DEVELOPMENT AND WEATHERABILITY OF BIO-BASED COMPOSITES OF STRUCTURAL QUALITY USING FLAX FIBER AND EPOXIDIZED SUCROSE SOYATE

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ABSTRACT

Composites having high bio-based content 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 dilute the resulting composite's bio-content and increases cost. To overcome these limitations while maintaining high bio-content, in this study, a newly developed biobased resin, epoxidized sucrose soyate (ESS), is combined with surface-treated flax fiber to produce novel bio-composites. Properties of manufactured composites were compared against those using epoxy resin reinforced with flax fiber. In addition to mechanical property evaluation, accelerated weathering was performed on the manufactured composites to evaluate the mechanical properties after exposing to UV and moisture. The results of this study revealed the successful production of bio-composites having properties that meet or exceed those

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of conventional pultruded members while having 85% bio-content. Moreover, composites using treated flax fiber and ESS resin showed less degradation in properties and appearance after accelerated weathering exposure.

Key Words: Biocomposites, degrading, natural fibers, natural resins, weathering.

1. Introduction

1.1. Bio-Composites and Natural Fibers

The available body of knowledge frequently discusses the manufacture of bio-composites incorporating natural fibers. However, many of these publications appear to discuss randomly oriented, short-fiber composites, or composites manufactured using specialized molds or equipment [1]. There appears to be little emphasis on the development of cost effective, scalable methods for producing high quality structural bio-composites. In addition, unfortunately, little success has been seen in attempts to produce largely bio-based 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 components possess their own particular negative aspects [2].

Bio-composites often incorporate natural fibers such as flax, jute, ramie, hemp, and kenaf [3-5]. Their binders are also often either partially or wholly comprised of resins derived from natural sources [6]. Natural fibers have several advantages over engineered fibers. For instance, they are renewable and can be produced relatively inexpensively, their low density translates into high specific properties such as modulus, as well as flexibility, strength, stiffness, impact resistance and superior vibration damping [7-10].

Because of the inherent variations existing in natural fibers [11], the prospect of producing composites using natural fibers poses significant hurdles if uniform, quantifiable, reproducible properties are desired [12]. In addition, resin-matrix compatibility issues are a universal hurdle to the use of natural fibers in composites. This incompatibility stems from inherent properties of the materials themselves. In addition, 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 less hydrophilic manner where it interfaces with the matrix. Moreover, due to high concentration of hydroxyl groups on the surface of the cellulose (main structural element of flax fiber), good wet-out and matrix adhesion are difficult to achieve with natural fibers in their virgin state [13]. Therefore, in the interest of improving composite performance through enhanced fiber/matrix interaction, a number of physical and chemical surface treatments have been investigated. Figure 1 shows the complex structure of flax fiber [13, 14].

Figure 1. a) cross section of flax fiber, b) structure of single fiber [13, 14].

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 [13, 15].

Dewaxing is another relatively simple fiber treatment which is accomplished by immersion of fibers in equal parts alcohol and benzene [16]. A. K. Mohanty et al. discuss treating natural fibers with maleated forms of polypropylene and polyethylene [17]. Wool and Thielemans reported 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 [18]. They have also achieved improved fiber/matrix interactions by introducing butylated kraft lignin to the matrix material prior to composite fabrication [18]. Treatment with silanes, though more commonly associated with glass fiber treatment, has proven useful for natural fibers as well [19, 20]. Other methods for chemically modifying natural fibers include acetylation [21], benzylation [22], and acrylation [23] as well as treatment with permanganate [24], peroxides [25], and isocyanates [26]. In addition, cold plasma treatment, corona discharge [27-30], dielectric barrier discharge [31], increase in surface carbonyl group content and porosity of fibers by ultrasound treatment [32] and exposure to ultraviolet radiation [33] have also been shown to improve the polarity of natural fiber.

1.2. Natural Resins

The majority of natural resins are derived from plant and animal oils and these natural oils can be described as triglycerides [34]. 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 [35]. When considering the superlative abundance of soybean oil compared to other vegetable oils, epoxidized soybean oil (ESO) is one of the most significant industrial compounds manufactured from vegetable oils [36, 37]. A depiction of the conversion of soybean oil into ESO can be seen in Figure 2 [38].

Figure 2. Soybean oil epoxidation adapted from [38].

While ESO has been used in a wide variety of applications [39-43], these are mostly limited to cases where it is used as an additive or modifier to an existing polymer technology. 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 [44]. Additionally, the aliphatic fatty acid chains of soy oil are flexible in nature. These factors limit the ability to achieve the desired physical and thermal properties using ESO alone, making it a poor choice for highly demanding applications [45, 46]. As a result, much effort is currently being made to develop modified forms of ESO that overcome these structural limitations.

Given that biobased resins suffer from the aforementioned limitations, much effort has been expended investigating methods of producing versions with respectable performance. Wool et al. have pursued various methods of modifying epoxidized forms of soy and other vegetable oils, including acrylation [47], maleinization [48], hydroxylation [1], and phthalation [38]. Adekunle et al. have produced methacrylated and acetic anhydride-modified soybean oil [49]. Sithique et al. have incorporated bismaleamides [50]. Thulasiraman et al. report having created a chlorinated ESO [51]. These modified ESOs are then usually blended with up to 35 wt% petrochemical based monomers such as styrene [46]. Despite the efforts 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 when crosslinked [52, 53]. Epoxidized sucrose soyate (ESS) is a unique bio-based epoxy resin based on sucrose and soybean oil, which is then epoxidized and thus it is 100% bio-based. Due to its chemical structure, it has a high number of epoxy groups per molecule which results in a high crosslink density when cured. It has also been shown that the rigid sucrose core makes a significant contribution to the properties of thermosets based on ESS [53, 54]. These factors are also what yield superior properties for ESS-based thermosets in comparison to epoxidized soybean oil (ESO), and allow for properties equivalent to thermosets derived from petrochemical epoxy resins. Thus, ESS has great potential to have a wide range of applications in protective coatings, structural adhesives and composites [52, 53].

To manufacture highly bio-based composites with properties and costs competing those of composites consisting of synthetic/manufactured constituents, three key elements are necessary: a resin system derived largely from renewable sources which exhibits performance similar to petrochemical based resins; a strong, inexpensive natural fiber that bonds well with bio-based 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 bio-composites rivaling their synthetic counterparts, while considering minimizing cost and maximizing renewable content. The investigation described 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) [55, 56]. This study will compare untreated fiber to NaOH treated and

crosslinker-pretreated fiber in terms of their performance when incorporated into composites. The composites prepared through the course of this study were also weathered via exposure to alternating cycles of ultraviolet (UV) radiation and water condensation. This treatment provided insight into the durability and long term performance of ESS resin and resulting composites and adds greatly to the existing body of knowledge.

2. Materials and Methods

2.1 Materials

The fiber used in this study was unidirectional flax fabric with the commercial name of Biotex obtained from Composites Evolution, Chesterfield, UK. Two different resins were used. The first resin which was used as control, was Araldite 8601 crosslinked with Aradur 8602. It is a commercially available epoxy/amine combination formulated specifically by Huntsman Corporation (The Woodlands, TX) for vacuum assisted resin transfer molding (VARTM) process. In addition, two different formulations of epoxidized sucrose soyate (ESS), were implemented. Both ESS formulations were crosslinked with methylhexahydrophthalic anhydride (MHHPA), and utilized 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst. The ESS was produced using samples of sucrose soyate (SEFOSE 1618U) obtained from Procter and Gamble chemicals (Cincinnati, OH). The MHHPA and DBU were obtained from Dixie Chemicals (Pasadena, TX) and Sigma Aldrich (St. Louis, MO), respectively. NaOH and 95% ethanol were purchased from the Department of Chemistry at NDSU. Properties of the epoxy resin and flax fiber from the literature is presented in Table 1.

Table 1. Literature Values for Flax and Epoxy Properties

Material properties	8601/Aradur [57, 58]	Flax Compiled	Flax [59]	Flax [60]	Flax [61]	Flax [62-65]
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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, ν_{12}	0.35	0.183	-	0.131–0.183	-	-

2.2 Fiber Treatments and Preparation

To treat the fibers, approximately 35 g of NaOH pellets were placed in a 4000 ml beaker and up to 3500 ml of 95% ethanol (100 ml/g NaOH) was added. The beaker was placed on a stirring hotplate and the solution was brought to a boil. A maximum of 45 g of fiber per liter of solution was then submerged in the solution for two hours. After two hours of treatment, the fibers were rinsed off with cold tap water until there was no treatment solution residue left in the fibers. Fibers were dried in a convection oven (Model 1370FM, VWR) at 80 °C for 12 hours.

A portion of the NaOH treated unidirectional flax fabric was subsequently treated by immersion in a 20 wt% solution of MHHPA in acetone. Approximately 460 g of fiber was immersed in a solution of 3.1 kg acetone and 0.62 kg MHHPA in a rectangular polypropylene tub with a lid. After 140 minutes at room temperature, the fiber was removed from the solution, rinsed with acetone and then placed in the oven for drying.

To determine whether the initial MHHPA treatment process was sufficiently aggressive, a sample of NaOH treated fiber was immersed in pure MHHPA for 24 hours. Following this step, a portion of the fiber was triple rinsed in acetone and after drying in the oven at 120 °C for an hour, the fiber samples were ground and incorporated into KBr pellets for Fourier transform infrared spectroscopy (FTIR) analysis.

To determine whether true fiber/crosslinker bonding is achievable, a third treatment regimen was undertaken as follows: First, NaOH treated fiber was 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 and the fiber was then oven dried at 80 °C for 23 hours, ground, and incorporated into KBr pellets for FTIR analysis. Second, In order to determine the likelihood of any reaction taking place between the fiber and the crosslinker, 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. Third, in order to determine the likelihood of any reaction occurring between the fiber and the crosslinker solution in acetone 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.

2.3 Panel Layup

To process the composite panels, vacuum assisted resin transfer molding method was used. A clean sheet of tempered glass was used as a mold surface. Twelve sheets of unidirectional flax fabric (75 g) were placed on a polytetrafluoroethylene (PTFE) sheet and then placed on the mold. The fabric was covered with a sheet of peel ply and bleeder cloth. Also, a caul plate was added on top of the materials. This caul plate served to provide both a uniform cross sectional area and a smooth upper surface of the final composite panel. Spiral tubing was placed at the ends of the fiber stack and everything was sealed under a vacuum bagging film. After mixing the resin and hardener and prior to infusion, the mixture was placed inside a vacuum chamber for 10 minutes at a vacuum pressure of 80 kPa to degas. During the infusion of resin, pressure was applied by placing a block of aluminum on top of the layup and using a shop press. This modification was done in order to achieve a higher fiber volume fraction. The maximum force applied on top of material was 4.5

metric tons. Figure 3 shows a schematic of the modified VARTM process used to manufacture composite panels for this study.

Figure 3. Modified VARTM process used to manufacture composite panels.

The mixing ratio for epoxy resin (Aradur 8601) to hardener ratio was 4:1 (by weight or volume). ESS Formulation 1 (ESS-F1) was mixed at an epoxide/anhydride molar ratio of 1/0.5, also incorporating 1.5 wt% DBU. ESS Formulation 2 (ESS-F2) was mixed at an epoxide/anhydride molar ratio of 1/0.75, also incorporating 1.5 wt% DBU. 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.

2.4 Characterization Methods

Test specimens were cut to proper dimensions for each mechanical test using a 65-10030 model Allied diamond saw. An Instron 5567 load frame was used to perform tensile, flexural and interlaminar shear strength (ILSS) tests. Tensile tests were performed according to ASTM D3039 on sample sets of five specimens per composite type. Three-point bending tests were performed per ASTM D790. ILSS tests were performed on five test specimens according to ASTM D2344.

The densities of five specimens per type of composite were determined using a Mettler Toledo 33360 density determination kit. The masses of the specimens 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 specimen in air, B is the weight of the specimen in distilled water, $\rho_{composite}$ is the density of the composite, and ρ_{water} is the density of the distilled water at room temperature.

Fiber volume fraction, 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} , was assumed to be 1.42 g/cm³ [66-68].

A second set of panels was produced with the intent of weathering them prior to conducting mechanical tests. The samples were 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/m².nm using a 40 w UVA-340 fluorescent lamp. Following 1000 hours of treatment, the samples were flipped and the other side was exposed to accelerated weathering in an identical manner. The same mechanical tests described above were performed on five specimens from each composite plate. 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. In addition, 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.

FTIR studies were conducted on various forms of MHPA and MHPA-treated fiber in an effort to better understand the interactions between the MHPA and the fiber. 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.

3. Results and Discussion

A target range for desired properties was defined based on commercial pultruded fiberglass composites available in literature [68-71]. Also, for purpose comparison, the results of all mechanical tests are normalized to a V_f of 50% and are presented in Table 4.

3.1. Unidirectional Fabric Composite, Unweathered

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

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 MHPA 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.

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. However, the best performance observed within a fiber treatment type was not consistent.

Table 4. Average Mechanical Properties of the manufactured Composites Produced

		Tensile Strength MPa	Tensile Modulus GPa	Flexural Strength MPa	Flexural Modulus GPa	Interlaminar Shear Strength MPa
	Target Properties	200-25	16-18	200-225	11-13	25-30
Unweathered	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	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

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. 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. 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. It was the untreated fiber that produced composites having the best flexural modulus. The highest 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.

The tendency for composites incorporating ESS-F1 to perform the most poorly is evident in the results for the ILSS tests. 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.

A comparison of the results for the NaOH treated and the MHHPA treated fabrics indicates 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, tests undertaken to determine the chemical composition of the MHHPA treated fiber (see below) failed to identify any chemical differences between the untreated and the MHHPA treated fibers.

3.2. Unidirectional Fabric Composite, Weathered

Samples of the composites 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. The

properties are shown in Table 1 and Figure 4 depicts the resulting changes in properties that occurred as a result of the exposure to artificial weathering.

Figure 4. Property change with artificial weathering.

Tensile strengths of the weathered samples were fairly similar across all composite types, though with slightly more variation than for the un-weathered 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. On average, 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 sample, with a decrease of 9.1%.

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 fared 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.

The flexural strengths of the weathered samples retained the un-weathered 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.

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 ESS-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 un-weathered values.

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. 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 un-weathered shear tests.

3.3. Weathered Unidirectional Fabric Optical Effects

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. 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 [73]. 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/m²·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. Prior to weathering, the panels were characterized by low reflectance. For this reason, gloss measurements taken at 85° are the most pertinent and have been presented in Figure 5. The results of gloss measurements taken before and after weathering show a significant decrease in 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. 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 5. a) 8601 gloss at 85° after 1000h UV-exposure, b) ESS F1 gloss at 85° after 1000h UV-exposure, c) ESS F2 gloss at 85° after 1000h UV-exposure.

Figure 6. a) Lightness difference (ΔL^*), b) Yellow color difference (Δb^*), after UV-exposure.

Figure 6 (a) shows the high ΔL^* values for the ESS resins, validating the observation that they experienced significant bleaching. Also, Figure 6 (b) 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.

3.4. MHHPA Fiber Treatment

As mentioned earlier, some of the fiber used in this study was treated with MHHPA prior to incorporation into a composite. It was expected that the MHHPA and fiber would react together forming a covalent bond and a reactive acid group so that the epoxy resin would behave as if it was crosslinking with the fiber itself. The desired end result of this process was covalent adhesion between the epoxy matrix and the fiber, and similarly exceptional composite properties as a result. Further analysis was performed in order to attempt to confirm this expectation.

The FTIR spectrum of the MHHPA treated fiber was obtained and compared to that of the NaOH treated fiber. The spectra, provided in Figure 7 (a) showed no discernible difference. In other words, the presence of MHHPA's carbonyl group was not confirmed. Figure 7 (b) shows the spectra resulting from three different fiber treatments: i) NaOH and MHHPA-treated, then subsequently washed in acetone; ii) NaOH and MHHPA-treated but not subsequently washed in acetone; iii) only NaOH treated. MHHPA's carbonyl peak at wavenumber 1710 cm^{-1} is present in the spectrum of unwashed fiber, but not in washed fiber. This suggests that MHHPA was not bonded to the fiber, but present as a residual deposit capable of being rinsed off by acetone.

To investigate whether the fiber and crosslinker are bonding, more treatments were performed on fibers. First, chopped NaOH treated fiber was aggressively refluxed in an MHHPA/acetone solution. As a result of this treatment, the fiber became firmly bound together into a sphere and required mechanical separation. Second, 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. The FTIR spectra of these treatments are showing in Figure 7 (c) and (d).

Figure 7. MHHPA treatment of flax fibers a) first treatment, b) second treatment, c) Reaction between ethanol and MHHPA (both pure liquid and solution), (d) Third MHHPA treatment of flax fibers.

The only difference noticed between the ethanol-MHHPA (orange) and ethanol-MHHPA/acetone (grey) reactions in Figure 7 (c) is the peaks indicative of the presence of acetone in the latter case.

Also, presence of a peak at 1704 cm^{-1} in the spectrum of unwashed fiber in Figure 7(d) indicates the presence of carbonyl group. The OH peak at 3424 cm^{-1} 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 8.

Figure 8. Reaction between flax fiber and MHHPA.

3.5. 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 petrochemical origin. As a consequence of their differing crosslinker content, the two ESS formulations have differing degrees of renewability. The exact percentages vary somewhat with the particular ESS batch's epoxide equivalent weight (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. 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 9. 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 9. 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-F1 resin 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%.

4. Conclusions

The results of this study suggest that a composite using biobased resin, ESS, can meet the requirements for a structural quality composite. All of the composites produced well exceeded the desired tensile and flexural properties. However, 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. This composite was the best in biocontent (83%), performing at least as well as a commercially available pultruded member in all property categories.

In accelerated weather testing the samples were exposed to equivalent of 6.4 months of 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. This was to be expected as this property is driven by the integrity of the fiber. Of the 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 and its flexural strength of 179.6 MPa, was 89.8% of the

objective. Its tensile and flexural moduli 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.

To conclude, it is shown in this study that biocomposites using ESS have the potential to be employed in structural application. However, the authors believe that future studies can still contribute to better understanding of this novel resin and greater development of biocomposites in more advanced applications. Future 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, 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. Finally, 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.

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Flax fiber /epoxidized sucrose soyate composite after accelerated weather exposure