THE RELATIONSHIP OF BARCOL HARDNESS AND INTERLAMINAR SHEAR STRENGTH IN GLASS REINFORCED POLYESTER COMPOSITE LAMINATES

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Materials Engineering Department

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Abstract

Chopped strand mat E-glass layers were impregnated with isophthalic marine laminating resin by hand lay-up techniques. Once the primary laminate reached the desired Barcol hardness value, the secondary laminate was applied and allowed to cure. These samples were bonded together at hardness values of 10, 30, 50, 70, and 90 Barcol. Lamination was conducted at 70°F with 35% glass fibers and 65% polyester resin catalyzed with 1.5% methyl ethyl ketone peroxide. The target thickness of each laminate was 6mm for short-beam shear testing requiring eight layers of glass and resin. Using the procedures outlined in ASTM D-2344, each sample set of ten specimens was short-beam shear tested using a 20mm span with 0.125in diameter load nose and supports. The short-beam shear testing of each specimen forced interlaminar shear between the primary and secondary layers, allowing for characterization of the bond strength at different hardnesses. After preliminary testing, all samples showed statistically significant differences with a trend of increasing bond strength with decreasing hardnesses. Twenty percent of the samples delaminated while the other sample failed under flexure loads. The samples that were bonded at higher hardnesses failed under lower loads in tension and compression rather than in shear. Three-point bend testing following ASTM 7264 was conducted to determine the flexural stiffness and strength properties of the samples to determine the validity of preliminary testing. After secondary testing was completed, the preliminary data was confirmed and conclusions were drawn. It was found that hardness does not affect the strength of adhesion in composite laminates. These results suggest that the use of this particular resin-fiber system could eliminate the sanding manufacturing step used during lamination.

Key Words: Materials Engineering, Composite, Fiberglass, Polyester, Resin, Lamination, Bend-Testing, Hardness, Short-Beam Shear, Barcol

1. Background

Composite industries utilize glass fiber-reinforced polyester (GFRP) laminates to produce boat hulls, aircraft fuselages, tubing, and a multitude of other products. GFRP laminates are used due to their increased tensile strength, insulating properties, and the cost effectiveness of each component compared to wood or steel. However, glass fibers have several shortcomings in typical applications due to their high hardness, low fatigue, and high density compared to other types of fibers[1]. There are five main forms of fiberglass: continuous strand roving, woven roving, chopped strands, chopped strand mat, and woven roving mat (Figure 1). All of these forms, combined with a particular resin system, are commonly used in many manufacturing industries. Polyester resin is the cheapest and most widely used matrix in conjunction with fiberglass. The curing of polyester is typically initiated with small quantities of catalyst; the catalyst most often used is a type of peroxide, such as methyl-ethyl-ketone peroxide (MEKP). In most manufacturing processes, several layers of fiberglass and polyester are applied to a part with a curing period in between applications. Determination of when to apply a secondary layer of fiberglass to acquire the strongest bond between laminates is key in reducing manufacturing time, cost, and the amount of material used. This bond strength can be measured by short-beam shear testing, which targets the adhesion strength between layers rather than the strength between the fiberglass and the polyester within a layer.

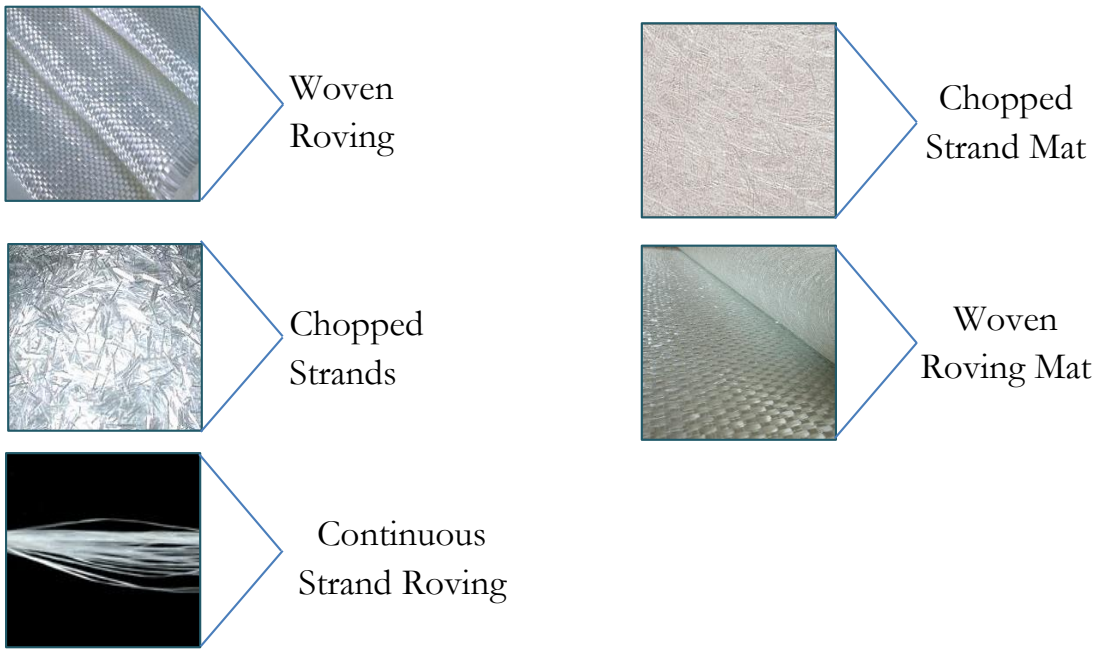

Figure 1: Five common forms of glass fibers for use in composite materials.[2]

In order to determine the quickest and strongest method of adhesion between composite laminates, a relation between adhesion and hardness needs to be generated, tested, and verified. In addition to creating a relationship between hardness and adhesive strength, both economic and manufacturing efficiencies must be considered. Currently, no method of relating the degree of cure to hardness has been established in developing lamination standards for maximum adhesive properties. While mechanical abrasion between lamination of excessive layers is used to maximize contact surface area, the chemical adhesion between laminates can be damaged and weakened. If a relationship is determined between the strength of adhesion and the hardness while laminating, abrading could be eliminated. Elimination of abrading could decrease time and resources required in a manufacturing setting. The goal of this project is to identify a relationship that can be used to determine the most efficient and strongest manner of applying secondary laminate layers to a primary layer.

1.1 Application Background

The most common use of fiberglass and polyester resin is in the production of parts and component molds for the boating industry. As of 2008, the marine industry was responsible for 11% of the composites market[3]. Boats were originally manufactured out of wood. This gradually led to using steel for larger ships, but the need for a material that was lighter than steel, and more resilient than wood, led to the use of fiberglass. A desire to optimize the lightness of wood with the resilience of steel led to the development of fiberglass boat parts. In the early 1920s, small parts within boats were manufactured with fiberglass. Due to the success of this material, fiberglass and polyester started to be used for the entire hull. The cost-effectiveness of glass fibers combined with its enhanced mechanical and physical properties over wood encouraged manufacturers to use fiberglass with polyester resin for all applications within a boat (Figure 2).

Figure 2: Examples of various applications of fiberglass within the marine industry. (a) An 8' small Livingston dinghy. (B) A 28' Cutwater pleasure cruiser. (C) A 224' naval minesweeper[11].

1.2 Realistic Constraints

Composites are replacing other materials, like woods and metals, every day. Composites are finding their place within an increasing number of industries; for example the military, marine, aviation, and automotive industries. Not only are the mechanical properties of composites similar or better than older materials, but composite applications are much more numerous. The identification of an accurate relationship between hardness and adhesion could reduce the manufacturing time of GFRP and minimize the cost of producing parts. Likewise, finding the optimal

hardness for adhesion could be used in any industry that utilizes secondary layers of fiberglass reinforced polyester laminates.

A reduction in manufacturing time lessens the environmental impact of open molding techniques by reducing the curing time of parts. With a reduction in the curing process time, emissions of styrene would be minimized and manufacturing-associated EPA requirements could be met more easily. Additionally, there is a 10% contribution to styrene emissions in the spray lay-up process due to the rate of application[4]. As such, styrene emissions could be reduced by determination of an optimal time for adhesion. Another advantage of decreasing the manufacturing time is a reduction in the labor necessary to produce each part.

Successful implementation of this laminating system could result in a reduction in material failures. For example, weak bonding in composite laminates can cause fiber pullout and delamination[5]. Delamination is a failure that occurs on a plane between adjacent layers with a laminate and is typically determined by the strength of the matrix (Figure 3). Delamination is the most common form of defect or cause of damage within a composite structure[6]. Delamination increases manufacturing time as well as the quantity of materials used. By increasing the strength of adhesion, the probability of delamination is reduced.

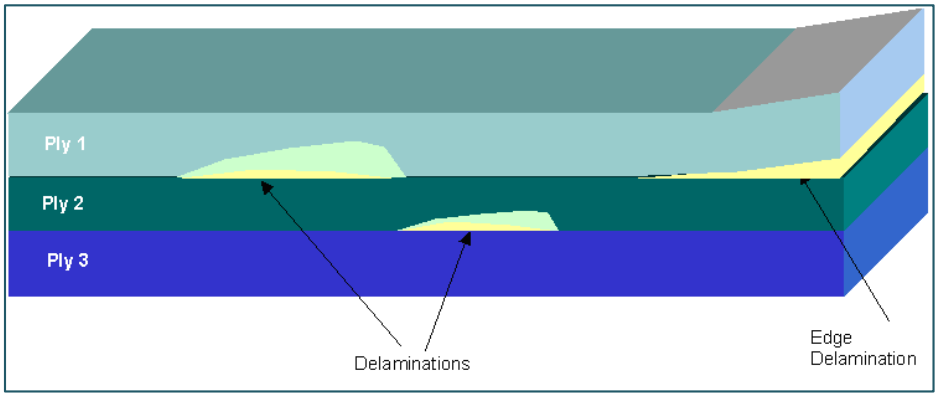

Figure 3: Diagram illustrating delamination within laminates as well as along the edge of a part[6].

The adhesion at the interface of two laminates can be improved by adding special coatings and coupling agents[5]. The interfacial strength can also be increased by mechanically abrading the surface with grinders, sand paper, and hours of labor. By determining when the maximum strength of adhesion is accomplished, the secondary lay-up can be applied without the need for abrasion, coatings, or coupling agents. The resulting reduction in labor time and materials used decreases the economic impact of each part on the producer. Labor can then be directed toward increasing the efficiency of the manufacturing processes.

1.3 Fiber-Reinforced Composites

Fiber-reinforced composites are structural materials that consist of two different components: a binder or matrix and reinforcements or fibers. The binder holds the reinforcements in place while protecting them. The matrix is the surrounding, continuous component within a composite, while the reinforcement provides strength, stiffness, and the mechanical properties of the composite. Early examples of fiber-reinforced composites are ancient Israelite mud bricks reinforced with straw and Mongolian hunting bows made of wood and glue. More recently, modern composites were sparked into recognition when Owens Corning Fiberglass began selling fiberglass as a reinforcement agent in 1937[3].

1.3.1 Glass Fiber Reinforcement

Glass fibers have been used for centuries to strengthen various applications, such as Renaissance era vases and pitchers. Fiberglass, in more recent years, has been commonly used as an insulating material. In WWII, when supplies of steel and other strategic materials were in high demand, fiberglass was combined with resin to create composite structures[3]. For many years after WWII, glass fibers were the only commercial reinforcements used in composites. Recently, within the last fifty years, the corrosion resistance of fiber-reinforced plastics has led to the replacement of

metals in many different applications such as car hoods, fenders, and other body components[7]. The low cost and advantageous properties of fiberglass continue to drive high demand for the material. For example, the manufacturing process of glass fibers is one reason the cost of fiberglass is lower than that of other reinforcing agents.

The raw materials used to manufacture glass fibers are silica sand, limestone, boric acid, and small amounts of clay, coal, and fluorspar. At around 2,300°F, these components are mixed and melted in refractory furnaces. There are two different methods of processing this molten material: marble processing and direct-melt processing. During marble processing, the molten glass is rolled into small marbles that ease transportation for later processing steps (Figure 4). These marbles are then re-melted and subjected to a formation bushing. This bushing consists of hundreds of small holes that are the resulting diameter of the fiber. After the molten glass is pushed through these holes, the glass is quenched with air and sometimes water. The resulting continuous strands are called filaments. A protective coating or sizing is applied to the filaments to help minimize damage without breaking or abrading the filaments. The filaments are then rolled and transported to curing and secondary processing. In the direct-melt process, the molten glass is forced through the bushing without forming marbles. The resulting fibers are identical to those of the marbling process.

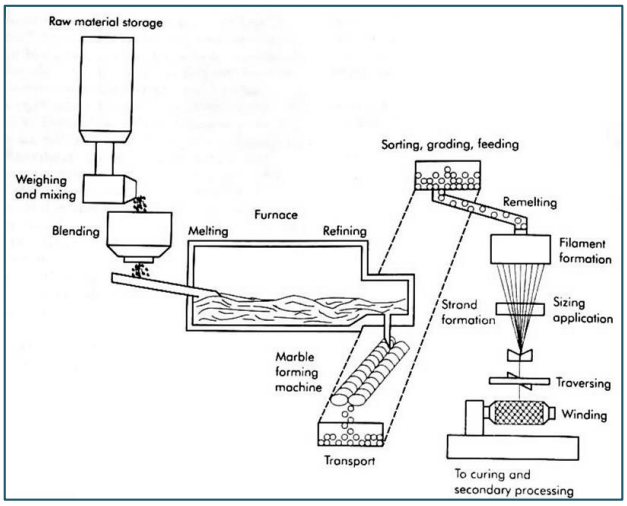

Figure 4: The marble melt process for production of continuous filament fiberglass.[3]

There are several types of glass fibers used for particular applications. E-glass, S-glass, C-glass, and quartz are the four types of glass fibers used for composites. E-glass was originally used when high electrical resistivity and strength were needed in electrical devices. Due to their low cost, E-glass is still the most widely used fiber in the composite applications, and less so for electrical ones. S-glass has the ability to retain its mechanical properties at higher temperatures while being 35% stronger than E-glass. S-glass is primarily used in advanced composites where carbon and Kevlar fibers are not used. C-glass is especially suited for chemically corrosive environments. Quartz fibers have less strength than the other three types, and are only used when electrical signal transparency or a higher glass transition temperature is desired. All of these types of fibers vary in their composition, and thus, mechanical properties.

Glass fibers have numerous applications in addition to the boating industry: light rail cars, roof structures, housings and cabinets, bath tub and shower units, and car bodies. Automotive manufacturing is another major market for glass fibers. For this market, glass fibers are used for body panels, air conditioning and heating ducts, and various small parts that utilize injection molding thermoplastic resins with glass fiber reinforcement. Many sporting goods utilize fiberglass as well; common applications of fiberglass include surf boards, snowboards, skis, skateboards, pole

vaulting poles, and arrows. Fiberglass is an easy and inexpensive method to improve the strength and stiffness of any part, which is why glass is used in many different industries.

1.3.2 Polyester Resin Matrix

There are three different types of matrix materials: polymeric materials, ceramic materials, and metallic matrix materials. Each type of matrix is chosen based upon its specific properties and how the matrix reacts with the reinforcement. The most common type of matrix material is a polymer. In a polymer matrix, single molecular units called monomers are linked together into short chains called oligomers that are then bonded together to create a polymer molecule (Figure 5)[8].

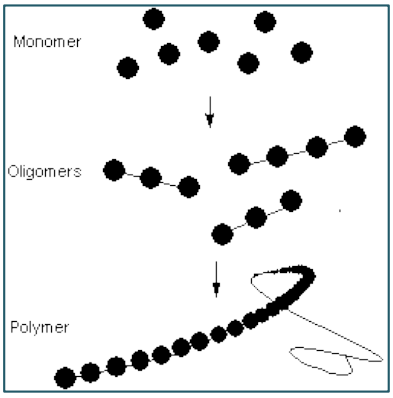

Figure 5: Linking of monomers to create oligomers to bond and create polymers that are used within matrix materials.[8]

Polyester is a polymer that is created through a condensation polymerization reaction in which two monomers with active end groups react with each other multiple times when mixed. This reaction results in the condensation or elimination of a byproduct molecule. Unsaturated polyester is the most commonly used thermosetting resin due to its low cost, ease of cure, and ease of molding. Despite having disadvantages like poor durability, brittleness, and air quality pollutants, polyester continues to dominate the resin market.

In the production of unsaturated polyester resin, glycols and diacids are combined to start the condensation reaction. The reactive groups on the glycol monomers are the alcohol (OH) groups located on the ends of the molecule. The reactive groups on the diacid molecule are the carboxylic acids (COOH). When the alcohol and the carboxylic acid react with one another, they form an ester. This ester is repeated in the polymer chain, thus forming the polyester resin with a byproduct of water (Figure 6).

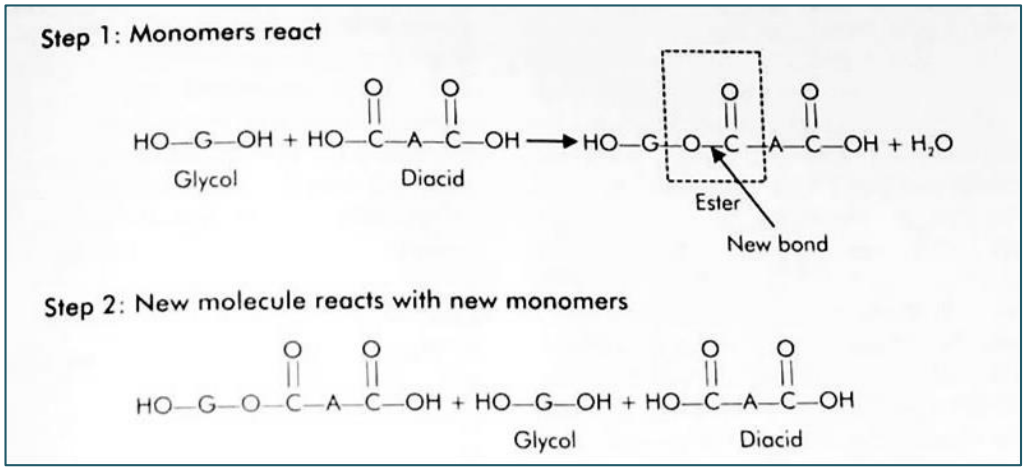

Figure 6: Condensation polymerization of a typical polyester.[3]

The properties of polyesters are dependent on several factors. Introduction of different additives to polyester slows or quickens the crosslinking reaction that occurs during curing. This crosslinking process is an exothermic reaction that produces significant heat while curing (Table I). In addition to altering reaction speeds, additives can change the color, viscosity, resulting hardness, and brittleness of the polymer. These properties can be ordered specifically from manufacturers or altered during the lamination process.

Table I: Polyester Additives Which Alter Reaction Speed

Slows Reaction	Quickens Reaction
Inhibitors: Absorbs free radicals, used to stop accidental crosslinking. **Fillers**: Calcium carbonate, calcium sulfate and talc add mass and absorb heat. **Oxygen**: Absorbs free radicals, used to quench system. **Molds**: The specific heat capacity of mold used to make parts acts as a heat sink.	**Styrene**: Acts as a solvent, used as a crosslinking agent. Excessive styrene will make final part brittle. **Initiators**: Peroxides typically are used to break apart and form free radicals. **Heat**: Increases chance of crosslinking. **UV Light**: Creates free radicals. **Accelerators**: Improves the efficiency of initiators.

In order to cure or harden a polyester resin, crosslinking must occur. Crosslinking is started when an initiator, most commonly an organic peroxide such as methyl-ethyl-ketone peroxide (MEKP), is mixed into the resin. Only a small amount of initiator is needed; a typical amount is 1.5-2% by volume of the resin used to cure a part. The initiator will then start the crosslinking reaction by splitting apart and forming free radicals. These unpaired electrons will seek out bonding sites on or nearby the polyester chain and produce a bond between one chain and another, therefore crosslinking the two chains.

The curing of polyester is critical in creating quality composite parts. The curing process is complex and is affected by the additives and the environment in which the part is being produced. A typical cure cycle will start with adding the initiator, causing a gelation point when the crosslinking starts changing the viscosity of the resin, and then will reach a final peak exotherm temperature (Figure 7).

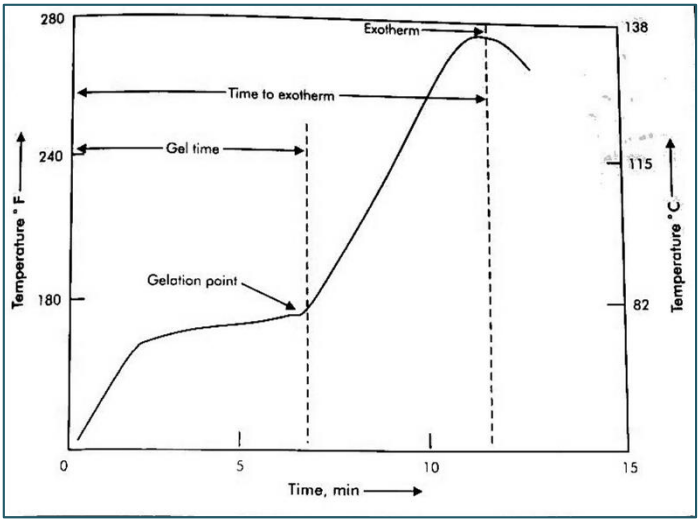

Figure 7: Curing process of most resin systems with gelation point and peak exotherm temperature.[3]

1.4 Manufacturing of Glass-Reinforced Polyester Composites

Several manufacturing techniques are used to creating GFRP laminates. Two major categories of manufacturing composites are open molding and closed molding processes. Open molding consists of laying fibers into an open mold and then applying resin. There are two methods of applying resin: lay-up molding and spray-up molding. Lay-up molding is used when complex shapes need to be produced and for the ease of adding inserts and stiffening (Figure 8).

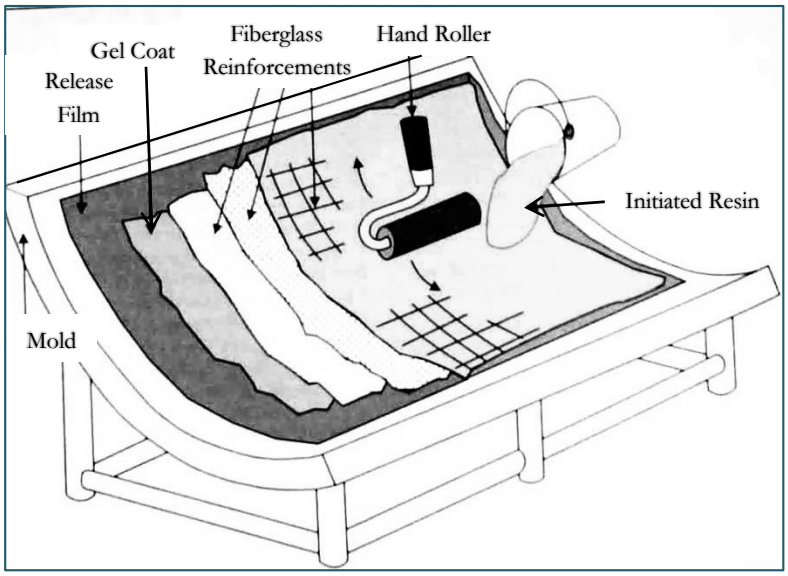

Figure 8: Hand lay-up process diagram.[3]

In the lay-up process, dry fibers are placed within a waxed mold cavity. Once all the dry materials are in place, the resin is applied with a hand roller. The hand roller is used to spread the resin and to remove any excess air within the fibers. Removing the air from the lay-up is critical for maintaining strength and decreasing the chance of crack propagation. Resin can also be applied to the fibers prior to being placed within the mold by using rollers or squeegees. Throughout the lay-up process, proper part thickness must be maintained to minimize shrinkage and to minimize the peak exotherm temperatures. If the desired thickness cannot be achieved in one lay-up, additional layers may be applied in a secondary bond. To maximize the strength between layers, the resins used in the secondary layer must be similar to those used in the first layer. Additionally, the secondary layer must be added before the primary layer is completely cured. The dual-layer associated increase in strength is due to the chemical bonding and adhering of the styrene between the two layers. If the first layer is allowed to cure for an excessive amount of time, contaminates can deteriorate the adhesion strength.

The second type of open mold processing is called spray-up molding. In spray-up molding, glass strands are cut and catalyzed resin is sprayed from a chopper gun onto a mold surface. Spray-up processing is typically used when parts are larger and less complex than those that use the hand lay-up process. The greatest advantage of the spray-up method is the decreased manufacturing time. Spraying both the fiberglass and the resin at the same time reduces the overall application time. The spray-up method has several disadvantages, including the need for special spraying equipment, a lack of control over fiber direction, and higher air pollution due to the atomizing of resin. Additional considerations for spray-up molding are that the spray equipment can only be operated by a trained operator, and that spray-up molding requires low viscosity resin to achieve proper wetting.

To apply the GFRP laminate, the operator sprays the resin and the chopped fibers onto the mold surface with an even coverage (Figure 9). If the coverage is not even, curing will occur at varying rates, which creates defects in the mold surface. The length of the chopped fibers can vary between projects, but is typically is 1-3 inches. The smaller fibers provide easier coverage around corners, but can weaken the part. Once the materials are sprayed on the surface, the surface is then rolled out as in the hand lay-up process. The rolling insures proper wet out and removes entrapped air which can cause voids in the finished composite.

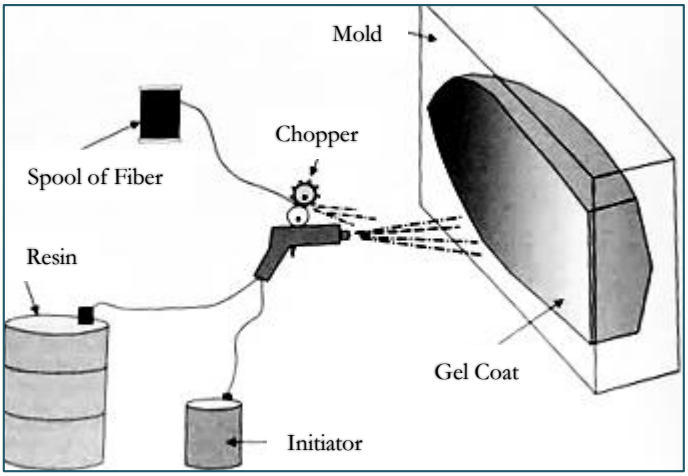

Figure 9: Spray-up molding technique used for large, less complex parts[3].

As in the hand lay-up process, additional layers can be added to the primary layer to increase the overall thickness. The additional layers may contain dye to distinguish them from the others, and must be added after the surface is mechanically abraded. This abrasion increases the mechanical bonding of the layers, but disrupts the chemical bonding that should take place between layers.

2. Materials and Methods

2.1 Fiberglass Reinforced Polyester

The tested samples were produced and cut with equipment provided by Cal Poly's Engineering Departments. The samples were cut from plates consisting of eight layers of laminated fiber-glass with a polyester matrix. The E-glass, fiber reinforcement was 1.5oz chopped strand mat with two inch fibers held in place by poly-vinyl alcohol (PVA). The PVA is deteriorated by the polyester resin, allowing for wetting out of the fibers. The matrix is an isophthalic polyester marine laminating resin produced by Composite Resource (Figure 10). This polyester resin contains surfacing agents to reduce the surface tension of liquids on the top of the laminates.

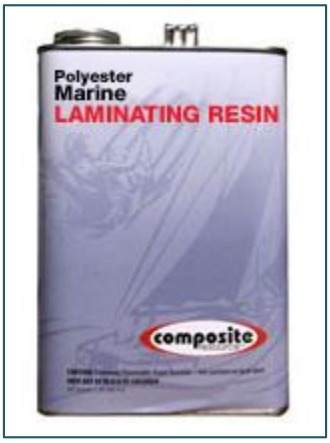

Figure 10*:* Isophthalic Polyester Marine Resin produced by Composite Resource, supplied by RevChem Composites.

The reduction in surface tension allows for increased adhesion of laminates as well as a tack-free surface once fully cured. The resin is UV-stabilized to minimize yellowing during exposure, and is pre-promoted to allow for easy application without the need to mix-in additives. The gel time is 13.5 minutes with a time to peak exotherm of 32 minutes. Each laminate was fabricated utilizing 60% resin and 40% glass at a temperature of 70°F. The resin was catalyzed with 1.5% MEKP and then applied to the first four layers of fiberglass. The samples were laminated using metal rollers to eliminate voids and bubbles. All laminating was done under a fume-hood to

capture the minimal VOCs eliminated while laminating. Once the laminates reached the desired hardness, the secondary laminate of four layers was applied to the sample.

2.2 Barcol Hardness Testing

Barcol hardness tests were performed using the Barber Colman Barcol impresser for soft materials, model GYZJ-935, following ASTM D 2583[9]. The hardness test characterizes the indentation hardness of materials by measuring the depth of penetration of the indenter point (Figure 11). A Barcol hardness tester is typically used to determine the degree of cure. The test specimen must be at least 1.5mm thick, and the testing must be conducted within 3mm of the edge of the specimen.

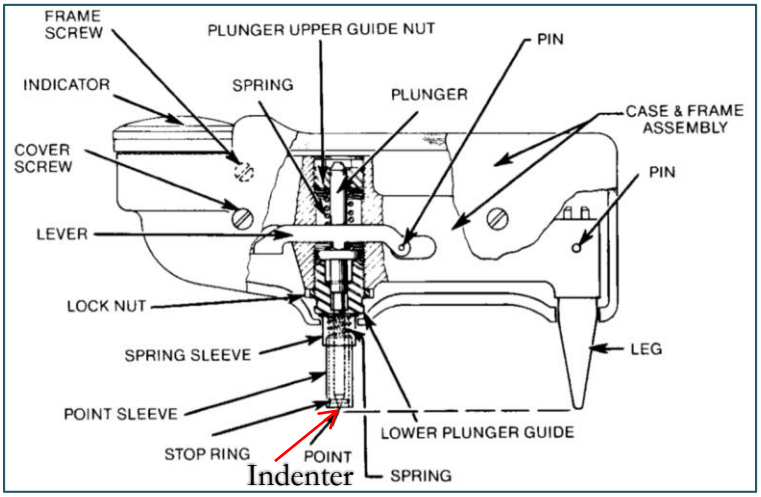

Figure 11*:* Schematic of the Barber Colman Barcol impresser hardness tester for soft materials illustrating internal components.

In the hardness test, the plates were supported across the entire sample to produce an even distribution of force. The test occurred on a stiff, hard, and supportive surface to minimize false data due to flexure in the material (Figure 12). Barcol hardness testing was conducted because of its current use in lamination plants for quality testing and comparison.

Figure 12: Barcol hardness test being conducted on a hard wood/metal surface with indenter on sample plate.

2.2.1 Test Procedure

Barcol testing was conducted at two minute intervals to determine the progression of hardness over time and to determine when to adhere the two laminates together. Once the primary laminate consistently registered the proper hardness, the secondary laminate was applied. Once the laminates were completed, both layers were allowed to fully cure overnight. The testing was completed in a uniform pattern allowing for twenty-five tests to be conducted on each sample plate (Figure 13). The indenter point and leg of the tester were placed parallel to the sample plate and pressure was applied. Once the force gauge reached a maximum value, the value was recorded and the next test point was checked. If the pressure was applied for too long, the force gauge would slowly drop off and the test would be invalid. Once all twenty-five test locations were checked and the averages calculated, the secondary laminates were applied.

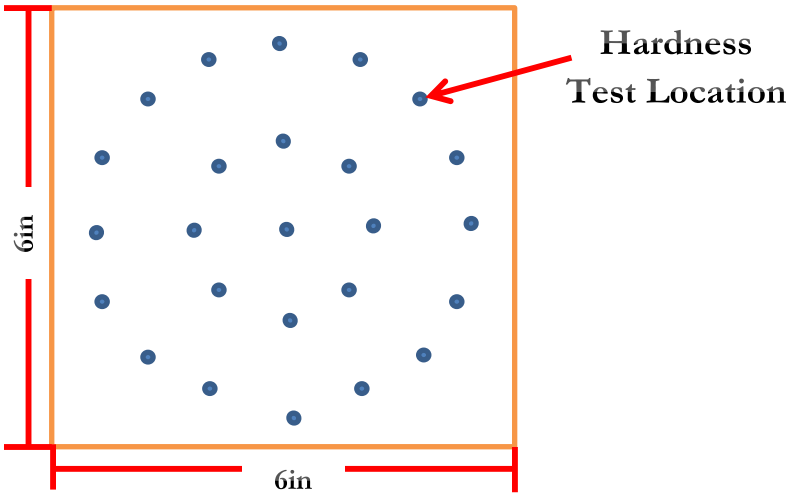

Figure 13*:* Illustration of sample test pattern for Barcol hardness testing. Test locations are a minimum of 3mm apart, and 3mm away from the edge.

2.3 Short-Beam Shear Testing

Short-beam shear testing provides an easy method to determine the interlaminar shear strength of composite laminates. Due to the random nature of chopped strand mat composites and the nature of the interlaminar strength, short-beam shear testing is best for comparing samples rather than calculating actual strength. The short-beam shear test also can determine the failure mode flexure or interlaminar failure, of each sample (Figure 14). The short-beam shear tests were conducted following ASTM D 2344[9]. This test method determines the short-beam strength used for quality control and process specification purposes. It can also be used for comparative testing of composite materials, provided that the failure modes are consistent between samples. Accurate reporting of observed failure modes is essential for data interpretation, especially in the determination of the initial damage modes.

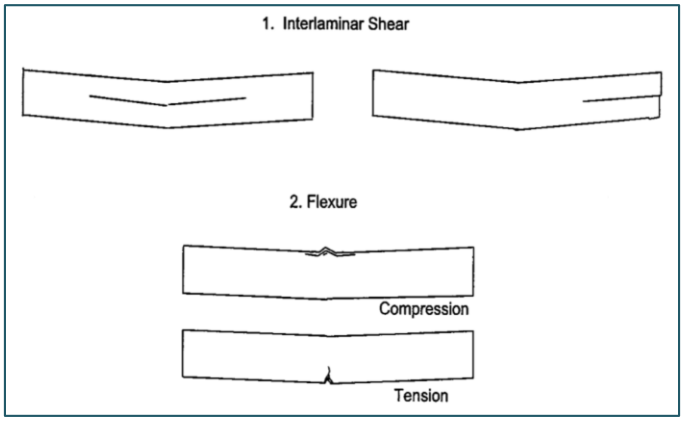

Figure 14: Failure modes induced by the short-beam shear test[9].

Although the short-beam shear test applies shear, the internal stresses within the samples are complex and flexure failure modes may occur. The stress state within short-beam shear samples shows a parabolic shear-stress distribution which theoretically resides on planes midway between the loading nose and the support span. Stress concentrations can occur under the loading nose and cause flexure failures if the loading nose is sufficiently small compared to the samples thickness[9].

2.3.1 Test Procedure

The short-beam shear test was conducted using center-loaded samples with the sample's ends resting on the two support noses. The loading nose was directly centered on the midpoint of the sample where the load was applied. Both the loading nose and the support noses had a diameter of 3.00mm. The ASTM standard recommends the use of five samples for each test condition. For this project, two sets of ten samples per set were produced at each test condition to maintain the statistical significance of the data. The short-beam shear samples were fabricated with a length-to-thickness ratio of 6.0 and a width-to-thickness ratio of 2.0. With each sample being 6mm thick, the length and width were calculated to 36mm and 12mm, respectively. Each laminate was cut using a tile saw without water to preserve the sample edges and the strength of the laminates. Each specimen was labeled for identification. Once

labeled, all samples were measured for width and thickness to calculate the shear strength after the test. The rate of crosshead motion was set to 1.0mm/min in the Blue Hill Software for testing on the Instron (Figure 15). The load was applied to the specimen until there was a load drop-off of 30%. Once the test was finished, the short-beam strength was calculated using Equation 1, shown below.

$$F^{sbs} = 0.75 * \frac{P_m}{b*h} \qquad \text{(Equation 1)}$$

F^{sbs} – Short-beam strength
P_m- Maximum load observed during test
b- Specimen width
h- Specimen thickness

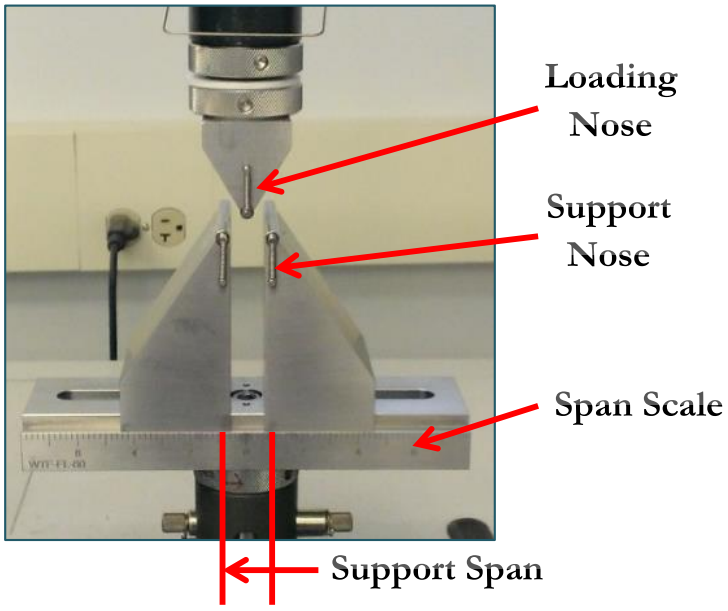

Figure 15: Test set-up for short-beam shear tests.

2.4 Three-Point Bend Testing

The three-point bend test determines the flexural stiffness and strength properties of the composite laminates. The test method utilizes a simply supported beam with center loading similar to short-beam shear testing with a larger support span and length to thickness ratio (Figure 16). To simplify calculations and

standardize geometry, loading is applied at one-half of the support span. The three-point bend test was developed for use with continuous-fiber-reinforced polymer composites. The test utilizes a 16:1 span-to-thickness ratio intended to develop long-beam strength instead of the short-beam shear strength. Compared to the short-beam shear test, the three-point bend test has design applications rather than only being for comparison purposes.

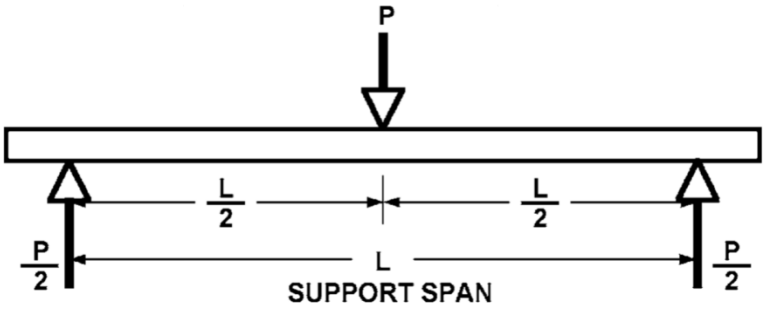

Figure 16*:* Schematic of three-point bend testing of a simply supported beam for composite materials[11].

2.4.1 Test Procedure

Each test was conducted following ASTM D 7264[10]. The loading nose and supports had cylindrical noses with a radius of 3.0mm. These samples were fabricated from the same plates and cut with the same tile saw as the short-beam shear samples. The sample length was 20% longer than the support span with the span being 104.0mm with the length being 145.0mm (Figure 17). A high span-to-thickness ratio was used to minimize the shear deformations to maximize the accuracy of flexural modulus determination. To increase the statistical validity of the test, ten samples were used for each test condition. The span was measured to the nearest 0.1mm when the fixture was set and confirmed for accuracy. The speed of testing was set at a rate of 1.0mm/min to allow for uniform strain across the surface of the sample. The test was stopped once the force dropped off by more than 30%. To obtain valid flexural strength data, the specimens had to fail on one of the two surfaces rather than by delamination. None of the samples failed at a specific flaw/defect, allowing for the

property values to be valid. Confirming the maximum flexural stress was calculated and recorded using Equation 2, shown below.

$$\sigma = \frac{3PL}{2bh^2} \qquad \text{(Equation 2)}$$

σ- Stress at the outer surface at mid-span of the specimen
P- Applied force
L- Specimen length
b- Specimen width
h- Specimen thickness

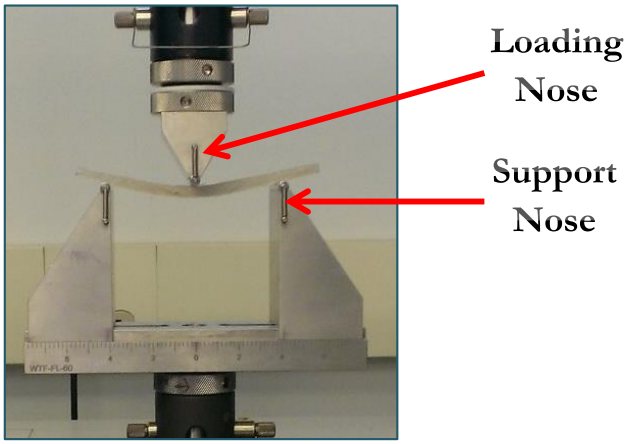

Figure 17: Three-point bend specimen in fixture at a span of 104mm with cross head movement at 1mm/min.

3. Results and Statistical Analysis

3.1 Barcol Hardness Test Results

To determine when lamination was to occur, the hardness and temperature progression had to be determined. Once the hardness was tracked and plotted, the time frame for lamination was determined for this resin system. These preliminary tests illustrated when the peak exotherm occurred, as well as when Barcol progression concluded (Figure 18). Temperature was determined using an infrared thermometer held six inches from the sample's surface. Lamination does not occur prior to the peak exotherm in manufacturing settings due to excessive shrinkage and warping of the final mold or part. With this resin system and the new Barcol tester, it was

determined that Barcol progression started twenty minutes after the peak exotherm. With this information, the test method and Barcol hardness testing unit were confirmed to be satisfactory. The first sample was laminated at a hardness of 10 Barcol and then laminations occurred in 20 Barcol increments (30, 50, 70, 90B). In order to compare these samples to industry standards, two samples had surface preparation; one sample was sanded and the other had a peel ply finish. The sample that was sanded is most similar to industry standard. The sample was thoroughly abraded with 120 grit sandpaper and blown off to remove dust. The peel ply sample was fabricated to illustrate another method of preparing the surface for lamination. After the first four layers were laminated, a peel ply fabric was applied to the surface and was allowed to cure. Once fully cured, the peel ply was then removed from the surface and the second four layers were then applied.

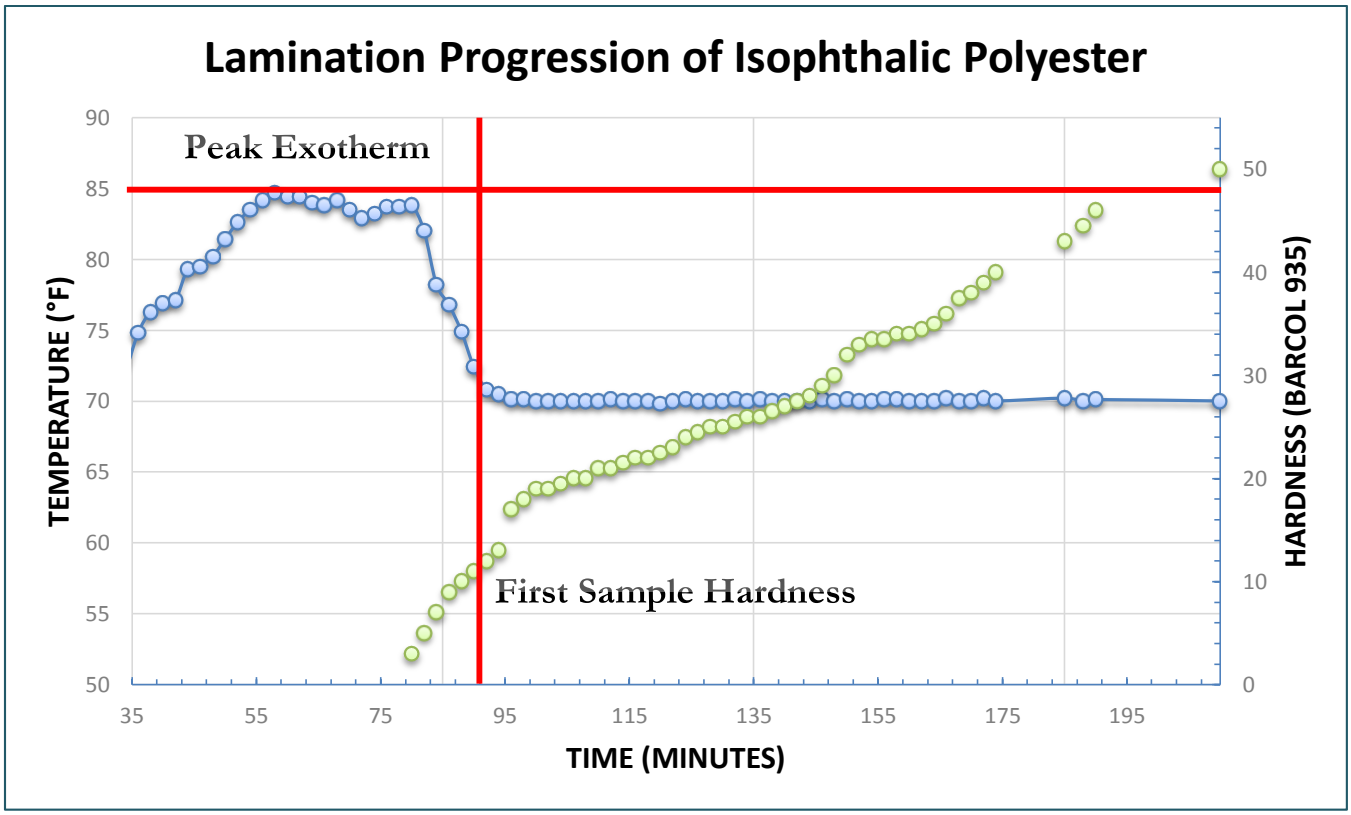

Figure 18: Variation of lamination temperature and Barcol hardness over time for isophthalic marine laminating resin.

Every sample was tested for hardness using the times predicted in the preliminary progression testing. Following the ASTM standard prescribed in Section 2.2 above, each sample was tested twenty-five times and the averages can be found in Figure 19. All samples were laminated within a 1 Barcol increment from the target value. All of the samples were statistically similar, therefore confirming the accuracy of the laminating schedule.

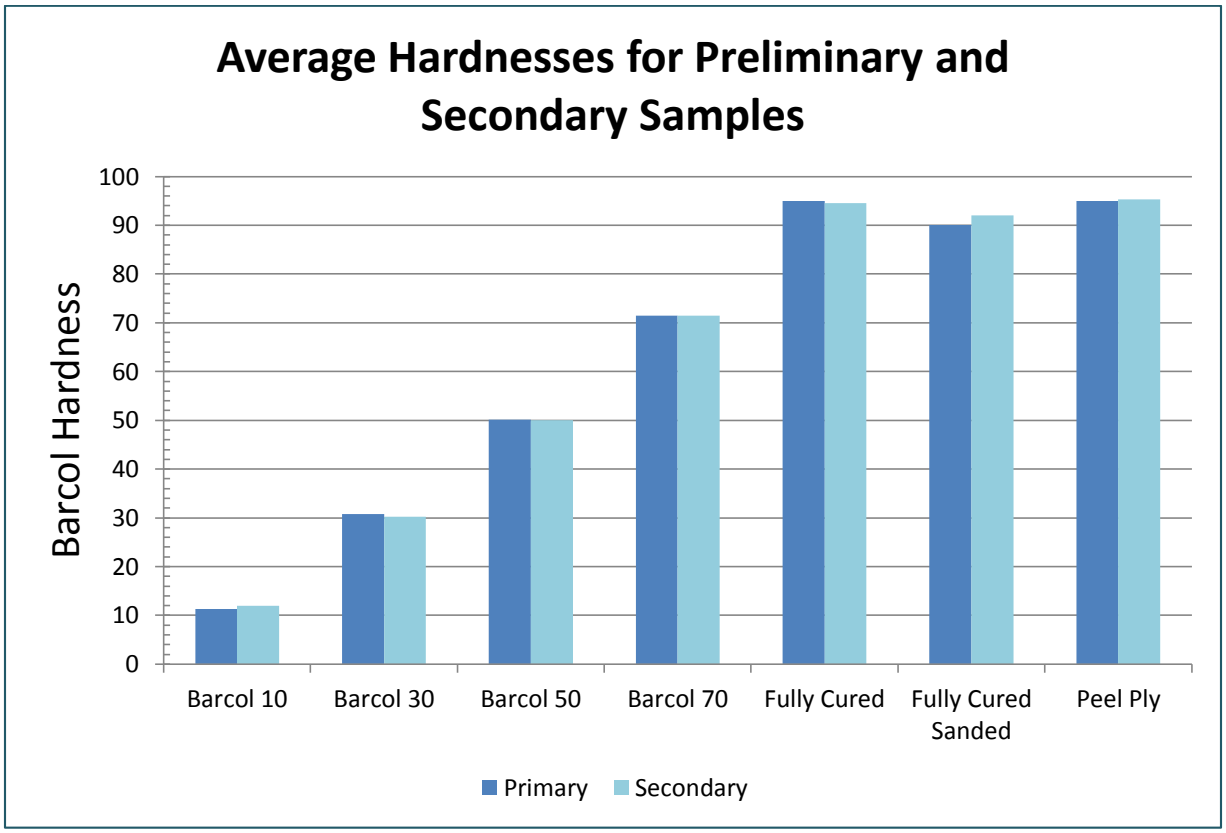

Figure 19*:* Average hardness values collected for each sample condition.

For comparison purposes, a Barcol of 95 was found to be the average fully cured hardness for this resin system. Samples were allowed to cure for two weeks prior to testing to take fully cured measurements. Industry specifications recommend that a part be fully cured in four hours, but the longest time a manufacturing plant would allow something to sit idle would be two weeks on average before adding additional layers. With this information, the extreme of two weeks was tested to gain a full

understanding of the Barcol progression. The fully cured, fully cured/sanded, and peel ply samples were all allowed to cure for a minimum of eight hours to reach a fully cured state with a Barcol between 90 and 95B.

3.2 Short-Beam Shear Test Results

Over 140 short-beam shear tests were conducted during the course of the project. Twenty samples were tested under each lamination condition. The primary data collected from the Barcol 10, 30 and 50 illustrated interlaminar failures, or delamination between the initial and secondary layers while the remaining data illustrated flexure failures in both tension and compression (Figure 20).

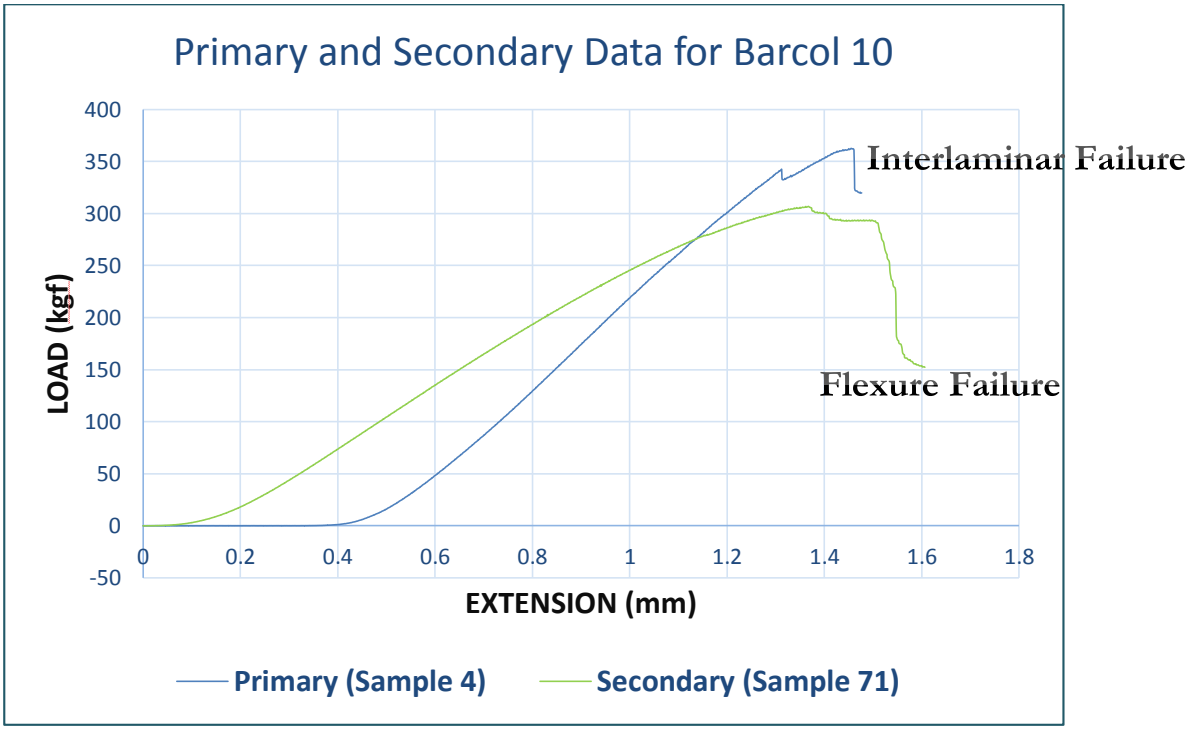

Figure 20: Representative curves for primary and secondary data for short-beam shear tests of Barcol 10.

It can be seen that the primary data illustrates an interlaminar failure due to the increased slope with sharp drop off in comparison to the flexural failure. The difference in failure modes tests the validity of the method. When different failure modes are present, the lamination of the panel must be validated. Over 78% of the samples followed the flexural failure mold all trending with the secondary line in

Figure 20. Due to the differences in failure mode, each sample was carefully inspected and the failure mode recorded. The maximum stresses generated during the short-beam shear test are generally similar, showing no trend or relation with hardness (Figure 21).

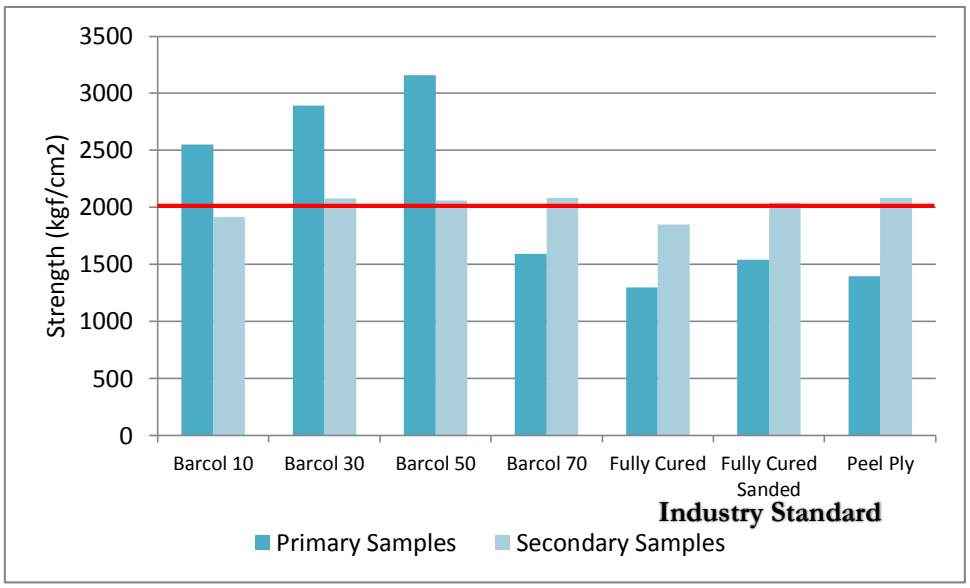

Figure 21: Comparison of strength between sample conditions and testing time for short-beam shear tests. The red line indicates the strength of the fully cured with sanding, industry standard sample.

Short-beam shear testing allowed for comparison of strength no matter the differences in failure mode. As shown in Figure 21, the strengths, calculated by Equation 2, of all of the secondary samples were considerably similar. The secondary data set had equivalent failure modes, therefore will be used for the basis of comparison. Those samples above the red line are stronger than those of the current industry standard. All of the samples are sufficiently strong, with the exception of the Barcol 10 and the fully cured without sanding for both sets of data. Comparing the strengths of different surface preparations, the fully sanded and the fully sanded with sanding samples illustrated the largest difference in values. This difference, although the greatest, is not statistically different. The strength values of all sample conditions are strong enough to indicate removing the sanding process would be beneficial in increasing efficiencies by reducing materials used, and reducing manufacturing time.

3.2.1 Statistical Analysis

Once the strength values were calculated, a two-sample t-test was performed to compare the two data sets. The t-test was performed using a 95% confidence interval with an alternative hypothesis of the sample populations being equal in value. The t-test revealed a p-value of 0.6148, indicating that there is not a statistically significant difference between the primary and secondary sample sets. Secondary statistics were performed on all short-beam shear samples to compare averages, standard deviations within the first and third quartile, and maximum and minimum values (Figure 22).

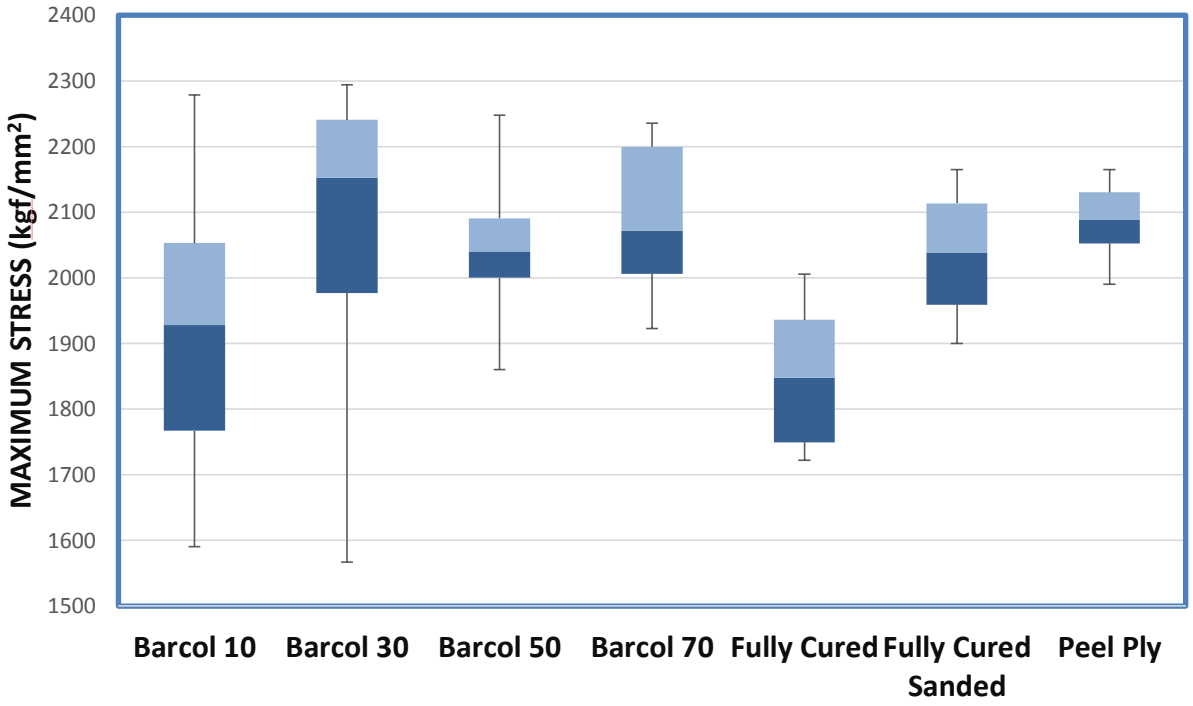

Figure 22: Box plot of average, maximum, minimum and first and third quartile for comparison between each sample condition for short-beam shear tests. The different colors indicate the first and third quartiles.

The box plot in Figure 22 illustrates the similarities and differences in each sample set. The fully cured sample without sanding is the closest to being significantly statistically different although through a t-test comparison a p-value of 0.0245 was determined, making the samples statistically similar. This p-value suggests statistical difference although it is much closer to the standard 0.05 than the majority

of the comparisons. The Barcol 10, 30 and 50 data have large ranges of values due to the primary data having a different failure mode.

3.3 Three-Point Bend Test Results

Three-point bend tests were performed on each of the sample conditions with the expectation of acquiring flexural properties. Five specimen were tested at each hardness value for statistical validity. Figure 23 represents the average values of all of the sample conditions demonstrating loading and extension. These samples do not have a specific trend similar to the short-beam shear samples. The three-point bend samples demonstrate a significantly lower load with larger extension while producing similar stress when compared to short-beam shear values. This difference is due to the differences in geometry between the two methods.

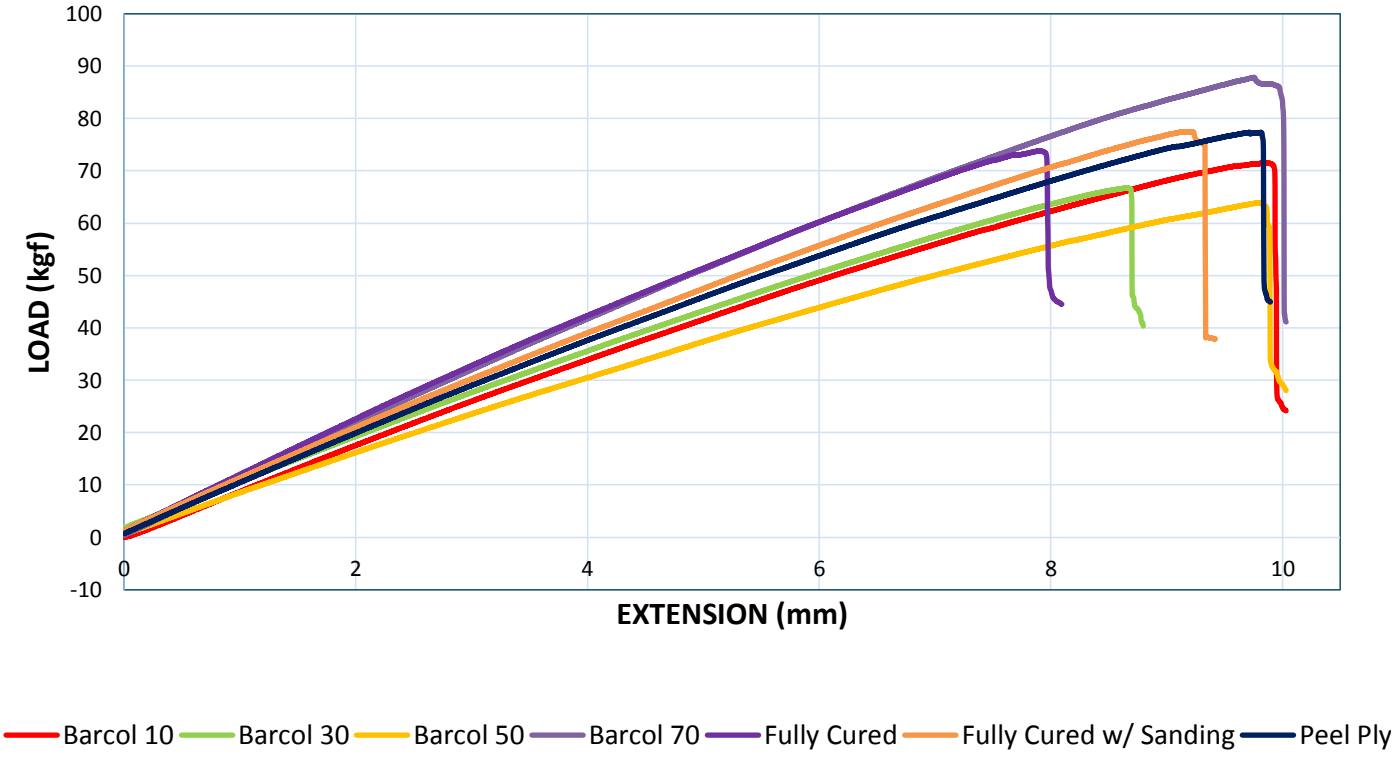

Figure 23: Three-point bend data for each sample condition illustrating the effects of varying geometry.

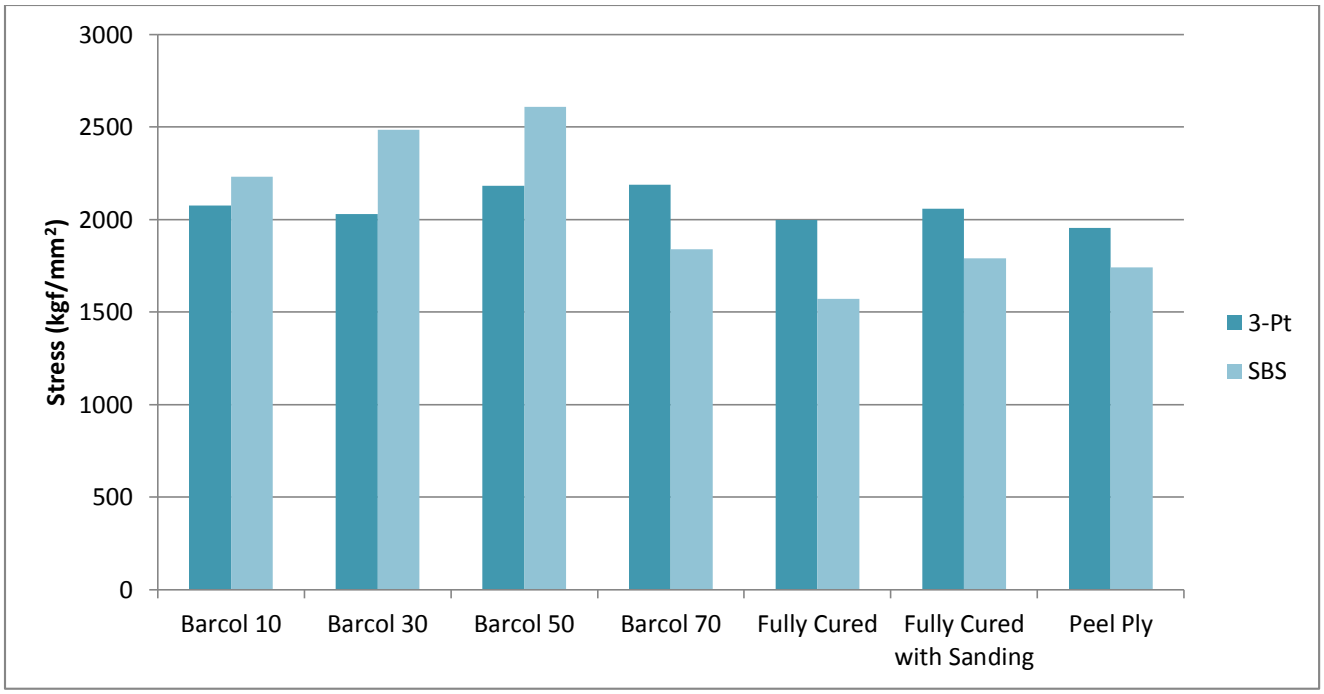

Figure 24*:* Comparison data of three-point bend strength and short-beam shear strength using Equation 2.

Three-point bend strength properly illustrates the laminates strength due to the stresses created in the samples. Due to the flexural failure mode of the short-beam shear samples, Equation 1 could not be used to determine the interlaminar strength of each sample. Instead, Equation 2 was used to calculate the strengths of both the short-beam shear and the three-point bend specimens, as seen in Figure 24. The short-beam shear data calculated represents an improperly dimensioned three-point bend test while maintaining statistical similarity between three-point testing and short-beam shear testing. The three-point bend data better represents the overall strength of the composite laminate, while the short-beam test better determines failure mode. When compared to one another the three-point strengths of each sample condition is stronger than the industry standard other than the peel ply and fully cured sample. This data further supports the elimination of the sanding manufacturing process.

4. Discussion

After finding the relationship between degree of cure and Barcol progression for this laminating system, the ability to determine a laminating schedule was possible. With this new insight, the project was able to proceed and became reproducible. The values found for this relationship were reproducible and can be applied in production settings given this resin system, or the determination of a new relationship for another system. Having the ability to start hardness measurements after peak exotherm validated testing following the high temperature. This information agrees well with industry standards and follows typical protocol.

Using short-beam shear testing, a determination of failure modes and a better understanding of interlaminar strength was provided to the project. With varying failure modes, the lamination method had to be rechecked. Determining the cause of the variation was found to be difficult. Without knowing the cause of the delamination in the first three sample sets, the data had to be checked for statistical similarity. Using the t-test, the data was confirmed to be similar and therefore testing proceeded. The remaining 140 samples all failed in the predicted mode of flexure failure. Short-beam shear testing revealed that the laminate strength was greater than the shear properties, thus increasing the ability to eliminate a surface preparation manufacturing step.

Three-point bend testing further focused the results on increased strength properties. The variation in strengths and non-relational trends leads to the assumption that as long as the strength of the laminates is greater than or equal to that of the industry standard, the sanding step could be removed from the manufacturing process without deteriorating the strength of the laminate. All of the samples but two meet these criteria making the sanding step not necessary.

This project further questions the validity of the short-beam shear test as a method for determining interlaminar shear strength in composite laminates. The simple loading condition induced during the test does not result in a simple failure mode. Without the test inducing pure shear force, Equation 1 becomes invalid and Equation 2 becomes the primary determination of stress. The short geometry of the sample creates a concentrated load under the loading nose increasing the complexity of the failure mode, further reducing the short-beam shear tests validity in design. The short-beam shear test is valid for use in comparison purposes, such as this project, but provides little clarity for results. There are two main problems with the short-beam shear test; the applied loading creates high local stress concentrations and non-uniform stresses occur throughout the sample due to their short geometry.

5. Conclusions

1. The preliminary test for temperature and hardness progression verifies the usability of the Barcol Hardness Tester in a production setting. The Barcol tester satisfies the requirements of measuring the degree of cure after peak exotherm with a fully cured sample being around 90-95 Barcol out of one hundred.

2. Although the Barcol Hardness Tester performed well under these conditions, one cannot conclude that the hardness dictates the interlaminar shear strength, due to the variations in strengths at different hardnesses.

3. The lamination schedule of composite panels utilizing this polyester resin system has a stronger interlaminar strength than that of the composite. Panels of this geometry will break in tension and compression before delaminating between layers.

4. Due to the sufficient strength in the composite panel in all of the test conditions, the sanding and surface preparation process of current manufacturing plants could be eliminated. With the elimination of this step, manufacturing time and material cost could be reduced or eliminated. The preparation does alter the ultimate strength, but not significantly enough to continue the sanding process.

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