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ORIGINAL PAPER

Enhancement of Mechanical Properties of Bio-Resin Epoxy/Flax Fiber Composites using Acetic Anhydride

Marc Li Loong[1] · **Duncan Cree**[2]

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Abstract Chemically treated acetic anhydride (AA) flax fiber mats were investigated. Bio-based epoxy resin and conventional epoxy resin unidirectional fiber composites were manufactured using a vacuum bagging technique. Flax fibers in the bio-resin composites were chemically treated with 1, 2, 3 and 4% (AA), while the fibers used with the conventional resin were not treated. The composites with the conventional resin were compared with the bio-resin in an untreated condition. A 2% AA treatment improved the bio-resin composite tensile strength, stiffness and bond shear strength by 55%, 58% and 7%, respectively. These three properties were evaluated and the results statistically analyzed using ANOVA. The AA reduced moisture absorption intake and improved adhesion of the fiber/matrix interface. The composites treated with 1–2% AA were most successful with a 65% moisture resistance. The scanning electron microscope was used to observe the fiber surface and fractured surfaces of the untreated and treated flax fibers. A chemical pre-treatment has improved the composite mechanical and moisture resistance over the non-treated fiber composites.

Keywords Epoxy bio-resin · Flax fiber · Acetic anhydride · Improved adhesion · Mechanical properties

✉ Duncan Cree
duncan.cree@usask.ca

[1] Department of Civil Engineering, Queen's University, Kingston, ON K7L 3N6, Canada

[2] Department of Mechanical Engineering, College of Engineering, University of Saskatchewan, Office 2B41, Engineering Building, 57 Campus Dr., Saskatoon, SK S7N 5A9, Canada

Introduction

Natural fiber reinforced polymer (NFRP) composites have been used in commercial applications requiring low strengths as early as 1986. Initial exploration was in the manufacturing of non-structural products such as roof segments and a post office mail box [1]. As knowledge and work experience with NFRPs developed over the years, an increase in interest for potential structural and infrastructure applications can be foreseen. NFRP composites contain environmentally friendly fibers and lower amounts of petroleum in the resin. The composites are lower cost along with acceptable mechanical (dependant on application) and moisture resistance. A study on infrastructure applications for natural fiber composites reported glass fibers used as a reinforcement in composite materials costs approximately $1.60 and $3.25, USD per kg, while flax fibers cost between $0.25 and $1.50 USD per kg [2]. Although the mechanical properties of glass fiber are superior, the cost of flax fibers are equivalent or below. A recent study found similar results where natural fibers were generally cheaper than glass fibers but highest for carbon fibers. In addition, the authors stated using natural fibers can cut production costs up to 30% compared to using glass fibers due to the lower consumption of energy and reduced tool wear [3]. The future of natural fibers used in composite materials appears to be promising according to market researcher Lucintel who have predicted the global natural fiber composite market will develop at a compound annual growth rate (CAGR) of 8.2% from 2015 to 2020 where the major sectors will be automotive, building and construction industries [4].

Projects with low to moderate design loads are suitable for NFRP composites such as pedestrian bridge girders and composite sandwich beams [5]. Other examples are panels and beams for roof construction [6] and I-beams [7]. More

recently, natural fiber fabric reinforced cementitious (FRC) composites [8] based on woven fabrics have been used as reinforcements in cement based composite materials for potential applications such as structural laminates, sandwich panels, ceilings, roofing sheets, on-ground floors and concrete tiles [9]. In an effort to improve the brittleness of geoploymer materials, fabric reinforced geopolymer (FRG) composites [8] consist of natural fiber based fabrics added into geopolymers. Applications are foreseen as low-cost construction materials in application such as slabs, shingles for siding, roofing, pipes, cooling towers and in the interior of building structures [10]. NFRP composites have also been used to strengthen concrete, masonry and timber structures in civil engineering applications [8]. In another study, NFRP tubes were investigated for their energy absorption capabilities. The results showed NFRP composites had comparable energy absorption capabilities to that of glass and/or carbon fiber reinforced composites (FRP) [11]. Flax NFRP tubes have been fabricated as permanent formwork for confinement of concrete applications. In an effort to replace the function of steel rebar, concrete was poured into NFRP tubes and found to increase the compressive and flexural properties of concrete [12].

Besides benefiting the environment and being derived from non-food related plants, flax fibers are commonly considered as composite reinforcements due to a number of factors such as its low cost, low density, high production annual yield and provides specific mechanical properties comparable to glass fibers [13]. In addition to the implementation of natural fibers as an environmentally friendly alternative, bio-based polymer epoxy resins have been studied as potential replacement for petroleum-based resins. These resins have a large portion of the carbon content replaced by a biomass origin [14, 15]. For example, bioresins have been manufactured using soybean oil. A study tested flax and hemp composites with an acrylated epoxidized soybean oil (AESO). The results indicated these composite materials met the strength requirements for housing applications such as roof/wall paneling and construction lumber [16]. In another work, structural beam panel composites were made of a foam core surrounded by a layer of soybean oil-based resin (AESO) and cellulose fiber. Testing revealed good mechanical performance suitable for a house roof structure [17].

Synthetic FRP composites externally bonded to concrete have been widely studied over a period of 30 years [18]. Wrapping concrete with FRP was reported to improve the compressive strength and ductility of unreinforced concrete [19]. Recently, there have been laboratory investigations on the use of externally bonded NFRP to concrete for reinforcement of beams and columns. For example, one study examined the durability of flax and glass fiber composite sheets bonded to concrete beams subjected to environmental aging immersed in 60 °C water for 63-days. The results showed the flax and glass composites retained 72% and 80%, respectively of their bond strengths compared to the control specimens [20]. A similar study reported the use of flax NFRP composite plates to reinforce concrete beams. The results showed the lateral load carrying capacity of flax fiber composites was comparable to glass fiber composites. The authors concluded flax composites were an effective external reinforcement material for strengthening concrete members [21]. In addition, concrete columns have been wrapped and strengthened with natural kenaf fiber and glass fiber composites. The results indicated the glass fiber composites provided a more effective confinement strength than the kenaf fiber composites. As future work, it was suggested to increase the thickness of the kenaf fiber composite wrapping for improved performance [22]. This current investigation evaluated the use of NFRP in a lap-splice configuration as a preliminary study which can further be implemented onto the exterior of concrete cylinders or beams.

Although natural fibers have good advantages, the main drawbacks are poor interfacial properties between the fiber and matrix and their high affinity for moisture. A chemical treatment with acetic anhydride (AA) or often referred to as an acetylation treatment of natural fibers is often used as a solution to these disadvantages in an attempt to produce more reliable results from the manufactured composites. The acetylation treatment reacts with the natural fiber through esterification by modifying the fiber chemical composition. Acetic anhydride ($(CH_3CO)_2$ O) is a commonly used reagent for acetylation. The surface of the fibers are chemically modified by AA which acetylates/substitutes the natural polymer hydroxyl groups with acetyl groups [23]. The reaction produces ester functions on the fiber surface. Acetic acid which is a by-product of the reaction is removed by rinsing in distilled water and drying prior to forming the composite material. This process aims to lower the hydrophilicity of the natural polymer in the cell walls and to cause plasticization of the cellulosic based fiber. The reaction decreases the affinity for moisture absorption from the lowered availability of hydroxyl groups and increases dimensional stability as the treated fibers do not shrink or swell as much as untreated samples [24]. Reduced moisture on the surface of the fibers was reported to have a better adhesion of the fiber/resin interface. For example, a previous study showed an acetylation treatment was able to reduce moisture uptake of jute fibers by 50% [25], while another study used an acetylation process to enhance the interface of flax/polypropylene composites [26].

The single fiber fragmentation tests (SFFT) has been used to evaluate the interfacial shear strength of conventional fibers. The SFFT proved to be a quick screening test for choosing a fiber that was suitable for a given matrix

such as glass fibers embedded in polyester resin [27]. SFFT has also been used on natural fibers. For example, one study evaluated single strand flax, hemp and cotton yarn embed in either polypropylene or polylactic acid matrices [28], while a more recent work investigated single strand flax yarn in a polypropylene matrix [29]. SFFT is a well-established micromechanical test for single strand yarn and can provide sufficient comparative results for interfacial properties of natural fibers [30].

The durability of flax fiber composites impregnated with conventional or bio-based resins needs to be addressed before it can be widely accepted in civil engineering applications. Natural fibers in composites have an affinity for moisture absorption and degradation can occur over time. In one study, the durability of flax fiber fabric was embedded in an epoxy matrix and submitted to an alkaline solution, seawater and water for 365 days. The alkaline ageing had the largest reduction in tensile and flexural properties, while the water had the least reduction [31]. Similarly, another study investigated the accelerated weathering of flax fabric/epoxy composites by submitting the specimens to a combined effect of ultraviolet radiation and water spraying for a duration of 1500 h. The tensile and flexural strengths were reduced by 30% and 10% respectively, compared to the control specimens [32].

Very few studies have evaluated the properties of AA treated unidirectional flax fiber mats incorporated into an epoxy bio-resin composite. The goal of this work was to increase the flax fiber strength, modify the surface of the fibers to improve their hydrophobicity and evaluate the compatibility of the bio-resin using an AA treatment. The measured properties consisted of tensile strength, single lap-splice bond strength and single fiber fragmentation test. Moisture absorption tests were conducted over a 15 day period. The scanning electron microscope (SEM) was used to view the surface morphology of the untreated and AA treated flax fibers as well as the fractured tensile surfaces of the composites.

Experimental

Materials

Biotex Flax Unidirectional mats with a fabric weight of 275 gsm were obtained from Composites Evolution Ltd., Chesterfield, UK. The average single strand flax yarn tensile strength and tensile modulus reported by the supplier were of 500 MPa and 50 GPa, respectively for fiber diameters 20 μm. The conventional petroleum based epoxy resin was Aeropoxy 2032 Laminating Resin with a PH3630 hardening agent, both obtained from PTM&W Industries, Santa Fe Springs, California, USA. A mix ratio of 100:27 (resin:hardener) by weight was suggested, providing a tensile strength of 68 MPa, tensile modulus of 2.9 GPa and elongation of 1.9%. The bio-based resin was Super Sap CPM/CPL (resin/hardener) obtained from Entropy Resins Inc., San Antonio, USA. This resin was manufactured with co-products of other industrial processes, creating a 31% bio-based end product. The manufacturer suggested a mix ratio of 100:40 by weight. The supplier data sheet reported a tensile strength of 62 MPa, tensile modulus of 3 GPa and elongation of 6%.

Methods

Composite Preparation

Composite sheets were produced using two successive techniques (hand lay-up and vacuum bag). Initially, the epoxy resins were applied to the flax fiber mats using a hand roller. The assembly was then put into a vacuum bag and sealed with sealant tape. The vacuum pressure applied to the sheets was 560 mm Hg (74.6 kPa) for 24 h, then cured at room temperature for another 24 h. The composites were further heated to 82 °C in a furnace for 20 min as suggested by the bio-based resin manufacturer to achieve full cure. Data for post-curing of conventional epoxy resin was not available, therefore the post-cure was conducted based on the bio-resin producer's information. Coupon specimens for the tensile and lap-splice tests were both cut from composite sheets with widths of 25 mm. After the flax composite sheets were manufactured, the fiber volume fraction were evaluated according to [33]. The fiber volume fraction of the untreated flax fibers bio-resin composite was estimated to be 23% for a double sheet composite with a thickness of 1.48 mm. Typical fiber volume fractions could be low as 20–40% if the fibers do not pack well together [34]. In contrast, vacuum bagging glass fiber/epoxy matrix unidirectional composites can reach a volume fraction as high as 60% [35]. Synthetic fibers tend to be solid, straight and parallel to one another which improves the fiber compactness, while natural flax fibers are relatively porous, soft and compressible which may require an additional pressure during vacuum bagging to improve fiber consolidation.

Preparation of SFFT Specimens

SFFT samples were fabricated using a custom-made aluminum mold as given in Fig. 1. The specimen dimensions had gauge lengths of 25 mm and a thickness of 5 mm, based on the SFFT dog-bone specimen used in a previous study on single strand yarn [36]. A random single strand flax yarn was carefully cut out of the flax mat and stretched across an individual mold slot. The fibers were

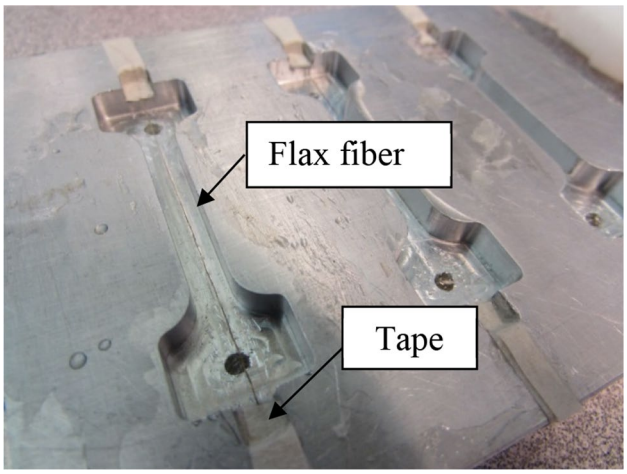

Fig. 1 SFFT aluminum mold with single strand flax yarn

secured at each slotted end by bonding the fiber ends with tape. Before pouring the bio-based epoxy resin mix into the mold, it was first placed in a Supersonic bath for 5 min. to remove as many air voids as possible. After pouring, the entire mold was placed in the Supersonic bath for another 5 min to remove bubbles formed during pouring. The specimens were cured for 24 h at room temperature, demolded and further post-cured at 82 °C for 20 min (identical to the composite curing procedure) before testing.

Flax mats were cut to lengths of 350 mm and 150 mm for tensile and lap-splice samples, respectively both with 350 mm widths. The mats were washed with distilled water to remove impurities and placed in an oven to dry at 105 °C for 12 h. The acetic anhydride concentrations selected in this work were based on the results of a previous study where 10% acetic anhydride was used on Kapok, Sisal, Jute and Hemp fibers for 1–3 h [37]. According to this study, the acetylation treatment used acetic anhydride with or without an acid catalyst (acetic acid). In the current study, a milder concentration without an acetic acid solution was used to adhere to the scope of this research project (e.g. natural fibers and bio-based resin). The acetic anhydride (99.5%) solution was made with concentrations of 1, 2, 3 and 4% by mass using distilled water. The treatment consisted of soaking the fiber mats in each solution for 60 min at 20 °C, followed by rinsing in distilled water and drying at 105 °C for 12 h before impregnating with resin.

Characterization

Mechanical Properties

Tensile strength coupons were obtained from double-layered flax mats cut in the longitudinal direction (unidirectional configuration) using a table saw. The ASTM D 3039 was used as a guideline to produce coupon dimensions of 350 mm in length and 25 mm in width as shown in Fig. 2. This dimension was selected to ensure failure in the gage length, away from the grips. The coupon thickness was 1.48 ± 0.08 mm based on the average of five readings along their length. End tabs measuring 40 mm long and 25 mm wide were used to reduce internal stresses incurred by the grips. Tension tests were performed on an Instron

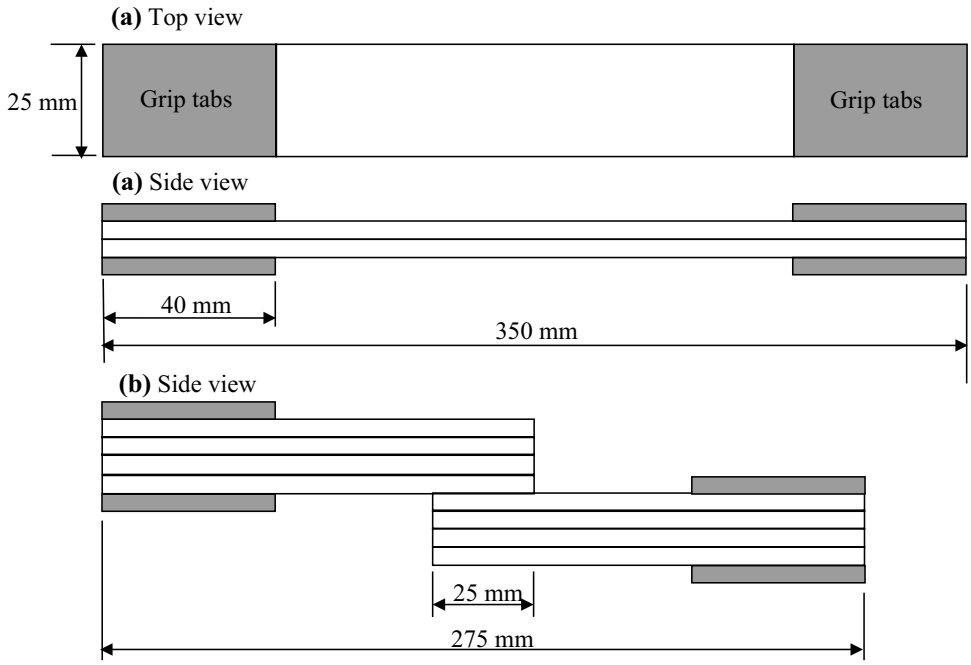

Fig. 2 Dimensions for **a** tensile coupons and **b** lap-splice coupons

8802 hydraulic testing system. The strain data was acquired using a 25 mm gauge length extensometer at a strain rate of 2 mm/min. The tensile strength results were based on the measured composite thickness. Each test value was an average of 10 samples.

Similar to tensile specimens, lap-splice bond shear strength coupons were fabricated by both hand lay-up and vacuum bagging techniques. The flax mats were first impregnated with the wet resin, then two 4-layer flax mats sheets were partially overlapped as illustrated in Fig. 2 according to the guidelines of ASTM D7616. The composites were cured identical to the procedure used for the tensile specimens. Grip tabs were also added to prevent grip failure. By trial and error, for a 25 mm width coupon, the overlap distance and number of sheets was determined to be 4-layers with a 25 mm overlap. These dimensions ensured the lap-splice coupons failed by complete delamination in the overlapping portion, rather than away from the lap-splice joint which would have measured the tensile strength of the coupons. The average of five thickness readings of the 4-layer lap-splice coupons were 3.48 ± 0.09 mm with an average overlap thickness of 6.78 ± 0.14 mm. The lap-splice bond shear strength was calculated based on the peak tensile strength during a delamination type failure in the overlapped area divided by the surface area of the lap-splice joint (e.g. length by the width) for an average of 10 samples per test.

For the single fiber fragmentation tests a total of 30 single strand flax yarn dog bone samples were tested with the bio-resin: 15 untreated flax fibers and 15 fibers treated with 2% AA. The AA concentration selected represented the best condition from the tensile results. The single strand flax yarns had an average diameter and tensile strength of 20 μm and 500 MPa, respectively. The SFFT were conducted on a Zwick-Roell Z020 with a 20 kN load cell and a strain rate of 0.5 mm/min. Loading was applied to the samples until the fiber fragments were maximized around the time the specimen began to neck but prior to specimen failure. Fragments were counted manually using an Olympus SZX series stereomicroscope with a 20×0.8 magnification, equipped with an Infinity 2 camera software.

Moisture Absorption of Composites

Flax composite sheets 350 mm by 350 mm were used to evaluate the environmental durability according to ASTM D5229. The coupons consisted of control sheets of untreated (0% AA) flax/bio-based epoxy composites and flax mats treated with concentrations of 1, 2, 3 and 4% AA. Prior to the water uptake tests, the composite sheets were dried in an oven at 105 °C for 12 h. The sheets were then immersed in a bath of distilled water for a total of 15 days at room temperature and weighed to 0.01 g every hour for the first 12 h, then every 12 h thereafter to monitor moisture uptake rate and final full saturation weight. After the sheets were removed from the water, surface water was removed using a paper towel for each weighing during the period to ensure the measurement was only absorbed water. The weight gain, W, for the moisture absorption was calculated according to the following equation:

$$W = \frac{(Ww - Wd)}{Wd} = 100\% \quad (1)$$

where W_w is the weight of the wet specimen at a time, t and W_d is the weight of the dry specimen.

Microstructural Characterization

The SEM was used to observe the morphology of the untreated and treated AA flax fibers as well as the fractured surfaces after the tensile strength tests. The SEM model was a JEOL JSM-6010 LV (Tokyo, Japan) and images were taken at an operating voltage of 15 kV. Prior to analysis, the samples were mounted on stubs, coated with a thin layer of gold using a sputter coater to improve the conductivity.

Statistical Analysis

Statistical analysis was performed using one-way analysis of variance (ANOVA) by means of Microsoft Excel 2010. The F-test was used with a level of significance of 0.05, which is a confidence level of 95%. ANOVA determined if any significant differences existed between the groups over the AA chemical treatments. In this study, the properties of tensile strength, tensile modulus and bond shear strength were measured at different AA concentrations, where the concentration of AA is the only variable that was changed throughout the test program. The results helped to identify if the chemical treatments on the flax fibers were able to provide a statistical improvement in mechanical properties of these flax fiber/bio-resin composites.

Results and Discussion

Mechanical Properties

As reported by both manufacturers' data sheets the pure conventional epoxy resin had a higher tensile strength compared to the pure bio-resin of 68 MPa and 62 MPa, respectively. Similarly, higher tensile strengths of a conventional epoxy resin without fibers was also observed from a study which compared five bio-resin epoxies to a synthetic epoxy [38]. The percentage of bio-material replacement played an important role in mechanical properties. Common petroleum based epoxies are generally derived from diglycidyl

ether of bisphenol A (DGEBA) monomers. The epoxy groups in DGEBA are highly reactive and produce a material with good mechanical properties. Replacing DGEBA with bio-based epoxies originating from plant oils tend to have lower properties due their monomers consisting of long aliphatic chains. Epoxy resins modified with natural oils are attributed to a lower reactivity of the epoxy groups which reduces their performance. In addition, it was shown that tensile strength of the conventional epoxy (68 MPa) is achieved at 1.9% of elongation whereas bio-epoxy gave 62 MPa at 6.0% of elongation. The difference between both composites can be due to the difference of behavior in elongation between both resins.

Untreated fiber composites consisted of a synthetic conventional epoxy resin (Control epoxy) and a bio-based epoxy resin (Control bio). The conventional and bio-resin epoxy composites control samples had tensile strengths of 60 MPa and 48 MPa, respectively as shown in Fig. 3. The tensile strength was slightly better for the composite containing the conventional epoxy as compared to the bio-resin by approximately 25%. The differences in tensile strength may have originated from a number of sources. For example, although the flax fiber mats were obtained from the same supplier, natural fibers are inherently variable in their properties. During manufacturing of the composites, the hand lay-up technique can also add variability in the mechanical strength results of the composites due to operator skill in the layup process. The adhesion of the resin system to the flax fiber surface could have also affected the results. Compatibility of the conventional and bio-based resin monomer types may be sources of variability. In general, epoxy resins with low viscosities may flow better into the flax mat than a higher viscosity resins. A flowable resin would act to increase the fiber surface wettability thereby improving the bonding between the fiber and the epoxy matrix. However, from the epoxy resin manufacturer's data sheets, the viscosity for the Aeropoxy 2032/PH3630 and the Super Sap CPM/CPL (resin/hardener) were reported to be similar at 25 °C, 880 cps and 800–875 cps, respectively.

All the flax fibers treated with AA were noted to improve in tensile strength. The trend from the four concentrations indicated the 2% AA treatment was ideal due to the maximum tensile strength produced. For example, when the flax fibers were treated with 2% AA, the tensile strength of the bio-based composite increased by 55% to 75 MPa. The effect of acetylation treatment on the flax fibers improve the tensile strength as compared to non-treated flax fiber/bio-resin composites. In a previous study on the acetylation of flax fiber/polypropylene composites, the authors suggested the increase in tensile strength of the modified fibers was due to the removal of lignin and hemicelluloses and increase in cellulose contents. In addition, the AA treatment was able to remove waxy materials, on the surface of the flax fibers and increased fiber–matrix interfacial strength. However, elevated concentrations of acetylation may damage the cellulose micro-fibrils [39]. In this study, concentrations above 2% for a soak time of 60 min indicated a reduction in strength as the concentration was increased. Augmenting the AA concentration to 3 and 4%, some degradation of the fibers may have occurred from fiber fibrillation as was apparent from the micrographs (Fig. 8c) in addition to the loss of hemicelluloses in the fiber from acetylation [40].

The tensile modulus of the epoxy bio-resin and epoxy conventional resin flax composites were 3.4 GPa and 3.2 GPa, respectively as shown in Fig. 4. Both resin systems produced a similar composite stiffness. From the manufacturer data sheets, the bio-based resin had a modulus of 3.0 GPa, while the conventional resin had a modulus of 2.9 GPa. With the addition of flax fiber mats, the tensile modulus increased by 13% and 10%, respectively. When the concentration of AA was 1–2%, the modulus was on average 5.4 GPa. The results showed an approximate improvement of 58% in stiffness could be achieved for the bio-resin composite with a 1–2% AA treatment. However, when the AA concentration increased to 3–4%, the modulus reduced

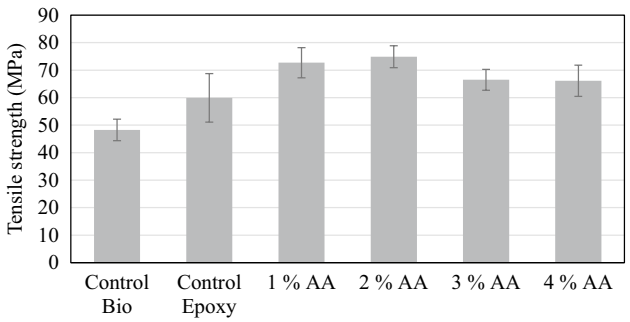

Fig. 3 Tensile strength of untreated and acetic anhydride treated flax fiber composites

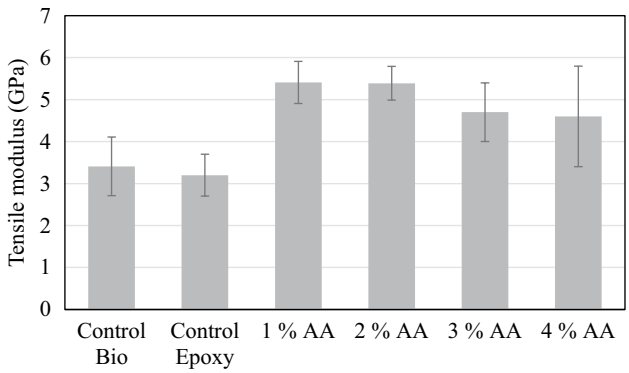

Fig. 4 Tensile modulus of untreated and acetic anhydride treated flax fiber composites

to 4.7 GPa. Depending on the application, 1–2% AA treated flax fibers impregnated with an epoxy based bio-resin could produce satisfactory modulus values. Overall, the modulus of the AA treated fiber composites increased compared to the non-treated fiber composites. Natural fibers are hydrophilic (affinity/attract water) due to the hydroxyl groups on the surface of the fibers while thermoset epoxy resins are hydrophobic (repels water). Due to this incompatibility, a low wetting and adhesion occur leading to reduced interfacial adhesion between the fiber and matrix [41]. The AA chemical treatment acted to promote dimensional stability by acetylation of hydroxyl functional groups on the flax fiber surface which were substituted with acetyl groups. By decreasing the number of hydroxyl groups, the polarity or affinity for water is reduced. The treatment improved the interface between the flax fibers and epoxy bio-resin by reducing moisture uptake, improving the wettability and promoting adhesion between fiber/matrix. Compatibility can be quantified by the enhanced properties resulting from better load transfer from fiber to fiber. A study observed the diameters of flax fibers reduced after an acetylation treatment which was assumed to have an influence on the modulus of the composite [39]. A reduction in diameter may increase the aspect ratio (l/d) of flax fibers and would tend to increase its modulus. This analogy is reflected in the composite modulus at 1–2% AA concentrations.

Single lap-splice coupon tests were conducted to evaluate the single lap-splice shear bond strength of non-treated and treated flax bio-based resin composites. In addition, the lap-splice bond strength helped to assess the effectiveness of the chemical treatments on the fiber-to-fiber interface. The tensile shear strength results of the bio-based resin composites with untreated flax fibers (Control bio) and AA treated fibers are shown in Fig. 5. The control samples with the bio-based resin produced an average strength of 6.0 MPa. The 1% AA treated fibers had a higher bond shear strengths than the control sample with an improvement of 18%. When the fibers were soaked in 2% AA, the bond shear strength increased slightly to 6.4 MPa. Increasing the concentration of AA above 2% resulted in a decrease of shear bond strength. The 3% and 4% AA groups, showed significantly lower shear strengths by approximately 3% and 22%, respectively as compared to the control sample. The typical failure of the bonded area failed predominantly by shear of the bio-resin epoxy in the bonded area.

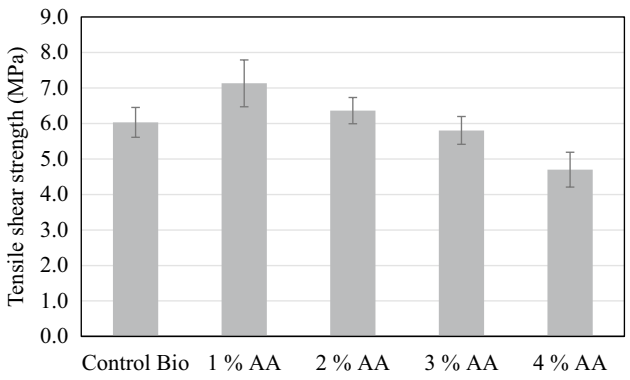

Fig. 5 Shear bond strength of untreated and acetic anhydride treated flax fiber composites

The composite to composite bond strength depends to some extent on the strength of the resin bonding the laminates together. As expected the fiber strength was higher than the overlap shear strength. When using untreated or acetic anhydride treated flax fiber bio-resin composites in an application where the composites are in tension, the results showed the lap-splice bond strength would be more critical than the strength of the tensile coupons. Maintaining a good adhesive bond in the lap-splice area is equally important as maintaining its tensile strength. Perhaps modifying the dimensions of the lap-splice area by increasing the overlap splice dimensions or utilizing a different epoxy for bonding may improve its performance.

The goal of the SFFT was to examine the micromechanical interaction between flax fiber reinforcement and the Super Sap bio-based epoxy resin. The process was to draw comparative results from the untreated and chemically treated single strand flax yarns by counting the number of fragments produced from a single tensile test. This method was also conducted on polyester glass fiber composites to quickly compare the adhesive strength between the fiber and the matrix [27].

The bio-resin used was semi-transparent and fiber fragments were easily observed. The fragmented untreated flax fiber embedded in the bio-resin was the control sample and is shown in Fig. 6a, while the single strand flax yarn/bio-resin treated with 2% AA sample is shown in Fig. 6b. Fiber fragments were defined by clear breaks in the fiber and are seen as white dots along the length of the fiber axis. Air voids in the resin could also be seen but were generally away from the fiber as circled in white for clarity (see Fig. 6a). In addition, the air voids did not affect the SFFT testing as no local crack formations were observed. The average fragments counted for the the untreated and treated 2% AA flax fibers was 15.9 ± 3.0 and 14.0 ± 3.0 for 25 mm gauge lengths, respectively. It can be seen there was a slight decrease (14%) in the number of fragments observed for the AA treated flax samples compared to the untreated fibers, which indicated an improvement in fiber/matrix adhesion. The AA treatment increased the fiber strength and made the flax fiber hydrophobic which resulted in better adhesion of the fiber/resin interface. The SFFT test was effective in calculating the individual fragments and enforced the use of an AA treatment to increase the properties of flax fiber composites. Single strand yarns are attributed to defects

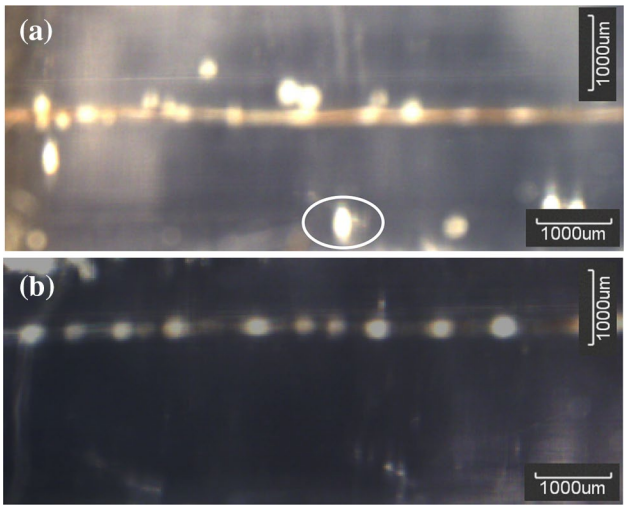

Fig. 6 Typical SFFT single strand flax yarn/bio-resin **a** control sample and **b** 2% AA sample (*white circle* indicates air void)

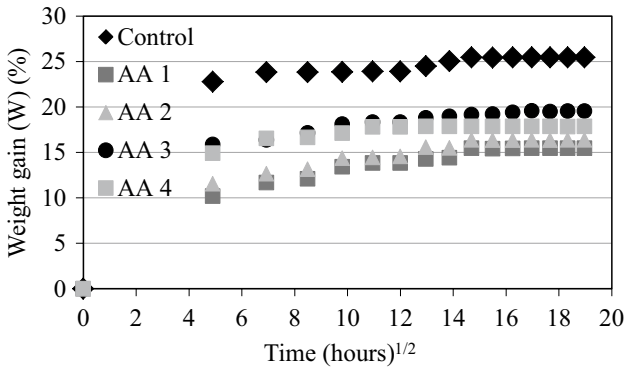

Fig. 7 Moisture absorption for AA treated flax/bio-resin composites immersed in water at 23 °C for different AA concentrations

and natural variability due to growing conditions from plant to plant which can affect the single strand yarn morphology. For example, a flax plant can have variability due to climate, soil conditions, water supply and temperature throughout the growing season. In addition the same plot of land can yield different fiber properties if one flax plant grows in the shade or in moist soil compared to a dryer soil. A way to mitigate these issues would be to increase the sample test size.

Composite Moisture Absorption

The effectiveness of moisture uptake resistance for the AA chemical treatment method was evaluated by monitoring water uptake and absorption quantity over 15 days. The acetic anhydride treated flax fiber results for the percent weight gain as a function of square-root of time are provided in Fig. 7. Compared to the control sample, all the treated samples showed an improvement in moisture resistance. The control, 1, 2, 3 and 4% acetic anhydride specimens had an initial linear water uptake from 0 to 25 h, with rates of 4.64, 2.08, 2.35, 3.04 and 3.03%/$h^{1/2}$, respectively. At the beginning of the test, the moisture intake was exponential as observed by the positive slope and gradually decreased until the composite specimens reached saturation. It can be observed that all the samples treated with acetic anhydride outperformed the control specimen in terms of initial rate of absorption and weight gain percentage, with 1% acetic anhydride being the ideal concentration. At the end of 15 days, the moisture absorption weight gain for the 1% AA treated sample was 15.4%, while the control sample was 25.5%. This represents a significant 65% improvement in moisture resistance. One of the main advantages of using the acetylation method was the plasticization of the flax fibers by replacing open hydroxyl groups with acetyl groups in order to decrease moisture affinity. Based on the results obtained from the four concentrations tested, 1% acetic anhydride treatment was the most effective for plasticizing process of flax fibers. The results were promising for the reduced use of AA concentrations and therefore maintaining a more environmentally friendly composite while lowering moisture uptake.

Microstructural Characterization

Some changes of the fiber morphology were observed between the untreated (as-received) and AA treated flax fibers as shown in the SEM micrographs of Fig. 8. In Fig. 8a, the untreated flax fibers had a rough surface containing mainly amorphous waxy cuticle layer material, as has been observed elsewhere [39]. The thickness of this layer varies along the length of the fibers. It was noted the flax fibers did not have a uniform geometry but had a shape resembling a polygon with four to six sides. At different intervals along the flax fiber, protrusion nodes were observed especially in Fig. 8b, which naturally occurs during plant growth. Some fibers had more than others which could be sources of weak points during loading. Figure 8b, c shows fibers after the acetylation process. In Fig. 8b, after the 2% AA treatment, the majority of the waxy material layers were removed leaving smoother fiber surfaces as compared to the unmodified fibers as occurred in a previous work on AA treated flax fibers [39]. However small amounts of material still remained on the surface of the fibers. In general, natural plant fibers are hygroscopic, due to the cellulose and hemicellulose constituents readily absorbing moisture. This AA reaction reduced moisture intake to produce hydrophobic fibers. In the presence of moisture, acetylated flax fibers tend to expand less than non-treated fibers therefore

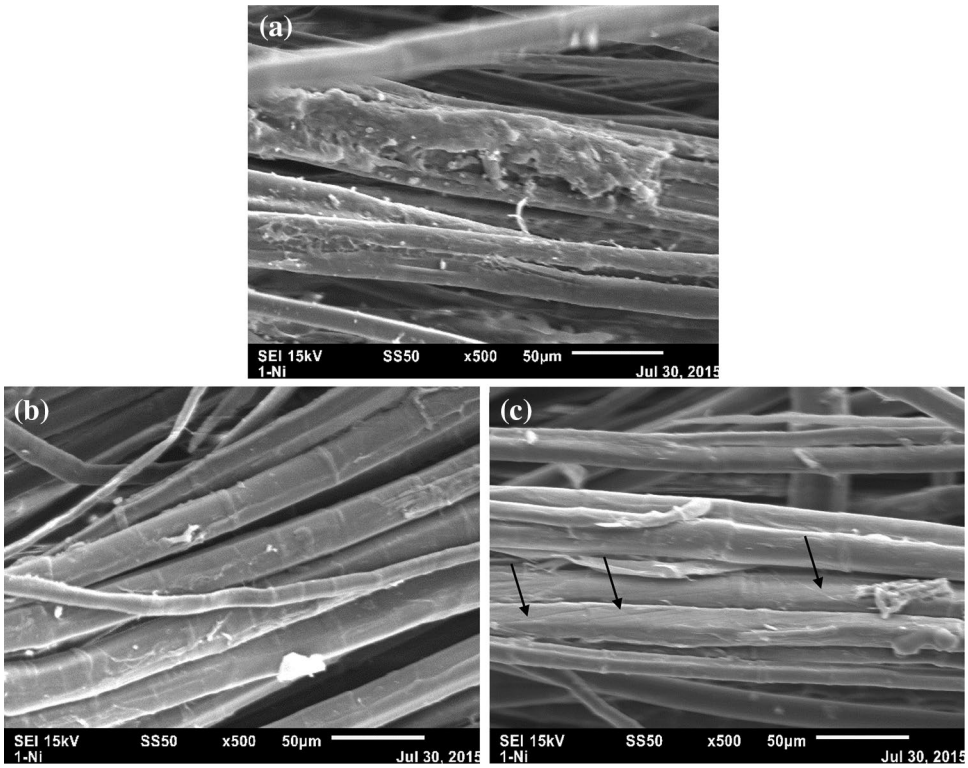

Fig. 8 SEM images of untreated and treated flax fibers: **a** untreated, **b** 2% AA and **c** 3% AA (*arrows* indicate micro-fibril fibrillation)

demonstrating more dimensionally stable fibers. By increasing the AA concentration to 3%, some single micro-fibril fibrillation may have occurred as shown in Fig. 8c and is depicted by fiber cracking. Fiber fibrillation is the process that forms micro-fibrils in natural based plants. In an acetylation treatment, the fibrillation occurs when an excess of wax, and pectin substances are leached out of the fiber which acts to reduce load transfer from micro-fibril to micro-fibril.

Composite tensile fractured surfaces of untreated (as-received) and treated fiber composites were investigated by SEM as given in Fig. 9. SEM showed there was a difference in untreated and treated flax fiber composites. For example, in both untreated composites, some fiber pull-out occurred as was observed by a number of empty cavities where fibers were present. The fibers shown in Fig. 9a, b failed with a greater length than those in Fig. 9c. In addition, the fiber surfaces were relatively smooth with little matrix adhered to their surface indicating a poor fiber–matrix interfacial bonding. As given in Fig. 9c, the AA treated fiber composites showed a better interfacial adhesion of the flax fibers with the bio-epoxy matrix as observed by the general reduced fiber pull-out. Failure was mainly due to tearing of short fibers. Some cellulose micro-fibrils were seen to protrude from individual fibers. The matrix failed in a brittle manner as characteristic of thermoset epoxy polymers which have the tendency to produce flat and smooth planes at the fractured surface as shown in Fig. 9.

Statistical Analysis

The ANOVA one-factor results obtained from Excel are given in Table 1 for tensile strength, tensile modulus and bond shear strength to compare untreated fiber composites with 1–4% AA treated fiber composites. Table 2 provides results for tensile strength, tensile modulus and bond shear strength to compare if significant differences existed between the 1, 2, 3 and 4% AA treatments only (without the effect of untreated fiber composites). The terms are as follows: between groups (BG), within groups (WG), sum of squares (SS), degree of freedom (Df), mean square (MS), F (F-test statistic), and Fcrit (critical value). The F-test determined if significant differences between groups occurred over the range of chemical treatment concentrations. If F is greater than Fcrit, the null hypothesis is rejected and the results have a significant difference in mean value. This would suggest the chemical treatments were not equally effective. If F is less than Fcrit the null hypothesis cannot be rejected and the results are not significantly different in mean values.

The analysis has confirmed that for all tests, the F is greater than Fcrit. The results suggest the flax fiber mats chemically treated with 1–4% AA incorporated into a bio-resin epoxy had a statistically significant change in strength and stiffness as the concentration of the chemical treatment increased compared to the untreated fiber bio-resin composite. Similarly, the ANOVA results for

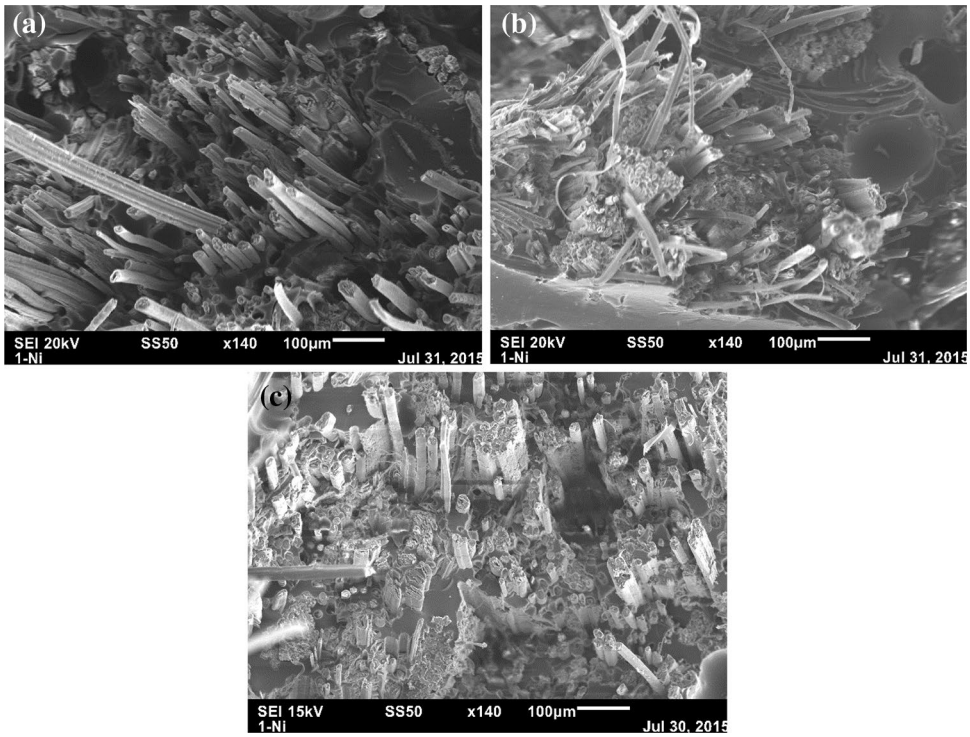

Fig. 9 SEM images of fractured flax fiber composites; **a** untreated control bio-epoxy and **b** untreated control epoxy resins and **c** AA treated control bio epoxy resin

1–4% AA treated fibers showed there was a significant difference in mean values between the treated composites (untreated fiber composite values were omitted). Overall the composites tested had a significant change in properties when the AA treatments were compared to the untreated fiber composites and when the AA treatments were compared to one another.

Table 1 ANOVA results at a 0.05 level of significance for tensile strength, tensile modulus and bond shear strength of flax fiber mats chemically treated with 1–4% AA concentrations compared to untreated bio-resin composites

Source of variation	SS	Df	MS	F	Fcrit
ANOVA results for tensile strength					
BG	4281.09	4	1070.273	46.05104	2.612306
WG	906.3992	39	23.241		
Total	5187.489	43			
ANOVA results for tensile modulus					
BG	26.49617	4	6.624042	25.51588	2.588836
WG	11.163	43	0.259605		
Total	37.65917	47			
ANOVA results for bond shear strength					
BG	17.43398	4	4.358494	3.753221	2.701399
WG	33.67676	29	1.161268		
Total	51.11074	33			

Conclusion

This study designed an acetic anhydride chemical treatment for unidirectional flax fiber mats to optimize composites with a bio-resin epoxy. The bio-resin composites were influenced by the concentration of the acetic anhydride treatment. Flax fibers soaked in 2% acetic anhydride for 1 h and further mixed with the bio-resin produced the best tensile strengths and modulus. Single lap-splice testing was evaluated to determine the lap-splice length and adhesive bond strength. The SFFT between the flax fiber and bio-epoxy resin provided comparative fiber/matrix adhesion results for untreated and chemically treated single strand flax yarns. The 2% acetic anhydride treated fibers produced a lower amount of fragments compared to the untreated flax control samples. The results are corroborated with the tensile results. All the AA treated samples showed moisture resistance improvements over the untreated fibers. The fibers treated with 1–2% acetic anhydride were most successful with an average moisture resistance improvement of 65% compared to the non-treated flax fibers. SEM revealed a 2% AA treatment was able to remove the majority of surface waxy materials, but 3% AA initiated fibrillation. SEM fractured surfaces showed improved interfacial adhesion of AA treated flax fiber composites as indicated by reduced fiber pull-out and tearing of shorter fibers. Statistical analysis using ANOVA suggested the chemical treatments on flax fiber mats incorporated into a bio-resin had significant statistical differences in tensile strength, tensile modulus

Table 2 ANOVA results at a 0.05 level of significance for tensile strength, tensile modulus and bond shear strength of flax fiber mats chemically treated with 1–4% AA concentrations compared to one another

Source of variation	SS	Df	MS	F	Fcrit
ANOVA results for tensile strength					
BG	517.72274	3	172.57424	6.738023	2.922277
WG	768.359	30	25.612		
Total	1286.08273	33			
ANOVA results for tensile modulus					
BG	5.33994	3	1.77998	9.06793	2.588836
WG	6.674	34	0.196294		
Total	12.01394	37			
ANOVA results for bond shear strength					
BG	17.39209	3	5.79736	3.60967	3.09839
WG	32.12129	20	1.60606		
Total	49.51338	23			

and bond shear strength. Therefore, the treatments had an effect on the mechanical properties of the flax fibers and of its composites.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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