

Asolectin from soybeans as a natural compatibilizer for cellulose-reinforced biocomposites from tung oil

Ashley Johns, Steven Morris, Kyle Edwards, Rafael Lopes Quirino

Chemistry Department, Georgia Southern University, Statesboro, Georgia 30460

Correspondence to: R. L. Quirino (E-mail: rquirino@georgiasouthern.edu)

ABSTRACT: The free radical copolymerization of tung oil, divinylbenzene, and n-butyl methacrylate results in bio-based thermosetting polymers with tunable properties. Biocomposites have been obtained by the reinforcement of such bio-based resins with α -cellulose. Asolectin from soybeans consists of a mixture of natural, polyunsaturated phospholipids. Because of its long, unsaturated fatty acid chains, and the presence of phosphate and ammonium groups, asolectin from soybeans is a good candidate for acting as a natural compatibilizer between the hydrophobic matrix and the hydrophilic reinforcement. In the current work, we investigate the changes in properties resulting from the addition of asolectin to a tung oil-based polymer reinforced with α -cellulose. An evaluation of the cure-kinetics of the tung oil-based resin has been conducted by dielectric analysis (DEA), and the final biocomposites have been thoroughly characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), Soxhlet extraction, and scanning electron microscopy (SEM). © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41833.

KEYWORDS: biomaterials; biopolymers and renewable polymers; cellulose and other wood products; composites; thermosets

Received 12 September 2014; accepted 4 December 2014

DOI: 10.1002/app.41833

INTRODUCTION

Aspirations to replace petroleum-derived materials with more environmentally friendly alternatives have resulted in the recent development of numerous bio-based resin systems. Among the bio-based resins recently developed, one can find polyurethanes,^{1,2} polyester amides,³ polyolefins,^{4–6} and cyanate esters.⁷ Many of these resins have been reinforced with inorganic materials, such as nanoclays,^{5,8} and glass fibers.^{9,10} Alternatively, petroleum-derived thermoplastics have been reinforced with natural fillers.^{11–13} In any of the aforementioned systems, there is an intrinsic incompatibility between a hydrophobic resin and a hydrophilic reinforcement. Improvements in filler–matrix interactions have been observed when maleic anhydride was added to the formulation of vegetable oil-based thermosetting resins reinforced with rice hulls,¹⁴ and wood flour.¹⁵

As an abundant and diverse biorenewable resource, plant oils have been used in the preparation of films, coatings, and resins with promising properties.^{16,17} Tung oil has 80% of its fatty acid chains being α -eleostearic acid, a triply conjugated fatty acid [Figure 1(A)]. The Carbon–Carbon double bonds in tung oil can readily react with vinyl comonomers, such as divinylbenzene, styrene, and dicyclopentadiene, via cationic, thermal, or free radical polymerizations, resulting in highly crosslinked polymer networks.^{16–18}

Cellulose is a linear, hydrophilic polysaccharide. It is a stiff homopolymer composed of repeating D-glucose units as shown in Figure 1(B).¹⁹ Due to their biodegradability, accessibility, exceptional mechanical properties, and high aspect ratio, cellulose nanocrystals have increasingly been used for the production of inexpensive materials.²⁰ Cellulose fibers have also been used as reinforcement in composites, such as in the addition of fibers from recycled newspaper, or α -cellulose short fibers, to poly(lactic acid).^{21,22} α -cellulose is a crystalline polymer with the highest degree of polymerization and stability amongst its analogues, β - and γ -cellulose, which are indeed classified as hemicelluloses.²³

Asolectin from soybeans is a mixture of phospholipids extracted from soybeans with an approximate composition of 25% phosphatidylcholine, 25% cephalin, 25% phosphatidylinositol, and small amounts of other phospholipids from soybeans.²⁴ Approximately 24% of the fatty acid chains in asolectin are saturated, 14% are mono-unsaturated, and 62% are poly-unsaturated.²⁴ A generic chemical representation of asolectin from soybeans is provided in Figure 1(C). Asolectin from soybeans has been frequently used in the synthesis of functional membrane proteins,^{25,26} and lipid bilayers for the study of transporting processes involving Cd⁺ and Pb⁺.^{24,26} To the best of our

Additional Supporting Information may be found in the online version of this article.

© 2015 Wiley Periodicals, Inc.

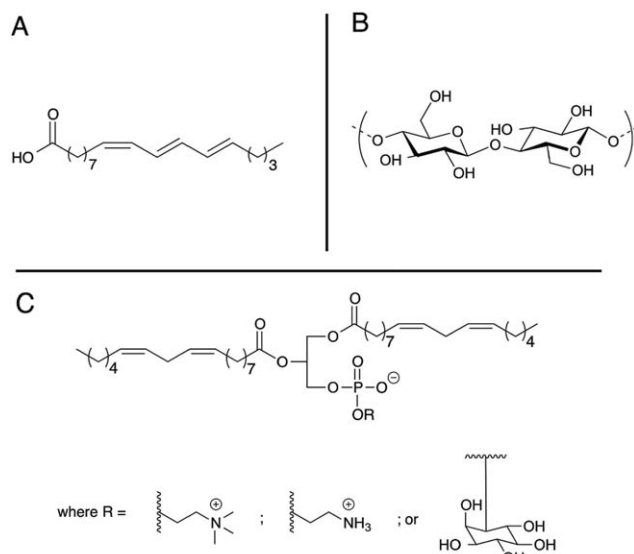


Figure 1. Chemical structure of (A) α -oleostearic acid, (B) α -cellulose, and (C) a generic chemical representation of asolectin from soybeans.

knowledge, there has been no report to date on the use of asolectin as a compatibilizer in bio-based composites.

It is hypothesized that the large number of polyunsaturated fatty acids in asolectin enables the molecule to be free radically polymerized in the presence of other reactive and compatible olefins. Due to obvious similarities in the structures of phospholipids and triglycerides, it is expected that a copolymer of tung oil and asolectin can be readily formed. The addition of asolectin in triglyceride-based polymers introduces highly polar phosphate and ammonium groups on the polymer structure. Such functional groups constitute a viable chemical handle, able to promote strong interactions with hydrophilic reinforcements, such as cellulose. Asolectin can then act as a good compatibilizer between hydrophobic matrices and hydrophilic reinforcements.

In the current manuscript we report the preparation of asolectin and tung oil-based thermosets reinforced with α -cellulose. Cure time, resin composition, and filler load have been established based on preliminary trials and dielectric analyses (DEA). The thermo-mechanical properties of resins and composites were evaluated by thermogravimetric analysis (TGA), differential

scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The composites have also undergone scanning electron microscopy (SEM) analysis and Soxhlet extraction with analysis of the extracts by proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy.

EXPERIMENTAL

Materials

n-butyl methacrylate (BMA), α -cellulose powder, tung oil, asolectin from soybeans, and di-*tert*-butyl peroxide (DTBP) were acquired from Sigma-Aldrich (St. Louis, MO) and used as received. Divinylbenzene (DVB) was purchased from TCI America (Portland, OR), and styrene was bought from Acros Organics (New Jersey, NJ).

Methods

Preparation of Tung Oil-Based Thermosetting Polymers. Predetermined amounts of tung oil, BMA, and DVB (as indicated in the discussion) were directly weighed in a 20-mL glass vial. A flow chart describing all steps involved in the synthesis of tung oil-based thermosets is provided in Figure 2. Various times and temperatures were applied, according to predetermined schedules indicated in the discussion, to achieve completely cured thermosets.

Preparation of Cellulose-Reinforced Biocomposites. Following the same procedure described for the synthesis of the thermosetting resins, α -cellulose was added to the glass vial right before the addition of the extra 5 wt % of DTBP. In preliminary trials, the addition of more than ~ 36 wt % of α -cellulose resulted in samples in which the relative volume of resin was not enough to wet all of the α -cellulose particles and form a continuous matrix phase. On the other hand, when less than 36 wt % of α -cellulose was added to the monomer mixture, the reinforcement precipitated in the glass vial during curing of the resin, leaving a layer of unreinforced polymer on top of the composites. Finally, adding 36–37 wt % of α -cellulose produced samples with only a very thin layer of unreinforced resin left. The composites discussed in this work have been prepared by adding 5 g of α -cellulose to 10 g of the desired comonomer mixture. α -cellulose was added in small increments, and as the mixture thickened, a spatula was used to thoroughly homogenize all of the components. DTBP was then mixed into the sample. The glass vial was capped and placed in a convection oven for the pre-set cure schedule. After curing, the thin layer of

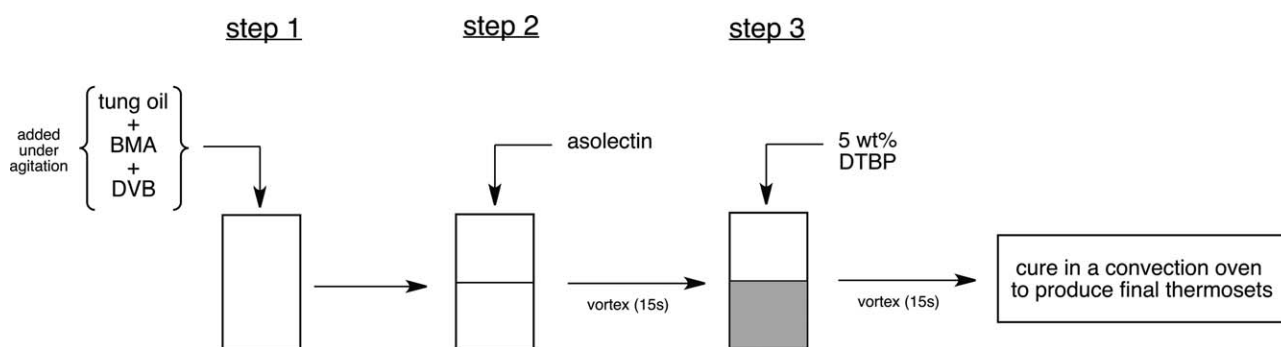


Figure 2. Flow chart showing the steps involved in the synthesis of tung oil-based thermosets.

Table I. Comonomer Composition of Selected Samples Prepared During Preliminary Data Assessment

Entry	Asolectin (wt %)	Tung oil (wt %)	BMA (wt %)	DVB (wt %)
1	10	10–20	60–50	20
2	10	30	40	20
3	10	40	30	20
4	10	50	20	20

unreinforced resin left on top of the composite was removed, and the remaining portion of the composite was weighed to calculate the final wt % of cellulose.

Characterization

To determine curing rates, DEA experiments were conducted with an Epsilon DEA 230/1 cure monitor (Netzsch Instruments North America LLC, Burlington, MA) equipped with a flexible probe that was immersed in the resin during curing. The cure was achieved in a convection oven kept at a constant temperature, as indicated in the discussion. The DEA tests were run for 24 h with frequencies ranging from 0.3 Hz to 10,000.0 Hz. The permittivity and loss factor of the samples were measured as a function of time. The results presented in the text correspond to a plot of ion viscosity ($\text{Ohm} \cdot \text{cm}$) versus time. The sample size used was ~ 10 g.

DSC experiments were conducted with a Q20 DSC instrument (TA Instruments, New Castle, DE). Tests were run in a N_2 atmosphere, and ~ 10 mg samples were heated from -30°C to 200°C at a rate of $10^\circ\text{C}/\text{min}$. A Q50 TGA instrument (TA Instruments, New Castle, DE) measured weight loss of samples (~ 10 mg) under an air atmosphere as a function of temperature. Samples were heated from room temperature to 650°C at a rate of $20^\circ\text{C}/\text{min}$.

A Q800 DMA (TA Instruments, New Castle, DE) with a tension fixture was used for all DMA experiments. Samples were cut into $23.0 \text{ mm} \times 10.0 \text{ mm} \times 2.2 \text{ mm}$ (length \times width \times thickness) segments; each segment was cooled to -60°C and heated to 150°C at a rate of $3^\circ\text{C}/\text{min}$ in iso-strain mode. Experiments were conducted under air at a frequency of 1 Hz and amplitude of $14 \mu\text{m}$. Three experiments were run for each sample. Results reflect the average of the three trials.

1–3 g composite samples underwent Soxhlet extraction for 24 h with dichloromethane. The solvent was removed from the extracts using a rotary evaporator. Soluble and insoluble materials were dried in a vacuum oven at 70°C overnight. After weighing the recovered materials, the soluble portions were dissolved in deuterated chloroform for ^1H -NMR spectroscopy analysis. The ^1H -NMR spectra were obtained on an Agilent MR400DD2 spectrometer (Santa Clara, CA) operating at 400 MHz.

SEM images were obtained in a JSM-760F Field Emission Scanning Electron Microscope (JEOL, Peabody, MA), using an accelerating voltage of 1.0 kV, lower detector scanning mode (LEI),

and an emission current of approximately $81 \mu\text{A}$. The images were collected on fracture surfaces of the composites.

RESULTS AND DISCUSSION

Preliminary experiments were conducted in order to determine the optimum resin composition. For a full list of compositions tested, please refer to Supporting Information Table S1. Each one of the preliminary samples tried has been cured at 140°C for 14 h, following previously established conditions²⁷ and was visually assessed. With an initial goal of creating a completely bio-based polymer from asolectin and tung oil, viable materials were only achieved when other reactive comonomers, such as divinylbenzene (DVB), *n*-butyl methacrylate (BMA), or styrene, were added in partial replacement of asolectin and tung oil. When either BMA, or styrene, were used as the only additional comonomers, the polymers formed were not fully cured in the heating time employed. Trials that incorporated varying quantities of DVB as the only additional comonomer resulted in rigid, but exceedingly brittle samples. From these trials, it was concluded that a combination of DVB and BMA is necessary to afford viable, fully cured polymers. By keeping the concentration of any two of the comonomers constant and varying the other two within 10 wt % at a time, it was possible to identify the optimum concentrations of asolectin (10 wt %) and DVB (20 wt %), as seen in Table I.

After determining the optimum concentrations of asolectin and DVB, variations in the amounts of tung oil and BMA resulted in the ideal polymer composition. While the compositions shown in Entries 2–4 (Table I) produced fully polymerized thermosets, Entry 3 (Table I) exhibited the fewest cracks or imperfections, and was therefore used in all following experiments denoted by TUN-ASO. The variation of that formulation in which asolectin was not included is henceforth called TUN, and has the following composition: 44.44 wt % of tung oil, 33.33 wt % of BMA, and 22.22 wt % of DVB.

DEA experiments were conducted in order to determine the optimal cure time and temperature for the ideal formulation established in the preliminary trials. In Figure 3, DEA curves at 120°C , 130°C , and 140°C are shown. The initial decrease in ion viscosity observed in the first 45 min of each one of the curves corresponds to an increase in ion mobility during initial heating of the monomer mixture and before polymerization starts. After ~ 45 min, polymerization begins, and a steady increase in ion viscosity occurs until full cure is reached and the ion viscosity plateaus. As can be clearly seen by a comparison of the slope of the curves after 35 min in Figure 4, the polymerization rate at 120°C is much lower than at 130°C or 140°C . After 10 h, the resin is still not fully cured when heated at either 120°C or 130°C . At 140°C , a fully cured sample is obtained after ~ 2 h 50 min.

To assess the cure-kinetic behavior of the system as a function of tung oil concentration, DEA experiments with samples of various resin compositions were carried out at 140°C (Figure 4). It can be clearly seen that for the sample containing 50 wt % of tung oil [Figure 4(C)], the polymerization is not completed within the experiment time (10 h). An early and short

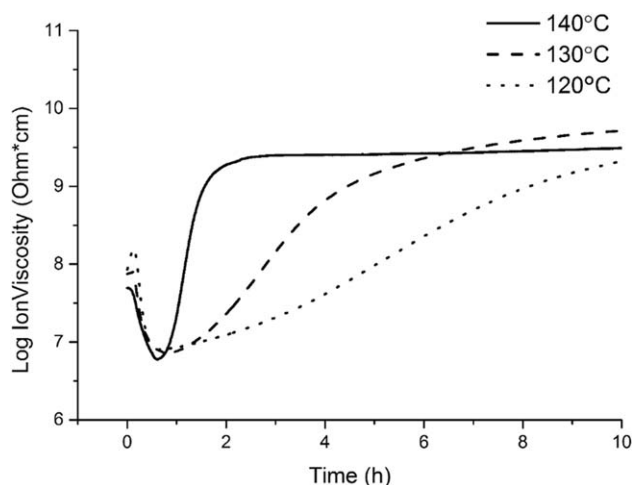


Figure 3. Dielectric analysis of tung oil-based thermosetting resins at 120, 130, and 140°C.

polymerization process has also been detected between 30 min and 45 min. This minor process may be related to the different reactivity of the resin components. It is possible that at this resin composition, a minor phase rich in one of the components starts to form before the polymerization of the bulk components takes place.

Samples with 30 wt % and 40 wt % of tung oil exhibit fairly similar DEA curves [Figure 4(A,B)], with polymerization times of 3 h 30 min and 2 h 50 min, respectively. Besides the slightly shorter polymerization time for the sample containing 40 wt % of tung oil, and its visual inspection, which revealed a sample with less imperfections than the sample with 30 wt % of tung oil, a slight shoulder can be seen at ~ 2 h in Figure 4(A). Similarly to the event observed in Figure 4(C), this feature suggests a partial phase separation of the polymer matrix at this composition. Although unconfirmed, it is possible that the slight decrease in ion viscosity after 3 h 30 min in Figure 4(A) might be related to secondary noncovalent interactions between polymer chains due to a change in the overall polarity of the resin by an increased concentration of BMA with respect to the other components. These noncovalent interactions can be easily broken at high temperatures, leading to an increase in ion mobility. Therefore, it is concluded that 40 wt % tung oil, 30 wt % BMA, 20 wt % DVB, and 10 wt % asolectin is the optimum resin composition for the system investigated, taking into account resin integrity and polymerization kinetics.

It is noteworthy that when curing a resin for 2 h 50 min at 140°C (cure Schedule I, Table II) the resulting polymer contained many structural imperfections, such as shrink cracks, bubbles, and voids. Therefore, lower temperature steps were added in an attempt to promote a milder heating of the sample, with a lower polymerization rate. Table II shows the different heating schedules tested.

By introducing a longer step at 130°C prior to the final stage at 140°C (cure Schedule II, Table II), the thermoset still contains many shrink cracks, indicating that the polymerization rate is still too fast. When the comonomer mixture is heated at 120°C

for 5 h 50 min prior to the final stage (cure Schedule III, Table II), a resin with no cracks resulted. In cure Schedules IV and V (Table II), the time of the initial heating stage at 120°C was varied. Cure Schedule IV produced a thermoset with no cracks, in the shortest time. When the final stage at 140°C is removed from the heating sequence (cure Schedule VI, Table II), the resulting sample isn't fully polymerized, as will be shown next in the DSC analyses.

The samples submitted to cure Schedules I–VI were evaluated by DSC in order to confirm completeness of the polymerization of all resin components. If polymerization is not complete for a given sample, an exothermic reaction occurs, as the heating employed during the DSC experiment reinitiates the polymerization process, resulting in exothermic peaks on the DSC curves of these samples. Figure 5 presents the DSC curves of samples submitted to cure Schedules I, IV, and VI. While both cure Schedules I and IV ensure that the resin is fully cured, according to the absence of exothermic peaks in their DSC curves (Figure 5), cure Schedule IV was selected as the ideal heating sequence because it resulted in a sample with no cracks. As mentioned previously, the sample submitted to cure Schedule VI, which excludes the final step of 2 h 50 min at 140°C, exhibits a definite exothermic peak at $\sim 180^\circ\text{C}$, demonstrating that the final heating step is crucial in order to ensure complete polymerization of the resin components.

In order to ensure that the temperatures employed in cure Schedule IV are compatible with all components of the proposed cellulose composites, and to evaluate the thermal stability of the resin, TGA curves of the resin without asolectin (TUN), pure asolectin, pure α -cellulose, and a composite (TUN-ASO-CELL) were obtained (Figure 6). The initial 10 wt % loss of pure asolectin and pure α -cellulose between 95°C and 150°C [Figure 6(A,C)] can be attributed to loss of adsorbed water, revealing the hydrophilic character of both species, which suggests a potential good compatibility between them. It can also

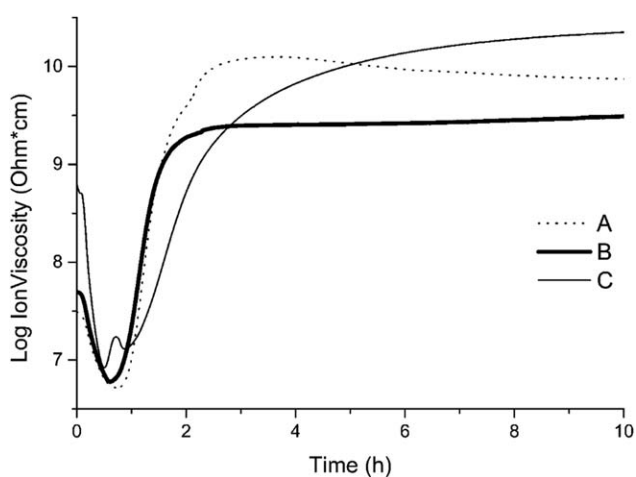


Figure 4. Dielectric analysis of tung oil-based thermosetting samples with various resin compositions. (A) 30 wt % tung oil, 40 wt % BMA, 20 wt % DVB, and 10 wt % asolectin; (B) 40 wt % tung oil, 30 wt % BMA, 20 wt % DVB, and 10 wt % asolectin; (C) 50 wt % tung oil, 20 wt % BMA, 20 wt % DVB, and 10 wt % asolectin.

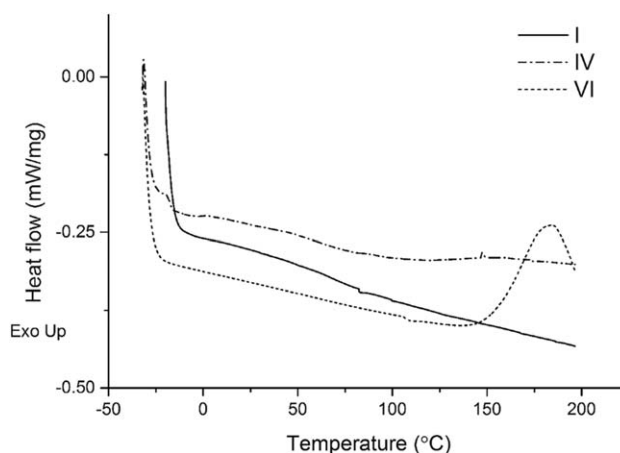
Table II. Heating Schedules Evaluated

Cure schedule	120°C	130°C	140°C
I	-	-	2 h 50 min
II	-	6 h 10 min	2 h 50 min
III	5 h 50 min	-	2 h 50 min
IV	3 h 50 min	-	2 h 50 min
V	1 h 50 min	-	2 h 50 min
VI	3 h 50 min	-	-

be observed that asolectin starts to degrade at $\sim 175^\circ\text{C}$, whereas pure α -cellulose and the tung oil-based resin without asolectin (TUN) start degrading at 280°C and 300°C , respectively. Therefore, the addition of α -cellulose and asolectin to the tung oil-based resin (TUN) decreases the overall thermal stability of the sample with respect to TUN alone [Figure 6(B,D)].

Another noticeable feature shown in Figure 6(A) is the ~ 20 wt % of residue in asolectin, whereas all other samples had insignificant amounts of residues. The residue composition has not yet been fully identified, but it can possibly be attributed to counter ions associated to the phosphate and ammonium groups in the phospholipids. Because of the relatively high residue content of pure asolectin, its T_5 was not observed (Table III, Entry 2). In the TGA curve of TUN-ASO-CELL [Figure 6(D)], it can be seen that ~ 4 wt % of residues are left at the end of the experiment, which can be attributed to the asolectin present in the composite. The trends for T_{90} and T_{50} (Table III) follow the expected pattern of having composites with temperatures intermediary between the pure resin without asolectin (TUN) and pure asolectin or cellulose. For T_{max} , asolectin and cellulose exhibit numbers significantly lower than TUN, reflecting their lower thermal stability (Table III, Entries 1–3). TUN, in fact, has two T_{max} s, corresponding, most likely, to the degradation of two distinct components (C–O bonds in triglycerides and C–C bonds in the polymer backbone, for example). Surprisingly, the composite TUN-ASO-CELL exhibits only one T_{max} at a value lower than that of the individual components (Table III, Entry 4). This can be an effect of the composite morphology, which will be addressed in more detail when discussing the SEM results.

When comparing the DSC curves of pure α -cellulose, TUN-ASO, and TUN-ASO-CELL (Figure 7), it can be clearly seen that no peaks can be detected for TUN-ASO in the temperature range investigated, showing not only that the sample is fully cured, but also that it is perfectly thermally stable below 200°C . The DSC curve of the composite TUN-ASO-CELL exhibits a broad endothermic peak centered at $\sim 95^\circ\text{C}$. Similar peaks have been observed in other bio-based composites, and were attributed to transitions in the ligno-cellulosic reinforcement.²⁸ Indeed, that peak matches a more intense peak, around the same temperature, in the DSC curve of pure α -cellulose [Figure 7(A)], which could represent a dehydration event in cellulose around 83°C , as previously described in the literature.²⁹ When α -cellulose is dried in a vacuum oven at 70°C overnight prior to the DSC experiment, no endothermic peaks are observed

**Figure 5.** DSC curves of tung oil-based thermosetting resins submitted to cure Schedules I, IV, and VI.

[Figure 7(D)], confirming that the endothermic event is most likely related to desorption of water.

DMA experiments evaluated the stress transfer ability of the polymers and composites prepared in this work. The DMA results are presented in Table IV and Figure 8. The addition of asolectin to the tung oil-based resin resulted in a decrease in the glass transition temperature (T_g) of the system (Table IV, Entries 1 and 2). The addition of α -cellulose to a tung oil-based resin devoid of asolectin causes an increase in T_g (Table IV, Entries 1 and 3), indicating that the presence of cellulose in the comonomer mixture interferes with the polymerization of the resin components. When a composite is prepared with a resin containing asolectin (TUN-ASO-CELL), a clear increase in T_g is observed with respect to the unreinforced resin (TUN-ASO) (Table IV, Entries 2 and 4). This indicates that asolectin is indeed promoting stronger interactions between the resin and the reinforcement. This effect will be more clearly analyzed when discussing storage moduli results.

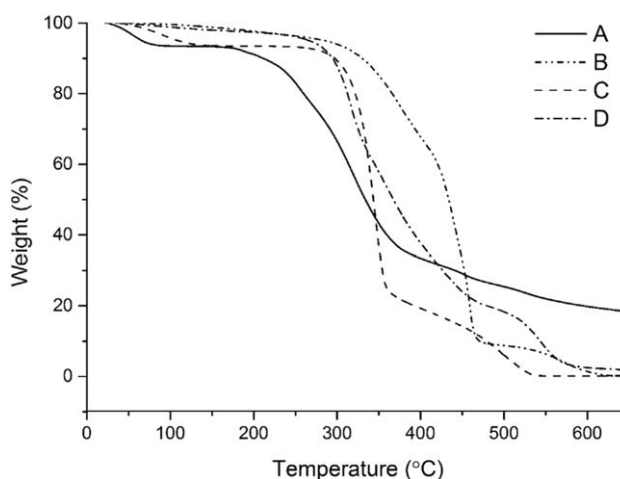
**Figure 6.** TGA of (A) pure asolectin, (B) pure polymer with 50 wt % of tung oil, 30 wt % of BMA, and 20 wt % of DVB (TUN), (C) pure α -cellulose, (D) TUN-ASO resin reinforced with 36 wt % of α -cellulose (TUN-ASO-CELL).

Table III. T_5 , T_{50} , T_{90} , and T_{max} for α -Cellulose, Asolectin, TUN, and TUN-ASO-CELL

Entry	Cellulose (wt %)	Asolectin (wt %)	T_{90} ($^{\circ}$ C) ^a	T_{50} ($^{\circ}$ C) ^b	T_5 ($^{\circ}$ C) ^c	T_{max} ($^{\circ}$ C) ^d
1	100	–	297	343	504	345
2	–	100	208	328	–	322
3	–	–	330	433	563	439, 458
4	36–37	10	294	367	562	316

^a T_{90} , temperature at which 90% of the original weight remains.

^b T_{50} , temperature at which 50% of the original weight remains.

^c T_5 , temperature at which 5% of the original weight remains.

^d T_{max} , temperature at maximum degradation rate.

The trends observed for the T_g s are also verified for the storage moduli at 25 $^{\circ}$ C and at the rubbery plateau, at $T_g + 50^{\circ}$ C. Indeed, the pure resin without asolectin (TUN) had a storage modulus of 714 MPa at 25 $^{\circ}$ C (Table IV, Entry 1). After addition of asolectin, that number decreased to 468 MPa (Table IV, Entry 2). This trend indicates that the addition of asolectin has a negative effect on the mechanical properties of the polymer, most likely related to its lower degree of unsaturation in comparison to tung oil, and its nonconjugated Carbon-Carbon double bonds, which contributes to a lower crosslink density. In Entry 3 (Table IV), the sample with cellulose, but no asolectin (TUN-CELL), exhibits higher storage moduli at 25 $^{\circ}$ C and at $T_g + 50^{\circ}$ C than its unreinforced counterpart (TUN), demonstrating that the addition of cellulose strengthens the polymer (Table IV, Entries 1 and 3). Despite the negative effect of adding asolectin to the resin, an improvement in the storage modulus at 25 $^{\circ}$ C and at $T_g + 50^{\circ}$ C is observed when asolectin is added to the composite (Table IV, Entries 3 and 4). This suggests that asolectin indeed plays the role of a compatibilizer between the hydrophobic polymer and the hydrophilic reinforcement. The highly polar phosphate groups on asolectin can strongly interact with the hydroxyl groups from cellulose. The enhanced interaction between the two components promotes a better stress transfer from the matrix to the reinforcement, resulting in higher stor-

age moduli, similarly to what has been observed in other bio-based systems.^{14,15}

It can be seen that drying cellulose prior to incorporating it to the composite doesn't significantly affect the T_g of the material (Table IV, Entry 5). In fact, the cellulose dehydration process discussed earlier occurs at a temperature lower than that required for initiating the cure of the resin (140 $^{\circ}$ C). Therefore, when the polymerization happens at an appreciable extent, the adsorbed water in cellulose has already been desorbed, exerting little effect in the cure kinetics of the system. The storage moduli at 25 $^{\circ}$ C and at $T_g + 50^{\circ}$ C of the composite prepared with dry cellulose is significantly lower than those measured for a sample prepared with regular cellulose (Entries 4 and 5, Table IV). It is believed that the extended drying period applied may have partially damaged cellulose's structure, compromising its performance as a reinforcing agent. Therefore, no obvious advantage was observed when drying cellulose prior to the preparation of composites.

The trends for storage modulus discussed above are particularly consistent for temperatures higher than -10° C (Figure 8). Below that temperature, the unreinforced resin containing asolectin (TUN-ASO) experiences storage moduli significantly higher than its counterpart made in the absence of asolectin (TUN). It is possible that at these low temperatures, the asolectin domains, due to their lower crosslink density, allow for a better packing of the polymer chains, resulting in a better ability to restore the energy input during the stress applied to the sample in the experiment. For the TUN-CELL sample, the incompatibility between cellulose and the hydrophobic resin becomes more important as the systems reach lower temperatures. Below -10° C, the presence of cellulose when no compatibilizer is used renders the system less efficient in restoring the energy after deformation. It is possible that for experiments run at low temperatures, much of the energy input is lost on the interface between matrix and reinforcement. When no cellulose is present, this effect is limited and higher storage moduli are observed for TUN-ASO and TUN below -10° C in comparison to TUN-CELL (Figure 8). When cellulose is covalently bonded to the matrix (TUN-ASO-CELL), the storage modulus is higher in the entire temperature range investigated, showing the efficient stress transfer from matrix to reinforcement.

From the Soxhlet extraction results, the solubles extracted from TUN totaled 3.3 wt % (Table IV, Entry 1). The addition of

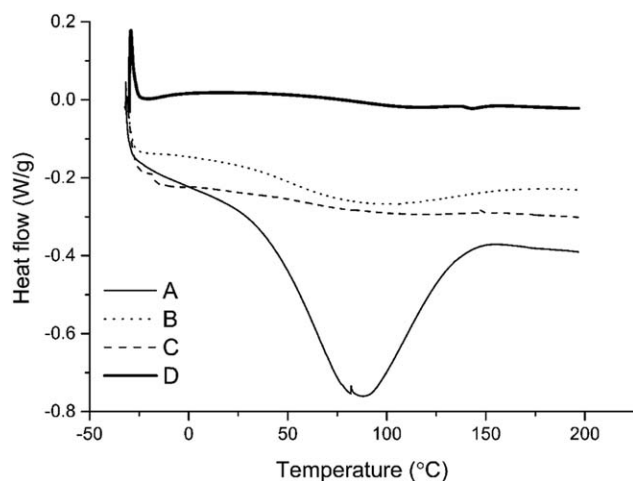


Figure 7. DSC curves of (A) pure α -cellulose, (B) TUN-ASO-CELL, (C) TUN-ASO, and (D) dry α -cellulose.

Table IV. DMA and Soxhlet Extraction Results for Tung Oil-Based Resins with and Without Asolectin and α -Cellulose

Entry	Asolectin (wt %)	Cellulose (wt %)	T_g ($^{\circ}\text{C}$)	E' at 25 $^{\circ}\text{C}$ (MPa)	E' at $T_g + 50^{\circ}\text{C}$ (MPa)	Wt % extracted
1	–	–	30	714	201	3.3
2	10	–	25	468	105	5.3
3	–	36–37	44	1231	391	4.9
4	10	36–37	34	1385	431	7.5
5	10	36–37 ^a	35	1013	322	7.9

^aCellulose was dried in a vacuum oven at 70 $^{\circ}\text{C}$ overnight prior to being incorporated into the composite.

cellulose and/or asolectin resulted in a slight increase in the amount of soluble materials recovered, with a larger increase for the addition of asolectin (Table IV, Entries 2–4). Nevertheless, the amount of soluble materials recovered is much lower than the 10 wt % of asolectin and/or the 36–37 wt % of α -cellulose added to the tung oil-based resin, suggesting that most of the composite components were incorporated into the final material. As expected, the use of dry cellulose doesn't represent a significant change in extractables in comparison to a composite made with regular cellulose (Entries 4 and 5, Table IV). The soluble materials extracted were analyzed by $^1\text{H-NMR}$ spectroscopy, and the obtained spectra are shown in Figure 9.

Figure 9(A) shows a typical $^1\text{H-NMR}$ spectrum of a triglyceride, with the characteristic set of peaks at 4.00–4.35 ppm corresponding to the glycerol methylenes, and the series of multiplets between 5.10 ppm and 6.40 ppm corresponding to the Hydrogens attached to sp^2 -hybridized Carbons of conjugated Carbon-Carbon double bonds in tung oil. Figure 9(B) shows the $^1\text{H-NMR}$ spectrum of asolectin, where all of the peaks <2.70 ppm coincide with peaks in the tung oil spectrum, indicating a very similar chemical structure. The most significant differences with respect to tung oil are in the disappearance of the glycerol methylene peaks at 4.00–4.35 ppm and the appearance of a series of new, low-intensity peaks in the same region, and a new peak at 3.25 ppm. These changes reflect the phospholipid backbone of asolectin, with a phosphate group and only one glycerol

methylene. The spectra in Figure 9(C,D) are very similar to that of tung oil. The characteristic glycerol methylene peak is present, and no peak at 3.25 ppm is detected. The absence of multiplets between 5.50 ppm and 6.50 ppm suggests the most of the soluble material recovered are oligomers of tung oil.

An SEM study revealed that in the absence of asolectin, a poor fiber-matrix interaction takes place, and can be noticed by fibers, on the crack surface, that do not have any matrix artifacts, indicating that cracks and failure originate and/or propagate at the interface between the resin and the reinforcement [Figure 10(A)]. When asolectin is added in the resin composition, there are stronger interactions between the resin and the cellulose fibers, and fibers with polymer artifacts are abundantly found all along the crack surface [Figure 10(B)].

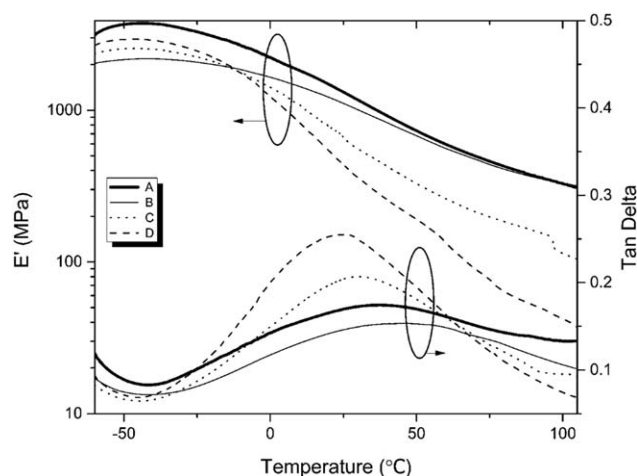


Figure 8. Tan Delta and storage modulus (E') curves of (A) TUN-ASO-CELL, (B) TUN-CELL, (C) TUN, and (D) TUN-ASO.

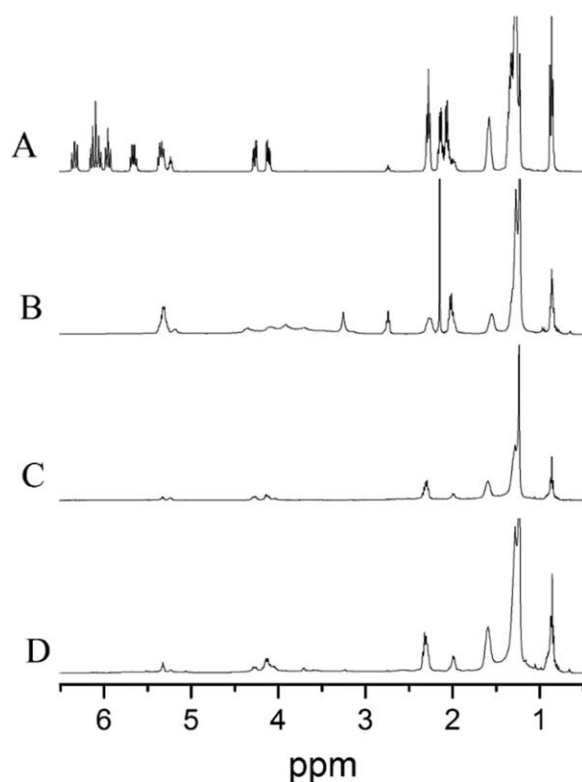


Figure 9. $^1\text{H-NMR}$ spectra of (A) tung oil, (B) asolectin, (C) tung oil-based resin with 50 wt % of tung oil, 30 wt % of BMA, and 20 wt % of DVB (TUN), and (D) tung oil-based resin with 40 wt % of tung oil, 10 wt % asolectin, 30 wt % of BMA, and 20 wt % of DVB (TUN-ASO).

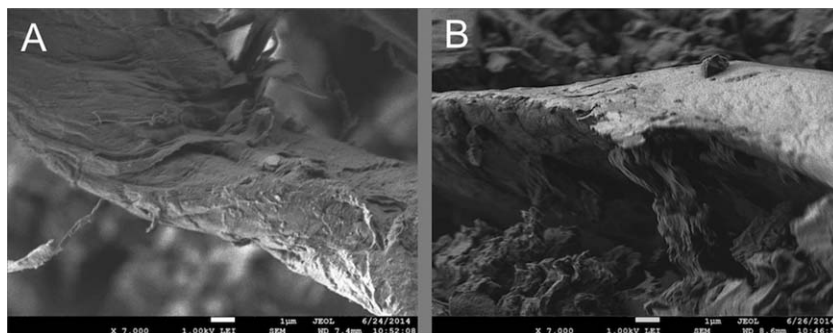


Figure 10. SEM images of (A) TUN-CELL composite and (B) TUN-ASO-CELL composite.

CONCLUSIONS

In this work, thermosetting resins resulting from the free radical copolymerization of DVB, BMA, asolectin, and tung oil were produced and analyzed. In the biocomposites produced, asolectin acted as a compatibilizer between the hydrophobic matrix and the hydrophilic cellulose reinforcement, promoting a better stress transfer between the two components and resulting in improved storage moduli. The appropriate amounts of DVB (20 wt %), BMA (30 wt %), asolectin (10 wt %), and tung oil (40 wt %) in the resin were polymerized in the presence of di-*tert*-butyl peroxide. DEA experiments were then conducted in order to establish the best cure time and temperature for the resin. An additional heating step was included to decrease the amount of cracks in the resin, resulting in a final curing schedule of 3 h 50 m at 120°C, followed by 2 h 50 m at 140°C. The absence of exothermic peaks in the DSC graph of TUN-ASO confirmed the complete polymerization of the resin. 36–37 wt % was determined as the optimal amount of cellulose to incorporate in the thermoset. The addition of asolectin and cellulose affects the degradation behavior of the biocomposite and resin, as demonstrated through TGA. Soxhlet extractions assessed the amount of unpolymerized materials in the resins and biocomposites. The total amount of soluble material extracted from TUN-ASO-CELL was 7.2 wt %. The extracts were determined to be mainly oligomers of tung oil by analysis of ¹H-NMR spectra. Data from DMA showed the effects that result from the addition of asolectin and cellulose to the resin with respect to glass transition temperature and storage modulus. The incorporation of asolectin resulted in a decrease of T_g . Overall, SEM and storage modulus data proved the hypothesis that asolectin acts as a compatibilizer between the resin and reinforcement. Indeed, an increase in storage modulus from 1231 MPa to 1385 MPa at 25°C is observed after addition of asolectin to a tung oil resin/cellulose composite.

The authors thank the College of Science and Mathematics and the Department of Chemistry at Georgia Southern University for the invaluable financial support.

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.
- 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**, *114*, 446.
- 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.
- Das, G.; Karak, N. *Prog. Org. Coat.* **2010**, *69*, 495.
- Thulasiraman, V.; Rakesh, S.; Sarojadevi, M. *Polym. Compos.* **2009**, *30*, 49.
- Espinoza-Perez, J. D.; Ulven, C. A.; Wiesenborn, D. P. *Transactions of the ASABE* **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.
- Quirino, R. L.; Larock, R. C. *J. Appl. Polym. Sci.* **2011**, *121*, 2050.
- Quirino, R. L.; Woodford, J.; Larock, R. C. *J. Appl. Polym. Sci.* **2012**, *124*, 1520.
- Liu, C.; Yang, X.; Cui, J.; Zhou, Y.; Hu, L.; Zhang, M.; Liu, H. *Bioresources* **2012**, *7*, 447.
- Montero de Espinosa, L.; Meier, M. *Eur. Polym. J.* **2010**, *47*, 837.
- Pfister, D. P.; Baker, J. R.; Henna, P. H.; Lu, Y. S.; Larock, R. C. *J. Appl. Polym. Sci.* **2008**, *108*, 3618.
- Klemm, D.; Heublein, B.; Fink, H.; Bohn, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 3358.
- Sanchez-Garcia, M.; Lagaron, J. *Cellulose* **2010**, *17*, 987.
- Huda, M.; Mohanty, A.; Drzal, L.; Schut, E.; Misra, M. J. *Mater. Sci.* **2005**, *40*, 4221.
- Wu, J.; Kuo, M. C.; Chen, C.; Hsu, Y.; Kuan, P.; Lee, K.; Fang, K.; He, J. *Polym.-Plas. Technol. Eng.* **2013**, *52*, 877.
- Brady, G. S. *Materials Handbook*; McGraw-Hill Book: New York, **1971**.

24. Navratil, T.; Sestakova, I.; Marecek, V. *Int. J. Electrochem. Sci.* **2011**, *6*, 6032.
25. Nozawa, A.; Nanamiya, H.; Tozawa, Y. *Methods Mol. Biol.* **2010**, *607*, 213.
26. Park, H.; Berrier, C.; Lebaupain, F.; Pucci, B.; Popot, J.; Ghazi, A.; Zito, F. *Biochem. J.* **2007**, *403*, 183.
27. Li, F.; Larock, R. C. *Biomacromolecules* **2003**, *4*, 1018.
28. Quirino, R. L.; Larock, R. C. *J. Appl. Polym. Sci.* **2009**, *112*, 2033.
29. Ciolacu, D.; Ciolacu, F.; Popa, V. I. *Cellulose Chem. Technol.* **2011**, *45*, 13.