

Sugarcane Bagasse Composites from Vegetable Oils

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ABSTRACT: Sugarcane bagasse composites have been prepared by the free radical polymerization of regular or modified vegetable oils with divinylbenzene and *n*-butyl methacrylate in the presence of dried, ground sugarcane bagasse. Various cure times and temperatures have been investigated to determine the optimum cure sequence for the new materials. The postcure time has also been varied, and an ideal postcure treatment of 1 h at 180°C at ambient pressure has given the best overall properties. The effect of varying the filler load and resin composition has been assessed by means of tensile tests, dynamic mechanical

analysis, thermogravimetric analysis, Soxhlet extraction, followed by proton nuclear magnetic resonance spectroscopic analysis of the extracts, and scanning electron microscopy. It has been observed that the initial washing and drying of the filler influence the filler–resin interaction and impact the final properties of the composites. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: composites; copolymerization; mechanical properties; vegetable oil; sugarcane bagasse

INTRODUCTION

The partial replacement of petroleum-derived plastics and composites by novel bio-based materials from inexpensive, renewable, and natural resources such as vegetable oils and agricultural residues has the potential to greatly impact the plastics and coatings industries. Such natural starting materials tend to be readily available in large quantities and at low price and can possibly afford more biodegradable materials than the virtually indestructible petroleum-based polymers. Furthermore, new bio-based materials may present properties not currently available in commercial petroleum products, with an overall intrinsic low toxicity. These characteristics make bio-based materials very appealing from an industrial point of view, and research in this area may lead to significant progress toward oil independence and sustainable industrial development.

Currently, a variety of chemicals and materials are prepared from vegetable oils, polysaccharides, wood, or proteins.¹ As an example, bio-oil and syngas are obtained from the pyrolysis of wood and agricultural wastes.² Soybean and corn proteins can be denatured and aligned to prepare protein-based bio-

polymers,^{3,4} and vegetable oils find wide use in paints,⁵ biocoatings,⁶ biofuels,⁷ and as building blocks for bio-based resins^{8–15} such as polyurethanes,^{8–10} polyester amides,¹¹ multicomponent thermosets,^{12–15} and cyanate esters.¹⁶ Some of these systems have been reinforced with nanoclays¹⁷ and glass fibers.^{18,19}

Alternatively, “green” composites can be prepared by the reinforcement of standard petroleum-derived thermoplastics, such as high-density polyethylene, with natural fillers, such as sugarcane bagasse²⁰ or wheat straw.²¹ Similarly, polypropylene has been reinforced with palm and coir fibers.²² There exist several other possible combinations of thermoplastics and natural fillers that are not explicitly cited here. More recently, some progress on the reinforcement of blends of petroleum-derived unsaturated epoxy resins and epoxidized soybean oil with hemp fibers has been reported.²³

In an effort to incorporate high biorenewable content into polymer blends, Lu and Larock¹⁵ at Iowa State University have developed a variety of vegetable oil-based thermosets with good thermal and mechanical properties. Cationic, free radical, and thermal copolymerization of regular and conjugated natural oils in the presence of various petroleum-based comonomers have yielded materials ranging from elastomers to rigid thermosets.¹⁵ The reactive sites in these vegetable oil-based systems are the carbon–carbon double bonds. Overall, the reactivity of the triglycerides toward the aforementioned polymerization processes can be significantly enhanced if the carbon–carbon double bonds in the

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fatty acid chains are isomerized and brought into conjugation.²⁴ More recently, the synthesis of bio-based polymers making use of alternative polymerization methods, including ring-opening metathesis polymerization⁶ and acyclic diene metathesis,²⁵ has also been investigated.

The cationic polymerization of vegetable oils¹⁵ in the presence of petroleum-derived comonomers avoids the entrapment of bubbles in the resin, which are usually seen when azobisisobutyronitrile is used as a free radical initiator. It also limits crack formation related to shrinkage of the resin during cure. Significant improvements in the properties of bio-based polymers can be obtained by simply reinforcing these cationic vegetable oil-based matrices with inorganic¹⁹ or natural fillers.^{26–28}

In the preparation of bio-based composites reinforced with soybean²⁶ and rice hulls,²⁷ it has been demonstrated that peroxide free radical initiators are effective in reacting with the carbon–carbon double bonds in the oils and the other comonomers used in the presence of lignocellulosic materials. The presence of bio-based filler particles minimizes shrinkage of the resin and only minimal microcracks have been detected by scanning electron microscopy (SEM) of the soybean hull composites.²⁶ Recent studies of natural filler-reinforced composites have suggested that maleic anhydride (MA) can serve as a good filler–resin compatibilizer and helps to improve the stress transfer from the matrix to the reinforcement, resulting in an overall increase in the mechanical properties.²⁷

These new bio-based composites contain up to 85 wt % of biorenewable content, including the resin and the filler.^{26–28} The technology involved in their preparation is remarkably simple and they have great potential in the automobile and construction industries.

Herein, we investigate the effects of cure parameters on the mechanical properties of vegetable oil-based thermosets reinforced with sugarcane bagasse. Our goal is to achieve the highest possible mechanical properties with the bio-based system under investigation. Vegetable oils with different numbers of carbon–carbon double bonds per triglyceride have been used for the preparation of the bio-based composites. Cure sequence, filler load, and resin composition have been varied, and the resulting properties of the composites have been assessed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile tests, dynamic mechanical analysis (DMA), and Soxhlet extraction, followed by proton nuclear magnetic resonance (¹H-NMR) spectroscopic analysis of the extracts. The results provide insight into the filler–resin interactions and the thermal stability of the filler present in the composite.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA). Divinylbenzene (DVB), MA, di-*t*-butyl peroxide (TBPO), and tung oil (TUN) were purchased from Sigma-Aldrich (St. Louis, MO). All were used as received. Soybean oil (Great Value Brand, Bentonville, AR) was purchased in a local grocery store, and Superb linseed oil was provided by Archer Daniels Midland (Red Wing, MN). Both oils have been conjugated using a rhodium catalyst, following a method developed and frequently used by our group.²⁴ The sugarcane bagasse was generously provided by the US Sugar Corporation (Clewiston, FL).

The sugarcane bagasse fibers were washed with water and dried at 50°C overnight. To ensure complete removal of moisture, after being ground to particle sizes <2.0 mm, the filler has been placed in a vacuum oven at 70°C overnight and has been impregnated with the resin right after the drying process.

General procedure for preparation of the bio-based composites

The crude resin was obtained by mixing the conjugated or regular vegetable oil, BMA, and DVB in a beaker. MA was melted in a hot water bath and quickly added to the crude resin mixture at room temperature under agitation, along with the free radical initiator TBPO. The natural fillers were impregnated with the crude resin and compression molded at 600 psi in a 6" × 6" steel mold to produce samples with a thickness of ~ 2.5 mm. The composites were then removed from the mold and post-cured in a convection oven at ambient pressure.

In an alternative procedure, the resin has been precured prior to compression molding in the presence of the fillers. This process did not afford viable materials, and the samples prepared by this method are therefore not discussed here.

In all composites produced, the resin has a vegetable oil content of 50 wt %, and the optimum amount of TBPO has been determined to be in preliminary tests an extra 5 wt % of the total resin weight. The homolytic cleavage of oxygen–oxygen bonds in TBPO initiates at 80°C, a temperature well below the boiling points of all of the comonomers used in this work. When the crude resin mixture is heated at the desired temperature (>140°C), the majority of the added free radical initiator has reacted and initiated polymerization of the resin components. Therefore, the loss of resin components due to evaporation inside the mold is not observed. This also prevents formation of bubbles in the final product. The

vegetable oil used and the amounts of BMA and MA have been varied, as indicated in the text, to produce composites of various compositions.

The total composite weight, including the sugarcane bagasse and the crude resin, is 100 g. The free radical initiator was carefully chosen taking into account the initiation temperature so that no loss of resin components by evaporation would occur. The filler load variations reported in this study were also carefully chosen so that no resin leakage from the mold is observed. As a consequence, no loss in weight has been detected before or after the cure of the composites.

Characterization of the composites

Tensile tests were conducted at room temperature according to ASTM D-638, using an Instron universal testing machine (Model 5569) equipped with a video extensometer and operating at a crosshead speed of 2.0 mm/min. Dogbone-shaped test specimens were machined from the original samples to give the following gauge dimensions: 57.0 mm \times 12.7 mm \times 4.5 mm (length \times width \times thickness, respectively). For each composite, seven dogbones were cut and tested. The results presented are the average of these measurements along with the calculated standard deviation.

DMA experiments were conducted on a Q800 DMA (TA Instruments, New Castle, DE) using a three-point bending mode with a 10.0-mm clamp. Rectangular specimens of 22.0 mm \times 8.5 mm \times 1.5 mm (length \times width \times thickness, respectively) were cut from the original samples. Each specimen was cooled to -60°C and then heated to 250°C at $3^{\circ}\text{C}/\text{min}$. The experiment was conducted using a frequency of 1 Hz and an amplitude of 14 μm under air. Two runs for each sample were carried out, and the results presented reflect the average of the two measurements.

Soxhlet extraction was conducted to determine the degree of incorporation of the resin components into the final thermoset. The amount of soluble material recovered after the extraction of 2.0 g of a composite sample with dichloromethane (CH_2Cl_2) for 24 h is an indication of the extent of resin polymerization and crosslink density. After extraction, the soluble materials were recovered by evaporating the CH_2Cl_2 under vacuum. Both soluble and insoluble materials were dried overnight at 70°C . The dried soluble fraction was then dissolved in deuterated chloroform (CDCl_3), and the corresponding ^1H -NMR spectrum was obtained using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA), operating at 300 MHz. The ^1H -NMR spectra helped to determine the identity of the soluble materials in each sample.

DSC experiments were performed on a Q20 DSC (TA Instruments) under a N_2 atmosphere over a temperature range of -20 to 400°C , while heating at a rate of $20^{\circ}\text{C}/\text{min}$. The samples weighed ~ 10 mg.

A Q50 TGA instrument (TA Instruments) was used to measure the weight loss of the samples under an air atmosphere. The samples (~ 10 mg) were heated from room temperature to 650°C at a rate of $20^{\circ}\text{C}/\text{min}$.

For the SEM analysis, a section of the sample was mechanically cut and shaved with a razor blade to provide a smooth cross section. The cut samples were examined using an Hitachi S-2460N variable-pressure SEM. The microscope was operated at 20 kV accelerating voltage, with 60 Pa of helium atmosphere, and a 25 mm working distance. Backscattered electron images were collected using a Tetra BSE detector (Oxford Instruments, Oxfordshire, United Kingdom) at $100\times$ magnification.

RESULTS AND DISCUSSION

Cure analysis

Cure time and temperature

In an effort to keep the cure times as short as possible, an appropriate cure sequence for the sugarcane bagasse composites has been investigated. Six different heating treatments have been applied to composites bearing 70 wt % of filler and a resin composed of 50 wt % of conjugated soybean oil (CSO), 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA. The mechanical properties of the corresponding materials have been compared, and the results are presented in Table I, along with the percentage of soluble material recovered after Soxhlet extraction of the samples.

Initially, two cure temperatures have been compared (Table I, entries 1 and 2), maintaining a postcure time of 2 h. When the composite is cured at 180°C for 5 h (Table I, entry 1), the resulting material is significantly degraded, and dogbone specimens cannot be obtained to conduct the tensile tests. The use of lower cure and postcure temperatures (Table I, entry 2) results in a completely cured material, with less degradation of the filler, as indicated by the higher storage modulus at 25°C . Although the material cured at 160°C for 5 h (Table I, entry 2) shows good mechanical properties, the dark color and the burnt smell observed, when demolding the sample, suggest that the fillers are still considerably degraded.

Finally, a two-step cure process has been tested, in which the sample is heated at 140°C for 3 h and at 160°C for another 3 h, before being submitted to the 2-h postcure step (Table I, entry 3). In this case, despite the overall longer time in the hot press, the sample was exposed to the maximum temperature

TABLE I
Tensile and Flexural Properties, Along with the Soxhlet Extraction Results, for Sugarcane Bagasse Composites Cured Under Various Cure Sequences^a

Entry	Cure temperature (°C)/time (h)	Postcure temperature (°C)/time (h)	<i>E</i> (GPa)	Tensile strength (MPa)	<i>E'</i> (MPa) at 25°C	Soluble content (wt %) ^b
1	180/5	200/2	–	–	1032	5
2	160/5	180/2	3.2 ± 0.5	10.0 ± 1.7	1272	6
3	140/3 160/3 ^c	180/2	2.9 ± 0.5	11.6 ± 1.5	597	5
4	140/3 160/3 ^c	180/0.5	2.5 ± 0.4	6.8 ± 1.3	2437	8
5	140/3 160/3 ^c	180/1	3.4 ± 0.4	12.6 ± 2.9	1137	6
6	140/3 160/3 ^c	180/3	–	–	1603	7

^a The filler/resin ratio is 70/30 and the resin composition is 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA.

^b Determined after Soxhlet extraction with CH₂Cl₂ for 24 h.

^c The cure sequence is composed of two stages.

for a shorter time and did not darken significantly or exhibit any burnt odor after the process. The results for the Young's modulus and tensile strength are comparable with those obtained for the sample cured at 160°C for 5 h (Table I, entry 2), as the difference between the numbers fall within the standard deviation of the measurements. Although a significantly lower storage modulus at 25°C is observed (Table I, entry 3 versus entries 1 and 2), there is only 1 wt % variation in the soluble content of the samples. In fact, the amount of soluble material recovered after Soxhlet extraction is inversely proportional to the degree of incorporation of the resin components into the final composite. The soluble content of samples cured at different temperatures (Table I, entries 1–3) is strong evidence that the extent of the reactions is very similar in those composites. These results, along with the much lower thermal stability of the filler with respect to the pure resin (see Fig. 2), indicate that the changes in the mechanical properties observed are a consequence of partial filler degradation, rather than differences in crosslink density and/or the extent of monomer incorporation into the matrix.

Although higher temperatures seem to degrade the core structure of the filler, longer cure times slowly degrade the least thermally stable components of the filler, affecting the interface between filler and resin, which results in poor stress transfer from the matrix to the reinforcement and a lower storage modulus. In conclusion, the two-step cure sequence has been chosen as ideal because of concerns about the thermal stability of the filler. A more thorough analysis of the filler's thermal stability will be presented later in the text when discussing the TGA results.

Postcure time

After establishing the ideal cure process, as discussed above, a study of the postcure time has been carried out. Samples with the same composition and submitted to the same cure sequence have been postcured for times varying from 0.5 to 3 h, and their mechanical properties and soluble content have been compared (Table I, entries 3–6). It has been previously shown that the postcure of vegetable oil-based composites reinforced with rice hulls is crucial to get a fully crosslinked material with maximum monomer incorporation into the matrix and the best mechanical properties possible.²⁸ Indeed, the postcure process ensures that any unreacted carbon-carbon double bonds in the polymers and oligomers formed during compression molding react, leading most likely to an increased crosslink density. In fact, the resin still contains reactive sites that can be used to improve the composite's properties after the initial compression molding step, with no evidence of significant filler degradation. An overall improvement in the mechanical properties can be achieved by postcuring the composite at an appropriate temperature and time.

When comparing samples postcured for 0.5 and 1 h (Table I, entries 4 and 5), it is apparent that the 0.5-h postcure step is not sufficient to fully cure the resin. Besides the significantly lower tensile properties, the sample postcured for 0.5 h still exhibits a strong odor of unreacted monomers, indicating that the resin components are not fully incorporated into the matrix. Further evidence of that is the relatively high percentage of soluble materials recovered after Soxhlet extraction of the material when compared with entry 5 (Table I). Interestingly, the sample

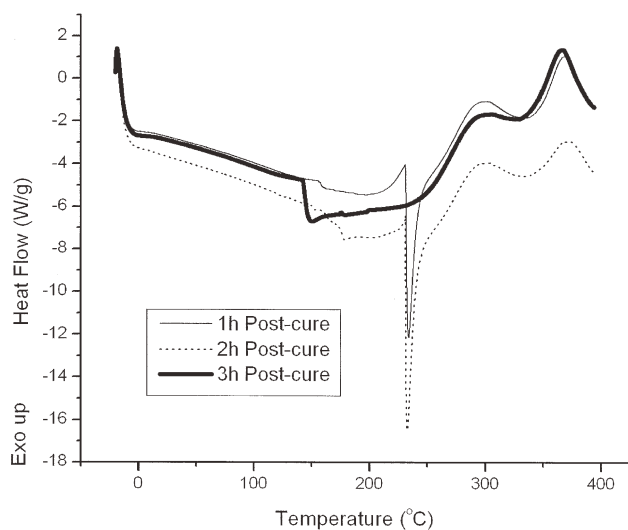


Figure 1 DSC curves for 70 wt % filled sugarcane bagasse composites postcured at 180°C for varying times. The resin composition is 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA, and the cure sequence consists of 3 h at 140°C, followed by 3 h at 160°C.

postcured for 0.5 h exhibits a significantly higher storage modulus. The DMA experiments have been repeated twice, and similar results have been found each time. This supports the hypothesis that longer heating times have a negative impact on the filler structure, especially at the filler–matrix interface.

When the postcure time is increased to 2 h (Table I, entry 3), the differences in the tensile properties, with respect to the sample postcured for 1 h, fall within the standard deviation of the measurements, and similar soluble contents are found. Nevertheless, a significant decrease in storage modulus is again observed.

The tensile properties of the sample postcured for 3 h could not be obtained because of severe degradation of the filler during the heat treatment (Table I, entry 6). The increase in storage modulus at 25°C with respect to entry 3 (Table I) does not follow the trend observed for the other samples and can possibly be related to nonhomogeneity of the material after degradation of the filler. Unfortunately, no more than two DMA specimens could be obtained for that particular sample to either confirm or discard the results presented. There is a slight increase in the soluble content that might be a consequence of fragmentation of the resin components, yielding CSO fragments and oligomers that can then be extracted during the Soxhlet extraction process.

Figure 1 depicts the DSC curves of samples postcured at the same temperature, but for different times. For clarity purposes, the sample postcured for 0.5 h has been omitted (individual DSC curves of all of the samples produced for the cure study are pro-

vided in the Supporting Information). When analyzing the DSC curve of the sample postcured for 1 h, some characteristic features are observed. There is a small exothermic peak at 156°C attributed to residual crosslinking of the matrix components. The sharp endothermic peak at 234°C is associated with initial thermal degradation of the filler, and all of the other peaks above 250°C are related to degradation of the different components of the materials being analyzed.²⁸ When the composite is postcured for 2 h, a very similar DSC curve is obtained, with the same features described for the sample cured for 1 h. There is only an increase in the temperature of the residual cure peak from 156 to 178°C. On the other hand, the sample postcured for 3 h gave a very distinct DSC curve. No exothermic peaks are detected. The endothermic peak occurs at a significantly lower temperature (149°C), and it is significantly less intense and broader than the ones observed in the other DSC curves. These results confirm that the 3-h postcure is responsible for extensive degradation of the material in comparison with the 1- and 2-h processes. Otherwise, except for the storage modulus, no significant differences have been found between composites postcured for 1 and 2 h. In view of these facts, the 1-h postcure has been chosen as the ideal and has been used in the preparation of all of the composites in the remainder of this project.

Filler load evaluation

The properties of sugarcane bagasse composites prepared with filler loads varying from 60 to 80 wt % are summarized in Table II. For comparison purposes, the properties of the unreinforced resin and the pure filler have also been included (Table II, entries 1 and 5, respectively). The resin, unless otherwise noted, is composed of 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA. The composites were cured for 3 h at 140°C, followed by another 3 h at 160°C, and postcured for 1 h at 180°C.

The reinforcing effect of sugarcane bagasse can be clearly observed when comparing the storage modulus results of the unreinforced resin and a composite containing 60 wt % of sugarcane bagasse (Table II, entries 1 and 2). Indeed, a fivefold improvement in E' at 25°C and an eightfold improvement in E' at $T_{g_2} + 50^\circ\text{C}$ (where T_{g_2} is the second glass transition temperature associated with the phase-separated resin, as explained when discussing the resin composition) are observed when sugarcane bagasse is added to the resin. When the filler content is increased from 60 to 80 wt % (Table II, entries 2–4), a decrease in the tensile properties is observed. As indicated by SEM images of soybean²⁶ and rice hull^{27,28}

TABLE II
Characterization of Sugarcane Bagasse Composites Containing Various Filler Loads^a

Entry	Filler load (wt %)	E (GPa)	Tensile strength (MPa)	E' (MPa)		T_7 (°C)
				At 25°C	At $T_{g_2} + 50^\circ\text{C}$	
1	0 ^b	–	–	152	56	327
2	60	3.9 ± 1.2	15.7 ± 2.2	760	447	273
3	70	3.4 ± 0.4	12.6 ± 2.9	1137	680	265
4	80	2.6 ± 0.1	9.8 ± 1.3	694	302	258
5	100 ^c	–	–	–	–	245

^a The composites were cured for 3 h at 140°C, followed by another 3 h at 160°C, and postcured for 1 h at 180°C. The resin composition is 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA.

^b Unreinforced resin containing 50 wt % of CSO, 35 wt % of BMA, and 15 wt % of DVB.

^c Nondried sugarcane bagasse without resin.

composites with similar resin compositions, the higher filler content leads to agglomeration of the lignocellulosic particles and formation of weak points within the composite structure.

In the three-point bending mode of deformation, an increase in the filler content from 60 to 70 wt % is beneficial to the flexural properties of the composite, as noted by an increase in the storage modulus (Table II, entries 2 and 3). This behavior is in contrast to what has been observed for the tensile properties, leading to the conclusion that with a filler load of 70 wt %, the particle agglomeration is not sufficient to have a negative impact on the flexural properties. Instead, the reinforcing nature of the sugarcane bagasse particles prevails, resulting in an increase in the storage modulus. When the filler content is increased to 80 wt %, there is an excess of filler, as discussed earlier for the tensile properties, and a decrease in the storage modulus is observed (Table II, entry 4).

Homogeneous composites containing less than 60 wt % of sugarcane bagasse could not be obtained. The filler deposited on the bottom of the mold, and significant resin leakage from the mold during the cure has been observed. The resulting material exhibited a rough surface and the properties could not be measured. Likewise, a mixture of filler and resin beyond the 80/20 ratio does not result in viable composites, as the materials crumble too easily when handled, which is a consequence of the lack of enough resin to hold the filler particles together.

The thermal stability of the sugarcane bagasse composites is strongly dependent on the filler content, as evident when comparing the T_7 values of the composites containing 60 to 80 wt % of sugarcane bagasse [Table II (entries 2–4) and Fig. 2]. T_7 represents the temperature at which 7 wt % of the material has degraded in the TGA experiment. By comparing the T_7 values of the unreinforced resin and the sugarcane bagasse alone (Table II, entries 1 and

5), it becomes evident that the sugarcane bagasse is significantly less thermally stable than the vegetable oil-based resin. Therefore, it is expected that a mixture of the two components would result in a material with a thermal stability between those observed for the filler and the resin individually. As the amount of filler increases in the composite (Table II, entries 2–4), a gradual decrease in the T_7 value is observed, and the degradation temperature approaches that of the filler alone (Table II, entry 5). This trend can be better visualized in Figure 2.

Figure 2 illustrates the TGA curves of the unreinforced resin, the sugarcane bagasse, and composites containing 60 to 80 wt % of sugarcane bagasse (individual TGA curves of all of the samples produced for the cure study are provided in the Supporting

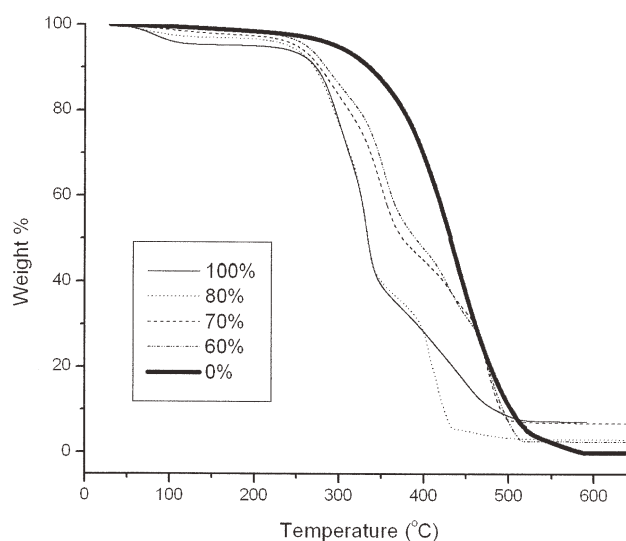


Figure 2 TGA curves for CSO-based composites reinforced with varying amounts of sugarcane bagasse. The resin composition is 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA, and the cure sequence consists of 3 h at 140°C, followed by 3 h at 160°C. The composites are postcured at 180°C for 1 h.

TABLE III
Characterization of Sugarcane Bagasse Composites with Various Resin Compositions^a

Entry	Oil (50 wt %)	BMA (wt %)	MA (wt %)	<i>E</i> (GPa)	Tensile strength (MPa)	<i>T</i> _{g1} (°C) ^b	<i>T</i> _{g2} (°C) ^b	<i>E'</i> at <i>T</i> _{g2} + 50°C (MPa)	Soluble content (wt %) ^c
1	CSO	35	–	3.0 ± 0.6	9.3 ± 0.4	15	115	676	4
2	CSO	20	15	3.9 ± 1.2	15.7 ± 2.2	–20	83	450	3
3	CLO	20	15	3.2 ± 0.4	13.8 ± 0.9	–24	76	1180	5
4	TUN	35	–	3.7 ± 0.7	16.2 ± 1.2	20	113	1169	2
5	TUN	20	15	3.5 ± 0.7	14.0 ± 0.7	10	74	895	7

^a The composites contained 60 wt % of filler and have been cured for 3 h at 140°C, followed by another 3 h at 160°C, and postcured for 1 h at 180°C.

^b Determined by DMA.

^c Determined after Soxhlet extraction with CH₂Cl₂ for 24 h.

Information). It is interesting to note that the thermal degradation of the unreinforced resin occurs in one major step, whereas that of the sugarcane bagasse can be divided into four well-defined steps. The first step corresponds to desorption of water from the filler structure and occurs between 80 and 110°C. The second step, from 251 to 320°C, corresponds to degradation of the hemicellulose. The third step, occurring in the 320 to 368°C temperature range, corresponds to degradation of the cellulose. The lignin component of biomass typically degrades over a wide range of temperatures.²⁸ In this case, the values determined from the derivative of the TGA curve (data not shown in Fig. 2) are 245–534°C.

The thermal degradation pattern observed for composites containing 60 to 80 wt % of the filler is similar to that obtained for the sugarcane bagasse alone, with four well-defined degradation stages. Significant differences are only observable in the degradation pattern after ~ 400°C, namely during degradation of the main resin components. In view of the results presented in this section, 60 wt % is considered to be the optimum amount of filler in these sugarcane bagasse composites, and this filler load has been used for the preparation of all composites in the remainder of this project.

Resin composition

It has been previously shown that changes in the resin composition can significantly affect the mechanical properties of bio-based composites.^{26,27} The use of vegetable oils with different numbers of carbon–carbon double bonds directly affects the crosslink density of the matrix and, as a consequence, differences in the tensile strength, and Young's and storage moduli have been observed when comparing CSO and conjugated linseed oil (CLO)-based rice hull composites.²⁷ Furthermore, the addition of MA as a filler–resin compatibilizer in vegetable oil-based rice hull composites has resulted in a significant improvement in the storage modulus

by promoting better stress transfer from the matrix to the reinforcement.²⁷ The chemical environment of the carbon–carbon double bond in MA is very similar to that of BMA, hence their similar reactivity toward free radical polymerization. The properties of sugarcane bagasse composites prepared with resins of various compositions are given in Table III.

From the results in Table III, it is evident that for composites prepared in the absence of MA, the choice of the oil used to prepare the resin has a strong influence on the tensile and flexural properties of the final composite material. Indeed, significant increases in the tensile strength and in the storage modulus at *T*_{g2} + 50°C are observed when TUN is used as the major resin component in comparison with CSO (Table III, entries 1 and 4). With an average of 7.9 carbon–carbon double bonds per triglyceride, TUN can form a matrix with a higher crosslink density than CSO (~ 4.5 carbon–carbon double bonds per triglyceride), which results in overall better mechanical properties. This hypothesis is supported by the soluble content recovered from the corresponding samples after Soxhlet extraction (Table III, entries 1 and 4). Indeed, the results obtained from the Soxhlet extraction of composites with different resin compositions give information about how much of the initial resin components have been incorporated into the final polymer. Although only 2 wt % of soluble material has been recovered from the sample prepared with TUN, a total of 4 wt % of soluble material has been recovered from the sample prepared with CSO. An exception to the trend of improved mechanical properties with the use of a more unsaturated oil is the Young's modulus. The difference in the stiffness of samples prepared with TUN and CSO is not significant and cannot be attributed to the structure of the oils used (Table III, entries 1 and 4).

For MA-containing composites (Table III, entries 2, 3, and 5), the relationship between the oil structure and the mechanical properties is not as clear as for the composites that do not contain MA. No

significant changes in the tensile properties are observed for samples prepared with different oils, as the results obtained for the Young's modulus and the tensile strength fall within the standard deviation of the corresponding measurements. When CLO (~ 6.0 carbon-carbon double bonds per triglyceride) is used as the major resin component, an increase in the storage modulus at $T_{g2} + 50^\circ\text{C}$ is observed when compared with the sample made from CSO (Table III, entries 2 and 3). However, a decrease in that number is observed when TUN is used (Table III, entry 5). The soluble content results are also opposite the expected trend, as more material is recovered from samples prepared with the more unsaturated oils. In fact, one would expect a higher reactivity and crosslink density when oils with a higher number of carbon-carbon double bonds per triglyceride are used as the major resin component, which would ultimately result in materials with improved mechanical properties and lower soluble content.

These results cannot be fully explained, but the deviation from the expected trends are possibly related to the initial treatment applied to the sugarcane bagasse. Although there is no solid evidence, a plausible explanation is that the wash and the extended drying to which the fillers have been submitted may have affected the surface of the lignocellulosic materials, and therefore altered their polarity, making them less hydrophilic. In that sense, MA no longer works as a compatibilizer between a hydrophobic matrix and a highly hydrophilic filler. On one hand, this leads to a better interaction between filler and resin even in the absence of MA. On the other hand, the addition of MA to the resin composition represents a decrease in the BMA content. As demonstrated previously with soybean and rice hull composites, the mechanical properties are also closely related to the BMA content of the resin.^{26,27}

The trend observed when comparing the mechanical properties of composites made with and without MA is further evidence of the poor compatibilizing effect that MA exhibits in this system. For CSO-containing composites (Table III, entries 1 and 2), the replacement of 15 wt % of BMA with 15 wt % of MA resulted in an expected increase in the tensile properties. Nevertheless, a significant decrease in the storage modulus at $T_{g2} + 50^\circ\text{C}$ is also observed. When TUN is the major resin component (Table III, entries 4 and 5), the addition of MA results in a decrease in all of the mechanical properties measured. The effect of substituting BMA by MA on the storage modulus can be better visualized in Figure 3, in which the curves of E' versus temperature for composites prepared with and without MA are plotted.

From a comparison of Figure 3(A,B), it is clear that the addition of MA to CSO-containing composites

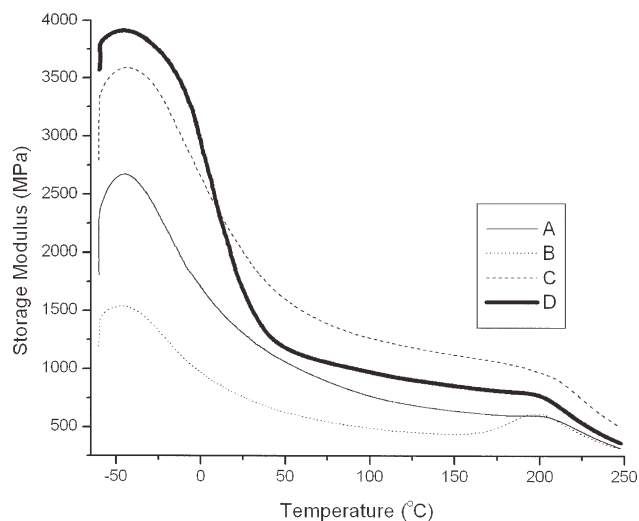


Figure 3 Storage modulus versus temperature for composites with the following resin compositions: (A) 50 wt % of CSO, 35 wt % of BMA, and 15 wt % of DVB; (B) 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA; (C) 50 wt % of TUN, 35 wt % of BMA, and 15 wt % of DVB; and (D) 50 wt % of TUN, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA. The composites possess a filler/resin ratio of 60/40 and have been cured for 3 h at 140°C and 3 h at 160°C and postcured for 1 h at 180°C .

results in a lower storage modulus throughout the temperature range investigated. For the TUN-containing samples [Fig. 3(C,D)], the results are a little more complex. Indeed, the expected trend of MA-containing materials exhibiting a higher storage modulus is observed for temperatures below 10°C . After that an inversion occurs and the MA-containing composite exhibits a lower E' . Beyond $\sim 210^\circ\text{C}$, a decrease in E' indicates initial degradation of the system.

A SEM study has been performed on sugarcane bagasse composites prepared with and without MA as part of the resin. The results are presented in Figure 4.

Unfortunately, because of the electronic properties of the filler, it is virtually impossible to distinguish between the matrix and the filler in the images obtained. The great morphological similarity between samples prepared with and without MA indicates that the presence of MA in the resin composition does not impart any significant visual improvement in the filler-resin interaction. In fact, one would expect that samples prepared without MA would exhibit more voids and gaps, especially in the filler-resin interface, as observed when a similar resin was reinforced with soybean²⁶ and rice hulls.²⁸ After interpretation of the SEM images, the observed decrease in mechanical properties when MA is incorporated into the resin can be attributed to a loss in the system's rigidity due to partial substitution of the known structural components DVB and BMA.

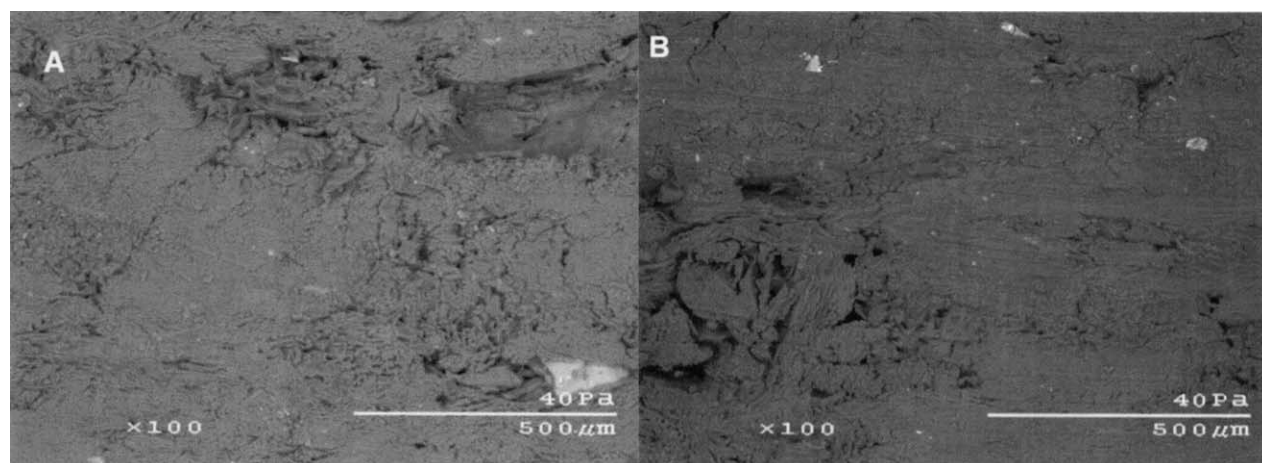


Figure 4 SEM images of sugarcane bagasse composites with resin compositions: (A) 50 wt % of tung oil, 35 wt % of BMA, and 15 wt % of DVB; and (B) 50 wt % of tung oil, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA. The composites have a filler load of 60 wt % and have been compression molded at 140°C for 3 h, 160°C for 3 h under 600 psi, followed by a postcure at 180°C for 1 h.

The $^1\text{H-NMR}$ spectra of the extract of sugarcane bagasse, CSO, and the extract of a composite containing 60 wt % of filler with a resin that is composed of 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA are presented in Figure 5. In the spectrum of the sugarcane bagasse extract [Fig. 5(A)], only protons in the aliphatic region have been detected. Although the substance extracted has not been thoroughly characterized and identified, the absence of characteristic peaks indicating functional groups and/or multiple bonds in the spectrum implies that this substance is, most likely, a hydrocarbon that could work as a plasticizer in the composite system. Nevertheless, only

5 wt % of that material has been recovered after Soxhlet extraction (data not included in Table II).

Figure 5(C) is representative of the extracts of all of the composites prepared in this work. The great similarity between Figure 5(C) and the spectrum of 100% conjugated soybean oil [Fig. 5(B)] is evidence that the vegetable oil is the major component extracted from the composite. This indicates that the vegetable oils used as the major resin components are significantly less reactive than the other comonomers present in the matrix. Indeed, a similar trend has been observed in previous works with soybean and rice hulls.^{26,28}

From the results in Table III, it is evident that all of the composites prepared exhibit two distinct T_g s, as determined by DMA. The appearance of two T_g s has been previously attributed to a phase separation of the resin due to a significant difference in the reactivity and rate of polymerization of the different comonomers that comprise the matrix.^{26,27} It has also been previously noted that when more unsaturated oils are used as the major resin component, the phase separation is avoided because of their increased reactivity, and as a consequence, only one T_g is observed.²⁷ Here, two distinct T_g s are observed for all of the composites prepared, regardless of the oil used. It is believed that the better filler–resin interaction imparted by the initial washing and drying of the filler makes the diffusion of larger molecules, such as triglycerides, more difficult, that is, molecules that can diffuse better, react faster, and get incorporated into the growing polymer chains preferentially, which results in the phase separation. It is interesting to note that the T_g s of samples prepared with MA are significantly lower than the ones observed for samples that do not contain MA when the same oil is used (Table III, entries 1, 2 and 4, 5).

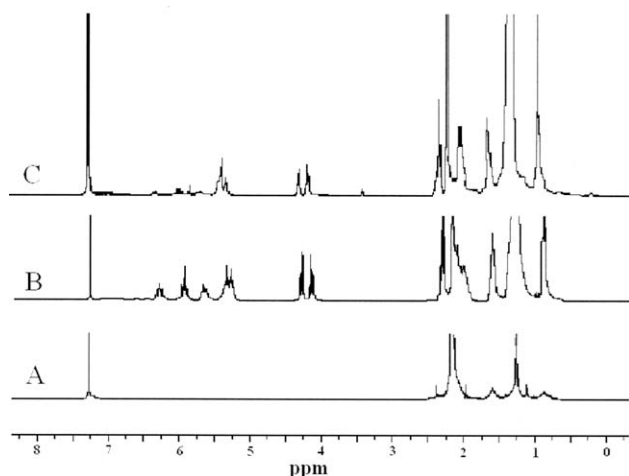


Figure 5 $^1\text{H-NMR}$ spectra of (A) the extract of sugarcane bagasse, (B) CSO, and (C) the extract of a composite containing 60 wt % of filler and a resin that is composed of 50 wt % of CSO, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA cured for 3 h at 140°C and for 3 h at 160°C, followed by a postcure at 180°C for 1 h.

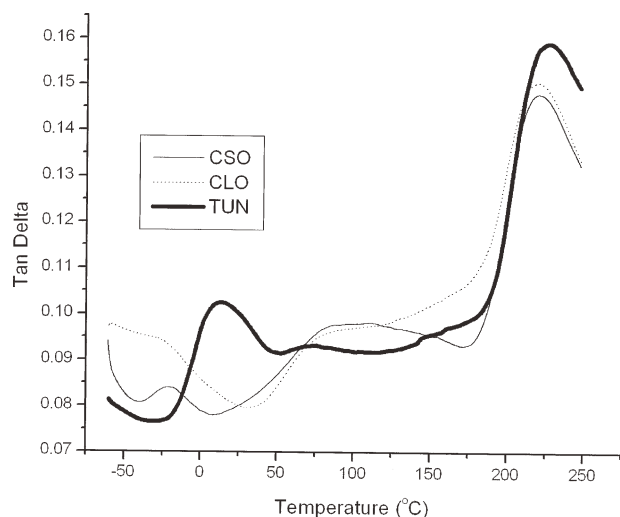


Figure 6 Tan δ curves for samples made with (A) CSO, (B) CLO, and (C) tung oil. The composites possess a filler/resin ratio of 60/40 and have been cured for 3 h at 140°C and 3 h at 160°C and postcured for 1 h at 180°C. The resin composition is 50 wt % of vegetable oil, 20 wt % of BMA, 15 wt % of DVB, and 15 wt % of MA.

A comparison of the tan δ curves of samples made with different vegetable oils is shown in Figure 6. It is noticeable that all samples exhibit two tan δ peaks, independent of the oil used, indicative of two distinct T_g s. The first T_g is attributed to the vegetable oil-rich phase, whereas the second T_g relates to a DVB-rich phase.

CONCLUSIONS

In this work, we have prepared vegetable oil-based thermoset composites reinforced with sugarcane bagasse. An initial cure sequence study showed that the changes in mechanical properties, observed when the sample is cured under different temperatures and times, are related to the thermal stability of the filler. However, the postcure step, carried out at ambient pressure, right after the cure of the material, has a great impact on the crosslink density of the resin, as shown by the Soxhlet extraction results. An optimum filler load of 60 wt % resulted in the most thermally stable and viable composites. Furthermore, better overall properties are obtained when more unsaturated oils are used as the major resin component. It has been shown that the initial washing and drying of the sugarcane bagasse affect the filler–resin interaction and result in a phase separation of the matrix, independent of the oil used in the preparation of the composites. Moreover, with a better interaction between resin and filler, MA no longer acts as a compatibilizer in the system, and an overall decrease in storage modulus is observed when MA is added to the resin composition.

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