

Preparation and Properties of Tung Oil-Based Composites Using Spent Germ as a Natural Filler

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ABSTRACT: Novel biocomposites have been prepared by the free radical polymerization of a tung oil-based resin using spent germ, the coproduct of wet mill ethanol production, as a filler. The effect of filler particle size, amount of filler, amount of crosslinker, and molding pressure on the resulting composites has been investigated. When compared to the pure resin, an increase in storage modulus is observed when filler is added to the matrix. The thermal stabilities of the resulting composites lie between the stabilities of the resin and the spent germ. Decreasing the particle size results in an increase in both the storage modulus and

the mechanical properties of the composites. As the amount of crosslinker, divinylbenzene, increases, an improvement in the thermal stabilities and mechanical properties is observed. The composites prepared are mainly composed of renewable resources, possess good thermal and mechanical properties, and have potential applications in the construction and automotive industries. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3618–3625, 2008

Key words: radical polymerization; renewable resources; composites; tung oil; spent germ

INTRODUCTION

The growing use and demand for petroleum-based plastics has caused environmental concerns and increased our dependence on foreign oil.¹ The persistence of these indestructible materials in the environment, a shortage of landfill space, concerns over emissions during incineration, and increasing oil prices have encouraged the development of biodegradable polymers and plastics from biorenewable resources.² Biopolymers from renewable natural resources have gained much attention because they are inexpensive and readily available.³

Natural oils are among the most promising renewable resources to be used for the production of biopolymers. Considerable recent research on the development of polymeric materials from these oils has been conducted. Wool and coworkers^{4,5} and Borrajo and coworkers⁶ have prepared rigid polymers from the free radical copolymerization of soybean oil monoglyceride maleates and linseed oil monoglyceride maleates, respectively, with styrene. Hazer and coworkers^{7,8} have reported the preparation of new biodegradable materials by the graft copolymerization of polymeric linseed and soybean oil-peroxides with styrene, methyl methacrylate, and *n*-butyl methacrylate. Polyurethane thermosets have been developed by Petrović and coworkers^{9,10} and Galia and

coworkers¹¹ by reacting various soybean oil polyols and epoxidized methyl oleate-based polyether polyols, respectively, with isocyanates. The preparation of epoxy resins has also been reported using epoxidized linseed,¹² soybean,^{12,13} and castor oils.¹³ Work in our group has mainly focused on the preparation of crosslinked networks by polymerization of the unfunctionalized double bonds in natural oils. Thermosets from regular and conjugated soybean oil,^{14,15} corn oil,¹⁶ linseed oil,^{17,18} tung oil,¹⁹ fish oil,²⁰ and various other vegetable oils²¹ have been prepared by cationic, thermal, and free radical polymerizations.

Fillers are often added to polymers to decrease cost and increase dimensional stability, strength, toughness, and environmental resistance.²² Composite materials have found many applications in the automobile, aircraft, military, sporting goods, and marine industries. The term biocomposites is broadly defined and can be used to describe composites resulting from bio-based resins and synthetic fibers, petroleum-based resins and natural fibers, or bio-based resins and natural fibers. The latter are often referred to as “green composites.”² Corn and soybean oil-based biocomposites have been successfully prepared using glass fibers as a phase reinforcer.^{23–25} The mechanical properties of the resulting materials are significantly improved, making these materials suitable for applications in automobile construction. Natural fibers, as a replacement for synthetic fibers, have gained much attention in the past several years, because of their low cost, low density, acceptable specific strength, renewability, and biodegradability.²

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Petroleum-based polymers reinforced with wood fibers have been extensively investigated in the past and these materials have found many applications in the automotive and construction industries. More recently, wood fibers have been replaced by agricultural fibers, underutilized agricultural coproducts, and crop residues. For example, flax and kenaf have been used to reinforce polypropylene (PP),^{26,27} high-density polyethylene (HDPE) composites have been prepared with cornstalks and corncobs,²⁸ and wheat straw, big blue stem grass, soybean hulls, and distillers dried grains and solubles (DDGS) have been used to reinforce both PP and HDPE.^{26,28,29} DDGS has also been used as a filler with a phenolic resin.³⁰ Recently, Wool and coworkers^{31,32} and Aranguren and coworkers³³ have reported the preparation of natural fiber composites using an acrylated epoxidized soybean oil (AESO), a modified AESO, or a linseed oil monoglyceride maleates-based matrix and wood flour, flax, hemp, cellulose, or pulp as a fiber or filler. When compared with the pure resin, considerable improvements in the physical and mechanical properties have been observed by the addition of fibers.

Tung oil, a triglyceride oil consisting primarily (~ 84%) of alpha-elaostearic acid (*cis*-9, *trans*-11, *trans*-13-octadecatrienoic acid), is an excellent drying oil typically used in the preparation of paints and varnishes.¹⁹ The high number of fatty acid side chains containing a conjugated triene makes it reactive toward free radical polymerization. DDGS and spent germ (SG) are the coproducts of dry mill and wet mill ethanol production, respectively. With the increased demand for ethanol as a fuel additive, the production of DDGS and SG are expected to increase dramatically. Finding new uses for these underutilized agricultural coproducts will increase their value and help offset ethanol production costs.³⁴ In this work, we report the preparation of tung oil-based composites using SG as a natural filler by a pressure molding process. The effect of filler particle size, amount of filler, amount of crosslinker, and the molding pressure on the structure and properties of the resulting composites have been investigated.

EXPERIMENTAL

Materials

The tung oil (TUN), divinylbenzene (DVB, technical-grade; assay 80% by gas chromatography, 20% ethylvinylbenzene), and *t*-butyl peroxide (TBPO) were purchased from Aldrich Chemical (Milwaukee, WI) and used as received. *n*-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA) and used as received. The ground SG was provided by Grain Processing Corporation of Muscatine, IA. The polytetrafluoroethylene (PTFE) release agent

MS-122DF was purchased from Miller-Stephenson Chemical (Morton Grove, IL).

Seven different particle sizes of SG were obtained using U.S. standard sieves. Unsieved means that the SG was used as received and mesh sizes of > 20, > 40, > 60, and > 80 correspond to particles that pass through a 20 (particles < 850 μm), 40 (particles < 425 μm), 60 (particles < 250 μm), and 80 (particles < 180 μm) mesh sieve, respectively. The mesh size 40 \times 60 corresponds to particles that pass through a 40 mesh sieve and are retained by a 60 mesh sieve (particles 250–425 μm), and 60 \times 80 corresponds to particles that pass through a 60 mesh sieve and are retained by an 80 mesh sieve (particles 180–250 μm).

The SG was also extracted to remove relatively unreactive corn oil before being used as a filler. The > 80 mesh SG was extracted for 24 h by Soxhlet extraction with refluxing methylene chloride as the solvent. This extracted SG was then used as a filler under the standard conditions listed below and the resulting composite is designated as ESG.

Preparation of TUN-based resin and composites

The TUN-based resin was prepared by bulk free radical polymerization. The designated amounts of TUN, BMA, and DVB were added together and stirred vigorously. The TBPO initiator was then added in the amount of 5 wt % of the total resin weight. This mixture was poured into a glass vial and cured at 130°C for 12 h and 140°C for 12 h. The following nomenclature is used: TUN represents tung oil and BMA and DVB represent the *n*-butyl methacrylate and divinylbenzene comonomers, respectively. For example, TUN50-BMA35-DVB15 corresponds to a resin prepared from 50 wt % TUN, 35 wt % BMA, 15 wt % DVB, and 5 wt % of this total weight was the amount of TBPO initiator used.

The composites were prepared using a compression molding process. The SG was dried in a vacuum oven at 70°C for 18 h. The designated amounts of TUN, BMA, DVB, and TBPO were mixed and cured using the above cure sequence. Just prior to the gel point (approximately 2 h), the resin was removed from the oven and added to the SG. This mixture was stirred until all the SG was wetted and was then placed in the cavity of the preheated (130°C) steel mold coated with the PTFE release agent. The mold was closed and cured at 130°C under the designated pressure for 4 h. The mold was then moved to an oven and cured under atmospheric pressure. Because an undetermined amount of resin and SG was forced out of the mold during the cure process, the reported amounts of SG are based on the initial amounts of SG and resin used. For example, for the composite containing 60% SG, 50 g of resin was added to 75 g of SG. The resin/SG

mixture was forced out to ensure that no air bubbles were present in the sample and only a small amount of material was lost. The standard composition and conditions used for preparing the composites were TUN50-BMA35-DVB15, > 80 mesh particle size, 50% SG, and 3000 psi molding pressure. When one variable was changed, the rest were held constant. In all cases, the matrix composition was TUN50-(BMA + DVB)50. For example, a composite designated DVB 20 refers to TUN50-BMA30-DVB20, > 80 mesh particle size, 50% SG, and 3000 psi molding pressure.

Characterization

Soxhlet extraction was used to determine the amount of soluble materials in the composites and to characterize the structures of the polymer resin and the resulting composites. A 4.5 g sample was extracted for 24 h with 110 mL of refluxing methylene chloride using 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 weighing. ¹H-NMR spectroscopic analysis of the soluble substances was carried out in CDCl₃ using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 300 MHz.

A Q50 TGA (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 the thermogravimetric analysis.

The dynamic mechanical properties of the resin and the resulting composites were obtained on a TA Instruments Q800 DMA using a three-point bending mode. A rectangular specimen of about 22 mm × 8.5 mm × 1.5 mm (length × width × thickness) was cut from the samples. Each specimen was cooled to –60°C and then heated at 3°C/min to 250°C at a frequency of 1 Hz under air.

The tensile tests were conducted at 25°C according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 10 mm/min. The dogbone-shaped test specimen (type-I specimen in ASTM D638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

Three-point bending tests were conducted at 25°C according to ASTM D790-93 using an Instron universal testing machine at a crosshead speed of 10 mm/min. A rectangular specimen of 65 mm × 14 mm × about 4.5 mm (length × width × thickness) was cut from the samples.

RESULTS AND DISCUSSION

Soxhlet extraction analysis

The microstructures of the resin and resulting composites were examined using Soxhlet extraction with methylene chloride as the refluxing solvent. Table I

TABLE I
Properties and Extraction Data of the Resin, Spent Germ, and Composites

Entry	Sample composition	DMA		TGA			Soxhlet extraction	
		T _g (°C)	E' (MPa) ^a	T ₁₀ (°C)	T ₅₀ (°C)	T _{max} (°C)	% Soluble	% Insoluble
1	Resin ^b	48	587	346	434	457	3	97
2	Spent germ ^c	–	–	252	316	298	14	86
3	Unsieved	20	661	266	417	430	5	95
4	> 20 Mesh	27	720	267	419	434	3	97
5	> 40 Mesh	27	744	267	419	433	5	95
6	> 60 Mesh	25	841	267	419	430	5	95
7	> 80 Mesh ^d	26	1,003	271	423	432	3	97
8	40 × 60 Mesh	26	1,013	270	417	433	4	96
9	60 × 80 Mesh	21	880	271	419	434	5	95
10	40% SG	37	989	276	425	433	2	98
11	45% SG	37	1,086	270	424	432	2	98
12	55% SG	16	586	267	418	429	5	95
13	60% SG	12	772	259	411	430	6	94
14	DVB 10	19	465	268	416	425	4	96
15	DVB 20	23 (61)	1,096	270	426	438	3	97
16	DVB 25	21 (57)	1,024	266	430	441	3	97
17	1,000 psi	20	745	271	420	431	4	96
18	2,000 psi	23	803	273	421	432	3	97
19	ESG	37	1,434	264	423	431	0	100

^a Storage modulus at 25°C.

^b TUN50-BMA35-DVB15.

^c > 80 mesh.

^d Represents the standard composition: 50% SG, DVB 15, and 3000 psi.

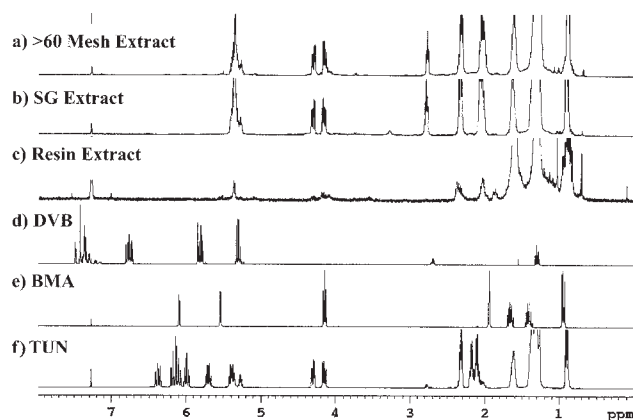


Figure 1 $^1\text{H-NMR}$ spectra of (a) extract of > 60 mesh composite, (b) extract of > 80 mesh SG, (c) extract of the resin TUN50-BMA35-DVB15, (d) DVB, (e) BMA, and (f) TUN.

gives the percentage of soluble materials for the resin, SG, and composites. Because of the multiple reactive C—C double bonds present in TUN and DVB, the resin is a highly crosslinked thermoset with a low amount of soluble materials. TUN is a triglyceride oil primarily composed of a fatty acid containing a conjugated triene, but also contains fatty acid side chains with nonconjugated double bonds. The wide range of chemical shifts for the vinylic protons (5.2–6.5 ppm) indicates that the carbon–carbon double bonds present in TUN are mostly conjugated [Fig. 1(f)]. The $^1\text{H-NMR}$ spectrum of the soluble portion of the resin [Fig. 1(c)] shows that it is primarily composed of unreacted tung oil. The oil appears to be nonconjugated, because of the small range of chemical shifts (5.3–5.4 ppm) evident for the vinylic protons. There also seems to be a very small amount of unreacted BMA or oligomers of BMA and TUN present in the soluble material. Because of the absence of peaks in the aromatic region, all the DVB was incorporated into the thermoset.

All the composites produced had a low amount of soluble materials ranging from 2 to 6% (Table I). The $^1\text{H-NMR}$ spectrum of the soluble portion of the > 60 mesh composite is shown in Figure 1(a). The soluble material is mainly composed of the crude corn oil present in the SG [Fig. 1(b)]. The > 80 mesh SG used in this study contained 14% corn oil (Table I, entry 2). This oil has a low degree of unsaturation (~ 3.9 C—C double bonds per triglyceride) compared to tung oil (~ 7.9 C—C double bonds per triglyceride) and the double bonds present in corn oil are nonconjugated. For these reasons, the corn oil is unreactive toward free radical polymerization. The soluble portion of the composite also contains a very small amount of unreacted BMA and possibly low molecular weight oligomers of BMA or TUN. The $^1\text{H-NMR}$

spectrum of the extracted > 60 mesh composite is representative of the soluble materials obtained from all composites [Fig. 1(a)].

The particle size of the filler (Table I, entries 3–9) appears to have no effect on the % soluble material extracted from the resulting composites with the soluble fractions varying from 3 to 5%. There seems to be a trend in the % soluble materials as the amount of SG is increased (entries 10–13). The % soluble materials increases from 2% for the 40% SG composite to 6% for the 60% SG composite. This was expected, because as more SG is added, more of the unreactive crude corn oil is present to be extracted. Another possibility for the increase in % soluble materials is that as more filler is added to the resin, the diffusion of the initiator or chain propagation is inhibited and the result is less crosslinking and a loose network structure. Similar results have been observed elsewhere.²³ As more DVB is added to the resin, the % soluble materials from the resulting composites decreases ever so slightly (entries 14–16). DVB is used as an effective crosslinker and as more DVB is added, the matrix becomes more highly crosslinked reducing the amount of soluble materials. The same trend is observed as the pressure is increased (entries 17 and 18). If the pressure is decreased, while holding the filler concentration constant, incomplete wetting of the filler by the resin is expected, resulting in an increase in voids and filler–filler agglomerations.³³ This makes the filler particles more accessible and the oil contained in the SG is more easily extracted. For the ESG composite (entry 19), most of the oil present in the SG was extracted prior to the preparation of the composite. Therefore, the corn oil that was extracted in all of the previous composites was absent and the resulting composite had 0% soluble materials.

Dynamic mechanical analysis

The room temperature storage moduli (E') and glass transition temperatures (T_g) for the resin and composites are given in Table I. The T_g data have been obtained from the peak position of the $\tan \delta$ curve. For the resin and all composites, the typical drop in E' at the glass transition temperature was observed. With the exception of the 55% SG and DVB 10 composites, the addition of SG increased the E' value of the composites over the entire temperature range studied. This increased stiffness is likely the result of the reduced mobility and deformation of the matrix caused by the addition of a filler.²³

As the larger particles are removed from the filler, it can be seen that E' increases (entries 3–7). E' increases from 661 MPa for the unsieved composite to 1003 MPa for the > 80 mesh composite. As the particle size in a composite decreases, the filler dis-

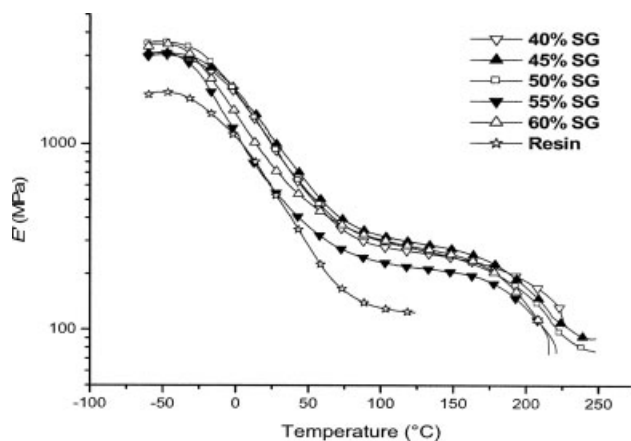


Figure 2 E' of the resin and composites prepared with differing amounts of SG.

persion and matrix-filler interaction, although it may be weak, should increase.³⁵ The increased interaction and interfacial adhesion would result in the higher modulus observed. But this trend was not observed when the fine particles were removed from the filler (entries 8 and 9). For the more uniform particle sizes, E' decreased from 1013 MPa for the 40×60 mesh composite to 880 MPa for the 60×80 mesh composite. Figure 2 shows the storage modulus as a function of temperature for the resin and the composites prepared with different amounts of SG. As described earlier, it is evident that as SG is added to the matrix, E' increases over the entire temperature range. The room temperature storage modulus initially increases when the amount of SG is increased from 40 to 45%. As the amount of SG is further increased, E' decreases from 1086 MPa to a low value of 586 MPa. Initially, the amount of crosslinker appears to have a dramatic effect on E' . When the amount of DVB increases from 10 (entry 14) to 15 wt % (entry 7), E' increases from 465 MPa for the DVB 10 composite to 1003 MPa for the DVB 15 composite, but increases very little when the amount of DVB is increased further. As expected, increasing the pressure caused an increase in E' from 745 MPa (entry 17) to 1003 MPa (entry 7). Increasing the pressure, while holding the amount of filler constant, should result in increased wetting of the filler and better filler-matrix interactions. The highest E' was observed for the ESG composite. By removing the corn oil from the SG, the resin is more easily absorbed into the filler, which could account for the increased stiffness. It is also possible that the corn oil present in the SG is having a plasticizing effect on all of the composites.

The T_g is considerably affected when SG is added to the resin. The resin has a T_g of 48°C and the resulting composites have glass transition temperatures ranging from 12 to 37°C . This decrease in T_g is

likely the result of a poor interaction between the filler and the matrix. The TUN and petroleum-based comonomers are hydrophobic in nature and the filler, with a large concentration of hydroxyl groups, is hydrophilic. Figure 3 illustrates the loss factor ($\tan \delta$) as a function of temperature for the resin and composites containing different amounts of SG. For all of the composites, two peaks in the $\tan \delta$ curve are observed. The first peak (lower temperature) corresponds to the primary relaxation process of the matrix and the second peak (higher temperature) is believed to correspond to the onset of degradation of the filler. Two reasons for this belief are: (1) the peak height increases as the amount of SG is increased, and (2) the onset of degradation of the filler/composites obtained from the TGA curves was observed to be $\sim 200^{\circ}\text{C}$. With all of the variables changed, there appeared to be no trend in the peak heights of the lower temperature $\tan \delta$ peak for the resulting composites.

As with the % soluble materials, there appears to be no effect on the T_g as the size of the particles is varied. When the amount of SG is increased from 40 to 60%, the T_g decreases from 37 to 12°C . There are two possible explanations for this result. One is that the initiator diffusion and chain propagation could be increasingly inhibited as the amount of filler particles increase, resulting in less crosslinking. Another possibility is that the unreactive corn oil present in the SG could have a plasticizing effect on the matrix. The T_g increases when the amount of DVB is increased from 10 to 15 wt % due to increased crosslinking. But as more DVB is added, two relaxation processes (peaks) are observed for the matrix in the $\tan \delta$ curve. The reactivity of the oil and the comonomers used in the matrix are very different. For the DVB 20 and DVB 25 composites, the large amounts of the more reactive DVB present at the beginning of

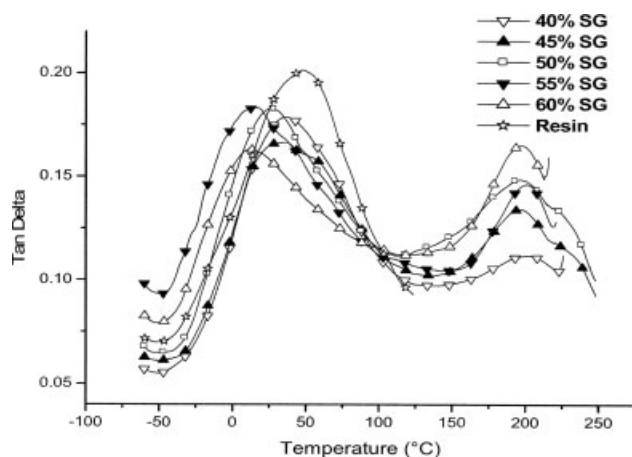


Figure 3 $\tan \delta$ curves for the resin and composites prepared with differing amounts of SG.

the reaction may result in a homopolymerization or copolymerization with BMA to form a “DVB-rich” phase. When the amount of DVB decreases, more oil is incorporated into the polymer to form an “oil-rich” phase. Each of these two phases have their own distinct relaxation processes: the “oil-rich” phase with a T_g of $\sim 20^\circ\text{C}$ and the “DVB-rich” phase with a T_g of $\sim 60^\circ\text{C}$. Similar results have been observed in previous work.^{21,23} The T_g increases from 20 to 26°C as the pressure is increased from 1000 to 3000 psi, most likely due to a decrease in voids and increased filler-matrix interactions discussed earlier. When the corn oil is removed from the SG, the T_g of the resulting composite increased from 26°C (entry 7) to 37°C (entry 19). As discussed earlier, this could be a result of the increased absorption of the matrix by the filler or the corn oil acting as a plasticizer.

Thermogravimetric analysis

Figure 4 shows the TGA curves of the resin, SG, and composites prepared with different amounts of SG. The curves of the composites with different amounts of SG are representative of all composites. The thermal degradation of the resin, SG, and composites can be separated into three stages. For the resin, the first stage, from 25 to 300°C , corresponds to the loss of unreacted oil and soluble materials. The second stage, from 300 to 475°C , likely involves degradation of the crosslinked insoluble resin and the last stage, from 475 to 650°C , involves oxidation of the char. No residue was left above 650°C . The first stage of degradation of the SG, from 25 to 125°C , represents the loss of water. The starch, protein, corn oil, and hemicellulose portions are lost in the second stage in the temperature range of 125 to 400°C .^{36–38} In the third stage, 400 to 650°C , the degradation of cellulose

is observed and approximately 5 wt % of residue is left after 650°C . For the composites, the first stage ranges from 25 to 350°C and corresponds to the loss of soluble materials, starch, protein, and hemicellulose. The second stage of degradation, from 350 to 500°C , represents loss of the crosslinked matrix. The final stage, from 500 to 650°C , is a result of the loss of cellulose and the oxidation of char. Approximately 4 wt % of residue remains after 650°C . Figure 4 indicates that the first and third stages of degradation for the composites are dictated by the filler. As more SG is added to the composite, an increase in the mass loss from 25 to 350°C and 500 to 650°C is observed.

The temperatures at 10% weight loss (T_{10}), temperatures at 50% weight loss (T_{50}), and temperatures at maximum degradation (T_{max}) are given in Table I for the resin, SG, and the resulting composites. It can be seen from the data that the resin is far more thermally stable than the SG. The degradation of the resin does not actually begin until 300°C , whereas the SG has lost nearly 60% of its mass by 350°C . As the particle size of the filler decreases (entries 3–9), the thermal stability tends to increase. When the particle size is changed from unsieved to > 80 mesh, T_{10} increases from 266 to 271°C and T_{50} increases from 417 to 423°C , but T_{max} seems to be unaffected. There is a large drop in the T_{10} and T_{50} values when the amount of SG is increased. T_{10} and T_{50} values decrease from 276 to 259°C and 425 to 411°C , respectively, when the amount of SG is increased from 40 to 60%. The T_{max} value also decreased, but to a lesser extent. As the amount of DVB increases (entries 14–16), the T_{50} and T_{max} values are most affected and no trend is observed for the T_{10} values. The T_{50} values increase from 416 to 430°C and the T_{max} values increase from 425 to 441°C when the DVB increases from 10 to 25 wt %. This was expected because of the increased crosslinking resulting from the larger amounts of DVB. Increasing the pressure appears to have little effect on the T_{10} , T_{50} , and T_{max} values, only causing small increases in these values (entries 17 and 18). Extracting the SG prior to preparing the composite (entry 19) has little effect on the thermal stability.

From the TGA data, the T_{10} values appear to be most affected by the filler, while the T_{max} values seem to be affected by the resin and T_{50} seems to be influenced by both the resin and the filler. For example, when the filler is varied, either the size or the amount (entries 3–13), the T_{10} and T_{50} values increase or decrease significantly, while little or no trend is observed for the T_{max} values. But when the resin is changed (entries 14–16), T_{50} and T_{max} change the most, while T_{10} appears to be unaffected. This is expected, because of the low thermal stability of the filler and the higher stability of the resin.

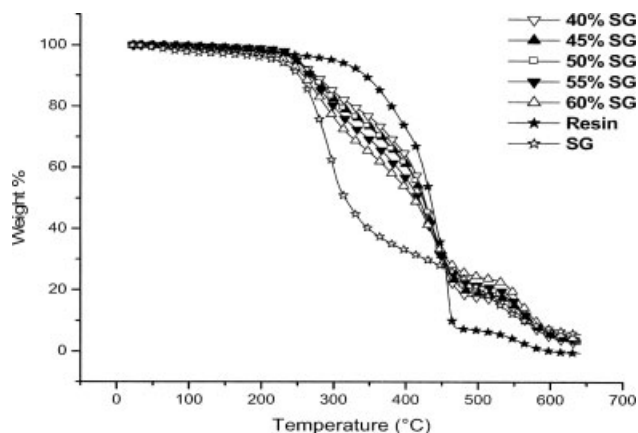


Figure 4 TGA curves for the resin, SG, and composites prepared from differing amounts of SG.

TABLE II
Mechanical Properties of the Composites

Entry	Sample composition	Young's modulus (MPa)	Tensile strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)
1	Unsieved	310 ± 6	5.5 ± 0.2	543 ± 63	5.8 ± 0.2
2	> 20 Mesh	421 ± 8	7.3 ± 0.3	657 ± 41	6.3 ± 0.7
3	> 40 Mesh	408 ± 11	7.5 ± 0.5	760 ± 22	10.3 ± 0.3
4	> 60 Mesh	410 ± 6	8.6 ± 0.4	728 ± 91	10.9 ± 0.9
5	> 80 Mesh ^a	470 ± 8	12.3 ± 0.6	991 ± 69	17.8 ± 0.9
6	40 × 60 Mesh	543 ± 11	7.6 ± 0.2	818 ± 82	11.9 ± 0.6
7	60 × 80 Mesh	494 ± 15	7.7 ± 1.4	895 ± 41	13.9 ± 0.9
8	40% SG	516 ± 15	13.1 ± 0.4	763 ± 35	18.6 ± 1.0
9	45% SG	525 ± 8	13.5 ± 0.5	906 ± 66	17.0 ± 0.8
10	55% SG	423 ± 9	9.1 ± 0.3	625 ± 66	10.0 ± 0.6
11	60% SG	335 ± 11	6.7 ± 0.3	938 ± 40	12.2 ± 0.5
12	DVB 10	196 ± 3	7.0 ± 0.4	295 ± 26	7.7 ± 0.1
13	DVB 20	678 ± 13	13.5 ± 0.6	1045 ± 86	20.2 ± 0.1
14	DVB 25	867 ± 17	12.4 ± 1.0	1228 ± 129	15.4 ± 0.6
15	1,000 psi	393 ± 18	8.9 ± 0.7	682 ± 15	12.5 ± 0.6
16	2,000 psi	388 ± 3	9.0 ± 0.5	638 ± 13	10.3 ± 0.4
17	ESG	746 ± 22	15.1 ± 1.2	1063 ± 47	24.8 ± 1.2

^a Represents the standard composition: 50% SG, DVB 15, and 3000 psi.

Mechanical properties

The mechanical properties of the composites are given in Table II. With an exception for the composites prepared with more uniform particles sizes (entries 6 and 7), the Young's modulus (E) and tensile strength (σ) increase as the particle size of the filler decreases. E and σ increase from 310 to 470 MPa and 5.5 to 12.3 MPa, respectively, as the particle size changes from unsieved to > 80 mesh (entries 1–5). Similar to the room temperature storage modulus, E stays relatively constant, while increasing the SG amount from 40 to 45% (entries 8 and 9). But as the amount of SG is further increased, E drops from a high value of 525 MPa for the 45% SG composite to 335 MPa for the 60% SG composite (entries 10 and 11). A similar trend is observed in σ , which drops from 13.5 to 6.7 MPa as the amount of SG increases from 45 to 60%. Increasing the amount of DVB from 10 to 25 wt % caused an increase in E from 196 to 867 MPa (entries 12–14). As the DVB is increased from 10 to 20 wt %, σ increases from 7.0 to 13.5 MPa, but increasing to 25 wt % causes a decrease in σ . It is possible that higher crosslinking reduces the number of conformations that the matrix can take on, while being under an applied force. When a crack becomes a failure, the matrix can disperse a lesser amount of energy, causing the decrease in σ . Similar results have been observed elsewhere.²³ No affect on E and σ is observed when the pressure is initially increased, but when the pressure is increased from 2000 to 3000 psi, both E and σ increase from 388 to 470 MPa and 9.0 to 12.3 MPa, respectively (entries 15 and 16). By removing the unreactive corn oil from the SG, increases in both the modulus and strength are observed (entry 17).

As expected, the flexural modulus and strength increase as the particle size of the SG decreases (entries 1–7). This is most likely the result of better filler dispersion and filler-matrix interactions obtained by using smaller particles. The flexural modulus increases from 543 to 991 MPa and the flexural strength increases from 5.8 to 17.8 MPa as the filler is changed from unsieved to > 80 mesh. With the exception of the 55% SG composite, the flexural modulus increases as the SG is increased from 40 to 45 wt %, but stays relatively constant as more SG is added (entries 8–11). The modulus increases from 763 MPa for the 40% SG composite to 991 MPa for the 50% SG composite. For the most part, the flexural strength decreases as more SG is added. The flexural strength decreases from 18.6 to 12.2 MPa as the amount of SG increases from 40 to 60 wt %. As with the Young's modulus, there is a large increase in the flexural modulus as the amount of crosslinker (DVB) increases. The flexural modulus increases from 295 to 1228 MPa when going from DVB 10 to DVB 25 (entries 12–14). The flexural strength also follows the same trend as the tensile strength. As the crosslinking of the matrix increases, the strength increases, but too much crosslinking results in a decrease in the strength of the composite. The flexural strength increases from 7.7 to 20.2 MPa, when the amount of DVB increases from 10 to 20 wt %, but decreases to 15.4 MPa, when the amount of DVB is further increased to 25 wt %. Increasing the pressure from 1000 to 2000 psi causes a drop in both the flexural modulus and strength (entries 15 and 16), but when going from 2000 to 3000 psi, the modulus and strength increase from 638 to 991 MPa and 10.3 to 17.8 MPa, respectively (compare entries 5 and 16).

As described earlier, the thermal and mechanical properties are improved when the corn oil is removed from the SG prior to preparation of the composite (entry 17). It is believed that the observed increase in the absorption of the matrix by the filler leads to a better filler-matrix interaction. The flexural modulus increases from 991 (entry 5) to 1063 MPa (entry 17) and the flexural strength increases from 17.8 to 24.8 MPa.

CONCLUSIONS

"Green composites" have been prepared from a free radical initiated, tung oil-based resin using SG as a natural filler. The matrix used in this study is highly crosslinked, causing the resulting composites to contain a low percent of soluble materials. This soluble portion is primarily composed of the corn oil present in the SG. The composites produced are quite thermally stable with T_{\max} values in the area of 430°C. In general, the thermal and mechanical properties of the composites are improved by decreasing the size of the filler. This is most likely the result of an enhanced interfacial adhesion and filler-matrix interaction. As more SG is added to the composite, the properties tend to decrease, due to the filler-filler agglomerations and an increase of voids expected when the amount of filler is increased, while holding the pressure constant. Divinylbenzene (DVB) is used as an effective crosslinker and, as expected, the thermal and mechanical properties of the composites increase as the concentration of DVB in the matrix increases. For the most part, as the pressure during the cure is increased, the properties increase. When decreasing the pressure, while holding the amount of filler constant, incomplete wetting of the filler by the matrix is expected, resulting in poorer properties. By removing the corn oil from the SG prior to composite preparation, an improvement in thermal and mechanical properties is obtained.

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