Composites from Northern Red Oak (*Quercus robur*) Leaves and Plant Oil-Based Resins

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ABSTRACT: Composite materials were successfully made out of plant oil-based resin and northern red oak (*Quercus robur*) leaves collected in the fall. The viscosities of the bio-based resins (MAESO and MAELO) were suited to high temperature resin transfer molding (RTM) and vacuum-assisted resin transfer molding (VARTM) processing. The leaves have a waxy epidermal surface layer that needs to be dewaxed prior to use in a composite part. We used different treatments (such as benzene–ethanol, boiling water, and strong detergent) to dewax the leaves; all three methods seem to give good results; but boiling water and strong detergent were considered the best treatments for the dewaxing of leaves and boiling water was considered the greenest dewaxing method. The compatibility between the resin and the leaves was improved with a silane treatment which resulted in composites with higher mechanical stiffness than the resin itself. With 10 wt % leaves, we obtained an improvement in the composite modulus of about 14% from which we could estimate the leaf modulus at about 5.3 GPa. An alternative method to produce biocomposites from leaves without the need for silane treatments consists in carbonizing the leaves first at 215°C for 12 h, and then at 450°C for 1 h. The composites made with leaves and bioresins derived from functionalized triglycerides have the potential for use in high volume applications with low costs such as housing, construction, civil infrastructure, toys, and furniture. The use of leaves as a biocomposite filler has several advantages including (a) reduced cost, (b) improved properties of the resin, (c) composites with high bio content, (d) removal of a waste material with subsequent prevention of burning with attendant health hazards, and (e) interesting design aesthetics for interior and exterior decoration. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: northern red oak (*Quercus robur*); leaves; bio-based composites; triglycerides; renewable resources; low cost; green materials

INTRODUCTION

Polymer and composite materials derived from petroleum-based materials are used in several fields, such as aerospace, automotive, marine, construction, civil infrastructure, consumer goods, and industrial applications. The depletion of petroleum reserves with increasing prices and a growing desire to move towards greener products, has created interest in materials from natural resources, such as vegetable oils and natural fibers. The Affordable Composites from Renewable Resources (ACRES) program at the University of Delaware has been actively designing monomers from plant triglycerides (TGD), using a broad range of chemical routes.[1,2] The chemically modified plant oils have been used to develop adhesives, foams, elastomers, and polymer composite matrix resins.[1–10] The ACRES group produced many different types of bio-based thermosets, such as acrylated epoxi-

dized soybean oil (AESO), maleinated acrylated epoxidized soybean oil (MAESO), maleinated soybean oil monoglyceride (SOMG/MA), and many others reviewed in Ref. 1. These bio-based resins have properties comparable to unsaturated polyester resins used in fiberglass composite applications with elastic modulus E ~ 2 GPa, fracture stress σ ~ 100 MPa and glass transition temperatures T_g ~ 100°C.

Synthetic fibers such as carbon, aramid, and glass are widely utilized as reinforcements in thermosets and thermoplastics matrix composites. In recent years, there has been a high interest in the employment of natural fibers. Natural fibers are typically grouped into four different types: leaf, bast, fruit, and seed, depending on their source. Leaf and bast fibers are generally used in composite processing. Examples of leaf fiber include sisal, henequen, and pineapple and bast fiber examples

include flax, hemp, ramie, cellulose and jute.[11–23] One of the major difficulties of natural fibers is that their properties are intrinsically dependent on where they are grown (locality), what part of the plant they are harvested from (leaf or stem), the maturity of the plant (age), and how the fibers are harvested and preconditioned in the form of mats or chopped fibers, woven or unwoven. These factors result in significant variation in properties compared with their synthetic fiber counterparts. Natural fibers have advantages, such as low density, high specific strength and modulus, limited requirements on processing equipments, minimal health problems, ease of surface modification, and availability as renewable natural resources. Natural fibers are much cheaper than synthetic fibers, and can be used as a replacement to the synthetic ones in many applications. Plant fibers are composed mainly of cellulose, hemicellulose, and lignin, plus some impurities near the surface. The chemical composition can help determine properties and end-use of the fibers. For instance, lignin facilitates reactivity, thus allowing better response to chemical modifications such as acetylation.[11] Higher cellulose content leads to higher stiffness and is most suitable for composite resin reinforcement.[11] The cellulose contains three hydroxyl groups which form hydrogen bonds; two of the hydroxyl groups form intermolecular bonds, while the third one forms intramolecular hydrogen bonds thereby improving stiffness at the molecular level.[11]

The presence of reactive groups (such as OH groups) in both fibers and resins is important to obtain a high interfacial energy with good adhesion at the fiber-matrix interface resulting in a composite with improved mechanical properties. However, many natural fibers have a layer of pectin and waxy substances to make them more water resistant and this can have a negative impact on the fiber-matrix interface strength. Thus, some surface treatments may be necessary to improve the composite properties. The behavior of natural fibers with liquid molding resins is potentially very different than their synthetic counterparts where for example the interfacial properties play a dominant role in controlling the properties of the glass fiber matrix interphase. Natural fibers tend to be highly porous (e.g., origin of the word "Straw" in drinks), can be laden with defects which detract from their intrinsic properties and have many internal surfaces with potentially different surface energies. Thus, the ideal resin for use with natural fibers should not only form an excellent composite matrix with good intrinsic properties but should also have sufficient compatibility and low viscosity to diffuse into the fibers, fill and heal the voids, create mechanical coupling with the matrix, and also provide good interfacial strength. Under these circumstances, the properties of the fibers in the composite can be improved compared with their intrinsic state.

The ACRES group studied the development of low-cost biocomposites,[1,13,14] where they used acrylated epoxidized soyoil (AESO) and natural fiber mats made of flax, cellulose, pulp and hemp. Recycled paper was used as a cheap resource of cellulose fiber and found to work well with AESO resin in terms of flow, impregnation, and surface bonding, giving a modulus of over five times that of the neat resin. These low-cost natural composites were found to have sufficient mechanical strength and properties suitable for applications in hurricane-resistant housing construction
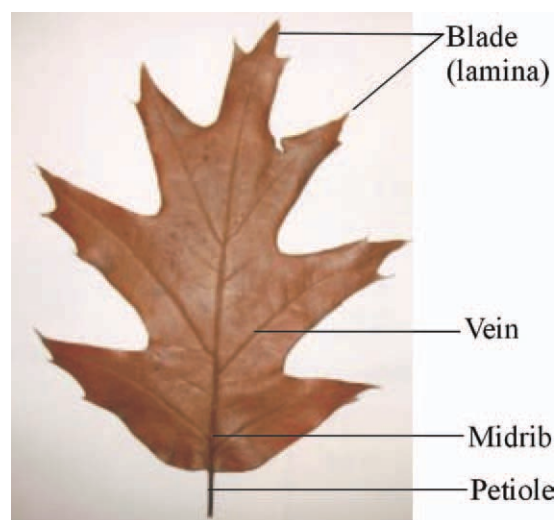

Figure 1. Northern red oak (*quercus robur*) leaf. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

materials, positive net energy housing, eco-leather, furniture and automotive parts.

In this article, we explore the development of very low-cost composites via the use of leaves obtained in the fall season from trees and bio-based resins from modified vegetable oils. In particular, we are interested in the use of Northern Red Oak (*Quercus robur*) leaves (Figure 1). These leaves are a low-cost renewable resource that until now have not been considered for the production of high value applications. In the forest they fall to the ground, decompose and restock the soil with nutrients, and also become food for numerous soil organisms vital to the forest ecosystem. But in cities and towns they are considered a waste; they are collected, composted, and often burned. In the United States, there are 30 million tons of leaves that are collected and burned every year.[24] Burning fallen leaves used to be standard practice across North America, but it can cause health problems, because they tend to burn slowly and thus generate large amounts of airborne particulates (fine bits of dust, soot and other solid materials) and may also contain hazardous chemicals such as carbon monoxide.

A leaf is a plant organ and consists typically of the following tissues shown schematically in Figure 2: the epidermis (skins that cover the upper and lower surfaces), the interior mesophyll, and an arrangement of veins (the vascular tissue). The epidermis is the outer multilayered group of cells covering the leaf; it forms the boundary separating the plant's inner cells from the external world. The epidermis provides several functions: protection against water loss, regulation of gas exchange, secretion of metabolic compounds, and (in some species) absorption of water. The epidermis is coated on the outer side with a waxy cuticle that prevents water loss. The interior of the leaf tissue is called the mesophyll, which is the primary location of photosynthesis in the plant. The veins are the vascular tissue of the leaf and are located in the spongy layer of the mesophyll. They are typical examples of fractal-like pattern formation (or venation) through ramification.
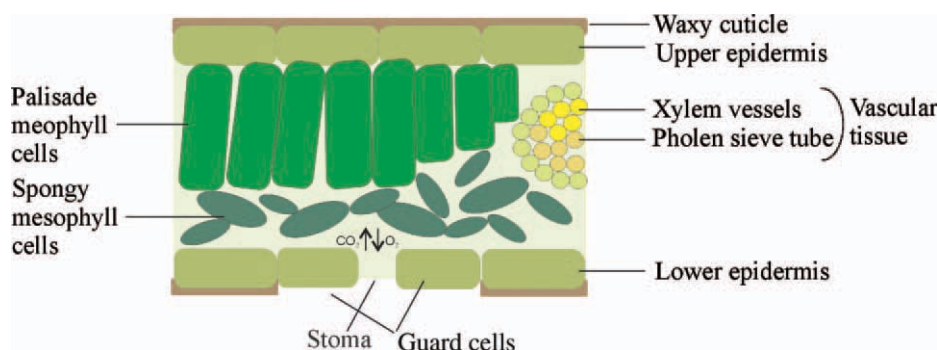
Figure 2. Leaf anatomy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The use of leaves as a biocomposite filler if successful has several advantages including (a) reduced cost, (b) improved properties of the resin, (c) green composites with high bio content, (d) removal of a waste material with subsequent reduction of health hazards, (e) interesting design aesthetics for interior and exterior decoration. The leaf-based composites have the potential for use in high volume applications with low costs such as housing, construction, civil infrastructure, toys, and furniture.

The objective of this study was to develop a novel low-cost bio-based composite material, produced by plant-oil based resins and Northern Red Oak (*Quercus robur*) leaves collected during the fall. For this purpose, two vegetable oil-based experimental resins were employed CREY4 [that contains maleinated acrylated epoxidized soybean oil (MAESO) and styrene] and CREY5 [that contains a mixture of MAESO, maleinated acrylated epoxidized linseed oil (MAELO) and styrene]. The viscosity and the gel time of these resins were studied due to the importance of liquid molding techniques utilized to produce large composite parts. In this work the mechanical properties of the composites were measured and we inquire if useful materials can be made with the leaves.

MATERIALS AND METHODS

Materials
Resins CREY4 and CREY5 were donated by Crey Bioresins Inc (Newark, Delaware) and were used as received. CREY4 contains 70 wt % MAESO with 30 wt % of styrene while CREY5 contains 55 wt % MAESO with 15 wt % of MAELO and 30 wt % of styrene. A free-radical initiator *tert*-butyl peroxybenzoate was purchased from Sigma-Aldrich. As a soap Palmolive was used (Palmolive-Colgate Company), and as a strong detergent Arm and Hammer laundry detergent (Church & Dwight Co., Inc.) was used. Benzene, ethanol (200 proof, absolute), and sulfuric acid were purchased from Fisher Scientific. Methacryloxypropyl-trimethoxysilane was obtained from Gelest. The Northern Red Oak (*Quercus robur*) leaves were collected during the fall season at the University of Delaware.

Mechanical Testing on As-Received Leaves
To evaluate the mechanical performance of the leaves, tensile testing was conducted on the single leaf strips. Specimen preparation for mechanical testing can be described as follows: strips of dimensions of 5 mm × 80 mm were cut carefully from the relatively large leaves and end-tabbed using cardboard and RT adhesives. Mechanical testing was conducted on samples using a mechanical tester with 20 lb (88.89 N) load- cell at 1.27 mm/min cross-head speed and 50 mm gauge length.

Treatment of the Leaves
Washing of the Leaves. All the leaves were washed and dried prior to being treated, as recommended by the EPA.[25] The leaves were placed in a solution with about 1 kg of distilled water and 20 g of soap; the temperature was raised to 70°C, and then left at that temperature for an hour. Then they were washed (five times) with distilled water to remove the detergent; and lastly they were dried in a vacuum oven at 70°C for 24 h.

Dewaxing of the Leaves. Three different treatments were used for dewaxing the leaves, (1) benzene–ethanol, (2) boiling water, and (3) strong detergent. The first method consisted of adding the leaves to a benzene–ethanol solution.[26] In this process, the leaves were placed in a solution of benzene and ethanol with a weight ratio of 2 : 1, respectively, for 72 h at room temperature, and then dried in a vacuum oven for 24 h at 70°C. The second treatment consisted in adding the washed leaves and distilled water in a 2 L glass reactor furnished with a condenser.[26] The water was boiled for 1 h and finally the leaves were dried in a vacuum oven for 24 h at 70°C. The last treatment used a strong detergent (SD) for dewaxing the leaves. In this case, different mass ratios of strong detergent (2, 5, and 10 wt % of SD) to water were used. The leaves were submerged in the solution of water and strong detergent at room temperature for 30 min. Then they were washed (five times) with distilled water to remove the detergent; finally, the leaves were dried in a vacuum oven for 24 h at 70°C.

Treatment with Silane. The dewaxed leaves were submitted to a silane treatment to improve the interfacial adhesion between the leaves and the resins. The dewaxed leaves were placed in the silane solution for 4 min, and finally dried in the vacuum oven for 24 h at 70°C. The silane solution (γ-MPS) was prepared by mixing an acid aqueous media (acetic acid solution 0.05N) with 1 wt % of methacryloxypropyl-trimethoxy silane.

Carbonized Leaves. Two different samples were prepared by this method. In the first sample, the washed leaves were placed in an oven with N_2 gas (with a gas flow of 90 mL/min). The temperature was ramped to 25°C in the course of 1 min, were it remained at that temperature for 3 h and then the temperature was ramped to 215°C in a period of 1 h where it stayed for 12 h, and finally ramped to 450°C in a period of 1 h where it remained for one more hour. The second sample thermal history was

Table I. Composites for Different Treatments Mixed with CREY4 and CREY5[a] Bio-Based Resins

Sample	Resin	Amount of bio–based Resin (g)	Treatment of the leaves[b]	Chop time (min)	Amount of leaves (g)	Amount of initiator (g)
I	CREY4	60	–	–	–	0.9
II	CREY5	60	–	–	–	0.9
III	CREY4	60	[c]	1	6.6	0.9
IV	CREY4	60	[c]	10	6.6	0.9
V	CREY4	60	bH_2O	5	6.6	0.9
VI	CREY4	60	bH_2O	1	6.6	0.9
VII	CREY4	60	bH_2O	10	6.6	0.9
VIII	CREY5	60	bH_2O	5	6.6	0.9
IX	CREY4	60	bH_2O and γ-MPS	5	6.6	0.9
X	CREY5	60	bH_2O and γ-MPS	5	6.6	0.9
XI	CREY4	60	B-E-S and γ-MPS	5	6.6	0.9
XII	CREY5	60	B-E-S and γ-MPS	5	6.6	0.9
XIII	CREY4	60	2 wt% SD	5	6.6	0.9
XIV	CREY4	60	5 wt% SD	5	6.6	0.9
XV	CREY4	60	10 wt% SD	5	6.6	0.9
XVII	CREY4	60	Carbonized-215°C	5	6.6	0.9
XVIII	CREY4	30	Carbonized leaves 215 and 400°C	5	3.4	0.45

[a]Curing conditions: 2 h at 90°C and then 2 h at 120°C, [b]bH_2O, Boiling water; B–E, benzene–ethanol; γ-MPS, silane solution; SD, strong detergent, [c]The leaves were only washed, no other treatment was conducted on these leaves.

different (no 450°C step). The temperature was ramped to 25°C in the course of 1 min where it remained for 3 h, and then ramped to 215°C in a period of 1 h where it stayed for 12 h.

Composite Processing

The treated leaves were chopped using a blender (Cuisinart®-pro-classic food processor). Then the bio-based resins were mixed with the chopped leaves using a mass ratio of 53 g of leaves to 487 g of resin; and afterward they were mixed with 1.5 wt % of the initiator (t-butyl perbenzoate). To prevent oxygen free radical inhibition, the resin was purged with nitrogen gas prior to transferring it to the mold. The resin was placed between two steel plates with a silicone rubber mold in the middle and then left in the vacuum for 10 min at a pressure of 20 psi. The composites were cured by the application of heat, for 2 h at room temperature followed by 2 h at 90°C and post-cured at 120°C for 2 h. The cured composite samples were then cut and polished for the dynamic mechanical analysis (DMA) analysis. Table I lists the 17 different composites prepared using the bio based resins (CREY4 and CREY5) and leaves.

Viscosity, Gel Time, and DMA Analysis

The viscosity of the bio-based resins was measured with a TA Instrument AR-G2 Rheometer (New Castle, DE). A cone-plate geometry with 40 mm diameter plates and a cone angle of 4° was used for all samples and three repeat runs were performed for each sample (CREY4 and CREY5). The effect of the temperature on the viscosity of the triglyceride-based cross-linkers was measured as follows: the samples were first equilibrated at 20°C and then the temperature was increased from 20 to 70°C at a rate of 1°C/min using a shear rate of 1 s^{-1}. The same rheometer was also used to obtain the gel point. The gel-time experiment

was conducted using 1.5 wt % initiator, at constant temperature (25 and 90°C) using a shear rate of 1 s^{-1}.

The thermo–mechanical properties of the samples were measured using DMA. Rectangular samples with approximate dimensions of 60 × 12 × 3 mm^3 were tested using a TA Instruments 2980 DMA in dual cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 μm while ramping the temperature from 20 to 180°C at a rate of 5°C/min. Three different experiments were run for each sample.

TGA Analysis

A thermogravimetric analysis (TGA) was done to determine the change in weight of the leaves with temperature. For this analysis, a Mettler Toledo TGA/DSC1 instrument was used. Ground, washed, and dried leaves were placed in a crucible with a total weight of 20.82 mg. The sample was heated from 25 to 600°C at a rate of 10°C/min in a Helium environment with a gas flow rate of 100 mL/min.

RESULTS AND DISCUSSION

Single Leaf Mechanical Properties

From tensile testing, stress–strain curves were generated and average properties were evaluated for single (as-received) leaves. Figure 3 shows stress–strain curves for the leaf samples. The stress–strain curves show progressive failure modes due to the successive fractures of the minor vines, where the load is mostly carried by the major vines, as observed from the fractured test samples (see Figure 4). The single dry leaf ultimate stress ranged from 2.5 to 3.2 MPa and the strain at break ranged from 0.014 to 0.028 (see Figure 3). The Young's modulus had an average value of 250 MPa, which is lower than expected. The
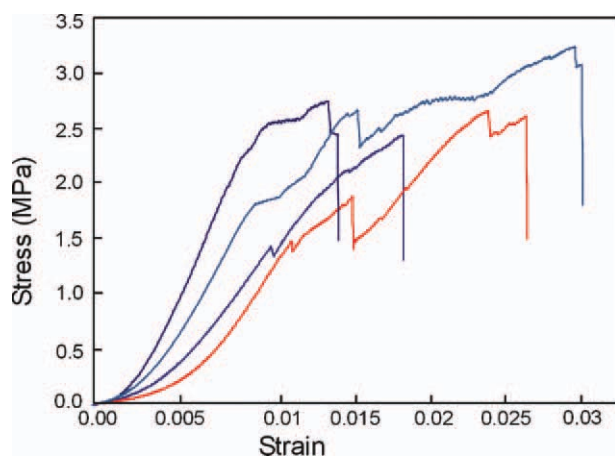
Figure 3. Stress–strain curves measured for several single northern red oak (*Quercus robur*) leaves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

measurement of the modulus value is very sensitive to the cross-section being used. In this work, a cross-section of 10×0.37 mm^2 was applied. To minimize these effects on the measured modulus, the leaves were chopped to a smaller size and embedded randomly in a resin matrix. The results will be discussed in the DMA section. Overall, the fluctuations in the mechanical properties measured for the received leaves of this study can be related to structural variability among the leaves, such as variation in thickness, size, and distributions of minor and major vine.

Dewaxing and Compatibility Results

In preliminary studies, we used vacuum-assisted resin transfer molding (VARTM) to produce a novel bio-based composite, with acrylated epoxidized soybean oil (AESO) and northern red oak (*Quercus robur*) leaves.[26] Figure 5 shows a picture of one of the panels obtained from this study. The leaves contain a waxy substance in their surface that must be eliminated to obtain an
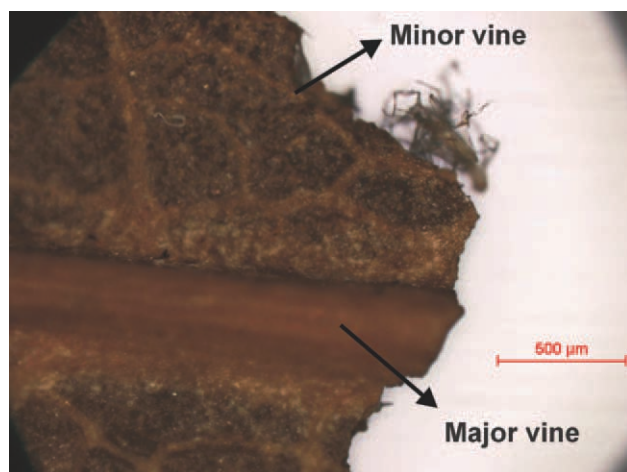
adequate impregnation between the leaves and the resin. We focused our attention on the elimination of the waxy substances from the surface of the leaves employing two different methods; the first one used a mixture of benzene and ethanol (B–E) and the second one consisted in the use of boiling water (bH$_2$O). Also, in that study the dewaxed leaves were treated with silane (γ-MPS) with the objective of improving the adhesion between the resin and the leaves. We found that both the dewaxed leaves with γ-MPS gave good compatibility between the AESO resin and the fiber, while the wettability with B–E and boiling water without treatment did not give acceptable results.

In this study, we decided to use chopped leaves instead of the whole leaves and to dewax them using three different treatments, the two mentioned above and a third one that consisted in the use of a strong detergent. Furthermore, the type of bio-based resin (MAESO and MAELO) was different from the one used in our previous study (AESO); we used resins that contained maleinated acrylated vegetable oils and due to their higher functionality should lead to composites with better mechanical properties than AESO.[1,2]

Red oak pollen is a well known allergen and potentially could cause some problems in the processing of red oak leaves and the final use of composite structures. This could involve worker exposure during processing and manufacturing and end-user exposure of finished materials, e.g., furniture. However, the 20–40 micron sized pollen particles are quite round or oval with an aspect ratio of 1–2 and are designed for distribution by wind such that the allergen activity occurs in humans by contact of the pollen with mucous membranes. Thus, the leaves contain at worst a light dusting of these pollen particles which can be readily removed by any of the washing treatments described herein. However, worker exposure could occur during the collection, chopping, prewashing and dewaxing treatments, and proper air control of the process needs to be maintained. If minute traces of pollen remain on the leaves after the washing process, resin infusion of the leaves during composite manufacturing would essentially encapsulate the pollen in a thermoset such that in the normal use

Figure 4. Fractured single leave test sample featuring the minor and major vines that can mostly carry the tensile load. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Composite panel prepared using VARTM with AESO and northern red oak (*Quercus robur*) leaves treated with B-E-γ-MPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
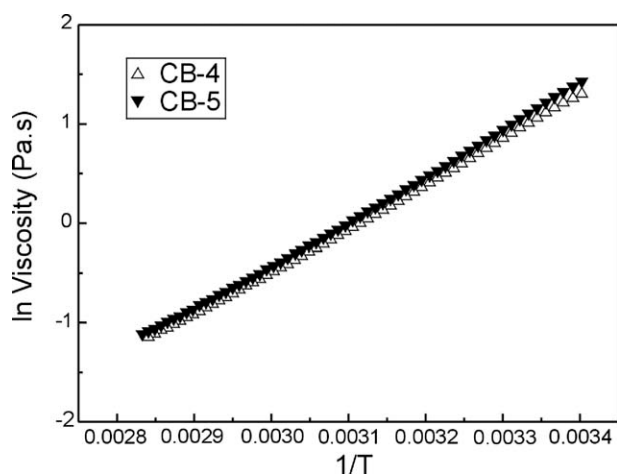
Figure 6. Viscosity as a function of temperature for CREY4 and CREY5 plant oil-based composite resins

of composite materials, contact with mucous membranes is expected to be negligible.

Resin Viscosity

Liquid molding technique, such as resin transfer molding (RTM) and VARTM are the processes of injecting reactive resins into a closed mold cavity containing fibrous pre-forms. During the resin injection, the viscosity of the resin increases due to the cure reaction. The increase of viscosity can result in the deformation of preforms and incomplete mold filling. Therefore, the knowledge of the viscosity and gel point development during the impregnation phase is important. The composite industry has established that the viscosity range for liquid molding resin should be between 0.2 and 1.0 Pa·s (200–1000 cP) in order to ensure good processability and properties.

Rheological measurements of the bio-based resins were performed to obtain changes in viscosity with temperature. The viscosity of all the samples decreased in an exponential manner with the temperature. The temperature dependence was modeled with the Arrhenius equation[27,28]:

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \quad (1)$$

where η is the viscosity (Pa·s), η_o is the prefactor, E_η is the activation energy for the viscous flow (J/mol), R is the ideal gas constant [8.314 J/(K mol)] and T is the absolute temperature (K).

The changes in viscosity with temperature for these two bio-based resins (e.g. CREY4 and CREY5) are plotted in Figure 6. The results for both resins nearly superimpose. The E_η obtained from the plot was 4413 J/mol for CREY4 and 4500 J/mol for CREY5. E_η increased slightly with the addition of more functional groups to the TGD structure (e.g., the initial content of C=C groups per TGD before the addition of the functional groups for CREY4 was ∼ 4.50 and for CREY5 was ∼ 4.95).[1,9,24,29] The functional groups increase the intermolecular interactions via hydrogen bonding and dipole–dipole interactions, which

increases E_η.[1,9,24,29] The molecular weight also increases slightly due to the addition of more carboxylic acids groups to the TGD structure.[1,9,24,29] So slightly higher Arrhenius parameters and viscosities were obtained for CREY5 compared to CREY4, due to higher molecular weight and polarity.

As shown in Figure 7 the initial viscosities of the resins at room temperature were higher than the requirement established by the composite industry (3.02 Pa·s and 3.38 Pa·s for CREY4 and CREY5, respectively), so it will not be possible to use these resins with VARTM at room temperature. However, we still can process our composites using higher temperatures. For example, at 90°C the viscosity of CREY4 was 0.25 Pa·s and of CREY5 was 0.30 Pa·s. Figure 7 also shows the experimental results on resins with the addition of 1.5 wt % of initiator at a constant temperature (25 or 90°C) using a shear rate of 1 s^{-1}. In this plot, we can observe that at 90°C the viscosity starts increasing in an exponential way after 150 min. We also note that the time required for the resin with the initiator to reach 5.0 Pa·s at room temperature was 140 min for CREY4 and 85 min for
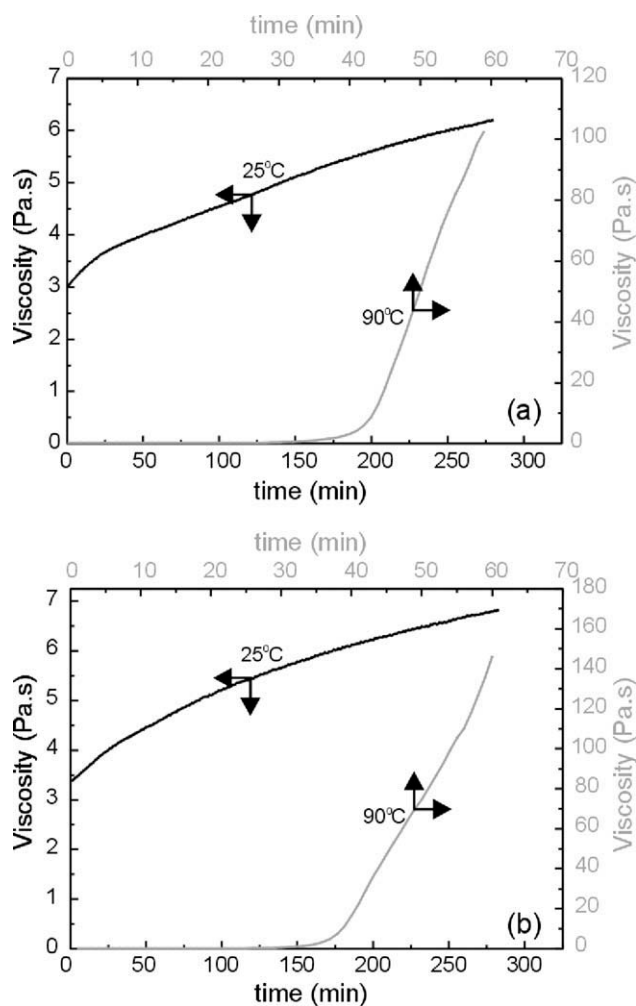

Figure 7. Viscosity as a function of the time for two different temperatures (25 and 90°C) using a shear rate of 1 s^{-1}. The samples consisted of the bio-based resin with 1.5 wt % of initiator, where (a) corresponds to CREY4 and (b) corresponds to CREY5.
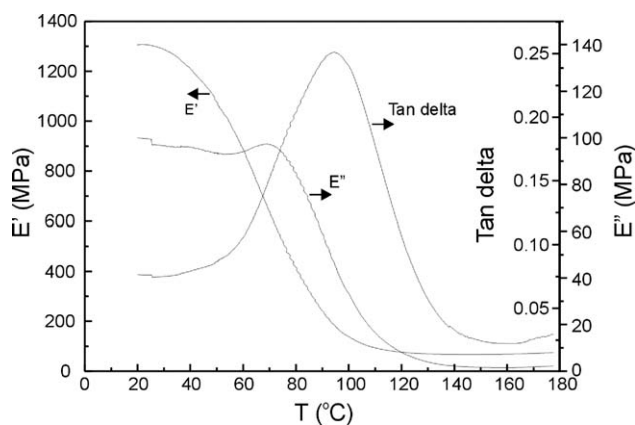
Figure 8. Dynamical mechanical behavior of the composites.

CREY5; and at 90°C it took 42 min for CREY4 and 37 min for CREY5. Due to the results obtained in this section we decided to cure our resins at higher temperatures to avoid any problem with the processability and quality of the resin and to decrease the curing time. The lower viscosity should also enhance resin infusion and diffusion into the interior of the leaves thereby reducing voids and defects and providing a greater opportunity for healing the defects and improving mechanical integrity.

Composite Modulus and Glass Transition

Composite parts were made from the differently treated leaves and bio-based resins (CREY4 and CREY5) as listed in Table I. The modulus and glass transition temperature (T_g) were measured at a temperature range of 20 to 180°C for the different composite specimens. Figure 8 shows typical dynamical mechanical behavior of one of the composites. The temperature at which the tan delta maximum occurs was used as a measure of

Table II. Glass Transition Temperature (T_g) and Storage Modulus (E') at 30°C for the Bio-Based Composites (CREY4 and Treated Leaves) as a Function of the Different Methods Used to Treat the Leaves

Sample	Leaf treatment method[a]	E' at 30°C (MPa)	T_g (°C)
I	–	1184	82.0
III	c 1 min[b]	310	83.1
IV	c 10 min[b]	1113	82.0
V	bH$_2$O, c 5 min	1210	84.5
VI	bH$_2$O, c 1 min	1140	84.2
VII	bH$_2$O, c 10 min	1345	83.6
IX	bH$_2$O and γ-MPS, c 5 min	1287	93.0
XI	B-E-γ-MPS, c 5 min	1229	91.2
XIII	2 wt% SD, c 5 min	1122	83.5
XIV	5 wt% SD, c 5 min	1182	83.0
XV	10 wt% SD, c 5 min	1236	83.2
XVI	Carbonized-215°C	1184	83.5
XVII	Carbonized-215°C–400°C	1221	90.8

[a] bH$_2$O, boiling water, B-E, benzene–ethanol; γ-MPS, silane solution; SD, strong detergent; c, chopped time, [b] The leaves were only washed, no other treatment was conducted on leaves.

the T_g. Tables II and III list the T_g and storage modulus (E') at 30°C of the bio-based composites as a function of the different methods employed to treat the leaves.

Between the washed leaves and washed–dewaxed bH$_2$O leaves, there was no difference in the value of the T_g; however, E' at 30°C increased from 1184 MPa to 1345 MPa when the leaves were dewaxed (see samples VIII, IX, XIII, and XIV; Table II) and chopped for 10 min. Comparing sample I and IX, one could deduce the leaf modulus E_L from a simple (lower bound) rule of mixtures using:

$$E_L = \phi_L E_C / [1 - \phi_M E_C / E_M] \qquad (2)$$

in which ϕ_L, E_C, ϕ_M, and E_M are the volume fraction of leaves, composite modulus, volume fraction of matrix and matrix modulus, respectively.

$$\phi_L = (\rho_M w_L) / (\rho_L w_M + \rho_M w_L) \qquad (3)$$

$$\phi_M = (1 - \phi_L) \qquad (4)$$

where ρ_L is the density of the leaf (which we assumed equal to 1 g/mL), w_L is the weight fraction of leaves, ρ_M is the density of the matrix (e.g., $\rho_M = 1.02$ g/mL), and w_M is the weight fraction of matrix in the composite. From Tables I and II, we have $\phi_L = 0.1$, $E_C = 1345$ MPa, $\phi_M = 0.9$, and $E_M = 1184$ MPa. From eq. (2), we then obtain the modulus of a chopped leaf as $E_L = 5290$ MPa. This value is modest by normal composite standards, e.g., fiberglass with typical E_c values ~ 10–20 GPa but it is still suited to such high volume composite applications such as furniture, housing construction, and packaging. If one were to make a higher leaf content composite, e.g., using $\phi_L = 0.5$ then eq. (2) would give the composite modulus as $E_C = 1935$ MPa. Thus, the composite properties can be improved using leaves, but most importantly, given the very low cost of the leaves, the resultant composite will have a proportionally lower cost and a high green content.

The leaves treated with different concentrations of strong detergent (2 to 10 wt %) at room temperature and chopped for 5 min had similar T_g values, but showed a slightly different storage modulus (see samples X to XII; Table II). The leaves dewaxed with 10 wt % of strong detergent (SD) had a slightly higher E' at

Table III. Glass Transition Temperature (T_g) and Storage Modulus (E') at 30°C of the Bio-Based Composites (CREY5 and Treated Leaves) as a Function of the Different Methods Used to Treat the Leaves

Sample	Leaf treatment method[a]	E' at 30°C (MPa)	T_g (°C)
II	–	1210	88.0
VIII	bH$_2$O and γ-MPS, c 5 min	1289	95.9
X	B-E and γ-MPS, c 5 min	1227	94.4
XII	bH$_2$O, c 5 min	1215	92.8

[a] bH$_2$O, boiling water; B-E, benzene–ethanol; γ-MPS, silane solution; c, chopped time.

30°C than the others due to a better dewaxing process that allowed better wettability between the leaves and the resin.

It can also be inferred from Table II comparing the different dewaxing treatments (where the leaves were chopped for 5 min) that the samples dewaxed with 10 wt % of SD had similar mechanical properties to those samples treated with bH$_2$O (samples III and X). So both procedures can be used as a green dewaxing method. Therefore, they can be considered as a good alternative to the organic solvent methods that are usually employed. The process with SD seems more profitable due to the high energy requirements of the bH$_2$O method; and therefore it will be better to conduct any dewaxing process at ambient temperature due to environmental and economic impacts.

The T_g and E' of the composites made from both resins can be found in Tables II and III. It can be observed that when CREY5 is used, products with higher T_g and E' are obtained. CREY4 is made from soybean oil, while CREY5 is made from soybean and linseed oils. As mention previously, this latter resin had more functional groups to the TGD structure which resulted in composites with improved mechanical properties.[1,29,30]

In our previous work with AESO, the leaves were dewaxed employing two treatments (B–E and bH$_2$O); using the B-Et treatment, we were able to obtain slightly higher mechanical properties than the composites prepared employing only the bH$_2$O method.[26] To improve the compatibility between the resin and the leaves, we subjected the dewaxed leaves to a silane (γ-MPS) treatment. We found that the composites prepared with natural resins (CREY4 and CREY5) and treated leaves with boiling water and γ-MPS led to samples with higher mechanical properties, higher T_g and E' (samples IV, V, XVI and XVII; Tables II and III). Therefore, the γ-MPS improves the adhesion between the matrix and the fibers, improving the mechanical properties. Analyzing Tables II and III, we can also infer that there is almost no difference between the resins without leaves and the resin with dewaxed leaves. This suggests that the advantage of incorporating leaves into the polymeric matrix is due to the efficient use of waste and the minimization of energy requirements and cost because there will be no need to burn the fall leaves collected in the cities and the leaves can provide composite reinforcement and material replacement. The unit operations processing costs (washing and drying) of the leaves are expected to add about $0.2–0.3/lb or $0.45–0.67/kg to the cost of the leaves. If collection costs are nominally $0.1/lb, this gives a leaf filler cost of about $0.3–0.4/lb. Since the resin cost is of order $1.5/lb, use of the leaf filler at 50 wt % gives a composite at a cost of $0.9–0.95/lb.

Carbonized Leaves
In this work, we inquired to see if carbonized leaves can be used to improve the mechanical properties, taking account of previous work done with carbonized chicken feathers.[31–33] Figure 9 shows the result of the TGA experiment for chopped leaves in an inert atmosphere. The leaves show considerable stability up to $T \sim 260°C$, above which a significant decrease in mass is observed from 300 to 500°C, with a maximum rate of degradation around 325°C. Using this data, we explored pyrolyzed samples subjected to 215°C for 12 h (sample VI) and 400°C for 1 h (sample VII) listed in Table I. Composite sample properties are shown in
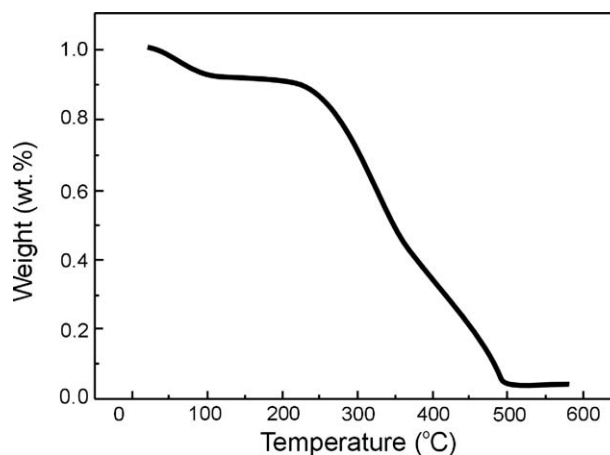

Figure 9. Result of the TGA experiment for chopped leaves in an inert atmosphere.

Table II. Sample VI gave carbonized leaves that had a fragile structure; therefore, the composites employed with this sample did not give composites with good properties. Sample VII gave a powder that was used as filler at about 10 wt % and using this specimen we were able to obtain a biocomposite with improved mechanical properties, where we observed an increase in modulus from 1184 to 1221 MPa and an increase in T_g from 82 to 91°C. The properties obtained with this sample were similar to the ones obtained with sample IV and V. More studies need to be done to understand the leaf pyrolysis process, but it seems as a good alternative to the silane treatment process.

CONCLUSIONS

Composite materials were successfully made out of plant oil-based resin and northern red oak (*Quercus robur*) leaves collected in the fall, achieving mechanical properties desired for some applications, such as furniture for homes, toys, and other applications. The following points are made in summary:

1. The viscosities of the bio-based resins (MAESO and MAELO) were suited to high temperature RTM and VARTM.
2. The leaves have an external epidermal surface cover of a waxy layer that does not allow a good adhesion between the resin and the leaf. Therefore, the leaves need to be dewaxed prior to its use in a composite part. In this work, we used different treatments (such as benzene–ethanol, boiling water, and strong detergent) to dewax the leaves; all three methods seem to give good results; but boiling water and strong detergent can be consider as a greener dewaxing method, and an alternative to the common organic solvent treatment.
3. After the dewaxing process, the compatibility between the resin and the leaves was improved with a silane treatment. With this treatment we were able to obtain low-cost natural composites with higher mechanical stiffness than the resin itself. With 10 wt % leaves, we obtained an improvement in the composite modulus of about 14% from which we could estimate the leaf modulus at about 5.3 GPa. This value is significantly higher than that obtained for dried leaf samples.

4. An alternative method to produce biocomposites from leaves without the need for silane treatments consists in carbonizing the washed leaves first at 215°C for 12 h, and then at 450°C for 1 h. The composite produced with carbonized leaves had similar properties to the composites produced with bio-based resin and dewaxed leaves treated with silane.

5. The composites made with leaves and bioresins derived from functionalized triglycerides have the potential for use in high volume applications with low costs such as housing, construction, civil infrastructure, toys, and furniture.

6. The use of leaves as a biocomposite filler has several advantages including (a) reduced cost, (b) improved properties of the resin, (c) composite with high bio content, (d) removal of a waste material with subsequent prevention of burning with attendant health hazards, and (e) interesting design aesthetics for interior and exterior decoration.

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