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New sheet molding compound resins from soybean oil. I. Synthesis and characterization

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Abstract

Thermosetting resins were synthesized from soybean oil, which are suited to sheet molding compound (SMC) applications. It was achieved by introducing acid functionality and C=C groups onto triglyceride molecules. The acid groups can react with divalent metallic oxides and/or hydroxides to form the sheet, while C=C groups undergo free radical polymerization. An acrylated epoxidized soybean oil (AESO), which has an average of 3.4 acrylates per triglyceride, was used as starting material. The hydroxyl groups on AESO reacted with maleic anhydride (MA) to render acid groups on the molecule. The resulting monomer was then copolymerized with 33 wt% styrene to form rigid polymers. Dynamic mechanical analysis showed storage moduli (E') for these polymers ranging from 1.9 to 2.2 GPa at room temperature, and the glass transition temperatures (T_g) in the range of 100–115 °C. Both the E' and T_g were increased by increasing the molar ratio of MA to AESO, and the transition from the glassy to the rubbery state was broadened by increasing the amount of MA. The effect of styrene as a comonomer was also examined, and a final formulation for SMC was optimized. The resulting resins exhibited appropriate viscosity during the SMC thickening process.

Keywords: SMC resins; Renewable resources; Dynamic mechanical analysis

1. Introduction

Sheet molding compound (SMC) is used extensively in the production of composite materials for use in the automotive, trucking, construction, civil infrastructure, aircraft, and military industries. In the USA market alone, the annual rate of consumption is more than 10^8 kg per year [1]. The molding compound consists of a mixture of fibers, fillers, additives, and a liquid molding resin. SMC was originally intended to replace sheet metal stamping in the automotive and related industries. The sheet is prepared such that it has sufficient initial properties at room temperature to be handled in the molding process before flow and cure in the mold. This is accomplished by using a thickening agent in the formulation, such as divalent cations, which complex with acid groups to produce a thickened, non-flowing resin. When heated in the mold, the labile divalent cation complex dissociates and the thickened resin viscosity drops rapidly. This allows flow and welding of the sheets in the mold, followed by free radical curing reactions at the higher temperatures. Manufacturing composite parts using these compounds are pursued because of their ability to mass-produce parts with a wide range of properties and sizes. Additionally, they have the ability to overcome many of the difficulties encountered in composites manufacturing, such as shrinkage and surface defects.

The most common resins used in SMC are the various unsaturated polyester resins, such as polyesters made from propylene glycol and maleic anhydride. These resins are synthesized using raw materials derived from petroleum. Replacing some, or all, of these petroleum-derived raw materials with renewable plant-based raw materials, such as soybean oil, is attractive, both economically and socially, as such raw materials are cheaper and their use contributes to global sustainability by not depleting scarce resources [2].

Soybean oil is one of many readily available renewable resources. Currently, most soybean oil is used for food

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applications. Refined soybean oil is composed of 99% triglycerides. These triglycerides are composed of eight different fatty acids ranging in length from 14 to 22 carbons long, as shown in Fig. 1(a). The average molecular weight of a triglyceride is approximately 871 g/mol with an average functionality of 4.6 carbon–carbon double bonds per triglyceride [3]. In the past, triglycerides and their fatty acid derivatives have been used as additives, such as mold release agents [4,5], coatings [6,7], or agents to improve the properties of various SMC [8]. In recent years, research has been done to develop rigid resins from soybean oil [9–13], but most of these resins were developed for conventional resin transfer molding processes [14]. Recently, Loza and McDaniel added soybean oil as a reactant in the traditional unsaturated polyester synthesis, and the final product showed promise for use in SMC applications. However, the soybean oil content in the final composition was not more than 17 wt% [15]. In this work, we report new SMC resins which contain approximately 50 wt% soybean oil.

For a resin to be suitable for use in SMC technology, it requires the chemical functionality to undergo thickening reactions with divalent metallic oxides and/or hydroxides to form the sheet as well as unsaturation for the free radical polymerization during the molding process [16]. In a previous work [9], we reported many different chemical pathways to synthesize rigid polymers from triglyceride-based monomers, such as acrylated epoxidized soybean oil (AESO). The synthetic route to AESO from soybean oil is shown in Fig. 1. First, the triglyceride molecules are epoxidized by the reaction of double bonds in the fatty acid with a peroxy acid to get epoxidized soybean oil (ESO) [Fig. 1(b)]. To introduce the acrylate functional group, the ESO is reacted with ethylenically substituted carboxylic acids, such as acrylic acid to form AESO [Fig. 1(c)]. Further modification of the AESO with functional groups such as cyclic anhydrides (e.g. maleic anhydride) renders acid groups and adds more unsaturation on the molecules as shown in Fig. 2, route A, the carboxylic acid groups on the half-esters can react with residual epoxy groups or hydroxyl groups on the triglycerides to oligomerize triglycerides (Fig. 2, route B). The resulting monomer is then copolymerized with 33 wt% styrene to form rigid polymers. These new polymers show mechanical properties comparable to commercial unsaturated polyesters and adequate thickening behavior.

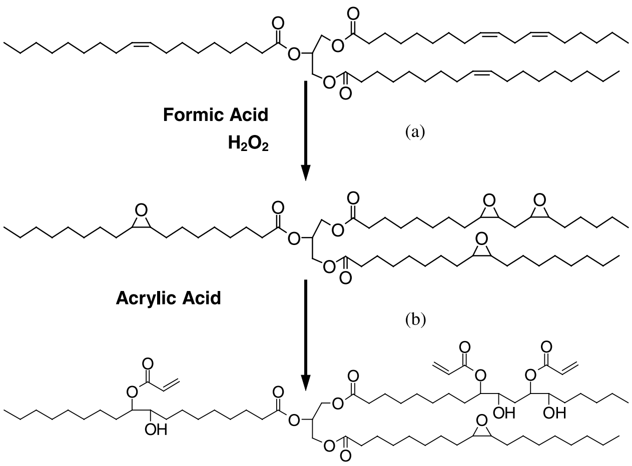

Fig. 1. Synthesis of acrylated epoxidized soybean oil (AESO) from soybean oil: (a) triglyceride molecule, (b) epoxidized soybean oil (ESO), and (c) acrylated epoxidized soybean oil (AESO).

2. Experimental

2.1. Chemicals

Acrylated epoxidized soybean oil was obtained in the form of Ebecryl 860 (UCB Radcure, Inc.). This AESO is acrylated with approximately 3.4 acrylates per triglyceride and an average molecular weight of 1200 g/mol. Maleic anhydride, *N*,*N*-Dimethylbenzylamine (BDMA), hydroquinone, styrene, and HPLC grade tetrahydrofuran (THF) were used as received from the Aldrich Chemical Co. Deuterated chloroform for the ^{1}H NMR analysis was obtained from Cambridge Isotopes Ltd. The initiator used for polymerization was *t*-butyl peroxy benzoate (Luperox$^{®}$ P) from Elf Atochem.

2.2. Synthesis of maleinated acrylated epoxidized soybean oil (MAESO)

Three different molar ratios of MA to AESO were examined as shown in Table 1. To synthesize the different maleic anhydride modified AESO monomers (MAESO), 50 g of AESO and 0.05 g of hydroquinone were first heated to 70 °C at a rate of approximately 1–2 °C/min, while being stirred. The necessary amount of MA (Table 1) was ground up finely and added at 70 °C. The mixture was then heated up to 80–90 °C, at which point the maleic anhydride dissolved, forming a homogeneous solution. The BDMA catalyst was then added in the amount of 1 g. Both the reaction temperature and reaction time were varied to see their effect on the resin viscosity and final properties.

2.3. MAESO characterization

The MAESO reaction was followed both by FTIR and ^{1}H NMR. The IR analysis was performed on an ATI

Table 1
The components of maleinization reaction

	Molar ratio (AESO:MA)	Weight ratio (AESO:MA)	Maleates added per TG
MAESO1	1:1	100:8.17	1
MAESO2	1:2	100:16.34	1.8
MAESO3	1:3	100:24.52	2.5

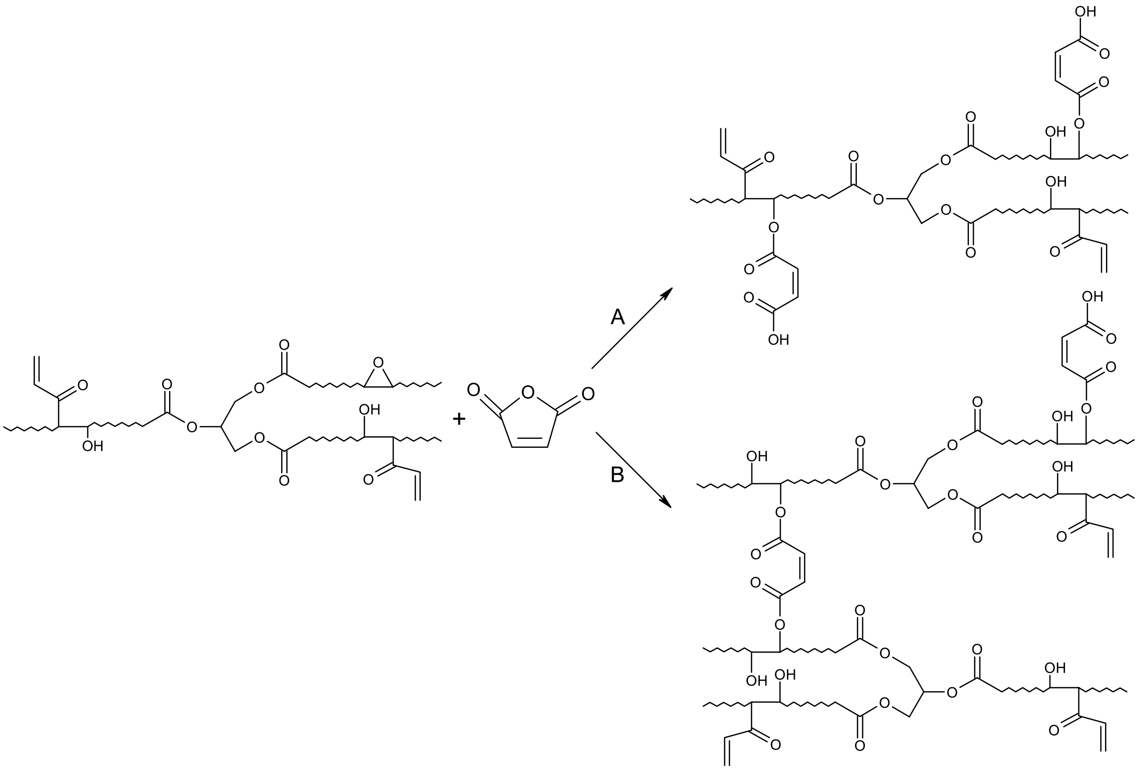

Fig. 2. Synthesis of maleinated acrylated epoxidized soybean oil (MAESO): (a) maleinization reaction and (b) oligomerization reaction.

Mattson FTIR spectrometer using KBr cells. ^1H NMR spectra were obtained on a Bruker AM250 NMR spectrometer. Approximately 100 mg of sample was dissolved in 1 ml of deuterated chloroform. To characterize the growth of high molecular species within the reaction, size exclusion chromatography (SEC) was used in conjunction with laser light scattering. A Perkin Elmer Series 200 SEC was used with two styrene–divinyl benzene columns in series. The first column's packing had a bead size of 5 μm, while the second column's packing had a mixed size ranging from 5 to 50 μm. The columns were run at 45 °C and samples were eluted with THF at a flow rate of 1 ml/min. The column effluent was monitored by an Optilab refractive index detector at 25 °C and a Minidawn low angle laser light scattering detector, both manufactured by Wyatt Technology. The refractive index increment (d*n*/d*c*) was used to determine the concentration of the species coming off the column. The value of d*n*/d*c* for MAESO was determined experimentally to be 0.1142 ± 0.0044 ml/g [17]. For the MAESO molecular weight determination, samples of concentration 4.0 mg/ml were prepared in HPLC grade THF. The scattering intensity and refractive index of each sample were used to calculate the number and weight average molecular weight using ASTRA® software (Wyatt Technology Corporation).

2.4. Polymer synthesis and characterization

Resins were prepared by blending soybean oil monomers (AESO and MAESO) with styrene and a free radical initiator. The soybean oil monomers were mixed with styrene in the ratio of 100 g monomer to 50 g styrene, corresponding to a 1:7 molar ratio. The free radical initiator, *t*-butyl peroxy benzoate (TBP), was then added in the amount of 1.5–2.0 wt% of the total resin weight. A Brookfield viscometer was used to measure the viscosity of the final resins at room temperature. Polymer samples were prepared by curing the resin in a vertical gasket mold. The vertical molds consisted of a silicon rubber mold (Dow Corning) sandwiched between two aluminum plates using binder clamps. The aluminum plates were 13.5 cm wide, 10.2 cm long, and 0.23 cm thick. The silicon rubber mold was 0.12 cm thick and the space for the liquid resin was 7 cm wide and 5 cm long. To prevent oxygen free radical inhibition, the resin was purged with nitrogen gas prior to transferring into the mold. The resin was cured at 110 °C for 2 h and post-cured at 150 °C for 2 h. Samples for dynamic mechanical analysis (DMA) were prepared to dimensions of $48 \times 10 \times 2.5$ mm. DMA was conducted in a three-point bending geometry on a Rheometrics Solids Analyzer II (Rheometric Scientific, Inc.). Temperature scans were run from approximately 25 to 180 °C at a heating rate of 5 °C/min with a frequency of 1 Hz and strain of 0.01%. The density of polymers was measured using a pycnometer. For the styrene comonomer study, MAESO2 was mixed with the desired amount of styrene. The initiator TBP was added in the amount of 2 wt% of the total weight of MAESO2 and styrene. It was then cured following the same procedure described above.

For the tensile test, resins were cured in the dog-bone mold at 90 °C for 2 h, 100 °C for 4 h, and post-cured at 150 °C for 1.5 h. The slower cure cycle for the tensile samples was necessary to produce samples without cracking. Samples were machined down to a thickness of approximately 3.2 mm. The samples were then conditioned at 50 °C for 24 h to remove any residual water. Tensile properties were measured using ASTM method D638. The tests were conducted at a constant cross-head speed of 1.27 mm/min on an Instron 4502 and at least five samples were tested.

2.5. Viscosity measurement and thickening behavior

MAESO2 and styrene were thickened with magnesium oxide paste (PLASTIGEL® liquid thickener PG-9033, Plasticolors, Inc.), which is a dispersion of 38 wt% reactive magnesium oxide (MgO) in an unsaturated, non-monomer containing polyester vehicle. In a 600 ml beaker, 100 g MAESO2 was mixed with 50 g styrene and 5.92 g MgO paste; the mixture was sealed and kept at room temperature. To inhibit the polymerization, 1 wt% of hydroquinone, based on the total weight of MAESO2 and styrene, was added. The viscosity change during the maturation was monitored using a Brookfield DV-I+ viscometer. When the viscosity of the resin was low, a HB1 spindle was used, and T-bar spindles (TA91-96) were used for the high viscosity. All measurements were done at room temperature using equipment manufactured by Brookfield Engineering Laboratories, Inc.

3. Results and discussion

3.1. Resin synthesis

Quantitative analysis of the starting material AESO was done using ^{1}H NMR as shown in Fig. 3. The fatty acid protons α to the carbonyl (a triplet peak in the 2.2–2.4 ppm range, peak 3) and methyl protons (0.9 ppm, peak 4) were used as internal standards as they remain unchanged during the course of the modification of triglycerides. The peaks from 5.8 to 6.7 ppm (peak 5) represent the three protons attached to the carbon–carbon double bond of the acrylate esters. According to the NMR spectrum, there are approximately 3.4 acrylates per triglyceride. Assuming for every acrylate group that is attached to a triglyceride via the epoxy group, a hydroxyl group appears as shown in Fig. 1, there should be 3.4 hydroxyl groups per triglyceride. These hydroxyl groups can also be esterified like a typical secondary alcohol at 75–120 °C [18]. The AESO has a negligible amount of epoxy left after acrylation, which would appear in the range of 2.8–3.26 ppm. Maleic anhydride reacts with the newly formed hydroxyl groups and residual epoxies on the triglycerides to form the half-ester (route A, Fig. 2). The reaction temperature was chosen to be less than 100 °C to inhibit possible condensation reactions (route B, Fig. 2) and other side reactions. During the reaction, FTIR was used to monitor the consumption of both the hydroxyl group and maleic anhydride. Fig. 4 shows the secondary hydroxyl group peak at 3384 cm^{-1}, being consumed, along with the 1779 and 1849 cm^{-1} peaks of the cyclic anhydride. NMR spectroscopy (Fig. 5) shows the consumption of the sharp anhydride vinyl protons at 7.1 ppm (peak 2) and the appearance of maleate ester vinyl protons at 6.35 ppm (peak 1). Since the reaction temperature is low, there are no fumarate ester vinyl protons forming, which would appear at 6.90 ppm. The appearance of COOH protons at 10 ppm (a broad peak 3) is additional evidence for the formation of maleate half-esters. Since both maleate half-ester and hydroxyl protons overlap with other protons, it is very difficult to correctly quantify the conversion. The total number of the maleate group N_{maleate} per triglyceride is estimated by measuring the total area of the maleate and acrylate peaks:

$$N_{\mathrm{maleate}} = \frac{1}{2}\left(\frac{A_{5.8\text{–}6.7\ \mathrm{ppm}}}{A_{\mathrm{proton}}} - 10.2\right) \qquad (1)$$

where 10.2 is subtracted to account for the total number of the protons attached to the carbon–carbon double bond of acrylate esters, and the factor of 1/2 accounts for the fact that each maleate group has two olefinic protons. A_{proton} is the area per proton per molecule, which is calculated by dividing the internal standard peak area by the number of protons per molecule that cause the resulting peak. Table 1 shows the amount of maleates added per triglyceride. The resulting AESO maleate (MAESO) is a very viscous liquid with a light yellow color.

3.2. Viscosity increase and molecular weight growth

During the synthesis of the MAESO monomer, there is an observable increase in viscosity as the reaction progresses. Fig. 6 shows the change of viscosity for MAESO+50 wt% of styrene vs. reaction time at two reaction temperatures, 80 and 90 °C. At both temperatures, the viscosity increases approximately linearly with the reaction time, and the increase in viscosity is much faster for 90 °C than 80 °C (the viscosity of MAESO3/styrene which reacted at 90 °C is not shown here because the gelation can start anytime). Although the room temperature viscosity of the resin for SMC application can range from 300 to 3000 cP, the lower viscosity is favored because the resin can better wet the fiber surface [1]. The increase in viscosity for these monomers can be related to the increase in molecular

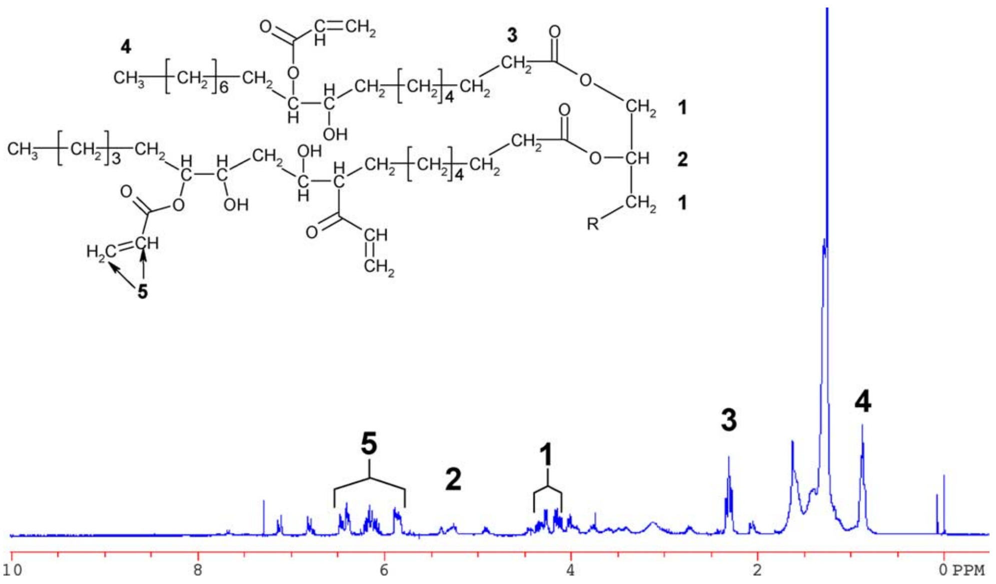

Fig. 3. ^{1}H NMR spectrum ($CDCl_3$) for AESO (Ebecryl 860).

weight and polarity [19]. SEC analysis shows that the viscosity increase mainly results from the molecular weight growth which is due to intramolecular or intermolecular addition of maleate half-esters to residual epoxies as shown in Fig. 2, route B. There are also other side reactions existing, such as the possible addition of hydroxyl groups to maleic anhydride or maleate double bonds, which cause the loss of double bonds and the increase in molecular weight [20,21]. Table 2 shows the average molecular weight of the resulting monomers increases with the reaction time. For example, after 6 h reaction at 90 °C, the average molecular weight for MAESO2 is 9107 g/mol, which means there are approximately 8 triglyceride molecules connected to each other. The viscosity of a polymer solution depends on four factors: temperature, solvent or solute content, polymer molecular weight, and polymer miscibility. For a miscible polymer solution, a power law equation, which expresses the effects of solute content and polymer molecular weight, can be used [22]:

$$\eta_z = KC^b M_w^a \tag{2}$$

where η_z is zero-shear viscosity, M_w is polymer molecular weight, C is polymer concentration, and K, a, b are constants. a is either between 2.5 and 1.0 for M_w below critical molecular weight, M_c, or between 3.3 and 3.6 for M_w above M_c. Since the critical entanglement molecular weight is on the order of 10^4 g/mol for most polymers, therefore a should be around 1.0. The molecular mass has a slightly different influence on the solution viscosity resulting from the different reaction temperatures. The data fitting shows the value of a is equal to 0.92 and 1.37 at 80 and 90 °C reaction temperature, respectively. The stronger effect of M on η at 90 °C reaction temperature can be attributed to the

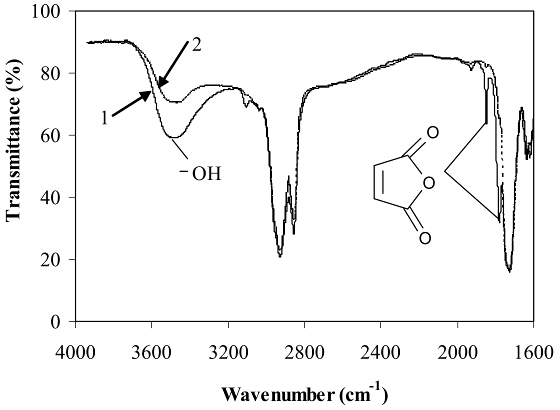

Fig. 4. FTIR shows the consumption of hydroxyl group and free maleic anhydride during maleinization reaction: (1) initial reaction, (2) final reaction.

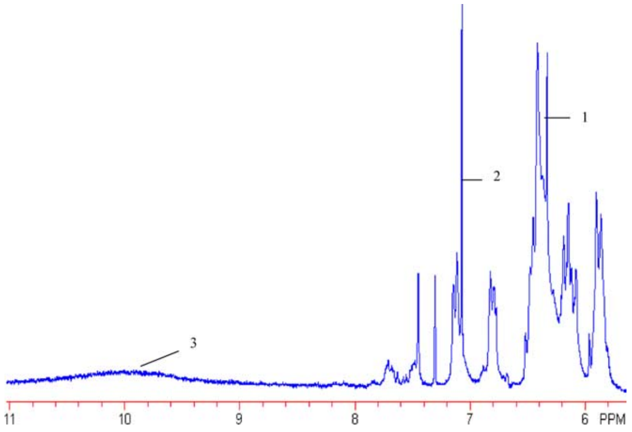

Fig. 5. Final ^{1}H NMR spectrum of maleinization reaction. Peak 1 represents the maleate half-ester, peak 2 represents unreacted maleic anhydride, and peak 3 is very broad which represents COO*H* protons (spectrum is offset for clarity).

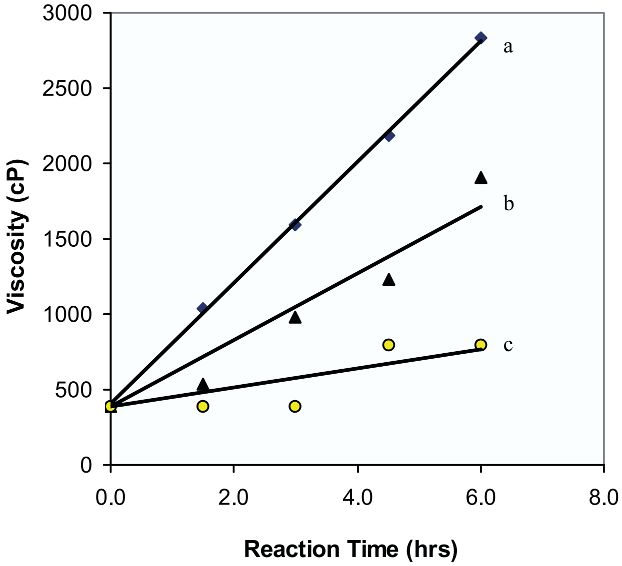

Fig. 6. The dependence of final resin viscosity on the reaction time during maleinization reaction: (a) MAESO2/styrene (reacted at 90 °C), (b) MAESO3/styrene (reacted at 80 °C), and (c) MAESO2/styrene (reacted at 80 °C).

formation of a partially cross-link network during the reaction which is not effectively shown in SEC molecular weight measurement. Therefore, the reaction temperature at 80 °C is preferred. The addition of carboxylic acid groups increases the polarity of the molecule, which can also cause the increase in viscosity. Because of viscosity problem, this reaction cannot be forced to completion by holding it for a longer time. From NMR analysis, approximately 0.2 and 0.5 mol free maleic anhydride per triglyceride for MAESO2 (~3.3 wt%) and MAESO3 (~8.2 wt%), respectively, is left in the system to take part in the final copolymerization.

3.3. Dynamic mechanical analysis

3.3.1. Effect of maleic anhydride

Fig. 7 shows the temperature dependence of the storage modulus E', loss modulus E'', and the loss factor tan δ for AESO polymer. In general, this polymer shows a broad transition from the glassy to the rubbery state due to the plasticizing characteristics of saturated fatty acids in the network and the different molecular structure of AESO compared to the aromatic styrene [17]. The polymer has a storage modulus of approximately 1.1 GPa at room temperature and a tan δ peak at 71 °C. Generally for most thermoset resins, the tan δ peak at a frequency of 1 Hz generally occurs at a temperature of 15 to 20 °C above the glass transition temperature (T_g), as measured by dilatometry or differential thermal analysis [23]. Thus, the T_g for AESO is approximately 56 °C (estimated by $(\tan\delta)_{\max} - 15$ °C), which is very low compared to most commercially available resins. The modification by MA provides more cross-link sites per triglyceride because it adds maleate functionality on the triglyceride and increases the molecular weight, as shown in the SEC measurement (Table 2). Fig. 8 shows the temperature dependence of the storage modulus and the loss factor of the MAESO polymers with various amounts of MA. Clearly, the storage modulus is increased significantly with more maleic anhydride. The transition from the glassy to the rubbery state is broadened by the addition of the maleic anhydride, which attributes to the increased cross-link density and heterogeneity of the molecular structure in the MAESO resins.

Table 2
Molecular weight increase during the maleinization reaction

Reaction time (h)	MAESO2, 80 °C	MAESO3, 80 °C	MAESO2, 90 °C
0	2292	2292	2292
1.5	2675	6720	4023
3.0	3395	6696	7053
4.5	3982	9284	7087
6.0	4455	12,840	9107

The modulus in the rubbery region greatly increases with increasing MA content; this increase is closely related to the cross-link density. Based on the kinetic theory of rubber elasticity, the experimental cross-link density (ν_e) of a polymer can be determined from the rubber moduli by the following equation [23]:

$$E' = 3\nu_e RT \tag{3}$$

where E' is the storage modulus of the cross-linked polymer in the rubbery plateau region above T_g, R is the gas constant and T is absolute temperature (K). The rubber modulus selected for calculating the cross-link density occurred at ~50 °C above the maximum in tan δ, where the modulus started to increase with temperature. As shown in Table 3, the typical value of cross-link density for these new SMC resins is above 3000 mol/m^3, which corresponds to a cross-link molecular weight M_c 367 g/mol.

Fig. 9 shows the temperature dependence of the loss factor (tan δ) for maleated soybean oil compared to acrylated soybean oil. The glass transition temperatures for these new polymers are in the range of 100–115 °C. Apparently, with the modification of MA, the single transition of the curves shifts to high temperatures, and the intensity of tan δ decreases with increasing the molar ratio of MA to AESO, which indicates increased cross-link density and lower toughness. The glass transition temperature of these polymers is very important because the T_g determines an upper bound for the use temperature of the

Table 3
Characteristics of maleinated acrylated epoxidized soybean oil polymers

	ρ (g/m^3)	ν_e (mol/m^3)	M_c
AESO	1.10	2993	367.52
MAESO1	1.1023	3615	304.86
MAESO2	1.1075	5435	203.77
MAESO3	1.1355	6322	179.60

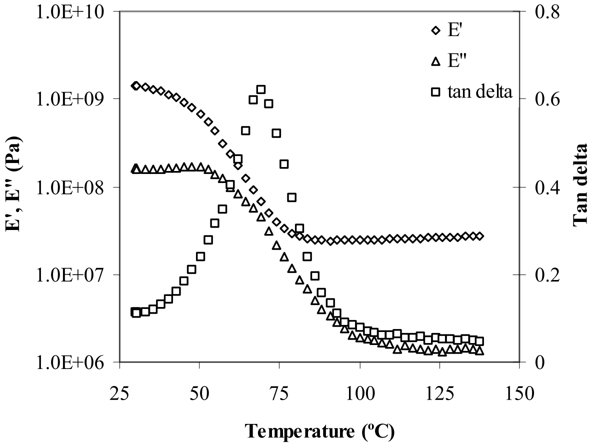

Fig. 7. Temperature dependence of the storage modulus E', loss modulus E'', and tan δ for AESO polymer.

polymers. Several models have been published to correlate the glass transition temperature of thermosetting polymers to the cross-link density [24–28]. As shown in Fig. 10, the glass transition temperatures of these new polymers exhibit a linear fit with the cross-link density, which is following the theory of Fox and Loshaek [25]:

$$T_g = T_{gL} + K_{FL}\nu \quad (4)$$

where T_{gL} is the glass transition temperature for an infinite straight chain polymer, K_{FL} is a universal constant, and ν is the cross-link density. The linear fit of the experimental data gives a value of 9.98 °C and 0.0176 m^3/mol for T_{gL} and K_{FL}, respectively.

3.3.2. *Effect of reaction time*

As we mentioned before, there is an observable viscosity increase during the maleinization reaction (Fig. 6), especially at higher reaction temperature, which results from the increased molecular weight. However, the longer reaction time has very little effect on the dynamical mechanical properties of the final polymers, as shown in Table 4. From Fig. 11, the cross-link density of the materials does show a dependence on the reaction time. The addition of MA to AESO and styrene without further reaction results a cross-link density of 4604 and 4720 mol/m^3 for MAESO2 and MAESO3, respectively. These correspond to the same entanglement molecular weights of 240 g/mol, which is not surprising since before the maleinization reaction, both MAESO2 and MAESO3 have the same cross-link functionalities. The cross-link density increases with reaction time until 90 min, reaching a cross-link density of 5435 and 5944 mol/m^3 for MAESO2 and MAESO3, respectively. After that, the cross-link density increases slightly. This behavior is consistent with the observation from ^{1}H NMR that the level of maleinization increases up to 90 min of reaction, after which the level of maleinization is constant. Although the molecular weight of the monomers continues to increase with further reaction, it has very little effect on the cross-link density and thermal mechanical properties of final materials. Therefore, the optimum maleinization reaction time was determined to be 90–120 min at 80 °C to reduce the viscosity problem for the further processing.

3.3.3. *Effect of comonomer*

The effect of styrene content was examined in this study to find the best formulation for SMC resins. From Fig. 12, with increasing content of styrene, the storage modulus at room temperature increases because of the introduction of the more rigid polystyrene segment. Fig. 13 shows the cross-link density at different styrene content using the storage modulus above T_g (ca. (tan $\delta)_{max}$ + 50 °C). The cross-link density increases with styrene content up to 20 wt% beyond which it decreases with increasing styrene concentration. Theoretically, the cross-link density should decrease linearly as the comonomer mass fraction increases. A possible reason for this contrast is that the maleates do not

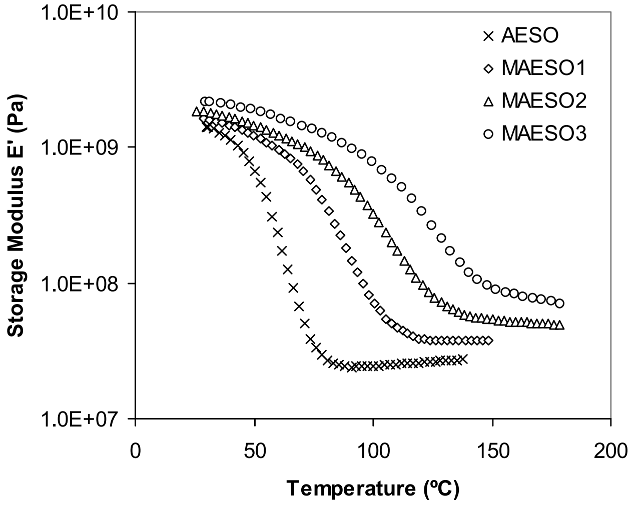

Fig. 8. Temperature dependence of the storage modulus E' for MAESO polymers at different molar ratios of MA to AESO.

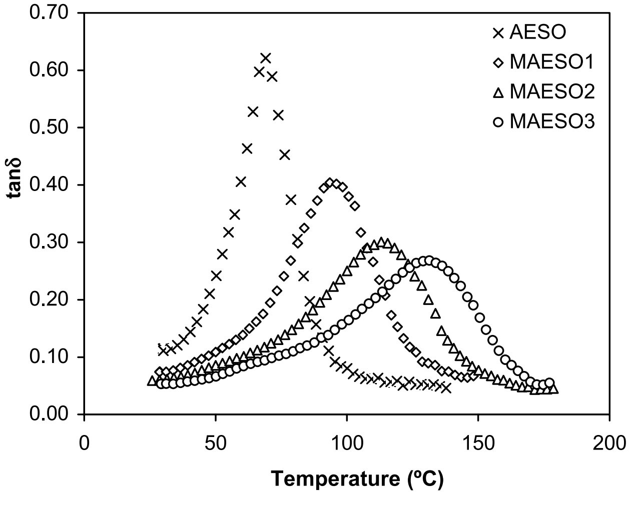

Fig. 9. Temperature dependence of the loss factor tan δ for MAESO polymers at different molar ratios of MA to AESO.

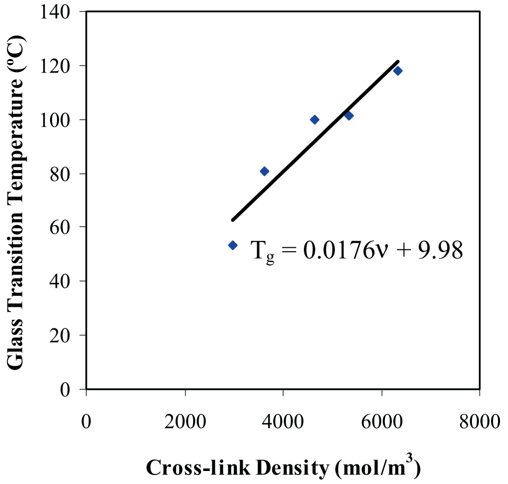

Fig. 10. The glass transition temperature of triglyceride-based polymers follows a linear fit with the cross-link density.

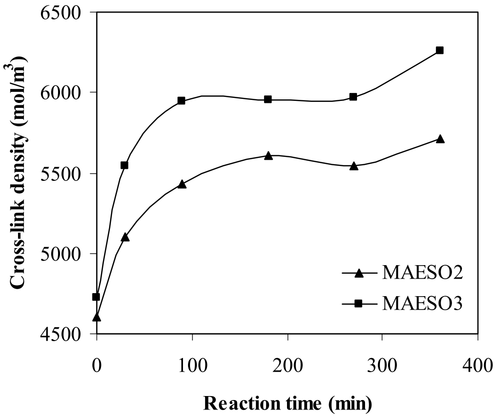

Fig. 11. The effect of reaction time on the cross-link density of MAESO polymers.

easily homopolymerize, but they can copolymerize readily with other comonomers, such as styrene [29]. Thus, the initial increase in styrene concentration increases the extent of curing as more maleates participate in the curing reaction resulting in an increase in cross-link density. However, further increase in styrene concentration increases the length of linear segments between cross-links, reducing the overall cross-link density. Fig. 13 also gives the information that approximately 20 wt% styrene can maximize the reaction extent of the maleate groups. The same behavior can be observed in the tan δ curves shown in Fig. 14. As the styrene concentration increases, the tan δ peak shifts to higher temperatures, but with an initial decrease in the sharpness up to 20 wt% styrene, which is due to the increase in the cross-link density. Beyond 20 wt% styrene, the tan δ peak no longer shifts to higher temperatures as much, but begins to sharpen. This behavior can be attributed to the formation of rigid polystyrene and a drop in the cross-link density. In general, with higher styrene concentration, the storage modulus and glass transition temperature are higher. To maximize the use of the bio-renewable content, and at the same time to optimize properties, the formula to be used for SMC applications is 66.7 wt% triglycerides-based monomer and 33.3 wt% styrene. Table 5 compares the properties of these triglyceride-based resins with those of commercial unsaturated polyesters, which are commonly used in the SMC applications. The viscosity of these new resins is in the reasonable range of viscosity for SMC applications. The thermomechanical properties are very comparable to those of unsaturated polyester. The storage modulus for these new polymers is in the range of 1.9–2.2 GPa, and the glass transition temperatures range from 100 to 115 °C. Table 5 also shows that these new resins display a Young's modulus in the range of 2.2–2.5 GPa and tensile strengths in the range of 41–44 MPa, which are below the unsaturated polyesters. However, the advantage gained is in the amount of renewable material in the resins. These new resins have a final pure soybean oil content of 40–50 wt%.

3.4. Thickening behavior

The essential feature of the SMC resins is to be able to chemically thicken during the maturation process. The viscosity of the SMC increases at least 1000-fold ($>10^6$ cP) which allows for easy handling and better glass fiber carrying capability during molding [1]. The most common method for thickening SMC involves the in situ reaction of carboxylic acid groups with oxides and/or hydroxides of Group IIA metals, such as MgO and $Mg(OH)_2$ [1,30]. The modification of AESO using MA successfully introduces enough acid functionality on the triglyceride molecules to promote thickening. Fig. 15 shows the viscosity change of the resin vs. thickening time for a typical formula. The viscosity increases quickly from 1200 cP to more than 10^6 in 48 h, after that, the viscosity increases slowly. This

Table 4
The storage modulus at room temperature and $(\tan \delta)_{max}$ vs. reaction time at 90 °C reaction temperature

RXN time (min)	MAESO2		MAESO3	
	$(\tan \delta)_{max}$ (°C)	E' (GPa)	$(\tan \delta)_{max}$ (°C)	E' (GPa)
0	112.30	1.9215	121.58	2.118
90	114.33	1.9306	130.48	2.1606
180	113.33	1.8958	131.21	2.1533
270	112.86	1.9119	129.90	2.1213
360	112.99	1.8847	129.86	2.1333

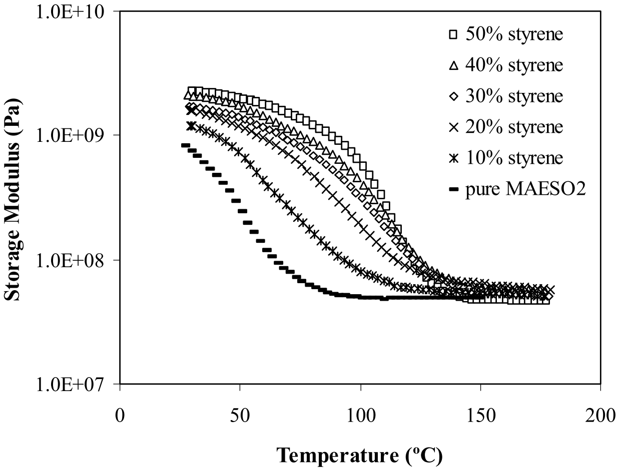

Fig. 12. Temperature dependence of the storage modulus E' behavior for MAESO2 polymers with various styrene concentrations.

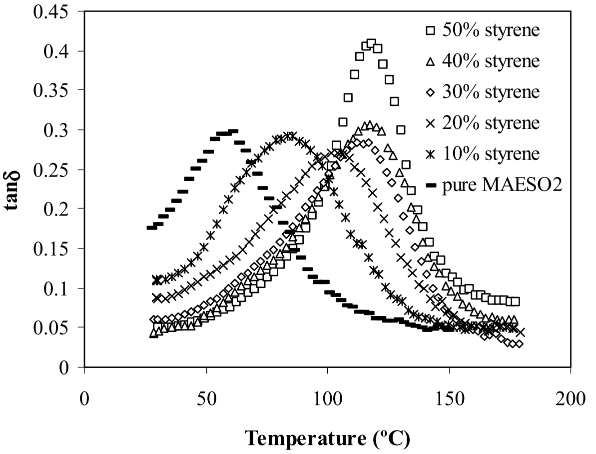

Fig. 14. Temperature dependence of the loss factor tan δ behavior for MAESO2 polymers at various styrene concentrations.

thickening behavior is very similar to that of unsaturated polyesters, but the viscosity increase is faster. Many factors, such as acid number, water content in the resin, and thickener concentration, affect the thickening behavior. However, adding the thickener can affect the curing of the resin. The detailed study for thickening and other mechanical properties of these new resins will be addressed in a future publication [31].

4. Conclusions

1. The modification of functionalized triglycerides (AESO) using MA adds more cross-link sites on triglyceride backbones and introduces acid functionality. The maleinization reaction is optimized to be 80 °C and 90–120 min to reduce possible condensation and side reactions.
2. The resulting monomer, MAESO, forms rigid polymers when it copolymerizes with styrene. Dynamic mechanical analysis shows that the moduli of the polymers at room temperature are in the range of 1.9–2.2 GPa, and the glass transition temperature is above 100 °C. Both of these properties are comparable to commercially available resins, such as unsaturated polyesters. The modification using maleic anhydride increases the cross-link density, which increases both the storage modulus and glass transition temperature. The transition from the glassy to the rubbery is also broadened. The glass transition temperature is proportional to the cross-link density of polymers.
3. Increasing the styrene concentration in the resin formula increases both the storage modulus and glass transition temperature. The cross-link density increases with styrene content up to 20 wt% beyond which it decreases with increasing styrene concentration. To maximize the use of the bio-renewable content, and at the same time to optimize properties, the formula is optimized to be 66.7 wt% triglyceride-based monomers and 33.3 wt% styrene.
4. The maleinization reaction successfully introduces a small amount of carboxylic acid functionality onto

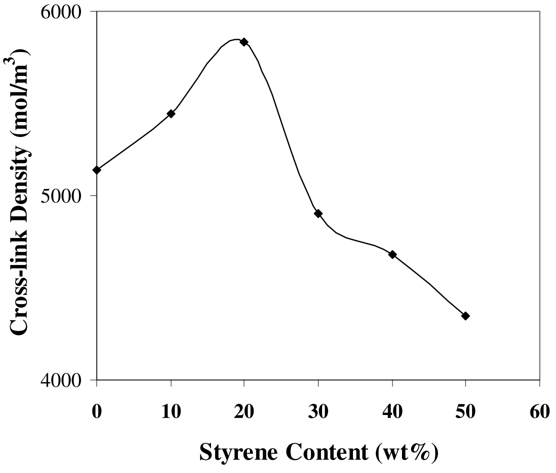

Fig. 13. Cross-link density at various styrene concentrations.

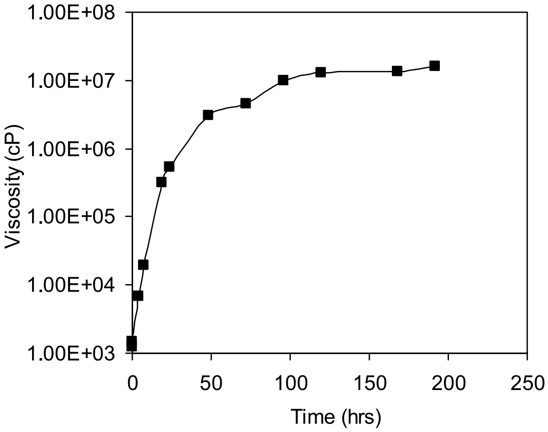

Fig. 15. Variation of resin viscosity as a function of time during thickening.

Table 5
Comparison to commercial unsaturated polyester resins

	Viscosity (cP)	E' at 30 °C (GPa)	$(\tan \delta)_{\max}$ (°C)	Tensile strength (MPa)	Young's modulus (GPa)
MAESO	800–1200	1.9–2.2	115–130	41–44	2.2–2.5
UPE[a]	1200	∼2.0	100	55–75	3.4

[a] The commercial unsaturated polyester resin containing 38 wt% of styrene [32].

triglycerides. During the thickening process with MgO paste, the compound forms a non-tacky leather-like sheet with more than 1000-fold viscosity increase. The behavior is very similar to that of commercial unsaturated polyesters. This formulated resin shows the promise to be used for SMC applications.

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