Development and Application of Triglyceride-Based Polymers and Composites

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ABSTRACT: Triglyceride oils derived from plants have been used to synthesize several different monomers for use in structural applications. These monomers have been found to form polymers with a wide range of physical properties. They exhibit tensile moduli in the 1–2 GPa range and glass transition temperatures in the range 70–120 °C, depending on the particular monomer and the resin composition. Composite materials were manufactured utilizing these resins and produced a variety of durable and strong materials. At low glass fiber content (35 wt %), composites produced from acrylated epoxidized soybean oil by resin transfer molding displayed a tensile modulus of 5.2 GPa, a flexural modulus of 9 GPa, a tensile strength of 129 MPa, and flexural strength of 206 MPa. At higher fiber contents (50 wt %) composites produced from acrylated epoxidized soybean oil displayed tensile and compression moduli of 24.8 GPa each, and tensile and compressive strengths of 463.2 and 302.6 MPa, respectively. In addition to glass fibers, natural fibers such as flax and hemp were used. Hemp composites of 20% fiber content displayed a tensile strength of 35 MPa and a tensile modulus of 4.4 GPa. The flexural modulus was ~2.6 GPa and the flexural strength was in the range 35.7–51.3 MPa, depending on the test conditions. The flax composite materials had tensile and flexural strengths in the ranges 20–30 and 45–65 MPa, respectively. The properties exhibited by both the natural- and synthetic fiber-reinforced composites can be combined through the production of "hybrid" composites. These materials combine the low cost of natural fibers with the high performance of synthetic fibers. Their properties lie between those displayed by the all-glass and all-natural composites. Characterization of the polymer properties also presents opportunities for improvement through genetic engineering technology. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 703–723, 2001

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INTRODUCTION

Polymers and polymeric composite materials have uses in aerospace, automotive, marine, infrastructure, military, sports, and industrial fields. These lightweight materials exhibit excellent mechanical properties, high corrosion resistance, dimensional stability, and low assembly costs. Polymers and polymeric composites are derived from petroleum reserves and as the number of applications of polymeric materials continues
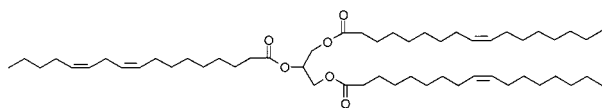
Figure 1 Triglyceride molecule, the major component of natural oils.

to increase, an alternative source of these materials becomes more important. Over the past 5 years, the Affordable Composites from Renewable Sources (ACRES) program at the University of Delaware has developed a broad range of chemical routes to utilize natural triglyceride oils as a basis for polymers and composite materials.[1,2] These materials have economical and environmental advantages over petroleum-based materials, making them an attractive alternative.

Natural oils, which can be derived from both plant and animal sources, are found in abundance in all parts of the world, making them an ideal alternative chemical feedstock. These oils are predominantly made up of triglyceride molecules, which have the structure shown in Figure 1. Triglycerides are composed of three fatty acids joined at a glycerol juncture. Most common oils contain fatty acids that vary from 14 to 22 carbons in length, with 0 to 3 double bonds per fatty acid. The fatty acid distributions of several common oils are shown in Table I.[3] In addition, there are exotic oils, which are composed of fatty acids with

other types of functionalities (e.g., epoxies, hydroxyls, cyclic groups, and furanoid groups).[4] Because of the many different fatty acids present, it is apparent that on a molecular level these oils are composed of many different types of triglycerides with numerous levels of unsaturation. With newly developed genetic engineering techniques, the variation in unsaturation can be controlled in plants such as soybean, flax, and corn.

In addition to their application in the foods industry, triglyceride oils have been utilized quite extensively to produce coatings, inks, plasticizers, lubricants, and agrochemicals.[5–11] Within the polymers field, the application of these oils as toughening agents has been investigated. There has been an extensive amount of work in their use to produce interpenetrating networks (IPNs), which has been reviewed by Barrett and co-workers.[12] The IPNs formed by triglycerides have been shown to increase the toughness and fracture resistance in conventional thermoset polymers. For example, Querishi and co-workers developed an IPN consisting of cross-linked polystyrene and an epoxidized linseed oil elastomer.[13] Similarly, Devia and co-workers produced IPNs with cross-linked polystyrene and castor oil elastomers.[14–16] Many other efforts have been made to utilize various types of triglycerides in the polymers field.[17–25] In all of the aforementioned work, the functional triglyceride was a minor component in

Table I   Fatty Acid Distribution in Various Plant Oils

Fatty Acid	#C: #DB	Canola	Corn	Cottonseed	Linseed	Olive	Palm	Rapeseed	Soybean	High Oleic[a]
Myristic	14 : 0	0.1	0.1	0.7	0.0	0.0	1.0	0.1	0.1	0.0
Myristoleic	14 : 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Palmitic	16 : 0	4.1	10.9	21.6	5.5	13.7	44.4	3.0	11.0	6.4
Palmitoleic	16 : 1	0.3	0.2	0.6	0.0	1.2	0.2	0.2	0.1	0.1
Margaric	17 : 0	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0
Margaroleic	17 : 1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Stearic	18 : 0	1.8	2.0	2.6	3.5	2.5	4.1	1.0	4.0	3.1
Oleic	18 : 1	60.9	25.4	18.6	19.1	71.1	39.3	13.2	23.4	82.6
Linoleic	18 : 2	21.0	59.6	54.4	15.3	10.0	10.0	13.2	53.2	2.3
Linolenic	18 : 3	8.8	1.2	0.7	56.6	0.6	0.4	9.0	7.8	3.7
Arachidic	20 : 0	0.7	0.4	0.3	0.0	0.9	0.3	0.5	0.3	0.2
Gadoleic	20 : 1	1.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0	0.4
Eicosadienoic	20 : 2	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0
Behenic	22 : 0	0.3	0.1	0.2	0.0	0.0	0.1	0.5	0.1	0.3
Erucic	22 : 1	0.7	0.0	0.0	0.0	0.0	0.0	49.2	0.0	0.1
Lignoceric	24 : 0	0.2	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0
Average #DB/triglyceride		3.9	4.5	3.9	6.6	2.8	1.8	3.8	4.6	3.0

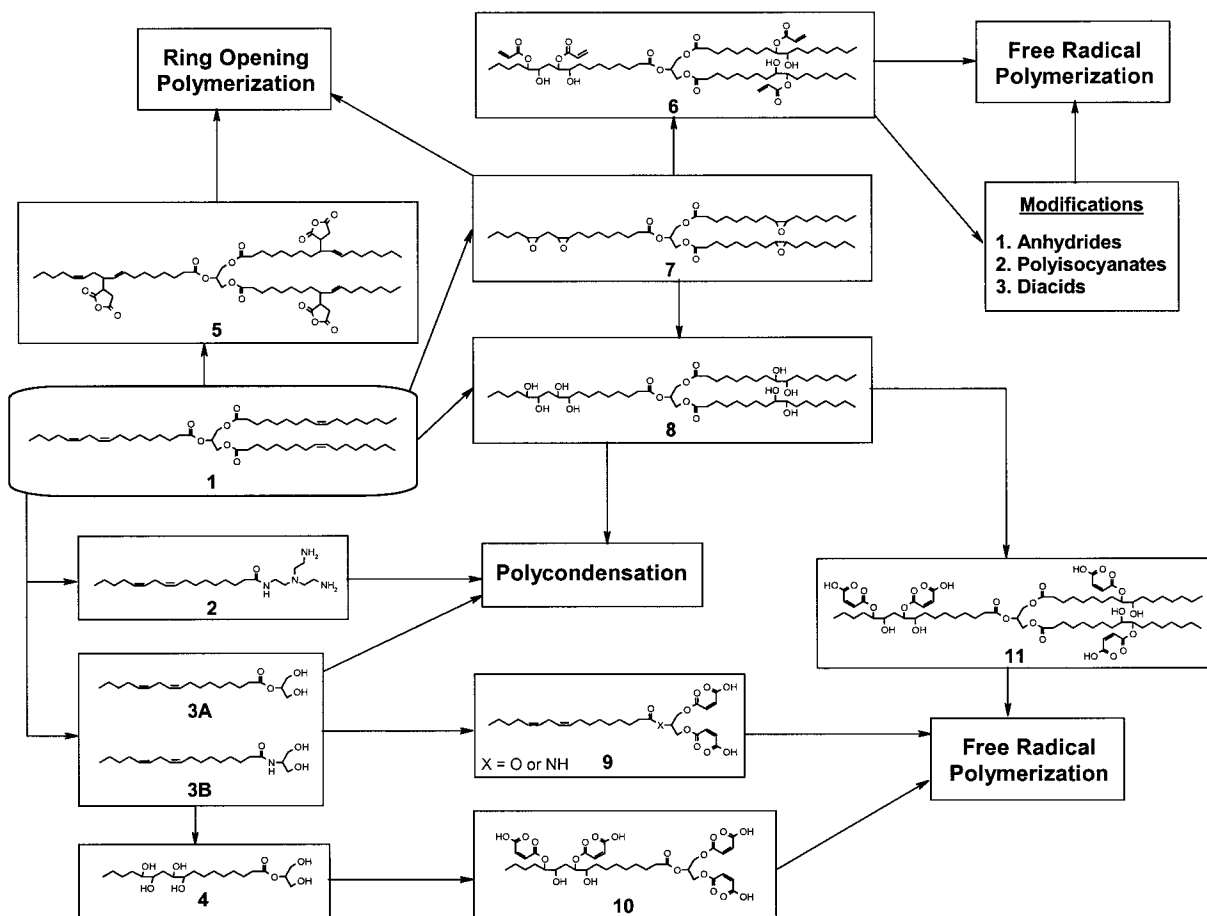[a] Genetically engineered high oleic acid content soybean oil (DuPont).

Figure 2 Chemical pathways leading to polymers from triglyceride molecules.[1]

the polymer matrix, acting solely as a modifier to improve the physical properties of the main matrix. Consequently, the triglyceride-based materials were low molecular weight, lightly crosslinked materials incapable of displaying the necessary rigidity and strength required for structural applications by themselves.

Synthetic Pathways for Triglyceride-Based Monomers

The triglyceride contains active sites amenable to chemical reaction; these sites are the double bond, the allylic carbons, the ester group, and the carbons alpha to the ester group. These active sites can be used to introduce polymerizable groups on the triglyceride using the same synthetic techniques that have been applied in the synthesis of petrochemical-based polymers. The key step, to reach a higher level of molecular weight and crosslink density, as well as incorporate chemical functionalities that are known to

impart stiffness in a polymer network (e.g., aromatic or cyclic structures), has been accomplished by several synthetic pathways, as illustrated in Figure 2.[1]

In structures 5, 6, 7, 8, and 11, the double bonds of the triglyceride are used to functionalize the triglyceride with polymerizable chemical groups. From the natural triglyceride, it is possible to attach maleates (5)[6,11] or convert the unsaturation to epoxy (7)[26–28] or hydroxyl functionalities (8).[29,30] Such transformations make the triglyceride capable of reaction via ring opening or polycondensation polymerization. These particular chemical pathways are also accessible via natural epoxy and hydroxyl functional triglycerides, as demonstrated by past work.[12,14–16] It is also possible to attach vinyl functionalities to the epoxy and hydroxyl functional triglycerides. Reaction of the epoxy functional triglyceride with acrylic acid incorporates acrylates onto the triglyceride (6), whereas reaction of the hydroxylated triglyceride with maleic anhydride incorpo-
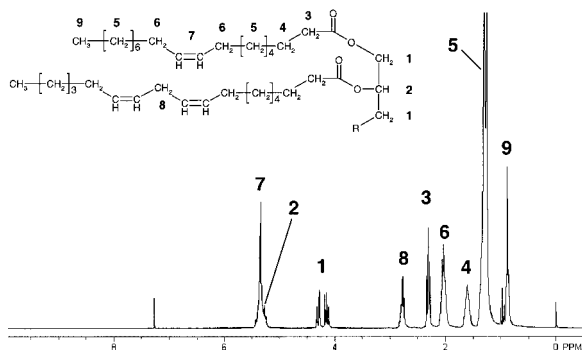
Figure 3 ^{1}H NMR spectrum (CDCl$_3$) of soybean oil (R represents a third fatty acid).

rates maleate half-esters and esters onto the triglyceride (11). These monomers can then be blended with a reactive diluent, similar to most conventional vinyl ester resins, and cured by free-radical polymerization.

The second method for synthesizing monomers from triglycerides is to convert the triglyceride to monoglycerides through a glycerolysis (3A) reaction or an amidation reaction (2, 3B).[31–36] Monoglycerides have found much use in the field of surface coatings, commonly referred to as alkyd resins, because of their low cost and versatility.[32] In those applications, the double bonds of the monoglyceride are reacted to form the coating. However, monoglycerides are also able to react through the alcohol groups via polycondensation reactions with a comonomer, such as a diacid, epoxy, or anhydride. Alternatively, maleate half-esters can be attached to these monoglycerides (9), allowing them to free-radically polymerize.

The third method is to functionalize the unsaturation sites as well as reduce the triglyceride into monoglycerides. This process can be accomplished by glycerolysis of an unsaturated triglyceride, followed by hydroxylation (4) or by glycerolysis of a hydroxy functional triglyceride. The resulting monomer can then be reacted with maleic anhydride, forming a monomer capable of polymerization by free-radical polymerization (10).

Although the structure of triglycerides is complex in nature, it is possible to characterize some aspects of it using proton nuclear magnetic spectroscopy (^{1}H NMR) and Fourier transform infrared (FTIR) spectroscopy. A typical ^{1}H NMR spectrum of soybean oil is shown in Figure 3 with peak assignments. The two sets of peaks at 4.0–4.4 ppm are produced by the four glycerol methylene protons per triglyceride.[4] The triplet set of

peaks at 2.3 ppm is produced by the six protons in the alpha position relative to the carbonyl groups. The peak at 0.9 ppm is produced by the nine methyl protons per triglyceride at the end of each fatty acid chain. These three groups of peaks provide a standard by which other peaks can be used to quantitatively characterize functional groups in the triglyceride.

In this work, we focus on three triglyceride monomers, shown in Figure 4, that have been found to be promising candidates for use in the composites and engineering plastics fields; they are acrylated epoxidized soybean oil (AESO), the maleinized soybean oil monoglyceride (SOMG/MA), and maleinized hydroxylated soybean oil (HSO/MA). These monomers, when used as a major component of a molding resin, have shown properties comparable to conventional polymers and composites, and these properties will be presented. Additionally, their use as a matrix in synthetic and natural fiber reinforced composites will be presented.

Acrylated Epoxidized Soybean Oil (AESO)

AESOs (Figure 4) are synthesized from the reaction of acrylic acid with epoxidized triglycerides. Epoxidized triglycerides can be found in natural oils, such as vernonia plant oil, or can be synthesized from more common unsaturated oils, such as soybean oil or linseed oil, by a standard epoxidation reaction.[37] The natural epoxy oil, vernonia
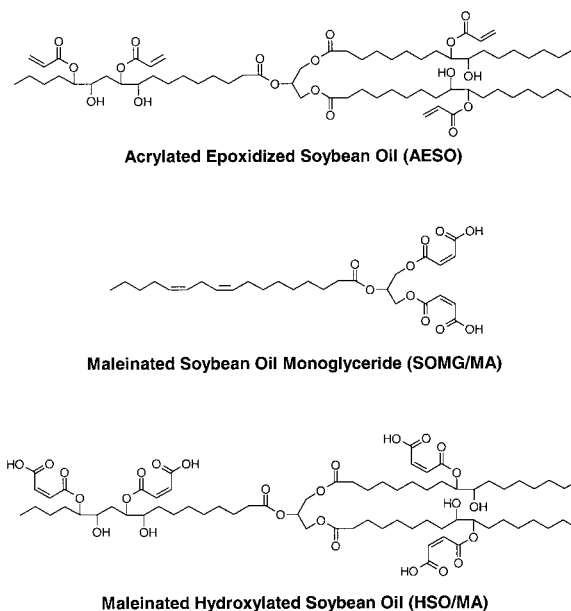

Acrylated Epoxidized Soybean Oil (AESO)

Maleinated Soybean Oil Monoglyceride (SOMG/MA)

Maleinated Hydroxylated Soybean Oil (HSO/MA)

Figure 4 Triglyceride-based monomers

oil, has an epoxy functionality of 2.8 epoxy rings per triglyceride.[13] Epoxidized soybean oil (ESO) is commercially available (e.g., Drapex 6.8, Witro Corp.) and is generally sold with a functionality of 4.1–4.6 epoxy rings per triglyceride, which can be identified via ^{1}H NMR.[20,38] Epoxidized linseed oil is also commercially available (Vikoflex 7190, Elf Atochem Inc.) when higher epoxy content is required.

These oils are predominantly used as an alternative plasticizer in polyvinyl chloride in place of phthalates.[39–41] However, research has been done to explore their use as a toughening agent.[20,23–25,42] With the addition of acrylates, the triglyceride can be reacted via addition polymerization. AESO has been used extensively in the area of surface coatings and is commercially manufactured in forms such as Ebecryl 860 (UCB Chemicals Company).[7,43,44] Urethane and amine derivatives of AESO have also been developed for coating and ink applications.[8,9,45]

The reaction of acrylic acid with ESO occurs by a standard substitution reaction and has first-order dependence with respect to epoxy concentration and second-order dependence with respect to acrylic acid concentration.[46] However, epoxidized oleic methyl ester displays second-order dependence on both epoxy and acrylic acid concentrations.[47] Although the reaction of ESO with acrylic acid is partially acid catalyzed by the acrylic acid, the use of additional catalysts is common. Tertiary amines such as N,N-dimethyl aniline, triethylamine, and 1,4-diazobicyclo[2.2.2]-octane, are commonly used.[38,48] Additionally, organometallic catalysts have been developed that are more selective, thereby reducing the amount of epoxy homopolymerization.[49,50]

AESO can be blended with a reactive diluent, such as styrene, to improve its processability and control the polymer properties to reach a range acceptable for structural applications. By varying the amount of styrene, it is possible to produce polymers with different moduli and glass transition temperatures (T_g). The polymer properties can also be controlled by changing the molecular weight of the monomer or the functionality of the acrylated triglyceride. Consequently, a range of properties and, therefore, applications can be found. Subsequent to the acrylation reaction, the triglyceride contains both residual amounts of unreacted epoxy rings as well as newly formed hydroxyl groups, both of which can be used to further modify the triglyceride by reaction with a number of chemical species (e.g., diacids, dia-
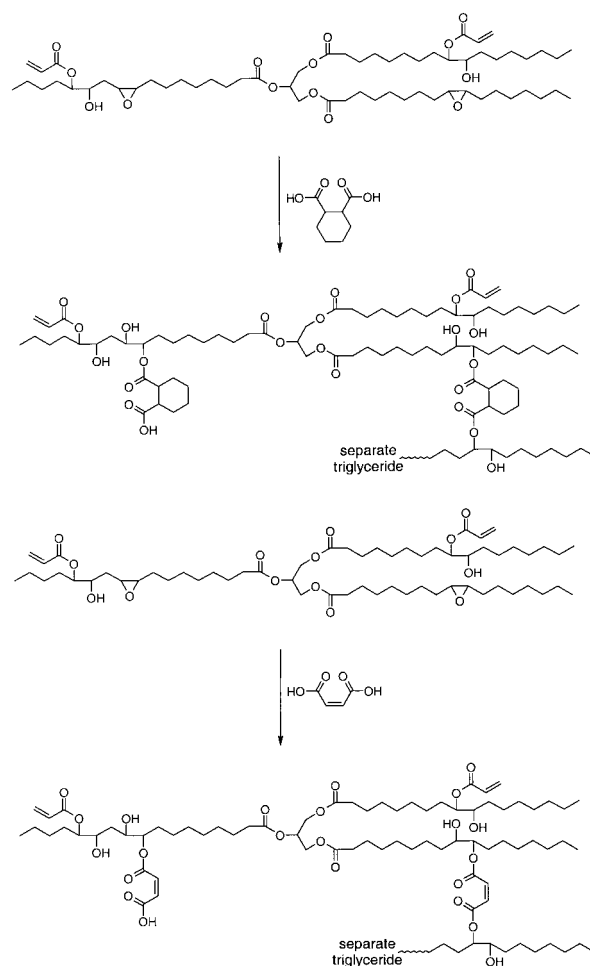

Figure 5 (A) Modification of AESO by reaction with cyclohexane dicarboxylic anhydride. (B) Modification of AESO by reaction with maleic acid.

mines, anhydrides, and isocyanates). The approach presented here is to oligomerize the triglycerides with reagents that have chemical structures conducive to stiffening the polymer, such as cyclic or aromatic groups. Reaction of the AESO with cyclohexane dicarboxylic anhydride (Figure 5A) forms oligomers, increasing the entanglement density as well as introducing stiff cyclic rings to the structure. Reaction of the AESO with maleic acid (Figure 5B) also forms oligomers as well as introduces more double bonds. Although it is desirable to maximize the conversion of hydroxyls or epoxies, at high levels of conversion, the viscosity increases dramatically. Eventually, this increase in viscosity can lead to gelation, so the reaction must be carefully monitored. After oligomerization, the modified AESO resin can be blended with styrene and cured in the same manner as the unmodified AESO resin.
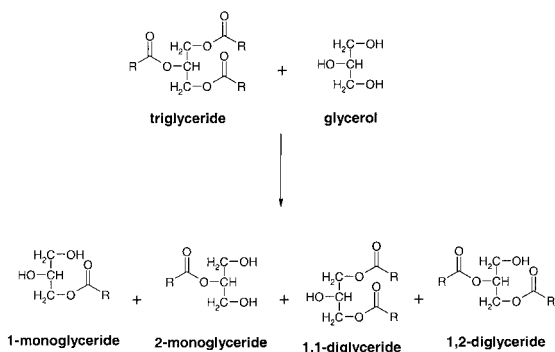
Figure 6 Glycerolysis of triglycerides to form mixture of mono- and diglycerides.

Maleinized Soy Oil Monoglyceride (SOMG/MA)

The SOMG/MA (Figure 4) is synthesized from the triglyceride oil in two steps.[33] The first step is a standard glycerolysis reaction to convert the triglycerides into monoglycerides. This reaction involves reaction of the triglycerides with glycerol, which has been reviewed in detail by Sonntag.[31] The product is generally a mixture of mono- and diglycerides, as illustrated in Figure 6. To aid in the conversion, excess glycerol can be used. Additionally, the reaction can be run in solvent or in the presence of an emulsifier catalyst.[34] After the reaction is completed, it is possible to separate a portion of the unreacted glycerol by rapidly cooling the product.[33] However, the presence of glycerol is not detrimental to the end polymer because it can be reacted with maleic anhydride in the same manner as the monoglycerides and incorporated into the end polymer network.

The maleinization of the SOMG mixture at temperatures <100 °C produces monoglyceride, diglyceride, and glycerol maleate half-esters. This reaction makes no attempt to produce a polyester, and the half-ester formation is expected to proceed at low temperatures in the presence of either acid or base catalysts without any byproducts. A good indication of the success of this reaction is to follow the signal intensity ratio of maleate vinyl protons to fatty acid vinyl protons (N_{MFA}) in the ^{1}H NMR spectrum. The use of 2-methylimidazole and triphenyl antimony as catalysts has been shown to be successful when conducting the reaction at temperatures of 80 to 100 °C, with a 3:2 weight ratio of glycerides to maleic anhydride (N_{MFA} = 0.85).[33,51] After these maleates have been added, the monoglycerides can react via addition polymerization. Because maleates are relatively unreactive with each other, the addition of

styrene increases the polymerization conversion as well as imparts rigidity to the matrix.

To increase the T_g and modulus of the SOMG/MA polymer, more rigid diols can be added during the maleinization reaction, which may increase the rigidity of the end polymer network. Two such diols are neopentyl glycol (NPG) and bisphenol A (BPA). Although their addition to the maleinization mixture will reduce the renewable resource content of the final resin, they should result in higher T_g values for the end polymer. The synthesis of maleate half-esters of organic polyols, including NPG and BPA, and the crosslinking of the resulting maleate half-esters with a vinyl monomer, such as styrene, has been reported in two patents.[52,53] The literature also abounds with examples of unsaturated polyesters prepared from NPG and maleic anhydride with some other polyols and diacids.[54–57] However, the copolymers of NPG and BPA bismaleate half-esters with SOMG maleate half-esters is new.

Here we present the properties of the SOMG/MA polymer as well as the effect of adding NPG and BPA on the mechanical properties of the final polymers. For this purpose, mixtures of SOMG/NPG and SOMG/BPA, prepared at the same weight ratio, were maleinized, and the copolymers of the resulting maleates with styrene were analyzed for their mechanical properties, which were compared with those of SOMG maleates.

Maleinized Hydroxylated Oil (HO/MA)

The maleinized hydroxylated oil (HO/MA) is synthesized in a manner similar to both the AESO monomer and the SOMG/MA monomer. The double bonds of unsaturated oils are used to attach the polymerizable groups, similar to the method used for the AESO monomer, by converting the double bonds of the triglyceride to hydroxyl groups. The hydroxyls can then be used to attach maleates, similar to the situation described for SOMG/MA synthesis. As can be seen in Figure 2, there are two routes to synthesize the hydroxylated triglyceride. The first path is through an epoxidized intermediate. By reacting the epoxidized triglyceride with an acid, the epoxies can be easily converted to hydroxyl groups.[29,58] Alternatively, the hydroxylated oil can be synthesized directly from the unsaturated oil in a manner similar to that described by Swern and co-workers.[30] After hydroxylation, the oil can be reacted with maleic anhydride to functionalize the tri-

glyceride with maleate half-esters. An anhydride-to-triglyceride molar ratio of 4:1 was used in all cases, and the reaction was catalyzed with *N,N*-dimethylbenzylamine. When the maleinization reaction is finished, the monomer resin can be blended with styrene as with the other resins presented here.

Triglyceride-Based Composite Materials

All of the resins presented here are suitable for use as a matrix in a composite material. Their low viscosity and method of curing make them ideal candidates for use in conventional resin transfer molding (RTM) processes. Most polymer matrix composites are made by embedding strong fibers, such as carbon, aramid, glass, or natural fibers, in a polymer matrix. The high strength and modulus of the embedded fibers impart strength and rigidity to the material that surpass that of the neat polymer.[59] Whereas most composite materials utilize synthetic fibers, such as carbon or glass, in recent years, natural fibers have attracted the attention of the composites community as a potential replacement because of the high cost of synthetic fibers. These natural fibers are based on cellulose and offer advantages of biodegradability, low density, nonabrasive nature, and low cost.

Depending on their origin, natural fibers can be grouped into seed, bast, leaf, and fruit qualities. Bast and leaf quality fibers are the most commonly used in composite applications. Examples of bast fibers include hemp, jute, flax, ramie, and kenaf. Leaf fibers include sisal and banana leaf fibers. Properties for these fibers include excellent tensile strength and modulus, high durability, low bulk density, good moldability, and recyclability. These natural fibers have an advantage over glass fibers in that they are less expensive, abundantly available from renewable resources, and have a high specific strength. Although high-performance carbon fibers remain superior to natural fibers in high-end applications, natural fibers have comparable properties to glass fibers in high-volume applications.[60] The properties of flax, jute, sisal, and hemp fibers are shown in Table II and compared with the commonly used E-Glass fiber.[61] The most notable natural fiber is the flax fiber, which has a modulus higher than that of E-glass. Flax is also less dense, thereby producing a lighter composite with good mechanical properties.

Numerous studies on the properties of natural fiber composites have appeared in the literature.

Table II   Properties of Natural and E-Glass Fibers[a]

Fiber	Density (kg/m^3)	Tensile Modulus (GPa)	Tensile Strength (GPa)
Flax	1500	100	1.1
Jute	1450	2.5–13	0.46–0.53
Sisal	1450	9.4–15.8	0.57–0.64
Hemp	1480	—	0.69
E-glass	2540	76	1.5

[a] Reference 61.

These studies have considered a range of natural fibers, including jute,[62–66] banana,[67] agave,[67] hemp,[67,68] flax,[68–70] bamboo,[71] pineapple,[72] and rubber wood.[73] For certain applications, the mechanical properties of natural fiber composites, such as those made from flax or hemp fiber, are not sufficient because of the low strength of these fibers. However, combining natural fibers with stronger synthetic fibers, like glass, could offer an optimum balance between performance and cost. These "hybrid" composites, which utilize two different types of fiber, have been examined in such forms as jute/glass hybrids with epoxy and polyester matrix materials.[74,75]

In all of the previous work, the natural fibers were combined with petroleum-derived matrix resins. The resins presented here offer the unique potential of combining natural fibers with resins based on natural renewable resources. Here we present the properties of glass-reinforced composite materials made from AESO resin as well as all natural fiber composite materials reinforced by flax and hemp fibers.[76] Additionally, we review the properties of hybrid composites manufactured from AESO-based resins reinforced with flax and glass fibers.[77]

EXPERIMENTAL

Acrylated Epoxidized Soybean Oil (AESO) Polymers

The AESO, shown in Figure 4, was examined for its ability to produce high T_g and high modulus polymers. A commercial form of AESO, Ebecryl 860 (UCB Chemical Company), was blended with various amounts of styrene to determine the effect of blending on mechanical and dynamic mechanical properties. The batch of Ebecryl 860
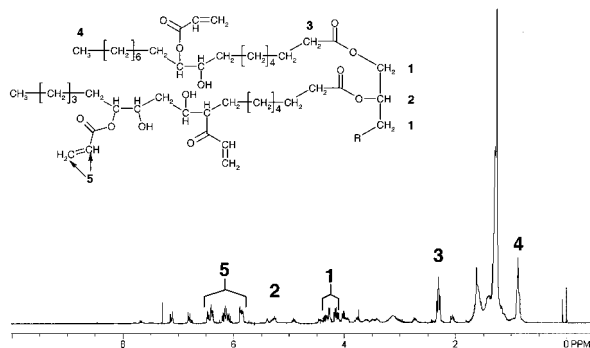
Figure 7 ^{1}H NMR spectrum (CDCl$_3$) for AESO (Ebecryl 860, UCB Chemicals Company).

used had an average functionality of ~3 acrylates per triglyceride as determined by ^{1}H NMR.[38] An example ^{1}H NMR spectrum of AESO is shown in Figure 7. Similar to soybean oil, the triplet peak at 2.3 ppm can be used as a basis for the protons present alpha to the carbonyls in the triglyceride. The three peaks in the range 5.8–6.5 ppm represent the three protons of the acrylate group.

Styrene monomer (Aldrich Chemical) was blended with the AESO along with a free radical initiator, 2,5-dimethyl-2,5-di(2-ethylhexanoyl peroxy)hexane (Witco Corp.). The addition of styrene to any type of unsaturated polyester is common practice in the composite liquid molding resin field. Its low cost and low viscosity improve the price and processability of the resin. For triglyceride-based polymers, the styrene also imparts a rigidity that the triglyceride does not naturally possess. The amount of initiator used was 1.5 wt % of the total resin weight (AESO + styrene). For tensile testing of the polymers, samples were prepared using a dogbone mold with dimensions in accordance with ASTM D 638. The resin was cured at 60 °C for 12 h followed by 125 °C for 1.5 h. Samples for dynamic mechanical analysis (DMA) testing were prepared by pouring resin into a rubber gasket between two metal plates covered with aluminum foil. Samples were cured at 65 °C for 1.5 h and post-cured at 125 °C for 1.5 h.

Tensile properties of the polymer were determined with an Instron 4502 instrument with Series II automated materials testing system v.4.05e (Instron Corp., Canton, MA). Samples were tested at a cross-head speed of 0.02 in/min. Strain measurements were taken using biaxial strain gages (CEA-06-125UT-350, Measurements Group Inc.) and Labview Data Analysis software (National Instruments). DMA was conducted in a three-point bending geometry on a Rheometrics

Solids Analyzer II (Rheometric Scientific Inc.). Temperature ramps were run from −125 to 120 °C at a ramp rate of 5 °C/min with a frequency of 1 Hz and strain of 0.01%.

Synthesis of Modified Acrylated Epoxidized Soybean Oil (AESO) Polymers

To improve the properties of the AESO-based resins, modified forms of the AESO were synthesized. These modifications involved partially reacting ESO with acrylic acid and reacting the remaining epoxies with anhydrides or diacids. A more detailed explanation of the synthesis of partially AESO can be found in other sources.[38] In summary, a mixture of ESO (Drapex 6.8, Witco Corp.) was mixed with a stoichiometric amount of acrylic acid (Aldrich Chemical) in a ratio of ~1500 g of ESO to 460 g of acrylic acid. Hydroquinone (Aldrich Chemical) was added as a free radical inhibitor in the amount of 0.07 wt % of the total weight of the reactants. In addition, 1,4-diazobicyclo[2.2.2]octane (Aldrich Chemical) was added to act as a catalyst, in the amount of 0.1 wt % of the weight of the total reactants. This mixture was reacted at 95 °C for ~11 h after which it was allowed to cool to room temperature. The resulting product had ~1.7 acrylates/triglyceride and 0.4 residual epoxies/triglyceride according to ^{1}H NMR analysis. The remaining 2.3 epoxies have been determined to be lost to epoxy homopolymerization.[38]

The first modification was the reaction of AESO with cyclohexane dicarboxylic anhydride (CDCA), as illustrated in Figure 5A. In a typical reaction, the synthesized AESO was reacted with 7.4% of its weight in CDCA (Aldrich Chemical) and 0.1% of its weight in 2-methyl imidazole (Aldrich Chemical), which catalyzes the reaction.[38] After reacting at 110 °C for ~3 h, the majority of anhydride and epoxy groups were consumed, as indicated by FTIR spectroscopy. The second modification was the reaction of AESO with maleic acid, as illustrated in Figure 5B. This modification was accomplished by reacting the synthesized AESO with 11% of its weight in maleic acid (Aldrich Chemical).[38] The reaction was held at ~80 °C for 4 h, during which time consumption of the epoxies was again confirmed by FTIR spectroscopy.

The modified resins were then blended with styrene and initiator in the amounts of 66 wt % modified AESO, 33 wt % styrene, and 1 wt % 2,5-dimethyl-2,5-di(2-ethylhexanoyl peroxy) hex-

ane initiator. After curing at 65 °C for 1.5 h and post-curing at 125 °C for 1.5 h, the polymers were analyzed for their dynamic mechanical properties and compared with the unmodified AESO resin.

Maleinized Soy Oil Monoglyceride (SOMG/MA) Resin Synthesis

The SOMG/MA shown in Figure 4 was synthesized by first breaking the triglycerides into monoglycerides and than functionalizing the alcohol groups with maleic anhydride. The glycerolysis reaction was done by heating the triglycerides in the presence of glycerol and a catalyst. In a typical reaction, glycerol (Atabay Inc.) was heated at 220–230 °C for 2 h under N_2 atmosphere to distill off any water present.[33] The amount of soybean oil reacted with the glycerol was 4 g of soybean oil (Cargill Inc.) to 1 g of glycerol, corresponding to a molar ratio of 4.75 mol of glycerol to 1 mol of triglyceride. The soybean oil was added in five portions to the glycerol, with each portion added at 1 h intervals. With the first portion of oil, commercial soap was added in the amount of 1 % of the total oil amount to act as an emulsifier and catalyst. The solution was heated at 230 °C under N_2, while being stirred. After 5.5 h, the reaction was immediately cooled to room temperature with an ice bath, causing glycerol to separate from the mixture. On removal of this layer, ~90% of the reaction solution, consisting of glycerides and glycerol, was recovered.

Maleinization of the mixture was accomplished by heating 60 g of glyceride/glycerol mixture up to ~80 °C with stirring. Then, 40 g of maleic anhydride (Aldrich Chemical) was added. As the anhydride melted, 0.6 g of triphenyl antimony (Aldrich Chemical) was added as a catalyst along with 0.01 g of hydroquinone. The reaction was complete after 5.5 h, according to FTIR and ^{1}H NMR, resulting in a mixture of maleinized glycerides and glycerol (SOMG/MA).[33]

Maleinized Soy Oil Monoglyceride/Neopentyl Glycol (SOMG/NPG/MA) Resin Synthesis

Modifying the procedure given in U.S. Patent 3,784,586,[53] SOMG/NPG/MA resin was synthesized as follows.[51] Forty-five grams of SOMG were placed into a 250-mL round-bottomed flask equipped with a temperature controller and a magnetic stirrer and heated to 125 °C. Then, 15 g of NPG (0.144 mol) were added to SOMG and, as the NPG melted, 58.3 g of maleic anhydride was

added. As the three compounds formed a homogenous solution, 0.06 g of triphenyl antimony catalyst and 0.015 g of hydroquinone were added. The solution was stirred for 6.5 h at 120 °C. ^{1}H NMR analysis of the product showed the formation of both the SOMG and NPG maleate and later fumarate vinyl groups.[33] The product was a light-yellow-colored viscous liquid at room temperature.

Maleinized Soy Oil Monoglyceride/Bisphenol A (SOMG/BPA/MA) Resin Synthesis

The preparation of maleates of BPA and ethylene and propylene oxide adducts of BPA has been reported in Gardner's patent.[52] For this work, SOMG and BPA were maleinized as a mixture.[51] First, 45 g of SOMG were placed into a 250-mL round-bottomed flask equipped with a temperature controller and a magnetic stirrer and heated to 125 °C. Then, 15 g of BPA (0.0657 mol) were added to SOMG and, as the BPA dissolved, 42.88 g of maleic anhydride (0.4375 mol) were added. As the three compounds formed a homogenous solution, 0.6 g of triphenyl antimony and 0.01 g of hydroquinone were also added. The solution was then stirred for 9 h at 125 °C until maleic anhydride consumption was complete. The ^{1}H NMR analysis of the product showed the formation of both the SOMG and BPA maleate and later fumarate vinyl groups.[33] The reaction product was an orange-colored viscous liquid (98 g) at room temperature.

Copolymerization of the Maleates with Styrene

The copolymerizations of SOMG/MA, SOMG/NPG/MA, and SOMG/BPA/MA with styrene were all run under the same conditions for comparison of the mechanical properties of the resulting polymers. For this purpose, a certain weight ratio of the maleate mixture was mixed with 35% of its own weight of styrene in a closed vial. All the maleate products were soluble in styrene. *tert*-Butyl peroxy benzoate radical initiator, 2% by weight of the total mixture, was added, and N_2 gas sparging and vacuum degassing were carried out for 5 min. The solution was then transferred into a rectangular rubber gasket mold that was sandwiched between two steel plates. The resin-filled mold was heated to 120 °C at 5 °C/min, and the resin was cured at this temperature for 3.5 h. It was then post-cured at 150 °C for 1 h. Samples were clear, homogenous, and free from voids or
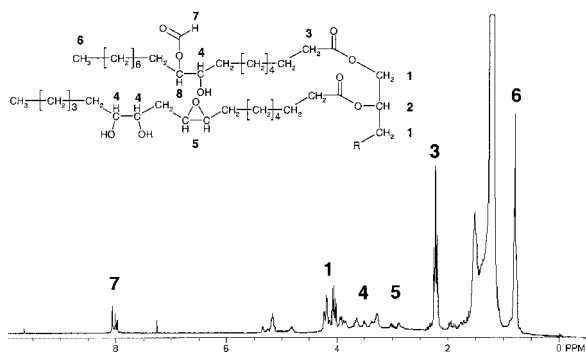
Figure 8 ^{1}H NMR spectrum (CDCl$_3$) of hydroxylated soybean oil. Treatment of the oil with formic acid and hydrogen peroxide results in conversion of the double bonds to hydroxy groups.

gas bubbles. The polymer samples were then polished and prepared for DMA. DMA was conducted in a three-point bending geometry on a Rheometrics Solids Analyzer II (Rheometric Scientific Inc.). Temperature ramps were run from 30 to 200 °C at a ramp rate of 5 °C/min with a frequency of 1 Hz and strain of 0.01%.

Maleinated Hydroxylated Oil (HO/MA) Polymer Synthesis

The maleinated hydroxylated oil (HO/MA) shown in Figure 4 utilizes the unsaturation of the triglyceride to incorporate polymerizable groups. This monomer was used in a series of experiments to understand how triglyceride structure can affect the synthesis and dynamic mechanical properties of the end polymer.[78] Olive oil (Aldrich Chemical), cottonseed oil (Sigma Chemical), soybean oil (Aldrich Chemical), safflower oil (Aldrich Chemical), linseed oil (Aldrich Chemical), triolein (Sigma Chemical), and a genetically engineered high oleic soybean oil (DuPont Company) were converted into hydroxylated maleinated oil resins (HO/MA). The levels of unsaturation for these oils are shown in Table I. The fatty acid chain lengths for all of these oils are between 17.5 and 18 carbons long, making the unsaturation level essentially the only difference among oils.

Hydroxylation of an oil was accomplished by vigorously stirring the oil (~100 g) in the presence of formic acid (150 mL) and 30% (aq.) hydrogen peroxide (55 mL) at 25 °C.[30,78] The reaction time was 18 h to reach a maximum conversion of double bonds. Formic acid, peroxide, and water were then removed from the hydroxylated oil by dissolving the reaction mixture in diethyl ether

and washing multiple times with water and then saturated (aq.) sodium bicarbonate until reaching a neutral pH. The solution was then dried by washing with saturated (aq.) sodium chloride and drying over sodium sulfate. Finally, the ether was evaporated off under vacuum. The extent of hydroxylation can be characterized by ^{1}H NMR. An example of a ^{1}H NMR spectrum is presented in Figure 8, with corresponding peak assignments.[78] The extent of hydroxylation has a linear dependence on the level of unsaturation. Generally, for every double bond present on the triglyceride, an average of 1.6 hydroxyls can be added to the triglyceride.[78]

The purified hydroxylated oil was reacted with maleic anhydride in a ratio of 1 mol of triglyceride to 4 mol of anhydride. The hydroxylated oil was heated to a temperature of ~80 °C and finely ground maleic anhydride (Aldrich Chemical) was then added. On dissolving of the anhydride, *N,N*-dimethylbenzylamine (Aldrich Chemical) was added to catalyze the reaction. The reaction was continued for 3 h and the extent of maleinization was determined by ^{1}H NMR. An illustrative ^{1}H NMR spectrum is shown in Figure 9.[78] Under these reaction conditions, the extent of functionalization seems to plateau in the range 2.1–2.8 maleates/triglyceride for all oils.[78] It was observed that ~20–25% of the maleates attached to the triglycerides isomerize to form fumarate groups (*trans* confirmation). Unreacted maleic anhydride remained in the resin and was polymerized during the cure reaction. The HOMA resins were then dissolved in styrene in a styrene/HOMA molar ratio of 7:1. Resins were cured with 2,5-dimethyl-2,5-di-(2-ethylhexanoylperoxy)hexane (Witco Corp.) at 65 °C for 1.5 h and post-cured
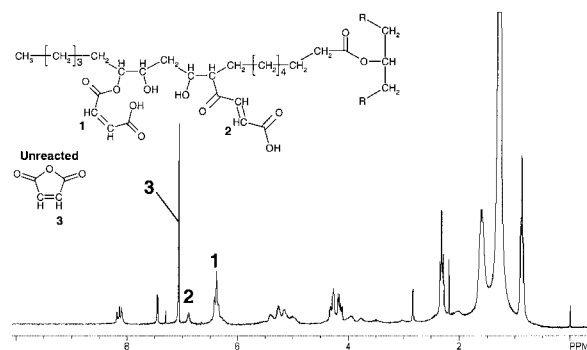

Figure 9 ^{1}H NMR spectrum (CDCl$_3$) of maleinized hydroxylated soybean oil. Peaks 1 and 2 represent the maleate half-esters and fumarate half-esters, respectively. Peak 3 represents unreacted maleic anhydride.

at 120 °C for 1 h. DMA was conducted in a three-point bending geometry on a Rheometrics Solids Analyzer II (Rheometric Scientific Inc.). Temperature ramps were run from 30 to 175 °C at a ramp rate of 5 °C/min with a frequency of 1 Hz and strain of 0.01%.

Manufacturing of Glass Fiber Reinforced Composites

The properties of glass fiber-reinforced composites made from the AESO and HSO/MA polymers were examined.[1] First, 1500 g of AESO (Ebecryl 860, UCB Chemical) was mixed with 750 g of styrene, 113 g of divinyl benzene, 18 g of cobalt naphthalate activator (Mahogany Company of Mays Landing Inc.), and 68 g of Trigonox 239 (Akzo Nobel) free radical initiator. The resin was infused into a glass fiber (50% volume fraction) preform (QM6408 E-Glass, 2 plies) by Seeman's Composite Resin Injection Molding Process (SCRIMP). The composite was cured for 12 h at room temperature and post-cured at 150 °C for 2 h. The properties were compared with those of a commercial high-performance vinyl ester resin, Dow PC-100 (Dow Chemical), containing the same fiber volume fraction and manufactured under the same conditions.

The HSO/MA composites were manufactured using resin composed of 100 g of HSO/MA monomer synthesized in the manner previously mentioned, 45 g of styrene, and 5 g of divinyl benzene. Next, 2.25 g of the initiator 2,5-dimethyl-2,5-di-(2-ethylhexanoylperoxy)hexane (Witco Corp.) were added, and the mixture was injected into a resin transfer mold containing two mats of glass fiber (TPI QM6408 glass fiber). The mold was heated at 65 °C for 1.5 h and post-cured at 120 °C for 1 h. Properties were compared with those of the vinyl ester resin Dow Derakane 411C50 (Dow Chemical) prepared under the same conditions.

The tensile, flexural, and compressive properties for both of these composites were measured in accordance with ASTM D 3039, ASTM D 790, and ASTM D3410, respectively.

Manufacturing of Flax and Hemp Composites

A more detailed outline of the method used to manufacture the flax and hemp composites can be found elsewhere.[76,79] Composites were manufactured using Durafiber Grade 2 flax fiber (Cargill Limited Inc.) and hemp fibers (Hemcore Limited) within AESO-based polymer. The hemp was obtained from in the form of a nonwoven mat with an oriented fiber direction.

The resin used in these all natural composites was prepared by blending AESO (Ebecryl 860, UCB Chemicals Co.) with styrene (Aldrich Chemical) and divinylbenzene (Aldrich Chemical) in the ratio 100:45:5 by weight. To initiate the free radical polymerization reaction, 1.5% of the total resin weight of 2,5-dimethyl-2,5-di-(2-ethylhexanoylperoxy)hexane (Witco Corp.) was added to the resin. The composite was manufactured using a resin transfer molding process. For the flax composites, flax fibers were uniformly arranged in the mold in a random mat. Hemp composites were made with two layers of the oriented hemp mats placed with their orientation perpendicular to each other. Resin was injected into the mold, and the composite was cured at 90 °C for an hour followed by a post cure at 110 °C for another hour. The tensile and flexural properties were measured in accordance with ASTM D 3039 and ASTM D 790, respectively.

Manufacturing of Glass–Flax Hybrid Composites

Hybrid composites were manufactured using glass (E-Glass woven fiber) and Durafiber Grade 2 flax fibers (Cargill Limited Inc.) in an AESO based polymer.[77] These were manufactured in symmetric and asymmetric manners. In the symmetric hybrid composites, a layer of flax fiber was sandwiched in between two layers of glass fiber. The asymmetric composites were produced by uniformly arranging the flax fibers at the bottom of the mold in a random mat and then placing the two layers of woven glass fabric on top.

The resin for these studies was prepared by mixing AESO (Ebecryl 860, UCB Chemicals Co.) with 50 parts per hundred by weight (phr) styrene (Aldrich Chemical), 4.5 phr Trigonox 239A free radical initiator (Akzo Nobel), and 1.2 phr cobalt naphthalate activator (Mahogany Company of Mays Landing Inc.). After injecting the resin into the mold, the composite was cured overnight at a pressure of 2.1 MPa at room temperature. The composite was then post-cured at 110 °C for 2 h. Following post-curing, the composite panels had fiber weight fractions in the range 0.31–0.40. Composites with glass–flax ratios 100:0, 80:20, 60:40, 40:60, and 0:100 were made. The tensile, compression, and flexural properties were measured in accordance with ASTM D 3039, ASTM D 3410, and ASTM D 790, respectively. Impact tests were conducted in accordance with ASTM D 3763.
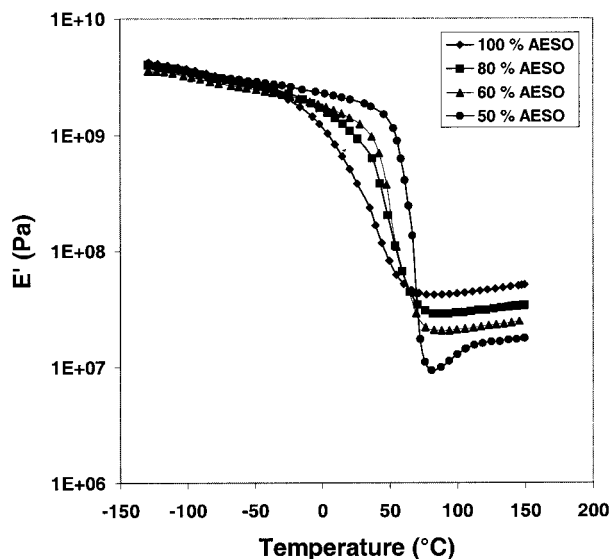
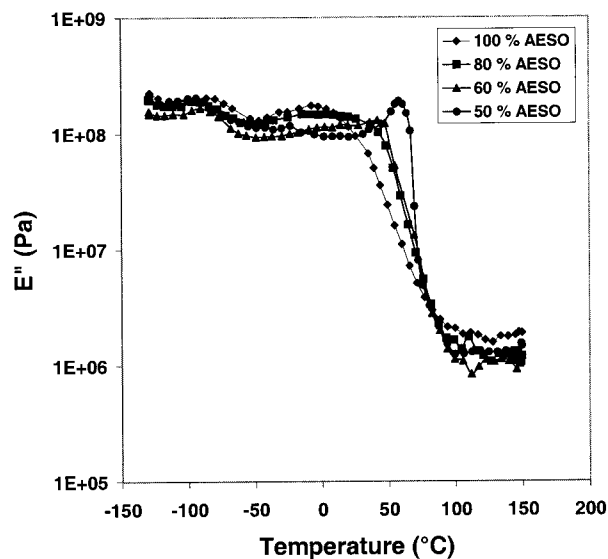**Figure 10** Storage modulus (E') of AESO–styrene co-polymer as a function of temperature.

Figure 11 Loss modulus (E'') of AESO–styrene copolymer as a function of temperature.

RESULTS AND DISCUSSION

Viscoelastic and Mechanical Properties of AESO–Styrene Polymers

The storage moduli, E', of the AESO–styrene neat polymers at various temperatures and compositions are shown in Figure 10. It is apparent that at room temperature ($\sim$25 °C), the polymers display moduli proportional to the amount of styrene present in the polymer, which is expected from the tensile properties presented earlier. Additionally, it can be seen that at room temperature all of the polymers are in the transition from the glassy region to the rubbery plateau. Even at temperatures as low as -130 °C, it does not appear that these polymers have reached a characteristic glassy plateau. At extremely low temperatures, all compositions exhibit essentially equal moduli of $\sim$4 GPa. At higher temperatures, the compositions show moduli inversely proportional to the amount of styrene present. According to rubber elasticity theory,[80] the lower styrene content polymers have a higher cross-link density, as observed in Figure 10.

The T_g is often designated by either the temperature at which the E'' value is at a peak or the temperature at which the tan δ exhibits a peak.[81] As shown in Figure 11, all of the AESO–styrene copolymers exhibit two peaks in E''. A minor relaxation occurs in the range -85–-95 °C, showing little dependence on composition. The much

larger relaxation, corresponding to the T_g, occurs in the range -10–60 °C, and also becomes sharper in nature with the addition of styrene. These peaks reflect themselves in the tan δ graph shown in Figure 12. The temperature at which these peaks occur exhibits a linear dependency on composition, increasing with the amount of styrene present in the system, as illustrated by Figure 13.

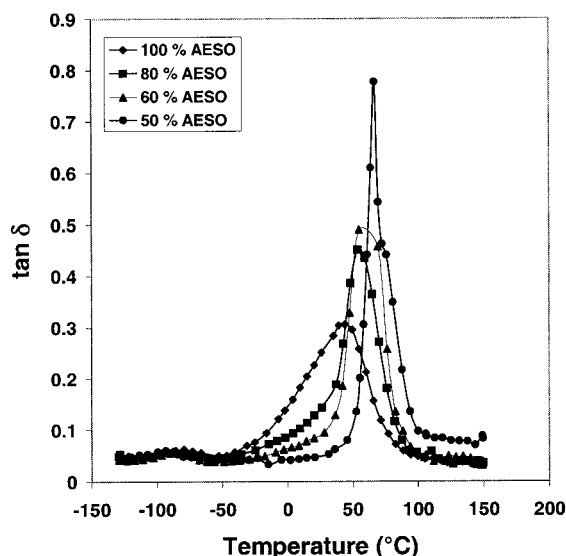The dynamic mechanical behavior just described is a combination of two factors, cross-link

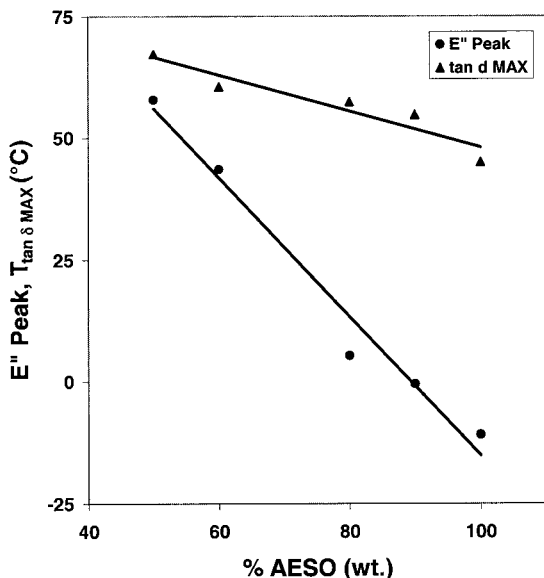**Figure 12** Dampening peak (tan δ) of AESO–styrene copolymer as a function of temperature.

Figure 13 Peak temperatures for E'' and tan δ for various compositions of AESO–styrene copolymer.

oleic content oil and synthetic triolein oil. The existence of some saturated fatty acids, though, can contribute to improved toughness and ballistic impact resistance.[82]

Tensile Properties of AESO–Styrene Copolymers

The tensile moduli of three AESO–styrene copolymers at room temperature are shown in Figure 14. The pure AESO polymer exhibits a modulus of $\sim$440 MPa. At a styrene content of 40 wt %, the modulus increases significantly to 1.6 GPa, which is a fourfold increase. In this region, the dependency on composition appears to be fairly linear. The ultimate tensile strengths of these materials, as shown in Figure 15, also show linear behavior. The pure AESO samples exhibit strengths of $\sim$6 MPa, whereas the polymers with 40 wt % styrene show much higher strengths of $\sim$21 MPa. Therefore, it is apparent that the addition of styrene drastically improves the properties of the end resin.

Dynamic Mechanical Behavior of Modified AESO Resins

The dynamic mechanical properties of the AESO polymers modified by CDCA and maleic acid were better than those of the unmodified polymers. As shown in Figure 16, the storage modulus at room temperature increases with both of these modifications. The storage modulus of the unmodified AESO resin at room temperature is 1.3 GPa,
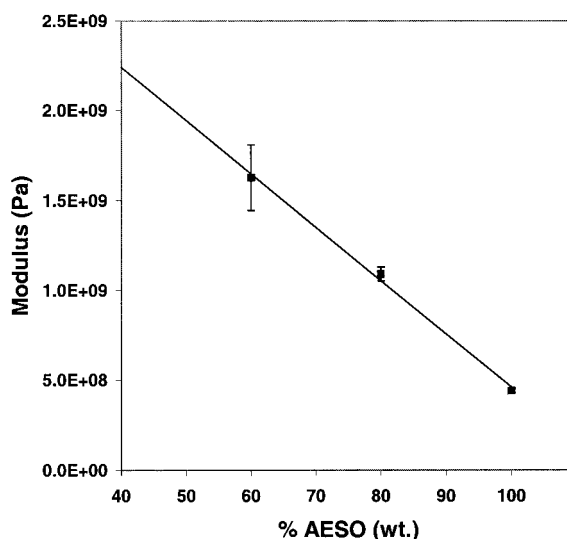
density and plasticization. As the amount of AESO is increased, the number of multifunctional monomers also increases. Therefore, the overall cross-link density is going to be greater with increasing amounts of AESO, as supported by the high-temperature moduli shown in Figure 10. Increasing the cross-link density slows the transition in E' from glassy to rubbery behavior. Additionally, the tan δ peak broadens and decreases in height.[81]. The other factor in the dynamic mechanical behavior, plasticization, is due to the molecular nature of the triglyceride. The starting soybean oil contains fatty acids that are completely saturated and cannot be functionalized with acrylates. Therefore, these fatty acids act in the same manner as a plasticizer, introducing free volume and enabling the network to deform more easily. The addition of even small amounts of plasticizer to polymers has been known to drastically broaden the transition from glassy to rubbery behavior and reduce the overall modulus.[81]

This plasticizer effect presents an issue that may be inherent to all natural triglyceride-based polymers that use the double bonds to add functional groups. However, with advances in genetic engineering capabilities, it may be possible to reduce this trend by reducing the amount of saturated fatty acids present, thus sharpening the glass–rubber transition. This issue will be addressed later in the properties of HO/MA polymers produced from genetically engineered high

Figure 14 Tensile modulus of AESO–styrene copolymers.
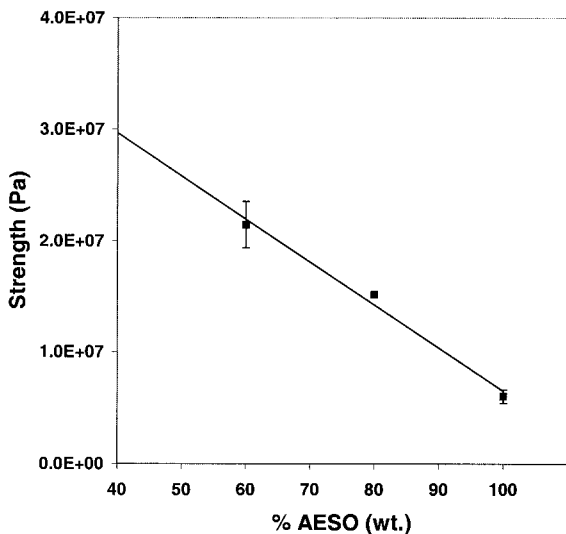
Figure 15 Ultimate tensile strength of AESO–styrene copolymers.

Figure 17 Damping peak (tan δ) of modified AESO resins as a function of temperature. Peaks in tan δ were found at 81 °C (CDCA modified) and 105 °C (maleic acid modified) compared with 79 °C for the synthesized AESO.

whereas the cyclohexane dicarboxylic anhydride modification increases the modulus to 1.6 GPa. The maleic acid modification provides the most improvement, raising the storage modulus to 1.9 GPa. The T_g, as indicated by the peak in tan δ , does not show any large increase from the anhydride modification, as shown in Figure 17. However, the maleic acid modification shifts the tan δ peak by almost 40 °C, showing a peak at 105 °C. The increased broadness of the peak can be attributed to increased crosslink density.
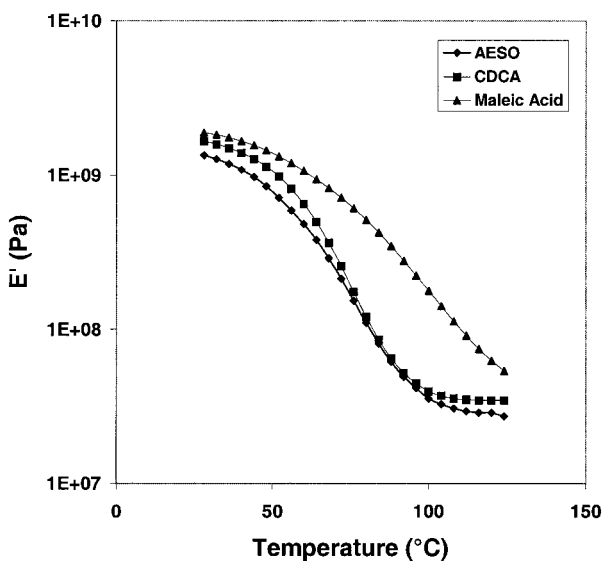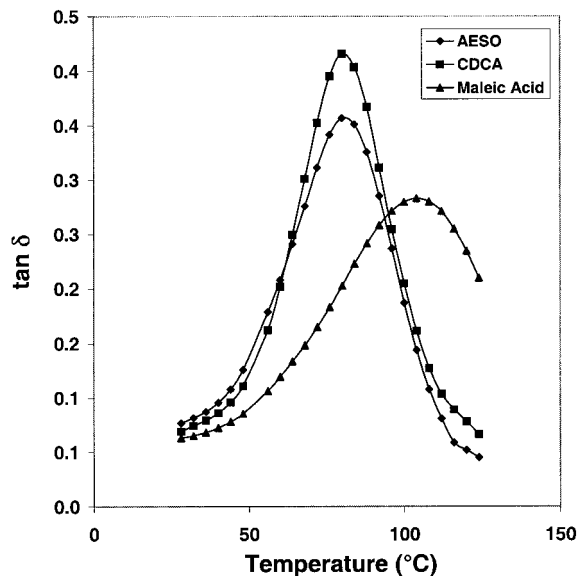
SOMG/MA Polymer Properties

As can be seen in Figure 18, the tan δ peak for the SOMG/MA polymer occurs at ~133 °C, and the polymer has an E' value of ~0.92 GPa at room temperature. It is apparent that the glass transition is rather broad due to the broad MW distribution of the SOMG maleates. The distribution of soy oil monoglyceride monomaleates, monoglyceride bismaleates, diglyceride monomaleates, and glycerol trismaleates has been confirmed by mass spectral analysis, which has been reported in a previous publication.[83] The tensile tests performed on the copolymers of SOMG maleates with styrene showed a tensile strength of 29.36 MPa and a tensile modulus of 0.84 GPa, as calculated from the force displacement graph.

SOMG/NPG Maleates (SOMG/NPG/MA)

The DMA of the SOMG/NPG/MA polymer showed a tan δ peak at ~145 °C and an E' value of 2 GPa at room temperature. The 12 °C increase in the T_g and the considerable increase in the modulus of the copolymers of SOMG/NPG/MA with styrene compared with that of SOMG/MA can be attributed to the replacement of the flexible fatty acid chains by the rigid methyl groups of NPG. The overall dynamic mechanical behavior of the
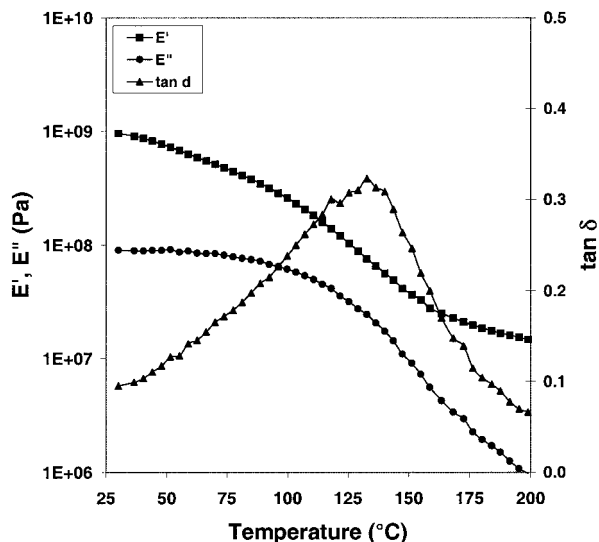

Figure 16 Storage modulus (E') of modified AESO resins as a function of temperature.

Figure 18 Dynamic mechanical behavior of SOMG/MA polymer.

SOMG/NPG/MA polymer was very similar to that of SOMG/MA, as shown in Figure 18. Despite the higher T_G and modulus, there remained a broad glass transition. The tensile strength of the SOMG/NPG/MA polymer was 15.65 MPa, whereas the tensile modulus was 1.49 GPa.

Maleinized pure NPG polymerized with styrene (NPG/MA) has been prepared to compare its properties with those of the SOMG/NPG/MA polymer.[51] DMA analysis of the NPG/MA showed a tan δ peak at ~103 °C and an E' value of ~2.27 GPa at 35 °C. The high T_G value observed for the SOMG/NPG/MA system (~145 °C) is attributed to a synergetic effect of both the NPG and SOMG because the T_G value observed for the NPG/MA system (~103 °C) is much lower. This difference is probably due to the incorporation of the fatty acid unsaturation into the polymer in the SOMG/NPG/MA system. The comparatively higher E' value observed for NPG/MA on the other hand explains the increase in the E' observed for the SOMG/NPG/MA system compared with that of the SOMG/MA system. The decrease in tensile strength of the SOMG/NPG/MA system compared with that of SOMG/MA may be attributed to a broader MW distribution of the former.

SOMG/BPA Maleates (SOMG/BPA/MA)

The DMA of this polymer showed a tan δ peak at ~131 °C and an E' value of 1.34 GPa at 35°C. The introduction of the rigid benzene ring on the poly-

mer backbone made a considerable increase on the modulus of the final polymer compared with that of SOMG/MA. The T_G of this polymer, however, was not very different from that of the SOMG/MA (133 °C). This similarity has been attributed to a lower yield in the maleinization of the BPA, as determined from ^{1}H NMR data.[51] Like the SOMG/NPG/MA polymer, the SOMG/BPA/MA displayed the characteristic gradual glass transition shown in Figure 18.

HO/MA Dynamic Mechanical Polymer Properties

The dynamic mechanical properties of the HO/MA polymers were better than those of the AESO polymers. Little variation was seen between the polymers made from the different oils. At room temperature, the storage moduli for all of the oils existed between 1.45 and 1.55 GPa, showing no dependence on saturation level. The dynamic mechanical behavior was very similar between the different oils, with the typical behavior being shown in Figure 19. The temperatures at which a maximum in tan δ was exhibited ranged from 107 to 116 °C, which are all substantially higher than that for the AESO base resin. These properties are fairly close to those shown by conventional petroleum-based polymers. However, the distinctive triglyceride behavior still exists, in that the glass transitions are extremely broad and that even at room temperature the materials are not completely in a glassy state. Again, these behaviors are probably due to the saturated fatty acids of the triglycerides that act as plasticizer.
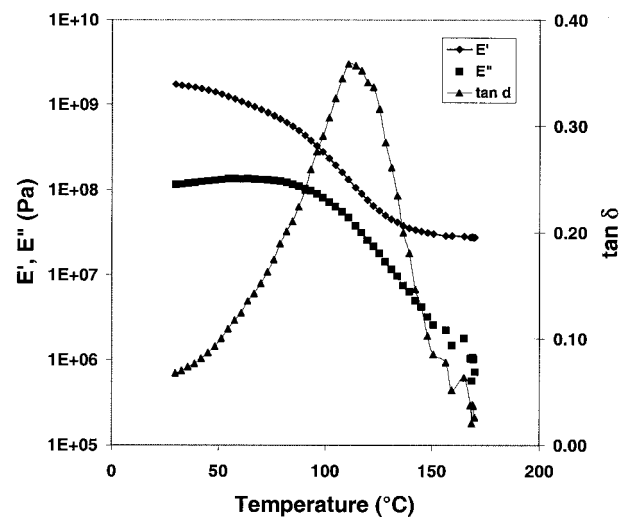

Figure 19 Representative dynamic mechanical behavior for HO/MA polymers.
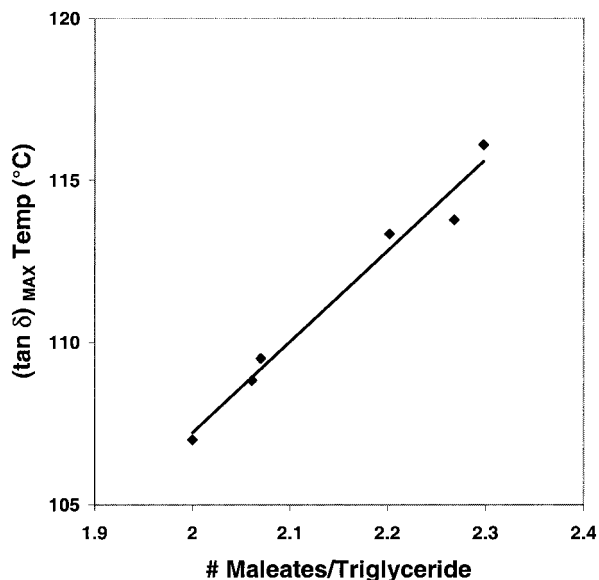
Figure 20 Peak in tan δ as a function of maleate functionality.

Although the extent of maleinization was approximately the same from oil to oil, it is possible to see how the slight differences affect the T_g. In Figure 20, the tan δ peak temperature has been plotted as a function of maleate functionality. Within this range, the behavior is linear, suggesting that if higher levels of functionalization are able to be reached, the properties should improve accordingly. However, it is expected that past a certain extent of maleate functionality, the properties dependence will plateau. Work is currently being pursued to test the limits of this behavior.

It was previously stated that the broadness in the glass transition may be inherent to all triglyceride-based polymers. However, work with genetically engineered oil and synthetic oil has shown that it is possible to reduce this characteristic.[78] The genetically engineered high oleic soybean oil has an average triglyceride functionality of 3 double bonds/triglyceride and the fatty acid distribution shown in Table I. The maleinized form of this oil had a maleate functionality of 2 maleates/triglyceride. The properties of polymers from this material were compared with those of polymers from triolein oil, which is monodisperse and consists only of oleic fatty acid esters (18 carbons long, 1 double bond). The maleinized triolein oil had a maleate functionality of 2.1 maleates/triglyceride. Thus, the only difference between the two oils is the fatty acid distribution of the high oleic oil versus the monodisperse triolein oil.

The dynamic mechanical properties of polymers made from these oils is shown in Figure 21. The T_G of these two polymers do not seem to differ much judging from either their tan δ peak or the inflection in the E'. However, the broadness of the transitions do differ. It is apparent that the triolein polymer has a sharper E' transition from the glassy region to the rubbery region. This difference is evident also in the tan δ peak, which has a higher peak height for the triolein polymer. The transition is not yet as sharp as petroleum-based polymers, probably because the triolein monomer has a functionality of only 2 maleates/triglyceride. Consequently, there is still a plasticizer effect present. However, this effect may be reduced by controlling the reaction conditions to reach higher conversions.

AESO and HSO/MA Glass Fiber Composites

The properties of the glass fiber-reinforced AESO composites are shown in Table III.[1] The physical properties are very close to those of the Dow PC100 resin. The tensile strength, tensile modulus, and compressive modulus all are similar to the properties of the vinyl ester resin. The only apparent shortcoming is in the compressive strength of the AESO resin, which can be attributed to the lower strength of the AESO neat polymer. However, according to DMA, the AESO com-
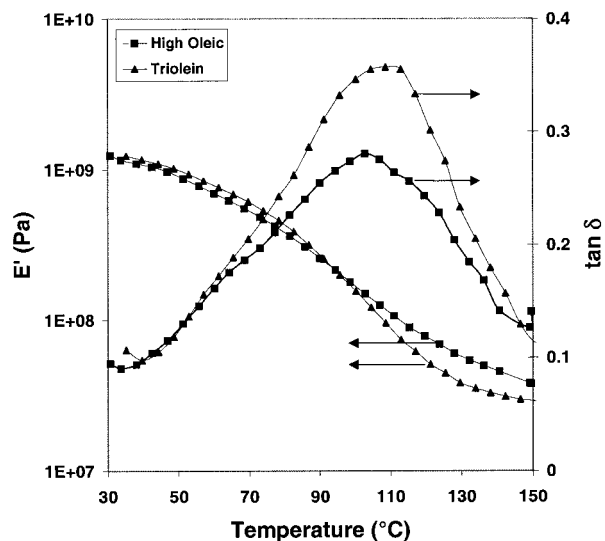

Figure 21 Dynamic mechanical properties of polymers made from maleinized hydroxylated high oleic oil and triolein oil. The monodisperse triolein displays a sharper transition from the glassy region to the rubbery region.

Table III Tensile and Compressive Properties of Glass Fiber-Reinforced AESO-Based Polymer and Dow PC100 Vinyl Ester Polymer

Polymer	Testing Direction	Tensile Strength (MPa)	Tensile Modulus (GPa)	Compressive Strength (MPa)	Compressive Modulus (GPa)
AESO	0°	463.2	24.8	302.6	24.8
Dow PC100	0°	458.4	23.8	420.5	23.4
AESO	90°	321.9	20.7	180.6	20.7
Dow PC100	90°	324.0	17.6	339.1	17.9

posite still displayed a T_G close to that of the neat polymer at ~80 °C. This value is much lower than the T_G of the vinyl ester polymer of ~128 °C.

The HSO/MA composite properties were even more successful at replicating the properties of a vinyl ester composite, as shown in Table IV. The flexural modulus and compressive strength for the HSO/MA composite were of same magnitude as those of the vinyl ester composite, whereas the flexural strength was slightly lower. Additionally, the T_G of the HSO/MA composite was ~128 °C, which equals that found for the vinyl ester composite.

These results indicate that although the properties of the neat based-based polymers are less than those of the vinyl ester polymers, the composite material properties are very similar. In tensile deformation, the fiber reinforcement is able to support the majority of the load, leading to an acceptable modulus and strength. The area in which improvement is needed is in compression deformation, where the polymer bears the majority of the stress.

Flax Composites

The tensile and flexural strength as a function of fiber content for the Durafiber grade-2 flax composites is shown in Figure 22. The tensile strength of the AESO–flax fiber composite had a

Table IV Flexural and Compressive Properties of HSO/MA-Based Polymer and Dow 411C50 Vinyl Ester Polymer

Polymer	Flexural Modulus (GPa)	Flexural Strength (MPa)	Compressive Strength (MPa)
HSO/MA	34.5	669	200
Dow DK 411C50	35.8	813	290

maximum value of 30 MPa at 34% fiber content, which is comparable to the tensile strength of the AESO neat resin (~30 MPa). The flexural strength showed a similar trend, exhibiting a maximum value at ~34% fiber content. The flexural moduli of these materials behaved similarly, showing a maximum at 34% fiber content, whereas the tensile moduli increased with fiber content, as illustrated in Figure 23. Other researchers have noticed this optimization phenomenon, which has been explained in terms of increasing fiber–fiber interactions as the fiber content increases.[60] This increase in fiber–fiber interactions reduces the level of fiber–matrix interaction, thereby weakening the composite. Percolation theory has also been used to explain this effect.[82]

Hemp Composites

Composites made of 20 wt % hemp fiber displayed tensile strength and modulus of 35 MPa and 4.4
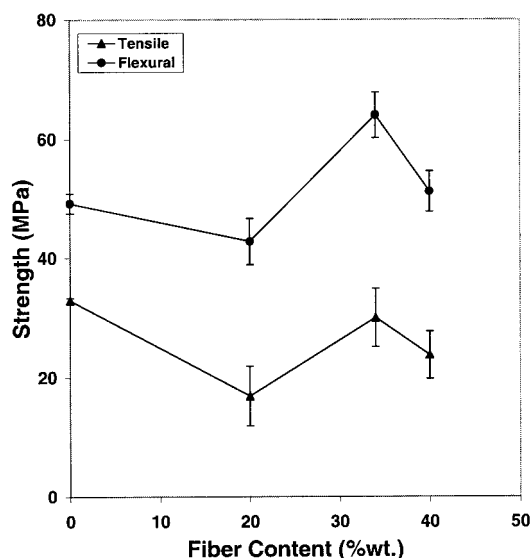
Figure 22 Strength dependence on composition for flax (Durafiber-grade 2)-reinforced AESO polymer.
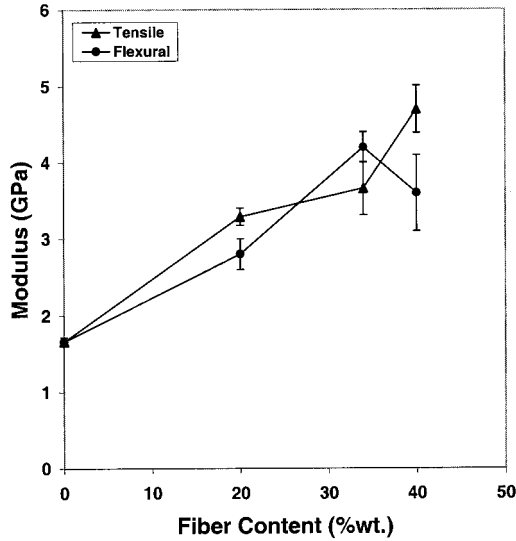
Figure 23 Modulus dependence on composition for flax (Durafiber-grade 2)-reinforced AESO polymer.

GPa, respectively. The flexural properties of the composites were anisotropic. Samples tested with the side of the composite in contact with the upper surface of the mold during the curing process resting on the supports display a yield strength of 35.7 ± 5.9 MPa and modulus of 2.6 ± 0.2 GPa. Samples tested with the side in contact with the lower surface of the mold during cure resting on the supports have a yield strength of 51.3 ± 2.7 MPa and modulus of 2.7 ± 0.2 GPa. Thus, the modulus does not appear to be affected by orientation, whereas the yield strength has a 44% increase. This increase in strength is substantial and can be attributed to the orientation of the fibers in the mat.

The mechanical properties of the all-natural composites are comparable to the properties shown by wood. For example, a typical hard wood has a tensile modulus of ~10 GPa, with a fracture stress of ~30 MPa when the stress is exerted parallel to the fiber axis and ~3 MPa when the stress is exerted normal to the fiber axis. The considerable advantage of the all-natural composites is that the unidirectional high properties of wood can be obtained in all directions for the randomly oriented fiber composite. In addition, the ease of manufacturing complex shapes via normal composite liquid molding operations provides a significant cost, as well as ease of fabrication, advantage for these materials.

Hybrid Composites

The tensile modulus, tensile strength, and compressive strength of the glass–flax hybrid composites for different glass–flax ratios and composite constructions are shown in Table V. As can be expected, these properties all increase with increasing glass fiber content. The 100% flax fiber-reinforced materials show a tensile strength and modulus of 26.1 ± 1.7 MPa and 1.9 ± 0.1 GPa, respectively. At the other extreme, the 100% glass fiber-reinforced materials show a tensile strength and modulus of 128.8 ± 1.1 MPa and 5.2 ± 0.1 GPa, respectively. As shown in Table VI, the asymmetric composites have tensile moduli very similar to those of the symmetric composites moduli. However, the tensile and compression strengths of the asymmetric composites were noticeably less than those of the symmetric composites. This difference is due to the different modes of failure exhibited by the two types of composites. The symmetric composites undergo tensile failure at the peak load, whereas the asymmetric composites fail by shear delaminating at the glass–flax interface because of the difference in the tensile moduli of the two fiber types.

The flexural properties of the glass–flax hybrid composites are shown in Table VII. The flexural modulus and strength for the glass fiber composite are much higher than those for the flax fiber

Table V   Tensile and Compression Properties of Symmetric Glass/Flax Hybrid Composites

Glass/Flax Ratio	Weight Fractions		Tensile Modulus (GPa)	Tensile Strength (MPa)	Compression Strength (MPa)
	Glass	Flax			
100/0	0.35	0.00	5.2 ± 0.1	128.8 ± 1.1	89.8 ± 3.2
80/20	0.25	0.06	3.5 ± 0.1	123.3 ± 1.2	71.6 ± 2.6
60/40	0.23	0.16	3.2 ± 0.1	109.1 ± 1.0	62.3 ± 3.1
40/60	0.16	0.24	2.9 ± 0.2	82.6 ± 1.4	33.6 ± 0.8
0/100	0.00	0.31	1.9 ± 0.1	26.1 ± 1.7	18.5 ± 2.4

Table VI   Tensile and Compression Properties of Asymmetric Glass/Flax Hybrid Composites

Glass/Flax Ratio	Weight Fractions		Tensile Modulus (GPa)	Tensile Strength (MPa)	Compression Strength (MPa)
	Glass	Flax			
80/20	0.25	0.06	3.4 ± 0.1	111.7 ± 2.1	65.3 ± 4.8
60/40	0.24	0.16	3.1 ± 0.1	90.6 ± 2.4	46.2 ± 0.6
40/60	0.16	0.25	2.7 ± 0.3	68.9 ± 2.1	30.1 ± 2.2

composite because of the higher modulus and strength of glass fibers. The 100% flax-reinforced composites display a flexural strength and modulus of 61.0 ± 3.4 MPa and 3.8 ± 0.2 GPa, respectively. The 100% glass fiber-reinforced composites have a flexural strength and modulus of 205.5 ± 4.5 MPa and 9.0 ± 0.2 GPa, respectively. Additionally, there is an obvious anisotropy in the behavior of the asymmetric composites depending on the surface that bears the load. The maximum flexural strengths were shown when the flax surface was the surface bearing the exerted load or impact. In such an orientation, the glass fibers bear a tensile load from the bending of the sample.

The impact energy of the hybrid composites ranged from 13.3 ± 0.3 to 28.7 ± 1.2 J. The maximum impact energy absorbed (28.7 ± 1.2 J) was shown by the asymmetric 40:60 glass/flax ratio composite when the flax surface was the load-bearing face. The energy absorption by the symmetric hybrid composites seems to be only marginally higher than that of the 100% glass fiber composite, a difference made even more in-

significant when considering the standard deviations.

CONCLUSIONS

Triglyceride oils are an abundant natural resource that has yet to be fully exploited as a source for polymers and composites. The different chemical functionalities allow the triglyceride to be converted to several promising monomers. These monomers, when blended with comonomers, form polymers with a wide range of physical properties. They exhibit moduli in the 1–2 GPa range and T_G ranging from 70 to 120 °C, depending on the particular monomer and the resin composition. DMA shows that the transition from the glassy to rubbery behavior is extremely broad for these polymers as a result of the triglyceride molecules acting both as cross-linkers as well as plasticizers in the system. Saturated fatty acid chains are unable to attach to the polymer network, causing relaxations to occur in the network. However, this transition can be sharpened

Table VII   Flexural Properties and Energy Absorption on Impact of Glass/Flax Hybrid Composites

Glass/Flax Ratio	Weight Fractions		Composite Construction	Loading/Impact Face	Flexural Modulus (GPa)	Flexural Strength (MPa)	Energy Absorbed (J)
	Glass	Flax					
100/0	0.35	0	—	—	9.0 ± 0.2	205.5 ± 4.5	16.5 ± 0.2
80/20	0.25	0.06	Symmetric	—	6.9 ± 0.2	130.3 ± 3.0	17.7 ± 1.9
	0.25	0.06	Asymmetric	Glass	6.3 ± 0.3	87.8 ± 3.9	13.3 ± 0.3
			Asymmetric	Flax	5.0 ± 0.1	189.0 ± 8.5	25.8 ± 1.1
60/40	0.23	0.16	Symmetric	—	6.0 ± 0.2	115.3 ± 2.5	18.0 ± 0.3
	0.24	0.16	Asymmetric	Glass	4.0 ± 0.3	80.1 ± 0.7	14.7 ± 0.3
			Asymmetric	Flax	4.7 ± 0.3	146.9 ± 5.5	27.6 ± 2.6
40/60	0.16	0.24	Symmetric	—	5.8 ± 0.5	83.3 ± 5.4	18.5 ± 0.2
	0.16	0.25	Asymmetric	Glass	3.8 ± 0.1	73.2 ± 7.5	15.1 ± 0.3
			Asymmetric	Flax	3.3 ± 0.4	111.1 ± 9.5	28.7 ± 1.2
0/100	0	0.31	—	—	3.8 ± 0.2	61.0 ± 3.4	1.4 ± 0.2

by reducing the saturation content, as demonstrated with the genetically engineered oil and pure triolein oil.

These resins are suitable for use in many molding processes to produce composite materials. At low glass fiber content (35 wt %), composites produced from AESO by resin transfer molding displayed a tensile modulus of 5.2 GPa and flexural modulus of 9 GPa. They also exhibit a tensile strength of 129 MPa and flexural strength of 206 MPa. At higher fiber contents (50 wt %), composites produced from AESO displayed tensile and compression moduli of 24.8 GPa each. The tensile and compressive strengths were 463.2 and 302.6 MPa, respectively. In addition to glass fibers, natural fibers, such as flax and hemp, can be used in the composite materials. Hemp composites of 20% fiber content display a tensile strength of 35 MPa and tensile modulus of 4.4 GPa. The flexural modulus was ~2.6 GPa and flexural strength was in the range 35.7–51.3 MPa, depending on the test conditions. The flax composite materials, also with AESO-based polymer, have tensile and flexural strengths in the ranges 20–30 MPa and 45–65 MPa, respectively. The properties exhibited by both the natural- and synthetic fiber-reinforced composites can be combined through the production of "hybrid" composites. These materials combine the low cost of natural fibers with the high performance of synthetic fibers, resulting in properties spanning a wide range.

This area of research sets a foundation from which completely new materials can be produced with novel properties. Work is being continued to optimize the properties of these materials and understand the fundamental issues that affect them. In this manner, more renewable resources can be utilized to meet the material demands of many industries.

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