Biocomposites Synthesized from Chemically Modified Soy Oil and Biofibers

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ABSTRACT: Composites with good mechanical properties were prepared from chemically modified soy oils and biofibers without additional petroleum-based polymers. These composites were prepared from maleic anhydride and epoxide functionalized soybean oils that were cured in the presence of various biofibers (e.g., kenaf, kayocell, protein grits, and solka-floc) by a flexible amine catalyst. Rigid thermosets characterized by a high-crosslink-density network and a high gel fraction were obtained. Fourier transform infrared was used to follow the cure reaction via the disappearance of the characteristic anhydride adsorptions. Composites with high tensile strength and low elongation were obtained when kenaf fibers were treated with (2-aminoethyl)-3-aminopropyl-trimethoxysilane and then added to the epoxidized/maleated soy matrix and cured with hexamethylenediamine. These biobased composites could provide inexpensive epoxy resin alternatives for a wide variety of industrial applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 69–75, 2006

Key words: biofibers; compatibilization; composites; thermosets

INTRODUCTION

A growing awareness of environmental issues has made the use of renewable resources and biodegradability an important consideration for industrial applications. Such agriculturally derived materials, when used as starting materials for biocomposites, in contrast to petroleum-based chemicals, provide a sustainable source of raw materials readily regenerated by photosynthesis. Both thermoplastic and thermoset matrix biocomposites have been described in the literature; the resin matrix is generally a biopolymer or a synthetic biodegradable polymer, and the reinforcing component is usually some biofiber (e.g., jute, flax, hemp, ramie, sisal, coir, and cotton). In our previous work, we reported on the rationale, design, and engineering of biobased materials[1-4] and elaborated on the advantages and disadvantages of biobased materials in comparison with traditional composites. Accordingly, one attractive source of starting materials for a resin matrix is soybean oil. Soybean oil is an abundant biorenewable resource composed of triglycerides containing glycerin with saturated and unsaturated long-chain fatty acids, as shown in Figure 1. As such, unfortunately, soy oil is not very reactive and must be chemically modified with suitable functional groups that can then be crosslinked to yield a thermoset matrix. As long as such reactive soy oil can be crosslinked and reinforced, it is expected to yield high-modulus, tough composite materials. In addition to this potentially attractive set of physical properties, soy-oil-based composites are expected to be cost-competitive, enhance global sustainability, and provide value-added agriculture products. Furthermore, biocomposites could be made to biodegrade when the matrix is broken down by lipase-secreting bacteria, or, alternatively, they could be made into long-lasting durable materials. Moreover, the use of natural fibers instead of traditional reinforcing materials such as glass fibers, talc, and mica provides further advantages in terms of lower cost, lower density, reduced tool wear, acceptable strength properties, energy recovery, and recyclability.

Currently, the most common chemical modification of soybean oil is the introduction of epoxy groups that replace some of the double bonds in the fatty esters. This epoxidation process was commercialized recently, and the modified oil is being used primarily as a process aid in poly(vinyl chloride) to improve its stability, flexibility, and processability. It is also being used in the preparation of adhesives for carpet backing, as a source of polyols for the preparation of rigid polyurethanes, and as a reactive modifier or diluent of epoxy resin systems.[5] The reaction of maleic anhydride with soybean oil has also been reported in the literature, and these chemically modified oils are used primarily in cosmetic applications as a component in shower gels, bar soaps, sunscreens, and skin-treatment products.[6]

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Palmitic Acid [16:0] ---- 11%

Stearic Acid [18:0] ---- 14%

Oleic Acid [18:1] ---- 23%

Linoleic Acid [18:2] ---- 53%
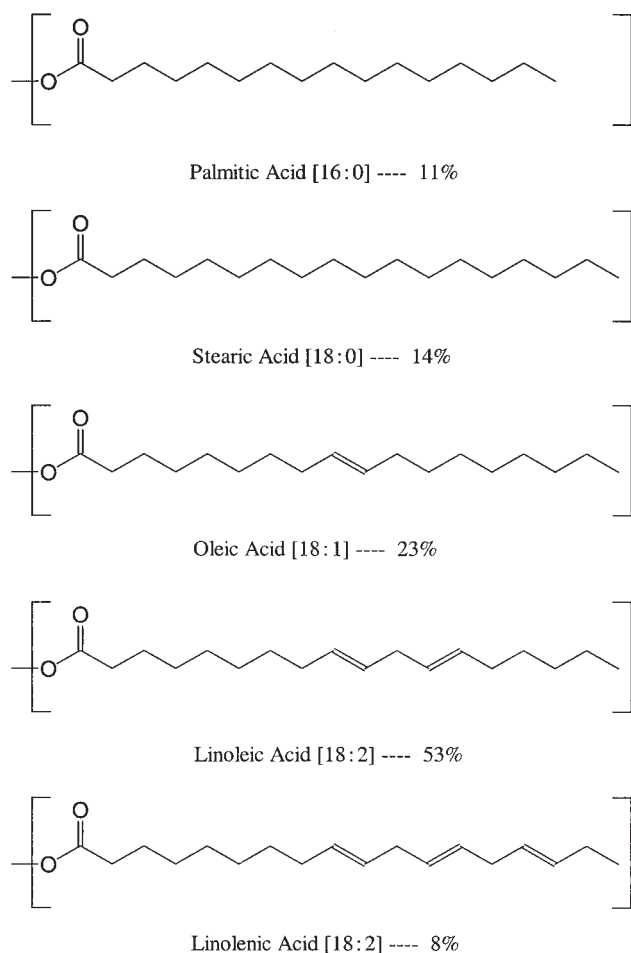
Linolenic Acid [18:2] ---- 8%

Figure 1 Five major fatty acid components in soybean oil.

Several researchers have investigated the use of chemically modified soybean oil in composites. However, the mechanical properties, primarily the tensile strength and stiffness, have been too low and thus limit their use in the marketplace. For example, an early work with epoxidized soybean oil (ESO) produced flexible, semiflexible, and rigid crosslinked polyesters.[7,8] Williams and Wool[9] prepared soy composites by the free-radical polymerization of acrylated ESO, which was then cured with styrene and divinylbenzene by resin-transfer molding in the presence of hemp and flax. These composites were reported to have mechanical properties comparable to those of commercially available synthetic resins. However, the use of petroleum-based polymers was essential to enhance the mechanical properties. Lu et al.[10] reported the preparation of clay nanocomposites based on functionalized triglycerides such as acrylated ESO, maleated acrylated ESO, and soybean oil pentaerythritol maleates combined with styrene. Another type of composite was prepared by Taveerne-Velduizen et al.[11] from soybean oil by thermoplastic processing in the presence of a binding agent such as an urea–

formaldehdye copolymer or a protein that was added to the soybean oil. Can et al.[12,13] focused on the preparation of copolymers from soy oil monoglycerides with styrene and soybean oil monoglyceride maleates with styrene. Zhu et al.[14] reported that epoxidized methyl soyate and epoxidized allyl soyate yielded resins that were highly reactive and provided a high degree of intermolecular crosslinking because of the addition of allyl soyate. These resins had higher modulus than similar resins obtained from unmodified ESO, and thus it was suggested that they could be suitable as composites for structural applications. Warth et al.[15] reported on the preparation of natural-fiber-reinforced soybean oil in polyester resin. Their work was based on networks of ESO and maleated soybean oil (MSO) with hemp and flax fibers (10 wt %), and they were able to achieve tensile strengths of 6.0 and 6.2 MPa, respectively.

The goal of this work was to synthesize tough composites from natural biofibers and chemically modified soybean oil with no additional styrene, polyester, or other petroleum-based polymers to supplement the soy matrix to enhance the mechanical properties. The soy-based composites were prepared by the combination of ESO with MSO or maleated methyl soyate (MMS) in the presence of selected biofibers. In contrast to previous studies, this work was focused on increasing the efficiency of the crosslink density and minimizing the sol fraction of the network to enhance the stiffness of the composites and eliminate possible bleeding out of the sol fraction from the gel network due to incomplete cure to avoid any adverse effects on the surface properties of the composites. It was thought that one common reason for a low gel fraction and incomplete cure in previous studies of epoxidized soy-based composites was related to incomplete cure between the epoxidized soy modified oil and the anhydride groups primarily due to the poor reactivity of the epoxy groups and steric hindrances. Thus, in this study, we explored the use of flexible spacer crosslinking amine catalysts [e.g., hexamethylenediamine (HMD) and 4-dimethylamino pyridine (4-DMAP)] that were expected to react with both epoxy- and anhydride-functional groups.

EXPERIMENTAL

Reagents and equipment

The soybean oil (Spectrum), one-third partially epoxidized soybean oil (Elf Atochem), and methyl soyate (Michigan Soybean Board) were used without further purification. Methylene chloride, maleic anhydride, isopropyl alcohol, HMD, 4-DMAP, and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane peroxide (L101) were purchased from Sigma–Aldrich (St. Louis, MO). Biofibers were obtained from American Fillers &
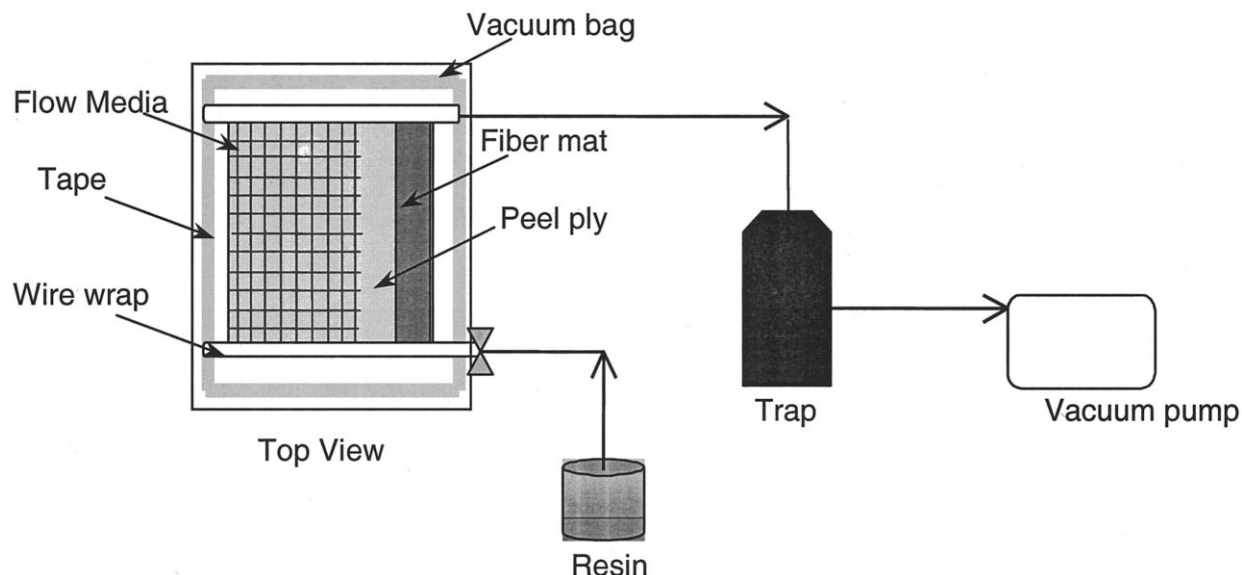
Figure 2 FTIR of functionalized soybean oils.

Abrasives, Inc., and (2-aminoethyl)-3-aminopropyl-trimethoxysilane was purchased from Gelest.

Fourier transform infrared (FTIR) spectra were run on a PerkinElmer model 1000 (Wellesley, MA) through the evaporation of a solution of a sample from the surface of NaCl crystals. The composites were cured in a Wabash Metal Products model CM02871. The mechanical properties were run after the aging of the samples for 3 days at 23°C and 50% relative humidity on a model SFM-20 tensile instrument made by United Testing Systems.

Maleation of soy oils

Although the reaction of maleic anhydride with soy oil to yield MSO has been reported in the literature,[16,17] a recently developed single-step, free-radical-initiated procedure that proceeds smoothly and gives high product yields was used.[18] Briefly, the reactions were carried out by the charging of maleic anhydride, soybean oil (or methyl soyate), and L101 into a 2-L Parr reactor equipped with a motorized stirrer, thermocouple, and heating element. The reactions were run for about 30 min at 150°C. At the end of each reaction, the reactor was connected to a vacuum pump for 30 min, and any volatile products were collected in a solvent trap immersed in an isopropyl alcohol/dry ice bath. The extent of the maleation reaction was determined by the acid number test with ASTM D 1980[19] and the iodine number per ASTM D 1959.[20] The data confirmed the addition of 1 mol of maleic anhydride/mol of soybean oil and the correspondent reduction of the double bond, as expected from this reaction. FTIR data (Fig. 2) of MSO, ESO, and soybean oil further show a characteristic absorbance of the

added succinic anhydrides around 1780 and 1850 cm^{-1}.

Cure reactions of MSO (or MMS) with ESO

Approximately equimolar amounts of MSO (or MMS) and ESO were combined with a catalyst in a beaker and placed in a silicone oil bath heated at 5°C/min while stirring with a magnetic stirrer. The gels were then removed and extracted in a Soxhlet apparatus for 3 days with methylene chloride as a solvent, and the gel fraction was determined. The results of the batch cure experiments are presented in Tables I and II. On the basis of these results, further cure studies were

TABLE I
Batch Curing Experiments in the Presence of a Base Catalyst

MSO (mol)	MMS (mol)	ESO (mol)	4-DMAP (wt %)	Temperature (°C)	Gel time (s)	Gel weight (%)
1	0	1	0	200	—	—
1	0	1	0.05	172	68	0.99
1	0	1	0.1	170	40	0.98
1	0	1	0.15	162	37	0.97
1	0	1	0.2	148	24	0.98
1	0	1	0.2	RT	—	—
0	1	1	0	200	—	—
0	1	1	0.05	185	98^a	0.78
0	1	1	0.1	164	57	0.74
0	1	1	0.15	158	51	0.82
0	1	1	0.2	152	32	0.75
0	1	1	0.2	RT	—	—

^{a} Gelation occurred over a long period of time or instantaneously.

TABLE II
Batch Curing Experiments in the Presence of a Diamine

MSO (mol)	MMS (mol)	ESO (mol)	HMD (wt %)	Temperature (°C)	Gel time (s)	Gel weight (%)
1	0	1	0	200	—	—
1	0	1	0.05	162	52	0.98
1	0	1	0.1	158	35	0.99
1	0	1	0.15	152	27	0.99
1	0	1	0.2	155	25	0.99
1	0	1	0.2	RT	—	—
0	1	1	0	200	—	—
0	1	1	0.05	164	61	0.97
0	1	1	0.1	162	58	0.99
0	1	1	0.15	159	46	0.98
0	1	1	0.2	148	33	0.99
0	1	1	0.2	RT	—	—

Figure 3 Preparation of soy-based composites by resin-transfer molding.

performed in an oven at 150°C. Each mixture was visually checked every few minutes. Initially, the reaction mixture was light yellow, and the catalyst was insoluble in the oil. However, after about 15 min at this temperature, a significant drop in the viscosity was noticed, and all the catalyst appeared to have dissolved in the matrix. Thereafter, the viscosity of the reaction mixture continuously increased, and the mixture turned slightly darker. The reaction was allowed to continue for 3 h, the gel was then removed from the oven and extracted in a Soxhlet apparatus for 3 days with methylene chloride as a solvent, and the gel fraction was determined. On the basis of these experimental conditions, biocomposites containing various fibers were prepared, as shown in Table III.

Resin-transfer molding

A measured weight of dried kenaf fiber mats sufficient to make 10 wt % composites was placed inside a rectangular mold. A flow medium was placed over the top of the fiber mat, and a vacuum bag was placed over the entire system, as shown in Figure 3. The reactants and catalyst were mixed at 60°C for 30 min and the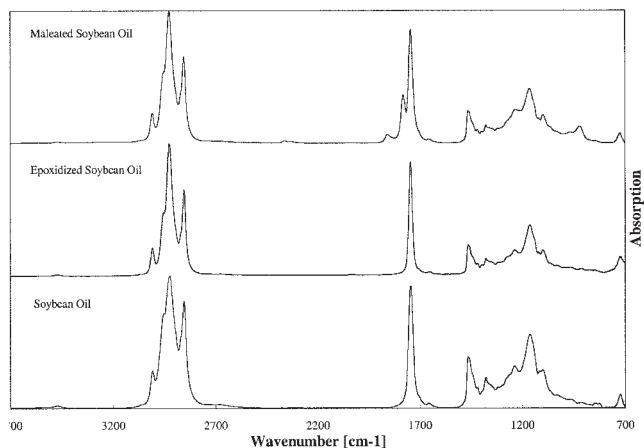n added to the fiber mat, and vacuum was applied to ensure that the fibers were completely saturated. The cure reaction was allowed to proceed for 3 h in a vacuum oven at 150°C.

Compression-molded cures

The catalyst was combined with ESO and impregnated into the biofiber (10 wt %), and the mixture was heated under stirring until the catalyst was completely dissolved. Then, MSO was added and thoroughly mixed, and the reaction mixture was poured into a rectangular mold and held at 150°C under 11 tons of pressure for 3 h. Samples were removed from the press after it was cooled to room temperature (RT) by the circulation of cooling water through the platens.

Surface treatment of kenaf fibers

Kenaf fibers were treated by a brief dip in a 2 wt % freshly prepared aqueous solution of (2-aminoethyl)-3-aminopropyl-trimethoxysilane. The fibers were then placed in a vacuum oven at 80°C and allowed to dry for 4 h.

TABLE III
Soy-Based Biofiber-Reinforced Natural Composites

| Reactants	Resin matrix characteristics	Biofiber
ESO + MSO	Viscous liquid	—
ESO + MSO + 4-DMAP	Soft and sticky solid	Kenaf, kayocell, protein grits, and solka-floc
ESO + HMD	Transluscent, highly viscous liquid	—
MSO + HMD	Tranparent, highly viscous liquid	—
ESO + MSO + HMD	Semirigid solid	Kenaf, kayocell, protein grits, and solka-floc
ESO + MMS	Liquid	—
ESO + MMS + 4-DMAP	Soft solid	Kenaf, kayocell, protein grits, and solka-floc
MMS + HMD	Tranparent, viscous liquid	—
ESO + MMS + HMD	Semirigid solid	Kenaf, kayocell, protein grits, and solka-floc
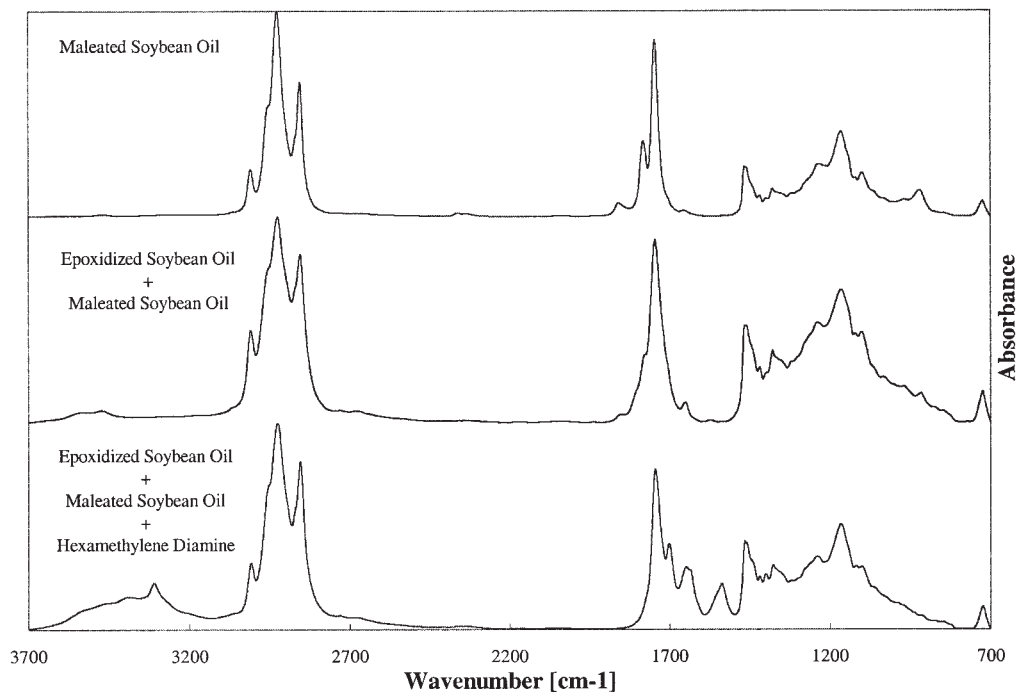
Figure 4 FTIR spectra of epoxidized and maleated functional soy oils.

RESULTS AND DISCUSSION

The crosslinking reaction between epoxy-functional polymers with anhydrides to yield a polyester resin is well known[21–23] and depends primarily on the reactivity of the anhydride, its molar ratio with respect to the epoxy groups, the concentration and efficiency of the cure catalyst, and the reaction conditions. In our study, the resin network was obtained by the reaction of epoxy-functional soy oil (ESO) and succinic anhydride functional soy oil (MSO or MMS) catalyzed by HMD or 4-DMAP. The cure was easily followed by the disappearance of the characteristic FTIR anhydride absorptions at 1780 and 1850 cm^{-1} (Fig. 4). The onset of gelation was directly proportional to the catalyst concentration and always appeared at lower temperatures when higher concentrations of the catalyst were used (Table I). However, the nature of the gels was greatly affected by the choice of the catalyst and the type of soy derivative that was used, as shown in Tables I and II. Thus, the HMD-catalyzed reaction between MMS and ESO produced a gel with a very high gel fraction (low sol content), but the same reaction catalyzed with 4-DMAP produced a poor gel with an unacceptably high sol content. Reactions between MSO and ESO for both catalyst systems yielded high gel fraction networks with essentially no weight loss after Soxhlet extraction. In contrast, the 4-DMAP-catalyzed reaction between MMS and ESO yielded a poor network with a high sol fraction.

These observations are in agreement with the curing mechanism of epoxy resins. It is generally agreed[24]

that a noncatalyzed cure starts by the reaction of anhydride with hydroxyl (which is always found with the epoxy group) to yield a monoester and a carboxylic group. The carboxylic acid group then reacts with an epoxide to form a diester with a hydroxyl group, which subsequently reacts with another anhydride. However, in the presence of amine catalysts, the cure reaction is initiated by the complex formation of the amine with a proton donor, and the active centers are the carboxylate and hydroxylate anions. The reaction mechanism in these cases depends to a great extent on the reactivity of the anhydride and, more importantly, on the type of amine catalyst. Apparently, in our case, the cure catalysis with 4-DMAP was not as efficient as the HMD catalysis.

The poor network with a high sol fraction that was obtained in the case of ESO/MMS was most likely due to the presence of the unreactive saturated palmitic and stearic components in the methyl soyate oil. Because maleation occurs across the double bonds, these fatty acids, which are present in the soy oil at about 15 wt % (Fig. 1), do not react with maleic anhydride and thus are not incorporated into the network. Hence, they merely act as a plasticizer and are easily removed from the resin by the Soxhlet extraction. The fact that reactions between MMS and ESO in the presence of HMD also resulted in high gel fractions with nearly no weight loss after extraction is most likely due to the rearrangement and formation of amide linkages with the carbonyl esters of the methyl soyate. Such ester saponification and amide formation allow for the sat-
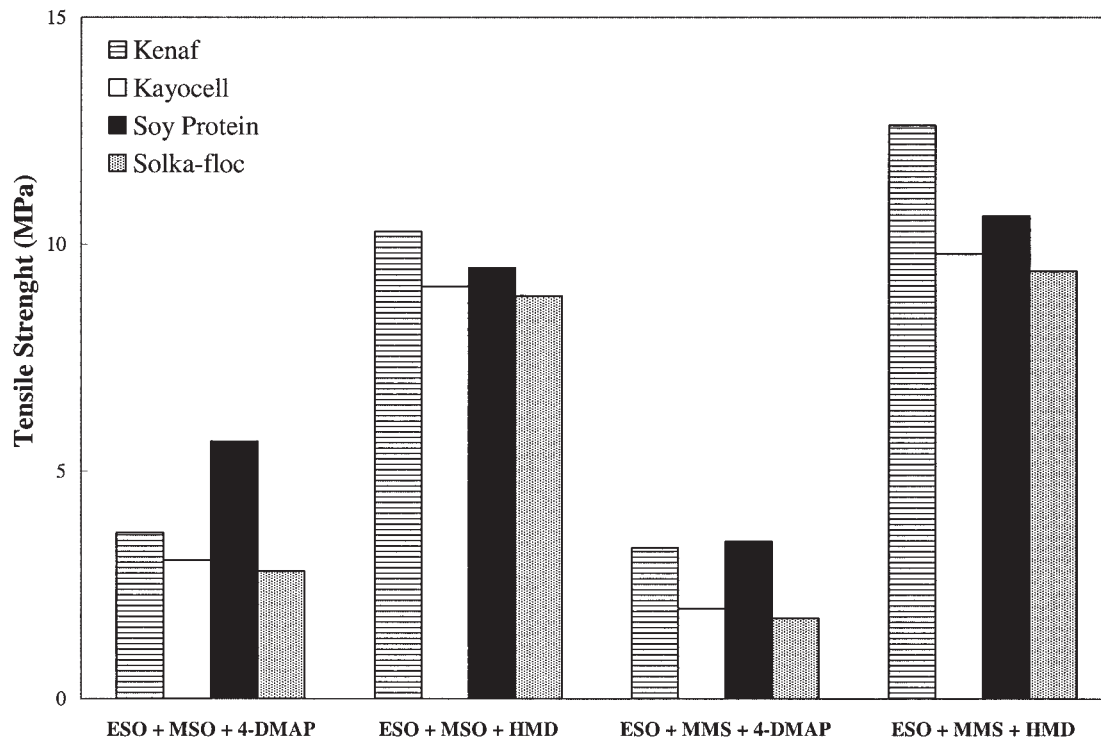
Figure 5   Tensile strength of composites prepared by compression molding.

urated components that carry no anhydride groups to be incorporated into the gel matrix through amide linkages.

The cured soy-based resins, especially those cured with HMS, were very rigid and brittle, unlike flexible and rubberlike resins prepared previously from ESO with succinic anhydride.[25] Apparently, the use of the succinic anhydride functional soy oil in combination with a flexible amine catalyst led to a more efficient network formation in comparison with similar ESO matrices that were cured with low-molecular-weight cycloaliphatic anhydrides and catalyzed by benzyldimethylamine.

The mechanical properties were greatly enhanced when these soy-based resins were reinforced with biofibers. Generally, the tensile strengths of such composites cured with HMD as a catalyst had the best tensile strengths. The types of biofibers or the soy matrix (ESO with MSO or with MMS) had only secondary impact (Fig. 5). In contrast, composites cured with 4-DMAP as a catalyst had relatively poor mechanical properties as a result of lower resin crosslink density. In fact, it was observed that composites made from MMS–ESO and cured with 4-DMAP had a significant sol fraction that diffused out of the sample upon aging.

The preparation of biocomposites by the incorporation of kenaf fibers provided the best reinforcement because of good interactions between the soy matrix and these lignin–cellulosic fibers (Fig. 5). Although the tensile strength of the composites cured with

4-DMAP were generally lower than those cured with HMD, good tensile strength was observed in the samples that were reinforced with soy proteins. It is possible that in this particular case the presence of free amino groups in the protein grits contributed to the fiber/matrix adhesion and consequently led to higher than expected tensile strength

Further enhancement in the mechanical properties was realized by surface treatment of the biofibers with the (2-aminoethyl)-3-aminopropyl-trimethoxysilane coupling agent before their incorporation into the matrix (Fig. 6). This coupling agent has been used extensively for the surface treatment of various fibers before.[26] It is effective at low concentrations: the amine-functional group enhances the solubility of the silane in water and at the same time provides multiple hydrogen bonding through interactions with hydroxyl groups on the surface of the fiber. After deposition, the amine groups further promote hydrolysis and condensation of the alkoxy groups on the silane to yield insoluble oligomeric polysiloxanes and a hydrophobic network on the surface of the fiber.[27] This surface treatment improved the adhesion between the resin and kenaf fibers and led to about 20% improvement in the tensile strength in comparison with similar composites for which kenaf fibers were dried but not treated. The effect of the surface treatment of the fibers was somewhat less pronounced in composites that were prepared by resin-transfer molding simply because of the difference in the wetting of the fibers in this process.
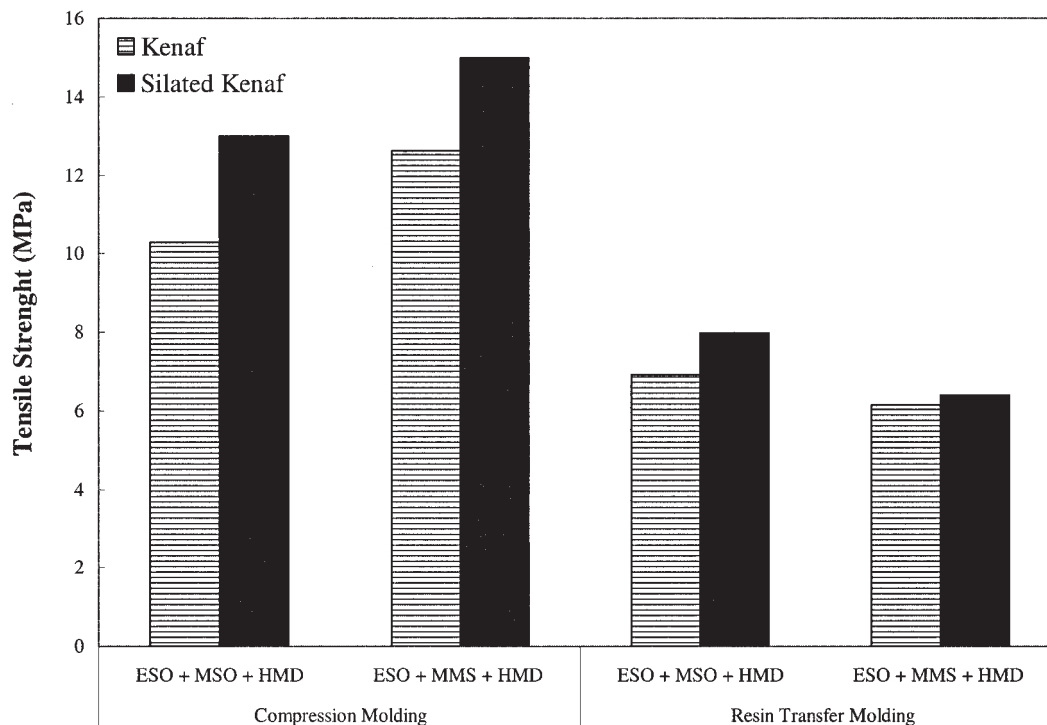
Figure 6 Effect of the aminosilane treatment of kenaf fibers on the tensile strength of soy-based composites.

CONCLUSIONS

Soybean oils and methyl soyate were chemically modified with suitable functional groups (e.g., epoxy and anhydride) that, in the presence of a flexible amine catalyst, reacted to create a three-dimensional crosslinked polyester matrix. The formation of these networks was followed by FTIR for different temperatures and reaction times. Biocomposites were then prepared by the curing of these soy-based resins in the presence of various biofibers (e.g., flax, Kayocell, protein grit, and solka-floc) with compression-molding and resin-transfer-molding techniques. Rigid network resins with high gel fractions were obtained when ESO was reacted with MSO with HMD as a catalyst. Composites with high mechanical strength were achieved when kenaf fibers were first treated with (2-aminoethyl)-3-aminopropyl-trimethoxysilane in the reinforcement of these soy-based matrix resins.

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