3.40**	**680**
Std dev	**1.90**		

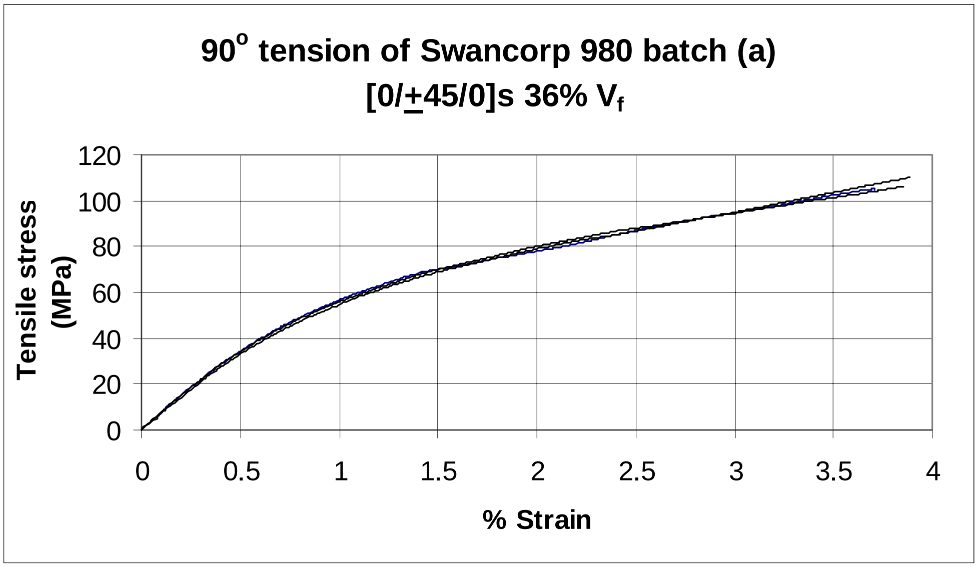
Results for 90° tension of [0/±45/0]s composites.

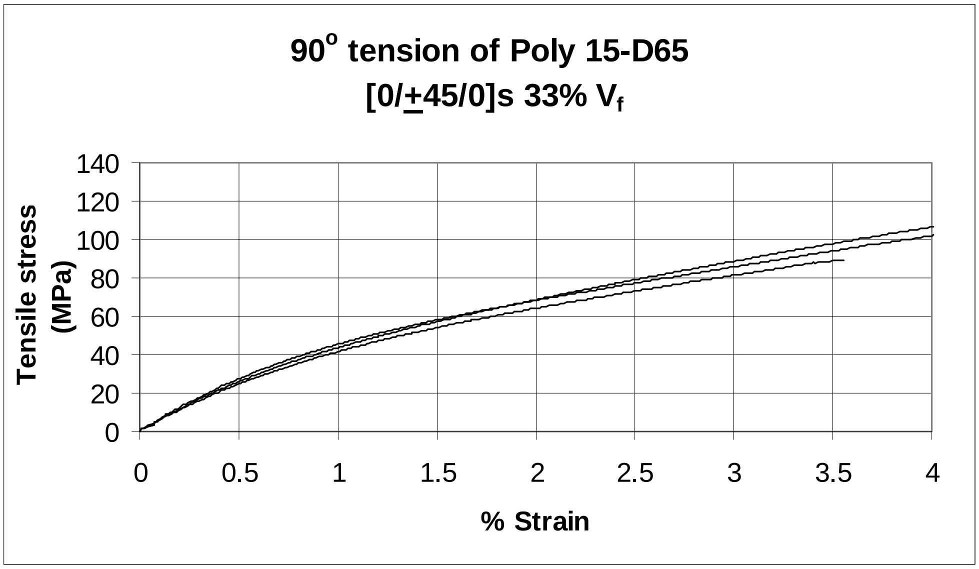
CoRezyn 63-AX-051	UTS (MPa)	Knee stress (MPa)	Tensile E (GPa)	Maximum % strain	(% V_f) Fiber volume
1T01	68.19	29.9	10.65	2.26	37.3
1T02	75.24	29.9	10.52	3.14	37.38
1T03	77.80	28.6	10.10	3.51	37.56
Average	**73.75**	**29.47**	**10.42**	**2.97**	**37.41**
Std dev	**4.06**	**0.61**	**0.23**	**0.52**	
Swancorp 980 (batch a)					
2T01	105.3	55.9	7.09	3.71	36.72
2T02	106.6	50.7	6.98	3.85	36.04
2T03	110.3	49.7	6.65	3.88	36.04
Average	**107.40**	**52.10**	**6.91**	**3.81**	**36.27**
Std dev	**2.12**	**2.72**	**0.19**	**0.07**	
Poly 15-D65					
3T01	89.4	37.6	5.47	3.51	38.48
3T02	117.9	37.9	5.65	5.42	38.62
3T03	116.1	39.9	5.57	4.68	38.48
Average	**107.80**	**38.47**	**5.56**	**4.54**	**38.53**
Std dev	**13.03**	**1.02**	**0.07**	**0.79**	
System 41					
4T01	108.5	60.9	11.66	3.02	42.25
4T02	122.1	60.4	11.75	3.8	42.84
4T03	110.5	60.1	11.48	3.34	42.31
Average	**113.70**	**60.47**	**11.63**	**3.39**	**42.47**
Std dev	**6.00**	**0.33**	**0.11**	**0.32**	
Derakane 411C-50 (39% Vf)					
ts411-1	57.61	35.4	9.25	4.39	39.15
ts411-2	54.77	36.6	9.24	4.92	39.02
ts411-3	56.59	36.6	9.45	4.01	39.28
Average	**56.32**	**36.20**	**9.31**	**4.44**	**39.15**
Std dev	**1.17**	**0.57**	**0.09**	**0.37**	
Derakane 411C-50 (35% Vf)					
t411-1	59.88	45.15	8.03	4.32	35.32
t411-2	58.56	44.44	8.13	3.95	35.59
t411-3	58.88	49.52	8.49	3.54	35.59
Average	**59.11**	**46.37**	**8.22**	**3.94**	**35.50**
Std dev	**0.56**	**2.25**	**0.20**	**0.32**	

Derakane 8084 (39% Vf)	UTS (MPa)	Knee stress (MPa)	Tensile E (GPa)	Maximum % strain	(% V_f) Fiber volume
ts8084-1	63.79	43.60	9.27	5.07	39.54
ts8084-2	67.44	44.90	9.52	4.04	39.54
ts8084-3	64.04	42.00	8.55	4.35	39.54
Average	**65.09**	**43.50**	**9.11**	**4.49**	**39.54**
Std dev	**1.66**	**1.19**	**0.41**	**0.43**	
Derakane 8084 (35% Vf)					
t8084-1	62.74	44.25	8.61	3.70	35.32
t8084-2	62.87	45.07	8.33	4.39	35.32
t8084-3	63.31	43.17	8.11	4.21	35.32
Average	**62.97**	**44.16**	**8.35**	**4.10**	**35.32**
Std dev	**0.24**	**0.78**	**0.21**	**0.29**	
SC-14					
tsc14-1	108.65	61.5	9.37	3.21	37.43
tsc14-2	120.75	60.9	9.51	4.73	37.83
tsc14-3	104.44	59.2	9.36	3.45	37.96
Average	**111.28**	**60.53**	**9.41**	**3.80**	**37.74**
Std dev	**6.91**	**0.97**	**0.07**	**0.67**	

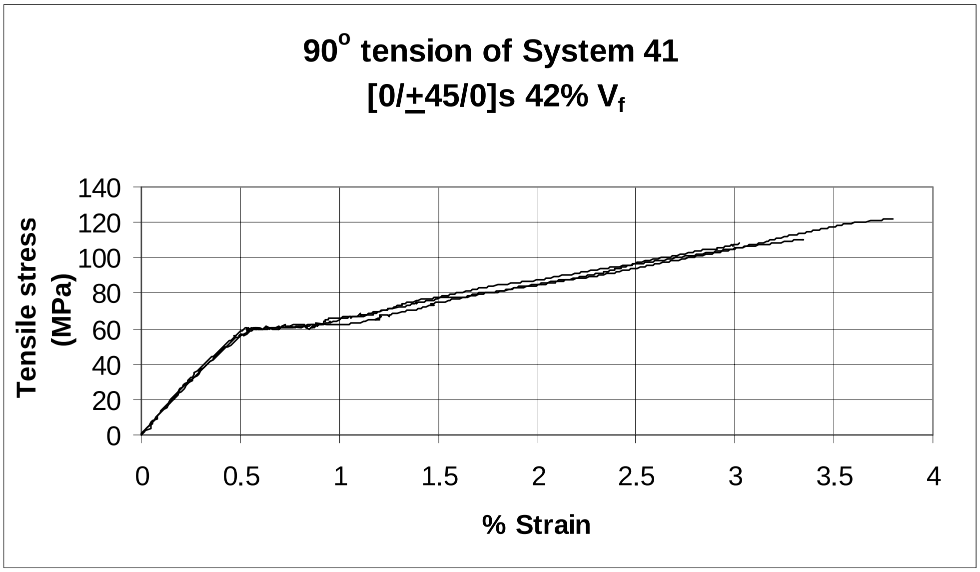
Stress-strain diagrams for 90° tensile test of [0/±45/0]s composites (3 specimens).



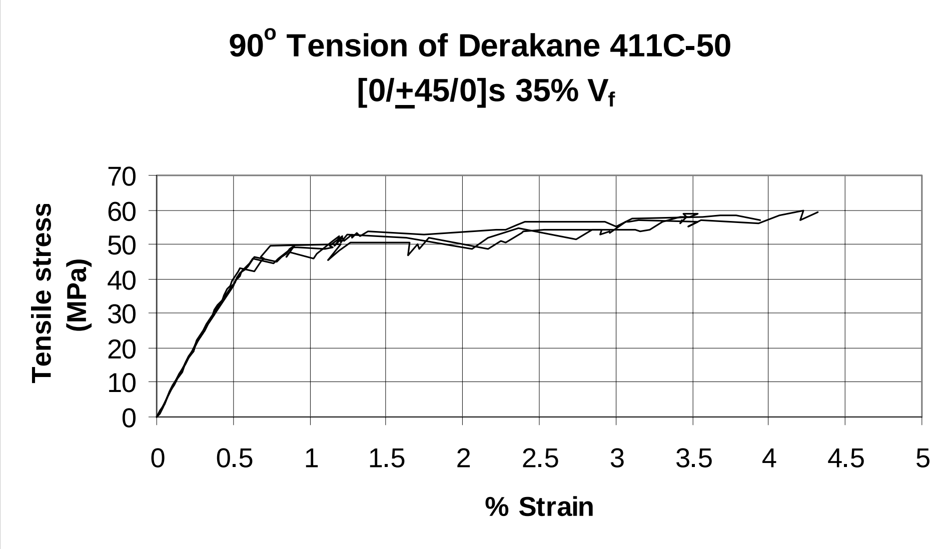


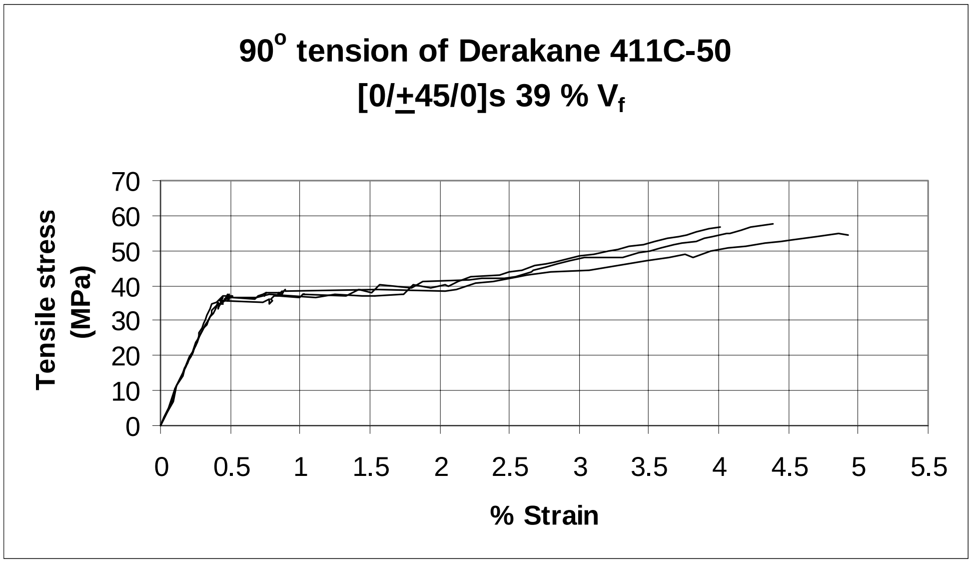


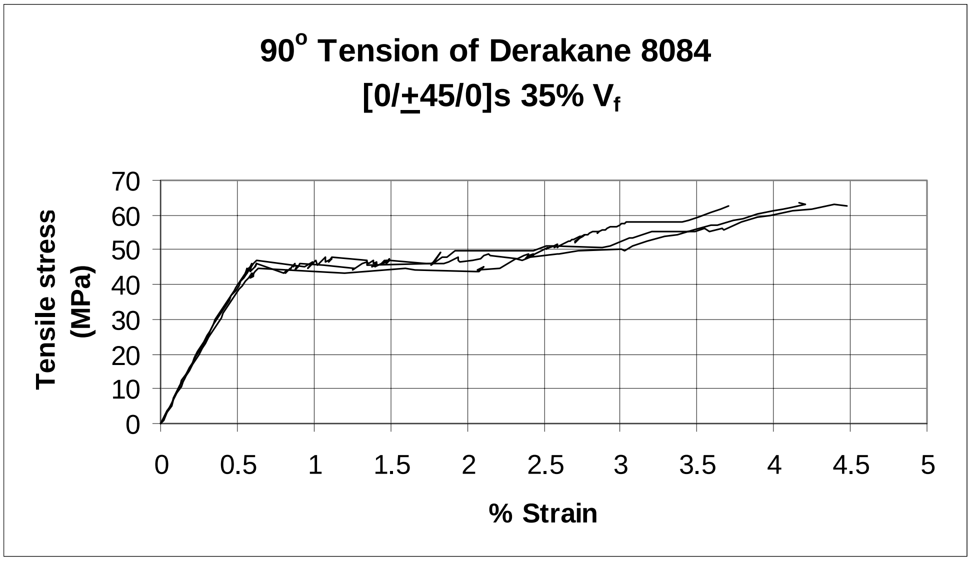
90^o tension of Poly 15-D65 [0/$\underline{+}$45/0]s 33% V_f

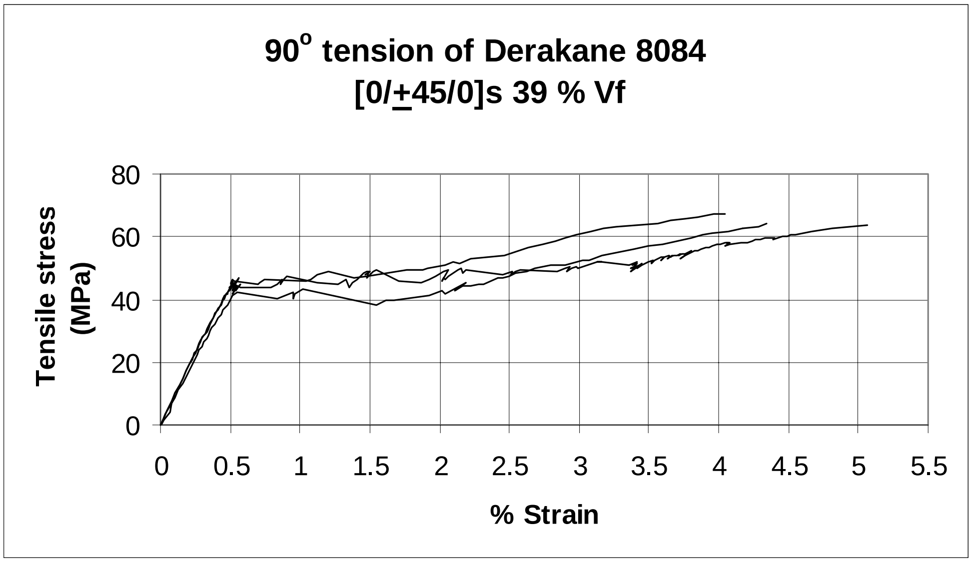


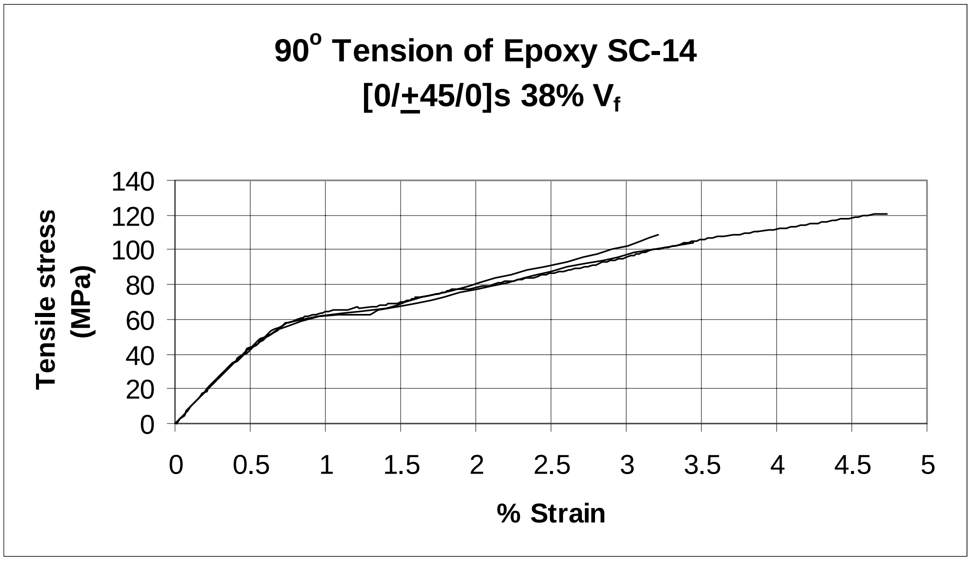
90^o tension of System 41 [0/$\underline{+}$45/0]s 42% V_f


90° Tension of Derakane 411C-50
[0/±45/0]s 35% V_f
Tensile stress (MPa)
70
60
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
% Strain


90° tension of Derakane 411C-50
[0/±45/0]s 39 % V_f
Tensile stress (MPa)
70
60
50
40
30
20
10
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
% Strain


90° Tension of Derakane 8084
[0/±45/0]s 35% V_f
Tensile stress (MPa)
0
10
20
30
40
50
60
70
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
% Strain


90° tension of Derakane 8084
[0/±45/0]s 39 % Vf
Tensile stress (MPa)
0
20
40
60
80
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
% Strain


90° Tension of Epoxy SC-14
[0/±45/0]s 38% V_f
Tensile stress (MPa)
140
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
% Strain

Results for 0° compression test of [0/±45/0]s composites.

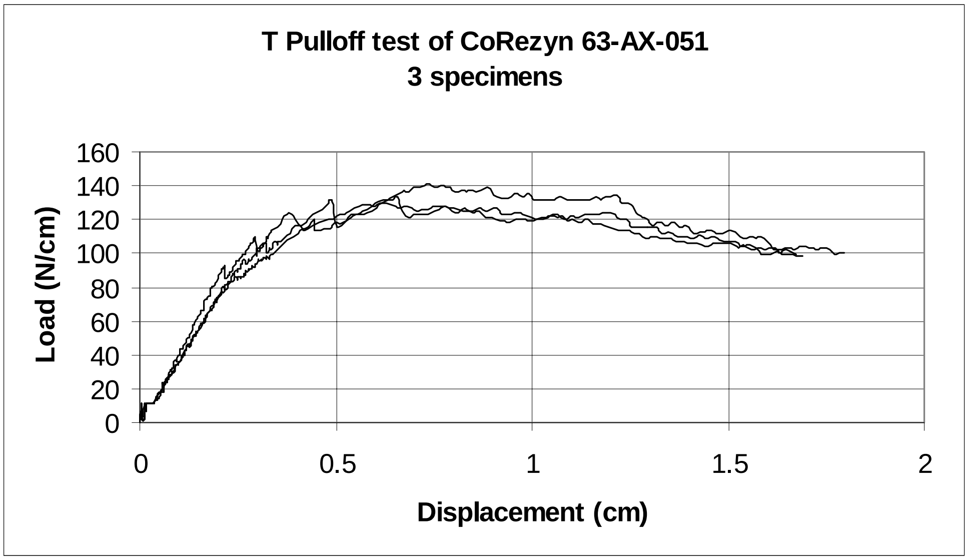
CoRezyn 63-AX-051	Compressive strength (MPa)	Maximum Load (kg)	thickness (mm)	V_f (%)
1C01	484.69	3768.88	2.98	37.38
1C02	541.04	4563.12	3.26	34.48
1C03	526.43	4329.06	3.18	35.32
Average	**517.39**	**4220.35**	**3.14**	**35.73**
Std dev	**29.24**	**408.13**		
Swancorp 980 (batch a)				
2C01	447.05	3411.45	3.00	37.17
2C02	397.06	3156.53	3.10	36.11
2C03	417.00	3364.28	3.14	35.72
Average	**420.37**	**3310.75**	**3.08**	**36.33**
Std dev	**25.17**	**135.63**		
Poly 15-D65				
3C01	404.12	3056.29	2.91	38.09
3C02	376.94	2960.58	3.01	37.04
3C03	355.75	2842.19	3.08	36.32
Average	**378.93**	**2953.02**	**3.00**	**37.15**
Std dev	**24.25**	**107.25**		
System 41				
4C01	596.63	4521.84	2.87	38.49
4C02	516.13	3904.05	2.83	38.95
4C03	590.64	4441.10	2.88	38.36
Average	**567.80**	**4289.00**	**2.86**	**38.60**
Std dev	**44.85**	**335.81**		
Derakane 411C-50 (39% Vf)				
411-1	432.86	3265.85	2.90	38.22
411-2	462.80	3457.72	2.84	38.75
411-3	458.42	3310.30	2.77	39.54
Average	**451.36**	**3344.62**	**2.84**	**38.84**
Std dev	**16.17**	**100.43**		
Derakane 411C-50 (35% Vf)				
t411c-1	587.88	4848.88	3.18	35.32
t411c-2	548.25	4526.37	3.20	35.06
t411c-3	581.05	4740.02	3.18	35.32
Average	**572.39**	**4705.09**	**3.18**	**35.23**
Std dev	**21.19**	**164.06**		

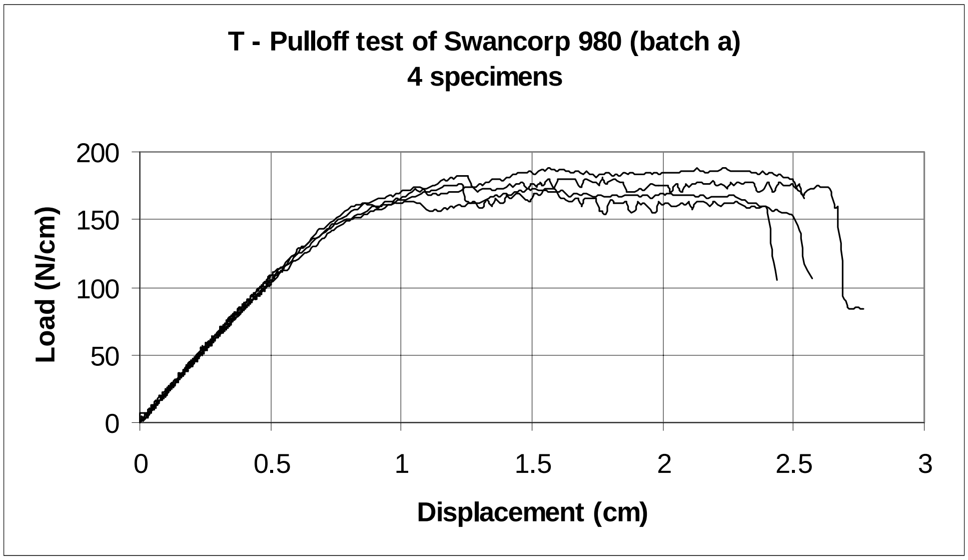
Derakane 8084 (39% Vf)	Compressive strength (MPa)	Maximum Load (kg)	Thickness (mm)	V_f (%)
808-1	470.76	3517.14	2.87	38.49
808-2	465.92	3436.40	2.82	39.02
808-3	448.12	3339.78	2.86	38.62
Average	**461.60**	**3431.11**	**2.85**	**38.71**
Std dev	**11.92**	**88.80**		
Derakane 8084 (35% Vf)				
t8084-1	510.16	4228.82	3.20	35.06
t8084-2	585.43	4862.48	3.20	35.06
t8084-3	528.76	4342.67	3.23	34.79
Average	**541.45**	**4477.99**	**3.21**	**34.97**
Std dev	**39.21**	**337.81**		
SC-14				
sc14-1	523.89	4089.11	3.02	36.91
sc14-2	527.16	4080.04	3.00	37.17
sc14-3	543.86	4209.32	3.00	37.17
Average	**531.64**	**4126.16**	**3.01**	**37.08**
Std dev	**10.71**	**72.16**		

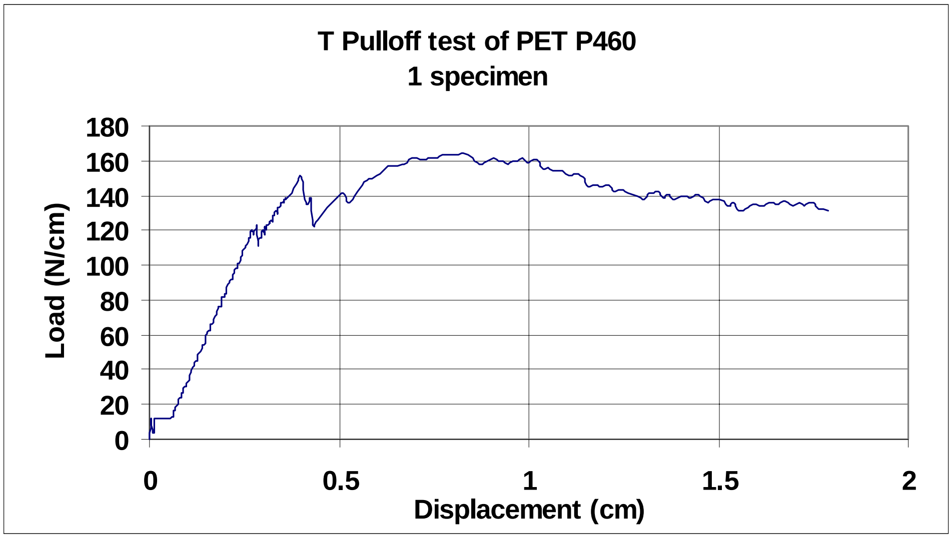
T-Pull off test results.

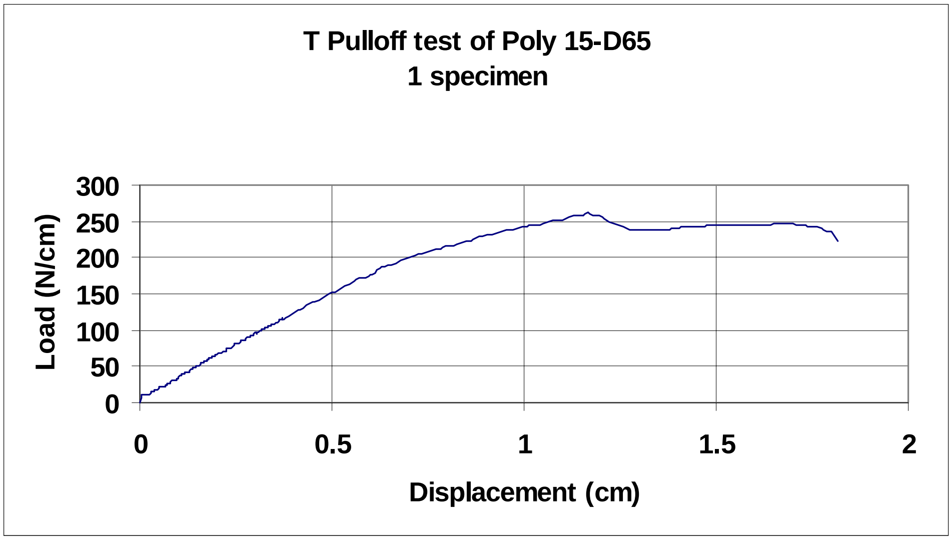
CoRezyn 63-AX-051 Specimen	Initial damage load (N/cm)	Displacement at initial damage (cm)	Maximum Load (N/cm)	Displacement at maximum load(cm)	Flange + Skin tickness (mm)
2601	82	0.23	134	0.68	5.62
2602	93	0.26	141	0.74	5.74
1505	86	0.22	129	0.63	6.37
Average	**87**	**0.24**	**135**	**0.68**	**5.91**
Std dev	**5.57**	**0.02**	**6.03**	**0.06**	
PET-P460					
2305	**120**	**0.3**	**164**	**0.84**	**6.69**
Swancorp 980 (batch a)					
2501	114	0.58	172	1.59	5.91
2502	108	0.51	176	1.24	5.88
2503	125	0.62	183	1.25	5.9
2504	123	0.6	188	1.56	5.93
Average	**119**	**0.58**	**182**	**1.35**	**5.90**
Std dev	**9.29**	**0.06**	**6.03**	**0.18**	
Derakane 8084					
2801	138	0.47	192	0.89	5.25
2802	150	0.51	195	0.91	5.15
Average	**144**	**0.49**	**194**	**0.90**	**5.20**
Std dev					
System 41					
2701	161	0.37	210	0.67	6.33
2702	175	0.39	207	0.67	5.99
Average	**168**	**0.38**	**209**	**0.67**	**6.16**
Std dev					
SC-14					
2901	140	0.6	198	1.91	5.37
2902	123	0.59	186	1.91	5.29
Average	**132**	**0.60**	**192**	**1.91**	**5.33**
Std dev					
Poly 15-D65					
2408	**141**	**0.46**	**262**	**1.16**	**6.54**

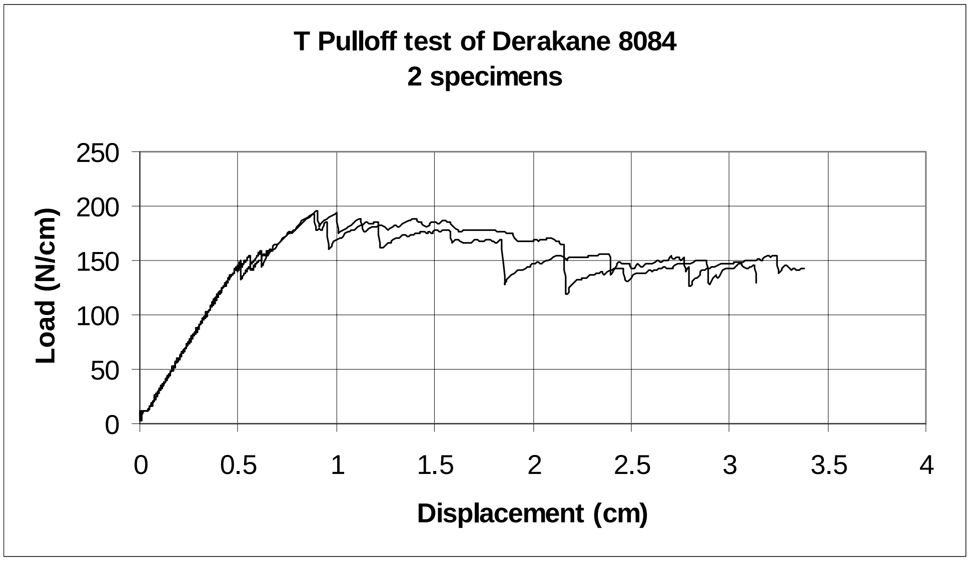
Load-displacement diagrams for T Pulloff tests.

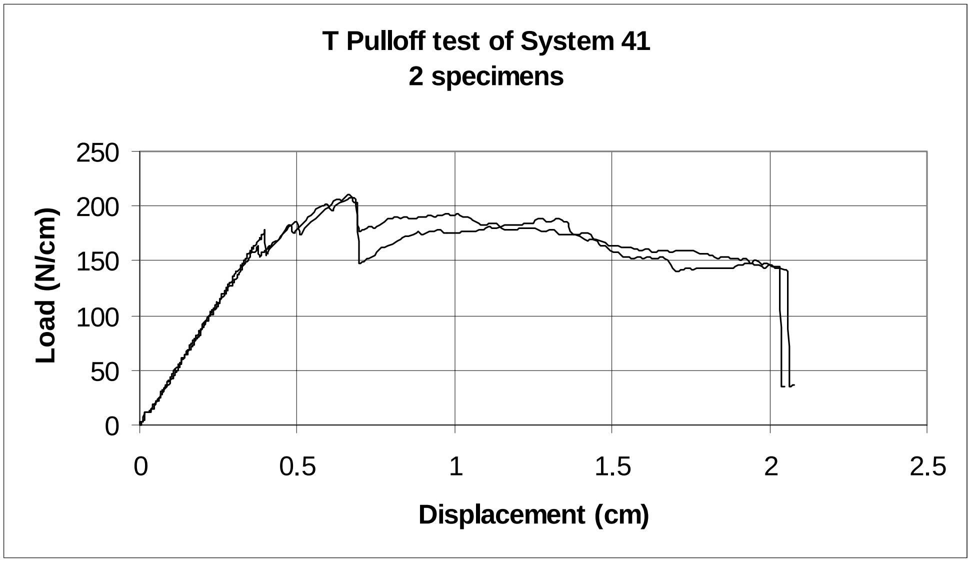


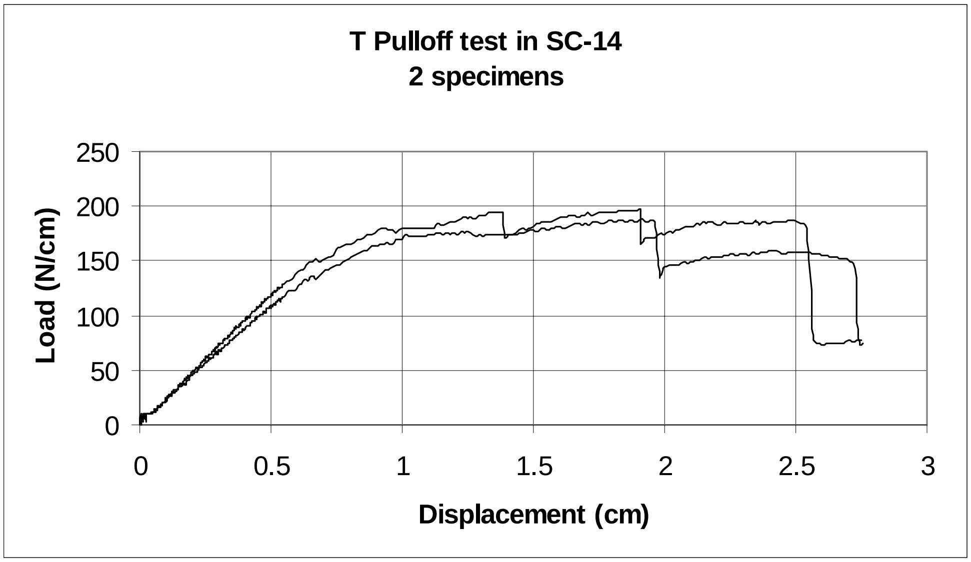



T Pulloff test of PET P460
1 specimen
Load (N/cm)
180
160
140
120
100
80
60
40
20
0
0
0.5
1
1.5
2
Displacement (cm)


T Pulloff test of Poly 15-D65
1 specimen
Load (N/cm)
300
250
200
150
100
50
0
0
0.5
1
1.5
2
Displacement (cm)


T Pulloff test of Derakane 8084
2 specimens
Load (N/cm)
250
200
150
100
50
0
0
0.5
1
1.5
2
2.5
3
3.5
4
Displacement (cm)


T Pulloff test of System 41
2 specimens
Load (N/cm)
250
200
150
100
50
0
0
0.5
1
1.5
2
2.5
Displacement (cm)


T Pulloff test in SC-14
2 specimens
Load (N/cm)
250
200
150
100
50
0
0
0.5
1
1.5
2
2.5
3
Displacement (cm)

Summary of DCB results for $[0]_6$ composites.

Polyester
CoRezyn 63-AX-051

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1011	162	179	345	5
1012	152		152	1
1013	139		139	1
1014	157	138	148	2
Average	**153**	**159**	**196**	Total Tests
Std Dev	**10**	**29**	**99**	7

Polyester PET P460

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1021	111	220	229	3
1022	232	297	264	2
1023	116	133	124	2
1025	139	239	189	2
1026	121	205	196	3
Average	**144**	**219**	**201**	Total Tests
Std Dev	**50**	**59**	**52**	12

Polyester Arotran Q6038

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1061	**153**	**309**	**235**	3

CoRezyn 63-AX-051 using bonded fabric with polyester veil (Veil-Veil)

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1111	202	258	326	5
1112	229	294	287	3
Average	**216**	**276**	**307**	Total Tests
Std Dev				8

CoRezyn 63-AX-051 using bonded fabric with glass Veil (Veil-Veil)

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1121	209	360	357	4
1122	167	187	226	3
Average	**188**	**274**	**292**	Total Tests
Std Dev				7

CoRezyn 63-AX-051 using bonded fabric with polyester veil (Glass-Glass)

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1131	130	116	143	3
1132	98	165	168	3
Average	**114**	**141**	**156**	Total Tests
Std Dev				6

Vinyl ester Swancorp 980 (batch a)

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1031	1308	1758	1869	4
1032	1635	1666	1908	5
1033	1754	2030	2060	3
1034	1066	1906	1855	3
Average	**1441**	**1840**	**1923**	Total Tests
Std Dev	**313**	**161**	**94**	15

Vinyl ester Derakane 8084

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1091	348	442	472	5
1092	335	671	496	3
1093	347	673	606	3
Average	**344**	**595**	**524**	
Std Dev	**7**	**133**	**71**	Total Tests
				11

Vinyl ester Derakane 411C-50

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1101	231	493	539	5
1102	238	298	343	3
Average	**234**	**396**	**441**	Total Tests
Std Dev				8

Vinyl ester Swancorp 901

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
901-1		193	306	3
901-2		230	299	3
901-3		200	262	3
Average		**208**	**289**	Total Tests
Std Dev		**20**	**24**	9

Vinyl ester Swancorp 901 & 980 (batch b)

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
100-1		552	638	3
100-2		560	587	3
100-3		595	679	3
Average		**569**	**635**	Total Tests
Std Dev		**23**	**46**	9

Vinyl ester Swancorp 980 (batch b)

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
980-1	670	846	803	4
980-2		641	708	3
980-3		1070	915	3
Average		**852**	**809**	Total Tests
Std Dev		**215**	**104**	10

Epoxy - System 41

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1041	240	263	294	5
1042	220	240	229	3
1043	196	189	215	3
Average	**219**	**231**	**246**	Total Tests
Std Dev	**22**	**38**	**42**	11

Epoxy SC-14

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1071	703	589	653	5
1072	591	511	584	4
1073	621	814	692	3
Average	**638**	**638**	**643**	Total Tests
Std Dev	**58**	**157**	**55**	12

Epoxy SC-12

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1081	379	445	511	5
1082	315	409	365	3
Average	**347**	**427**	**438**	Total Tests
Std Dev				8

Polyurethane Poly 15-D65

Specimen	G_{IC} (a) initial (J/m^2)	G_{IC} (b) (J/m^2)	Overall G_{IC} (J/m^2)	Tests Performed
1051	2411	2752	2512	4
1052	2914		2914	1
Average	**2663**	**2752**	**2713**	Total Tests
				5

Individual DCB test results.

CoRezyn 63-AX-051

Specimen	b= 2.5146 cm		**initial a (cm)**		Overall	
1011	disp (mm)	load (kg)	**4.72**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	5.66	2.31	4.89	**161.92**	344.80	176.23
b)	6.56	2.28	5.28	**178.77**		
c)	10.78	3.02	5.65	360.74		
d)	13.33	3.26	6.17	449.95		
e)	17.70	3.41		572.63		

	b= 2.48 cm		**initial a (cm)**		Overall	
1012	disp (mm)	load (kg)	**4.75**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	5.61	2.17	4.84	**151.63**	151.63	

	b= 2.48 cm		**initial a (cm)**		Overall	
1013	disp (cm)	load (kg)	**4.73**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	5.04	2.21	4.88	**139.28**	139.28	

	b= 2.53 cm		**initial a (cm)**		Overall	
1014	disp (mm)	load (kg)	**4.75**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	5.64	2.28	4.87	**157.22**	147.73	13.43
b)	5.69	2.03		**138.23**		

Polyester PET P460

	b= 2.54 cm		**initial a (cm)**		Overall	
1021	disp (mm)	load (kg)	**4.44**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	4.11	2.07	4.52	**110.78**	228.97	123.12
b)	6.20	2.77	4.80	**219.63**		
c)	8.55	3.46	5.13	356.50		

	b= 2.56 cm		**initial a (cm)**		Overall	
1022	disp (mm)	load (kg)	**4.53**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	6.37	2.87	4.96	**231.82**	264.48	46.18
b)	8.40	3.05		**297.14**		

	b= 2.52 cm		**initial a (cm)**		Overall	
1023	disp (mm)	load (kg)	**4.47**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	4.34	2.04	4.67	**115.73**	124.29	12.10
b)	4.82	2.20	4.80	**132.85**		

	b= 2.53 cm		**initial a (cm)**		Overall	
1025	disp (mm)	load (kg)	**0.91**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	0.25	8.61	1.26	**138.64**	189.06	71.29
b)	0.65	7.95	1.43	**239.47**		

	b= 2.52 cm		**initial a (cm)**		Overall	
1026	disp (mm)	load (kg)	**0.48**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	0.10	10.24	1.29	**120.83**	195.62	70.45
b)	0.38	11.95	2.21	**205.29**		
c)	1.06	9.30	2.63	260.74		

Polyester Arotran Q6038

	b= 2.37 cm		**initial a (cm)**		Overall	
1061	disp (mm)	load (kg)	**1.05**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	0.30	8.80	1.58	**153.15**	234.90	78.00
b)	0.87	9.04	2.11	**308.51**		
c)	1.18	6.98	2.44	243.04		

CoRezyn 63-AX-051 using bonded fabric with polyester veil (Veil-Veil)

	b= 2.54 cm		**initial a (cm)**		Overall	
1111	disp (mm)	load (kg)	**2.43**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	1.76	4.80	2.89	**201.68**	326.47	115.39
b)	2.55	5.06	2.97	**258.28**		
c)	3.02	5.33	3.15	314.90		
d)	3.44	5.55	3.23	351.33		
e)	4.50	6.26	3.39	506.15		

	b= 2.54 cm		**initial a (cm)**		Overall	
1112	disp (mm)	load (kg)	**2.49**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	1.97	5.02	2.81	**229.49**	287.91	55.62
b)	2.85	5.00	3.17	**294.01**		
c)	3.63	5.13	3.64	340.23		

CoRezyn 63-AX-051 using bonded fabric with glass Veil (Veil-Veil)

	b= 2.54 cm		**initial a (cm)**		Overall	
1121	disp (mm)	load (kg)	**2.43**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	1.87	4.70	2.66	**209.38**	356.95	105.44
b)	2.83	5.82	2.87	**360.12**		
c)	3.42	5.85	3.14	405.28		
d)	4.30	5.72	3.41	453.03		

	b= 2.52 cm		**initial a (cm)**		Overall	
1122	disp (mm)	load (kg)	**2.29**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	1.36	4.81	2.68	**166.90**	226.32	86.21
b)	1.78	4.81	2.97	**186.86**		
c)	2.94	5.64	3.45	325.20		

CoRezyn 63-AX-051 using bonded fabric with polyester veil (Glass-Glass)

					Overall	
	b= 2.54 cm		**initial a (cm)**		GIC (J/m^2)	Stdev
1131	disp (mm)	load (kg)	**2.47**	GIC (J/m^2)	142.82	34.69
a) Initial	1.50	3.69	2.85	**129.94**		
b)	1.83	3.13	3.26	**116.41**		
c)	2.93	3.50	3.72	182.11		

	b= 2.55 cm		**initial a (cm)**		Overall	
1132	disp (mm)	load (kg)	**2.48**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	1.23	3.44	2.73	**97.97**	168.12	71.71
b)	1.96	4.00	3.00	**165.09**		
c)	2.78	4.53	3.31	241.30		

Vinyl ester Swancorp 980 (batch a)

	b= 2.51 cm		**initial a (cm)**		Overall	
1031	disp (mm)	load (kg)	1.69	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.67	14.15	1.98	**1308.20**	1868.50	459.61
b)	3.45	17.28	2.26	**1757.57**		
c)	4.61	16.79	2.66	2001.36		
d)	6.59	16.63	3.17	2406.86		

	b= 2.53 cm		**initial a (cm)**		Overall	
1032	disp (mm)	load (kg)	**1.74**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	3.03	16.13	1.89	**1634.51**	1907.56	289.89
b)	3.13	17.32	2.14	**1666.00**		
c)	4.32	16.47	2.38	1936.70		
d)	4.97	16.01	2.76	1944.67		
e)	7.06	15.83	2.93	2355.90		

	b= 2.53 cm		**initial a (cm)**		Overall	
1033	disp (mm)	load (kg)	**1.77**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.85	18.72	2.02	**1753.84**	2059.81	321.96
b)	3.62	19.48	2.13	**2029.91**		
c)	4.52	19.42	2.61	2395.68		

	b= 2.52 cm		**initial a (cm)**		Overall	
1034	disp (mm)	load (kg)	**1.75**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.21	14.48	1.89	**1066.45**	1855.03	764.57
b)	3.51	17.59	2.06	**1905.55**		
c)	4.60	19.90	2.47	2593.09		

Vinyl ester Derakane 8084

	b= 2.55 cm		**initial a (cm)**		Overall	
1091	disp (mm)	load (kg)	**2.46**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.50	5.92	2.52	**348.39**	471.56	127.52
b)	2.97	6.50	2.80	**442.14**		
c)	4.44	7.29	3.13	668.69		
d)	4.22	4.89	3.38	381.63		
e)	5.48	5.53	3.60	516.94		

	b= 2.54 cm		**initial a (cm)**		Overall	
1092	disp (mm)	load (kg)	**2.50**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.60	5.56	2.89	**335.36**	495.96	168.48
b)	4.97	6.73	3.18	**671.33**		
c)	5.11	5.16	3.94	481.19		

	b= 2.52 cm		**initial a (cm)**		Overall	
1093	disp (mm)	load (kg)	**2.42**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.52	5.71	2.55	**346.96**	605.54	232.41
b)	3.91	7.49	2.93	**672.64**		
c)	5.42	7.37	3.26	797.01		

Vinyl ester Derakane 411C-50

	b= 2.53 cm		**initial a (cm)**		Overall	
1101	disp (mm)	load (kg)	**2.50**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.13	4.65	2.63	**230.61**	538.78	212.59
b)	3.56	6.28	2.98	**493.07**		
c)	5.07	6.08	3.18	599.53		
d)	5.42	5.55	3.42	549.23		
e)	7.49	6.45	3.80	821.46		

	b= 2.53 cm		**initial a (cm)**		Overall	
1102	disp (mm)	load (kg)	**2.54**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.31	4.51	2.66	**238.00**	343.27	133.52
b)	2.88	4.74	3.10	**298.37**		
c)	4.78	5.51	3.48	493.46		

Vinyl ester Swancorp 901

	b= 2.55 cm		**initial a (cm)**		Overall	
901-1	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			2.41		306.48	110.61
b)	1.59	5.08	2.85	**193.30**		
c)	3.25	6.30	3.70	414.32		
d)	4.37	4.58	4.88	311.81		

	b= 2.55 cm		**initial a (cm)**		Overall	
901-2	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			2.30		299.41	73.30
b)	1.78	5.13	2.41	**229.80**		
c)	2.30	5.31	2.61	292.53		
d)	2.97	5.72	2.85	375.91		

	b= 2.55 cm		**initial a (cm)**		Overall	
901-3	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			2.40		262.46	56.85
b)	2.06	4.04	2.66	**199.92**		
c)	2.87	4.99	2.88	310.98		
d)	3.30	4.17	3.11	276.49		

Vinyl ester Swancorp 901& 980 (batch b)

	b= 2.55 cm		**initial a (cm)**		Overall	
100-1	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			2.58		637.64	75.36
b)	3.81	6.49	3.04	**552.06**		
c)	5.64	6.49	3.77	694.08		
d)	8.28	5.26	4.41	666.78		

	b= 2.54 cm		**initial a (cm)**		Overall	
100-2	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			2.73		587.47	24.37
b)	4.14	6.35	3.19	**559.74**		
c)	5.74	5.72	3.86	597.18		
d)	8.23	4.90	4.87	605.49		

	b= 2.55 cm		**initial a (cm)**		Overall	
100-3	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			2.58		678.75	73.53
b)	3.76	7.08	2.91	**594.97**		
c)	5.33	6.94	3.44	732.61		
d)	6.91	6.12	4.23	708.65		

Vinyl ester Swancorp 980 (batch b)

	b= 2.55 cm		**initial a (cm)**		Overall	
980-1	disp (mm)	load (kg)	**2.06**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.74	8.75	2.45	**670.36**	803.26	113.38
b)	4.11	8.75	2.94	**845.75**		
c)	5.54	7.03	3.77	761.82		
d)	9.30	6.58	5.04	935.10		

	b= 2.55 cm		**initial a (cm)**		Overall	
980-2	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			**2.26**		707.60	60.17
b)	3.48	7.21	2.84	**641.23**		
c)	5.49	6.49	3.41	723.01		
d)	7.67	5.85	4.42	758.57		

	b= 2.59 cm		**initial a (cm)**		Overall	
980-3	disp (mm)	load (kg)		GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial			2.26		914.94	144.08
b)	4.19	10.16	2.80	**1070.41**		
c)	5.13	7.53	3.35	785.90		
d)	7.65	6.85	3.96	888.52		

Epoxy - System 41

	b= 2.49 cm		**initial a (cm)**		Overall	
1041	disp (mm)	load (kg)	**1.34**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	0.69	7.95	1.64	**240.44**	293.55	54.63
b)	0.97	7.50	2.05	**263.05**		
c)	1.43	6.81	2.57	279.57		
d)	2.18	6.03	3.00	302.14		
e)	3.23	6.01	3.85	382.53		

	b= 2.58 cm		**initial a (cm)**		Overall	
1042	disp (mm)	load (kg)	**1.39**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	0.60	8.88	1.63	**219.97**	229.19	10.14
b)	0.83	8.30	1.98	**240.05**		
c)	1.13	6.97	2.19	227.57		

	b= 2.8 cm		**initial a (cm)**		Overall	
1043	disp (mm)	load (kg)	**1.40**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	0.74	7.06	1.71	**196.01**	215.11	39.52
b)	0.80	7.63	2.04	**188.77**		
c)	1.26	8.03	2.43	260.55		

Epoxy						
SC-14	b= 2.47 cm		**initial a (cm)**		Overall	
1071	disp (mm)	load (kg)	**1.59**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	1.68	11.21	2.14	**703.00**	653.34	65.85
b)	2.48	8.55	2.44	**589.26**		
c)	3.57	8.52	3.13	741.91		
d)	5.15	6.21	3.66	606.79		
e)	6.85	5.61	4.10	625.73		

	b= 2.47 cm		**initial a (cm)**		Overall	
1072	disp (mm)	load (kg)	**1.85**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	1.86	9.87	2.16	**591.19**	583.87	114.32
b)	2.32	7.99	2.28	**510.56**		
c)	3.20	8.90	2.83	742.57		
d)	3.62	6.46	3.65	491.16		

	b= 2.5 cm		**initial a (cm)**		Overall	
1073	disp (mm)	load (kg)	**2.22**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.60	8.99	2.44	**620.51**	692.27	106.05
b)	3.93	8.62	3.03	**814.08**		
c)	5.04	6.57	3.40	642.21		

Epoxy						
SC-12	b= 2.53 cm		**initial a (cm)**		Overall	
1081	disp (mm)	load (kg)	**2.34**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.43	6.26	2.81	**379.05**	510.95	109.50
b)	3.71	5.79	3.22	**444.79**		
c)	5.57	5.87	3.83	591.84		
d)	7.07	4.56	4.18	489.64		
e)	9.58	4.86	5.41	649.46		

	b= 2.53 cm		**initial a (cm)**		Overall	
1082	disp (mm)	load (kg)	**2.34**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	2.23	5.69	2.73	**315.16**	365.09	47.31
b)	3.39	5.66	3.20	**409.24**		
c)	4.27	4.77	3.49	370.87		

Polyurethane Poly 15-D65

	b= 2.57		**initial a (cm)**		Overall	
1051	disp (mm)	load (kg)	**1.93**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	4.20	19.40	2.36	**2410.92**	2512.33	163.07
b)	6.40	17.71	2.67	**2751.64**		
c)	7.57	14.81	3.13	2406.57		
d)	9.55	14.23	4.14	2480.19		

	b= 2.56		**initial a (cm)**		Overall	
1052	disp (mm)	load (kg)	**2.06**	GIC (J/m^2)	GIC (J/m^2)	Stdev
a) Initial	5.00	20.90		**2914.28**	2914.28	

Results for Enf tests of $[0]_6$ composites.

CoRezyn **63-Ax-051** Specimen	crack length from support center a (cm)	load (kg)	h (mm)	V_f	EL*(GPa)	GIIC (J/m^2)
1012	3.77	38.92	1.69	0.40	33.15	1169
1013	2.33	51.71	1.72	0.39	32.56	724
1014	1.86	74.84	1.68	0.40	33.36	1037
Average	**2.66**	**55.16**	**1.69**	**0.40**	**33.03**	**977**
Std dev	**0.99**	**18.21**	**0.02**	**0.01**	**0.42**	**229**
Polyester PET-P460						
1021	2.18	83.46	1.70	0.40	32.92	1729
1022	3.55	54.88	1.73	0.39	32.42	1848
1023	3.86	47.17	1.73	0.39	32.31	1679
1025	3.90	56.25	1.89	0.35	29.41	2072
Average	**3.77**	**52.77**	**1.78**	**0.37**	**31.38**	**1866**
Std dev	**0.19**	**4.89**	**0.09**	**0.02**	**1.70**	**197**
Polyester Arotran Q6038						
1061	1.02	85.27	1.97	0.33	28.04	305
Vinylester Swancorp 980 (batch a)						
1031	1.89	124.28	1.91	0.35	29.21	2358
1032	2.67	102.51	1.95	0.33	28.40	3017
1033	3.13	100.24	1.96	0.33	28.29	3972
Average	**2.57**	**109.01**	**1.94**	**0.34**	**28.63**	**3116**
Std dev	**0.63**	**13.27**	**0.03**	**0.01**	**0.50**	**812**
Vinylester Derakane 411C-50						
1101	2.49	81.65	1.56	0.43	35.45	2620
1102	3.70	54.43	1.57	0.43	35.22	2495
Average	**3.09**	**68.04**	**1.57**	**0.43**	**35.34**	**2557**
Std dev						
Vinylester Derakane 8084						
1091	1.86	95.25	1.57	0.43	35.17	1992
1092	2.65	82.10	1.54	0.43	35.86	3054
1093	3.09	69.40	1.57	0.43	35.29	2867
Average	**2.53**	**82.25**	**1.56**	**0.43**	**35.44**	**2638**
Std dev	**0.62**	**12.93**	**0.02**	**0.00**	**0.37**	**567**

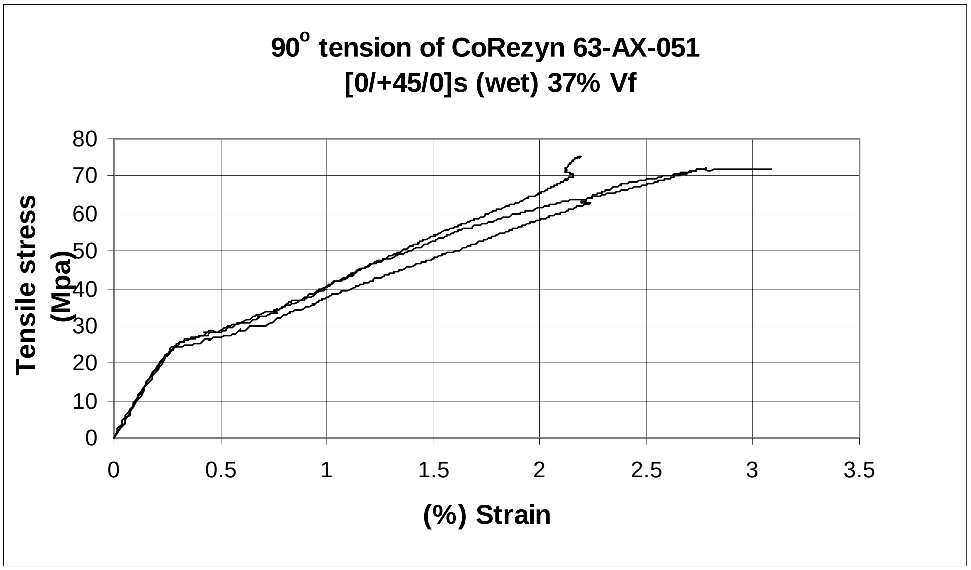
Epoxy System 41 Specimen	crack length from support center a (cm)	load (kg)	h (mm)	V_f	EL*(GPa)	GIIC (J/m^2)
1041	1.74	141.07	1.89	0.35	29.39	2593**
1043	2.95	102.51	1.89	0.35	29.53	3776
Average	**2.35**	**121.79**	**1.89**	**0.35**	**29.46**	**3776**
Std dev						
Epoxy SC-14						
1071	1.89	119.75	1.72	0.39	32.64	2769
1072	2.91	83.01	1.72	0.39	32.63	3110
1073	3.19	84.82	1.71	0.39	32.65	3791
Average	**2.66**	**95.86**	**1.72**	**0.39**	**32.64**	**3223**
Std dev	**0.68**	**20.71**	**0.00**	**0.00**	**0.01**	**520**
Epoxy SC-12						
1081	2.41	80.29	1.57	0.43	35.27	2350
1082	2.98	70.31	1.57	0.43	35.17	2710
Average	**2.69**	**75.30**	**1.57**	**0.43**	**35.22**	**2530**
Std dev						
Polyurethane Poly 15-D65						
1051	2.33	121.56	1.99	0.32	27.60	3145**

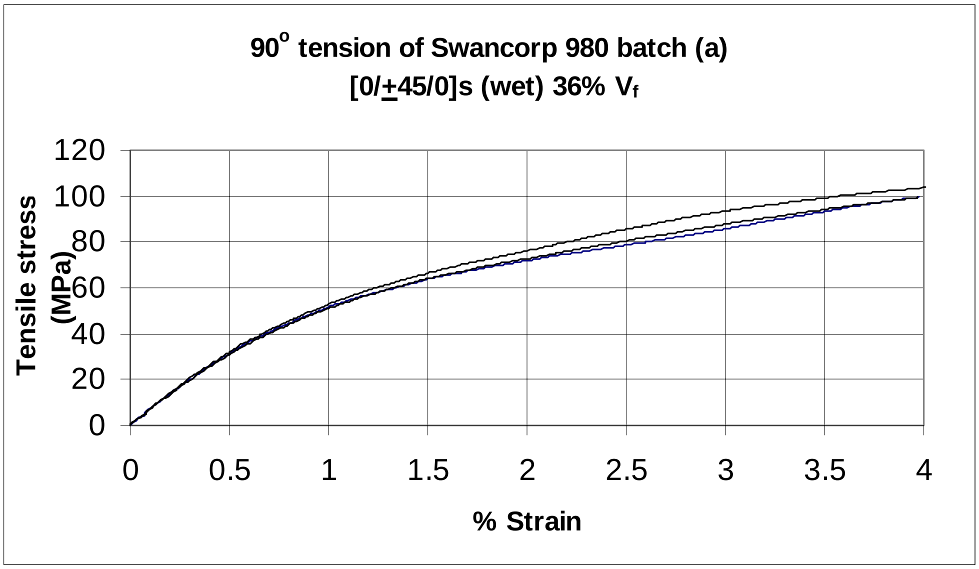
** Specimens failed in compression, no crack propagation occurred.

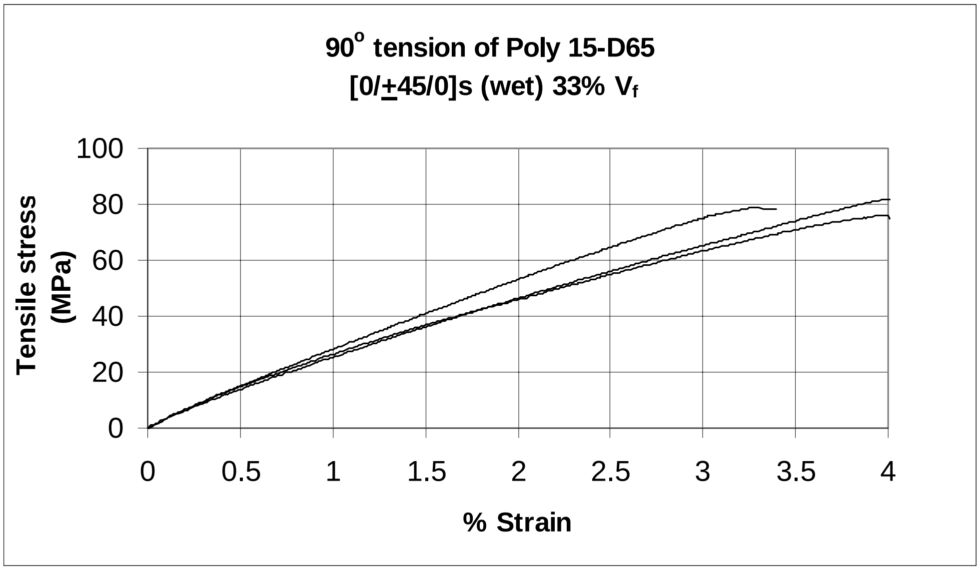
Results for 90° tension test of [0/±45/0]s wet composites after 330 hrs.

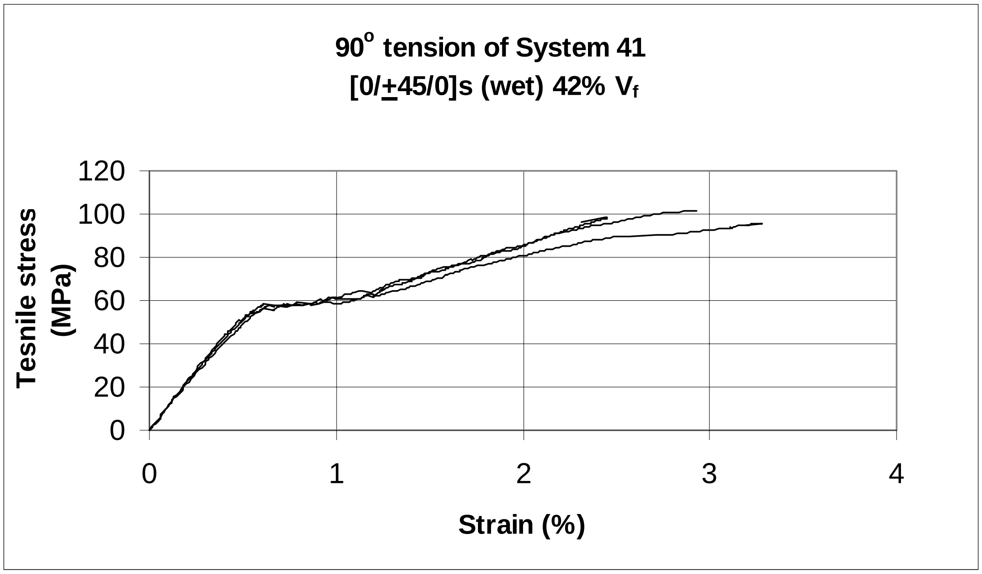
CoRezyn 63-AX-051	UTS (MPa)	Knee stress (MPa)	Tensile E (GPa)	Maximum % strain	Fiber Volume (Vf)
1T04	77.17	27.02	8.94	2.95	36
1T05	71.92	28.44	8.68	2.78	36
1T06	75.83	28.3	9.02	2.79	36
Average	**74.97**	**27.92**	**8.88**	**2.84**	**36.00**
Std dev	**2.23**	**0.64**	**0.15**	**0.08**	
Swancorp 980 (batch a)					
2T04	99.67	50.13	6.33	3.94	36
2T05	99.71	49.27	6.59	3.97	35
2T06	105.06	46.96	6.88	4.31	36
Average	**101.48**	**48.79**	**6.60**	**4.07**	**35.67**
Std dev	**2.53**	**1.34**	**0.22**	**0.17**	
Poly 15-D65					
3T04	81.31	28.68	3.1	3.3	37
3T05	82.37	22.57	2.73	4.06	37
3T06	76.11	28.5	2.91	3.98	37
Average	**79.93**	**26.58**	**2.91**	**3.78**	**37.00**
Std dev	**2.74**	**2.84**	**0.15**	**0.34**	
System 41					
4T04	101.62	57.92	9.69	2.93	42
4T05	101.93	56.89	10.74	2.45	40
4T06	96	57.9	10.06	3.28	38
Average	**99.85**	**57.57**	**10.16**	**2.89**	**40.00**
Std dev	**2.73**	**0.48**	**0.43**	**0.34**	

Results for 0° compression test of [0/+45/0]s wet composites after 330 hrs






90° tension of Poly 15-D65
[0/±45/0]s (wet) 33% V_f
Tensile stress (MPa)
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
4
% Strain


90° tension of System 41
[0/±45/0]s (wet) 42% V_f
Tesnile stress (MPa)
120
100
80
60
40
20
0
0
1
2
3
4
Strain (%)

Results for 0° compression test of [0/±45/0]s composites after water absorption.

CoRezyn 63-AX-051	Compressive strength (MPa)	Maximum Load (kg)	thickness (mm)	Vf (%)
1C04	433.77	3552.52	3.13	35.72
1C05	470.15	3753.46	3.06	36.44
1C06	401.64	3277.64	3.12	35.85
Average	**435.19**	**3527.87**	**3.10**	**36.00**
Std dev	**34.28**	**238.87**		
Swancorp 980 (batch a)				
2C04	411.90	3243.17	3.09	36.11
2C05	403.95	3295.30	3.19	35.13
2C06	432.77	3376.10	3.07	36.37
Average	**416.21**	**3304.86**	**3.12**	**35.87**
Std dev	**14.88**	**66.98**		
Poly 15-D65				
3C04	245.45	1888.30	2.97	37.43
3C05	291.35	2261.60	2.97	37.43
3C06	259.68	2046.14	3.02	36.90
Average	**265.49**	**2065.35**	**2.99**	**37.25**
Std dev	**23.50**	**187.39**		
System 41				
4C04	518.68	3517.14	2.57	41.58
4C05	510.62	3756.63	2.67	40.46
4C06	587.18	4622.08	2.91	38.09
Average	**538.83**	**3965.28**	**2.72**	**40.04**
Std dev	**42.07**	**581.27**		