

Novel Thermosetting Resins for SMC Applications from Linseed Oil: Synthesis, Characterization, and Properties

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ABSTRACT: New thermosetting resins for applications of sheet-molding compounds (SMCs) were successfully synthesized from linseed oil, which is the most molecularly unsaturated of all plant oils. The carbon-carbon double bonds were opened by epoxidation, followed by acrylation, and then maleinization, which provided more crosslink sites and added acid functionality on the triglyceride molecules to develop thickening. Dynamic mechanical analysis showed that the storage modulus of these new polymers was approximately 2.5 GPa at 30°C, and the glass-transition temperature was above 100°C. During maturation the resins

reached a molding viscosity quickly and stayed stable. Mechanical tests showed a flexural strength of 100 MPa and a flexural modulus of 2.8 GPa. Thermogravimetric analysis showed a single degradation ranging from 300°C–480°C, which was a result of the carbonization of the crosslinked network. These bio-based resins are promising as replacements of some petroleum-based resins in the SMC industry. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2481–2488, 2006

Key words: renewable resources; thermosets; synthesis; mechanical properties

INTRODUCTION

In recent years polymers developed from renewable resources have attracted much attention because of their environmental and economic advantages.^{1,2} Among those polymers obtained from agricultural resources, natural oils have been the main resources.^{2–6} In a previous work, we reported sheet-molding compound (SMC) resins developed from soybean oil, the cheapest and most affordable oil.^{7,8} Unfortunately, the mechanical properties of the resulting polymers were still inferior to those of commercial unsaturated polyesters. As part of a continuing effort, these new SMC resins have been synthesized from linseed oil, which is from flax. Although linseed oil is quite expensive, it is the most highly molecularly unsaturated of all plant oils, which gives it a high potential to synthesize rigid polymers with high stiffness. Linseed oil contains 5 wt % palmitic acid, 3 wt % stearic acid, 20 wt % oleic acid, 15 wt % linoleic acid, and more than 56 wt % linolenic acid, which contains three carbon-carbon double bonds; it has an average of 6.4 double bonds.⁹ Linseed oil is most commonly used in the coating industry because of its dry-oil characteristics.^{10,11} A variety of crosslinked polyesters also have been devel-

oped by UV-curing epoxidized linseed oil alone¹² or with dicarboxylic acid anhydride,^{9,13} but the mechanical properties of these polyesters were well below those of commercially available resins, and these synthetic methods could not meet the requirements for SMC applications. SMC resins require the chemical functionality to undergo thickening reactions with divalent metallic oxides and/or hydroxides as well as to be unsaturated for polymerization during the molding process.¹⁴

Linseed oil is composed mainly of triglyceride molecules, with a typical structure shown in Figure 1. Triglycerides are composed of three fatty acids connected by a glycerol center through ester linkages. The fatty acids range in length from 14 to 22 carbon atoms with 0–3 double bonds per fatty acid.¹⁵ Figure 2 shows the synthetic route of maleinized, acrylated, epoxidized linseed oil (MAELO). Because the carbon-carbon double bonds on triglycerides are not free-radical polymerizable, polymerizable unsaturation was introduced by opening double bonds with epoxidation, followed by acrylation. The residue epoxy groups and the newly formed hydroxyl groups can be further modified by cyclic anhydrides, such as maleic anhydride. This step is crucial because it not only increases the crosslinking sites per triglyceride but also provides sufficient acid functionality, which can coordinate or associate with divalent metal ions to form complexes during the thickening process.³ This causes a more than 1000-fold increase in viscosity. The thickening can reduce the segregation of reinforcement during molding and decrease polymerization shrinkage.¹⁴

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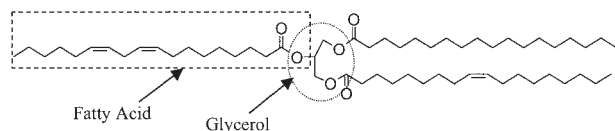


Figure 1 Molecular structure of a typical triglyceride molecule.

When these functionalized triglycerides are blended with comonomers such as styrene, they form rigid polymers by free-radical polymerization. In this article we report the results of our study of the thermomechanical behavior, thickening ability, and mechanical properties of these new SMC resins made from linseed oil.

EXPERIMENTAL

Materials

An epoxidized linseed oil (Vikoflex 7190) from Elf Atochem was used as obtained. It had a molecular weight of approximately 974.2 g/mol and contained approximately 6.2 epoxy groups per triglyceride. Acrylic acid, maleic anhydride, *N,N*-dimethylbenzylamine (DMBA), hydroquinone, and styrene were obtained from Aldrich Chemical Company and used as received. The catalyst AMC-2, supplied by Aerojet Chemicals, was used as received. The initiator, methyl ethyl ketone peroxy (MEKP; Witco Inc.), was used as received.

Monomer synthesis and characterization

The epoxidized linseed oil was reacted with excess acrylic acid to maximize the level of acrylation.¹⁶ An excess of 0.1 mol acrylic acid per mole of epoxy groups was used. In a 125-mL Erlenmeyer flask, 70 g of epoxidized linseed oil, 0.14 g of AMC-2, and 0.23 g of hydroquinone were vigorously stirred at 75°C. Then 35.4 g of acrylic acid was added in five aliquots during the course of the reaction in order to reduce the amount of epoxy homopolymerization. The first aliquot was added when the temperature reached 70°C. On the addition of the acrylic acid, the solution became bright green in color. This was probably because of the interaction of the acid with the chromium-based catalyst (AMC-2). When the acid was consumed, as measured by pH paper, the reaction mixture became brown in color. When this occurred, the next aliquot of acrylic acid was added. An aliquot of acrylic acid was added after 2 h even if the reaction mixture had not turned brown. The overall reaction was maintained for 12 h. The product was analyzed using proton nuclear magnetic resonance (¹H-NMR) to determine the extent of acrylation and epoxy consumption. A

small sample (~1 g) of the product was dissolved in ethyl ether (Fisher Scientific, ACS Certified) and was washed by distilled water three times. An aqueous solution of saturated sodium bicarbonate (Fisher Scientific, ACS Certified) was then added until the pH paper indicated that it was neutral. Next, a saturated sodium chloride (Fisher Scientific, ACS Certified) solution was added to eliminate any water remaining in the organic phase. The mixture was dried over anhydrous sodium sulfate (Fisher Scientific, ACS Certified) to eliminate any residual water. Finally, the sodium sulfate was filtered out, and the excess ether was evaporated in a vacuum oven. Approximately 100 mg of extracted oil were dissolved in 1 mL of deuterated chloroform (99.9% chloroform with 0.1% tetramethylsilane; Cambridge Isotope Laboratories, Inc.). A Bruker AM250 NMR spectrometer was used to collect all spectra.

The acrylated, epoxidized linseed oil (AELO) was further reacted with maleic anhydride to provide more crosslink sites and to add acid functionality. To reduce the cost, AELO was used without further extraction after the acrylation reaction because unreacted acrylic acid can copolymerize with styrene in the final polymerization reaction. Two ratios of AELO to maleic anhydride were examined in order to understand their effects on the polymer properties. These ratios corresponded to 1:2 (MAELO2) and 1:3 (MAELO3) AELO: maleic anhydride molar ratios, which corresponded to 100:16.34 and 100:24.52 AELO: maleic anhydride weight ratios. A higher ratio of ma-

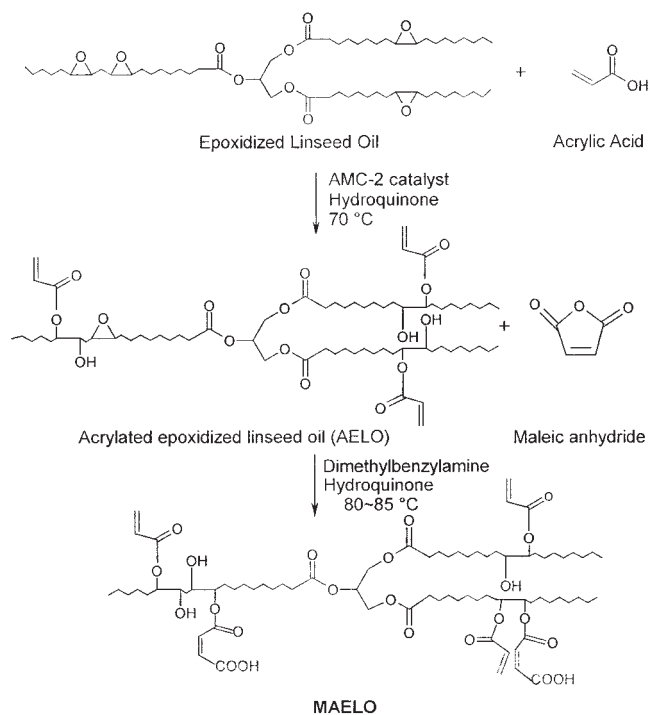


Figure 2 Synthesis of linseed oil-based SMC monomers.

leic anhydride was not used because gelation can easily occur. To synthesize the different maleic anhydride-modified AELO monomers, the AELO (200.0 g) and 0.01 wt % hydroquinone was heated to 60°C at a rate of approximately 1°C–2°C/min while being stirred. The necessary amount of maleic anhydride was ground up finely and added to the reaction at 60°C. The reaction was then heated to 80°C–85°C. Once the maleic anhydride was dissolved and a homogeneous solution was formed, 2.0 wt % DMBA was added. The reaction was kept for 1.5 h.

Viscosity measurement and thickening behavior

The mixture of MAELO and styrene was thickened with magnesium oxide paste (PLASTIGEL® liquid thickener PG-9033; Plasticolors, Inc.), which is a dispersion of 38 wt % magnesium oxide in an unsaturated, nonmonomer-containing polyester vehicle. In a 600-mL beaker, 100 g of MAELO was well mixed with 50 g of styrene and 5.92 g of MgO paste (MgO was 1.5 wt % of the total weight of MAELO and styrene); the mixture was well sealed and kept at room temperature. To inhibit polymerization, 1.0 wt % hydroquinone based on the total weight of MAELO and styrene also was added. The viscosity change during maturation was monitored using a Brookfield DV-I+ viscometer. When the viscosity of the resin was low, a HB1 spindle was used; when viscosity was high, T-bar spindles (TA91-96) were used. All measurements were done at room temperature.

Polymer synthesis and characterization

Resins were prepared by blending functionalized linseed oil monomers with styrene and a free-radical initiator. The AELO or MAELO was mixed with styrene in a ratio of 100 g of linseed oil-based monomer to 50 g of styrene. The free-radical initiator, MEKP, was then added in an amount of 1.5 wt % of the total resin weight. Polymer samples were prepared by casting the resin into a vertical gasket mold, curing it at 90°C for 2 h, and postcuring it at 150°C for 2 h. To prevent oxygen free-radical inhibition, the resin was purged with nitrogen gas prior to curing. Samples for dynamic mechanical analysis were prepared to dimensions of approximately 48 × 10 × 2.5 mm. Dynamic mechanical analysis was conducted in a three-point bending geometry on a Rheometrics Solids Analyzer II (Rheometric Scientific Inc.). Temperature ramps were run from approximately 25°C to 180°C at a ramp rate of 5°C/min with a frequency of 1 Hz and a strain of 0.01%. Samples for the flexural test were prepared to dimensions of approximately 63.5 × 12.7 × 3.2 mm. Flexural strength and modulus were measured according to ASTM D 790-95a with a crosshead

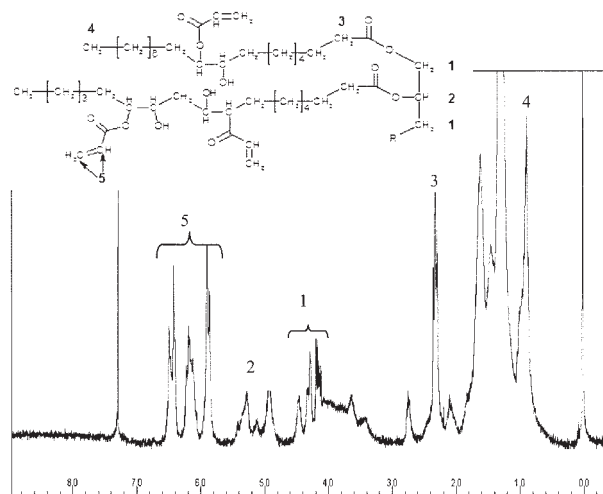


Figure 3 $^1\text{H-NMR}$ spectrum of acrylated epoxidized linseed oil.

speed of 1.27 mm/min. For accuracy, at least five specimens were measured.

The thick plates for the fracture test were cured in a slow curing cycle (80°C for 2 h, 90°C for 4 h, and postcuring at 150°C for 2 h) to inhibit cracking. The plates were then machined into samples that were 55.88 × 12.7 × 6.35 mm. Central V-shape notches were machined in the bars using a diamond cutter. Then a sharp razor blade was slid in one motion across the machined notch. The total depth of the notch obtained by machining and generation of the razor blade was the crack length (a), which was chosen so that $0.45 < a/W < 0.55$, where W is sample width. The samples were tested at a crosshead speed of 1.27 mm/min. The critical-stress-intensity factor, K_{1C} , and critical strain energy release rate, G_{1C} , were calculated according to ASTM D 5045-99.

A TA Instruments thermogravimetric analyzer, Q500, was used to measure the weight loss of the cured sample under a helium atmosphere. Approximately 4.0 g of sample was heated from room temperature to 600°C at a heating rate of 20°C/min. Helium was fed to the combustion chamber at a rate of 50 mL/min.

RESULTS AND DISCUSSION

Monomer synthesis

La Scala et al. showed that using a 0.1 molar excess of acrylic acid could maximize the acrylation level of epoxidized triglycerides to a level of acrylation of more than 90%.¹⁶ Figure 3 shows the $^1\text{H-NMR}$ spectrum of acrylated epoxidized linseed oil. The peaks from 5.8 to 6.7 ppm (peak 5) represent the three protons attached to the carbon-carbon double bond of acrylate esters. Fatty acid protons, α to the carbonyl,

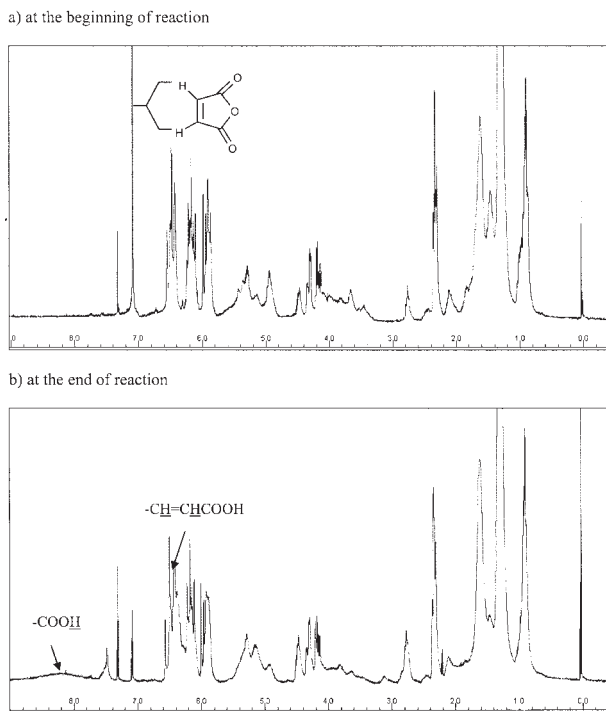


Figure 4 $^1\text{H-NMR}$ spectrum of maleinization reaction.

were used as internal standards as they remained unchanged during the course of the modification of the triglycerides. These protons are indicated by a triplet peak in the range of 2.2–2.4 ppm (peak 3). Acrylate groups were calculated to be 5.7–5.8 per triglyceride. The reaction was completed because there was no epoxy peak left, which would have appeared from 2.8 to 3.2 ppm. Because epoxidized linseed oil has an average of 6.2 epoxy groups, there were 0.4–0.5 epoxy groups lost in homopolymerization. Assuming that for every acrylate group attached to a triglyceride, a hydroxyl group appears, there were 5.7–5.8 hydroxyl groups per triglyceride. These secondary hydroxyl groups can be esterified at 75°C–120°C.¹⁷ To eliminate the possible condensation and side reaction, the reaction temperature was kept at 80°C–85°C. Figure 4 shows the $^1\text{H-NMR}$ spectrum of the reactant mixture at the beginning and end of maleinization. It shows the consumption of the sharp anhydride vinyl protons occurred at 7.1 ppm. The appearance of maleate ester vinyl protons at 6.35 ppm and COOH protons at 8–9 ppm is other evidence of the reaction. Figure 5 shows the effect of reaction time on the extent of the maleinization reaction. The HO–MA reaction was quick. Most maleates were added to the triglyceride molecules in the first 30 min; after that, the number of maleates slowly increased until 90 min had elapsed. This reaction built viscosity so fast because of the possible condensation reaction such that it could not be forced to completion by holding it for a longer time. For both molar ratios, there was approximately 0.25

free maleic anhydride/triglyceride left. When this resulting pre-polymer copolymerized with 33.3 wt % styrene, it formed a transparent rigid polymer by free-radical polymerization.

Viscosity changes during thickening

It is a common process in the SMC industry to thicken the resins for easy handling and good fiber carrying capability, and this process differentiates the SMC resins from general liquid molding resins. The most common method for thickening SMC involves an *in situ* reaction with alkaline earth oxides or hydroxides or diisocyanate compounds.^{14,18–20} The thickening process based on diisocyanate is fast, and the viscosity of the resulting compound is very stable, but the viscosity does not decrease upon heating because of strong covalent bonds. In this work, MgO paste was used as a thickener because of its low cost and high efficiency. A mechanism of thickening unsaturated polyesters using MgO is shown in Figure 6.¹⁴ First, a basic salt formed by the reaction of MgO with a carboxylic group; it continues to react with another carboxylic acid group to form a neutral salt (Scheme A{SCHEME A}). The chain extension resulted in increased molecular weight and consequently in higher viscosity. At the same time, the magnesium ion was able to interact with a carbonyl oxygen to form a 3-D coordinate that dramatically increased the viscosity (Scheme B{SCHEME B}). Figure 7 shows the viscosity increase during thickening at room temperature for MAELO2 resin system with a 1.5 wt % thickener. The initial viscosity was 2160 cP, which is in the desirable region for SMC applications. The viscosity then in-

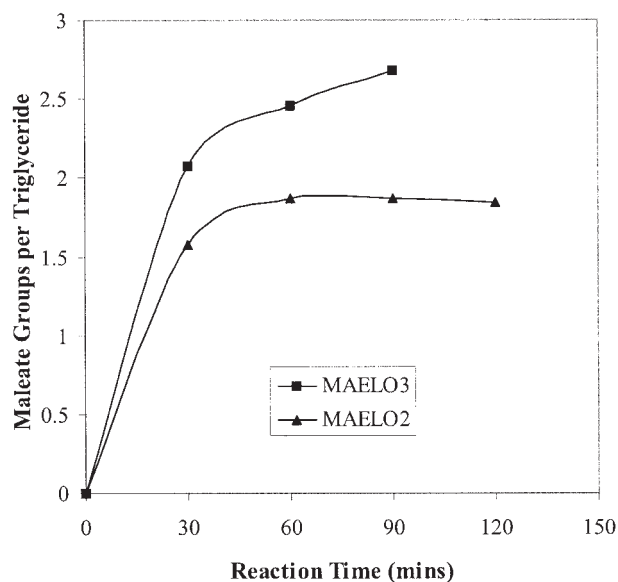


Figure 5 Addition of maleate to the triglyceride molecules versus reaction time.

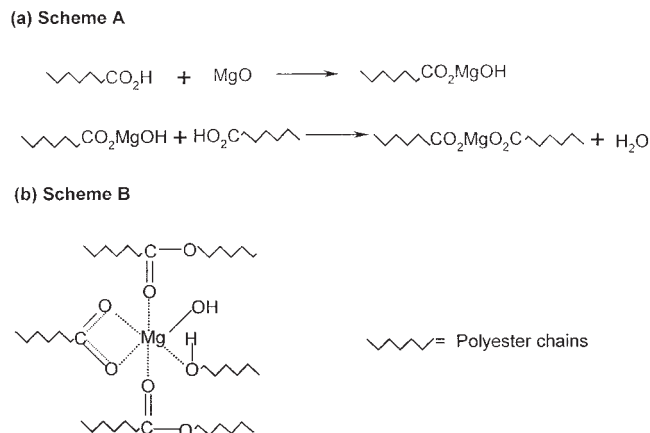


Figure 6 Thickening mechanism of unsaturated polyesters.

creased dramatically upon thickening and reached 10^7 cP after approximately 6 h. After that, the viscosity increased slowly. Compared to the thickening behavior of commercial unsaturated polyesters, this process was much faster. A possible reason for this is that in the distribution of carboxylic acid groups on fatty acid backbones, some triglyceride molecules may have di- or tricarboxylic functional groups; thus, the system can form a crosslinked network much easier, which dramatically increases viscosity. This faster process can minimize the amount of compound inventory that must be maintained; however, the fast-building viscosity may not allow a good fiber wet-out.

Dynamic mechanical properties

Figure 8 shows the dynamic mechanical behavior of the MAELO2 system. It had a storage modulus of 2.34 GPa at 30°C, and the $\tan \delta$ peak appeared at 120.55°C. It is well known that the $\tan \delta$ peak at a frequency of 1 Hz generally occurs at a temperature of 15°C–20°C above the glass-transition temperature, as measured

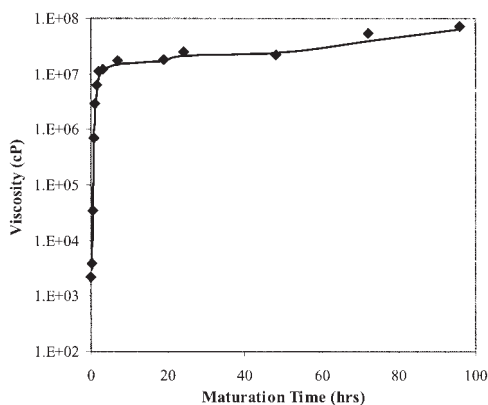


Figure 7 Fast viscosity increase of the MAELO2/styrene/1.5 wt % MgO system during thickening.

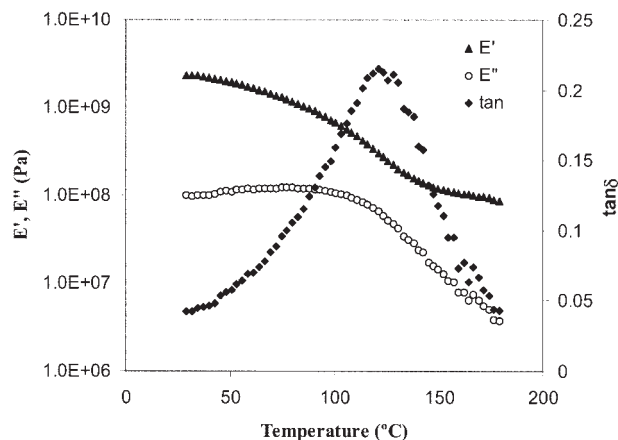


Figure 8 Dynamic mechanical behavior of MAELO2 system as a function of temperature.

by dilatometry or differential thermal analysis. Thus, the glass-transition temperature for MAELO2 was above 100°C, very similar to that of other commercially available resins. In general, it showed a broad transition from the glassy to the rubbery state, which is mainly because of the plasticizing characteristics of triglycerides and the chemical heterogeneity, in which there were differences in the overall chemical composition from different molecular structures in the system. Here there was MAELO, which has long fatty acid chains, free maleic anhydride, and aromatic styrene.

Figure 9 shows the temperature dependence of the storage modulus, E' , with various amounts of maleic anhydride. Acrylated epoxidized linseed oil can form rigid polymer when polymerized with comonomers such as styrene, which can be used for the general

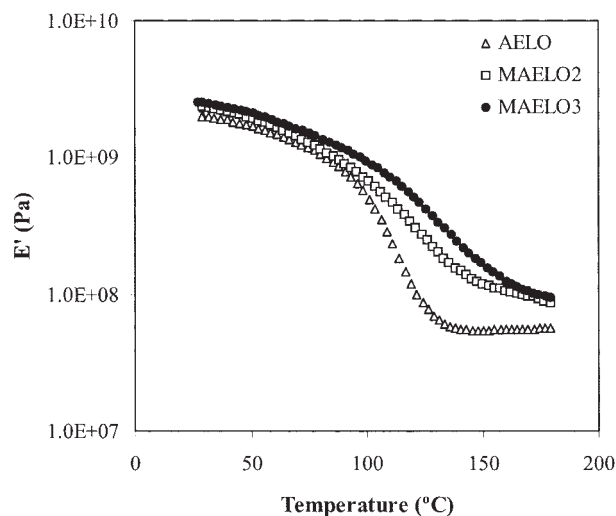


Figure 9 Temperature dependence of the storage modulus for polymers from linseed oil at various amounts of maleic anhydride.

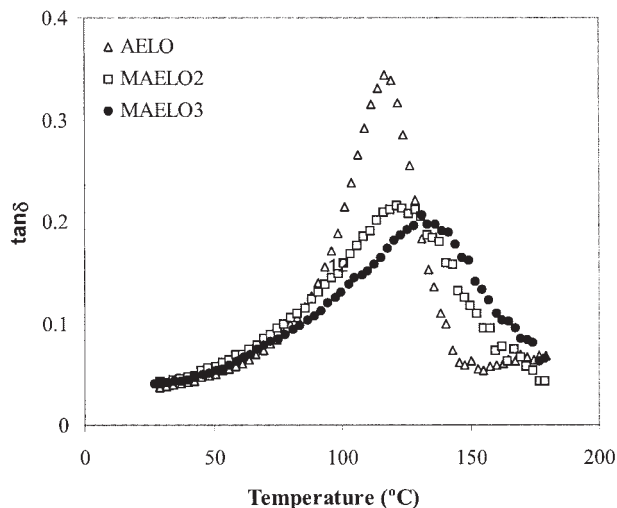


Figure 10 Temperature dependence of the loss factor, $\tan \delta$, for polymers from linseed oil at various amounts of maleic anhydride.

liquid molding processes, but it cannot meet the requirements for SMC applications. Further modification with maleic anhydride not only adds sufficient acid functionality onto the triglyceride molecules but also adds more polymerizable unsaturation. As shown in Figure 9, with maleic anhydride modification, the storage modulus increased with an increasing molar ratio of MA to triglycerides, which is a result of the increased molecular weight and crosslink density. With the higher ratio of MA to AELO (3:1), the MAELO3 had a storage modulus of 2.51 GPa. The transition from the glassy to the rubbery state was broadened by MA modification, which resulted from increased crosslinking density and the heterogeneity of the molecular structure in the system resulting from the copolymerization. Figure 10 shows the temperature dependence of the loss factor, $\tan \delta$, also known as damping, which is a very sensitive indicator of crosslinking. As expected, the $\tan \delta$ peak shifted to higher temperatures and the intensity of the $\tan \delta$ decreased with increasing amounts of MA. This is understandable because an increase in crosslink density greatly restricts the motion of the triglyceride molecule, and the amount of energy that could be dissipated in the system is greatly decreased.

Using the kinetic theory of rubber elasticity, the crosslinking density (ν_e) of a crosslinked polymer can be determined by the following equation²¹:

$$E' = 3\nu_e RT$$

where E' is the storage modulus of the crosslinked polymer in the rubbery plateau region above T_g (ca. $T_g + 40^\circ\text{C}$), R is the gas constant, and T is the absolute temperature (K). The crosslink densities of these new

resins were calculated to be 5.05×10^3 , 7.69×10^3 , and $8.45 \times 10^3 \text{ mol/m}^3$ for AELO, MAELO2, and MAELO3, corresponding to crosslink molecular weights, M_c , of 217.8, 143.0, and 130.1 g/mol, respectively. It was noticed that with more maleic anhydride modification, the increase in crosslinking density was not very significant. This was possibly because of the side reactions during the maleinization reaction, which caused loss of maleate double bonds by the addition of hydroxy groups to the double bonds.²² It is also possible that the crosslinking became less efficient with further increases in the functionality level on the triglyceride backbones because of intramolecular polymerization.²³

Mechanical properties and thermostability

Figure 11 shows the mechanical behavior of the AELO and MAELO systems obtained by the flexural test. The deformation of these polymers at room temperature under an applied load was typical of brittle plastics in terms of stress and strain. Table I summarizes the flexural properties of these polymers and compares them to the polymers derived from soybean oil and commercial unsaturated polyesters. Soybean oil averages 4.6 carbon-carbon double bonds. Originally much more unsaturated, these new linseed-oil-based polymers showed a flexural strength of approximately 100 MPa and a modulus of 2.8 GPa, which were much higher than those of the polymers derived from soybean oil. Their properties are very comparable to those of commercial resins such as ortho-unsaturated polyester and iso-unsaturated polyester that are commonly used in the SMC industry.

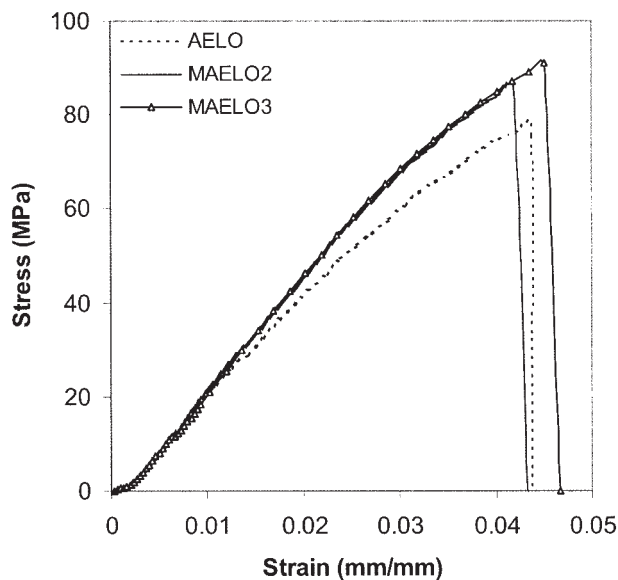


Figure 11 Flexural stress-strain curves for polymers prepared from linseed oil.

TABLE I
Flexural Properties of MAELO Resins Compared to Those of Commercial Unsaturated Polyesters

Resins	Flexural strength (MPa)	Flexural modulus (GPa)	Strain (mm/mm)
AELO	78.73 ± 1.84	2.31 ± 0.05	0.045
MAELO2	95.6 ± 3.13	2.78 ± 0.08	0.044
MAELO3	99.87 ± 2.50	2.79 ± 0.03	0.049
MAESO2 ^a	77.06 ± 1.50	2.03 ± 0.08	0.069
Ortho-UPE	80	3.45	
Iso-UPE	130	3.59	

^a Polymer made from soybean oil using the same synthetic route as MAELO2.²⁷

Figure 12 shows the load-displacement behavior of MAELO2 polymers from the fracture test. The failure type is completely clear. Again, this polymer showed a brittle characteristic. K_{1C} and G_{1C} were calculated to be 0.3135 MPa · m^{1/2} and 107 J/m², respectively. Compared to most commercial polymers, the toughness of these new polymers was low. It is well known that epoxidized plant oil can be used in epoxy polymers as a toughening agent because the latter have flexible fatty acid chains.²⁴ In this work, an effort was made to produce polymers with high stiffness. Thus, more reactive functional groups were introduced to the backbone of the fatty acids, and the crosslink density increased. The effect of high crosslink density is twofold: it greatly increases the mechanical properties of the resulting polymer, but it also restricts the mobility of the fatty acid backbone of the triglyceride molecules, which causes a decrease in toughness of the polymers. This behavior is very similar to other crosslinked polymer networks, such as epoxy²⁵ and vinyl ester/styrene networks.²⁶ With increasing crosslink density, the network structure will be more rigid, which limits the development of a local plastic zone at the crack tip, thus reducing the degree of energy dissipation.

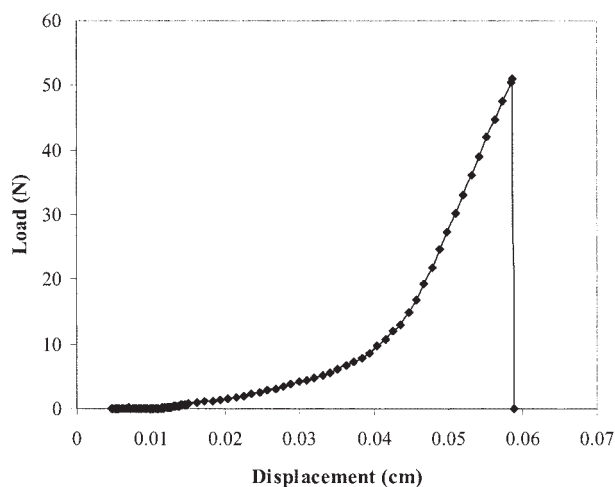


Figure 12 Load-displacement curve for MAELO2 polymer from the fracture test.

The thermogravimetric curves (Fig. 13) show that there was only a single degradation process for the MAELO2 polymer. The degradation occurred in the temperature region of 300°C–480°C, with the maximum rate of decomposition reached at 412.3°C. The degradation is a result of the decomposition of the crosslinked polymer network and random scission of the linear chains.

CONCLUSIONS

New bio-based resins for use in SMC applications were synthesized from linseed oil. The triglyceride molecules were first epoxidized, followed by the acrylation and maleinization reaction. These functionalized triglycerides were then mixed with 33.3 wt % styrene to form unsaturated polyesterlike resins. When thickened with MgO paste, it showed a very fast viscosity rise during the maturation process and slight increase during the room temperature storage. They formed rigid polymers by free-radical polymerization with the storage moduli ranging from 2.34 to 2.51 GPa at 30°C and a glass-transition temperature above 100°C. The flexural strength and modulus were approximately 100 MPa and 2.8 GPa, respectively. The

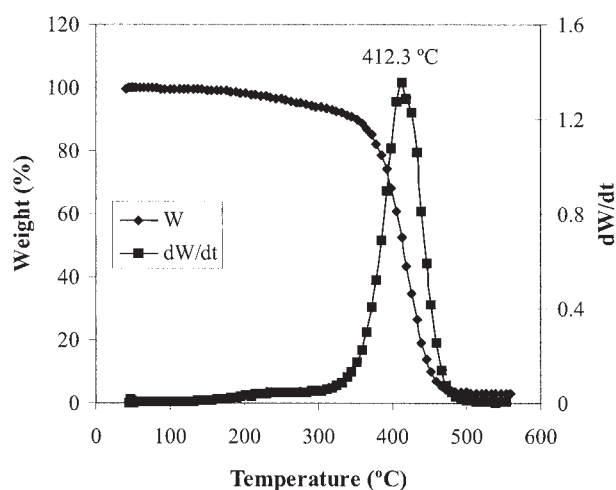


Figure 13 TGA curve for MAELO2 polymer.

toughness of these polymers was low because of the high crosslink density. The thermogravimetric analysis (TGA) curve showed a single degradation in the range of 300°C–480°C, which corresponded to the decomposition of the crosslink structure. These new bio-based resins showed properties very comparable to those of the commercial unsaturated polyesters, and they showed promise as replacement petroleum-based polymers in the SMC industry.

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