

Pyrolyzed Chicken Feather Fibers for Biobased Composite Reinforcement

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ABSTRACT: An environment friendly, green composite design was demonstrated by producing an almost completely biorenewable and affordable material. Mildly pyrolyzed chicken feather fibers (PCFF) were incorporated in acrylated epoxidized soybean oil (AESO) and methacrylated lauric acid (MLAU)-based thermosetting resin to provide reinforcement in low density and rubbery polymer applications. The mechanical properties of the polymer composite, such as storage modulus, tensile modulus, tensile strength, and fracture energy were directly proportional to the fiber content. Varying the fiber content up to 32 wt % allowed for a wide tuning of mechanical properties (i.e., 20–300 MPa storage modulus and 10–150 MPa range at room temperature). Upon subjecting the CFFs to a strategic pyrolysis thermal history, the formation of isopeptide and ester bonds with limited protein backbone scission resulted in mechanical fiber integrity. Thermally stabilized PCFF have the potential for utilization in composite manufacturing, where typical manufacturing temperatures, especially in thermoplastic extrusion, exceed the untreated biobased fiber degradation temperature (215°C). © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Natural fibers are considered an inexpensive and renewable resource to replace synthetic petroleum-based fibers. The chemical and physical properties of natural fibers on the mechanical properties of thermoplastics and thermosetting polymer matrices have been investigated.^{1–8} However, these studies were limited to cellulose-based fibers due to the inherent impact resistance and load bearing nature of the predominantly bast fibers. The inherent properties of the cellulose-based fibers are a result of the straight chain microfibril secondary structure of the fibers, which are supported by strong covalent and hydrogen bonds.⁹ Unlike cellulose-based fibers, protein-based fibers, such as wool and chicken feather fibers (CFF) predominantly possess an α -helix structural conformation. The α -helices are supported axially by hydrogen bonds, which are weaker but more flexible than covalent bonds. Therefore, CFF have higher flexibility than cellulosic-based fibers. Additionally, their relatively low density and cost are advantages that can be attractive for many composite applications. The utility of CFF as a reinforcement or filler in composites has been investigated previously and these materials have shown great promise.^{10–13}

Composite manufacturing processes, particularly with thermoplastic melts, typically require high temperatures.¹³ Unfortu-

nately, high temperatures can result in natural fiber degradation and subsequent deterioration of the composite properties. CFF structural changes as a function of temperature were explored by Senoz et al.¹⁴ The analysis revealed pyrolysis pathways to prepare thermally stable, crosslinked, intact fibers. These pyrolyzed chicken feather fibers (PCFF) have higher thermal resistance (up to 450°C) than untreated CFF and can be reliably used in high temperature composite applications.

Epoxy, vinyl ester, and unsaturated polyester resins derived from petrochemical feedstock are widely used in polymer composites. These resins consist of multiple reactive sites that are suitable for crosslinking in these thermoset polymers. Functionalized, triglyceride-based resins are biobased and have displayed great potential as a biorenewable, crosslinking substitute.¹⁵ For example, soybean oil is composed of up to 99%¹⁶ unsaturated triglyceride molecules. The unsaturated sites are suitable for conversion to maleanated, acrylated, epoxidized, or hydroxylated functionalities.^{15,17} Among these functionalized triglyceride-based resins, AESO (acrylated epoxidized soybean oil) has been studied extensively^{15,17} and manufactured commercially.

Because of the relatively high viscosities of the crosslinkers, reactive diluents are incorporated into the resins to reduce manufacturing costs. Additionally, reactive diluents can provide better

polymer matrix properties by inducing what is termed “the chain extension effect” and by providing higher extents of polymerization.¹⁸ However, reactive diluents, such as styrene, are hazardous air pollutants (HAP) and volatile organic compounds (VOC). Furthermore, a large portion of styrene evaporates during composite processing and, unfortunately, can continue to emit during the lifetime of the part. Previous research by Ziaee, et al. has shown that up to 40% of the styrene in vinyl-ester resins is unreacted even after cure.¹⁹ Therefore, replacement of these reactive diluents with biobased, environmentally friendly substitutes is desired. Previous research conducted by La Scala et al. has shown that methacrylated lauric acid (MLAU) is an attractive fatty acid-based reactive diluent,^{20–22} particularly when a flexible polymer matrix is desired.

The main objective of this article was to demonstrate the utilization of thermally stable PCFF in polymer composites. Composites were prepared from PCFF reinforcement in a matrix derived from AESO crosslinking agent with MLAU as the reactive diluent. The effects of the PCFF weight fraction and method of pyrolysis on the composite properties were investigated.

EXPERIMENTAL

Sample Preparation

Chicken feather fibers (CFF) were supplied by the Feather Fiber Corporation (Nixa, MO). The details of the CFF pyrolysis process has been described by Senoz et al.²³ Basically, the CFF were pyrolyzed in a nitrogen atmosphere at 215°C for 2 h (PCFF-1) and 10 h (PCFF-3). A set-point temperature of 215°C was employed to pyrolyze the CFF below their crystalline melting temperature near 225°C. The pyrolysis was achieved in a Thermolyne Type F6000 box furnace with a constant 100 mL min⁻¹ N₂ purge. Fibers were washed with sufficient distilled water and toluene, dried under vacuum at 60°C overnight, and stored in a desiccator before use. The PCFF with the desired fiber content were placed in a mold designed for resin transfer molding (RTM) processing. A stock liquid molding resin consisting of 50–50 wt % AESO : MLAU was prepared and stored after degassing. The chemical structures of AESO (Ebercryl 860; Cytec Surface Specialties, Smyrna, GA) and MLAU (Applied Poleramic, Benicia, CA) are illustrated in Figure 1. Prior to transferring the resin to the fiber loaded mold, a free radical initiator, Trigonox 239, and a catalyst, cobalt naphthenate (CoNap), were mixed thoroughly into the resin. The Trigonox 239 (AkzoNobel Polymer Chemicals LLC, Chicago, IL) and CoNap (Aldrich, Milwaukee, WI) masses used were 1.5 and 0.375 wt %, respectively, of the total resin mass. The mixture was subsequently degassed at room temperature for 20 min and then transferred into the mold using a VARTM process. The composites were cured at room temperature for 2 days and postcured at 100°C for 3 h.

Resin Viscosity

Monomer and resin viscosities were obtained on a TA Instruments AR-G2 rheometer. Measurements were performed isothermally at 25°C controlled by a Peltier plate ($\pm 0.1^\circ\text{C}$ error). A 20 mm 1° steel cone with a truncation gap of 25 μm and a minimum sample volume of 0.04 mL was utilized. The shear

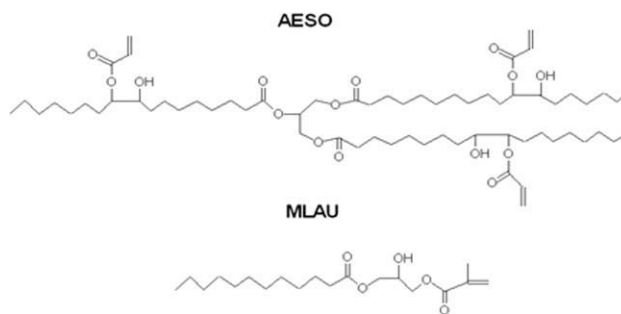


Figure 1. Molecular structures of AESO and MLAU monomers.

rate was swept from 1 to 100 s⁻¹ collecting 21 data points to observe any non-Newtonian behavior. At a given shear rate, the shear stress was measured every 2 s. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive points.

Composite Densities

To obtain the densities of the composites, each composite was weighed in air and pure water. The density values were calculated from the measured weights by using Archimedes principle. Each density value was determined after three consecutive measurements on different samples.

Mechanical Tests

Dynamical Mechanical Analysis. Thermo-mechanical properties of the cured resins were measured using dynamic mechanical analysis (DMA). Rectangular samples with approximate dimensions of 3 × 13 × 60 mm³ were tested using a TA Instruments Q800 DMA in single frequency mode using a dual cantilever clamp. The samples were tested at 1 Hz with an amplitude of oscillation of 5 μm while ramping the temperature from -100 to 90°C at a rate of 2°C min⁻¹. Samples were isothermally cooled at -100°C for 20 min prior to the temperature ramps. Each composite type was tested three times to ensure reproducibility and standard deviations were calculated based on these successive runs. The glass transition temperature (T_g) was taken as the temperature at which the maximum of the tan δ occurred.

Tensile Tests. The tensile moduli of the composites were obtained using an Instron 5567 with a 500-N load cell. Vishay Micro-Measurements strain gauges were used to obtain strain readings with high accuracy. The samples had approximate dimensions of 2.5 × 13 × 80 mm³. Each composite type was tested three times to ensure reproducibility and standard deviations were calculated based on these successive runs. Fractured surface images of the composites were obtained using a Hitachi TM-1000 Tabletop Microscope SEM.

RESULTS AND DISCUSSION

Resin Viscosity

The viscosities of AESO, MLAU, and 1 : 1 AESO : MLAU are reported in Table I. As can be seen, the viscosity of AESO is high and considerably higher than the upper and lower viscosity limits of 800 and 300 cP, respectively, for optimum liquid molding processing.²⁴ The high viscosity of AESO is attributed to its

Table I. Viscosity of the Monomers at Room Temperature

Monomer	Viscosity (cP)
AESO	26960 ± 23
MLAU	38.28 ± 0.27
1 : 1 AESO-MLAU	668.4 ± 3.4

bulky chemical structure, polarity and intermolecular hydrogen bonding.²⁵ Compared to AESO, MLAU is composed of a single, saturated, 12 carbon fatty acid chain. These qualities give MLAU a significantly lower viscosity (38 cP) which is only one order of magnitude higher than styrene (1 cP).²⁰ Thus, a 1 : 1 mixture of AESO and MLAU monomers brought the viscosity within the optimum liquid molding viscosity window.

Composite Densities

The densities of 1 : 1 AESO-MLAU composites containing various amounts of fibers in the range of 0–32 wt % are shown in Table II. A clear density trend is not observed with respect to fiber content and the densities fall in the range of 1.03–1.10 g cm⁻³. Hong et al.¹² reported similar density values for the soybean oil–styrene-based composites. Even though at 5% CFF loading, the composite densities slightly increase with respect to the heat treatment time, a similar trend is not observed at 32% CFF loading. It is likely that the process conditions result in small density variations due to potential air bubble entrapment. However, all composites exhibit low densities of order 1 g cm⁻³ indicating that the densities of the fibers are close to that of neat AESO-MLAU resin.

Dynamical Mechanical Analysis

Senoz et al.¹⁴ showed that PCFF, which were pyrolyzed at 215°C contained sufficient amounts of disulfide and nondisulfide crosslinks to keep them intact and retain their fibrous character in aqueous solutions. Therefore, the thermo-mechanical properties of composites with PCFF reinforcement became an area of interest for soft and rigid composites. The storage modulus (E') and $\tan \delta$ values obtained from DMA provide insight into the viscoelastic properties of the CFF and PCFF reinforced biobased composites. Figure 2 shows E' vs. T of the composites containing PCFF-1 in the range of 0–32 wt %. In the low temperature region, a distinct glassy plateau was not obtained because of the resin's nature. This behavior was also observed in AESO-styrene

Table II. Densities of 1 : 1 AESO-MLAU Composites with Varied Amounts of Untreated and Pyrolyzed CFF

Fiber type	Fiber content (wt %)	Density (g cm ⁻³)
Pure matrix	0	1.081 ± 0.002
Untreated CFF	5	1.059 ± 0.026
Untreated CFF	32	1.078 ± 0.022
PCFF-1	5	1.077 ± 0.011
PCFF-1	8	1.087 ± 0.007
PCFF-1	19	1.080 ± 0.011
PCFF-1	32	1.068 ± 0.016
PCFF-3	5	1.085 ± 0.002

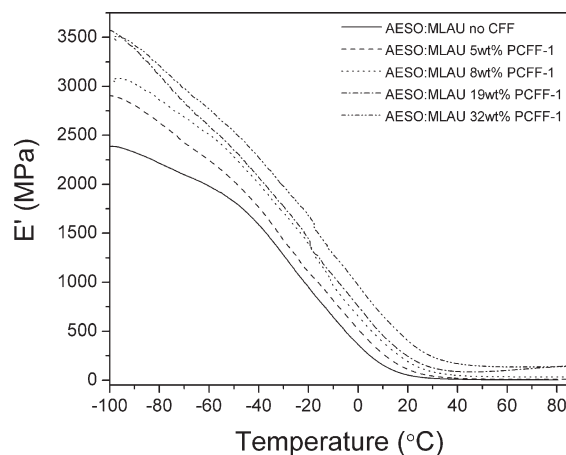


Figure 2. Storage modulus of 1 : 1 AESO-MLAU composites with varied amounts of PCFF-1 (2 h heat treated at 215°C) as a function of temperature.

composites.^{12,15} As the PCFF-1 content increased, the storage modulus of the composites increased within the experimental temperature range. Moreover, Figure 3 shows that the composites with pyrolyzed fibers exhibit a higher storage modulus than those reinforced with untreated fibers (CFF) in the glassy regime. However, as the temperature increases above $T_g \approx 20^\circ\text{C}$, the storage moduli converge and eventually approach that of the neat AESO-MLAU polymer matrix. Encouraging is the fact that the storage moduli of the heat-stabilized PCFF reinforced composites are improved compared to the nonheat-treated CFF composites. The modulus reinforcement is further illustrated in Figure 4 where the storage moduli at 25°C are plotted as a function of fiber content. As can be seen, the reinforcement by PCFF-1 resulted in an order of magnitude increase in the composite storage modulus and is directly proportional to the fiber content. Additionally, the storage moduli of the composites with 5 wt % fiber loading are essentially

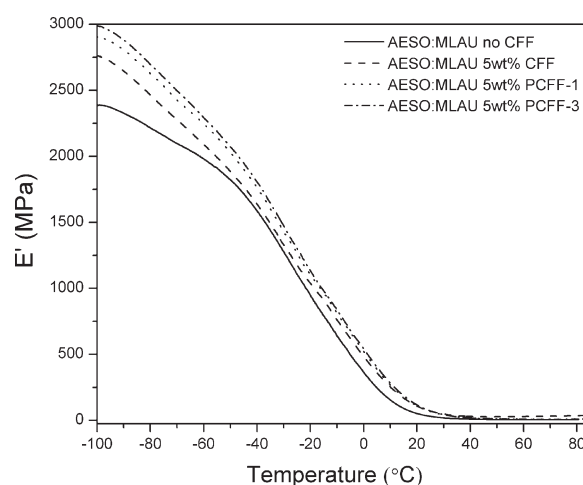


Figure 3. Comparison of the effect of fiber and fiber type on the storage modulus of the 1 : 1 AESO-MLAU composites as a function of temperature.

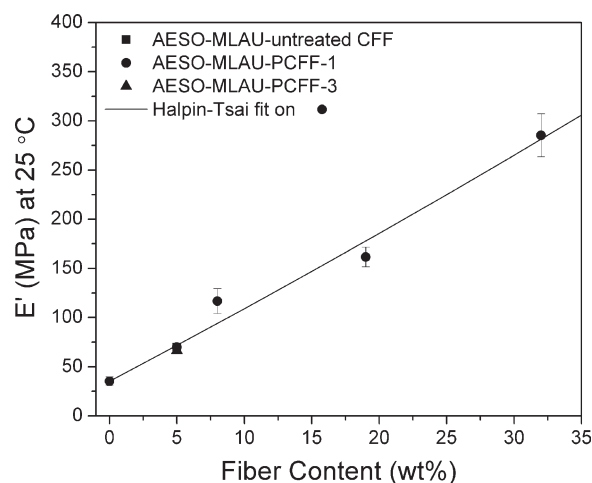


Figure 4. Comparison of the effect of fiber, fiber type, and fiber content on the storage modulus of the 1 : 1 AESO-MLAU composites at 25°C.

independent of fiber type which indicates the stability of the heat treated fibers.

The Halpin-Tsai method^{26,27} can be used to estimate the fiber modulus from the composite and the matrix modulus. According to this model, the composite modulus, E_c is expressed by:

$$E_c = E_m \frac{(1 + \zeta \eta f)}{(1 - \eta f)} \quad (1)$$

where the factor η is given by:

$$\eta = \frac{\frac{E_F}{E_M} - 1}{\frac{E_F}{E_M} + \zeta} \quad (2)$$

Here, E_F and E_M are the modulus of the fibers and the matrix, respectively, ζ is the geometric factor (related to the fiber aspect ratio), and f is the fiber volume fraction. The storage modulus data of AESO-MLAU-PCFF-1 composites at room temperature in Figure 4 were fitted to the Halpin-Tsai equation by varying E_F and ζ and using the least squares method. The storage modulus and geometric factor of PCFF-1 at room temperature was calculated as $E_F = 922$ MPa and $\zeta = 110$, respectively, with a goodness of fit parameter $R^2 = 0.979$. Assuming the same geometric ζ factor, the calculated storage modulus, E_F , of untreated CFF and PCFF-3 by the Halpin Tsai method were very similar to that of PCFF-1. The similar fiber modulus values were the result of the crosslinking process of CFF at 215°C during pyrolysis. The control over the composite storage modulus in a wide range between 10 and 300 MPa can be useful for room temperature soft composite applications such as suggested for Eco-Leather.¹⁷

The T_g s of the composites were determined to be in the range of 23–29°C, using the $\tan \delta$ method, as shown in Figures 5 and 6. The glass transition temperatures of the composites are considerably lower by design than that previously reported for the AESO-styrene composites^{12,15}; for Eco-leather applications, the T_g values should be in the vicinity of room temperature.

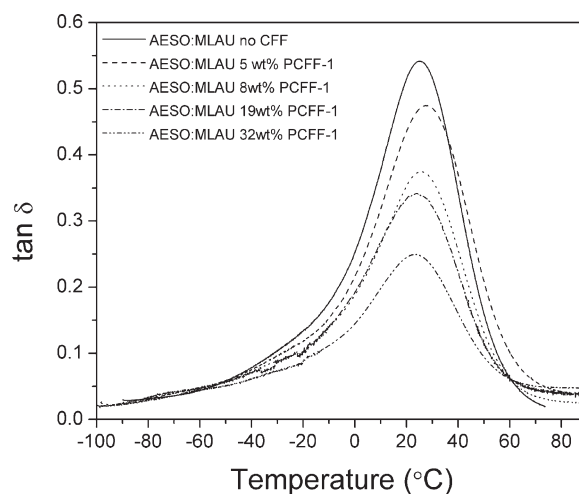


Figure 5. $\tan \delta$ of AESO-MLAU composites with various amounts of PCFF-1 (2 h heat treated at 215°C) as a function of temperature.

The aromatic side chain of styrene provides the polymer matrix with structural rigidity and, in turn, a higher T_g . On the other hand, the rather long fatty acid side chain of MLAU increases the liquid fraction in the mixture, and suppresses the temperature at which rigid, solid, percolated fractal structures can form.^{28–30} The MLAU also acts as a plasticizer and provides backbone flexibility and increased linear chain lengths to the network structure. Additionally, AESO contains a percentage of saturated, long chain fatty acids that also increase flexibility, lower T_g , and may exhibit affinity for the fatty acid side chains of MLAU.¹⁵ As seen in Figures 5 and 6, the T_g did not change remarkably with respect to fiber content and type.

The maximum $\tan \delta$ is an indication of the damping behavior of a polymer. A high $\tan \delta$ maximum is a sign of good damping properties which is useful against vibrational fatigue failure and noise in various applications.³¹ The 1 : 1 AESO-MLAU resin by itself is quite flexible in the glass transition region due to the abundance of long, fatty acid side chains that restrict the

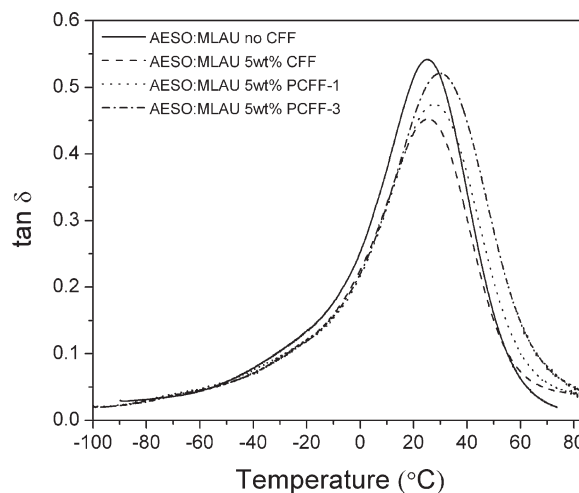


Figure 6. Comparison of the effect of fiber and fiber type on the $\tan \delta$ of the 1 : 1 AESO-MLAU composites as a function of temperature.

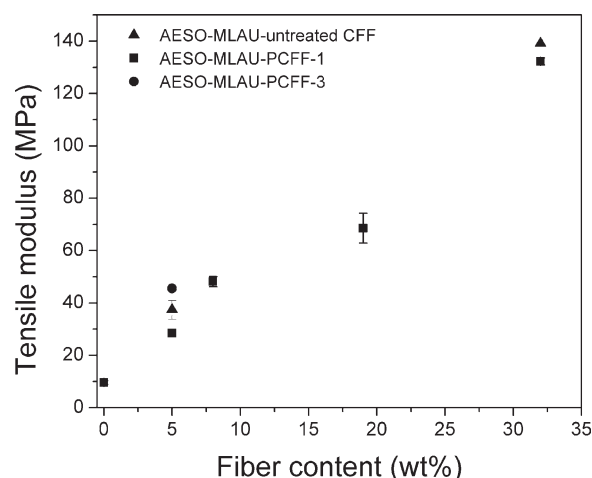


Figure 7. Comparison of the effect of fiber, fiber type, and fiber content on the tensile modulus of the 1 : 1 AESO–MLAU composites.

crosslinking density. The integration of the fibers into the composites limits the motion of polymer proportional to the fiber content; consequently, lowers the energy dissipation during the glass transition and, thereby, lowers the maximum $\tan \delta$ value. As seen in Figure 5, the $\tan \delta$ peak maximum gradually decreased from 0.55 to 0.25 as the fiber content increased. All composites displayed broad glass transitions. Broad peaks indicate a variety of vibrational modes in the composite. The copolymerization of AESO and MLAU may result in some heterogeneity in the polymer matrix. For example, local concentrations of MLAU and saturated fatty acid side chains of AESO can result in variations in polymer rigidity, thereby, producing various vibrational modes.^{31,32}

Tensile Testing

The tensile moduli of the composites are illustrated in Figure 7. In general, the composite tensile modulus increases with fiber content. The 1 : 1 AESO–MLAU resin exhibits a tensile modulus of 10 MPa, while the addition of 32 wt % PCFF-1 increased the tensile modulus above 130 MPa. Similar to the storage moduli of the composites, the tensile moduli gave a linear relationship with respect to fiber content. The contributions of untreated CFF and PCFF-1 to the stiffness of the composites are very similar at both 5 and 32 wt % fiber loading. On the other hand, at 5 wt % loading the 10-h crosslinked fibers (PCFF-3) exhibit a higher stiffness than the untreated CFF suggesting a higher degree of fiber crosslinking. Senoz et al.¹⁴ showed that 215°C was high enough to initiate disulfide cleavage in the feather keratin matrix. At the same time this temperature was also sufficiently high to form crosslinks that hold the fiber molecules intact. Both PCFF-1 and PCFF-3 were about 80 wt % insoluble in water indicating a highly crosslinked structure. However, the soluble portion of PCFF-3 in 2-mercaptoethanol solution (a disulfide bond breaking agent) gave a larger amount of high molecular weight particles compared to PCFF-1. Therefore, pyrolysis of CFF at 215°C increases the amount of nondisulfide linkages such as amide and ester bonds. The higher tensile modulus of the PCFF-3 composites might be due to higher amount of these crosslinks within the fiber bulk. In general,

Table III. Tensile Properties of CFF and PCFF Containing 1 : 1 AESO–MLAU Composites

Fiber type	Fiber content (wt %)	Energy absorption (kJ m ⁻²)	Fracture stress (MPa)	Fracture strain
Pure matrix	0	0.600	0.50	0.051
Untreated CFF	5	2.202	1.86	0.055
Untreated CFF	32	6.966	5.30	0.048
PCFF-1	5	1.377	1.27	0.049
PCFF-1	8	2.733	2.18	0.057
PCFF-1	19	4.260	3.73	0.053
PCFF-1	32	7.566	6.22	0.052
PCFF-3	5	1.243	1.46	0.036

tensile tests indicate that the mechanical performance of the fibers is at least maintained during heat treatment at 215°C. However, the apparent lower modulus of the CFF (1 GPa) in the MLAU/AESO matrix at T_g compared to AESO/ST (3 GPa) below T_g leads us to suspect that the softer MLAU migrated to the PCFF interface and gave reduced stiffness values in the composites. This effect can increase toughness at impact but may reduce long time fatigue. However, for these materials experiencing mechanical trauma in the vicinity of T_g , it may be possible to get self-healing of mechanical damage at the fiber–matrix interface if a soft layer is present on the fibers.²⁸ For highly rigid composites, soft fiber–matrix interfaces are usually considered in a highly negative light, but for softer composites as envisaged herein, this interface may be quite beneficial. The soft interface effect also results in facile fiber pullout, as demonstrated in the next paragraph.

The fracture stress and fracture adsorption energy were also found to be directly proportional to the fiber loading in all fiber types, as shown in Table III. The fracture strain data did not show a specific trend with respect to fiber loading and remained

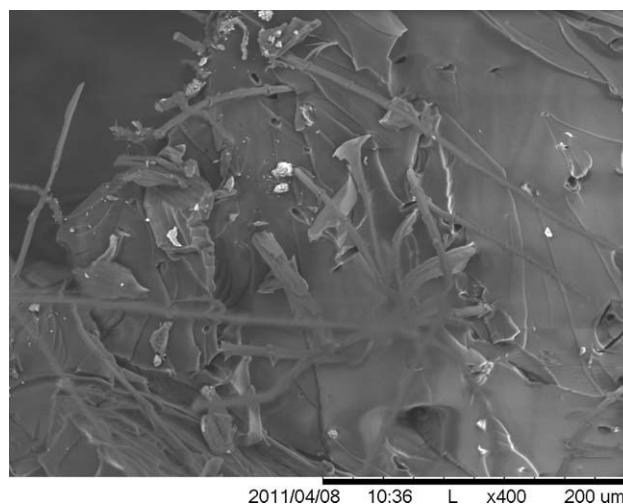


Figure 8. Fracture surface of 1 : 1 MLAU–AESO with 5 wt % untreated CFF.

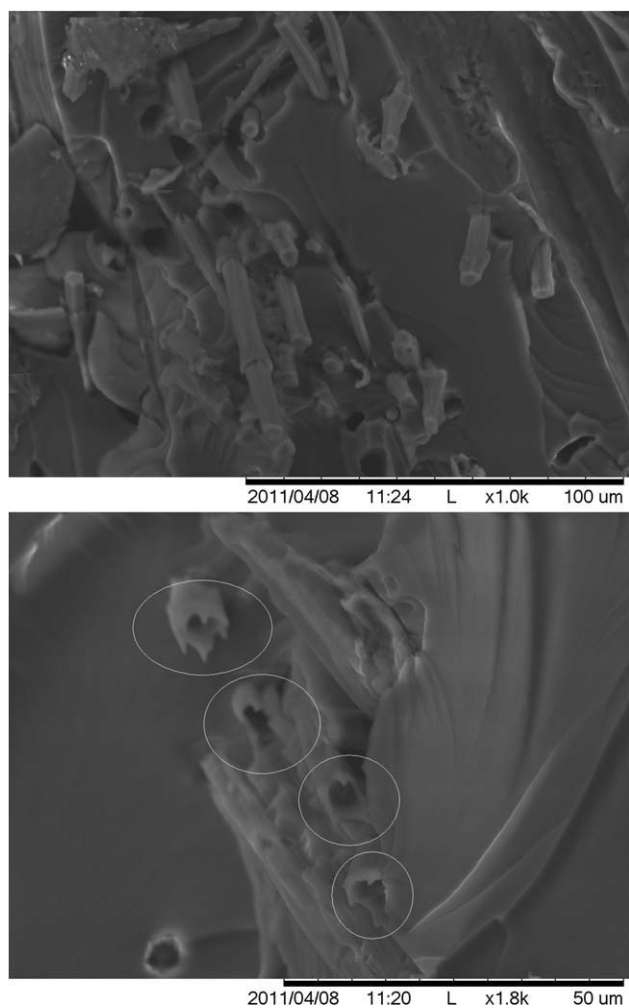


Figure 9. Fracture surface of 1 : 1 MLAU–AESO with 8 wt % PCFF-1; fiber nodes where fracture occurred are circled in the bottom image.

near 5%. However, at 5% fiber loading, the untreated CFF containing composite gave larger fracture strain compared to ones with heat treated CFF, which is a consequence of the shrinkage and breaking of the fibers due to the thermal degradation.

During tensile testing, fracture took place correctly at the center of the gauge length and not in the grips in all samples. Extremely long fibers were clear on the fracture surface of the composites containing untreated CFF; see Figure 8. This is a good indication of extensive fiber pullout with reduced adhesion between fibers and the polymer matrix. Because of poor interactions between fibers and the matrix, the surface between fibers and matrix becomes the weakest point during stress application. Consequently, fibers were pulled out following the fracture of the matrix. The number of fiber pullouts was lower and pullout lengths were much shorter on the fracture surfaces of composites that contained PCFF-1 as shown in Figure 9. This is an indication of enhanced interfacial bonding.³³ However, lack of matrix residues on the fibers shows that the fiber–matrix adhesion could be further improved. In addition, numerous PCFF-1 broken from the node segments can be observed in the bottom image of Figure 9. These nodes are located on the fibers

roughly every 40 μm along the fiber axis. At these junction points, one fiber segment penetrates through the cross-section of another segment. The geometry of the nodes provides a low cross-sectional area where stress reaches a local maximum. Therefore, these locations turned out to be vulnerable points for fracture for these fibers and, in turn, for the biobased composites.

CONCLUSIONS

Completely biorenewable, affordable, and partially agricultural waste containing composites were prepared by using modified chicken feather fibers and biobased resins. The biobased resin mixture had a suitable viscosity value for liquid molding techniques and polymerization of this resin resulted in polymers that have low densities, in the range of 1.0–1.1 g cm^{-3} , and were at the glass transition at room temperature. The incorporation of 32 wt % untreated or pyrolyzed chicken feather fibers into the matrix resulted in a 15-fold increase in the storage and tensile moduli. The comparison of pyrolyzed and untreated CFF did not give differences in the degree of reinforcement to the composites. Although the nondisulfide crosslinking protects fibers from mechanical deterioration at high temperatures, they did not provide stronger fibers.

The results in this study showed that untreated or pyrolyzed chicken feather fibers in AESO–MLAU-based composites do not only act as inexpensive filler, but also as a reinforcement media for the composites. The prepared composites may be used for lightweight rubbery polymer applications. Composite property tuning for a desired application can be accomplished by controlling the fiber loading. Additionally, due to the enhanced thermal stability of the PCFF, liquid molding techniques can be implemented in the preparation of CFF reinforced thermoplastics without the worry of fiber degradation during processing.

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