

Cationically Cured Natural Oil-Based Green Composites: Effect of the Natural Oil and the Agricultural Fiber

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ABSTRACT: Green composites were produced from various cationically cured natural oil-based resins and agricultural fibers. The natural oils and agricultural fibers of interest included corn, soybean, fish, and linseed oils and corn stover, wheat straw (WS), and switchgrass fibers. The effects of the types of natural oil and agricultural fiber on the structure and thermal and mechanical properties of the composites were studied using Soxhlet extraction, thermogravimetric and dynamic mechanical analysis, and tensile testing. The green composites, with agricultural fiber loadings of 75 wt %, have thermal stabilities up to 275°C.

The Young's moduli and tensile strengths of the composites ranged from 1590 to 2300 and 5.5 to 11.3 MPa, respectively. In general, an increase in the degree of unsaturation of the natural oil resulted in improvements in the thermal and mechanical properties of the composites. The WS fibers tended to give composites with the best thermal and mechanical properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1392–1400, 2012

Key words: composites; cationic polymerization; renewable resources

INTRODUCTION

The recent volatility in the crude oil market and concerns over the environment have encouraged many industries to focus on the production of greener materials. The plastics and composites industries are no exception. Although poly(lactic acid) has gained the most attention in the plastics industry, there has also been a lot of interest given to the use of natural oils as a feedstock for plastic materials.^{1–3} Natural oils have a triglyceride structure with a high functionality per molecule, which leads to crosslinked thermosetting resins, and are annually renewable, are available in large quantities, and have historically been very inexpensive. In the composites industry, natural fibers are seen as a viable replacement for synthetic fibers because they are biorenewable, biodegradable, and very inexpensive and yet have a high specific strength and stiffness.

Green composites is the term often given to composites prepared from both a biobased filler and a biobased matrix. Work concentrating on the use of functionalized natural oils to prepare green composites has been carried out extensively in the past. Most researchers have used acrylated or methacrylated epoxidized soybean oil, vegetable oil monoglyceride maleates, or epoxidized vegetable oils to produce biobased resins and have reinforced these materials with various lignocellulosic fibers, generally, hemp, flax, or kenaf.^{4–12} Research on the preparation of green composites from unfunctionalized natural oils has either taken advantage of the double bonds already present in the oil to produce thermosetting resins or made use of the hydroxyl groups present in castor oil to produce polyurethanes, which have been reinforced with natural fibers.^{13,14}

The green composites produced in our group have used a range of agricultural fibers to strengthen biobased resins prepared by the free-radical copolymerization of conjugated vegetable oils through the carbon–carbon double bonds present in the triglyceride. Spent germ,¹⁵ the coproduct of wet-mill ethanol production, soybean hulls,¹⁶ corn stover (CS),¹⁷ and wheat straw (WS)¹⁸ have all been used to reinforce resins based on tung oil, conjugated soybean oil (CSOY), or conjugated linseed oil (CLIN). In this study, we also used CS, WS, and switchgrass (SWG) as natural fiber reinforcements but instead focused on resins produced by the cationic copolymerization of conjugated natural oils, such as corn, soybean, fish, and linseed oils. Plastics produced by the

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cationic copolymerization of these oils with styrene (ST) and divinylbenzene (DVB) have been studied in the past by our group,^{19–22} and biocomposites have been prepared by the reinforcement of some of these resins with glass fibers^{23,24} or clays.^{25,26} These previously prepared cationically cured natural oil-based plastics and composites were produced at low temperatures using long cure times, whereas the composites produced in this study were cured at much higher temperatures in order to reduce the cure time. To this date, no green composites have been prepared from cationically cured natural oil-based resins and natural fibers.

CS and WS are the residues remaining after corn and wheat grain harvest, and the 2005 Billion Ton study estimated that 75 and 11 million tons of each, respectively, are available annually in the U.S.²⁷ SWG is a perennial warm-season grass native to North America. A large amount of interest has been given to these fibers, particularly CS and SWG, as a feedstock for cellulosic ethanol production, but they are also being looked into as a reinforcement for plastics. Nearly all of the research in this area has focused on the production of composites from petroleum-based thermoplastics or thermosets, but some have used these fibers as a reinforcement for soy protein-, starch-, and acrylated epoxidized soybean oil-based plastics.^{28–37} The fiber composition and ash content of the CS, WS, and SWG are given in Table I. As can be seen, the fiber composition of the agricultural fibers varies little, but there are notable differences in the ash content.

The annual global productions of soybean, corn, fish, and linseed oils are approximately 26.5, 2.3, 1.1, and 0.8 million tons, respectively.³ The main use of corn and soybean oils is in the food industry, but more recently, they have also been used as a feedstock for biodiesel production. Fish oil is typically used in aquaculture. However, with its nutritional benefit, fish oil is increasingly finding direct use in human foods and capsules.³⁸ Being highly unsaturated, linseed oil is most often used as a drying oil for surface coatings.³⁹ In this work, we studied the effect of the variation of the natural oil and the agricultural fiber on the structure and thermal and mechanical properties of the resulting cationically cured composites.

EXPERIMENTAL

Materials

The soybean and corn oils were purchased in a local supermarket. Menhaden fish oil was supplied by Omega Protein (Houston, TX) and the linseed oil was supplied by Archer Daniels Midland (Decatur, IL). The oils were conjugated to produce conjugated

TABLE I
Composition of the Agricultural Fibers Used^a

Agricultural fiber	Cellulose (mass %)	Hemicellulose (mass %)	Lignin (mass %)	Ash (mass %)
CS	35	23	19	12
WS	33	26	18	5
SWG	33	23	17	10

^a Taken from the U.S. Department of Energy Biomass Feedstock Composition and Property Database.

corn oil (CCORN), CSOY, conjugated fish oil (CFO), and CLIN according to our previously published procedure.⁴⁰ The extent of conjugation was calculated to be in the range 95–100%. ST, DVB (assay 80% by gas chromatography, 20% ethylvinylbenzene), and boron trifluoride diethyl etherate (BFE) were purchased from Sigma-Aldrich Corp. (St. Louis, MO) and were used as received. The release film, Wrightlon 5200, was supplied by Airtech International, Inc. (Huntington Beach, CA). The CS was collected directly from a forage harvester on the Iowa State University Sorenson research farm in Boone County, Iowa. The WS was collected directly from the Iowa State University Burkey research farm in Boone County, Iowa. The SWG was supplied by Chariton Valley Resource Conservation and Development, Inc. (southern Iowa). These three agricultural fibers were ground to pass through a 2 mm screen with a Wiley mill.

Preparation of the natural oil-based resins and composites

The natural oil-based resins were prepared by bulk cationic polymerization. The monomer mixture was prepared by adding 45 wt % conjugated natural oil, 25 wt % ST, and 25 wt % DVB together with vigorous stirring. Before the initiator was added, the resin mixture was cooled in a dry ice/acetone bath. The BFE initiator was modified to ensure a homogeneous polymerization by the mixture of 3 wt % initiator with 5 wt % conjugated oil. The modified BFE initiator was then added to the monomer mixture, and this mixture was stirred, poured into a glass mold, and cured at 180°C for 4 h. In all cases, the composition of the resin was 50 wt % conjugated natural oil, 25 wt % ST, and 25 wt % DVB. The following nomenclature is used: a polymer designated CSOY corresponds to a resin prepared from 50 wt % CSOY, 25 wt % ST, and 25 wt % DVB, and 3 wt % of this total weight was the amount of BFE initiator used.

The composites were prepared using a compression molding process. The resin was mixed as described earlier and then added to the agricultural fiber, which was dried in a vacuum oven at 70°C for approximately 18 h before use. This mixture was

TABLE II
Fatty Acid Compositions of the Natural Oils Used

Natural oil	C=C bonds ^a	Fatty acid composition (%)									
		C14 : 0	C16 : 0	C18 : 0	C18 : 1	C18 : 2	C18 : 3	C20 : 4	C20 : 5	C22 : 5	C22 : 6
Corn	4.0	<1	11	2	25	60	1	—	—	—	—
Soybean	4.5	<1	11	4	23	54	8	—	—	—	—
Fish ^b	5.7	10	20	3	9	2	2	2	13	3	8
Linseed	5.9	<1	5	4	19	24	47	—	—	—	—

^a Number of carbon-carbon double bonds per triglyceride.

^b Contains less than 2% of several other fatty acids.

stirred by hand until all of the agricultural fiber was wet and was then placed in the cavity of the steel mold lined with the release film. The mold was closed and cured at 180°C for 4 h under a pressure of 400 psi. Once the mold was cooled to room temperature, the composite was removed and postcured at 180°C for 1 h. In all cases, the matrix composition was 50 wt % conjugated natural oil, 25 wt % ST, and 25 wt % DVB, and the agricultural fiber loading was 75 wt %. For example, a composite designated CFO-WS refers to a composite prepared with a resin containing 50 wt % CFO, 25 wt % ST, 25 wt % DVB, and 75 wt % WS as the filler.

Characterization

Soxhlet extraction was used to determine the amount of soluble materials in the agricultural fibers, pure resins, and composites and to characterize the structure of the resulting composites. A 4.5 g sample was extracted for 24 h with 110 mL of refluxing methylene chloride with a Soxhlet extractor. After extraction, the resulting solution was concentrated on a rotary evaporator, and both the soluble and insoluble materials were dried in a vacuum oven at 70°C overnight before they were weighed. ¹H-NMR spectroscopic analysis of the soluble substances was carried out in CDCl₃ with a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz.

A Q50 thermogravimetric analysis (TGA) instrument (TA Instruments, New Castle, DE) was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from room temperature to 650°C at a heating rate of 20°C/min. Generally, a 10–12 mg sample was used for TGA.

The dynamic mechanical properties of the resins and the resulting composites were obtained on a TA Instruments Q800 dynamic mechanical analysis (DMA) machine in tension mode. A rectangular specimen of about 25 × 8.5 × 1.5 mm³ (Length × Width × Thickness) was cut from the samples. Each specimen was cooled to -120°C and then heated under air at 3°C/min to 200°C at a frequency of 1 Hz.

The tensile tests were conducted at 25°C according to ASTM D 638 with an Instron universal testing

machine (model 4502, Norwood, MA) at a crosshead speed of 10 mm/min. The dogbone-shaped test specimen (type I specimen in ASTM D 638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

RESULTS AND DISCUSSION

Fatty acid composition of the natural oils

As mentioned before, natural oils are made up of triglycerides, and what distinguishes one from another is their fatty acid composition. Table II gives the fatty acid composition and the number of C—C double bonds per triglyceride for corn, soybean, fish, and linseed oils. The vegetable oils used in this work (corn, soybean, and linseed oils) tend to be rich in palmitic (C16 : 0), stearic (C18 : 0), oleic (C18 : 1), linoleic (C18 : 2), and linolenic (C18 : 3) acids. Fish oil, on the other hand, has a relatively low amount of C18 fatty acids and instead contains significant amounts of saturated fatty acids and long-chain, highly unsaturated fatty acids. The different fatty acid composition for each oil leads to a variation in the degree of unsaturation. Corn oil, with significant amounts of oleic and linoleic acids and very little linolenic acid, has a relatively low degree of unsaturation (~ 4.0 C—C double bonds), whereas linseed oil, with nearly 50% linolenic acid, has a higher degree of unsaturation (~ 5.9 C—C double bonds). The different levels of C—C double bonds results in resins with different crosslink densities, which should affect the thermal and mechanical properties of the pure resins and resulting composites. Typically, we have seen that more highly unsaturated oils give plastics and composites with improved thermal and mechanical properties.^{17,22–24} Fish and linseed oils both have approximately the same number of C—C double bonds per triglyceride, but their fatty acid compositions are very different. The C—C double bonds in linseed oil are fairly evenly distributed throughout the triglyceride molecule, whereas fish oil has significant amounts of saturated fatty acids and then longer chain fatty acids with four or more C—C double bonds. Although the

TABLE III
Extraction Data and Thermal Stability of the Resins and Composites

Entry	Sample	Soxhlet extraction	TGA ^a	
		Percentage soluble materials	T ₁₀ (°C)	T ₅₀ (°C)
1	2 mm CS	<1	259	319
2	2 mm WS	<1	266	311
3	2 mm SWG	3	292	348
4	CCORN resin	15	386	472
5	CSOY resin	15	383	471
6	CFO resin	19	297	466
7	CLIN resin	13	399	471
8	CCORN-CS	8	291	370
9	CSOY-CS	8	294	377
10	CFO-CS	7	294	378
11	CLIN-CS	5	299	390
12	CCORN-WS	9	297	403
13	CSOY-WS	9	297	407
14	CFO-WS	7	295	403
15	CLIN-WS	6	299	423
16	CCORN-SWG	7	299	381
17	CSOY-SWG	7	299	389
18	CFO-SWG	7	300	378
19	CLIN-SWG	5	300	394

degree of unsaturation for these two oils is the same, the crosslinking in the resulting resins should be considerably different. The large amount of saturated fatty acid side chains in fish oil will not get incorporated into the polymer chains and will, thus, act as a plasticizer, which should give a softer material than materials derived from linseed oil.

Soxhlet extraction analysis

The percentage of soluble materials from the agricultural fibers, pure resins, and composites are given in Table III. The agricultural fibers used in this study generally contained a low amount of soluble materials (entries 1–3). Although the ¹H-NMR spectra are not shown, the extracts were mainly composed of a fatty substance (triglyceride oil, fatty acids, etc.).

With the exception of the resin prepared from CFO, the percentage of soluble materials changed very little as the natural oil was varied (entries 4–7). It decreased slightly from 15% for the CCORN-based resin to 13% for the resin from CLIN. The higher amount of soluble materials for the CFO-based resin (19%) was likely the result of the high saturated fatty acid content present in CFO. Because more than a third of the fatty acid chains in CFO are saturated, it is likely that some of the triglyceride molecules contain two saturated fatty acid side chains. These molecules, with a low potential to crosslink, should have more readily formed oligomers that were soluble in methylene chloride. A representative ¹H-NMR spectrum of the extract from the CLIN-

based resin is given in Figure 1. Regardless of the natural oil, the ¹H-NMR spectra of the resin soluble extracts were alike and were also similar to the spectra of soluble extracts from cationically cured natural oil-based resins previously prepared in our group.^{20,22} Earlier studies indicated that the extracts mainly contained unreacted oil, initiator fragments (peak at 4.1 ppm), and oligomers composed of oil and the aromatic comonomers (broad peak above 7 ppm).

The composites contained between 5 and 9% soluble materials. From the data in Table III, it can be seen that the amount of soluble materials in the agricultural fibers appeared to have little effect on the amount of soluble materials in the resulting composites. For example, the 2 mm SWG had the highest amount of soluble materials, yet the composites reinforced with SWG tended to have the lowest percentage of soluble materials. Also, when taking into account the percentage of soluble materials of the individual components (fibers and resin), the composites tended to have a higher than expected amount of soluble materials. This was particularly true for the CS and WS composites. The higher than expected percentage of soluble materials for the composites is likely the result of a lower crosslinked resin. It is likely that the addition of fibers inhibited chain propagation during the polymerization and resulted in less crosslinking.

Although the percentage of soluble materials varied little for the composites and may be within the experimental error, the overall trend appears to be that a more highly unsaturated natural oil gives a lower percentage of soluble materials. For example, with the CS composites, the percentage of soluble

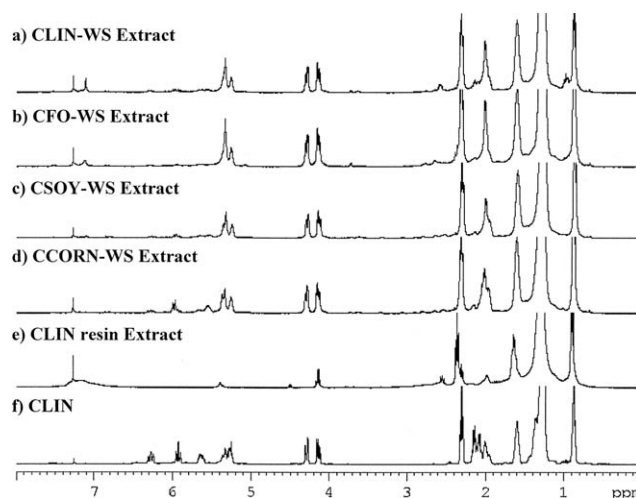


Figure 1 ¹H-NMR spectra of the extracts from (a) the CLIN-WS composite, (b) the CFO-WS composite, (c) the CSOY-WS composite, (d) the CCORN-WS composite, (e) the CLIN resin, and (f) CLIN.

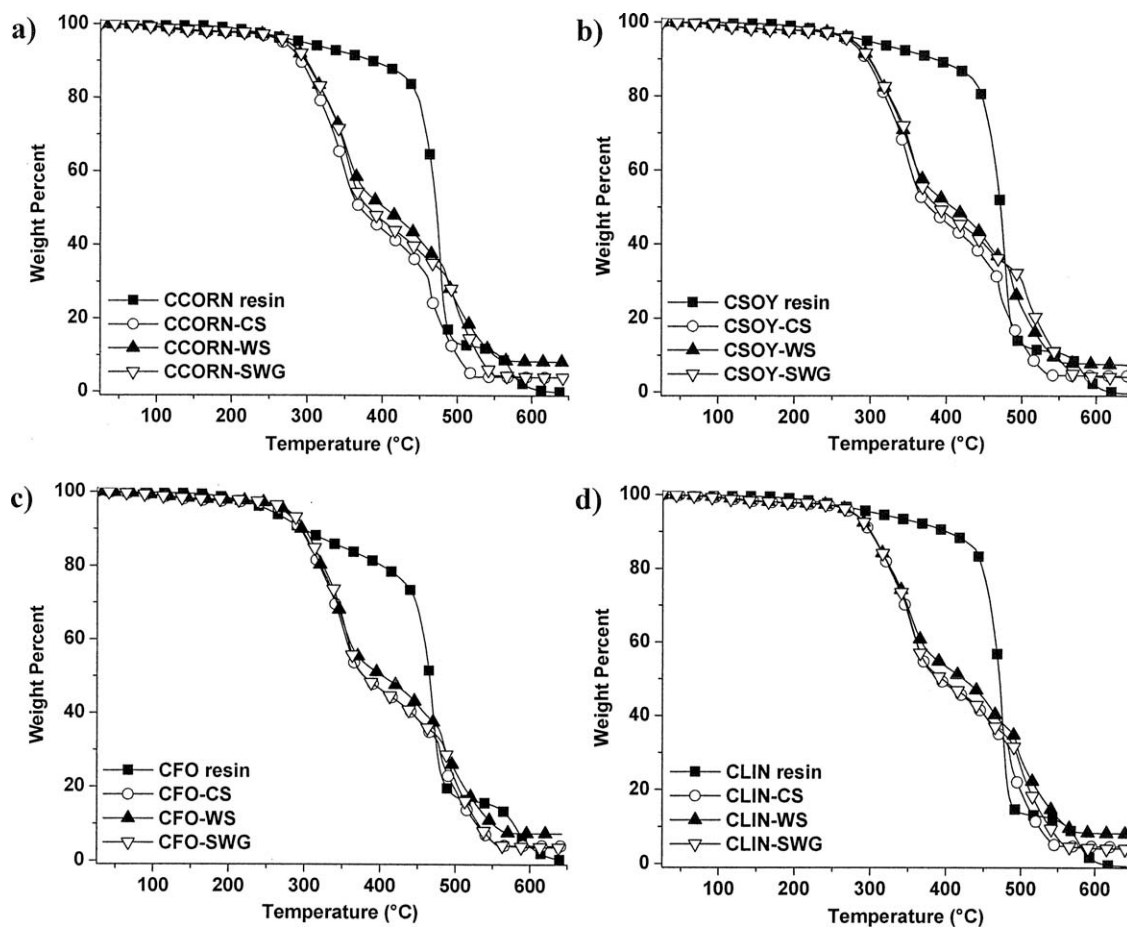


Figure 2 TGA curves for the pure resins and composites prepared from (a) CCORN, (b) CSOY, (c) CFO, and (d) CLIN.

materials stayed constant at 8% for the CCORN- and CSOY-based composites (entries 8 and 9), decreased to 7% for the CFO-based composite (entry 10), and decreased further to 5% for the CLIN-based composite (entry 11). With regard to the fiber, the WS composites tended to have the highest amount of soluble materials, followed by CS, and then SWG. For the CCORN-based composites, the composite reinforced with WS contained 9% soluble materials, the CS composite contained 8% soluble materials, and the SWG composite contained 7% soluble materials. From the $^1\text{H-NMR}$ spectra of the soluble extracts from the composites [Fig. 1(a–d)], it was seen that the soluble material was essentially unreacted natural oil or oligomers mostly composed of natural oil. All of the spectra of the composite extracts are not shown, but it was observed that the composition of the extracts was only dependent on the type of the natural oil and not on the agricultural fiber. While the spectra for extracts from the composites prepared from different oils were very similar, the peak in the aromatic region at 7.1 ppm became more prominent as the number of C–C double bonds in the oil increased. These aromatic protons were from ST or DVB comonomers, most likely contained in

low-molecular-weight oligomers, along with the natural oil.

TGA

The temperature at 10% weight loss (T_{10}) and the temperature at 50% weight loss (T_{50}) for the agricultural fibers, pure resins, and composites are given in Table III, and the TGA curves for the pure resins and composites are given in Figure 2. From the TGA curves, we observed that the pure resins were far more thermally stable than the resulting composites and that both the resins and composites essentially degraded in three stages. For the resins, the first stage, up to about 450°C, corresponded to the loss of the unreacted oil and low molecular weight oligomers. The second stage, from 450 to 500°C, corresponded to degradation of the crosslinked resin and char formation, and the char was oxidized in the final stage, greater than 500°C. With the exception of the CFO-based resin, the TGA data in Table III suggests that the initial thermal stability of the resins was somewhat dependent on the degree of unsaturation of the natural oil, whereas no effect was observed at higher temperatures. T_{10} remained

TABLE IV
Thermomechanical Properties of the Resins and Composites

Entry	Sample	DMA			Tensile properties		
		T_g (°C)	E' at 25°C (MPa)	E' at 150°C (MPa)	E (MPa)	σ (MPa)	ε (%)
1	CCORN resin	82	1030	— ^a	460 ± 20	13.9 ± 0.5	22 ± 4
2	CSOY resin	84	1040	— ^a	470 ± 10	14.7 ± 0.3	25 ± 2
3	CFO resin	108	1230	— ^a	630 ± 110	18.8 ± 0.2	10 ± 3
4	CLIN resin	97	1520	— ^a	920 ± 120	25.1 ± 1.0	10 ± 4
5	CCORN-CS	-23, 97	1970	1310	1590 ± 70	7.0 ± 0.7	1 ± 0
6	CSOY-CS	-15, 97	1950	1280	1790 ± 70	8.2 ± 0.2	1 ± 0
7	CFO-CS	9, 94	2120	1330	1870 ± 100	8.6 ± 0.7	1 ± 0
8	CLIN-CS	-14, 98	2290	1490	1960 ± 100	11.3 ± 0.8	1 ± 0
9	CCORN-WS	-18, 98	2410	1610	2050 ± 110	8.1 ± 0.9	1 ± 0
10	CSOY-WS	-32, 101	2580	1750	2160 ± 100	8.3 ± 0.8	1 ± 0
11	CFO-WS	-12, 96	2810	1810	2300 ± 170	8.4 ± 0.4	1 ± 0
12	CLIN-WS	-15, 97	2970	1930	2280 ± 120	10.7 ± 0.7	1 ± 0
13	CCORN-SWG	-13, 99	1950	1230	1710 ± 160	6.7 ± 1.6	1 ± 0
14	CSOY-SWG	-11, 100	2170	1400	1800 ± 90	6.5 ± 0.6	1 ± 0
15	CFO-SWG	97	2310	1400	1850 ± 170	5.5 ± 0.9	1 ± 0
16	CLIN-SWG	-6, 101	2480	1570	1920 ± 90	8.5 ± 0.9	1 ± 0

^a The pure resin DMA specimens broke below 150°C.

relatively constant at 386 and 383°C for the CCORN- and CSOY-based resins, respectively, and increased to 399°C for the resin prepared from CLIN, but T_{50} stayed constant at about 471°C, regardless of the vegetable oil used. The lower thermal stability for the CFO-based resin, particularly at the lower temperatures, was likely the result of the high amount of saturated fatty acids contained in CFO. This led to a higher amount of soluble materials in the CFO-based resin, which was lost at lower temperatures.

One of the drawbacks of natural fibers is their low thermal stability (Table III, entries 1–3). By replacing 75 wt % of the resin with agricultural fibers, it was observed decreases of about 100°C for the T_{10} and T_{50} values. As shown in Figure 2, the first stage of degradation for the composites occurred up to 275°C and corresponded to the loss of water, unreacted oil, and low molecular weight oligomers. In the final two stages, the resin and fiber components (cellulose, hemicellulose, and lignin) of the lignocellulosic fillers decomposed, but because the degradation of the fiber components is very complex when in an oxidative atmosphere, it was not possible to determine where each degraded.⁴¹ With regard to the natural oil, the composites tended to become more thermally stable as the degree of unsaturation increased. The CFO-WS and CFO-SWG composites were exceptions to this rule. For example, for the CS composites, T_{10} and T_{50} increased from 291 to 299 and 370 to 390°C, respectively, as the natural oil was changed from CCORN to CLIN (entries 8–11). Again, the lower than expected thermal stability for the CFO-based composites was likely the result of the high saturated fatty acid content in CFO and,

therefore, the likelihood of forming low molecular weight oligomers.

Figure 2 shows a comparison of the thermal stability of the composites as the agricultural fiber was changed and the natural oil-based resin was kept constant. As with the percentage of soluble materials, the thermal stability of the agricultural fibers did not affect the thermal stability of the resulting composites. Even though the thermal stability varied significantly for each agricultural fiber (entries 1–3), initially, changing the fiber had little effect on the thermal stability of the composites. At higher temperatures, the WS composites tended to be the most stable, followed by SWG, and then CS. For example, with the CLIN-based composites, T_{50} decreased from 423°C for the WS composite to 394°C for the SWG composite, and further to 390°C for the CS composite. Meanwhile, for the same CLIN-based composites, T_{10} basically stayed constant at 300°C.

DMA

The room temperature and rubbery storage moduli E' , and glass-transition temperatures (T_g) for the pure resins and the resulting composites are given in Table IV. As seen from the E' versus temperature curves given in Figures 3(a–d), the pure resins exhibited dynamic mechanical properties typical of our thermosetting natural oil-based plastics.⁴² While in the glassy state at lower temperatures, the modulus remained relatively constant. At about 0°C, a large decrease in E' was observed, which corresponds to the onset of segmental mobility in the polymer network, but because the samples yielded

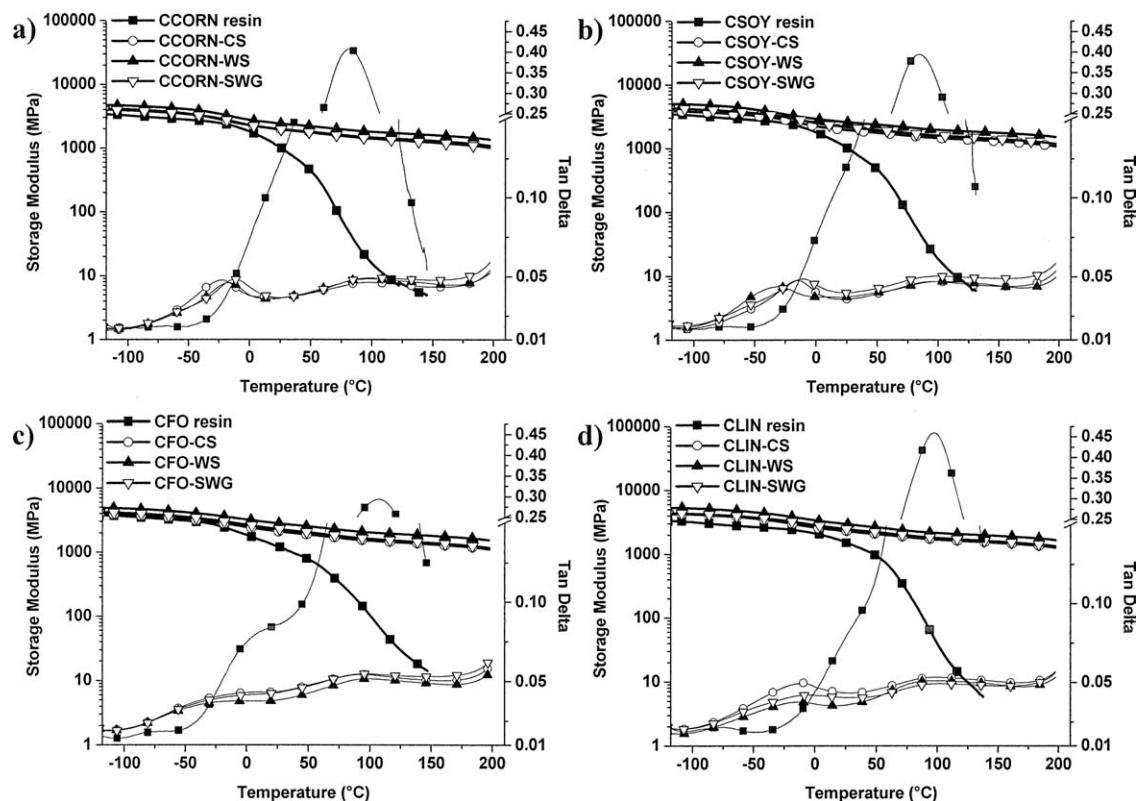


Figure 3 E' and $\tan \delta$ curves for the pure resins and composites prepared from (a) CCORN, (b) CSOY, (c) CFO, and (d) CLIN.

at higher temperatures, the resins did not exhibit the typical rubbery plateau. The room temperature E' of the resins tended to be directly related to the degree of unsaturation of the natural oil. E' increased from 1030 to 1520 MPa when the oil was changed from CCORN (~ 4.0 C–C double bonds) to CLIN (~ 5.9 C–C double bonds).

The addition of agricultural fibers to the resins caused an increase in E' over the entire temperature range but particularly at higher temperatures. The dramatic increase in E' in the rubbery region was a result of the reduction in the mobility and deformability of the resin caused by the stiff lignocellulosic fibers.⁴³ Increasing the number of C–C double bonds in the natural oil and, therefore, the crosslink density of the matrix, led to an increase in the stiffness of the composites over the entire temperature range. For the composites reinforced with WS (entries 9–12), the room temperature and rubbery plateau E'' 's increased from 2410 and 1610 MPa for the CCORN-based composites to 2970 and 1930 MPa for the CLIN-based composites. From the E' curves in Figure 3, it can be seen that the WS fibers led to composites with the highest stiffness. The SWG composites tended to be slightly more rigid than the CS composites, but both these fibers gave composites with significantly lower E'' 's than the composites from WS. For example, the room temperature and rubbery E'' 's for the composite designated CFO–WS

were 2810 and 1810 MPa, respectively (entry 11). When the WS fibers were replaced with SWG, the same moduli decreased to 2310 and 1400 MPa (entry 15), whereas the CFO–CS composite had room temperature and rubbery E' values of 2120 and 1330 MPa (entry 7).

The T_g 's listed in Table IV were taken from the peaks of the $\tan \delta$ versus temperature curves, which are given in Figure 3. It should be noted that a break in the y axis was inserted to account for the large difference in the peak heights for the pure resins and composites. For the most part, increasing the degree of unsaturation of the natural oil increased the T_g of the resulting plastic. The T_g of the pure resin increased from 82 to 97°C as the natural oil was changed from CCORN to CLIN. The higher T_g for the CFO-based resin appeared to be the result of a phase separation in the resin. When looking at Figure 3(c), a strong shoulder peak around 0°C was observed in the $\tan \delta$ curve for the CFO-based resin that was not present in the curves of the other natural oil-based resins. This indicated a slight phase separation in the CFO-based resin and may have been a result of the difference in reactivities of the saturated and highly unsaturated fatty acid side chains present within CFO. The CFO molecules with a significant amount of saturated fatty acid side chains would have been far less reactive toward polymerization than the natural oil molecules with

highly unsaturated side chains. The more reactive, highly unsaturated CFO molecules should have gotten incorporated into the polymer chains first, leading to a highly crosslinked, rigid phase. As their concentration decreased, more of the highly saturated CFO molecules would have gotten incorporated and given a softer phase with a lower crosslink density.

Adding agricultural fibers to the resin resulted in dramatic decreases in the $\tan \delta$ peak heights and also caused a phase separation in the matrix. The large decrease in the peak height could have been a result of two things: (1) the reduced mobility of the polymer chains caused by the addition of stiff agricultural fibers and (2) because the peak height is a relative measure of the amount of polymeric material taking part in the transition, a reduction was expected as the resin was replaced by the fibers.^{43,44} The phase separation in the matrix was most likely a result of the agricultural fibers inhibiting the mobility of the monomers and propagation of the polymer chains. This inhibition should have been more dramatic for the larger, high molecular weight natural oil molecules and limited their ability to be incorporated into the polymer chains. This would have led to a rigid phase that was rich in the ST and DVB comonomers and a softer phase that was rich in the natural oils. Each of these phases has its own T_g : the oil-rich phase with a T_g of about -15°C and the ST/DVB-rich phase with a T_g of about 100°C . Similar results have been observed in our previous work on composites.^{17,18} From Figure 3, it can be observed that, with the exception of the CFO-based composites, all of the $\tan \delta$ curves for the composites appeared pretty similar. With the CFO-based composites, there was no strong peak for the oil-rich phase but instead more of a shoulder. The T_g 's varied somewhat for all of the composites, but no real trend was observed as the natural oil or agricultural fiber was varied.

Mechanical properties

The Young's moduli (E), tensile strengths (σ), and elongations at break (ϵ) for the resins and composites are given in Table IV. E and σ are also displayed graphically in Figure 4. The pure natural oil-based resins displayed tensile properties typical of rigid plastics. Increasing the number of C–C double bonds in the natural oil increased the strength and stiffness of the resulting plastic but also made it more brittle. E increased from 460 to 920 MPa, σ increased from 13.9 to 25.1 MPa, and ϵ decreased from 22 to 10% as the number of C–C double bonds per triglyceride was increased from about 4.0 in CCORN to about 5.9 in CLIN.

When the agricultural fibers were added to the resins, a nearly threefold increase in the stiffness of

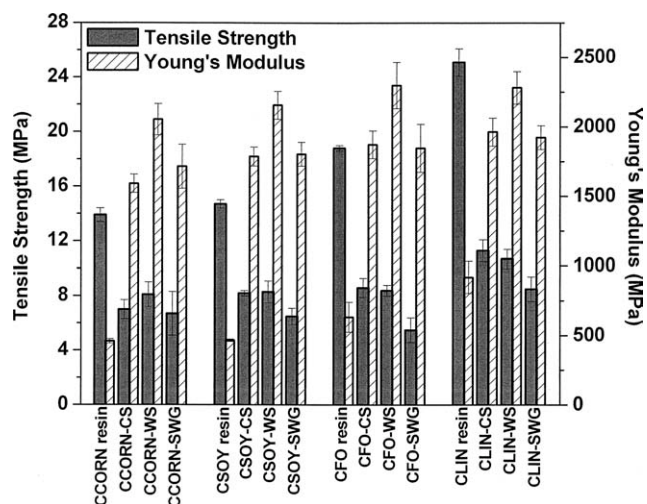


Figure 4 E and σ values for the pure resins and composites.

the materials was observed, but the strengths were approximately halved, and the materials became much more brittle. The enhanced stiffness of the composites could be attributed to the stiff lignocellulosic fibers, whereas the decreased strength and brittle nature of the composites was likely a result of the poor interfacial interaction between the hydrophobic natural oil-based matrix and the hydrophilic lignocellulosic fibers. For the most part, increasing the crosslink density of the matrix by increasing the degree of unsaturation of the natural oil caused increases in the stiffness and strength of the composites. For example, with the CS composites, E and σ increased from 1590 to 1960 and 7.0 to 11.3 MPa, respectively, when changing from a CCORN-based resin to a CLIN-based resin (Table IV, entries 5–8). Regardless of the type of natural oil or the agricultural fiber, ϵ stayed constant at 1%. From Figure 4, we can better see the effect of the agricultural fiber on E and σ when the natural oil was held constant. The WS fibers definitely gave composites with the highest modulus, whereas the composites from CS and SWG fibers had about the same stiffness. For example, for the CFO-based composites, E decreased from 2300 MPa for the WS composite to 1870 and 1850 MPa for the CS and SWG composites, respectively. With regard to σ , the CS and WS fibers gave composites with approximately the same strength, and the SWG fibers gave the weakest composites. The CFO–CS and CFO–WS composites had σ values of 8.6 and 8.4 MPa, respectively, whereas σ decreased to 5.5 MPa for the CFO–SWG composite.

CONCLUSIONS

Cationically cured resins based on corn, soybean, fish, and linseed oils were reinforced with CS, WS,

and SWG fibers to produce green composites. The composites prepared were much more brittle and had lower σ 's than the pure resins, but the addition of fibers also resulted in a roughly threefold increase in the stiffness when compared to the pure resins. Because of the low thermal stability of the agricultural fibers, the composites had a lower thermal stability than the natural oil-based pure resins but were still stable up to 275°C. Natural oils with a higher number of C=C double bonds per triglyceride typically give composites with improved thermal and mechanical properties. Of the three agricultural fibers studied, the composites prepared with WS as a reinforcement tended to have the best thermal and mechanical properties.

Although some of the mechanical and thermal properties of the composites were inferior to the properties of the pure resins, it is important to note that the biorenewable content of the composites was about 88%, compared to 50% for the resins. The high annually renewable content of these composites should make them appealing to the automotive, construction, and furniture industries. Although these composites are somewhat weak, it is expected that they should still find nonstructural applications, such as automotive panels, wall panels, ceiling tiles, window frames, furniture, and doors, in the previously mentioned industries.

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