

# Soybean and Linseed Oil-Based Composites Reinforced with Wood Flour and Wood Fibers

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**ABSTRACT:** Composites consisting of a conjugated linseed or soybean oil-based thermoset reinforced with wood flour and wood fibers have been prepared by free radical polymerization. The thermoset resin consists of a copolymer of conjugated linseed oil (CLO) or conjugated soybean oil (CSO), *n*-butyl methacrylate (BMA), divinylbenzene (DVB), and maleic anhydride (MA). The composites were cured at 180°C and 600 psi and postcured for 2 h at 200°C under atmospheric pressure. The effect of varying filler load, time of cure, filler particle size, origin of the fillers, and resin composition has been assessed by means of ten-

sile tests, DMA, TGA, Soxhlet extraction followed by <sup>1</sup>H-NMR spectroscopic analysis of the extracts, and DSC. The best processing conditions have been established for the pine wood flour composites. It has been observed that the addition of MA to the resin composition improves the filler-resin interaction. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1520–1528, 2012

**Key words:** composites; copolymerization; mechanical properties; conjugated vegetable oil; wood flour; wood fibers

## INTRODUCTION

With the current desire to find replacements for petroleum-derived chemicals and materials, several bio-based resin systems have been developed in the past few years.<sup>1–15</sup> These biopolymers consist of linseed and soybean oil-based resins,<sup>1–8</sup> polyurethanes,<sup>1,2</sup> polyester amides,<sup>3</sup> multicomponent thermosets,<sup>4–7</sup> and cyanate esters.<sup>8</sup> Some of these systems have been reinforced with inorganic fillers, such as nanoclays<sup>9,10</sup> and glass fibers.<sup>11,12</sup> Another approach, adopted by several authors, for the preparation of “green” composites, is the reinforcement of standard petroleum-derived thermoplastics with a variety of natural fillers.<sup>13–19</sup> Only recently, some progress on the reinforcement of blends of petroleum-derived unsaturated epoxy resins and 10 wt % of epoxidized soybean oil with natural fillers has been reported.<sup>20</sup>

The Larock group at Iowa State University has focused its initial efforts in the study of bio-based thermosets on high natural oil content (~40–60 wt %) materials.<sup>21–24</sup> The cationic copolymerization of modified vegetable oils and other vinylic comonomers results in homogeneous bio-based materials

with a smooth surface.<sup>25</sup> Due to the problems associated with the cure of vegetable oil-based systems in the presence of free radical initiators, such as the entrapment of bubbles in the resin and crack formation, free radical resins received little attention in the early stages of our research.<sup>23</sup> The thermal copolymerization of such systems has also been investigated, but the process is not considered to be practical due to the high temperatures and long times required to obtain viable materials.<sup>26</sup>

More recently, in an attempt to improve the mechanical properties of the aforementioned bio-based polymers, the Larock group has used inorganic<sup>27,28</sup> and natural fillers as reinforcements for the preparation of “green” composites.<sup>29–33</sup> The natural filler-reinforced composites contain up to 85 wt % of bio-based materials, including the resin and the filler.<sup>29–33</sup> In the preparation of such materials, it has been demonstrated that free radical initiators are quite effective in crosslinking the carbon–carbon double bonds in the oils and the other monomers used. The presence of ligno-cellulosic filler particles minimizes shrinkage of the resin and only minimal microcracks have been detected by scanning electron microscopy (SEM) of soybean hull composites.<sup>30</sup> Recent results from the study of natural filler-reinforced composites in the Larock group suggested that maleic anhydride (MA) can serve as a good filler-resin compatibilizer and help improve the stress transfer from the matrix to the reinforcement, resulting in an overall increase of the mechanical properties.<sup>32,33</sup>

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With an estimated annual production of 21.2 billion pounds in 2007,<sup>34</sup> soybean oil is one of the most prevalent vegetable oils in the United States. Soybean oil consists of a triglyceride with a fatty acid composition of 11% palmitic acid, 3% stearic acid, 22% oleic acid, 55% linoleic acid, and 9% linolenic acid.<sup>35</sup> The total average number of carbon-carbon double bonds per triglyceride in soybean oil is 4.5.<sup>36</sup> When these carbon-carbon double bonds are isomerized and brought into conjugation using methodology developed by the Larock group and widely used by us,<sup>37</sup> soybean oil can readily polymerize and crosslink in a free radical process to form a rigid thermoset. With a similar fatty acid composition (4% stearic acid, 19% oleic acid, 15% linoleic acid, 57% linolenic acid, and 5% of other fatty acids), but a higher degree of unsaturation (6.0 carbon-carbon double bonds per triglyceride), linseed oil is also a potential bio-based monomer for the preparation of "green" composites.<sup>23</sup>

The use of wood flour and wood fibers as reinforcements in the preparation of "green" composites is known.<sup>13,15</sup> However, in most cases, petroleum-derived thermoplastics have been used as the matrix.<sup>13,15</sup> Here, we report the preparation of soybean and linseed oil-based thermosets reinforced with pine, oak, and maple wood flours and a mixture of hardwood fibers. Parameters, such as cure time, filler load, filler particle size, origin of the filler, and resin composition, have been varied and the resulting properties of the "green" 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 (<sup>1</sup>H-NMR) spectroscopic analysis of the extracts. After analysis of the results, optimal conditions have been suggested for the preparation of such composites, and the effect of MA as a filler-resin compatibilizer has been verified.

## EXPERIMENTAL

### Materials

*n*-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA). DVB, MA, and *t*-butyl peroxide (TBPO) 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 ADM (Red Wing, MN). The carbon-carbon double bonds in both oils have been isomerized and brought into conjugation using a rhodium catalyst, following a method developed and frequently used by our group.<sup>37</sup> The products contain conjugated carbon-carbon double bonds, like in a 1,3-diene, and

will be referred to in the text as conjugated oils. The wood flours of different particle sizes and wood fibers were provided by American Wood Fibers (Schofield, WI). The fillers were dried overnight at 70°C in a vacuum oven right before impregnation with the resin to improve filler-resin compatibility.

### General procedure for preparation of the composites

#### Wood flour composites

The crude resin was obtained by mixing the conjugated vegetable oil, BMA, and DVB in a beaker. MA was melted in a hot water bath and quickly added to the crude resin mixture under agitation, along with the free radical initiator TBPO. The natural fillers were manually mixed with the crude resin in a large beaker using a spatula, resulting in thorough impregnation of the fillers. The impregnated fillers were then transferred to a 6 in. × 6 in. mold, and compression molded at 180°C and 600 psi. The composites were removed from the mold and postcured in a convection oven for 2 h at 200°C at ambient pressure. In all composites produced, the resin has a conjugated 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 amounts of DVB, BMA, and MA have been varied, as indicated in the text, to produce composites of various compositions.

#### Wood fiber composites

Due to the very low density of the wood fibers, and the difficulties associated with handling that material, only one composite has been prepared using mixed hardwood fibers, which exhibit a wide variation in the aspect ratio, as reinforcement. The aspect ratio of the mixed wood fibers has not been determined by us, and the fibers have been used as received. Following the same procedure described for the preparation of the wood flour composites, the wood fibers were impregnated with a resin containing 50 wt % of conjugated linseed oil (CLO), 35 wt % of BMA, 15 wt % of DVB, and an extra 5 wt % of the total resin weight of TBPO. The final filler to resin ratio obtained was 50/50. The mixture was compression molded at 130°C and 400 psi for 5 h, and postcured in a convection oven at 150°C for 2 h at ambient pressure. For comparison purposes, a pine wood flour (particle size diameter <310 μm) composite was prepared using the same parameters.

### Characterization of the composites

Tensile tests were conducted at room temperature according to ASTM D-638 using an Instron universal

TABLE I  
Tensile Tests, DMA, and Extraction Results for Pine Wood Flour Composites with Varying Filler Loads

Entry	Filler load (wt %) <sup>a</sup>	E (GPa)	Tensile strength (MPa)	E' at 130°C (MPa)	T <sub>g1</sub> (°C)	T <sub>g2</sub> (°C)	Soluble fraction (%) <sup>b</sup>
1	— <sup>c</sup>	—	—	44	−51	37	13
2	60	1.5 ± 0.1	9.1 ± 1.0	739	1	75	8
3	70	1.8 ± 0.1	9.5 ± 2.0	946	−4	78	8
4	75	2.8 ± 0.9	9.5 ± 1.6	1033	−3	85	9
5	80	2.8 ± 0.9	11.7 ± 2.4	1072	4	79	5
6	85	3.3 ± 0.4	10.5 ± 0.7	1026	7	61	4

<sup>a</sup> Filler particle size diameter <310 μm. Cure conditions: 180°C and 600 psi for 5 h, followed by a postcure step at 200°C and ambient pressure for 2 h.

<sup>b</sup> Determined by Soxhlet extraction.

<sup>c</sup> Unreinforced resin containing 50 wt % of CSO, 35 wt % of BMA, and 15 wt % of DVB.

testing machine (model 5569) equipped with a video extensometer and operating at a crosshead speed of 2.0 mm/min. Dog bone-shaped test specimens were machined from the original samples to give the following gauge dimensions: 57.0 mm × 12.7 mm × 4.5 mm (length × width × thickness, respectively). For each composite, seven dog bones were cut and tested. The results presented in the text 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 × 8.5 mm × 1.5 mm (length × width × thickness, respectively) were cut from the original samples. Each specimen was cooled to −60°C and then heated at 3°C/min to 250°C. 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 in the text reflect the average of the two measurements.

Soxhlet extraction was conducted to determine the amount of soluble materials in the composites. A 2.0 g sample of each composite was extracted for 24 h with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). After extraction, the solubles were recovered by evaporating the CH<sub>2</sub>Cl<sub>2</sub> under vacuum. Both soluble and insoluble materials were dried overnight at 70°C. The dried soluble fraction was then dissolved in deuterated chloroform (CDCl<sub>3</sub>) and the <sup>1</sup>H-NMR spectrum was obtained using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) operating at 300 MHz. The <sup>1</sup>H-NMR spectra helped to identify the solubles in each sample.

A Q50 TGA instrument (TA Instruments, New Castle, DE) 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°C/min.

DSC experiments were performed on a Q20 DSC instrument (TA Instruments, New Castle, DE) under

a N<sub>2</sub> atmosphere over a temperature range of −20 to 400°C, while heating at a rate of 20°C/min. The samples weighed ~10 mg.

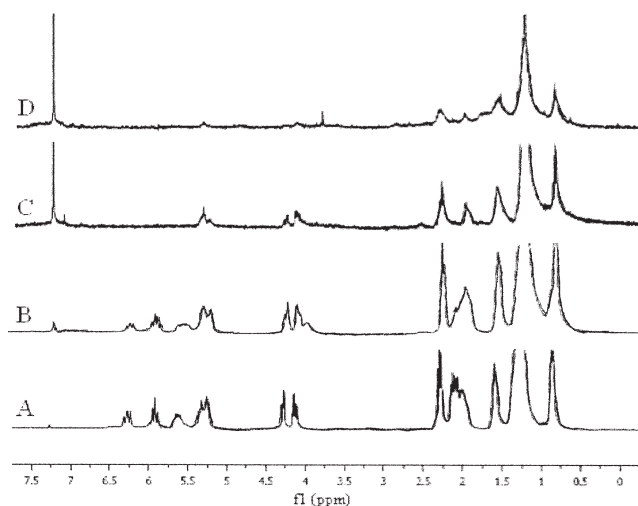
## RESULTS AND DISCUSSION

### Filler load evaluation

To determine the optimal filler to resin ratio for the preparation of wood flour composites, samples containing 60 to 85 wt % of pine wood flour have been prepared and their mechanical properties have been measured by tensile tests and DMA. Table I summarizes the results obtained for composites with a constant resin composition equal to 50 wt % of conjugated soybean oil (CSO), 35 wt % of BMA, and 15 wt % of DVB. The pine flour particle size diameter was also held constant at <310 μm. The composites have been cured at 180°C and 600 psi for 5 h, followed by a postcure step at 200°C and ambient pressure for 2 h.

From the tensile test results presented in Table I, one can see an overall increase in both the Young's modulus and the tensile strength of the composites with increasing filler loads. The increase in the tensile properties is clearer for filler loads comprised between 60 wt % and 75 wt %. Beyond that point, the differences in Young's modulus fall within the standard deviation associated with the measurements. Although a high value of 3.3 GPa is observed for the sample containing 85 wt % of pine wood flour, there is no statistical difference between the samples. The same situation is observed for the tensile strength of samples containing 80 wt % and 85 wt % of filler. In this case, the strength peaks at 11.7 MPa, for the sample prepared with 80 wt % of pine flour, but the difference with respect to the sample containing 85 wt % of pine flour falls within the standard deviation of the two measurements.

When the flexural properties of samples prepared with varying amounts of pine flour are compared, a clear increase in the storage modulus at 130°C (well



**Figure 1**  $^1\text{H-NMR}$  spectra of (A) conjugated soybean oil (CSO), (B) extract of a resin containing 50 wt % of CSO, 35 wt % of BMA, and 15 wt % of DVB, (C) extract of a pine wood flour composite containing an 80/20 filler to resin ratio and cured for 4 h, (D) extract of pine wood flour.

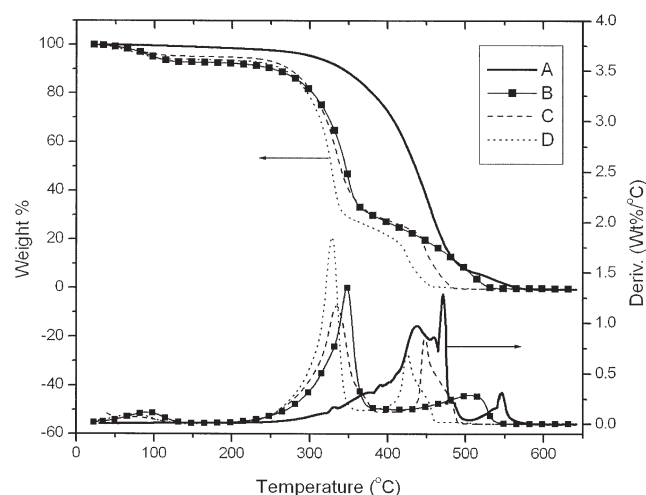
above the detected  $T_g$ 's) is observed when the filler load is increased from 60 wt % to 80 wt %. This increase reflects the reinforcement imparted by the filler, which is a consequence of the stress transfer from the matrix to the filler particles, avoiding dissipation of the energy in polymer chain motions and therefore yielding a higher storage modulus. An even higher effect is obtained when comparing the unreinforced resin and the sample containing 60 wt % of the filler. In that case, there is approximately a 17-fold improvement in the storage modulus. Nevertheless, as noted in our previous work with soybean and rice hulls,<sup>30,32</sup> when the filler load is exceedingly high (85 wt %, Table I), the amount of resin in the system is not enough to bind all of the filler particles, leading to filler agglomeration and formation of weak points in the composite morphology that negatively impact the storage modulus.

Another interesting observation from the flexural tests is the presence of two distinct  $T_g$ 's for the systems presented in Table I. This phenomenon has been observed and analyzed previously by us and is attributed to a phase separation of the resin due to the very distinct reactivity of the comonomers toward free radicals, most noticeably CSO and DVB.<sup>30,32</sup>

The soluble content recovered after Soxhlet extraction of the composites bearing different filler loads is also presented in Table I. The soluble content of the pure resin corresponds to 13 wt %, and it has been identified as being mainly unreacted CSO.<sup>30</sup> Indeed, the  $^1\text{H-NMR}$  spectrum of the resin extract [Fig. 1(B)] matches very closely that of pure CSO [Fig. 1(A)], except for small peaks at 4.0 ppm and 7.0 ppm in the spectrum of the resin extract. Those peaks are

most likely related to either residual unreacted BMA and DVB respectively, or to noncrosslinked oligomers containing those units. Some differences in the pattern of the 1.9 to 2.2 ppm signal are also observed when comparing Figure 1(A,B). Those differences are possibly related to the presence of BMA, DVB, and/or noncrosslinked oligomers in the extract of the resin. It is, however, extremely hard to attribute the observed differences in that range to specific components of the system due to the extensive overlap of signals related to aliphatic protons of the various resin components.

Pine wood flour only yields 9 wt % of an unidentified soluble material (result not shown in Table I). Thus, it is expected that an increase in the filler content will result in a decrease of the recovered solubles after Soxhlet extraction as is observed in Table I. The material extracted from the wood flour is rich in carbon-hydrogen bonds as evidenced by the peaks in the 0.8 to 2.5 ppm range [Fig. 1(D)] with the possibility of the presence of carbon-carbon double bonds and/or oxygenated functional groups evident from the small peaks located at 3.7 ppm and 5.3 ppm. Since this material has not been identified yet, it is impossible to predict what role it plays in the system studied. When analyzing the spectrum of a composite extract [Fig. 1(C)], it is possible to identify most of the features found in the spectrum of the resin extract, confirming that the majority of what is extracted comes from the matrix and is most likely unreacted CSO and trace amounts of the other comonomers. The intensity of the solvent peak (7.26 ppm) indicates how concentrated the solutions used



**Figure 2** TGA and DTA curves of (A) an unreinforced resin with the following composition: 50 wt % of CSO, 35 wt % of BMA, and 15 wt % of DVB; (B) pine wood flour; (C) a composite containing 70 wt % of pine wood flour (particle size diameter  $<310\ \mu\text{m}$ ) and 30 wt % of resin A; and (D) a composite containing 80 wt % of pine wood flour (particle size diameter  $<310\ \mu\text{m}$ ) and 20 wt % of resin A.

**TABLE II**  
**Tensile Tests, DMA, and Extraction Results for Pine Wood Flour Composites Cured at 180°C and 600 psi for Different Times, and Postcured at 200°C for 2 h at Ambient Pressure**

Entry	Cure time (h) <sup>a</sup>	<i>E</i> (GPa)	Tensile strength (MPa)	<i>E'</i> at 130°C (MPa)	<i>T</i> <sub>g1</sub> (°C)	<i>T</i> <sub>g2</sub> (°C)	Soluble fraction (%) <sup>b</sup>
1	5	2.8 ± 0.9	11.7 ± 2.4	1072	4	79	5
2	4	4.3 ± 1.1	12.4 ± 1.1	742	3	93	4
3	3	3.1 ± 0.6	12.3 ± 1.9	704	-2	77	6
4	2	3.3 ± 0.7	13.9 ± 1.6	831	2	90	5
5	1	3.5 ± 0.9	13.0 ± 0.9	1292	-1	71	5
6	0.5	3.1 ± 0.6	11.4 ± 1.2	864	-7	97	5

<sup>a</sup> Filler particle size diameter <310 μm. Filler/resin ratio = 80/20.

<sup>b</sup> Determined by Soxhlet extraction.

to obtain the corresponding spectra were. It is noteworthy that only a very small amount of extract has been recovered from samples C and D, resulting in more dilute samples and more intense solvent peaks.

The thermal stability of the wood flour composites can be assessed by a comparison of the TGA curves of some selected samples shown in Figure 2. Due to the high filler load present in the composites [70 wt % and 80 wt %, Fig. 2(C,D), respectively], their thermal degradation profile more closely resembles that of the pure pine wood flour [Fig. 2(B)] rather than the resin [Fig. 2(A)]. After the initial loss of water by the filler particles (around 100°C, Fig. 2), the composites and the pure filler start to degrade at approximately 225°C, whereas the pure resin only starts degrading at approximately 275°C. Thus, the fillers are less thermally stable than the resin.

It is interesting to note that despite the higher thermal stability of the resin system, the composites degrade slightly faster than the pure filler. This is confirmed by the first peak of the DTA curves (*T*<sub>max1</sub>). While the pure filler exhibits a *T*<sub>max1</sub> of 348°C, samples C and D exhibit a *T*<sub>max1</sub> of 334°C and 329°C, respectively. This first degradation peak can be attributed to the hemicellulose component of the lignocellulosic materials.<sup>30,32</sup> The negative effect that the resin has on the thermal stability of the wood flour differs from our earlier data using soybean and rice hulls as reinforcements,<sup>30,32</sup> and is not yet fully understood. The other DTA peaks observed for samples B, C, and D are, most likely, a combination of the degradation of cellulose, lignin, and some of the resin components. The degradation pattern of the resin is more complex and it is hard to attribute the DTA peaks for sample A (Fig. 2) to specific components of the system. Nevertheless, it is noteworthy that *T*<sub>max1</sub> occurs at approximately 445°C for the pure resin, a much higher temperature than that observed for the composites or the pure filler.

Given the results presented so far for composites made with different amounts of filler, an 80/20 filler to resin ratio yields a composite with the overall best mechanical properties. Furthermore, despite the

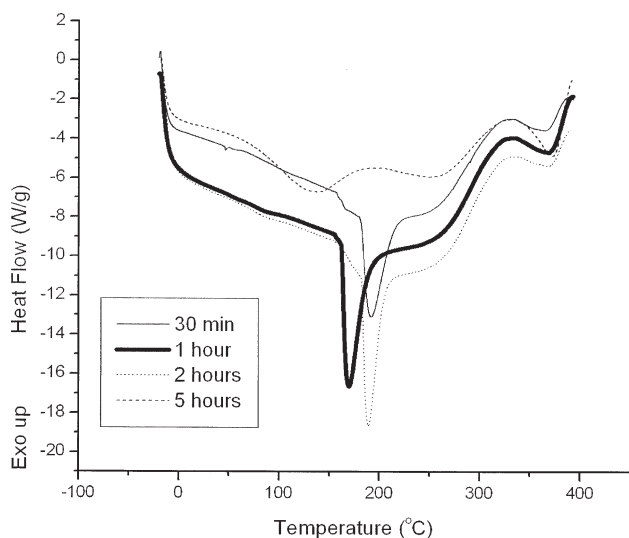
statistical equivalence of the tensile properties of samples containing 80 wt % and 85 wt % of wood flour, and taking into account the processability of the crude resin and wood flour mixture, the 80/20 filler to resin ratio proved to be the most practical one to handle before curing. Therefore, this filler load has been used in the preparation of all composites in the remainder of this work.

#### Cure time analysis

To determine the best cure time for the system, pine wood flour composites with a constant filler to resin ratio of 80/20, and a constant resin composition (50 wt % of CSO, 35 wt % of BMA, and 15 wt % of DVB) have been prepared and cured at 600 psi and 180°C for different times. The results from the tensile tests, DMA, and Soxhlet extraction are presented in Table II.

When the cure time is varied from 30 min to 3 h, there is no significant variation in the Young's modulus of the pine wood flour composites as the differences between the values fall within the standard deviations of the measurements. The Young's modulus reaches its maximum at 4.3 GPa when the composite is cured for 4 h, but once again, no statistical differences have been found between the samples cured for 4 and 5 h. For the tensile strength, with the exception of the sample cured for 30 min, all the other composites exhibit values that range within the standard deviations of the measurements. These results indicate that although very little variation is obtained in the tensile properties by varying the cure time, a 30-min cure is inappropriate due to the very low tensile strength obtained. This is probably because the resin is not completely cured after such a short time. On the other hand, a 4 h cure sequence results in the stiffest material and is therefore considered the optimum cure time for the preparation of wood flour composites.

With respect to the storage modulus at 130°C, there is no obvious trend between the values observed and the cure time. A maximum storage modulus is observed when the composite is cured



**Figure 3** DSC of composites cured at 180°C and 600 psi for different times, and postcured at 200°C and ambient pressure for 2 h. The composites have a filler/resin ratio of 80/20, and a resin composition of 50 wt % of CSO, 35 wt % of BMA, and 15 wt % of DVB.

for 1 h. However, the results suggest a tendency for  $E'$  to increase with cure time for cure sequences lasting between 3 and 5 h.

During the cure, two competing phenomena are responsible for the minor variation in the mechanical properties measured as a function of the cure time. Indeed, one would expect the tensile and flexural properties to improve significantly with cure time as the crosslink density of the resin increases and further reactions of the comonomers are expected to yield stiffer and stronger materials. Furthermore, it has been shown that the postcure step is essential for achieving a fully crosslinked resin.<sup>32</sup> This finding supports the claim that samples submitted to the same postcure conditions exhibit a similar crosslink density, and similar properties as a consequence. However, degradation of the filler components starts at fairly low temperatures (see Fig. 3), and the loss of properties due to partial filler degradation under the cure conditions is a possibility. With both phenomena occurring simultaneously, one effect compensates for the other and this is reflected in the overall measurements, as can be seen in Table II.

It has been previously shown, with rice hull composites cured at different temperatures, that a cure temperature of 180°C maximizes the crosslinking of the resin, resulting in materials with better properties.<sup>32</sup> A cure temperature of 130°C has been employed in the preparation of a wood flour composite, resulting in a sample with significantly lower properties than the one cured at 180°C (compare the results presented in Tables I and IV).

Once again, two distinct  $T_g$ 's have been observed for the wood flour composites prepared with CSO

(Table II). As discussed earlier, this is a result of a phase separation due to the difference in reactivity of the comonomers that form the matrix of the composites. The lower  $T_g$ , most likely associated with a CSO-rich phase, varied from -7 to 4°C in a nonregular pattern, as the cure time increased from 30 min to 5 h. The higher  $T_g$ , most likely related to a DVB-rich phase, shows a broader variation from 71 to 97°C within the same cure time range. These results show that the phase separation does not depend on the cure time and that the DVB-rich phase is readily formed at the cure temperature (180°C), even when the cure only lasts for 30 min. Once the DVB-rich phase is formed and the concentration of free DVB monomer has dropped, the CSO-rich phase starts to form. Surprisingly, the change in soluble material with cure time is minimal, which suggests that both phases are mostly formed within the first 30 min of the cure, and that only a small amount of the monomers are left unreacted. For the remainder of the time, during longer cure sequences, processes such as crosslinking, polymer chain growth, and oligomer incorporation into the matrix occur, resulting in materials with slightly better mechanical properties.

Another evidence of the effect of the cure time on the composites is shown in Figure 3, where the DSC plots of composites cured for different times are pictured. Composites cured for 3 and 4 h have been omitted due to their similarity to the composite cured at 2 h and to achieve better quality plots.

As discussed in our previous publication on soybean hull composites,<sup>30</sup> the exothermic peaks occurring after 250°C in the DSC of ligno-cellulosic composites correspond to the decomposition of hemicellulose and cellulose from the filler. Since the composition of the materials is the same for all four samples shown in Figure 3, no significant variation is detected between 250°C and 400°C. The sharp heat absorption observed between 150°C and 200°C for samples cured between 30 min and 2 h is attributed to volatilization of compounds during hemicellulose thermal degradation, as previously demonstrated with soybean hull composites.<sup>30</sup> This peak occurs at 190°C for samples cured for 30 min and 2 h. It is unclear to us why a lower temperature was obtained for the composite cured for 1 h. However, the main focus of the present discussion is the change in the resin using different cure sequences. Regarding the DSC of the composite cured for 5 h, the endothermic peak is much less intense, and appeared at a considerably lower temperature (135°C). This is an indication that the exceedingly long cure time initiated the thermal degradation of the filler, and, therefore, less energy was required during volatilization of the compounds in the DSC experiment.

The most important feature of the DSC curves shown in Figure 3 is a change in the baseline

**TABLE III**  
**Filler Particle Size, Filler Origin, and Resin Composition Effects on the Properties of Wood Flour Reinforced Composites**

Entry	Filler	Resin composition <sup>a</sup>	Particle size (μm)	<i>E</i> (GPa)	Tensile strength (MPa)	<i>T</i> <sub>g1</sub> (°C)	<i>T</i> <sub>g2</sub> (°C)	<i>E'</i> at 130°C (MPa)
1	Pine flour	CSO-DVB-BMA35	<470	3.2 ± 0.6	8.3 ± 0.8	2	69	879
2	Pine flour	CSO-DVB-BMA35	<310	4.3 ± 1.1	12.4 ± 1.1	3	93	742
3	Pine flour	CSO-DVB-BMA35	<224	2.7 ± 0.7	9.9 ± 0.7	-1	72	686
4	Pine/maple flour	CSO-DVB-BMA35	-	1.6 ± 0.1	7.5 ± 1.0	-8	70	388
5	Pine flour	CLO-DVB-BMA35	<310	3.8 ± 1.9	15.7 ± 1.9	-	54	1559
6	Pine flour	CLO-DVB-BMA20-MA15	<310	4.0 ± 0.9	17.6 ± 1.9	17	109	2244
7	Maple/oak flour	CLO-DVB-BMA20-MA15	<470	2.1 ± 0.4	8.5 ± 2.5	11	91	600
8	Maple/oak flour	CLO-DVB-BMA20-MA15	<310	1.8 ± 0.3	8.1 ± 2.2	-12	62	2223
9	Maple/oak flour	CLO-DVB-BMA20-MA15	<224	2.5 ± 0.5	11.3 ± 2.3	-9	59	1064

<sup>a</sup> All resins have 50 wt % of conjugated vegetable oil, and 15 wt % of DVB. The wt % of BMA and MA is indicated by the numbers following the corresponding acronyms.

occurring right before the heat absorption. This feature is clearly seen at 160°C for the composite cured for 30 min, and is most likely related to further cure of the resin, as discussed for soybean hull composites.<sup>30</sup> The same feature, although much less intense is observed, at the same temperature, for the composite cured for 1 h, indicating that a longer cure time indeed results in a more complete cure of the resin. For the composite cured for 2 h, the change in the baseline is much smoother and actually hard to detect, corroborating the idea that a longer heating time results in further cure of the resin. The aforementioned feature is completely nonexistent in the DSC of the composite cured for 5 h. In fact, in this instance, the resin is completely cured, but the filler is significantly degraded, and a burnt smell has been noticed when removing the composite from the mold after preparation.

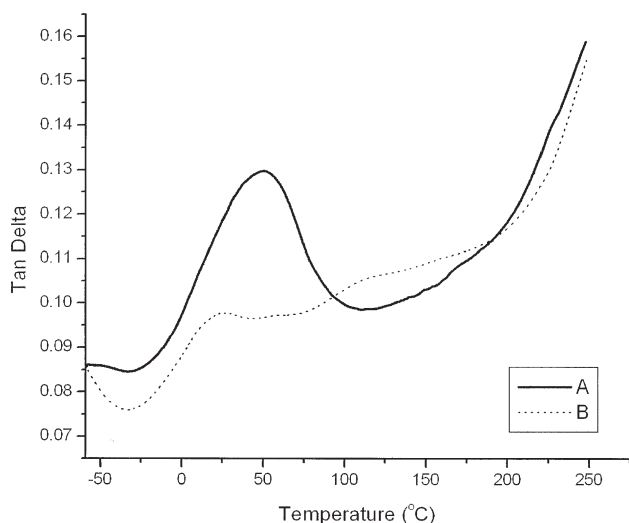
#### Filler particle size, filler origin, and resin composition effects

Table III shows the properties of composites made with different wood flours containing varying particle sizes and resin compositions. Comparing the properties of composites made with pine wood flour of different particle sizes (entries 1–3, Table III), it is evident that the overall best values have been obtained from the composite prepared with particles <310 μm (entry 2, Table III). The only exception being the storage modulus at 130°C, for which the composite prepared with filler particles <470 μm (entry 1, Table III) exhibited the highest value. We have observed previously with soybean hulls that the use of fillers of smaller particle sizes tends to result in a better dispersion of the resin and higher mechanical properties.<sup>30</sup> Larger particles, on the contrary, agglomerate more easily, forming weak points in the composite.<sup>30</sup> Here, probably due to a difference in the filler structure and composition (grain

shell vs. ground wood), a different trend is observed. The optimum intermediate particle size (<310 μm) most likely prevents agglomeration of the filler. This trend changed when maple/oak composites were prepared with a resin that contains the compatibilizer MA (entries 7–9, Table III). In that case, the expected trend of smaller particle sizes (<224 μm) yielding composites with better properties is verified. Once again the exception being the storage modulus at 130°C, for which the highest value is observed for the composite prepared with particles <310 μm (entry 8, Table III).

Another interesting aspect from Table III is that the use of mixed wood flours gives worse properties than when a pure wood flour is used in the preparation of the composite. This is true for the pine/maple mixed flour (entry 4, Table III), when compared with the pure pine flour (entries 1–3, Table III). One reason for the observed pattern is that the maple flour originally used to prepare the mixture appears to have very low mechanical properties. Unfortunately, we could not get samples of pure maple flour to prepare a control composite and test that hypothesis. A similar situation is observed for composites made with maple/oak mixed flours (entries 7–9, Table III). Although the mechanical properties measured for the maple/oak composite (entry 8, Table III) are overall lower than the ones measured for the pine wood flour composite with the same resin composition and particle size (entry 6, Table III), no controls have been prepared with pure oak, and/or pure maple wood flours.

When CSO is replaced by CLO in pine flour composites (entries 2 and 5, Table III), a significant improvement in tensile strength and storage modulus at 130°C is observed. These results support the idea that a higher number of carbon–carbon double bonds in the oil (linseed oil has on average 6.0 carbon–carbon double bonds per triglyceride, while soybean oil only possesses 4.5 carbon–carbon double



**Figure 4** Tan delta curves of pine flour composites with resin composition: 50 wt % CLO, 35 wt % BMA, and 15 wt % DVB (A); and 50 wt % CLO, 20 wt % BMA, 15 wt % DVB, and 15 wt % MA (B). Both composites had a filler/resin ratio of 80/20 and have been cured for 4 h at 180°C and 600 psi, and postcured at 200°C for 2 h at ambient pressure.

bonds per triglyceride) gives a more crosslinked and stronger material. A similar trend has been observed and recently published by us for soybean and linseed oil-based rice hull composites.<sup>33</sup> As for the Young's modulus of the CSO- and CLO-based composites compared here (entries 2 and 5, Table III), the values measured fall within the standard deviation of the method used and therefore cannot be considered statistically different. The appearance of one single  $T_g$  for the CLO-containing composite (entry 5, Table III) is again a result of the higher reactivity of CLO in comparison to CSO, due to its higher number of carbon-carbon double bonds. By reacting faster, CLO is incorporated into the polymer matrix at approximately the same rate as the other comonomers, resulting in a single phase.

When maleic anhydride (MA) is added to the resin formulation, it acts as a compatibilizer between the hydrophobic matrix and the hydrophilic filler. MA can also be polymerized through a standard free radical reaction of its reactive carbon-carbon double bond, which allows it to be easily incorporated into the polymer matrix. It is also known that

the anhydride unit can be easily opened in the presence of nucleophiles at elevated temperatures, which should allow the appended anhydride to interact with the ligno-cellulosic fillers rich in carbohydrates.

A comparison of entries 5 and 6 in Table III shows that the addition of MA to the resin formulation in partial replacement of BMA results in a slight improvement in the mechanical properties. Young's modulus and tensile strength are slightly higher for the MA-containing sample, but the values still fall within the standard deviation of the measurements. The storage modulus measured at 130°C, on the other hand, shows a significant improvement, increasing from 1559 MPa to 2244 MPa after the addition of MA, which supports better stress transfer from the resin to the reinforcement, and indicates that a better filler-resin interaction has been obtained with MA.

Interestingly, the presence of MA in the resin system seems to have an influence on the  $T_g$ 's observed and the corresponding phase separation. Two distinct  $T_g$ 's have been found for a pine flour composite containing MA (entry 6, Table III), even when CLO is used as the major resin component. The same phase separation is observed in all maple/oak composites (entries 7–9, Table III). A plausible explanation for this phenomenon is that when the polymer chains containing MA units start to form, the favorable interactions between MA and the filler restrict the movement and the dispersion of the growing chains, which ultimately results in the observed phase separation, regardless of the reactivity of the oil used to prepare the resin. A comparison of the tan delta curves of pine flour composites prepared with and without MA is presented in Figure 4.

### Wood fiber composites

For comparison purposes, samples containing mixed hardwood fibers and pine wood flour have been prepared with the same filler/resin ratio and resin composition. The resin was composed of 50 wt % of CLO, 35 wt % of BMA, and 15 wt % of DVB and the filler/resin ratio used was 50/50. As mentioned earlier, a cure sequence of 5 h at 130°C and 400 psi, followed by a postcure step of 2 h at 150°C and ambient pressure, was used for both composites.

**TABLE IV**  
Properties of Pine Flour and Hardwood Fiber Composites

Entry	Filler	$E$ (GPa)	Tensile strength (MPa)	$T_g$ (°C)	$E'$ at 130°C (MPa)
1 <sup>a</sup>	Pine flour	1.3 ± 0.4	2.6 ± 0.6	62	152
2 <sup>a</sup>	Mixed hardwood fiber	2.3 ± 0.2	18.4 ± 1.5	70	1051

<sup>a</sup> Both composites have a 50/50 filler/resin ratio and a resin composition of 50 wt % of CLO, 35 wt % of BMA, and 15 wt % of DVB. The cure employed corresponds to 130°C for 5 h at 400 psi, followed by a postcure of 2 h at 150°C and atmospheric pressure.



The properties of both samples are summarized in Table IV.

From the results presented in Table IV, the use of hardwood fiber as a reinforcement resulted in a composite with much higher mechanical properties than the composite reinforced with pine wood flour. The Young's modulus increased from 1.3 GPa to 2.3 GPa, while the tensile strength and storage modulus at 130°C showed a sevenfold improvement. This increase in mechanical properties is most likely related to the higher aspect ratio and fibrous nature of the wood fibers in comparison with wood flours, where the particles exhibit a more spherical geometry. Also noteworthy is the presence of only one  $T_g$  for both composites due to the use of CLO as the major resin component.

### CONCLUSIONS

In this work, we have studied composite systems where the matrix is a free radical copolymer of BMA, DVB, and either conjugated soybean oil or linseed oil. These thermosets have been reinforced with pine, maple, and oak flours, and a mixture of hardwood fibers. First, we evaluated different filler amounts for pine wood flour composites and determined that a filler load of 80 wt % was the most practical for the preparation of such composites. Then, we examined the effect of cure time on the final properties of the pine flour composites. The results indicate that little variation in the mechanical properties is obtained when the cure time varies from 30 min to 5 h. TGA and DSC experiments indicated that this is a result of factors that compensate for each other. While longer cure times help to completely cure the resin and tend to increase crosslink density and monomer incorporation into the matrix, it is also responsible for partial thermal degradation of the filler components, which impacts the properties negatively. Optimum particle size has been shown to depend on the filler composition, and composites made with mixtures of flours containing oak exhibit worse mechanical properties than pure pine flour composites. It has been verified that MA is a good filler-resin compatibilizer for the composites studied, because its presence imparts a significant increase in the storage modulus of the composites. Finally, a comparison between wood fiber and wood flour composites indicates that the composites reinforced with fibers show significantly higher mechanical properties.

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### References

- Ashraf, S. M.; Ahmad, S.; Riaz, U. *Polym Int* 2007, 56, 1173.
- Wang, C.; Yang, L.; Ni, B.; Shi, G. *J Appl Polym Sci* 2009, 114, 125.
- Sharma, H. O.; Alam, M.; Riaz, U.; Ahmad, S.; Ashraf, S. M. *Int J Polym Mater* 2007, 56, 437.
- Gultekin, M.; Beker, U.; Guner, F. S.; Erciyas, A. T.; Yagci, Y. *Macromol Mater Eng* 2000, 283, 15.
- Bhuyan, S.; Holden, L. S.; Sundararajan, S.; Andjelkovic, D.; Larock, R. C. *Wear* 2007, 263, 965.
- Sharma, V.; Banait, J. S.; Kundu, P. P. *J Appl Polym Sci* 2009, 111, 1816.
- Zhan, M.; Wool, R. P. *J Appl Polym Sci* 2010, 118, 3274.
- Zhang, G.; Zhao, L.; Hu, S.; Gan, W.; Yu, Y.; Tang, X. *Polym Eng Sci* 2008, 48, 1322.
- Sharma, V.; Banait, J. S.; Kundu, P. P. *J Appl Polym Sci* 2009, 114, 446.
- Das, G.; Karak, N. *Prog Org Coat* 2010, 69, 495.
- Thulasiraman, V.; Rakesh, S.; Sarojadevi, M. *Polym Comp* 2009, 30, 49.
- Espinoza-Perez, J. D.; Ulven, C. A.; Wiesenborn, D. P. *Trans Am Soc Agric Biol Eng* 2010, 53, 1167.
- Lundin, T.; Cramer, S. M.; Falk, R. H.; Felton, C. *J Mater Civil Eng* 2004, 16, 547.
- Liu, H.; Wu, Q.; Zhang, Q. *Bioresour Technol* 2009, 100, 6088.
- Xu, Y.; Wu, Q.; Lei, Y.; Yao, F. *Bioresour Technol* 2010, 101, 3280.
- Schirp, A.; Loge, F.; Aust, S.; Swaner, P.; Turner, G.; Wolcott, M. *J Appl Polym Sci* 2006, 102, 5191.
- Jarukumjorn, K.; Suppakarn, N. *Compos B* 2009, 40, 623.
- Srebrenkoska, V.; Gaceva, G. B.; Dimeski, D.; Maced J Chem Chem Eng 2009, 28, 99.
- Haque, M. M.; Hasan, M.; Islam, M. S.; Ali, M. E. *Bioresour Technol* 2009, 100, 4903.
- Haq, M.; Burgueno, R.; Mohanty, A. K.; Misra, M. *Compos Sci Technol* 2008, 68, 3344.
- Li, F.; Hasjim, J.; Larock, R. C. *J Appl Polym Sci* 2003, 90, 1830.
- Li, F.; Larock, R. C. *Biomacromolecules* 2003, 4, 1018.
- Henna, P. H.; Andjelkovic, D. D.; Kundu, P. P.; Larock, R. C. *J Appl Polym Sci* 2007, 104, 979.
- Valverde, M.; Andjelkovic, D.; Kundu, P. P.; Larock, R. C. *J Appl Polym Sci* 2008, 107, 423.
- Xia, Y.; Henna, P. H.; Larock, R. C. *Macromol Mater Eng* 2009, 294, 590.
- Kundu, P. P.; Larock, R. C. *Biomacromolecules* 2005, 6, 797.
- Lu, Y.; Larock, R. C. *Macromol Mater Eng* 2007, 292, 863.
- Lu, Y.; Larock, R. C. *Macromol Mater Eng* 2007, 292, 1085.
- Pfister, D. P.; Larock, R. C. *Bioresour Technol* 2010, 101, 6200.
- Quirino, R. L.; Larock, R. C. *J Appl Polym Sci* 2009, 112, 2033.
- Bhuyan, S.; Sundararajan, S.; Pfister, D.; Larock, R. C. *Tribol Int* 2010, 43, 171.
- Quirino, R. L.; Larock, R. C. *J Appl Polym Sci* 2011, 121, 2039.
- Quirino, R. L.; Larock, R. C. *J Appl Polym Sci* 2011, 121, 2050.
- U.S. Soybean oil Production 1982. [http://www.soystats.com/2008/page\\_21.htm](http://www.soystats.com/2008/page_21.htm), 2008. Accessed on 8 January 2011.
- Li, F.; Larock, R. C. *Polym Int* 2003, 52, 126.
- Li, F.; Larock, R. C. *J Polym Environ* 2002, 10, 59.
- Andjelkovic, D. D.; Min, B.; Ahn, D.; Larock, R. C. *J Agric Food Chem* 2006, 54, 9535.