DEVELOPMENT OF BIOBASED COMPOSITES OF STRUCTURAL QUALITY

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ABSTRACT

Highly biobased composites with properties and costs rivaling those consisting of synthetic constituents are a goal of much current research. The obvious material choices, vegetable oil based resins and natural fibers, present the challenges of poor resin properties and weak fiber/matrix bonding, respectively. Conventional methods of overcoming poor resin quality involve the incorporation of additives, which dilutes the resulting composite's bio-content and increases cost. To overcome these limitations while maintaining high bio-content and low cost, epoxidized sucrose soyate is combined with surface-treated flax fiber to produce biocomposites. These composites are fabricated using methods emphasizing scalability and efficiency, for cost effectiveness of the final product. This approach resulted in the successful production of biocomposites having properties that meet or exceed those of conventional pultruded members. These properties, such as tensile and flexural strengths of 223 and 253 MPa, respectively, were achieved by composites having around 85% bio-content.

ACKNOWLEDGMENTS

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CHAPTER 1. INTRODUCTION

Composites are valued because of their high strength, low weight, and relative ease of manufacture into myriad configurations and structures. The earliest manufacture of composite materials incorporated naturally derived components. For example, most ancient Mesopotamian building projects employed bricks made of clay reinforced with straw. Over recent decades, composite technology has come to rely heavily on petroleum-based resins and man-made fibers in the pursuit of more reliably and highly performing products. Paralleling this shift toward synthetic materials is the rapid expansion of uses and applications for composite materials. This not only raises concerns of sustainability issues during their manufacture, but their non-biodegradability also raises environmental concerns associated with their end-of-life disposal. With these concerns in mind, a relatively recent surge has been seen in the area of developing viable applications for biobased composites. These bio-composites often incorporate natural fibers such as flax, jute, ramie, hemp, and kenaf. Their binders are also often either partially or wholly comprised of resins derived from natural sources.

Unfortunately, little success has been seen in attempts to produce largely biobased composites of sufficient strength for use in structural applications. In general, it has been true that high performance and high levels of renewable content are mutually exclusive. Neither the fiber reinforcement nor the resin material is solely responsible for this. Rather, natural versions of both phases possess their own particular negative aspects.

Basic resins derived from natural sources lack the properties needed to produce composite materials of note. When not being simply overlooked in favor of more highly performing petrochemical resins, they require a high degree of modification in order to bolster their properties. Further blending with conventional resins is often also necessary. While the

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resins resulting from such machinations often have passable properties, an unfortunate side effect is the notable reduction of the resin's renewable content. Of course, the cost to achieve these mediocre gains, in terms of process complexity as well as material cost and biocontent reduction, raises questions as to the practicality of such approaches. However, a newly developed biobased thermoset resin, epoxidized sucrose soyate (ESS), is notably different than resins produced through the afore-mentioned dilution and modification approaches. Despite being entirely biobased, it shows the potential for overcoming the performance limitations of currently available bioresins.

The prospect of producing composites using natural fibers poses significant hurdles if uniform, quantifiable, reproducible properties are desired. This is because the properties of natural fibers vary greatly from growing season to growing season among their regions of origin. Variations in practically any of the conditions in which a plant is grown have the potential to affect the quality of the fiber obtained from that plant. In addition, age of the fibers, storage environment, and methods used to separate them from the plant source also impact the fibers' properties (1). Beyond fiber variability problems, resin-matrix compatibility issues are a universal hurdle to the use of natural fiber in composites. This incompatibility stems from inherent properties of the materials themselves. The resins are hydrophobic in nature, while natural fibers are hydrophilic. Overcoming this requires treating the fiber in order to modify its surface chemistry, making it behave in a more hydrophobic manner where it interfaces with the matrix.

CHAPTER 2. BACKGROUND/LITERATURE REVIEW

2.1. Natural Fiber

The topic of natural fibers includes a wide array of materials and origins. Perhaps the smallest general category could be that of mineral fibers such as asbestos. Another category, animal fiber, includes several general types: feathers, silks, and hairs. Plants are a third source of natural fiber, which provides a broad range of types of various lengths and properties. While each of these categories of natural fiber can conceivably be employed in a composite material, for the purposes of this discussion the focus will be on plant fiber. As such, it is implied that future references to 'natural fiber' is intended to refer specifically to plant fiber.

2.1.1. Natural Fiber Types

Natural fibers originating from plants can be grouped into four or five general categories: leaf, seed/fruit (sometimes categorized separately), stalk, and bast fibers (2,3). Fibers obtained from the leaves of certain plants have found use in composites. Included in this group are the curaua, henequen, manila, palm, pineapple, screw pine, and sisal fibers (4). Coir, cotton, kapok and oil palm are examples of seed or fruit fibers. Based on their source, it can easily be inferred that these fibers are fairly short in comparison to other types. As their name implies, stalk fibers are taken from the stalk of their source plant. Examples of this type include the straw of cereal crops such as wheat, rice and barley, as well as bamboo and other grasses. Wood fiber is also considered a member of this category. Bast fibers come from the phloem, or nutrient-conducting tissue of a plant (5). This category includes such fibers as banana, flax, hemp, jute, kenaf, mesta, ramie, and rattan (4,6). As may be expected based on the part of the plant from which they are obtained, bast fibers are among the longest natural fibers available. They also include some of

the strongest natural fibers available. As a result, bast fibers are often a first choice when composites with optimal strength are desired.

2.1.2. Natural Fiber Structure

In general, plant based fibers are made up of similar constituents, though often in varying combinations and configurations. Table 1 lists the makeup of several common natural fibers (7,8). The most critical of the components is cellulose, which provides the majority of the strength for the fiber. Cellulose makes up anywhere from 61% to 83% of the fibers included in the table. In addition to cellulose, other components include hemicellulose, lignin, pectin and various waxes (9). Each of these materials has its own characteristic mechanical properties which contribute to the overall properties of a fiber. As such, natural fibers can rightly be considered composites in and of themselves.

In these composite fibers, the reinforcing component is cellulose fibrils. What can be considered the matrix is the collection of amorphous components such as lignin, pectin, and hemicellulose that bind the fibrils in place (10). Figure 1 illustrates the complex structure of natural fiber (11). Within a primary wall are three secondary walls, all of which surround the central hollow lumen. Each wall contains helically wrapped microfibrils having diameters ranging from 10-30 nm (12). The winding direction of these fibrils alternates with each

Table 1. Structural Compositions of Natural Fibers (7,8)

Fiber type	Cellulose (wt.%)	Lignin (wt.%)	Hemicellulose (wt.%)	Pectin (wt.%)	Wax (wt.%)
Jute	61-71.5	12-13	13.6-20.4	0.2	0.5
Flax	71	2.2	18.6-20.6	2.3	1.7
Hemp	70.2-74.4	3.7-5.7	17.9-22.4	0.9	0.8
Ramie	68.6-76.2	0.6-0.7	13.1-16.7	1.9	0.3
Sisal	67-78	8.0-11.0	10.0-14.2	10.0	2.0
Cotton	82.7	0.7-1.6	5.7	-	0.6

secondary wall layer. The central secondary wall, S2, is by far the thickest and contributes the majority of the fiber's mechanical properties (12).

Just as orientation of the fibers in a conventional composite influence the composite's properties, so too does the microfibrillar angle impact the properties of natural fibers. Specifically, low microfibrillar angles equate to higher strength fibers (13).
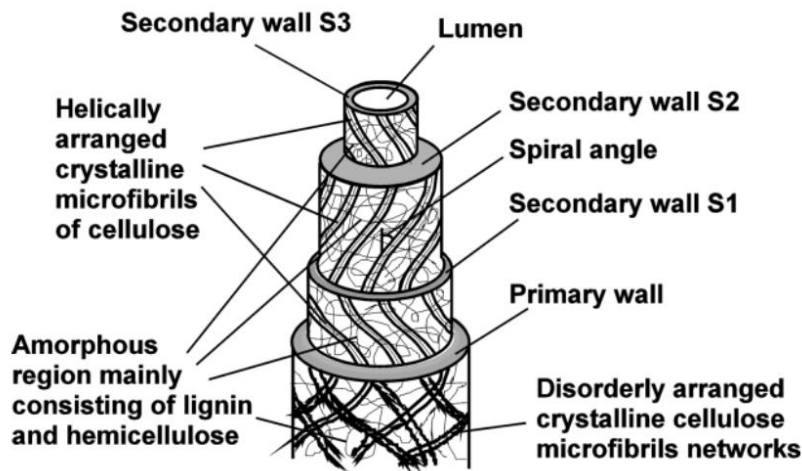
Figure 1. Natural fiber structure (11).

2.1.3. Natural Fiber Qualities

Natural fibers have a number of characteristics distinguishing them from engineered fiber. Some of these qualities contribute to their appeal and utility. Other qualities are not nearly so beneficial and detract from their usefulness.

2.1.2.1. Natural Fiber Advantages

The advantages of natural fiber over engineered fibers are numerous and varied. Firstly, they are renewable and can be produced relatively inexpensively. Their low density translates into high specific properties such as modulus, flexibility, strength, stiffness, and impact resistance (12,14–16). They are safer to handle and do not abrade manufacturing equipment or irritate skin, translating to further cost savings and ease of use. They are excellent electrical

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insulators. Also, their hollow lumen results in respectable acoustic dampening qualities (12). Natural fibers also exhibit superior vibration damping (16).

2.1.2.2. Natural Fiber Disadvantages

In addition to those positive qualities outlined above, natural fibers possess a number of deleterious traits that require cognizance on the part of the user. The qualities of natural fibers vary with such factors as growing season, region of origin, age, storage environment, processing methods, and genetic variation (1). Low degradation temperatures limit processing and service temperatures to below 200 °C (12). Natural fibers also have a hydrophilic nature, which results in a poor ability to adhere to non-polar, more hydrophobic polymer matrix materials. This high moisture absorption also leads to swelling of composites and production of voids at the fiber matrix interface, reducing the composite's dimensional stability as well as its mechanical properties (12). Also, while their biodegradability is often considered a favorable property, the chance of premature degradation is a concern.

2.1.4. Fiber Harvesting and Processing

The cultivation of bast plants is generally not undertaken with the goal of obtaining both a seed harvest and fibers of optimum quality. This is a consequence of the timing of seed and fiber development. Fibers obtained once the seed has fully matured are generally more brittle and coarse than those obtained at an earlier stage of seed development. In addition, fibers are more easily decorticated and separated when harvested prior to full seed maturity (17).

Following harvest, the pectin cementing the fiber to the rest of the stem is removed through a process called retting. This is generally accomplished in one of five ways: dew, water,

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enzymatic, chemical, and mechanical retting (17,18). The particular process employed

significantly influences the quality of the fiber obtained in the end (10).

2.1.4.1. Dew Retting

Frequently employed in areas with limited water, dew retting involves leaving the plant

stems lying in the field. Over a three to six week timeframe, moisture and microorganisms from

the soil decompose the hemicellulose and pectin, separating the stem and the fibers. Fibers

retted in this way are generally coarser and are darker in appearance than water retted fiber.

Additionally, seasonal variations cause inconsistent results year to year (10,18).

2.1.4.2. Water Retting

Traditionally, water retting is accomplished by submerging bundles of stalks in bodies of

standing or running water. As the water soaks in to the center of the stalk, the inner cells swell

causing the outer layers to burst. This facilitates more rapid influx of additional moisture and the

anaerobic bacteria responsible for the breakdown of the pectin. This process generally takes one

to two weeks. However, a variation of the process exists in which warm water is employed.

Under 28 to 40 °C conditions, the process only takes three to five days. In either case, the

process of water retting results in fiber of consistently good quality, as well as the generation of

large quantities of polluted wastewater (10).

2.1.4.3. Enzymatic Retting

Enzyme retting results in fine fibers of reliable consistency. Taking between 2 to 24

hours, this is one of the faster retting methods. While it provides undamaged fiber of exceptional

strength, the costs associated with enzyme retting are significantly greater that with any other

method (10).

2.1.4.4. Chemical Retting

A modified form of heated water retting utilizes chemical action to further accelerate the retting process. The dissolution of pectin can be facilitated through the use of one of several chemicals, including chlorinated lime, sodium hydroxide (NaOH), potassium hydroxide (KOH), sulfuric acid, and sodium carbonate (17).

2.1.4.5. Mechanical Retting

Mechanical retting can be employed to separate the fiber from the rest of the stalk, provided that it has either been partially retted or fully dried. With this method, a hammermill is used to separate the fibers. This method is not nearly so dependent on weather and microbial action. However, the quality of fiber produced using this method is quite low (10,18).

2.1.5. Fiber Surface Treatments

Natural fibers show good mechanical properties given their low density. However, good wet-out and matrix adhesion are difficult to achieve with natural fibers in their virgin state. This is due, in large part to the high concentration of hydroxyl groups on the surface of the cellulose, which imparts a hydrophilic nature to the fiber. In the interest of improving composite performance through enhanced fiber / matrix interaction, a number of physical and chemical surface treatments have been investigated.

Alkali treatment, also known as mercerization, is one of the more notable chemical treatment methods. It both increases the number of surface hydroxyl groups on a fiber, and it splits fibers into finer fibrils by removing the lignin and hemicellulose binding them together (19). Dewaxing is another relatively simple fiber treatment which is accomplished by immersion of fibers in equal parts alcohol and benzene (20). A. K. Mohanty et al. discuss treating natural

fibers with maleated forms of polypropylene and polyethylene (21). Wool and Thielemans report that deposition of a layer of pine kraft lignin on natural fibers enhances their matrix interactions and theorize that direct reaction of fibers with the lignin would provide further enhancement (22). They have also achieved improved fiber/matrix interactions by introducing butyrated kraft lignin to the matrix material prior to composite fabrication (23). Treatment with silanes, though more commonly associated with glass fiber treatment, has proven useful for natural fibers as well (24,25). Other methods for chemically modifying natural fibers include acetylation (26), benzoylation (27), and acrylation (28) as well as treatment with permanganate (29), peroxides (30), and isocyanates (31).

Cold plasma treatment and corona discharge are two time tested methods of physically modifying surface chemistries (32,33). The plasma treatments can be carried out either in a vacuum (34) or under atmospheric conditions (35). Miller et al. have reported the effects of using dielectric barrier discharge to modify the surface of cellulose samples (36). Laine et al. have reported slight increases in surface carbonyl group content and porosity of fibers subjected to ultrasound at 23 kHz (37). Finally, exposure to ultraviolet radiation has also been shown to improve the polarity of natural fiber (38).

2.1.6. Flax Properties

New methods for separating fiber have decreased the production cost of flax and increased the consistency of its strength and thickness. Even though the available literature still reports a wide range of properties for flax, as shown in Table 2, these new processing techniques have decreased its cost enough that many now consider it a viable replacement for glass fiber in composites (39).

Table 2. Literature Values for Flax and Epoxy Properties

Material properties	8601/ Aradur (40,41)	Flax Compiled	Flax Bledzki et al. (42)	Flax Baley (43)	Flax Bos (44)	Flax Other Sources (45–48)
Density (kg/m^3)	**1120**	**1400 – 1500**	1500	---	1400	---
Tensile modulus (GPa)	**2.22**	**12 – 100**	100	38.9 – 69.2	50 – 70	12 – 85
Tensile strength (GPa)	**0.0543**	**0.5 – 2**	1.1	0.853 – 1.825	0.5 – 1.5	0.6 – 2
Max elongation (%)	**6**	**1 – 4.11**	---	2.43 – 4.11	2 – 3	1 – 4
Transverse modulus (GPa)	**2.22**	**9.7 – 17.1**	---	9.7 – 17.1	---	---
Shear modulus, G_{12} (GPa)	**0.822**	**2.4 – 3.4**	---	2.4 – 3.4	---	---
Poisson's ratio, v_{12}	**0.35**	**0.183**	---	0.131 – 0.183	---	---

Despite the broad range of potential values for engineering properties of flax fiber, the range of properties present in a particular batch of fiber can be expected to be much narrower. This is due to the fact that the individual fibers within a batch have most likely experienced similar growing, processing and storage conditions.

2.2. Natural Resins

Natural resins can be derived from a wide array of sources. However, perhaps the majority are derived from botanical and animal oils. All of these natural oils can be described as triglycerides. That is, a set of three long-chain fatty acids connected to glycerol through ester linkages. These fatty acids usually incorporate a chain that is 18 carbon atoms in length, though certain exceptions to this rule have been observed. For instance, chains up to 26 carbon atoms in length have been observed in certain fish oils (49).

2.2.1. Natural Oils

A large variety of fatty acid types are extant within the universe of natural oils. A partial listing of these fatty acids, along with their structures, can be viewed in Figure 2 (50). Some, such as linoleic and linolenic acid, are fairly common. Others, such as ricinoleic acid, are not. As can be seen, these fatty acids can contain varying numbers of unsaturated double bonds between carbon atoms, as well as a small handful of other moieties. Within each variety of natural oil, the pool of potential fatty acids narrows. However, there is still a great degree of variation between individual triglyceride molecules within the given variety of natural oil. In addition, the average fatty acid content of a particular oil can be expected to vary with such factors as seasonal, regional, and genetic variations. For instance, seed oils produced in warm climates generally contain larger concentrations of saturated fatty acids than otherwise identical seed oils produced in cool climates (49).

Each variety of natural oil exhibits its own characteristic level of ability to cure into a solid, crosslinked form. Some harden fully, others do not harden at all, while still others fall somewhere in between. This has led to the classification of these oils into three general categories: drying, semidrying, and non-drying. An oil's drying ability is a function of its ability to undergo auto-oxidation and crosslinking as a result of the presence of conjugated double bonds and diallylic groups within its constituent fatty acid chains (49).

There are a number of differences between conjugated and nonconjugated drying oils in terms of their curing mechanisms. As a result, there is not a unified method to precisely quantify the drying characteristics of both types. However, it can be noted that double bonds are present in both cases. The prevalence of these double bonds in a particular oil, and its resulting stereochemistry, are among the primary factors influencing its chemical and physical properties

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(51). Quantification of these double bonds has proven to be a useful method of predicting the behavior of oils. This is accomplished through a determination of an oil's iodine value. This method utilizes iodine's reactivity with olefin moieties to quantitatively determine the concentration of double bonds in a particular sample. This value, defined as the number of grams of iodine consumed by 100 grams of oil under standardized conditions, is used to characterize natural oils. Drying oils, having iodine values greater than 130, auto-oxidize when exposed to air, ultimately resulting in a crosslinked solid. Semi-drying oils, having iodine values between 100 and 130, partially auto-oxidize with exposure to air, usually resulting in a soft, tacky, partially crosslinked material. Non-drying oils, having iodine values lower than 100, do not auto-oxidize significantly in air and remain liquid (50). The auto-oxidation mechanism of drying oils is shown in Figure 3 (52).

Figure 2. Natural Fatty Acid Examples (50)**.**
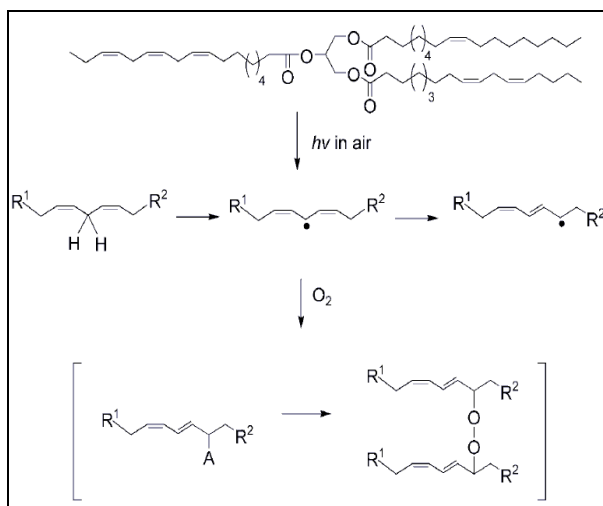
Figure 3. The auto-oxidation of drying oils. (52).

Drying oils, such as tung and linseed oils, can be employed directly. However, their properties, and therefore their suitable applications are somewhat limited. Consequently, natural oils are often chemically modified prior to use in an effort to convert them into a more robust form.

As can easily be deduced from the correlation between an oil's iodine number and its ability to crosslink via auto-oxidation, the double bonds are the reactive sites that make it possible to generate polymers from bio-oils. It can also, then, be easily concluded that bio-oils containing the highest number of these double bonds are of the greatest use in the development of biobased resins such as epoxies.

The most important commodity oils are listed in Table 3 (50). Included in the table is information regarding the average number of double bonds per oil molecule. Linseed oil, with 6.6 double bonds per triglyceride, is clearly superior when it comes to number of double bonds. Sunflower, soybean and corn oils are next with 4.6, 4.5, and 4.4 double bonds per molecule, respectively. However, while linseed oil represents a miniscule fraction of total global natural oil

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production, production of soybean oil exceeds that of any other natural oil. In fact, at 26.52

million tons per year, there is more soybean oil produced globally than all the other high double-

bond oils combined. As a result, soy oil garners most of the attention in the development of

biobased polymers in the United States (53).

Table 3. Production, Compositions, and Properties of 17 Important Commodity Oils (50)

Natural oil	Average annual production [10^6 tons]	Double bonds [a]	Iodine value [mg/100 g]
Soybean	26.52	4.6	117-143
Palm	23.53	1.7	44.58
Rapeseed/Canola	15.29	3.8/3.9	94-120/110-126
Sunflower	15.29	4.7	110-143
Groundnut	5.03	3.4	80-106
Cottonseed	4.49	3.9	90-119
Coconut	3.74	-	6-11
Palm kernal	2.95	-	14-24
Olive	2.52	2.8	75-94
Corn	2.3	4.5	102-130
Fish	1.13	-	104-110
Linseed	0.83	6.6	168-204
Sesame	0.76	3.9	103-116
Castor	0.53	2.7	82-88
[a] Average number of double bonds per triglyceride.			

2.2.1.1. Epoxidized Soy Oil

The three-member cyclic ether of the epoxy functional group is among the most useful of

the potential products of olefinic fatty acids. Consequently, epoxidation is the most common

chemical alteration of natural oils (53). There are a number of methods by which these oxirane

rings can be added to olefinic compounds. Perhaps the most common of which was first

reported by Nikolaus Prileschajew in 1909, and has since come to be known as the Prileschajew

reaction (54). In this method, treatment with peroxyacids converts the double bonds to the

familiar oxirane ring of epoxies. This process is illustrated in Figure 4 (55). Conveniently,

peroxyacids can be produced *in situ* through the combination of a peroxide and a carboxylic acid such as formic acid or acetic acid.
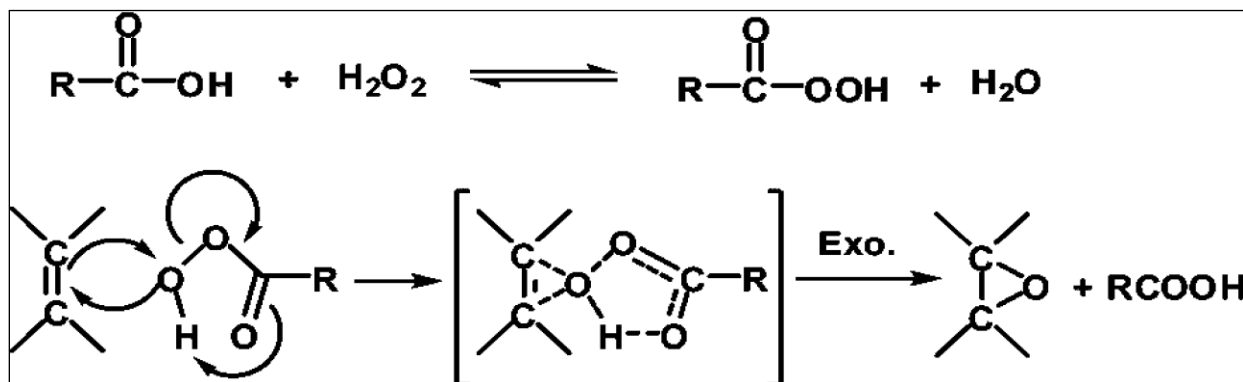
Figure 4. Reaction mechanisms for in situ epoxidation with peroxyacid (55).

This process is perhaps the most commonly utilized alkene epoxidation method. It has the advantage that its essential reagents are easily obtained at low cost (55,56). On the other hand, it achieves low selectivity and often results in the opening of epoxide rings. This ring opening is considered to be more severe when formic acid is used. As a result, acetic or other carboxylic acids are favored in order to limit the negative aspects of this process (57).

As alluded to earlier, epoxides are extremely useful starting materials for a plethora of compounds as a result of their highly reactive oxirane moiety (58). When considering the superlative abundance of soybean oil compared to other vegetable oils, it goes without saying that epoxidized soybean oil (ESO) is one of the most significant industrial compounds manufactured from vegetable oils (59). A depiction of the conversion of soybean oil into ESO can be seen in Figure 5 (60).
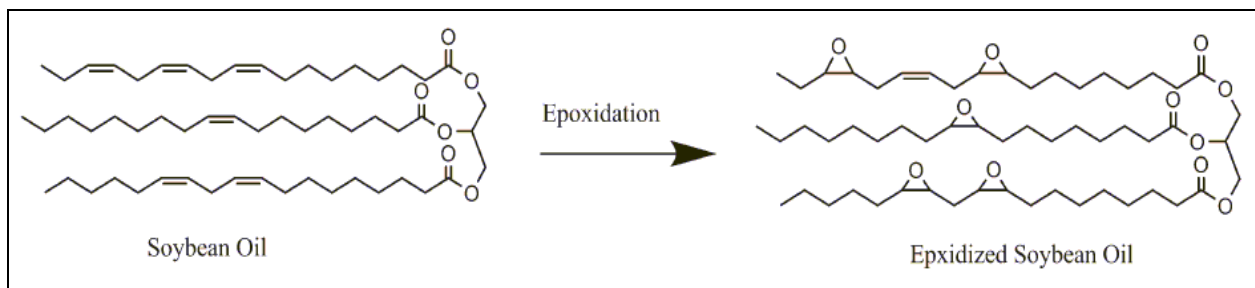
Figure 5. Soybean oil epoxidation (60).

The list of applications for which ESO is used is quite long. Arguably, its most commonly cited industrial application is as a plasticizer for polyvinyl chloride (51,61). It also sees use in the adhesive backing of carpets, and is regularly used as a diluent or reactive modifier in other epoxy resins (62). It can serve as a lubricant: at high temperatures when its epoxide rings are intact, and at low temperatures if the rings have been opened (63). ESO is also used in the formulation of cationic UV-cured coatings (64).

The potential application of ESO depends on factors such as oxirane number, purity, and iodine number. Specifications for commercial ESO's are iodine number less than 2.5 and oxirane number of 6.5% (61). Corma et al. point out that the double bond concentration inherent to natural oils themselves limits their potential oxirane number to around seven percent (57). It would then follow that the specification for commercial ESO's calling for an oxirane number of 6.5% would equate to an approximate conversion rate of 93%. However, Gerbase et al. note that ESO's intended for use as reactive diluents of alkyd resins are more suitable when only partially epoxidized. They also note that the ability to tailor the degree of epoxidation provides the opportunity to adjust properties such as compatibility and viscosity (56).

While ESO has been used in a wide variety of applications, these are mostly limited to cases where it is used as an additive or modifier to an existing polymer technology. In theory, ESO could also be implemented as the primary material in a polymer. However, there are certain

realities that have thus far limited its application in this manner. ESO's potential oxirane concentration (oxirane number) is limited due to the relatively low concentration of olefin moieties found in natural oils (57). Compounding this issue further, the ESO's epoxide groups are located in secondary positions, meaning they are sterically hindered. Consequently, full crosslinking is very difficult to achieve, and intramolecular bonding is common (65). Additionally, the aliphatic fatty acid chains of soy oil are flexible in nature. These factors limit the ability to achieve significant physical and thermal properties using ESO alone, making it a poor choice for higher demand applications (50,66). As a result, much effort is currently being made to develop modified forms of ESO that overcome these structural limitations.

2.2.2. Natural Resin Improvement Efforts

Much effort has been expended investigating methods of producing biobased resins with respectable performance. Wool et al. have pursued various methods of modifying epoxidized forms of soy and other vegetable oils, including acrylation (67), maleinization (68), hydroxylation (69), and phthalation (60). Adekunle et al. have produced methacrylated and acetic anhydride-modified soybean oil (70). Sithique et al. have incorporated bismaleamides (71). Thulasiraman et. al. report having created a chlorinated epoxidized soybean oil (72). These modified ESOs are then usually blended with up to 35 wt% petrochemical based monomers such as styrene (66). Despite the effort applied in this area, the results generally fail to produce competitive resins without significantly diluting their "greenness." A notable exception, however, is the relatively recent development by Webster et al. of an epoxidized sucrose ester vegetable oil resin, epoxidized sucrose soyate, which exhibits exceptional performance (55,73).

2.3. Composites

Broadly speaking, composites are materials made up of two or more materials, separated by distinct boundaries on a macroscopic level. Each of these materials either serves as reinforcement or as a binder for the reinforcement. The vast majority of the structural properties of a composite are provided by the reinforcement. The binder defines the shape of the composite, keeping the reinforcing material aligned in the desired direction. In addition, the binder serves as the vehicle by which loads are transferred to the reinforcements and also encapsulates the reinforcement, protecting it from damage. While a wide array of materials can be considered composites, most would likely readily associate the term with those materials composed of thin fiber reinforcement material bound by a polymer resin matrix. Indeed, in the case of this discussion, this is precisely the type of composite under consideration. More specifically, this discussion will focus on continuous fiber reinforced composites using thermoset resins, as opposed to those reinforced with short fibers or particulates and those utilizing thermoplastic matrices.

Composites have a number of qualities making them more desirable than traditional monolithic engineering materials. Foremost among these is their high stiffness and strength to weight ratios. In addition, many polymer matrix materials are relatively inert, lending high environmental stability to the overall structure. Furthermore, these materials can provide unique combinations of properties that are unavailable with more conventional materials (74). For instance, since their properties are strongly anisotropic (i.e. directionally dependent), structures made from composites can have finely tailored properties in any desired direction. Additional qualities they can possess are a low to nearly zero coefficient of thermal expansion, low thermal conductivity, and high damping capacity (75).

There are several general methods of composite manufacture. These methods include hand lay-up, resin transfer molding (RTM), and pultrusion. As its name implies, the hand lay-up method involves processing the composite manually. This can be accomplished either by first soaking the fiber in resin and then placing it in the desired location, or by first placing the fiber and then applying the resin to it. With RTM, the fiber is held inside a mold as the resin is either injected into it using pressure or drawn in under a vacuum. In the latter case, the method is referred to as vacuum assisted resin transfer molding (VARTM). In either the case of hand lay-up or with RTM/VARTM, best results are obtained when the infused fiber is compressed during cure. With pultrusion, continuous fibers are coated in resin and subsequently drawn through a heated die, resulting in a continuous composite of constant cross-section.

The array of applications for composites is vast and is continually increasing. Early adopters were the aerospace, automotive and sports industries where cutting edge performance supersedes cost considerations. However, virtually all industries have now adopted composites in one form or another. Many of the current applications of composites are in non-structural uses, such as interior panels in automobiles. However, for the purposes of this discussion the most relevant applications are those where composites are employed in structural applications. For example, Hollaway cites several examples of civil structures manufactured using pultruded components. Prominent among these were examples of bridges incorporating composite girders or decking materials or both (76). Indeed the highest volume of structural composites is produced using pultrusion due to the unrestricted lengths and relative ease with which it can produce common structural geometries such as rods, tubes, and beams.

2.3.1. Synthetic Composites

To date, virtually all examples of man-made structural composites are composed of synthetic materials. In the cases of the highest demand applications, the constituents would be high performance materials such as carbon or aramid fibers in an epoxy resin. In lower demand applications the reinforcement is likely to be E-glass fiber. The reinforcement in such cases would likely be either an epoxy or polyester resin. A recent in-house study has demonstrated that composites of E-glass infused with an epoxy resin using the VARTM method can be expected to exhibit tensile and flexural strengths of 537 and 635 MPa respectively. They also exhibited tensile and flexural moduli of 40.7 and 31.1 GPa respectively, as well as a short beam strength of 39.5 MPa. It is worth noting that these properties were obtained from a composite having a V_f of 0.51. This performance is significantly greater than those properties of commercially available pultruded members. For example, San Diego Plastics, Inc. reports tensile and flexural strengths of 200-225 MPa, tensile modulus of 16-18 GPa, flexural modulus of 11-13 GPa, and interlaminar shear strength of 25-30 MPa (77). It may be useful to note that a recent study of commercial pultruded fiberglass structural beams found an average V_f of 0.42 (78).

2.3.2. Biocomposites

In general, the term "biocomposite" has been used to refer to composites incorporating some amount of biobased material (12). ASTM standards have defined a "biobased product" as one containing biobased materials as a noteworthy percentage of its total mass (79). ASTM standards further define "biobased materials" to be those containing organic carbon and produced via biological processes in the recent past (80,81).

The available body of knowledge frequently discusses the manufacture of biocomposites incorporating natural fibers. However, many of these publications appear to discuss randomly

oriented, short-fiber composites, or composites manufactured using specialized molds or equipment (69). There appears to be little emphasis on the development of cost effective, scalable methods for producing high quality structural biocomposites.

CHAPTER 3. OBJECTIVES

Highly biobased composites with properties and costs rivaling those of composites consisting of synthetic/manufactured constituents are highly desirable. To achieve this, three key elements are necessary: a resin system derived largely from renewable sources which exhibits performance similar to petro-chemical based resins; a strong, cheap natural fiber that bonds well with biobased resins; and an efficient method of composite manufacture capable of achieving high fiber loading. As yet, the current state of the art in the areas discussed above have not been combined in a focused effort to achieve levels of performance in biocomposites rivaling synthetics, while also minimizing cost and maximizing renewable content. The investigation proposed herein will seek to identify ways to accomplish these goals by investigating how critical design variables impact the performance of ESS and flax fiber composites.

To date, composites produced in preliminary investigations have incorporated two resin formulations consisting of different ratios of ESS and the crosslinker Methyl Hexahydrophthalic Anhydride (MHHPA). A study of the efficacy of several formulations of ESS and their comparison to a commercially available epoxy resin will contribute to the optimization of composites based on this novel high performing biobased resin.

This study will also compare untreated fiber to NaOH treated and crosslinker-pretreated fiber in terms of their performance when incorporated into composites. Factors to be considered will be complexity, cost, and "greenness" of each treatment process. In addition to fiber treatment, composite performance is strongly influenced by fiber alignment. After treatment, fiber is currently prepared for infusion by hand in a time consuming process. Streamlined methods of fiber treatment, detangling, separation, straightening, and alignment will be sought.

Infusion of the relatively viscous ESS resin is accomplished through a standard VARTM process, followed by the application of external pressure using a shop press with heated platens. Finding an ideal balance between pre-warming the resin prior to infusion, to reduce viscosity, and post-infusion pressure application to eliminate excess resin, will allow optimal fiber loading of 50-55%.

In preliminary studies, the methods described above have produced composites approaching, but not matching, those achievable through the use of synthetic materials. Additional fiber configurations and hybridizations with manufactured materials such as E-glass will be investigated in order to identify the minimum amount of manufactured material necessary in order to produce composites rivaling those of purely synthetic/manufactured materials. Common properties of pultruded fiberglass composites will be used as a standard by which the performance of this study's results will be judged.

Composite properties will be verified through several basic tests. Procedure A of ASTM Standard D790 will be employed to perform flexural analysis. ASTM Standard D3039 will be utilized to test tensile properties. Shear properties will be evaluated using the short beam strength test outlined in ASTM D2344.

The composites prepared through the course of this study will also be weathered via exposure to alternating cycles of ultraviolet (UV) radiation and water condensation. This treatment will provide insight into the durability and long term performance of the resin and resulting composites.

In an effort to enhance understanding of the physical mechanisms affecting the performance of various treatments and methods, scanning electron microscopy (SEM) will be used to examine the fiber-matrix interface at the point of fracture. In addition, Fourier transform

infrared spectroscopy (FTIR) spectra will be obtained for the untreated and treated flax fibers in order to assess the efficacy of the treatment methods.

More specifically, the objectives of this project are to:

1. Optimize natural fiber preparation techniques to maximize performance while minimizing production cost and environmental impact

2. Optimize the manufacture of natural fiber composites using a modified VARTM process

3. Compare the performance of composites of various types of fiber treatment and resin formulation

4. Identify the optimum natural/glass fiber ratio to maximize renewable content while achieving performance required for structural applications

5. Assess relative degree of interfacial bonding by examining failure surfaces with SEM

6. Assess efficacy of fiber treatment through FTIR spectroscopy

CHAPTER 4. MATERIALS AND METHODS

4.1. Materials

4.1.1. Fiber Types

This study utilized flax fiber in two forms. The first was a loose form of linen from Harbin, Heilongjiang, China, which was water retted and processed by hand. This resulted in a nearly pristine fiber. It was natural color and had suffered very little mechanical damage. Each fiber was quite long, approaching three feet in length, enabling the manufacture of panels containing truly continuous fiber.

The second fiber was in the form of a unidirectional flax fabric marketed under the name Biotex, which was produced by Composites Evolution in Chesterfield, UK. The fiber in this fabric was more mechanically processed than the Chinese linen. The fibers, whose lengths were around 5 cm, were twisted into yarns of approximately 3 mm diameter. Around these yarns was twisted a fine polyester carrier thread. The fabric consisted of 11 of these yarns per cm and was available in a 23 cm wide roll.

4.1.2. Resins

Two different resins were used over the course of this study. The first of which is Araldite 8601 crosslinked with Aradur 8602 (8601). It is a commercially available epoxy/amine combination formulated specifically by Huntsman Corporation for VARTM applications. This resin was used as a control. In addition, two different formulations of the second resin, ESS, were implemented. Both ESS formulations were crosslinked with MHHPA, and utilized 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst. The ESS was produced by the Coatings and Polymeric Materials Department (CPM) at North Dakota State University (NDSU) using samples of Sucrose Soyate obtained from Procter and Gamble. The MHHPA and DBU were also

obtained from CPM who in turn obtained them from Dixie Chemicals (Pasadena, Texas) and Sigma Aldrich (St. Louis, Missouri), respectively.

4.1.3. Fiber Treatment Materials

NaOH and 95% ethanol were purchased from the Department of Chemistry at NDSU. The crosslinker pretreatment material, MHHPA, is the same as mentioned above.

4.1.4. Composite Layup Materials

Frekote 770 NC (Loctite) was used as a release agent. PTFE coated fiberglass fabric (Item #8577k81, McMaster Carr), peel ply (Bleeder Lease® B, Airtech), and bleeder cloth (Part 1779, Fibre Glast) were also used. Tacky tape (SM 5142, Northern Composites) was used to secure the bagging film (Dahlar®, Airtech). Two types of tubing: spiral tubing (Item #41156, US Plastic Corp.) and Excelon vacuum tubing (Item #54446, US Plastic Corp.) were used.

4.2. Fiber Treatments and Preparation

4.2.1. Loose Fiber

Loose Chinese linen was mercerized using the following method. Up to 35 g of NaOH pellets were massed on a scale (SP2001, Ohaus Corp., Pine Brook, NJ) and placed in a 4000 ml beaker (VWR). To this, up to 3500 ml of 95% ethanol (100 ml/g NaOH) was added and the beaker was placed on a stirring hotplate (Model MS23, Precision). A 5.08 cm PTFE coated stirbar was added and a cover was placed over the beaker. The heat on the plate was then turned to its highest setting of 9 and the stirrer was set to 4, which was the highest setting employable without causing the stirbar to jump out of the rotating magnetic field. Once the NaOH pellets were fully dissolved and the 10g/L solution had begun to boil, the heat on the stirplate was adjusted to 6.75, and the stirrer was turned off. A 130 g bundle of loose Chinese linen was then

submerged in the solution and the cover was again placed atop the beaker. Note, the bundle of fibers had been pre-trimmed to a length of approximately 2 cm greater than the dimensions of the composite panel into which they are intended to be incorporated. In order to ensure a stoichiometrically sufficient quantity of reagent was available to fully treat the fiber, a maximum of 45 g of fiber per L of solution was observed.

After two hours of treatment in the boiling solution, the beaker was removed from the heat and the solution was decanted off. The beaker was then filled with cold tap water and the fiber bundle was grasped by hand and was gently agitated in a swirling motion to wash the brown tea-like treatment residue into the water. The beaker was then drained and refilled and the process repeated until the rinse water no longer became brown. Following this, small clumps of the fiber were removed from the beaker and held under running water for a final rinse. Finally, the fibers of these small clumps were straightened by hand while still wet and then laid on a clean tray (Model 83T-6, MainStays, Walmart).

Additional rinse water was removed and fibers were further straightened by pressing down on an end of the clump of fibers with one hand to hold the fibers in place while the edge of the other hand was used like a squeegee and run along one half of the fibers; this was repeated in the other direction for the other half of the fibers. This final rinsing, straightening and squeegeeing of the small clumps of fiber was repeated until all the fiber had been transferred to the tray. The fibers were then covered with brown trifold paper towels and the tray was placed in a convection oven (Model 1370FM, VWR) at 80 °C for at least 12 hours to dry. Once dry, the fibers were carefully separated by hand and realigned. Throughout the fiber treatment process described above, any readily removable shive was picked out by hand.

4.2.2. Unidirectional Flax Fabric

Prior to treatment, the 23 cm wide fabric was cut into lengths of 22.8 cm. These swatches were then cut in half along the direction of the fiber. This resulted in 11.5 cm by 22.8 cm sheets of fabric which is of slightly greater dimensions than those of the intended panel. The preparation of the NaOH/ethanol solution and treatment of the fabric was carried out in the same manner as described above for loose fiber. In this case, a stack of 24 pre-cut sheets of fabric were mercerized in the 3500 ml solution. Following treatment, the solution was decanted off and the beaker refilled with cold tap water. One at a time, each sheet was carefully separated from the others and held under a stream of gently flowing tap water. Once the fibers were sufficiently rinsed, the sheet was placed on a brown trifold paper towel and then covered with another paper towel. Each subsequent sheet was separated, rinsed and placed atop the previous and again covered with a paper towel. Once all sheets had been rinsed, they were transferred, one at a time, to a clean tray, and straightened by grasping the ends of each yarn between thumb and forefinger and stretching. While placing the sheets on the tray, an effort was made to correct any separation of the yarns in the transverse direction that had occurred as a result of rinsing. Once straightened and placed on the tray, each sheet was covered by a half piece of dry paper towel before the next sheet was stacked on top of it. Once all the sheets were straightened and stacked, the stack was covered with paper towels and the tray was placed in the oven to dry as described above.

4.2.2.1. MHHPA Treated Unidirectional Flax Fabric

A portion of the NaOH treated unidirectional flax fabric was subsequently treated by immersion in a 20 wt% solution of MHHPA in acetone. More specifically, a 72 sheet (462.7 g) stack of fiber was immersed in a solution of 3.1 kg acetone and 0.62 kg MHHPA. The solution

was contained in a rectangular polypropylene tub with a lid (Ziploc brand). The stack of fiber was agitated by compressing and releasing several times in order to drive out any retained air pockets and ensure full wetting of the fiber. The lid was then placed on the tub. After 140 minutes at room temperature, the fiber was removed from the solution, the tub was rinsed with acetone, and the fiber was returned to the tub. The tub was filled with clean acetone and the fiber was again compressed and released several times to ensure thorough rinsing. This process was repeated two more times so that the fiber was ultimately triple rinsed in acetone. Following this, the fiber was again carefully straightened and stacked on a clean tray, covered and placed in the oven, following the same method employed during treatment with NaOH.

4.3. Panel Layup

The layup of the fibers in preparation for infusion via a VARTM process was much the same regardless of fiber type. In both cases, a flat 30.5 cm x 30.5 cm x 1.3 cm tempered glass tooling surface was cleaned and treated with five layers of Frekote. Once it was dry, acetone was used to remove the Frekote from within 2 cm of the edges of the glass plate. A 30.5 cm-square frame of two sided pliable tape (i.e. tacky tape) was then applied to this newly cleaned edge of the tooling surface. A 27.9 cm x 27.9 cm sheet of PTFE coated fabric was then placed inside the frame of tacky tape. The fiber was then placed in the center of this fabric. In the case of loose fiber, approximately 60 g of fiber was distributed evenly over a 10.15 cm x 20.3 cm area, with the fiber aligned as well as possible in the longer direction. In the case of unidirectional fabric, 12 sheets of the fabric, with a total mass of approximately 75 g, were stacked atop each other with all their yarns aligned on the same axis. A 27.9 cm x 27.9 cm sheet of peel ply was then draped over the fiber, followed by a 12.7 cm x 22.9 cm piece of bleeder cloth. Finally, the addition of a caul plate modified the setup from that of a basic VARTM process. The 10.15 cm x

20.3 cm x 2 mm aluminum caul plate was wrapped in the PTFE coated fabric and placed on top of the bleeder cloth, centered over the fiber with its long axis oriented in the same direction as that of the fiber. This caul plate served to both provide a uniform cross sectional area and a smooth upper surface of the final composite panel.

12.7 cm long pieces of spiral tubing were placed at the narrow ends of the fiber stack, with the excess of both tubes protruding beyond the fiber in the same direction. This excess spiral tubing was wrapped around inlet and outlet tubes. A 38 cm square sheet of bagging film was then affixed to the tacky tape, sealing the layup inside.

In order to debulk the fiber and to remove as much residual moisture and other volatiles as possible from the fiber, the glass plate and its contents were then placed on the lower platen of a heated press (973214A, Carver). Following this, the temperature of the platen was set to 65 °C, the inlet line was clamped shut, and a vacuum of 26 in Hg was applied to the layup by attaching the outlet line to a resin trap (2 ½ gal paint tank, Central Pneumatic) and vacuum pump (0528-101Q-8G588DX, GAST). This debulking process was allowed to continue for at least one hour.

4.4. Resin Preparation

In the case of each resin, 140 g was prepared in a 250 ml Tri-Pour beaker (US Plastic Corp., Lima, OH) for incorporation into each panel. The specific details of the preparation varied with resin type and are detailed below.

4.4.1. Araldite 8601

Literature provided by Huntsman states that, when mixed at a 4:1 ratio, 8601 has a gel time of 70 minutes at 25 °C (40). For the purposes of this project, the components were

combined as prescribed and mixed thoroughly by carefully stirring by hand so as to introduce as few bubbles as possible in the process. The resin was then placed inside a vacuum chamber for 10 minutes at a vacuum pressure of 23 in. Hg. Once degassing was completed, the resin was removed from the vacuum chamber and was then ready for infusion into the fiber.

4.4.2. ESS Formulation 1

ESS Formulation 1 (ESS F1) was mixed at an epoxide/anhydride molar ratio of 1/0.5, also incorporating 1.5 wt% DBU. The necessary quantity of each compound varies with the epoxide equivalent weight (EEW) of a given batch of ESS. The following equations are used to determine the ratios of each component in order to achieve the desired ratio:

$$grams\ ESS = \frac{desired\ mass}{1 + \dfrac{1}{EEW * 0.5 * 168.2\ ^g/_{mol}} + 0.015\left(1 + \dfrac{1}{EEW * 0.5 * 168.2\ ^g/_{mol}}\right)}$$

$$grams\ MHHPA = \frac{grams\ ESS}{EEW * 0.5 * 168.2\ ^g/_{mol}}$$

$$grams\ DBU = 0.015(grams\ ESS + grams\ MHHPA)$$

In order to prevent an undesired complex between the MHHPA and DBU, the ESS was measured out first. The DBU was then added and thoroughly mixed in by hand. Following this, the MHHPA was added and the mixture was again thoroughly blended by hand.

Reduction of the resin's viscosity was desirable for ease of infusion as well as to facilitate the rise of air bubbles inadvertently introduced during mixing. For this reason, the cup containing the mixed resin was placed on top of the half-closed vent of the convection oven which was operating at 80 °C. After 30 minutes, the resin was ready for infusion into the fiber.

4.4.3. ESS Formulation 2

ESS Formulation 2 (ESS F2) was prepared in much the same way as ESS F1. However, in this case it was mixed at an epoxide/anhydride molar ratio of 1/0.75, also incorporating 1.5 wt% DBU. The equations used to determine the necessary component ratios are:

$$grams\ ESS = \frac{desired\ mass}{1 + \dfrac{1}{EEW * 0.75 * 168.2\ ^g/_{mol}} + 0.015\left(1 + \dfrac{1}{EEW * 0.75 * 168.2\ ^g/_{mol}}\right)}$$

$$grams\ MHHPA = \frac{grams\ ESS}{EEW * 0.75 * 168.2\ ^g/_{mol}}$$

$$grams\ DBU = 0.015(grams\ ESS + grams\ MHHPA)$$

4.5. Fiber Infusion

Infusion of the fiber whose layup was described in section 4.3 was accomplished using the same basic VARTM method for all composites produced, however minor specific details varied depending on the resin and fiber types.

Following the introduction of the resin, the method employed deviated from a standard VARTM operation in that a 10.15 cm x 20.3 cm x 2.4 cm block of aluminum was placed on top of the layup directly over, and in the same orientation as the caul plate. Following this, the press in which the layup was resting during infusion was employed to apply an external pressure on the composite in order to increase the fiber volume fraction (V_f) of the final product. In the case of loose fiber, the maximum force known to still result in sufficient wet-out was 2.5 metric tons. For the unidirectional fabric, the maximum force was 4.5 metric tons.

4.5.1. 8601 Infusion

Prior to infusion with the 8601 resin, the fiber which has been debulked as described in section 4.3 was allowed to cool by turning off the heated platens. Once the press and fiber layup had cooled to room temperature, the resin was infused at a vacuum pressure of 22 in Hg, which is low enough to prevent its hardener from boiling. Following the infusion of all 140 g of resin, the inlet line was clamped off. The aluminum block was then placed atop the layup and the maximum force allowable for the given fiber type was applied. In order to prevent the fiber from spreading out in the transverse direction as the excess resin was squeezed out, this force was applied at a rate no greater than one metric ton per minute. Following the application of the maximum force, the excess resin, now surrounding the fiber, was allowed to travel into the outlet line before it was clamped off. The resin infused fiber was then allowed to cure in this state overnight before being removed.

4.5.2. ESS Infusion

In order to maintain a lower resin viscosity and facilitate infusion, the platen and fiber were infused while still at the 65 °C debulking temperature. The resin was infused at a vacuum

pressure of 22 in Hg. When the fiber was half infused, the set point temperature of the platens was increased to 85 °C. The inlet was clamped off once the full 140 g of resin had been drawn into the fiber. The aluminum block, which in this case had been preheated to 80 °C in the convection oven, was then placed atop the layup, and the set point temperature of the press was increased to 120 °C. Following this, the maximum force allowable for the given fiber type was applied as described in the previous section. The layup was then allowed to remain in the press for two hours beyond the time the actual temperature of the platens reached 120 °C. At which point, the layup was removed from the press in order to stop the curing process. In order to prevent uneven cooling, the composite was carefully separated from the hot glass plate and the aluminum caul plate.

4.6. Composite Testing

4.6.1. Mechanical Test Sample Preparation

Once the panels were cool and cured, the edges were trimmed of any fiber-less excess resin using scissors (Klein Tools model 23015), and subsequently massed. Following this, a wet saw (Allied) with a segmented diamond blade (65-10030, Allied) was used to remove the small border region of the composite that had not been compressed by the caul plate. The thickness of the remaining coupon was measured. The wet saw was again used to cut the coupon into samples of appropriate dimensions for the tests outlined in the following sections. Once cut, the samples were washed under running tap water, blotted with a paper towel and placed in a desiccator (Dricycler 134041, Boekel Scientific). Once dry, the scissors were used to trim any strands of fiber the saw had left on the edges of the samples. They were then returned to the desiccator to condition for at least 48 hours. Prior to testing, the samples were labeled using a Sharpie marker and their dimensions were recorded.

4.6.2. Tensile Tests

An Instron model 5567 load frame was used to perform tensile tests per ASTM Standard D3039 on sample sets of five specimens per composite type (82). The widths of the specimens were 2.5 times their thicknesses, and were at least 10 cm long. The test frame was equipped with MTS Syntech grips and a 5.08 cm extensometer (632.25B-20, MTS). The specimens were tested to the point of tensile failure at a constant displacement rate of 2.0 mm/min. Strain data, as well as loads at failure were captured and used to calculate the tensile properties of each sample set. Ultimate tensile strengths were calculated using:

$$\sigma_t = \frac{P_t}{A}$$

where σ_t is tensile stress, P_t is the applied tensile force, and A is the original cross sectional area. Tensile moduli were determined utilizing data captured by the extensometer by identifying the slope of a chord drawn between data points at each end of the initial linear section of the stress-strain curve.

4.6.3. Flexural Tests

Three-point bending tests were performed per procedure A of ASTM Standard D790 using the Instron model 5567 load frame (83). Test samples adhered to the standard's prescribed dimensions of 3.2-6 mm thickness, length of 16*thickness + 20%, and width of 2-4 times the thickness. Sample sets, consisting of up to six specimens per composite type, were tested to the point of flexural failure over a support span of 16 times the mean thickness of the sample set. The diameters of the supports in contact with the samples were 3.17 mm, and the diameter of that portion of the fixture applying the load was 6.34 mm. The test rate was determined utilizing the following equation specified by the standard:

$$R = \frac{0.01L^2}{6d}$$

where L is the support span and d is the sample thickness.

Force and displacement data were captured and used to calculate the flexural properties of each set of samples, again via equations provided by the standard. The flexural stress equation is:

$$\sigma_f = \frac{3PL}{2bd^2}$$

where σ_f is flexural stress, L is the support span, P is the applied load, b is the sample width, and d is its thickness. The flexural strain equation is:

$$\epsilon_f = \frac{6Dd}{L^2}$$

where ϵ_f is flexural strain, D is deflection, d is the sample thickness, and L is the support span. As with tensile modulus, flexural modulus was determined by identifying the slope of the elastic portion at the beginning of the flexural stress-strain curve.

4.6.4. Interlaminar Shear Tests

As specified by ASTM Standard D2344, the samples prepared for determination of interlaminar shear strengths (ILSS) of the composites had a thickness of no less than 3 mm and no greater than 6 mm. Widths were twice the thickness and lengths were six times the thickness. The sample sets of six specimens per composite type were flexed at a rate of 1.0 mm/min while supported by a span of four times the thickness using the Instron model 5567 load frame. As with the flexural tests, the diameters of the supports in contact with the samples were 3.17 mm, and the diameter of that portion of the fixture applying the load was 6.34 mm. Results from

samples not showing evidence of tensile or compressive failure at their surfaces were accepted as valid. All others were disregarded. As specified in the standard, the interlaminar shear strength of the samples was calculated using:

$$F = 0.75 \frac{P_{max}}{bh}$$

where F is the shear strength, P_{max} is the maximum applied load, b is the sample width, and h is its thickness.

4.6.5. Density Tests

The densities of five specimens per type of composite were determined using a Mettler Toledo 33360 density determination kit in a mass balance (AB204-S/FACT, Mettler Toledo). The masses of the samples were obtained when measured directly as well as while submerged in distilled water at room temperature. The densities were calculated by:

$$\rho_{composite} = \frac{A}{A - B} \cdot \rho_{water}$$

where A is the weight of sample in air, B is the buoyancy of the sample in distilled water, $\rho_{composite}$ is the density of the composite, and ρ_{water} is the density of the distilled water at current room temperature.

The densities of the sample sets were averaged and the V_f of each composite was calculated by:

$$V_f = \frac{\rho_{composite}}{\rho_{fiber}} \cdot \frac{W_{fiber}}{W_{composite}}$$

where W_{fiber} is the weight of fiber in the composite, and $W_{composite}$ is the final weight of the composite. The density of the fiber, ρ_{fiber}, is assumed to be 1.42 (84).

4.6.6. Sample Weathering

In addition to those samples prepared for testing immediately following production, a second set of panels was produced with the intent of weathering them prior to conducting mechanical tests. Once produced, they were trimmed of their uncompressed borders as described in section 4.6.1. Following this they were labeled and their edges were sealed in a polyurethane resin (BladeRep LEP 9, Mankiewicz Coatings LLC, Charleston, SC) in order to prevent moisture absorption by the fibers exposed as a result of trimming. The sealant was allowed to cure for 1 hour. The samples were then placed into a QUV accelerated weathering chamber (Model QUV/S, Q-Lab, Westlake, OH) and one side of them was exposed to alternating cycles of ultraviolet (UV) radiation and water condensation, each for 4 hours at 40 °C. The chamber produced an irradiance of 0.5 W/m^2·nm using 40 w UVA-340 fluorescent lamp. Following 1000 hours of treatment, the samples were flipped and the other side was exposed in an identical manner. Following this, the samples were sectioned and tested as described above. However, as a portion of each panel was covered with sealant, the area of usable panel was decreased somewhat compared to the unweathered panels. Consequently, the sample sets consisted of five tensile specimens, four flexural specimens, and six to seven ILSS specimens per composite type.

4.6.6.1. Additional steps and measurements

Images were taken of each of the panels in order to provide visual evidence of their state prior to weathering. Once the exposure of the first side of the panels was complete, images were again taken of both the weathered and unweathered sides of each sample.

A micro-TRI-gloss meter (BYK, Columbia, MD) was used to measure the gloss of the weathered samples at angles of 20°, 60°, and 85°. These measurements were made at 0, 200, 450, 679, 778, and 992 hours.

The CIELAB color space values of the weathered composites were measured using a Macbeth Color-Eye 7000 (X-Rite Inc, Grand Rapids, Mi) operating in reflectance mode. This data was used to calculate the color changes each panel underwent as a result of weathering.

4.6.7. SEM

Failed tensile samples of selected panels were examined at the Electron Microscopy Center at NDSU. These samples were unweathered untreated 8601, unweathered untreated ESS F1, unweathered untreated ESS F2, weathered untreated ESS F2, unweathered NaOH ESS F2, and unweathered MHHPA F2. Each of these samples were sputter coated with gold-palladium (Model SCD 030, Balzers, Liechtenstein) after having been mounted to aluminum bases using adhesive carbon tabs. A JEOL JSM-6490LV scanning electron microscope (JEOL, Peabody, Massachusetts, USA) at an accelerating voltage of 15 kV in the secondary electron contrast mode was used to generate the images.

4.7. MHHPA Fiber Treatment Study

To further investigate the efficacy of the MHHPA pre-treatment of the fiber, efforts were made by Adlina Paramarta of NDSU's Coatings and Polymeric Materials Department to quantify the degree to which the crosslinker was added to the fiber surface (85). The first test was an acid number titration. This was followed by FTIR analysis. Further FTIR studies were conducted on various forms of MHHPA and MHHPA-treated fiber in an effort to better understand the interactions between the MHHPA and the fiber.

4.7.1. Acid Number Titration

A sample of approximately 0.25 g of the MHHPA treated fiber was cut to a length of 2.5 cm and tested per ASTM Standard D465-05. The fiber was added to a 50:50 wt% mixture of isopropyl alcohol and toluene. A 0.05 N solution of KOH was then titrated into it until any acid in the solution had been neutralized.

4.7.2. FTIR

Samples of each of the unidirectional fabric fiber treatment types were ground in a cryomill (Spex Sample Prep 6750 Freezer/Mill, Model 6750, S/N 05026) for two minutes and then incorporated into KBr (Specac P/N 3610) pellets. Thirty two scans were taken for each specimen over the range of 4000 to 400 cm-1 at a resolution of 4 cm-1 using an FTIR spectrometer (Thermo Scientific Nicolet 8700) equipped with vendor software.

4.7.3. MHHPA Treatment Two

To determine whether the initial MHHPA treatment process was simply not sufficiently aggressive, a sample of NaOH treated fiber was immersed in pure MHHPA for 24 hours. Following this, a portion of the fiber was triple rinsed in acetone. After drying in an oven at 120 °C for an hour, the fiber samples were ground and incorporated into KBr pellets for FTIR analysis.

4.7.4. MHHPA Treatment Three

To determine whether true fiber/crosslinker bonding is achievable, a third treatment regimen was undertaken. In this case, three scenarios were explored.

4.7.4.1. Fiber Treatment

First, NaOH treated fiber was chopped to a length of 1.27 cm and immersed in a 20 wt% solution of MHHPA in acetone. This solution was then refluxed for 17 hours at 60 °C. A portion of the fiber was triple rinsed in acetone. The fiber was then oven dried at 80 °C for 23 hours, ground, and incorporated into KBr pellets for FTIR analysis.

4.7.4.2. Alcohol MHHPA Reaction

In order to determine the likelihood of any reaction taking place between the fiber and the crosslinker, a simplified model was devised. Ethanol was used in place of the fiber. This primary alcohol was expected to be more reactive than the fiber's secondary OH groups, and thus more easily provide evidence of an anticipated interaction. This ethanol and pure MHHPA were refluxed at 60 °C for 17 hours.

4.7.4.3. Alcohol MHHPA Acetone Reaction

In order to determine the likelihood of any reaction taking place between the fiber and the crosslinker solution in acetone, a model similar to that described above was implemented. In this case, the ethanol was added to a 20 wt% solution of MHHPA in acetone. Following a 17 hour reflux at 60 °C, the clear solution was allowed to cool.

CHAPTER 5. RESULTS AND DISCUSSION

As mentioned earlier, there was a significant difference in the conformation of the two fiber types used in this study. This, and the ensuing difference in the maximum external force allowable before too little resin was extant in the composite, resulted in different average fiber loading between composites of the two fiber types. Also, there were slight variations between panels within each fiber's set of composites. For this reason, results were normalized to a Vf of 50% and presented in Table 4 below. This approach is acceptable based on the generally held assumption that there is a linear relationship between Vf and properties over small Vf ranges.

Table 4. Average Mechanical Properties of the Composites Produced

		Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Short Beam Strength (MPa)
	Target Properties	200 - 225	16 - 18	200 - 225	11 - 13	25 - 30
Unweathered Loose Fiber	Untreated 8601	158.1 ± 21.7	31.1 ± 4.0	194.6 ± 24.6	18.2 ± 1.2	12.6 ± 1.6
	Untreated ESS F1	154.2 ± 6.8	42.9 ± 11.8	252.4 ± 24.2	18.8 ± 1.8	22.3 ± 3.2
	Untreated ESS F2	152.6 ± 16.0	37.5 ± 11.3	340.3 ± 28.2	26.9 ± 2.8	25.6 ± 2.5
	NaOH 8601	312.4 ± 30.8	40.8 ± 5.4	242.0 ± 22.5	22.6 ± 3.4	23.3 ± 0.3
	NaOH ESS F1	109.9 ± 2.8	25.5 ± 9.3	159.1 ± 16.7	17.0 ± 0.5	19.4 ± 0.5
	NaOH ESS F2	178.3 ± 38.9	38.8 ± 10.5	259.5 ± 12.4	19.5 ± 2.8	25.4 ± 1.8
Unweathered Unidirectional Fabric	Untreated 8601	230.9 ± 20.6	26.8 ± 2.0	200.9 ± 10.5	21.0 ± 1.6	23.2 ± 0.7
	Untreated ESS F1	194.3 ± 7.6	25.0 ± 2.8	163.9 ± 2.2	15.5 ± 0.8	15.8 ± 0.3
	Untreated ESS F2	210.5 ± 11.1	26.5 ± 2.6	229.0 ± 13.1	18.9 ± 1.0	23.4 ± 0.2
	NaOH 8601	225.3 ± 8.0	27.4 ± 1.8	232.6 ± 2.4	17.6 ± 0.7	33.0 ± 1.3
	NaOH ESS F1	203.2 ± 15.8	25.0 ± 2.2	174.8 ± 5.5	9.8 ± 0.5	20.1 ± 1.5
	NaOH ESS F2	209.4 ± 5.7	24.2 ± 1.6	216.1 ± 8.3	12.6 ± 0.3	26.6 ± 0.6
	MHHPA 8601	202.2 ± 9.7	26.2 ± 1.5	233.1 ± 11.3	19.0 ± 0.4	25.5 ± 0.4
	MHHPA ESS F1	203.0 ± 17.2	23.1 ± 1.9	193.4 ± 12.2	15.7 ± 0.6	19.6 ± 0.6
	MHHPA ESS F2	222.9 ± 8.5	25.3 ± 5.0	253.3 ± 2.3	18.8 ± 0.2	29.9 ± 0.7
Weathered Unidirectional Fabric	Untreated 8601	179.0 ± 7.0	19.5 ± 1.8	143.5 ± 4.8	12.0 ± 0.9	16.1 ± 1.0
	Untreated ESS F1	163.8 ± 7.9	17.7 ± 1.0	117.7 ± 3.7	11.8 ± 0.3	12.4 ± 0.9
	Untreated ESS F2	177.2 ± 8.6	20.5 ± 1.6	148.6 ± 5.2	12.7 ± 0.7	17.8 ± 0.9
	NaOH 8601	198.0 ± 6.6	26.7 ± 1.9	200.7 ± 3.6	14.8 ± 0.6	24.8 ± 1.0
	NaOH ESS F1	157.3 ± 3.9	21.7 ± 1.5	139.7 ± 8.6	12.7 ± 0.8	16.3 ± 1.0
	NaOH ESS F2	174.9 ± 3.6	22.7 ± 1.8	179.6 ± 1.9	14.9 ± 0.5	22.1 ± 0.6
	MHHPA 8601	183.7 ± 5.6	24.4 ± 1.6	194.2 ± 5.5	13.8 ± 0.1	23.8 ± 1.5
	MHHPA ESS F1	141.7 ± 4.5	19.9 ± 2.4	143.1 ± 7.2	13.2 ± 0.4	15.6 ± 0.5
	MHHPA ESS F2	159.4 ± 2.6	19.8 ± 2.3	172.5 ± 3.0	14.8 ± 0.4	21.7 ± 0.6

Note: properties exceeding the upper end of the target range are highlighted green. Those falling within the range are highligted yellow.

5.1. Loose Fiber Composite

5.1.1. Loose Fiber Composite Tensile Strength

There was negligible difference in the tensile strengths of composites of untreated fiber, with each composite demonstrating an average tensile strength of around 150 MPa. This lack of variation in result is predicable given the fact that the tensile properties of these composites are nearly entirely based on those of the incorporated fiber.

In the case of the panels incorporating NaOH treated fiber, however, greater variability was observed in their tensile strengths. The panel using 8601 had an average tensile strength of 312 MPa. The ESS F1 and F2 panels averaged 110 and 178 MPa, respectively. This increased variability cannot be attributed simply to increased processing, which would imply greater mechanical damage incurred by the fiber. If this was the case, the measured strengths would likely have been consistently lower than those obtained using untreated fiber. The irregularity in the results is likely more a study in the impact of improving processing technique with practice. (The 8601 panel was the last of the set to be manufactured.) It should be observed that the exceptional result for this panel is also likely partly due to an overestimation of its tensile strength as a result of normalizing its unusually low V_f of 36 up to 50. However, even without normalization, the performance of this sample set was excellent. Its average tensile strength was 225 MPa, which is at the top end of the target property range. Assuming the validity of the normalization of this result to a V_f of 50 would mean that a tensile strength of 156% of the minimum target property was achieved using the loose fiber layup techniques outlined above.

5.1.2. Loose Fiber Composite Flexural Strength

The flexural strengths of the composites of untreated loose fiber showed a clear progression of increasing properties from 8601 resin to ESS F1 to ESS F2. The average

strengths observed for each were 195, 252, and 340 MPa, respectively. The maximum value, provided by the ESS F2, was 170% of the minimum target property.

The results for flexural strengths of composites of NaOH treated loose fiber were more varied. Those incorporating 8601 and ESS F2 were essentially the same at 242 and 259 MPa, respectively. The performance of the panel using ESS F1 was less impressive at an average strength of 159 MPa. Overall, the only panel that did not perform at or above the benchmark range was this panel of ESS F1 resin and NaOH treated fiber.

5.1.3. Loose Fiber Composite Tensile Modulus

Perhaps the most striking feature of the results for tensile modulus of loose fiber composites, as seen in Table 5, is the large degree of uncertainty in the results. This is quite likely another example of the impact of poor fiber alignment. These large standard deviations make it difficult to identify the best performing composite, but it is possible to say with certainty that the panel of 8601 resin and NaOH treated fiber outperformed 8601 with untreated fiber and ESS F1 with treated fiber. Even with the uncertainty, it can be seen that all the types of panels met or exceeded the benchmark.   Ignoring the error bars, the best observed average tensile modulus, seen with ESS F1 and untreated fiber, was 268% that of the minimum target. Meanwhile, the lowest average tensile modulus of 25.5 GPa was seen with ESS F2 and NaOH treated fiber.

5.1.4. Loose Fiber Composite Flexural Modulus

As with flexural strength, flexural modulus showed a pattern of increasing performance among panels of untreated fibers going from 8601 resin, with an average value of 18.2 GPa, to ESS F1 and ESS F2, with values of 18.8 and 26.9, respectively. Unlike the results for flexural

strength, however, in this case there is not enough difference between 8601 and ESS F1 to indicate statistical significance.

Another similarity between the flexural results is that the ESS F1 resin shows the poorest performance among the composites of NaOH treated fiber with an average value of 17.0 GPa. The averages for 8601 and ESS F2 with mercerized fiber were 22.6 and 19.5 GPa, respectively.

The uncertainty in the results makes it difficult to identify a clearly superior composite, however it would appear to be either the ESS F2 with untreated fiber, or 8601 with NaOH treated fiber. The highest average value, seen for ESS F2 with untreated fiber, performed at 245% of the low end of the goal. While the ESS F2 with treated fiber seems to be the poorest performer, even it surpassed the benchmark by 155%.

5.1.5. Loose Fiber Composite ILSS

Within the subset of panels incorporating untreated fiber, ILSS tests showed a trend of performance increase with 8601 resin's average of 12.6 MPa at the low end and with ESS F1 and ESS F2 at the high end averaging 22.3 and 25.6 MPa, respectively. In the area of panels manufactured with NaOH treated fiber, the ESS F2 was the least impressive with an average shear strength of 19.4 MPa. 8601 followed with a strength of 23.3 MPa. The best of this group was ESS F2 with a strength of 25.3 MPa. While none of the results were exceptional, it is worth noting that the two ESS F2 results, meet the minimum requirements set forth in this project, with a third being within the realm of possibility.

5.1.6. Loose Fiber Composite Observations

Whenever statistically different, the commercially available resin was consistently the poorest performer of the untreated fiber composites, and ESS F2 was the most promising.

Among the composites incorporating mercerized fiber, ESS F1 was consistently the poorest performer, though not always to a statistically significant degree.

The area of ILSS was the most challenging from a results standpoint. Also, the obvious influence of fiber alignment and layup technique on the resulting composite properties makes it impossible to render a definite determination as to the efficacy of each particular fiber-resin combination, based on these results. Despite these challenges, it has been demonstrated that composites incorporating loose flax fiber can achieve properties on par with those demanded of structural quality materials. While further improvements to fiber straightening and layup technique can be expected to yield even better results, the inherently random nature of the fibers' current alignment irregularities renders impossible any attempt at quantification of the magnitude of the existing property deficit. Therefore, the potential upper limit to the obtainable properties is rather difficult to ascertain.

There is one potential exception to the expectation that improved fiber alignment will result in improved properties. It is possible that the three-dimensionally intermingled nature of poorly aligned and wavy fiber provides an inherent resistance to longitudinal shearing. If this is the case, it would also not be unexpected that this contribution to shear strength would be inversely related to the degree of fiber alignment and straightening.

5.2. Unidirectional Fabric Composite, Unweathered

As detailed previously, one of the goals of this study was to identify efficient methods for producing high performance biobased composites. A key part of the strategy for ameliorating the challenges associated with working with flax fiber was to produce a set of composites using unidirectional flax fabric rather than loose fiber.

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5.2.1. Unweathered Unidirectional Fabric Tensile Strength

Although there was more variability between composites of untreated fiber in the case of unweathered unidirectional fabric than there was with loose fiber, there is less variability overall. Indeed, the difference between the best and worst averages amongst the panels was only 37 MPa, as opposed to the 202 MPa span seen with loose fiber. In addition, the results are much more coherent, with smaller standard deviations than the analogous loose fiber results. This reduction in variability, both in average strengths and in degree of error, can be attributed to the format of the fiber reinforcement. The greater consistency in fiber alignment of the fabric compared to loose fiber has resulted in greater consistency in results. Also, the low degree of variability between resin types is to be expected, as the tensile properties of the samples originate almost entirely from their fiber reinforcement.

The greatest average strength of 231 MPa belonged to the composite consisting of 8601 and untreated fiber, while the worst average, 194 MPa, was that of the ESS F1 and untreated fiber composite. These values were 116% and 97.0% of the low end of the goal.

5.2.2. Unweathered Unidirectional Fabric Flexural Strength

The results of the three-point bend tests on samples of unidirectional flax show a consistent pattern. Composites incorporating ESS F1 failed under a lower stress than did the other samples of similar fiber treatment type. The best performance observed within a fiber treatment type was not consistent, however. Overall, there also appears to be a progressive improvement in properties with the extent of fiber treatment.

In the case of the MHHPA treated fiber, the maximum average flexural strength of 253 MPa was seen with ESS F2 resin. The untreated fiber composites' minimum average flexural strength was 164 MPa. Expressed differently, these values were 127% and 82.0% of the

minimum target property. As with tensile strength, there was less error inherent in the results for unidirectional fabric as opposed to those for loose fiber.

5.2.3. Unweathered Unidirectional Fabric Tensile Modulus

As with the results of loose fiber composites, the tensile modulus data reported here shows a larger degree of scatter in the results than those of the other mechanical tests. However, as with the other results reported in this section, the tensile modulus data for unidirectional fabric composites were more consistent than those of the results for the comparable tests on loose fiber composites. Even though there is a lower margin of error in the results of this type for unidirectional fabrics, it is still not possible to declare a particular composite configuration to be superior to another. This is because it is also true that there is less variability in the average moduli of the various composites, causing them to lie within the others' ranges of error.

Ignoring the errors associated with the results, the best average tensile modulus was 27.4 GPa for NaOH treated fiber with 8601 resin. Similarly, the worst average tensile modulus was 23.1 GPa for MHHPA treated fiber with ESS F1 resin. These translate to 171% and 144% of the minimum benchmark, respectively. This means, of course, that all the coupons greatly exceeded the goals in the area of tensile modulus.

5.2.4. Unweathered Unidirectional Fabric Flexural Modulus

In the case of flexural modulus, it was once again seen that results for ESS F1-containing composites were the lowest amongst each particular fiber type. It is also true that, where the results were statistically significant, the best performing resin within each fiber type was the 8601 resin. The NaOH treated fibers appear to have produced the poorest performing composites in this area. The worst of all, ESS F1 with NaOH treated fiber, showed an average

flexural modulus of 9.85 GPa, which is 89.6% of the minimum goal. Unexpectedly, it was the untreated fiber that produced composites having best flexural modulus. The greatest result, 21.0 GPa, or 191% of the goal, was with untreated fiber and 8601 resin.

It may be possible that this unanticipated result of lower flexural modulus for treated fiber may stem from the removal of the amorphous components of the fiber. To illustrate, consider a piece of yarn compared to a candle wick. The fibers of the wick are infused with wax, and as a result, the wick is somewhat more able to carry a compressive load before buckling than is the dry yarn. In the case of the flax fiber, the process of mercerization strips out the wax, pectin, and hemicellulose binder from between the microfibrils. In the imagery of the analogy, this essentially converts a candle wick into dry yarn. If the epoxy resin does not fully replace the lost material during composite fabrication, this would leave the fiber less able to carry a compressive load. Since half of a flexed material is under compressive loading, it would follow that it would not perform as well as it would if the microfibrils were fully infused with, and supported by, the epoxy resin.

5.2.5. Unweathered Unidirectional Fabric ILSS

Again, the tendency for composites incorporating ESS F1to perform the most poorly is evident in the results for the ILSS tests. Also, there is again much less error associated with the results of unidirectional fabric than those for loose fiber. Unlike those for loose fiber, there are several results that meet or even exceed the minimum target property. The greatest average result, seen with NaOH treated fiber and 8601 resin, was 33.0 MPa. The lowest result, seen with untreated fiber and ESS F1, was 15.8 MPa. These correlate to 132% and 63.3% of the minimum target property, respectively.

5.2.6. Unweathered Unidirectional Fabric Observations

In the case of composites incorporating unidirectional fabric, there appears to be a tendency for those containing ESS F1 to perform more poorly than the others. This trend is not universal. However, in the examples where this is not the case, there is not a statistical difference between the ESS F1 sample and its competitor for last place. It is not as clear, though, which of the remaining resins performs the best.

Overall, the results for unidirectional fabric composites showed much less error within each type of result than was seen with loose fiber composites. This demonstrates the significantly greater degree of consistency that can be achieved using the fabric. However, the properties obtained using unidirectional fabric were nearly all lower than those obtained using loose fiber. The only exception is in the area of ILSS. The lower shear strength provided by loose fiber is counterintuitive given the fact that the unidirectional fabric provides discreet lamina between which shear failure can be expected to more easily occur than in three-dimensionally intermingled loose fiber. It should probably be noted, however, that considerable difficulty was experienced in obtaining shear failure during the testing of samples incorporating loose fiber. Consequently, the reported values for these composites may be somewhat smaller than their true shear strength. If so, this would at least partially account for the unexpected result. Also, this would mean that the difference in performance in this area between the composites of loose fiber and unidirectional fabric may be smaller than reported.

There are some additional factors that likely contributed in small ways to the difference in performance between the fiber types. As noted earlier, there was a significant difference in the lengths of individual fibers between the two. In addition, the sizing on the fabric likely produced some variation in the efficacy of the mercerization for it versus the Chinese linen. The

significance of the effect is not known, however. Furthermore, the twist of the fibers in the unidirectional fabric guarantees that all fibers are slightly off-axis.

A comparison of the results for the NaOH treated and the MHHPA treated fabrics would appear to indicate that pretreating with the crosslinker has had some effect: the flexural strengths and moduli of coupons utilizing MHHPA treated fabric were greater than those of solely NaOH treated fiber. However, as discussed in section 5.5, tests undertaken to determine the chemical composition of the MHHPA treated fiber failed to identify any difference between it and the NaOH treated fiber.

5.3. Unidirectional Fabric Composite, Weathered

Samples of the composite produced in this study were subjected to accelerated weathering conditions intended to simulate exposure conditions that would potentially be experienced by composites employed in real-world applications. Specifically, the condensation and UV radiation cycles emulate exposure to humidity & precipitation, and exposure to sunlight, respectively. Figure 6 depicts the resulting losses in properties suffered by these samples.
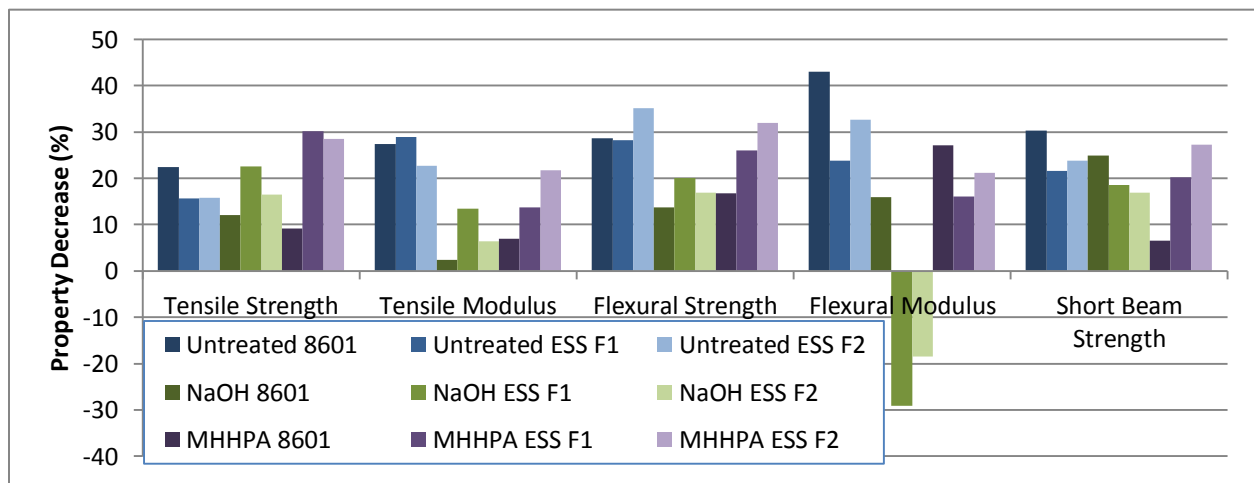

Figure 6. Percent property decrease with weathering.

5.3.1. Weathered Unidirectional Fabric Tensile Strength

The tensile strengths of the weathered samples were fairly similar across all composite types, though with slightly more variation than for the unweathered samples. While there was greater variation between panel types, the standard deviations of the test results within each particular type of panel showed a tendency to be much smaller. The trend of ESS F1 panels to perform at a lower level than equivalent ESS F2 and 8601 is evident as well. Overall there is a decrease in performance in the weathered samples versus the unweathered. On average, the tensile properties of the samples decreased by 19.2 %. The largest decreases were seen in the MHHPA ESS F1 and MHHPA ESS F2 panels, with decreases of 30.2 and 28.5 %, respectively. The lowest decrease was seen in the properties of the MHHPA 8601 panel, with a decrease of 9.1%.

5.3.2. Weathered Unidirectional Fabric Flexural Strength

The flexural strengths of the weathered samples retained the unweathered samples' overall appearance of increasing strengths from untreated, to NaOH treated, to MHHPA treated fibers. The tendency for ESS F1 panels to be weaker than their counterparts was also retained. Overall, the standard deviations within each sample set are smaller. On average, the flexural strengths decreased by 24.3%. The greatest decrease, 35.1%, was seen with the untreated ESS F2 panel. The smallest decrease of 13.7% was seen with the NaOH 8601 panel.

5.3.3. Weathered Unidirectional Fabric Tensile Modulus

The tensile moduli of the weathered samples also showed decreased variability within each particular sample type. Overall, the NaOH treated fiber composites showed the best resiliency. The MHHPA treated fiber composites faired quite well also. The average

weathering-induced decrease in tensile modulus was 15.9%. The greatest decrease of 29.0% was seen with Untreated ESS F1. The smallest loss of 2.4% was seen with NaOH 8601.

5.3.4. Weathered Unidirectional Fabric Flexural Modulus

As with tensile modulus, the greatest decrease in flexural moduli was observed with the composites incorporating untreated fiber. Continuing the trend observed above, there is an overall decreased variability in the results of each particular type of composite. Again, the poorest performers were the untreated fiber composites, while the NaOH treated composites appeared to fare the best. The greatest property loss was experienced by the untreated 8601 panel, which decreased by 42.9%. Unexpectedly, the weathered NaOH ESS F1 and F2 panels showed *increases* in their flexural moduli by 29.1 and 18.5%, respectively. However, as they do not appear to be abnormally large in comparison to the properties of similar samples, it is likely that this result is a product of abnormally low unweathered values.

5.3.5. Weathered Unidirectional Fabric ILSS

As with the other properties, the category that fared the worst overall was that which incorporated untreated fiber. The greatest loss of 30.3% was suffered by the untreated 8601 sample. However, while the untreated composites fared the most poorly overall, the 2nd worst performer was MHHPA ESS F2 with a loss of 27.2%. The best performer, with a loss of 6.5%, was MHHPA 8601. The average loss in shear strength across all sample types was 21.1%. Contrary to the results seen for the other properties, the average error inherent in the results of this set was slightly greater than it was for the unweathered shear tests.

5.3.6. Weathered Unidirectional Fabric Observations

In most cases, the uncertainty associated with the test results seemed to decrease as a result of weathering. Also, in most cases, those composites incorporating untreated fiber suffered the greatest decrease in properties. The tendency for the unweathered ESS F1 panels to perform at a slightly lower level than the other resin types was observed in the weathered panels too. However, the ESS F1 panels did not exhibit a penchant for greater property loss with weathering than the other resins. Therefore, the retained trend of lower performance of ESS F1 is likely due to the properties of the panel prior to weathering, rather than a result of the weathering itself. Excluding the NaOH ESS F1 and F2 panels, the panels that suffered the lowest average deterioration across all the properties were the NaOH and MHHPA 8601 panels. Their average losses were 13.8 and 13.3%, respectively.

5.3.7. Weathered Unidirectional Fabric Optical Effects

Prior to weathering, the panels were characterized by low reflectance. For this reason, measurements taken at 85° are the most pertinent and have been presented in Figures 7-9. The results of gloss measurements taken before and after weathering show a significant decrease in
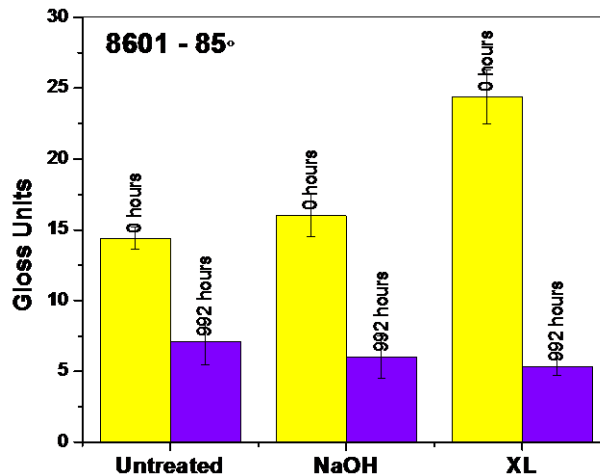

Figure 7. 8601 gloss at 85° after 1000h UV-exposure.

glossiness of the 8601 panels. In contrast, the ESS panels did not show a statistically relevant change. This tendency for 8601 to degrade more than the ESS resins can be attributed to its many aromatic rings, which are known for their UV induced degradation.
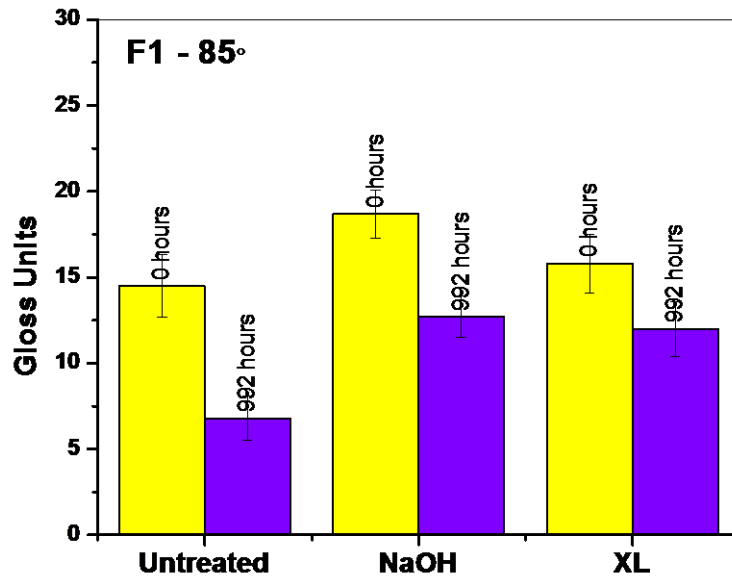

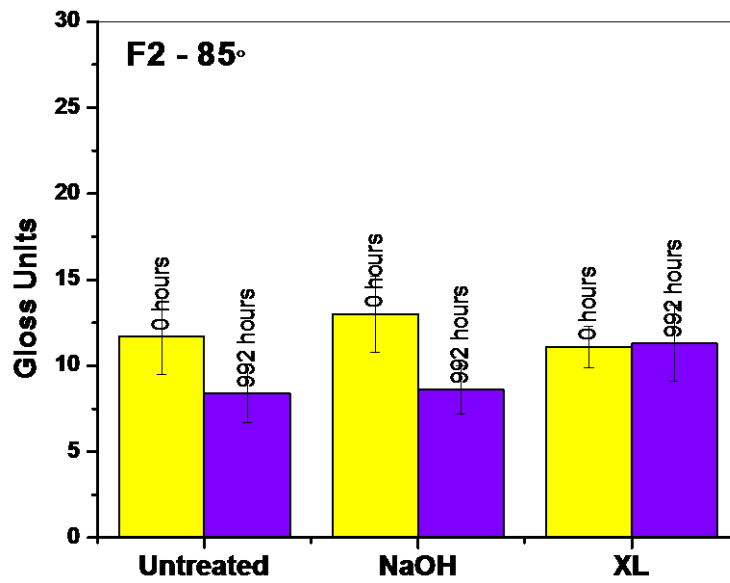**Figure 8.** ESS F1 gloss at 85°after 1000h UV-exposure.

Figure 9. ESS F2 gloss at 85° after 1000h UV-exposure.

Before and after images of the composites show that those made with the ESS resins bleach with exposure. The 8601 panels showed a change with weathering also, but upon simple visual inspection of the images, it is less apparent what the nature of the change is. The color difference measurements are useful in quantifying the changes. Figure 10 shows the high ΔL* values for the ESS resins, validating the observation that they experienced significant bleaching.

Figure 11 shows relatively high Δb* values for the 8601 composites compared to those incorporating the ESS resins. This indicates that the 8601 panels yellowed significantly more than the ESS panels, which is not unexpected given its greater aromatic content.
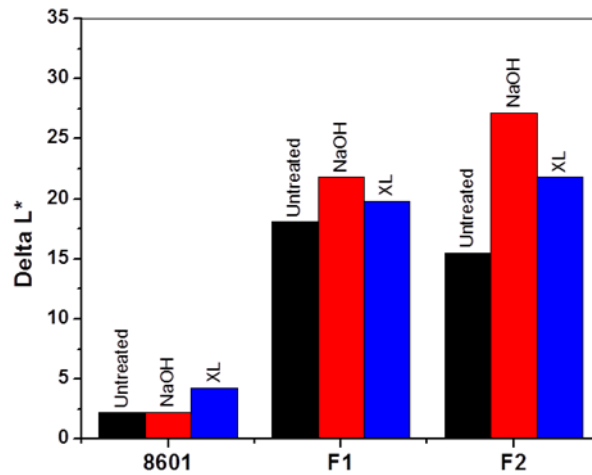
**Figure 10.** Lightness difference (ΔL*) after UV-exposure.
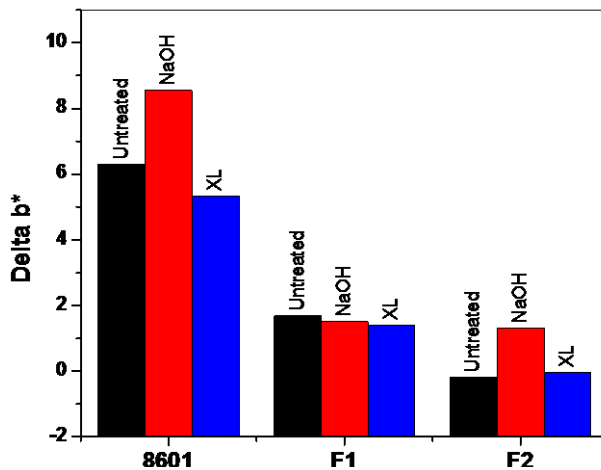
Figure 11. Yellow color difference (Δb*) after UV-exposure.

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5.4. Resin Performance
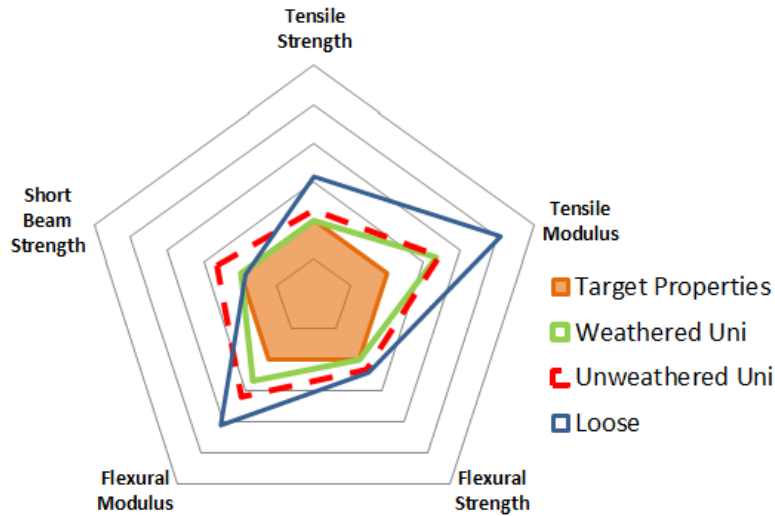
5.4.1. Araldite 8601

As can be seen in Figure 12, composites using the 8601 resin and untreated unidirectional fabric essentially meet the performance goals in the areas of tensile strength, flexural strength, and short beam strength. They fare even better in the areas of tensile and flexural moduli. When weathered, this composite experienced marked property degradation, though still performed passably in the areas on tensile strength, tensile modulus, and flexural modulus. The loose fiber version of this composite performed less admirably than its unidirectional counterpart in the areas of tensile and short beam strength.

When the fiber was treated in NaOH, the overall performance of each of these types of composites improved. This can be seen in Figure 13. The unidirectional fabric composite showed a slight overall improvement in both the unweathered and weathered versions. The gains seen in the weathered composite are such that it now meets the performance goals. Similarly, the loose fiber composite is also now quite adequate in all areas.
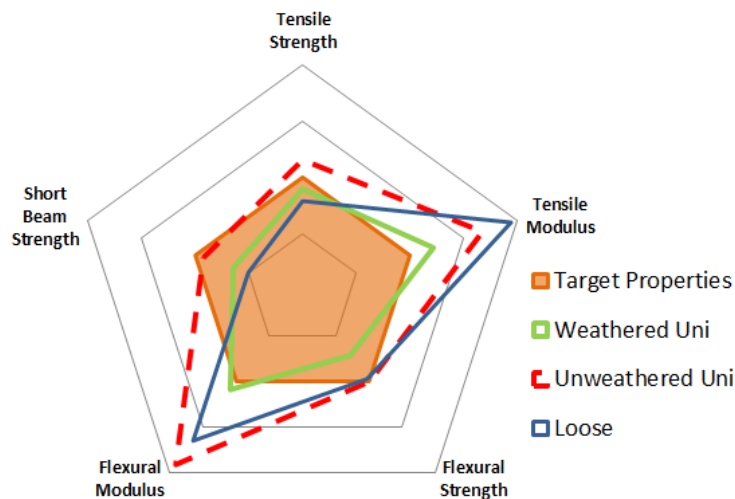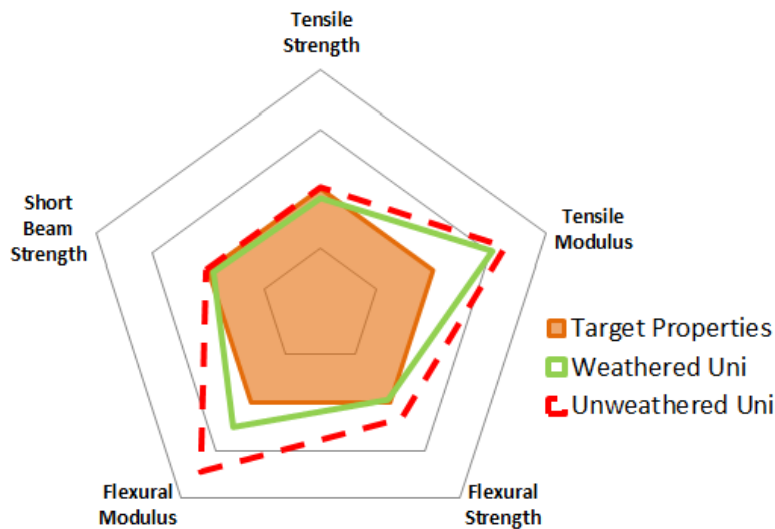

Figure 12. Untreated fiber and 8601 resin (normalized to 50% V_f).

Figure 14 shows that, with the exception of a slight improvement of flexural modulus and a slight decrease in short beam strength for unweathered unidirectional fabric composites, those versions of these composites incorporating fiber treated with MHHPA performed largely the same as those with NaOH treated fiber.
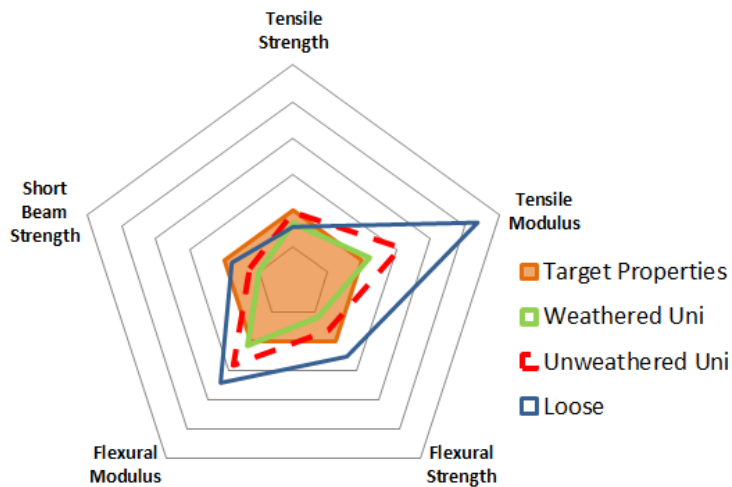

Figure 13. NaOH fiber with 8601 resin (normalized to 50% V_f).

Figure 14. MHHPA fiber with 8601 resin (normalized to 50% Vf).

5.4.2. ESS F1

As can be seen in Figure 15, composites using untreated unidirectional fabric and the

ESS F1 resin essentially meet the performance goal in the area of tensile strength, and exceed

them for tensile and flexural moduli. As expected, this composite experienced property

degradation when weathered, though not to the extent that the comparable 8601 composite did.

While it still performed passably it the areas of tensile and flexural moduli, the other properties,

if not previously lacking, now perform at an unacceptable level. In contrast to the comparable

8601 composite, the loose fiber version of this composite performed more admirably than its

unidirectional counterpart in all areas except tensile strength.

Figure 15. Untreated fiber with ESS F1 resin (normalized to 50% V_f).

When the fiber was treated in NaOH, the individual properties of the composite

maintained roughly the same significance relative to the others (tensile modulus vs. tensile

strength, etc.) This can be seen in Figure 16. In general, the unidirectional fabric composite

showed a slight overall improvement in both the unweathered and weathered versions.

Curiously, the weathered iteration of this composite performed better in the area of flexural

modulus than did its unweathered counterpart. As mentioned in section 5.3.4, this is likely due to

an abnormally low unweathered value. While the weathered version of this composite generally

fared better than the comparable untreated fiber composite, it still only meets the property goals in the area of tensile and flexural moduli. This is true of the loose fiber version as well.

Figure 17 shows that, excepting a slight decrease of flexural modulus and the questionable flexural modulus result of the previous composite, those incorporating fiber treated with MHHPA performed largely the same as those with NaOH treated fiber.
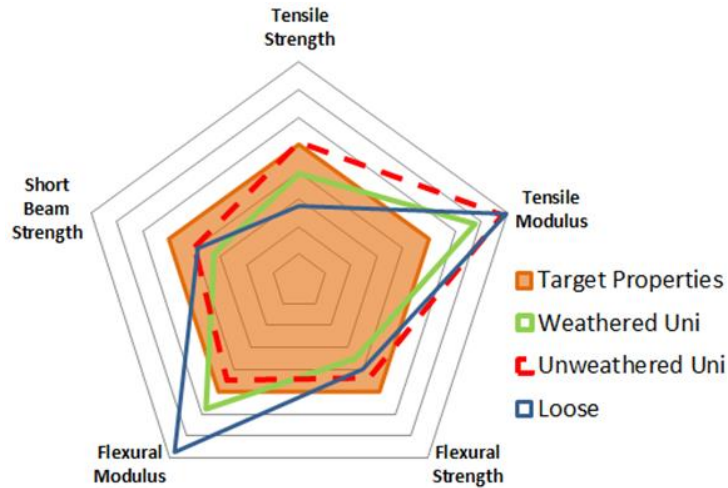
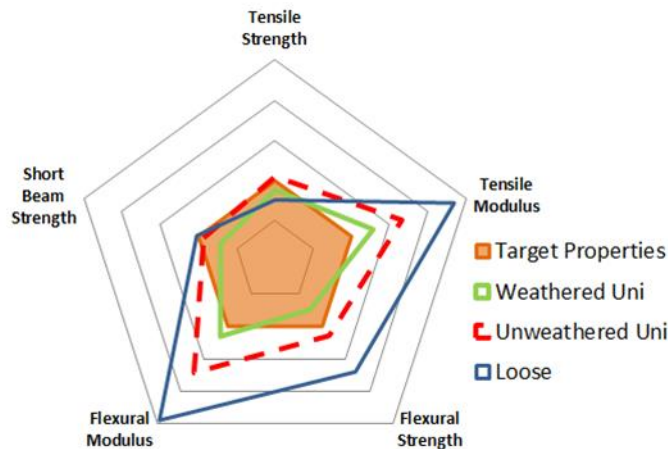**Figure 16.** NaOH fiber with ESS F1 (normalized to 50% V_f).
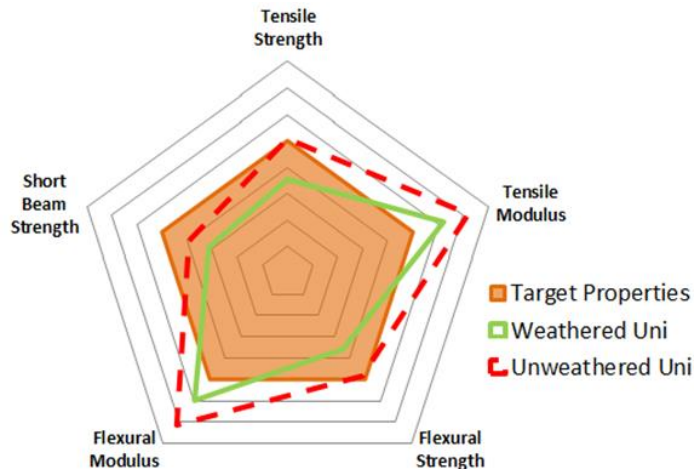
Figure 17. MHHPA fiber with ESS F1 (normalized to 50% V_f).

5.4.3. ESS F2

As can be seen in Figure 18, composites using untreated unidirectional fabric and the ESS F2 resin essentially meet the performance goals in all areas provided they are unweathered. The unweathered version of this composite fared slightly less well than the comparable 8601 composite. However, weathering resulted in a reversal whereby the ESS F2 composite had greater properties than the 8601. Despite its properties not deteriorating as significantly as the 8601, weathering left this composite underperforming in the areas of tensile, flexural, and short beam strengths. While it still performed passably it the areas of tensile and flexural moduli, the other properties, if not previously lacking, now perform at an unacceptable level. As with the ESS F1, the loose fiber version of this composite performed more admirably than its unidirectional counterpart in all areas except tensile strength. It is also worth noting that the overall performance of the loose fiber composite incorporating ESS F2 is better than comparable composites incorporating other resin types.

When the fiber was treated in NaOH, the overall performance of the composite incorporating ESS F2 and unweathered unidirectional fabric was better than that of the ESS F1 composite. In this instance, all properties meet the performance goals, though generally not to

Figure 18. Untreated fiber with ESS F2 resin (normalized to 50% V_f).

any impressive degree. As can be seen in Figure 19, the weathered version of this composite

largely maintains its properties, though, with the exception of the moduli, the properties drop

slightly below the target. As with the comparable ESS F1 composite, the unweathered flexural

modulus appears to be abnormally small. As with the weathered version of the ESS F1

composite, the weathered version of this ESS F2 composite generally fared better than the

comparable untreated fiber composite. The loose fiber version of this composite fared

substantially better than that of the ESS F1 composite, though it still underperformed slightly in

the areas of short beam and tensile strength.

Figure 20 shows that the MHHPA treated version of the ESS F2 composite performed

markedly better than the equivalent NaOH composite. This composite now exceeds the goals in

all areas. When weathered, this composite performs about as well as the NaOH composite, but

outperforms the equivalent ESS F1 composite.
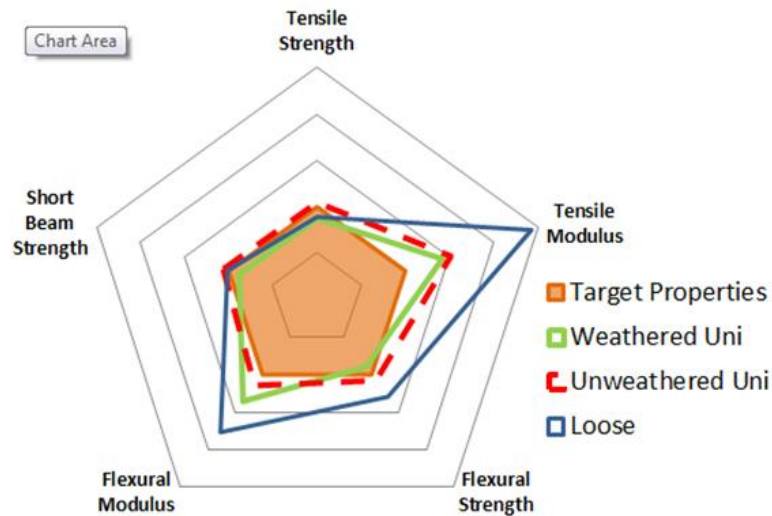
Figure 19. NaOH fiber with ESS F2 resin (normalized to 50% V_f).
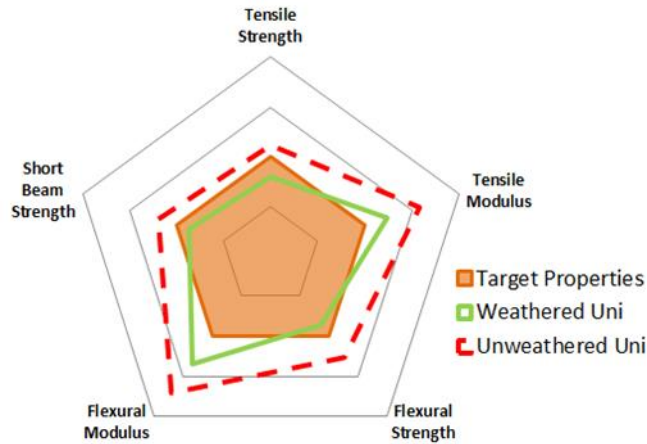
Figure 20. MHHPA fiber with ESS F2 resin (normalized to 50% V_f).

5.5. Biocontent

The fiber and resin components of the composites produced are substantially biobased. ESS resin itself is 100% renewable, while the MHHPA and DBU are assumed to be of entirely petrochemical origin. As a consequence of their differing crosslinker content, the two ESS formulations then have differing degrees of renewability. The exact percentages vary somewhat with the particular ESS batch's EEW, but in all cases they are very nearly 74% for F1 and 66% for F2.

Untreated and NaOH treated flax fiber is entirely biobased. Theoretically, a small percentage of the MHHPA treated fiber's weight is not biobased, however a definitive quantification of this percentage proved difficult to ascertain. (See section 5.5 for further explanation). For the purpose of discussion, a generous 5% of the total weight of these fibers was assumed to be non-biobased.

The biocontent of the panels produced in this study is graphed in Figure 21. Within each particular resin type, there is a small amount of variability in the results. These slight differences are not entirely a result of differences in the biocontent of the fiber types, since the MHHPA treated fiber is the only one that is not fully renewable. In the case of the ESS resins, these differences can be partly attributed to slight variations in resin mixing ratios from panel to panel. However, while the mix ratio of 8601 resin does not impact the overall biocontent of the panels incorporating it, panels of this resin type also exhibit variation in overall renewability. Indeed, the variability observed between the 8601 composites is greater than that observed between either of the ESS composite sets. This is a strong indicator that simple variation in V_f is a primary cause of this variability in overall biocontent. This is further evidenced by the fact that the composites using loose fiber are generally lower in renewable content than panels of comparable fabric type.
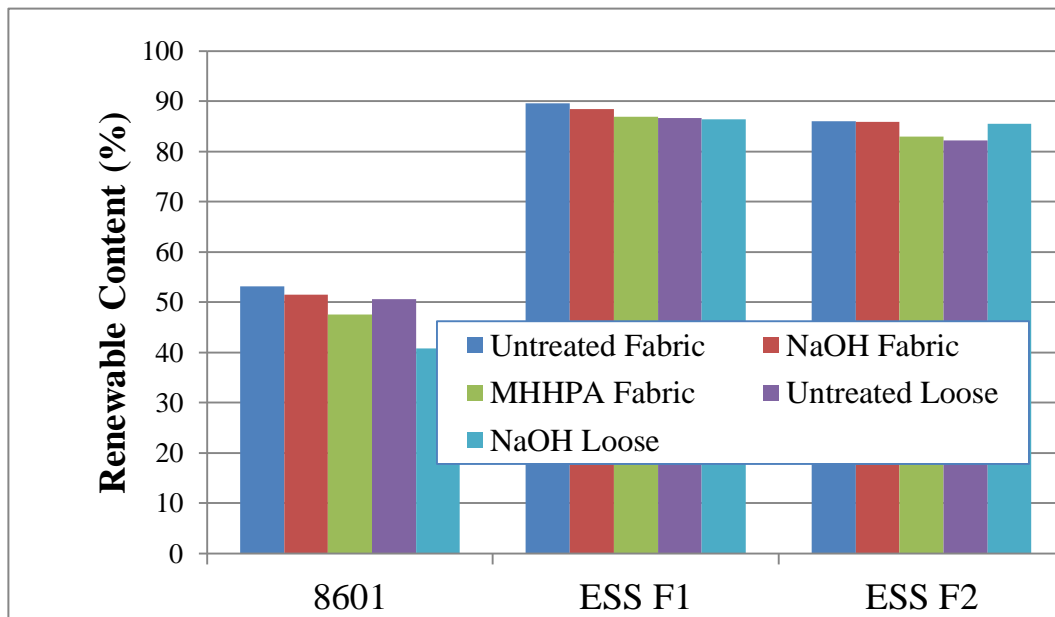
Figure 21. Flax composite renewable content by weight.

For each resin, untreated unidirectional fabric resulted in composites having the highest renewable content. The ESS F1 resin, having the highest renewable content, produced composites with the greatest overall biocontent. As such, untreated unidirectional fabric with ESS F1resin produced the panel with the highest biocontent of 89.6%. This fabric with ESS F2 and 8601 resins produced the highest biocontent panels for these resins. Their renewable content values were 86.1% and 53.2%, respectively. On average the panels produced using 8601 resin resulted in a 48.7% biocontent, ESS F1 averaged 87.6% and ESS F2 averaged 84.5%.

5.6. MHHPA Fiber Treatment Study Results

As mentioned earlier, some of the fiber used in this study was treated with MHHPA prior to incorporation into a composite. The hope was that the MHHPA and fiber would so strongly associate that the epoxy resin would behave as if it was crosslinking with the fiber itself. The desired end result of this process was superlative adhesion between the epoxy matrix and the fiber, and similarly exceptional composite properties as a result. The following sections describe tests that were conducted in attempts to verify the validity of these hopes (85).

5.6.1. Acid Number Titration

There was no discernable difference between titrations of the fibers and control titrations of the alcohol/toluene solution without fiber. It was concluded that either MHHPA was not present in the sample, or that this method was not appropriate for this type of sample.

5.6.2. MHHPA Treatment One

Following the failure of acid number titration to provide insight into the MHHPA content of the treated fiber, the FTIR spectrum of the fiber was obtained and compared to that of NaOH treated fiber. The spectra, provided in Figure 22, showed no discernible difference. Most notably, the MHHPA-treated sample showed no new peak at wavenumber 1710 cm^{-1}, which would have indicated the presence of MHHPA's carbonyl groups.
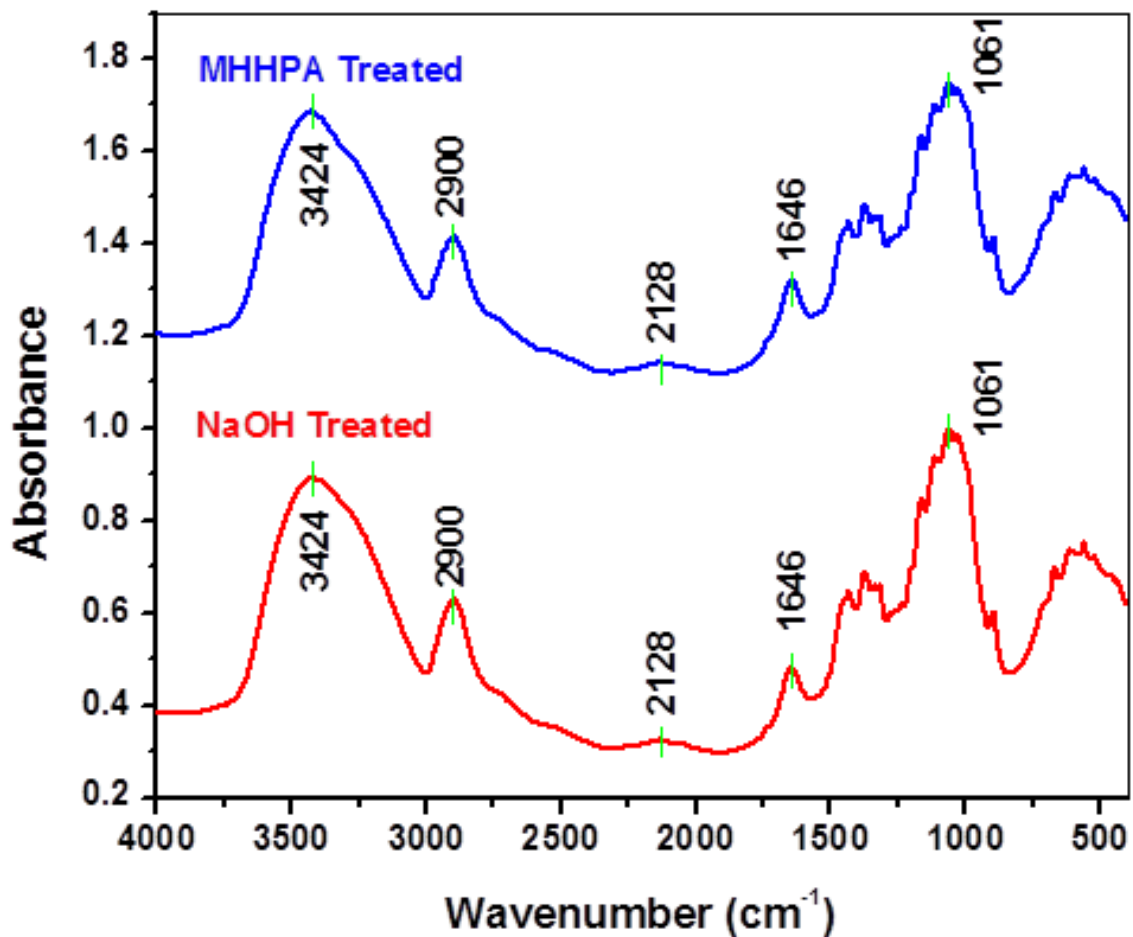
Figure 22. MHHPA treatment of flax fibers, version 1.

5.6.3. MHHPA Treatment Two

To further investigate, additional efforts to understand the interactions between MHHPA and –OH functional groups were undertaken. The spectra resulting from three different fiber treatments were obtained and compared to the spectrum of MHHPA itself. The treatments were: 1) NaOH and MHHPA-treated, then subsequently washed in acetone; 2) NaOH and MHHPA-treated but not subsequently washed in acetone; 3) only NaOH treated. The resulting spectra are compared in Figure 23. MHHPA's carbonyl peak at wavenumber 1710 cm^{-1} is present in the spectrum of unwashed fiber, but no peak appears when washed. This suggests that MHHPA was not bonded to the fiber, but present as a residual deposit capable of being rinsed off by acetone.
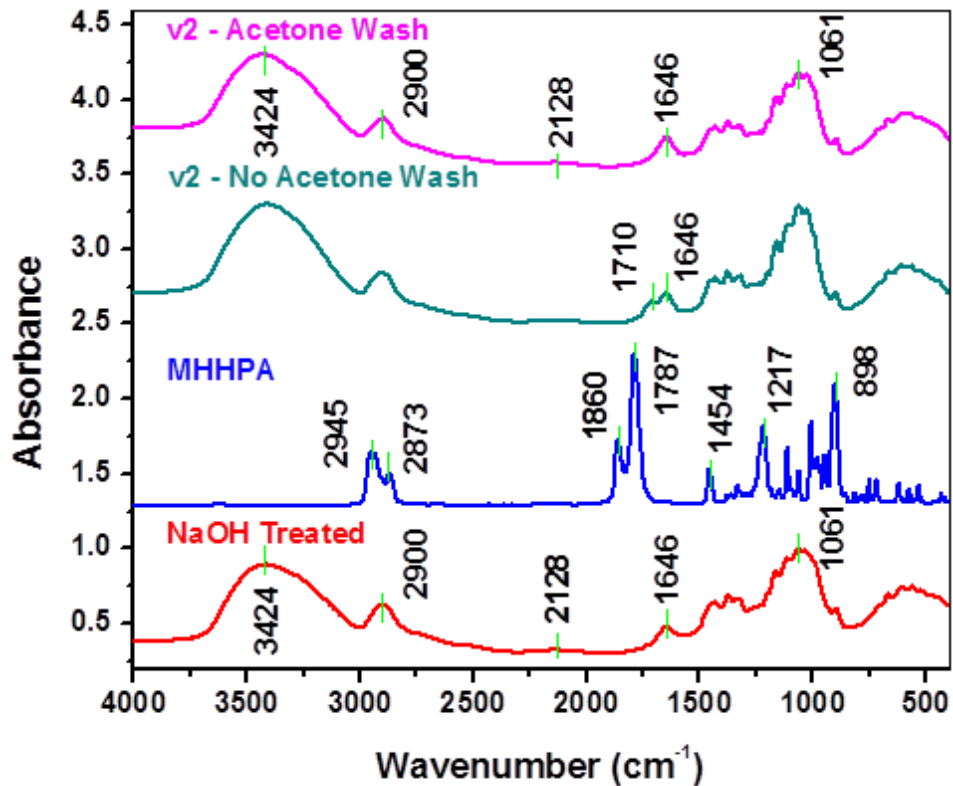

Figure 23. MHHPA treatment of flax fibers, version 2.

5.6.4. MHHPA Treatment Set Three

As mentioned earlier, the finding that the MHHPA had not bonded to the fiber prompted further study into the likelihood that fiber/crosslinker bonding is achievable under any conditions. This additional study took place in three phases.

The first step was to treat chopped NaOH fiber by aggressively refluxing it in an MHHPA/acetone solution. As a result of this treatment, the fiber became firmly bound together into a sphere and required mechanical separation.

The second step repeated the first, but used a simplified model. The fiber was replaced by ethanol, and pure MHHPA was used in place of the crosslinker/acetone solution. Aggressive refluxing of this combination produced no visually apparent change to the solution.

Given that the first step seemed to indicate that something was occurring to cause the fiber to bind together, while the second step did not appear to indicate a reaction, a third step was devised to determine if a model of intermediate complexity would demonstrate evidence of reaction. In this trial, ethanol, acetone and MHHPA were aggressively refluxed. During cooling following the reflux, a white precipitate formed which subsequent heating to 50 °C failed to re-dissolve.

5.6.4.1. MHHPA Treatment Set Three Discussion

The FTIR spectra produced by the products of the various tacks undertaken in treatment set three can be viewed in Figures 24 and 25. Comparing the ethanol-MHHPA (orange) and ethanol-MHHPA/acetone (grey) reactions in Figure 24, there appear to be no noteworthy differences aside from peaks indicative of the presence of acetone in the latter case.
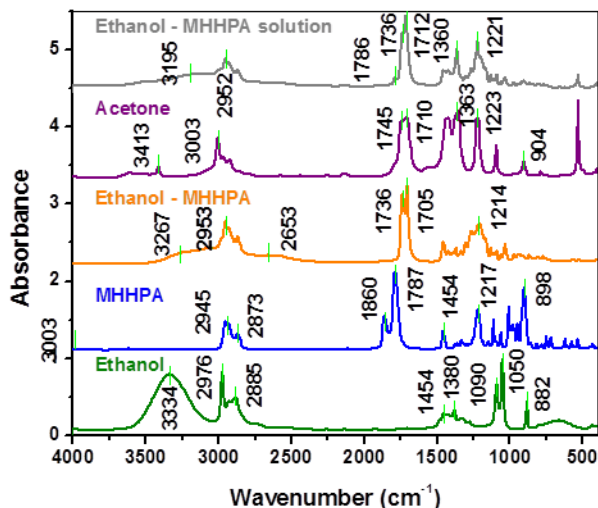
Figure 24. Reaction between ethanol and MHHPA (both pure liquid and solution).

Figure 25 shows the results of the third attempt at MHHPA treatment of fiber. As with the results of MHHPA fiber treatment two in Figure 22, there was no difference between the curves for the (green) acetone-washed and the (red) NaOH treated fiber. There was, however, a peak indicative of the presence of a carbonyl group in the (purple) spectrum of the unwashed fiber. In this case, the peak was located at 1704 cm^{-1}. Unlike the curves for treatment two, the OH peak at 3424 is significantly reduced for the fiber that had been refluxed with the crosslinker in acetone, but not subsequently rinsed in acetone. This peak reappears once the fiber has been rinsed in acetone. The reduced peak would seem to indicate that the increased heat employed in fiber treatment three successfully effected interactions between the MHHPA and the fiber's hydroxyl groups. However, the reappearance of the peak following the acetone rinse indicates that the interaction between the two is not a strong one, but rather merely the alcohol-anhydride hydrogen bonding association depicted in Figure 26.
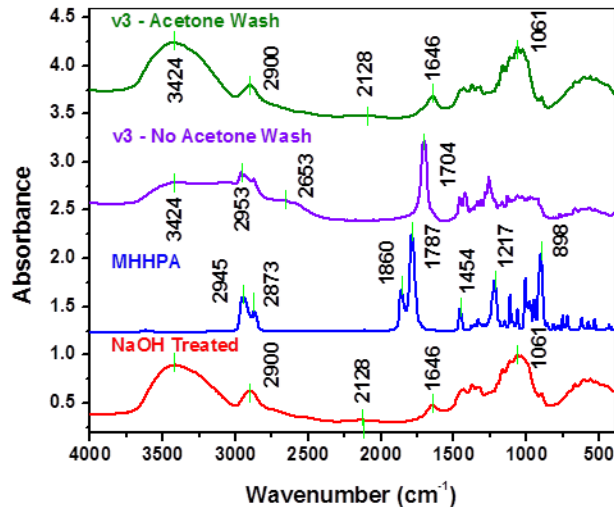
Figure 25. Third MHHPA treatment of flax fibers.
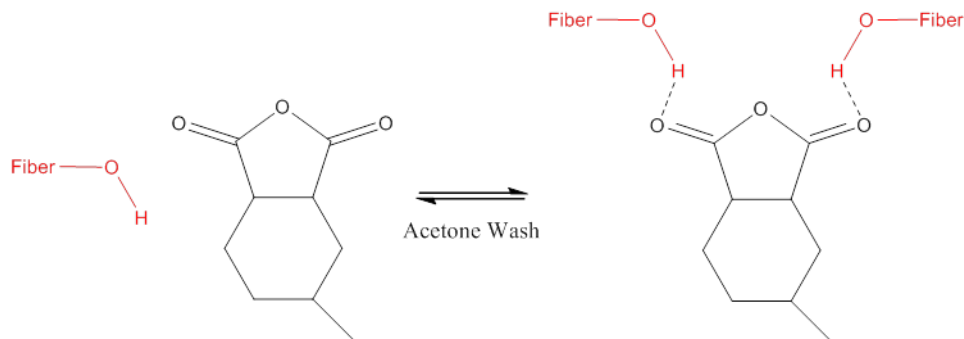
Figure 26. Reaction between flax fiber and MHHPA.

5.7. SEM Results

The SEM images presented in Figure 27 show examples of pulled out fibers for several of the composite types. For the unweathered untreated 8601 and ESS F1, the fibers appear to be fairly clean with only a small amount of adhered resin. Unweathered untreated ESS F2 appears to show a fiber sheathed in resin. This was characteristic of the sample as a whole. The majority of the pulled out fibers were found in this state. The weathered version of this composite, however, was characterized by fairly clean fibers. Unweathered NaOH ESS F2 showed increased resin adherence. In this example, the back side of the fiber appears to be sheathed in resin, while the front is not. Other fibers from this sample (not shown in Figure 27) were fairly

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clean with amounts of adhered resin that were similar to the other relatively clean fibers. Unweathered MHHPA ESS F2 showed a surprising trend. All examples of pulled out fiber that were located possessed a large amount of crystalline looking detritus.

The images presented in Figure 28 show examples of matrix fracture surfaces and the state of the fibers in these locations. For unweathered untreated 8601 there are several holes where fiber pulled out. There is also a gap around most of the fibers where the matrix is not bonded. It is interesting to note that there is a circular synthetic carrier fiber present on the left side of the image which stands out in contrast to the polygonal profiles characteristic of flax fiber. The image of unweathered untreated ESS F1 does not show the gaps between fiber and matrix. Again, a round synthetic fiber can be seen in the upper left hand corner of the image. Both the weathered and unweathered untreated ESS F2 samples show small amounts of gapping around fibers. They also both contain examples of a resin sheath coating a fiber. The unweathered NaOH ESS F1 image shows a dramatic gap between a fiber bundle and neighboring matrix. It also shows separation between fibers that were previously so closely associated that no resin exists between them. The image for unweathered MHHPA ESS F2 shows little gapping around fibers and also shows that most fibers failed in close proximity to the matrix fracture.
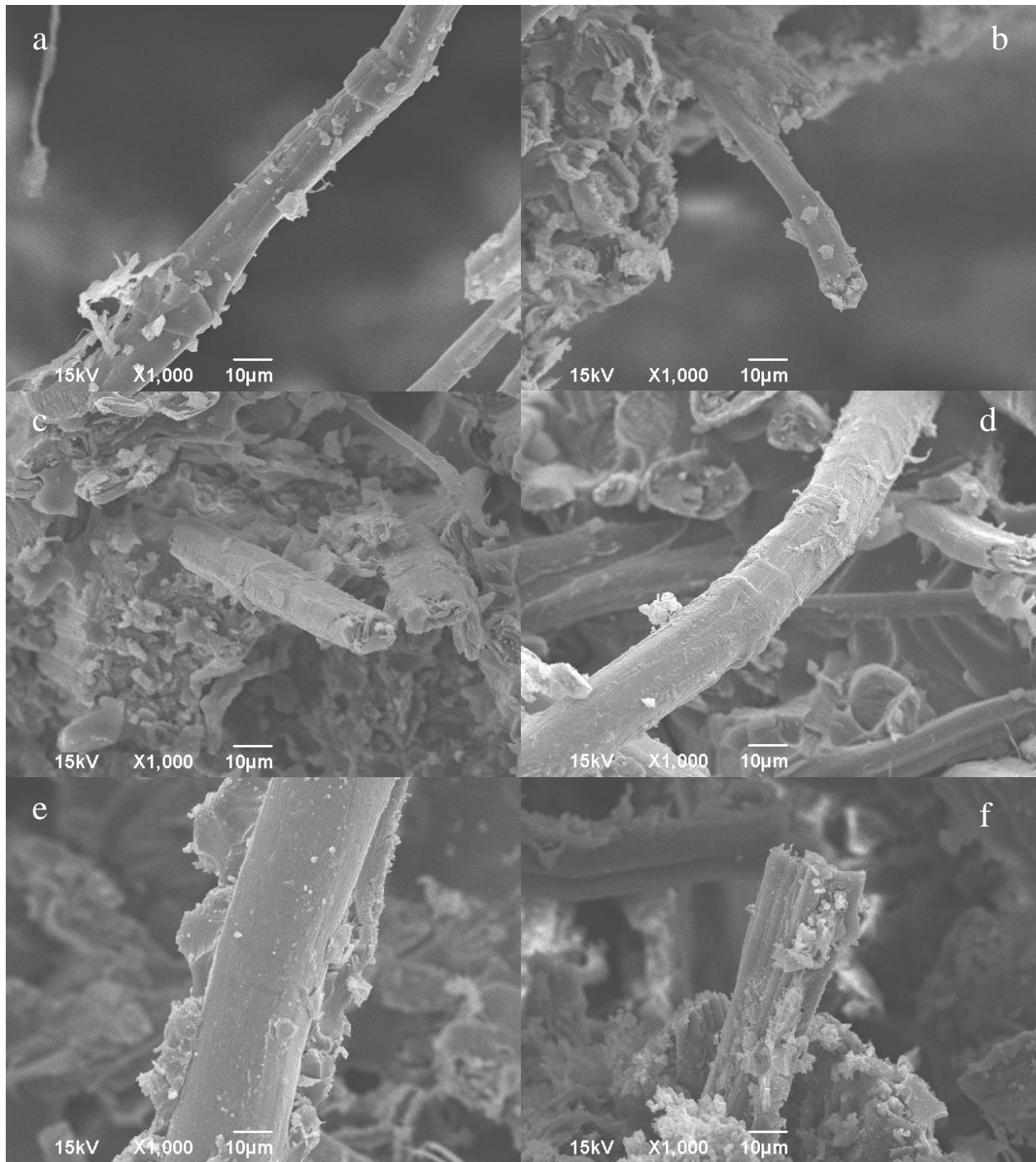
Figure 27. Fiber pullout for selected composites:

a) Unweathered untr. 8601 b) Unweathered untr. ESS F1 c) Unweathered untr. ESS F2

d) Weathered untr. ESS F2 e) Unweathered NaOH ESS F2 f) Unweathered MHHPA ESS F2.
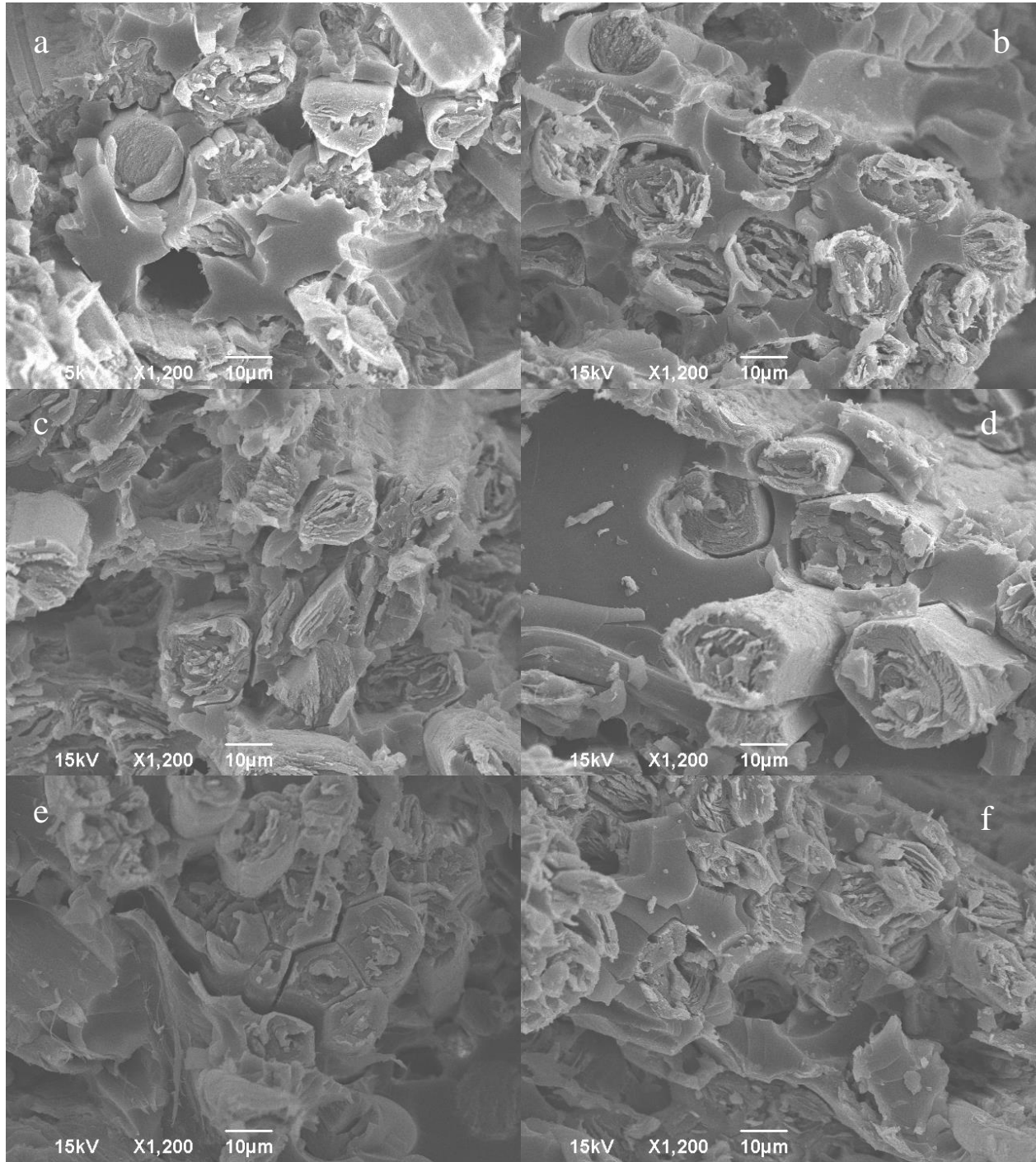
Figure 28. Matrix fracture surface for selected composites:

a) Unweathered untr. 8601 b) Unweathered untr. ESS F1 c) Unweathered untr. ESS F2

d) Weathered untr. ESS F2 e) Unweathered NaOH ESS F2 f) Unweathered MHHPA ESS F2.

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5.8. Further Discussion

Throughout this study, several different batches of ESS were used. As alluded to in section 4.4.2, each of these batches had a different EEW and, therefore, different amounts of resin and catalyst required in order to arrive at a desired formulation (i.e. ESS F1 or F2). It is worth pointing out that it has been assumed that this EEW variation does not impact the consistency of the final results.

CHAPTER 6. CONCLUSIONS

6.1. Fiber Type

At the outset of this study, it was assumed that ESS would provide a significant improvement over conventional biobased resins, though it would still require a modicum of glass fiber if structural quality properties were to be achieved. However, the results presented in the previous chapter clearly show that a composite meeting the requirements set forth in the objectives of this project can be met without the addition of glass fiber. Tensile strengths exceeding 156% of the objective were realized using loose fiber. The fact that this result was obtained using the 8601 resin is largely irrelevant as this property is almost entirely driven by the strength of the reinforcing material. All of the composites produced well exceeded the desired goal for tensile modulus. The best result of 42.9 GPa, or 268% of the desired performance, was achieved using untreated loose fiber and ESS F1. The greatest flexural strength was obtained using untreated loose fiber and ESS F2. It exhibited a flexural strength of 340.3 MPa, or 170% of the stated goal. This fiber and resin combination also produced the greatest flexural modulus: 26.9 GPa, or 245% of the objective. Producing composites of exceptional short beam shear strength proved to be more challenging, regardless of the resin employed. However, many of the ESS F2 composites fared respectably well. The best of these, MHHPA ESS F2 in unidirectional fabric, exhibited a short beam strength of 29.9, which was 120% of the goal. In fact, overall, this material is the best high biocontent composite, performing at least as well as a commercially available pultruded member in all property categories. This well performing composite contained 83.0% renewable content. In addition to proving that glass reinforcement is unnecessary, it has been shown that both fiber types have positive and negative qualities. Composites with superlative, albeit variable, qualities were achieved using loose fiber. Conversely, more

consistent, but less impressive results were achieved when using unidirectional fabric. In addition, the variability in results observed in the composites using loose fiber is unlikely to instill great faith in structural products using it. Barring a need for properties greater than can be provided by the fabric, it is likely that its consistency in performance will be of greater value than will loose fiber's superior results.

6.2. Fiber Processing

Results obtained from composites of loose fiber underscore the necessity of good fiber alignment. This testifies to the fact that continued refinements in fiber treatment and manufacturing techniques will likely play a deciding role in the successful commercial fabrication of structural quality biocomposites. For example, the results of section 5.1.1 demonstrate that even if it is intended that loose fibers be employed without undergoing surface treatment, their alignment, and the resulting composite properties, can be significantly improved if they are first wetted and straightened. However, the total time required to rinse and prepare loose fiber was around 10 hours per composite, compared to around 2 hours for the fabric. Barring further improvements in the methods used to prepare the fiber, or informed compromises being made in the quality of the fiber preparation as is currently undertaken, the increased time and labor incurred in so doing significantly nullifies any process savings obtained by skipping the surface treatment.

6.3. Composite Manufacture

The amount of external pressure applied to infused fiber generally dictates the V_f of the resulting composite. As a result, greater pressure results in greater properties, provided that the pressure is not so great that there is no longer sufficient matrix to transfer load between fibers. Through a process of trial and error using 8601 resin while practicing the techniques utilized in

this project, it was found that external loads of 2.5 and 4.5 metric tons (1.189 and 2.140 kPa) were best for untreated versions of loose fiber and fabric, respectively. However, it has never been confirmed that these loadings are ideal for layups consisting of treated fibers, nor has it been confirmed for other resins. It is possible that the pressures used were not ideal in all cases.

6.4. Weathering

It is generally acknowledged that lab based accelerated weathering methods cannot be directly correlated to an equivalent degree of natural weathering using some sort of universal formula. This is a consequence of variations in the characteristics of each specific material. In addition, there is inherent variability in environmental conditions from season to season as well as between geographical regions. However, in an effort to provide some semblance of a benchmark by which the two methods can be correlated, a technical paper making this comparison was published by Q-Lab, the manufacturer of the chamber used in this study (86). The epoxy used in that report was a glossy gray primer over a steel substrate, which is a weak correlation to the epoxies used in this study. However, if this example is examined as it is, it can be found that the report implies an observed acceleration factor of 7.9 over 1000 hours of exposure. Assuming a linear correlation between irradiance and acceleration factor, accounting for the different irradiance levels employed during this study and that one (0.5 vs 0.85 $W/m^{2 \cdot}nm$) would suggest that the acceleration factor for this study's composites is 4.6. This would mean that they underwent the equivalent of 6.4 months of natural weathering.

On average, weathering caused a 21% decrease in properties. However, both fiber treatments appeared to result in improved resistance to property degradation. This effect was particularly noticeable with the 8601 resin. In general, weathering appeared to have the smallest effect on the tensile properties of the panels. Of course, this is to be expected as this property is

driven by the integrity of the fiber, which was protected from damage by the surrounding resin. Of those highly biobased composites presented in this work, the best overall material for use in environmentally exposed settings appears to be NaOH ESS F2. Its tensile strength was 174.9 MPa, or 87.5% of the goal. Similarly, its flexural strength of 179.6 MPa, was 89.8% of the objective. Its tensile and flexural moduli, 22.7 and 14.9 GPa, respectively, were 141.9% and 135% of their benchmarks. Lastly, the short beam shear strength of this composite was 22.1 MPa, which was 88.4% of the goal.

6.5. One Final Conclusion

In refutation to those who doubt its likelihood, it is has been demonstrated that it is indeed possible for an individual with three kids 5 and younger to complete a Master's degree in a new field without consuming any coffee or energy drinks.

CHAPTER 7. FUTURE WORK

7.1. Additional Resin Formulation

Structure-property studies of the matrix resin system could provide useful insight into the impact of such variables as epoxy functionality, anhydride crosslinker, catalyst type, loading, and curing conditions on properties such as modulus, impact resistance, glass transition temperature, thermal stability, water sorption, and durability. In addition, it would be worthwhile to confirm the validity of the assumption that variations in EEW from batch to batch do not impact the consistency of the properties exhibited by each formulation.

7.2. Additional Fiber Treatment

It is expected that continual refinements to the techniques used in fiber treatment will further increase the cost effectiveness of the process, as well as the performance and biocontent of the resulting material. Improved processing methods, such as the use of supporting screens and a shower of rinse water rather than a concentrated stream of water would improve the efficiency of post treatment rinsing while also reducing fiber dis-alignment. Another specific avenue that could be pursued is the possibility that the efficacy of the MHHPA pre-treatment could be improved through the use of a catalyst and a greater treatment temperature.

7.3. Additional Composite Manufacture

Continuing refinements to the techniques used in composite manufacture are expected to further improve the cost effectiveness of the process, as well as increase the performance and biocontent of the resulting material. As mentioned above, a systematic study of the external pressure applied to composites of varying fiber treatments would be beneficial and likely result in further property improvements. Another avenue that may be worth considering is the

hybridization of loose flax and unidirectional fabric. The goal of this would be to achieve a final product that approached the consistency of the fabric and the superlative properties of the loose flax.

7.4. Additional Testing

In the future, tests could be conducted to determine the durability of the matrix resin. Similarly, structure-process-property relationships could be established for the biocomposites produced with regards to durability when used as a structural construction grade material.

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