Development and characterization of flax fiber reinforced biocomposite using flaxseed oil-based bio-resin

Anup Rana, Richard W. Evitts

Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 5A9
Correspondence to: A. Rana (E-mail: anup.rana@usask.ca)

ABSTRACT: In this study, acrylated epoxidized flaxseed oil (AEFO) resin is synthesized from flaxseed oil, and flax fiber reinforced AEFO biocomposites is produced via a vacuum-assisted resin transfer molding technique. Different amounts of flax fiber and styrene are added to the resin to improve its mechanical and physical properties. Both flax fiber and styrene improve the mechanical properties of these biocomposites, but the flexural strength decreases with an increase in styrene content. The mass increase during water absorption testing is less than 1.5% (w/w) for all of the AEFO-based biocomposites. The density of the AEFO resin is 1.166 g/cm^3, which increases to 1.191 g/cm^3 when reinforced with 10% (w/w) flax fiber. The flax fiber reinforced AEFO-based biocomposites have a maximum tensile strength of 31.4 ± 1.2 MPa and Young's modulus of 520 ± 31 MPa. These biocomposites also have a maximum flexural strength of 64.5 ± 2.3 MPa and a flexural modulus of 2.98 ± 0.12 GPa. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41807.

INTRODUCTION

During the last two decades, several studies have been performed on natural fiber reinforced biocomposite materials.[1–4] Biocomposites have been developed using both synthetic polymers and biopolymers.[1–5] Synthetic polymers are derived from non-renewable sources; hence, there is a paradigm shift toward developing renewable materials such as biopolymers. Biopolymers have been derived from various sources like starch, sugar, cellulose, and plant oils.[6] There have been several studies done on synthesis of polymers using vegetable oil and these biopolymers have shown comparable properties at reduced cost.[7] Natural plant oils are predominantly made up of triglycerides. Triglycerides contain many active sites amenable to chemical reactions; these include the double bond, the allylic carbons, the ester group, and the carbon alpha to the ester group. These active sites can be used to introduce polymerizable groups on the triglyceride molecule, which is similar to the synthesis of synthetic polymers.[1,8–10] Most of the polymers that are developed from triglyceride oil involve intermediate process such as epoxidation.[11,12] During an epoxidation reaction an oxygen atom is introduced into a compound containing an unsaturated carbon-carbon bond to form a three-member ring.[13]

Plant oils have been used to produce different polymers such as polyurethane, polyester, polyether, and polyolefin.[14–16] Significant research has been performed on bio-resin produced from soybean oil; large quantities of oil are produced and they have high amounts of unsaturated fatty acids. Different grades of soybean oil polymers have been developed and they are categorized based on their physical and mechanical properties.[17–20] Several vinyl polymers have also been developed from plant oil by various polymerization techniques.[21] Flaxseed oil has high level of unsaturation similar to soybean oil since its main content is also linolenic acid.[1] Linolenic acid contains three double bonds, which is advantageous for initiating polymerization reactions. Flaxseed oil is also known as linseed oil in most part of the world.[22] Flaxseed oil has been studied by many researchers for its drying properties for commercial applications such as in oil-based paints, varnish, putty, and linoleum.[22,23] Sunflower oil, castor oil, and linseed oil have been investigated for their potential for polyurethane production for paint formulation.[1] It has been reported in the literature that sometimes triglyceride-based oil polymers shows low rigidity and strength.[8] To impart additional rigidity and strength to the resin, styrene can be used as an additive.[24]

Natural fiber can be used to reinforce plant-based bio-resin. Flax fiber possesses the highest strength amongst reported different natural cellulosic fibers used to develop biocomposite material.[2–4] The principal constituent of flax fibers is cellulose, with smaller amounts of hemicellulose, lignin, pectins, oils, and waxes.[25] Properties of fibers such as density, ultimate tensile

strength, and the Young's modulus depend upon the internal structure and the chemical composition.[26,27] Natural fibers are hydrophilic in nature due to the presence of cellulose and hemi-cellulose, which is a major problem in biocomposite development. The hydrophilic natural fiber and hydrophobic polymer matrices have poor interfacial adhesion. Several chemical treatments like have been used to improve the fiber–polymer interface by surface modification.[25,28] Alkaline and silane treatments are commonly adopted by most of the researchers. Adding a coupling agent improves the chemical compatibility at the fiber/matrix interface.[25]

Different grades of biocomposites have been developed using natural fiber and various biopolymers.[5,8,19,29,30] PLA has been investigated to develop various biocomposites with different natural fibers such as kenaf and flax fiber.[31] Bio-resin studies on biodegradable biocomposites from soy-based bio-resin have indicated its potential commercial use in packaging and in the production of interior panels for the construction industries.[5] Epoxidized soybean oil and cellulosic fiber have been used to develop biodegradable biocomposite for structural building material.[32]

Canada is the largest producer of flax worldwide and hence abundant raw material is available for developing new renewable flax-based bio-products for commercial application. In this study, acrylated epoxidized flaxseed oil (AEFO) resin synthesized from flaxseed oil was used to develop flax fiber reinforced biocomposites. Different amounts of silane-treated flax fiber and styrene content were added to AEFO bio-resin to develop several biocomposites via vacuum-assisted resin transfer molding. The physical (density, water absorption) and mechanical (tensile, flexural, hardness) properties of AEFO-based biocomposites were determined. AEFO resin had low water absorption characteristics and a density of 1.166 g/cm^3. The flax fiber reinforced AEFO-based biocomposites (flax fiber 10% w/w) have a maximum tensile strength of 31.4 ± 1.2 MPa Young's modulus of 615 ± 31 MPa, maximum flexural strength of 64.5 ± 2.3 MPa, and a flexural modulus of 2.98 ± 0.12 GPa. In this article, the effects of flax fiber and styrene content on these properties are presented.

EXPERIMENTAL

Materials

In this research, Saskatchewan grown 100% pure cold-pressed flaxseed oil from Herbal Select and 99% pure flax fiber provided by Biolin Research Inc., Saskatoon was used. Hydrogen peroxide (30% v/v aqueous solution), formic acid (85%), and ethyl ether were from Fisher Scientific (NJ, USA). Sodium bicarbonate, sodium chloride, and anhydrous sodium sulphate were from EMD Chemical Inc. (Gibbstown, NJ, USA). Acrylic acid and triethoxyvinylsilane (97%) were from Sigma Aldrich (St. Louis, MO, USA) . Styrene (99%) was purchased from Alfa Aesar (Heysham, UK) and t-butyl peroxybenzoate (98%) was from Acros Organics (NJ, USA).

Chemical Treatment of Flax Fiber

The flax fiber was treated with 5% (w/w) NaOH solution and later treated with an alcohol water mixture (60 : 40) containing

Table I. Investigated AEFO: Styrene Weight Ratios

S.No		Weight ratio	Sample ID
1	AEFO: Styrene	100%:0% [a]	AEFO
2	AEFO: Styrene	90% :10%	AEFO10S
3	AEFO: Styrene	80% :20%	AEFO20S
4	AEFO: Styrene	70% :30%	AEFO30S
5	AEFO: Styrene	60% :40%	AEFO40S
6	AEFO: Styrene	50% :50%	AEFO40S

[a] Control sample with 0% flax fiber.

2.5% (w/w) triethoxyvinylsilane as a coupling agent for 1 h. The treated flax fiber was placed in a dryer for 24 h at 50°C to reduce the moisture content to 2% (w/w).

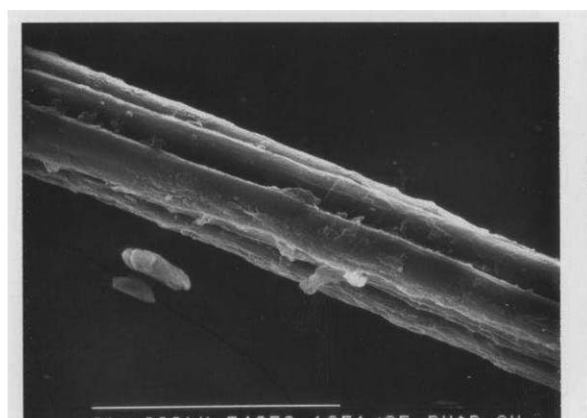### Development of Acrylated Epoxidized Oil-Based Biocomposite

Flaxseed oil was used to produce the acrylated epoxidized flaxseed oil (AEFO) resin. The flaxseed oil was mixed with formic acid and hydrogen peroxide in a volume ratio of 50 : 15 : 45; the flaxseed oil was first mixed with formic acid (85%), and then hydrogen peroxide (30% v/v) was added drop-wise to the solution. The solution was vigorously stirred at 45°C for 18 h using magnetic stirrer at 200 rpm. This process generated the epoxidized flaxseed oil (EFO). The EFO was then dissolved in ethyl ether and washed with saturated sodium bicarbonate solution until a pH of approximately 7 was reached. The mixture was further washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. The remaining hydrogen peroxide and formic acid in the epoxidized oil were removed in the washing step.[8] The oil and water phase was separated using the separation funnel. Then the ether was removed by heating the oil to temperature of 50°C.

The epoxidized flax oil was mixed with the acrylic acid in a weight ratio of 1 : 3 in an Erlenmeyer flask. Higher amount of acrylic acid was added to maximize the level of acrylation. The mixture was stirred at 250 rpm using a magnetic stirrer at a temperature of 75°C for 6 h. The acrylic acid was added in aliquots to reduce the amount of epoxy homopolymerization during the course of reaction. Then, the resin was produced by adding the styrene to the AEFO with 1.5% (w/w) of the free-radical initiator, t-butyl peroxybenzoate. Styrene was added to the AEFO in the five different weight ratios presented in Table I.

The AEFO-based resin was reinforced with silane-treated flax fiber. The silane-treated flax fiber was placed in the vacuum-assisted mold. The resin was transferred in the vacuum-assisted mold containing the flax fiber and the mold was cured at 100°C for 1 h and post-cured at 125°C for 2 h. Three levels of flax fiber content (2%, 5%, and 10% w/w) were used to investigate the effect of flax fiber content in the biocomposite.

Characterization of Acrylated Epoxidized Flaxseed Oil-Based Biocomposite

The effect of silane treatment on flax fiber surface was studied using the images captured by scanning electron microscope-

Figure 1. Effect of flax fiber content on water absorption characteristics of AEFO biocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SEM 505 (Philips, Holland). The fiber surface was coated with thin layer of gold in vacuum using S150B sputter coater (BOC Edwards, Wilmington, MA) to provide a required electrical conductivity to capture the SEM images.

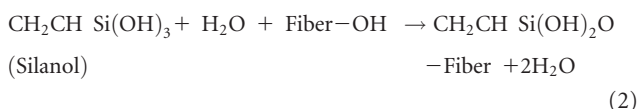The water absorption characteristics were studied using the ASTM D570 test method.[33] Rectangular test specimens (76.2 ± 0.2 mm × 25.4 ± 0.2 mm × 3.2 ± 0.2 mm) were used during the test and the increase in mass after 24 h immersion in water was calculated to the nearest 0.01%.

Five rectangular samples (76.2 ± 0.2 mm × 25.4 ± 0.2 mm × 3.2 ± 0.2 mm) were used to determine the density of the biocomposite. The mass of the samples was measured at room temperature using a Galaxy 160D weighing scale (OHAUS Scale Corporation, USA). The volumes of the biocomposite samples were measured using a gas-operated pycnometer (Quantachrome Corporation, USA). The density of the biocomposite samples was determined as the mass per unit volume and expressed in grams per cubic centimeter. The actual density was compared with the ideal density. Ideal density of the biocomposite was determined using the equation based on density and mass fractions of polymer and fiber, respectively.[34]

Biocomposite samples were subjected to the tension test described in ASTM D638.[35] A familiar dog bone type specimen of thickness of 3.2 ± 0.2 mm was machined for the test. The test specimens were conditioned at a temperature of 23°C ± 2°C and a relative humidity of 50% ± 5% for 40 h prior to the test. The tensile test was performed at a crosshead speed of 5 mm/min for five samples and each test was performed until tensile failure occurred. The tensile strength and the Young's modulus were determined from the test results.

The biocomposite samples were subjected to the flexural test according to ASTM D790.[36] Five rectangular cross section samples of dimension 64 ± 0.2 mm × 12.7 ± 0.2 mm × 3.2 ± 0.2 mm were tested. The test specimens were conditioned at a temperature of 23°C ± 2°C and a relative humidity of 50% ± 5% for 40 h prior to the test. The test samples behaved as a beam during the test. The flexural strength and flexural modulus were determined from the test results.

The hardness of the biocomposites was measured by determining the Rockwell hardness number using ASTM D785 test method.[37] The test specimens of thickness 6.4 ± 0.2 mm were conditioned at a temperature of 23°C ± 2°C and a relative humidity of 50% ± 5% for 40 h prior to the test. A HRLW tester, 60 KGF forces and 1/4" ball indenter was used to evaluate the hardness. The hardness number of each biocomposite sample is reported as an average of 10 readings.

RESULTS AND DISCUSSION

Physical Properties of AEFO Biocomposites

Water absorption by the biocomposite may affect its dimensional stability and mechanical properties; hence, low water absorption characteristics are desirable. The water absorption of the AEFO-based biocomposite increased with an increase in flax fiber content as shown in Figure 1. Since natural fibers are hydrophilic in nature, adding them to polymers will increase the amount of water absorption of the polymer.[38]

It was found that the biocomposite with the highest flax fiber content (i.e., 10% w/w flax fiber) had an increase in mass of less than 1.5% (w/w) which is acceptable for most biocomposite applications; the water absorption ability of flax fiber was reduced by silane treatment. The coupling agent triethoxyvinylsilane provides a coating on the flax fiber surface that reduces the water absorption. No significant effect was found on the water absorption characteristics by changing the styrene percentage from 0 to 50% (w/w) in AEFO-Styrene resin formulation (Figure 2). In literature, the mass increase during water absorption test for similar biopolymer acrylated epoxidized soybean oil (AESO) is given as 0.5%.[39]

SEM images of untreated and silane-treated flax fiber are given in Figure 3. The SEM image of untreated flax fiber shows the presence of waxy substances like lignin and pectin on the fiber surface. After silane treatment, the waxy material is removed and layer of coupling agent triethoxyvinylsilane is more readily coated on flax fiber surface. The reaction mechanism of silane treatment is shown in eqs. (1) and (2).[40,41]

$$CH_2CHSi(OC_2H_5)_3 + 3H_2O \rightarrow CH_2CH\,Si(OH)_3 + 3C_2H_5OH$$

(Triethoxyvinylsilane)   (Silanol)

(1)

Figure 2. Effect of styrene content on water absorption characteristics of AEFO biocomposite. The uncertainty presented in the figure is at the 95% percentile confidence level.

a) Untreated flax fiber

b) Silane treated flax fiber

Figure 3. SEM images of untreated and silane treated flax fiber.

$$CH_2CH\ Si(OH)_3 + H_2O + Fiber-OH \rightarrow CH_2CH\ Si(OH)_2O$$

(Silanol) $-Fiber\ +2H_2O$

(2)

The density of biocomposite plays an important role in commercial applications to develop low-density and high strength
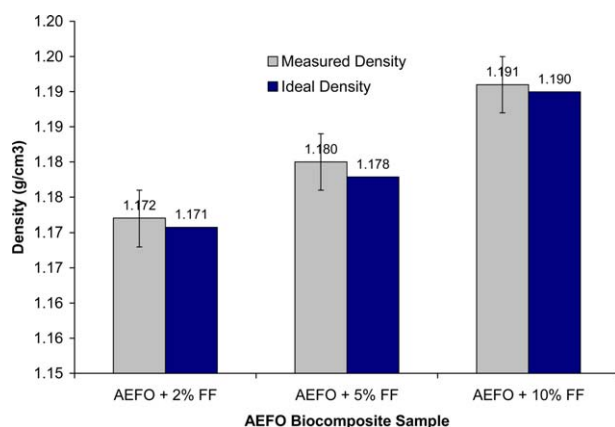
Table II. Densities of AEFO-Styrene-Based Biocomposite Samples

S. No	Biocomposite sample	Density (g/cm^3)
1.	AEFO + 10% FF	1.191 ± 0.004
2.	AEFO10S + 10% FF	1.180 ± 0.005
3.	AEFO20S + 10% FF	1.170 ± 0.004
4.	AEFO30S + 10% FF	1.166 ± 0.005
5.	AEFO40S + 10% FF	1.156 ± 0.003
6.	AEFO50S + 10% FF	1.151 ± 0.006

% FF: percentage of flax fiber content (wt/wt).

products. The densities of AEFO biocomposites with different flax fiber contents are shown in Figure 4. The flax fiber has a higher density (1.461 g/cm^3) than the AEFO resin (1.166 g/cm^3). Therefore, as expected, the density of the AEFO-based biocomposite increases with an increase in the flax fiber content. The comparison of measured density and ideal density is also shown in Figure 4. It can be inferred from the comparison results that the biocomposite did not have any significant cavity or pores since the density determined was as expected; the vacuum-assisted resin transfer molding technique eliminates most of the air bubbles during the molding process and develops a high quality product.

Table II indicates that the density of the AEFO biocomposite decreases with increasing styrene content due to the lower density of styrene (0.909 g/cm^3).

Mechanical Properties of AEFO Biocomposites

The tensile strength of the AEFO biocomposites developed with different flax fiber contents are shown in Figure 5. Increasing the flax fiber from 0 to 10% (w/w) increases the tensile strength of AEFO biocomposite from 29.8 MPa to 31.4 MPa. Flax fiber has high tensile strength and hence it serves as reinforcement in the biocomposite. Silane treatment also improves the interfacial adhesion and the tensile strength because this treatment creates a cross-linked network of fiber and polymer due to covalent bonding.[25,42] Many studies have also confirmed that the

Figure 4. Effect of fiber loading on density of AEFO-based biocomposite samples. The uncertainty presented in the measured density is at the 95% percentile confidence level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
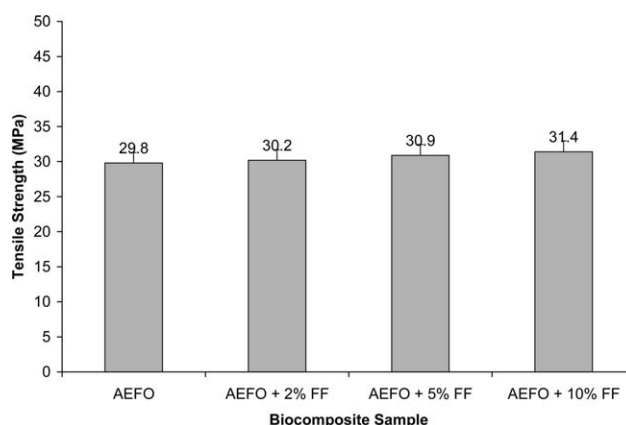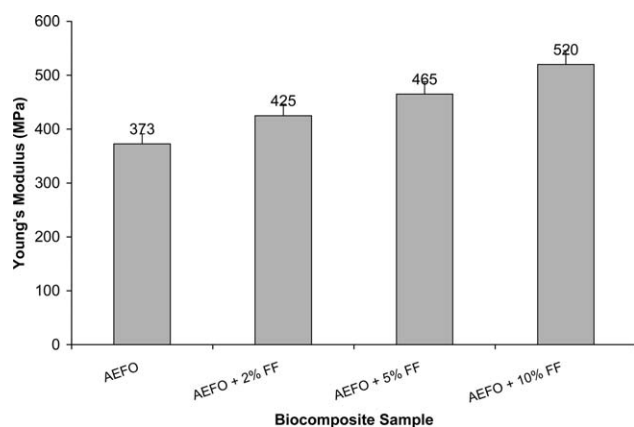

Figure 5. Effect of flax fiber content on tensile strength of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.
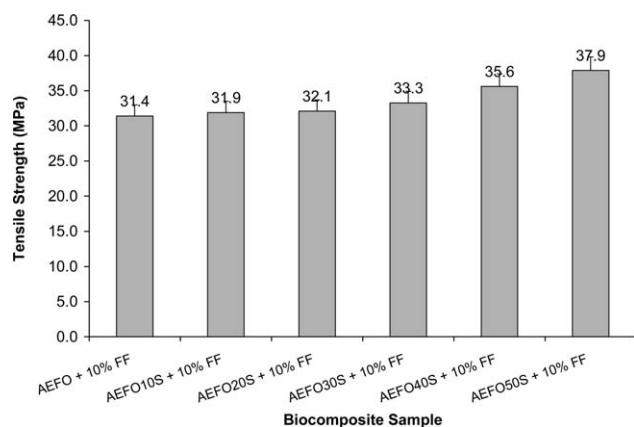
Figure 6. Effect of styrene content on tensile strength of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.
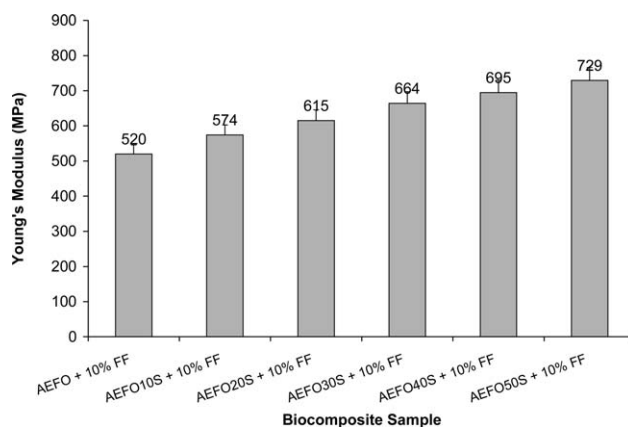

Figure 8. Effect of styrene content on Young's modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.

addition of natural fiber to polymer matrices increases the tensile strength.[29,43,44]

To improve the tensile strength of AEFO biocomposites, styrene was added to the AEFO biocomposite. Styrene imparts rigidity to the polymer and hence improves the tensile strength of biocomposites. As expected, an increase in styrene content significantly increases the tensile strength (Figure 6). There was approximately a 21% increase in tensile strength with a addition of 50% (w/w) styrene to the AEFO biocomposites. The tensile strength of the AEFO is comparable to the literature value of tensile strength ($\approx$ 30 MPa) of AESO resin.[8]

Similarly, flax fiber also increases the Young's modulus significantly. Figure 7 shows that increasing the flax fiber content from 0 to 10% (w/w) increases the Young's modulus from 373 MPa to 520 MPa. It has been reported that the Young's modulus increases significantly when cellulosic material is added to acrylated epoxidized soybean oil resin.[19] The addition of styrene to the composite/polymer matrix increases the rigidity of the composite.[8] Figure 8 illustrates that an increase in styrene content in the AEFO biocomposite increases the Young's modulus

significantly. However, an increase in rigidity also increases the brittleness of the AEFO biocomposite.

The flexural test is used to determine the flexural strength and the flexural modulus of the AEFO biocomposite. It was found that, as with tensile strength, an increase in flax fiber content increased the flexural strength significantly (Figure 9). Similar observations were reported for other natural fiber-based biocomposites by several researchers.[25,45,46] The flexural strength of AEFO biocomposite increases from 53.5 ± 2.3 MPa (0% flax fiber) to 64.5 ± 2.3 MPa (10% flax fiber) when flax fiber was added to AEFO resin. Researchers also reported that flexural load induces both compressive and tensile stresses during the flexural test.[25] Flax fiber possesses high strength and the silane treatment further improves the fiber-polymer interfacial adhesion. The results shown in Figure 9 confirm that flax fiber has a good interfacial bonding with the AEFO polymer. Similar results have been reported for AESO; AESO composite with 0% fiber has a flexural strength of 34.8 MPa.[39] As reported earlier, the addition of styrene increases the rigidity and brittleness. The addition of styrene to AEFO biocomposite decreases the flexural strength as shown in Figure 10. This can be explained by the
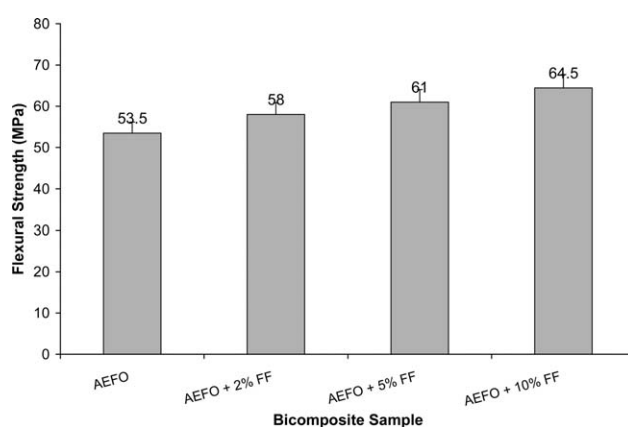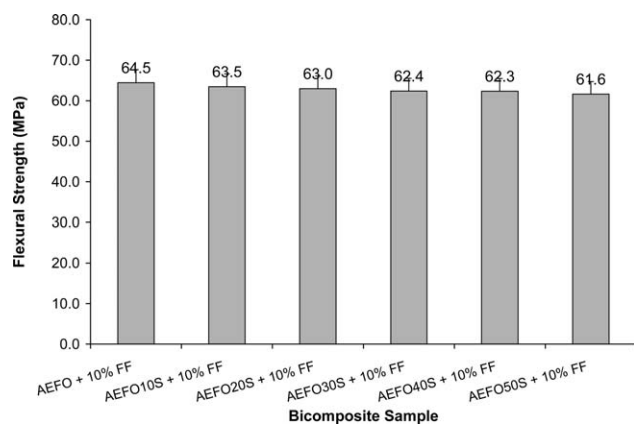

Figure 7. Effect of flax fiber content on Young's modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.
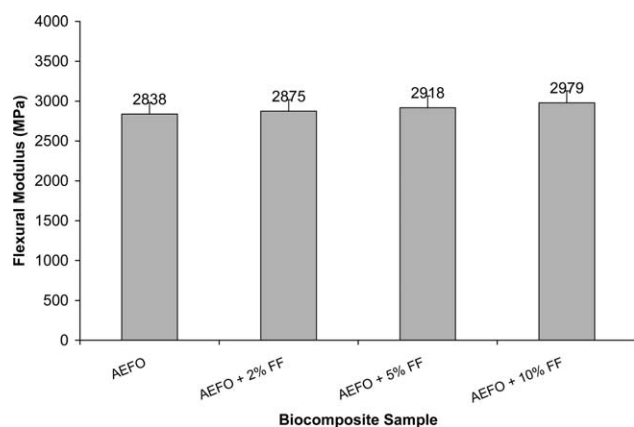

Figure 9. Effect of flax fiber content on flexural strength of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.

Figure 10. Effect of styrene content on flexural strength of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.

Figure 12. Effect of styrene content on flexural modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.

fact that an increase in brittleness decreases the flexibility; hence the flexural strength also decreases.

The trends in flexural modulus were similar to those of the Young's modulus. It was found that flexural modulus increased with an increase in flax fiber and styrene content as indicated in Figures 11 and 12, respectively. Flexural modulus of pure AEFO sample (0% flax fiber) was found 2.838 ± 0.121 GPa and it increases to 2.979 ± 0.121 GPa with 10% flax fiber loading. This result can also be attributed to the better fiber-polymer interfacial adhesion and rigidity provided by the styrene. In literature, the flexural modulus of AESO is reported as 0.896 GPa.[39]

Hardness measures resistance to bending, scratching, abrasion, and indentation. The Rockwell hardness number measures the indentation hardness, which helps in characterizing the viscoelastic behavior of the material. Intermolecular forces have a significant effect on the hardness. The results shown in Figure 13 illustrates that the addition of flax fiber increases the Rockwell hardness number of the AEFO biocomposites, which implies that the hardness of the biocomposites has increased. It has been reported that similar behavior has been observed for polypropylene-based biocomposites.[47] The hardness of a

material is related to the modulus in such a way that an increase in modulus will increase the hardness too.[47]

Hardness is also directly related to rigidity. Since the styrene content increases the rigidity of the biocomposite, the hardness of composite will also increase. Figure 14 illustrates the hardness for different styrene amounts in the composite material. As expected, the Rockwell hardness number increases with an increase in the styrene content.

CONCLUSIONS

In this study, acrylated epoxidized flaxseed oil (AEFO) resin synthesized from flaxseed oil was used to develop flax fiber reinforced biocomposites via a vacuum resin transfer molding method. The biocomposites exhibited good physical and mechanical properties.

The mass increase during the water absorption test was found to be less than 1.5% (w/w) for all AEFO-based biocomposites, which is generally acceptable in biocomposite industries. The styrene content had no significant effect on the water absorption characteristics. The density of the AEFO resin (1.166 g/cm^3) was found to be higher than that of styrene (0.909 g/cm^3)

Figure 11. Effect of flax fiber content on flexural modulus of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.
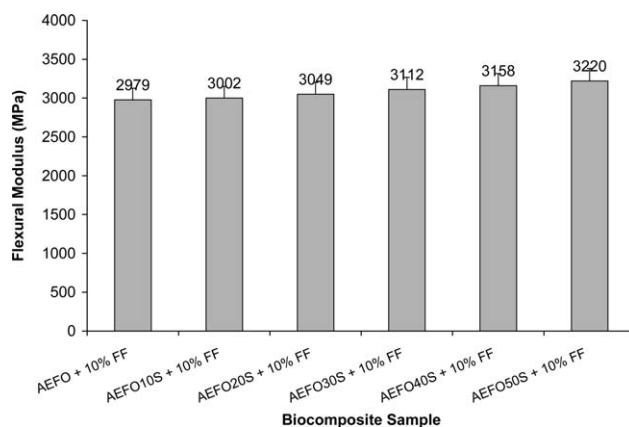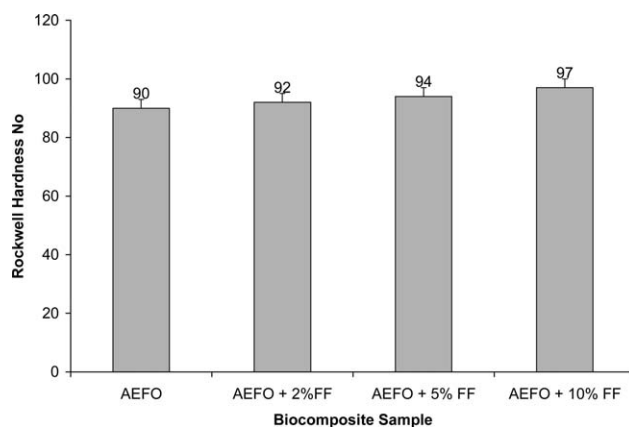

Figure 13. Effect of flax fiber content on hardness of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.
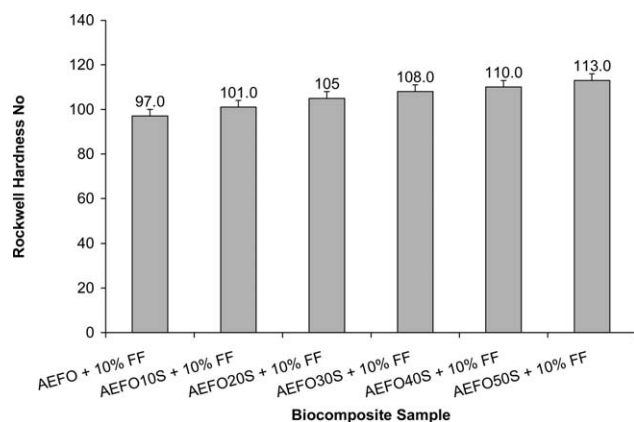
Figure 14. Effect of styrene content on hardness of AEFO biocomposites. The uncertainty presented in the figure is at the 95% percentile confidence level.

and lower than that of flax fiber (1.461 g/cm^3). Flax fiber loading improved the mechanical properties of the AEFO biocomposite. An increase in flax fiber content increased the tensile strength, Young's modulus, flexural strength, flexural modulus, and the hardness of the AEFO biocomposite. It was found that styrene improves the tensile strength and the Young's modulus of AEFO biocomposites but decreases the flexural strength. Both flax fiber and styrene content were found to increase the hardness of AEFO based biocomposite.

The AEFO biocomposite with 10% (w/w) flax fiber had a tensile strength of 31.4 ± 1.2 MPa and a Young's modulus of 520 ± 31 MPa. It also exhibited a flexural strength of 64.5 ± 2.3 MPa and a flexural modulus of 2.98 ± 0.12 GPa.

ACKNOWLEDGMENTS

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