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Fatty Acid-Based Comonomers as Styrene Replacements in Soybean and Castor Oil-Based Thermosetting Polymers

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ABSTRACT: In this study, a fatty acid-based comonomer is employed as a styrene replacement for the production of triglyceride-based thermosetting resins. Styrene is a hazardous pollutant and a volatile organic compound. Given their low volatility, fatty acid monomers, such as methacrylated lauric acid (MLA), are attractive alternatives in reducing or eliminating styrene usage. Different triglyceride-derived cross-linkers resins were produced for this purpose: acrylated epoxidized soybean oil (AESO), maleinated AESO (MAESO), maleinated soybean oil monoglyceride (SOMG/MA) and maleinated castor oil monoglyceride (COMG/MA). The mechanical properties of the bio-based polymers and the viscosities of bio-based resins were analyzed. The viscosities of the resins using MLA were higher than that of resins with styrene.

Decreasing the content of MLA increased the glass transition temperature (T_g). In fact, the T_g of bio-based resin/MLA polymers were on the order of 60°C, which was significantly lower than the bio-based resin/styrene polymers. Ternary blends of SOMG/MA and COMG/MA with MLA and styrene improved the mechanical properties and reduced the resin viscosity to acceptable values. Lastly, butyrate kraft lignin was incorporated into the bio-based resins, ultimately leading to improved mechanical properties of this thermoset but with unacceptable increases in viscosity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1000–1010, 2011

Key words: vegetable oils; fatty acids; lignin; renewable resources; thermosets; mechanical properties

INTRODUCTION

Polymer and composite materials derived from petroleum-based materials have uses in several fields, such as in aerospace, automotive, marine, infrastructure, consumer goods, and industrial applications. Due to the depletion of petroleum combined with increasing prices and a growing desire to move toward greener products, there is increased interest to replace nonrenewable materials with those made from natural resources, such as vegetable oils. In particular, the affordable composites from renewable resources (ACRES) program at the University of Delaware has been actively designing various monomers from soybean oil and other plant triglycerides (TGD), using a broad range of chemical routes.^{1,2} These monomers include SMC resins,³ as well as epoxidized fatty acids and plant oils modified with acrylate or maleate groups.^{1–8} The resulting polymers range from soft rubbers to rigid thermosets with varied applications such as elastomers, composites, adhesives, and foams.^{1–8}

The ACRES group has developed different triglyceride-derived cross-linkers, such as acrylated epoxidized soybean oil (AESO), maleinated acrylated epoxidized soybean oil (MAESO), maleinated soybean oil monoglyceride (SOMG/MA), maleinated castor oil monoglyceride (COMG/MA), and many others.^{1–8} They have reported that the glass transition (T_g) of AESO was ~ 70°C,^{1,2} and for MAESO the T_g varied between 90 and 110°C depending of the molar ratio of AESO to maleic anhydride employed in the maleination reaction^{1–3}; however, the viscosity of the latter was too high, even with the introduction of the reactive diluent. The glass transitions of these triglyceride-derived cross-linkers can be increased by employing SOMG/MA and COMG/MA, ~ 124 and ~ 130°C, respectively.^{1,2,5,6} In all cases, styrene was employed as a copolymer to reduce the viscosity of the resin, using in most resins ~ 30–35 wt % of the reactive diluent.

Resins derived from petroleum and modified vegetable oils typically contain high concentrations of reactive diluents (e.g., styrene) to reduce their viscosity for resin transfer molding. Styrene is a hazardous air pollutant (HAP) and a volatile organic compound (VOC) and poses significant environmental and health risks; therefore, its replacement with alternative monomers is advantageous on many

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levels. Recently, La Scala et al. and Can et al. develop modified fatty acids that can be employed as an alternative to styrene in the production of polymers employing vinyl ester (VE) and unsaturated polyesters resins.^{9–11} Employing blends of VE resin, methacrylated fatty acids (MFA), and only 10–20 wt % styrene generates materials with properties similar to commercial compounds. They also showed that MFAs are an excellent alternative to styrene, because of their lower cost, reduced volatility, non-HAP/VOC nature, and reduced health and environmental risks.

The aim of this study was to replace part or all the styrene with MFA monomers in thermosetting resins with plant oil derived cross-linkers and evaluate the mechanical properties. For this purpose, different triglyceride-derived cross-linkers like AESO, MAESO, SOMG/MA, and COMG/MA were produced. Methacrylated lauric acid (MLA) has been found to be an optimum combination of low cost and high performance in terms of producing resins with relatively low viscosities and high glass transition temperatures (T_g).⁹

Lignin, one of the most abundant renewable resources, is a polymeric material and a major component of wood, found primarily in cell walls of hardwoods and softwoods.¹² Its highly aromatic structure is ideal for use as a renewable substitute in various petroleum-based materials. Currently, lignin is predominantly considered as a waste product in the paper pulping process, as in most instances, it is burned and used as a fuel as a means of energy recovery in the aforementioned process.¹³

During the extraction of lignin from wood (i.e., alkali digestion), polymeric structure linkages are severed leading to sites with highly polar hydroxyl groups. These functional groups present a challenge for lignin use in high-value applications, because they render lignin insoluble in most common solvents.^{13–23} However, chemical modification of lignin can improve polymer-lignin compatibility by introducing reactive sites.^{16–23} The available hydroxyl groups on the lignin molecule are reactive and local centers of high polarity are capable of hydrogen bonding.¹⁹ Modification of these reactive nuclei results in an effective alternation of the lignin solubility behavior.^{20,21} Lignin has been reacted with carboxylic acids anhydrides to allow it to free radically polymerize.²¹ Lignin-based epoxy resins have then been produced by epoxidation of the anhydride-modified lignin.²² Recent work in the ACRES group employed chemical modified lignin in thermosetting polymers and composites, where they found that the mechanical properties of the matrix improved with the addition of the modified lignin.^{16–18} In this study, lignin was added to bio-based resins to improve polymers properties and allow for high bio-based content in the resin.

MATERIALS AND METHODS

Materials

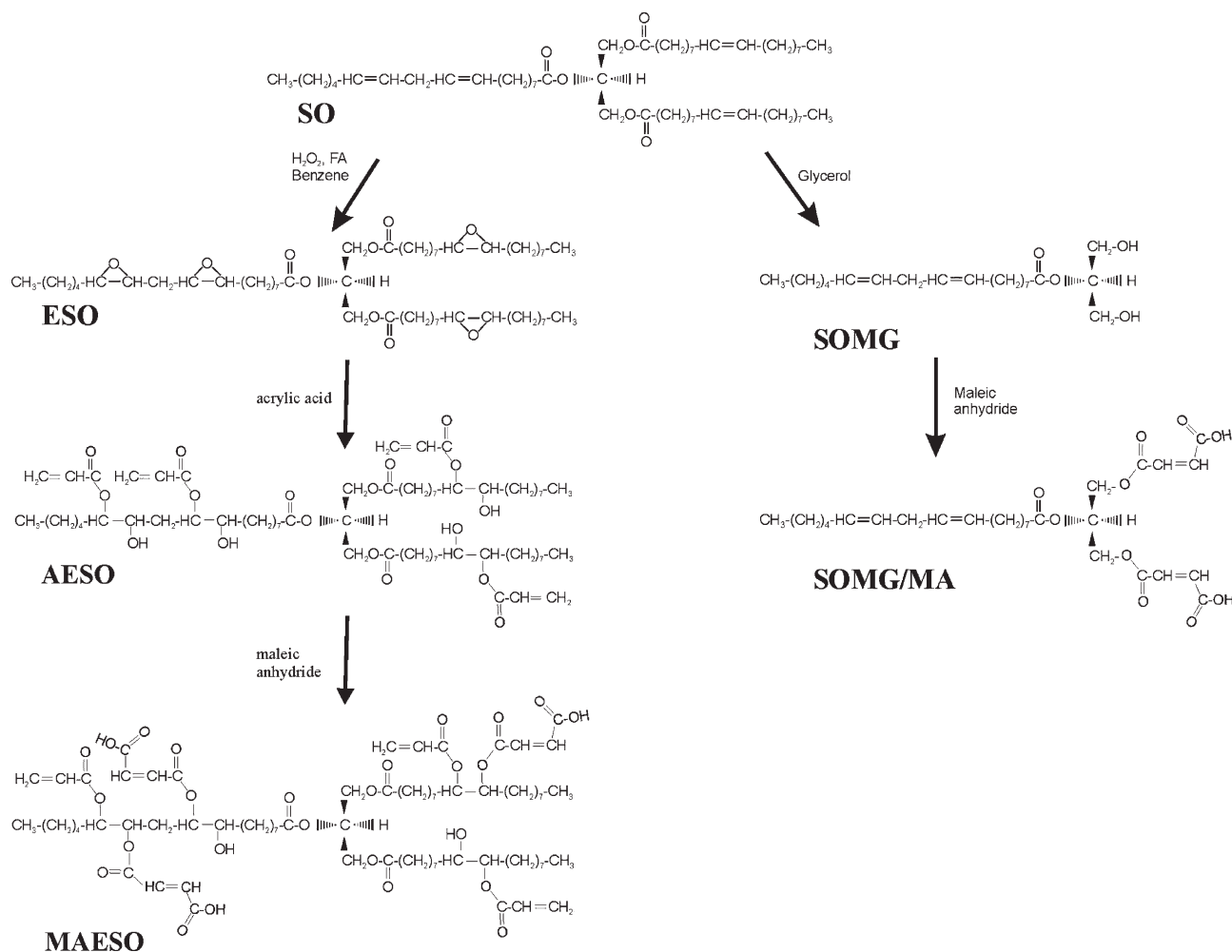
Castor oil, soybean oil, glycerol (99.5%), maleic anhydride (99%), hydroquinone (99%), calcium hydroxide (99+%), N,N-dimethylbenzylamine (99+%), 2-methylimidazole, styrene (99% pure), butyric anhydride (98%), tert-butyl peroxybenzoate, and chloroform-D with 0.03 %v/v of TMS were purchased from Sigma-Aldrich (St. Louis, MO). Ethyl ether (anhydrous), hydrogen peroxide (30 wt %), and cyclohexane (99% pure) were obtained from Fisher Scientific (Pittsburg, PA). Hardwood kraft lignin (PC-1369) was obtained from Westvaco (Stamford, CT); it contains about 1 hydroxyl group per phenyl propane unit with almost 25% aliphatic hydroxyl groups and 75% aromatic hydroxyl groups.¹⁸ MLA was purchased from Applied Poleramics (Benicia, CA).

Synthesis of epoxidized soybean oil (ESO)

Soybean oil (SO) was epoxidized (Scheme 1) at low temperature, with performic acid generated *in-situ*, using benzene as a diluent for the organic phase, to minimize oxirane ring opening.^{24,25} The molar ratio of hydrogen peroxide (H_2O_2)/formic acid (FA)/SO unsaturation (double bonds) was 10/2/1. First, soybean oil, benzene, and FA were placed together into a well-stirred, round-bottom glass reactor kept at room temperature. Then, dilute (30 wt %) hydrogen peroxide was added dropwise after which the reactor temperature was slowly raised to 40°C, to complete the reaction. This procedure requires 22 h to complete the reaction. Formic acid and H_2O_2 were removed by washing the resin multiple times with water and then with saturated (aq.) sodium bicarbonate until a neutral pH was attained. The solution was then dried by washing with saturated (aq.) sodium chloride and drying over sodium sulfate. Finally the benzene was removed by evaporation under vacuum.

Synthesis of AESO

A mixture of ESO was mixed with a stoichiometric amount of acrylic acid (Scheme 1).^{1,2} Hydroquinone was added as a free radical inhibitor in the amount of 0.07 wt % of the total reactant's weight, whereas 1,4-diazobicyclooctane was added as a catalyst in the amount of 0.1 wt % of the total reactant's weight. A mixture of the acrylic acid, hydroquinone, and catalyst was prepared in a beaker and added to the 50 mL ESO, in a three-neck reaction vessel. The mixture was stirred with a magnetic stir bar and brought up to the reaction temperature of 95°C and reacted for about 11 h after which it was allowed to cool to



Scheme 1 Chemical pathways employed to produce the triglyceride-based cross-linkers from soybean oil.

room temperature. The acrylated oil was ether extracted to remove free acrylic acid. Finally the ether was removed by evaporation under vacuum.

Synthesis of MAESO

About 50 g of AESO and 0.05 g of hydroquinone were first heated to 70°C at a rate of 1–2°C/min, while being stirred.^{1–3} A molar ratio of AESO to MA of 1 : 2 was employed and was added at 70°C to the AESO/hydroquinone mixture. The mixture was then heated to 80–90°C, at which point the MA dissolved, forming a homogeneous solution. The *N,N*-dimethylbenzylamine catalyst was then added in the amount of 1 g. The reaction was stopped after 6 h.

Synthesis of SOMG/MA

The glycerolysis reaction was performed by heating the SO in the presence of glycerol and catalyst (Scheme 1).^{1,2,7} The glycerol was placed with the $\text{Ca}(\text{OH})_2$ (catalyst; in the amount of 0.65 wt % of the total oil amount) in a four-necked round-bottom

flask equipped with a N_2 gas inlet, a mechanical stirrer, thermometer, and a calcium drier; and heated at 230°C for 2 h under N_2 atmosphere to evaporate any water present. Then SO was added in 5 portions to the glycerol, with each portion added at 1 h intervals. The mass ratio of soybean oil reacted with glycerol was 4 g of SO to 1 g of glycerol, corresponding to a molar ratio of 4.75 mol of glycerol to 1 mol of triglyceride. The solution was heated at 230°C under N_2 , whereas being stirred for 5.5 h.

The maleinization of the SOMG (Scheme 1) was accomplished by heating at 80°C while stirring 100 g of SOMG.^{1,2,7} Then, 67 g of the maleic anhydride was added; a ratio of 3 mol of SO to 7 mol of maleic anhydride. When the anhydride melted, 1 g of 2-methylimidazole was added as a catalyst along with 0.1 g of hydroquinone. The total reaction duration was 5.5 h.

Synthesis of COMG/MA

The glycerolysis reaction of castor oil (Scheme 1) was conducted according to the procedure described

by Can and coworkers,⁶ employing 100 g of castor oil, 21.9 g of glycerol, and 1.22 g of Ca(OH)₂. The molar ratio employed was 1 mol of CO to 2.4 mol of glycerol. For the maleination reaction (Scheme 1), 98.08 g of maleic anhydride, 0.22 g hydroquinone were added to the product obtained from the glycerolysis step, and the reaction mixture was heated to 90°C. The molar ratio used was 3 mol of OH groups castor oil to 10 mol of maleic anhydride. The mixture was stirred at this temperature until the anhydride melted, then 0.318 g of N,N-dimethylbenzylamine was added, and the reaction temperature was stabilized at 98°C and maintained at this temperature for 5 h.

Synthesis of butyrate lignin

The chemical modification of lignin was produced as described by Thielemans et al.^{16–18} Kraft lignin and butyric anhydride were added in a 1 : 2 weight ratio. 80 g butyric anhydride was heated to 50°C in a reactor and melted. Then 40 g of lignin was added to the reactor along with 1 g of 2-methylimidazole. The mixture was kept under heat and N₂, while being stirred vigorously. The solution was removed from heat after 4 h. 500 g of ethyl ether was added to the solution to separate the butyrate lignin. The butyrate lignin was then decanted and washed with a series of 3 × 500 mL of distilled water. Finally, 200 mL of cyclohexane was added to the butyrate lignin to extract the modified lignin mixture. After decanting the lignin again, the remaining cyclohexane evaporated, whereas the lignin was dried under vacuum for 12 h. The lignin, which was in clusters, was then powdered using a mortar and pestle.

Copolymerization of the triglyceride-derived cross-linkers with a comonomer

SOMG/MA and COMG/MA were copolymerized with styrene and/or the MLA, and mixed with t-butyl perbenzoate initiator at 2 wt % of the total mixture. AESO and MAESO were copolymerized with styrene and/or the MLA and 1.5 wt % of t-butyl perbenzoate. To prevent oxygen free radical inhibition, the resin was purged with nitrogen gas prior to transferring it to the mold. The resin was placed between 2 steel plates with a silicone rubber mold in the middle and cured by the application of heat. SOMG/MA and COMG/MA were cured at 90°C for 2 h, 120°C for 2 h, and 160°C for 1 h.^{1,2,6,7} AESO and MAESO were cured at 90°C for 2 h and postcured at 120°C for 2 h.^{1,2} All polymer samples were then polished and prepared for DMA analysis. The above resins with added modified lignin in the amount of 5 wt % were cured employing the same amount of initiator and curing conditions described above.^{16–18}

Nuclear magnetic resonance (NMR) analysis

¹H NMR was used to monitor the different modified vegetable oils.^{1–3,6,7,26–34} The NMR samples were prepared by dissolving 60 mg in 0.6 mL of CDCl₃. A Bruker AV400 (400.16 MHz) Spectrometer (Bruker, Germany) was used for all measurements, which were performed at 20°C with 16 scans of each sample.

All the samples analyzed in NMR contained the following peaks: $-(CH_2)_n-$ at 1.1–1.4 ppm, terminal $-CH_3$ at 0.8–1.0 ppm, $\alpha-CH_2-(C=O)-O-$ at 2.2–2.4 ppm and $\beta-CH_2-(C=O)-O-$ at 1.7–1.9 ppm.^{1–3,6,7,26–34} To be able to estimate the conversion of the reactions studied in this work, any of the above peaks can be employed as an internal standard. Also, in SO, ESO, AESO, and MAESO the following δ -values can be observe: 4.0–4.4 ppm that corresponds to $-CH_2-CH-CH_2-$ glycerol methylene protons and 5.1–5.3 ppm related to $-CH_2-CH-CH_2-$ glycerol methine protons.^{1–3,6,7,26–34}

In the case of SO peaks related to the double bonds can be find, in particular to $-CH-$ protons of the double bonds at 5.3–5.4 ppm, $-CH_2$ protons adjacent to two double bonds at 2.8 ppm and $\beta-CH_2$ adjacent to the double bond at 2.01–2.06 ppm.^{26–28,33} For ESO, all the peaks related to the double bonds disappear and peaks related to the oxirane group appear at: 2.8–3.3 ppm related to $-CH-$ protons of the epoxy ring, 1.8–2.0 ppm to $-CH_2$ protons adjacent to two epoxy groups and 1.4–1.55 ppm $\beta-CH_2$ adjacent to epoxy group.^{29,30,33} AESO has the set of peaks from 5.8–6.7 ppm that represents the three protons of the acrylate group, and the peak from 5.0–5.5 ppm that corresponds to the proton geminal to ester groups.^{1,2,31–33} For every acrylate group attached to a triglyceride, a hydroxyl group appears and the corresponding peak appears at 3.26–4.2 ppm. Also, some small peaks of the epoxide (2.8–3.3 ppm) still remain after the acrylation. For MAESO, the peaks in the NMR spectrum related to the maleic acid ester that was attached to the double bond appeared at 6.35–6.88 ppm and a peak corresponding to the remaining hydroxyl groups appeared at 3.26–4.2 ppm.^{1–3} Two protons of the carbon-carbon double bond corresponding to the free maleic anhydride appeared at 7.1 ppm. The N,N-dimethylbenzylamine peak appears at 7.75 ppm.

The following equations (extracted from reference 9) were employed to estimate the number of C–C bonds, epoxy and other functional groups per TGD. The number of carbon-carbon double bonds per TGD, was calculated by⁵:

$$U = \frac{1}{2} \left(\frac{A_{5.3-5.4 \text{ ppm}}}{A_{\text{proton}}} - 1 \right) \quad (1)$$

where A_{proton} is the area per proton per molecule, 1 is subtracted to account for the coincident glycerol

methane proton, and the factor of $\frac{1}{2}$ accounts for the fact that there are 2 olefinic protons per unsaturated site. The area per proton per molecule (A_{proton}) can be estimated by dividing the peak area of the selected internal standard ($A_{\text{internal standard}}$) by the number of protons per molecule that cause the resulting peak (p):⁵

$$A_{\text{proton}} = \frac{A_{\text{internal standard}}}{p} \quad (2)$$

The areas of the terminal $-\text{CH}_3$, peak, $\alpha\text{--CH}_2\text{--(C=O)--O--}$, $\beta\text{--CH}_2\text{--(C=O)--O--}$ and glycerol peak have a ratio of 9 : 6 : 6 : 4.⁵

The number of epoxy group per TGD (E) was calculated measuring the epoxy peak area⁵:

$$E = \frac{A_{28-3.26 \text{ ppm}}}{2 A_{\text{proton}}} \quad (3)$$

where the factor 2 accounts for the fact that there are two epoxy protons per epoxide group.

The number of attached acrylated groups (N_A) was estimated by the following equation⁵:

$$N_A = \frac{A_{5.8-6.7 \text{ ppm}}}{3 A_{\text{proton}}} \quad (4)$$

where the factor of $\frac{1}{3}$ accounts for the three protons attached to the $\text{C}=\text{C}$ of the acrylate groups. N_A can also be calculated using the peaks that represent the proton geminal to the ester group:

$$N_A = \frac{A_{5.0-5.5 \text{ ppm}}}{A_{\text{proton}}} - 1 \quad (5)$$

where 1 is subtracted because the glycerol CH also appears in this range.

The number of attached maleate half-ester groups (N_{Maleate}) and fumarate half-ester groups (N_{Fumarate}) was calculated by the following equation⁵:

$$N_{\text{Maleate}} + N_{\text{Fumarate}} = \frac{A_{5.0-5.5 \text{ ppm}}}{A_{\text{proton}}} - N_A - 1 \quad (6)$$

The percentage conversion of i groups (X) to j groups (e.g., X of $\text{C}=\text{C}$ groups to epoxy groups) for all the reactions was calculated as:

$$X = \left(\frac{(i^0 - i)}{i^0} \right) 100 \quad (7)$$

where i^0 is the initial number of i groups per TGD.

SOMG contains the following peaks at: 4.2 ppm that is characteristic of $-\text{CH}_2\text{--(O)--(C=O)--(CH}_2\text{)}_n$, 5.1 ppm that corresponds to $-\text{CH--(O)--(C=O)--}$

$(\text{CH}_2)_n$, 2.01–2.06 ppm related to $-\text{CH--OH}$; $-\text{CH}_2\text{--OH}$ and the three peaks related to the double bond described already for SO.^{1,2,7,34} COMG has a similar peak assignment as SOMG except the peaks related to $-\text{CH=CH--CH}_2\text{--CH=CH--}$, with an additional multiple peak at around 3.62 ppm that is the characteristic of the methane protons that are connected to the hydroxyl (CH--OH).^{1,6} Also, the final concentration of glycerol, mono-, di-, and triglycerides was determined by GC³⁵ employing a reference method, using a Shimadzu GC-17ATF unit and an Agilent column: DB-5HT 15 m, 0.32 mm, 0.10 μm . NMR spectroscopy of SOMG/MA and COMG/MA shows the appearance of maleate and fumarate ester vinyl protons at 6.35 ppm and 6.9 ppm, respectively.^{1,6,7} Also, the disappearance of the 3.7 ppm peak, because of the CH--OH protons and the appearance of CH--OCO of a peak at 5.05 ppm (fatty acids connected to maleate functionality). The conversion was calculated following the disappearance of the 3.7 ppm peak employing eq. (7), also eq. (6) was employed to calculate the number of attached maleate half-ester groups and fumarate half-ester groups. Two protons of the carbon-carbon double bond corresponding to the free maleic anhydride appeared at 7.1 ppm, and they were employed to estimate the remaining maleic anhydride.

Viscosity analysis

The effect of viscosity on the chemically modified soybean oil was measured with a TA Instrument AR-G2 Rheometer (New Castle, DE). A cone and plate geometry with 40 mm diameter plates was used for all samples and repeat runs were performed for all the samples. The effect of the temperature over the viscosity of the triglyceride-based cross-linkers were measured; the samples were first pre-equilibrated at 20°C and then the temperature was increased from 20 to 70°C at a rate of 1°C/min employing a shear rate of 1 s^{-1} .

Dynamic mechanical analysis

Thermo-mechanical properties of the samples were measured using dynamic mechanical analysis (DMA). Rectangular samples with approximate dimensions of $60 \times 12 \times 3 \text{ mm}^3$ were tested using a TA Instruments 2980 DMA in dual cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 μm while ramping the temperature from 20 to 180°C at a rate of 5°C/min. Three different ramp experiments were run for each sample.

To be able to explain the effects of comonomers on the mechanical properties, it is useful to calculate the cross-link density (ν ; mol/m^3). The cross-link density can be estimated from experimental data

TABLE I
Functionality and Conversion of the Different Reactions

Reaction	Group	Final amount of groups per TGD ^a	Conversion (%)
SO	unsaturation site	4.62 ± 0.069	
Epoxidation of SO	epoxy	4.50 ± 0.099	98
Acrylation of ESO	acrylates	3.97 ± 0.10	88
	OH	3.97 ^b	
Maleination of AESO	maleic/fumaric acid ester	1.30 ± 0.036	65
	acrylates	3.97 ± 0.15	
	OH	2.67 ^b	
	unreacted MA	0.70 ± 0.021 ^c	
Synthesis of COMG	OH	2.87 ^d	
Synthesis of SOMG	OH	1.95 ^d	
Maleination of COMG	maleic/fumaric acid ester	2.40 ± 0.074	84
	OH	0.40 ^b	
	unreacted MA	0.87 ± 0.041 ^c	
Maleination of SOMG	maleic/fumaric acid ester	1.66 ± 0.055	85
	OH	0.26 ^b	
	unreacted MA	0.67 ± 0.023 ^c	

^a TGD (triglyceride).

^b Inferred from a functional group balance.

^c Number of the initial MA measured that remains unreacted.

^d Estimated from the percentage composition obtained employing a reference method.

using rubber elasticity theory. Thermosets behave as rubbers above T_g . At small deformations, rubber elasticity theory predicts that the modulus E' , of an ideal elastomer with a network structure is proportional the cross-link density (ν , mol/m³) according to the following equation.^{1-7,36}

$$E' = 3 \nu R T = \frac{3 \rho R T}{M_c} \quad (8)$$

where E' is the rubbery modulus (Pa), R is the universal gas constant [8.314 (Pa m³)/(mol K)], T is the absolute temperature (K), ρ is the density of the sample (1.1×10^6 g/m³ was approximated for all samples) and M_c is the molecular weight between cross-links (g/mol). The temperature and rubbery modulus were determined for the calculation of eq. (8) at $T_g + 40^\circ\text{C}$. The temperature at which the peak in the tan delta presents a maximum was considered the glass transition temperature of the material.

RESULTS AND DISCUSSION

NMR analysis of triglyceride-based cross-linkers

Scheme 1 shows the synthetic pathways employed in this work to produce the triglyceride-based cross-linkers from soybean oil. The first route involved transforming the unsaturated sites of SO into epoxy groups (by performic acid generated *in-situ*) and then producing AESO via oxirane ring opening with an acrylic acid. Also, AESO was reacted with maleic anhydride producing MAESO. Figure 1 and Table I show the conversion and functionality of all synthe-

ses performed in this work. The reaction of C=C to epoxy after 22 h gave a final conversion of 98.3%, where the final amount of epoxy groups per TGD was 4.50. The starting material (SO) contained 4.62 double bonds per TGD. The conversion was estimated by NMR, using peaks related to the double bond and epoxy group, as explained in the analysis section. The conversion of the acrylation reaction is plotted in Figure 1. The final percentage conversion was 88.3 as calculated from the epoxy group in the NMR spectra. AESO contained 3.97 acrylate groups and 3.97 OH groups, this latter group was inferred from a functional group balance. Figure 1 also shows the reaction of the OH groups and the remaining epoxy groups with maleic anhydride for the production of AESO/MA, where the final product (per TGD) contained 3.97 acrylate groups, 1.3 maleate, and 2.67 OH groups with 35% of the maleic anhydride remaining unreacted after the maleination reaction.

The second route in Scheme 1 generated monoglycerides from the reaction of triglycerides with glycerol. This reaction was performed employing two types of oils, soybean, and castor oil. The resulting SOMG contained 79.3% of monoglyceride, 11.1% diglyceride, 31.0% triglyceride, and 8.6% of glycerol. The COMG had 74.2% of monoglyceride, 12.2% diglyceride, 4.5% triglyceride, and 9.1% of glycerol. Both products were estimated employing the reference method, the OH groups were estimated employing this composition.³⁵ These products were reacted with maleic anhydride to generate maleinated monoglycerides oils with conversions of 85% and 84% for SOMG and COMG, respectively, as

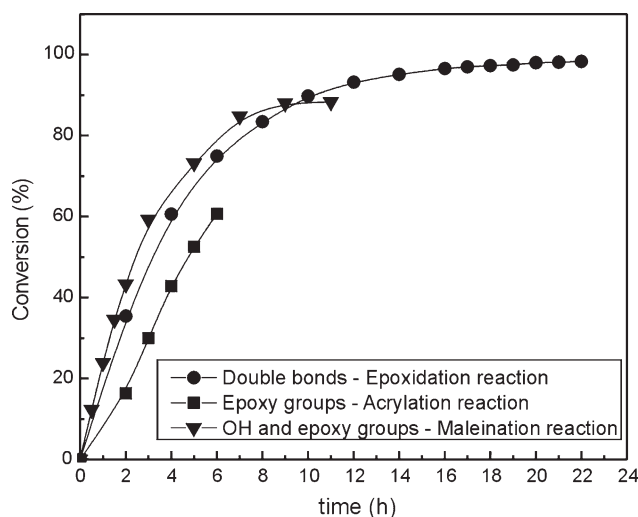


Figure 1 Conversion versus time of (a) double bonds in the epoxidation of soybean oil by performic acid generated in-situ, (b) epoxy groups in the acrylation reaction of epoxidized soybean oil, and (c) OH groups and the remaining epoxy groups with malic anhydride.

shown in Figure 1 and Table I. SOMG/MA contained 1.66 maleate (carboxylic groups) per TGD while COMG/MA contained 2.4. In addition, 28.9% and 26.1% of the maleic anhydride remained unreacted after the maleination reaction for SOMG/MA and COMG/MA, respectively.

Rheological measurements of resins

Liquid molding is used to manufacture many thermosetting polymers and composite parts. Vacuum-assisted resin transfer molding (VARTM) is a common manufacturing process for composites. The composite industry has established that the viscosity for liquid molding resin should be between 0.2 and 1.0 Pa.s (preferably <0.5 Pa.s) to ensure good processability and properties. At viscosities greater than 1 Pa.s, voids may occur in the part, the time required for injection increases and there can be

problems with fiber wetting during the composite preparation. So the triglyceride-derived cross-linkers by their own cannot be used without a diluent in a liquid molding process. In industrial processes, resins are blended with reactive diluents, usually styrene, to meet the above requirements.

Rheological measurements were performed for bio-based resins as a function of triglyceride cross-linker, diluent type and diluent content. The viscosity of all the samples decreased in an exponential manner with temperature. The temperature dependence was modeled with the Arrhenius equation [eq. (9)]^{37,38}:

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \quad (9)$$

where η is the viscosity (Pa.s), η_0 is the prefactor, E_η is the activation energy for the viscous flow (J/mol), R is the ideal gas constant [8.314 J/(K mol)], and T is the absolute temperature (K). Calculation of η_0 involves extrapolating to infinite temperature. Therefore, an accurate measurement of this prefactor is very difficult, and it requires a much more sensitive experiment than the one employed in this work.

The viscosities and Arrhenius parameters of the bio-based cross-linkers employing MLA as a comonomer were considerably higher than the triglyceride-cross-linker resins with styrene because MLA had a higher viscosity than styrene (0.05 Pa.s and 0.0007 Pa.s at 25°C, respectively) as shown in Table II. It can be observed that the viscosity ratio between the cross-linking triglyceride with 35 wt % of MLA compared with the same bio-based cross-linker with 35 wt % of styrene was ~ 4.5 . Figure 2 shows changes in viscosity with the temperature for the 65 wt % of AESO with 35 wt % of comonomer (MLA and styrene). E_η increased linearly with decreasing styrene content. Styrene is a non-polar small molecule that behaves as a solvent, decreasing the intermolecular interactions among the larger and more polar triglyceride monomers. However, MLA

TABLE II
Viscosity of the Bio-based Triglyceride at Room Temperature and Arrhenius parameters

Bio-based triglyceride	MLA (wt %)	Styrene (wt %)	η (Pa.s) ^a	η_0 (Pa.s)	E_η (kJ/mol)
AESO	33	0	2.24 ± 0.19	2.67 × 10 ⁻⁹	56.1
	23	10	1.56 ± 0.06	3.1 × 10 ⁻⁹	50.6
	10	23	0.82 ± 0.07	1.19 × 10 ⁻⁸	44.6
	0	33	0.48 ± 0.03	6.56 × 10 ⁻⁸	39.1
MAESO	33	0	7.27 ± 0.24	6.86 × 10 ⁻¹⁰	72.0
	0	33	1.66 ± 0.13	9.05 × 10 ⁻⁹	50.1
SOMG/MA	35	0	1.36 ± 0.16	3.42 × 10 ⁻¹⁰	52.8
	0	35	0.32 ± 0.06	8.19 × 10 ⁻⁸	32.1
COMG/MA	35	0	1.89 ± 0.21	9.16 × 10 ⁻¹⁰	54.8
	0	35	0.39 ± 0.03	3.32 × 10 ⁻⁸	33.8

^a At 25°C.

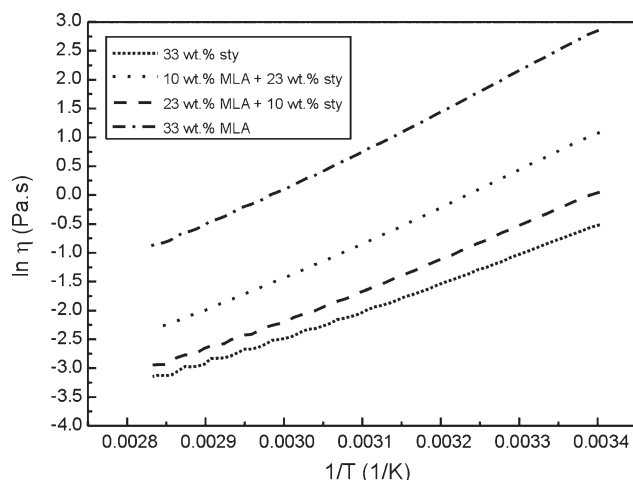


Figure 2 Viscosity as a function of temperature for 65 wt % of AESO copolymerized with metracrylated lauric acid (MLA) or/and styrene (sty).

contains hydroxyl-ester groups, which induce hydrogen bonding.^{5,39} The increase in activation energy with the addition of MLA is evidence that the polar interactions are the main cause for the increase in the viscosity of the resin. When the E_η (or viscosity) is too high, the pressure driving force in liquid molding techniques is not enough to push the viscous resin into the gaps in between the fibers before the resin cures; consequently, viscous resins will produce a composite part with high content of voids.

Also, Table II shows the Arrhenius parameter (E_η and η_0) for the different triglyceride-derived cross-linkers. MAESO has a higher E_η than AESO. This can be explained by analyzing the functionality of each triglyceride cross-linker resin: MAESO contains 1.3 carboxylic acids, 3.97 ester linkages, and 2.67 OH groups (per TGD), while AESO has 3.97 of ester linkages and 3.97 OH groups (per TGD). Higher Arrhenius parameters in MAESO are due to two factors: higher molecular weight and polarity.^{1,40} These groups increase intermolecular interactions via hydrogen bonding and dipole-dipole interactions, which increase E_η .^{1,40} Also, the increase in molecular weight from the addition of carboxylic acids groups influences the parameters.^{1,40}

Both maleinated monoglycerides have lower E_η than MAESO given their functionality and molecular weight are lower. As shown in Table II AESO had a slightly higher viscosity and activation energy than the maleinated monoglycerides, because of the higher molecular weight and polarity of AESO (the functionality of each TGD cross-linker is shown in Table I). But in both maleinated monoglyceride, and also in MAESO, there is still unreacted maleic anhydride in the bio-based resins, therefore the viscosity value will also be influenced by the polarity of this molecule.

Comparing SOMG/MA to COMG/MA, the latter resin had a slightly higher E_η due to the type of veg-

etable oil employed. Castor oil contains an extra OH group in its fatty acid (12-hydroxy-9-*cis*-octadecenoic acid) compared with SO. As shown in Table I, COMG and SOMG contain 2.8 and 1.92 OH groups per TGD, respectively. Thus COMG has more OH groups to react with the maleic anhydride during the malienization reaction, leading to a product with higher content of carboxylic acids and OH functionalities, and thus higher polarity resulting in higher Arrhenius parameters.

Thermo-mechanical properties of bio-based polymers

Thermo-mechanical properties were measured employing DMA. Table III lists the glass transition temperature (T_g) and the storage modulus (E') at 30°C of the bio-based thermoset polymers measured as a function of the comonomer concentration (MLA and/or styrene). Figure 3 shows the storage and loss modulus as a function of the temperature and the comonomer content for SOMG/MA. It can be inferred from the plot that at room temperature all the polymers are in the transition from the glassy region to the rubbery plateau. In addition, the maximum loss modulus decreased as the styrene content decreased; some triglyceride cross-linkers samples did not have a distinct loss modulus peak for this reason, the temperature at which the tan delta maximum occurs was used to measure the T_g . Also, it can be observe that the modulus of this resin improved as the styrene content increased. The storage modulus at a given temperature and the temperature at which the peak in the loss modulus occurred increased as the styrene content in the resin increased. This trend was observed for all the triglyceride cross-linkers (Table III), where it can be inferred that the E' (at 30°C) ratio of styrene versus MLA for the bio-based cross-linkers had a value of approximately 6.35. Figure 4 plots T_g as a function of the amount of styrene for AESO, MAESO, SOMG/MA, and COMG/MA; as shown, the maleinated monoglyceride vegetable oils had higher T_g and modulus compared with AESO and MAESO; where $T_{g\text{COMG/MA}} > T_{g\text{SOMG/MA}} > T_{g\text{MAESO}} > T_{g\text{AESO}}$; this same trend was observed for E' , more detail information about this has already been discussed elsewhere.¹⁻⁸ From Figure 4 and Table III shows that T_g of this resin decreased as the styrene content decreased; and the T_g ratio of styrene versus MLA for the triglyceride cross-linkers was approximately 2.26. Increasing concentrations of styrene led to an improved DMA character because of the aromatic nature of styrene, imparts rigidity to the polymeric matrix. The storage modulus at a given temperature and the temperature at which the peak in the loss modulus occurred increased approximately

TABLE III
Mechanical Properties of the Bio-based Thermoset Polymers

Bio-based triglyceride	MLA (wt %)	Styrene (wt %)	T_g (°C)	E' (MPa) ^b	v (mol/m ³)	Mc (g/mol)	T_g (°C) ^c	T_g (°C) ^{c,d}	E' (MPa) ^{b,c}
AESO	33	0	27 ± 0.3	128 ± 2.1	3.57 × 10 ³	3.1 × 10 ²	35 ± 1.2	38	100 ± 2.7
	23	10	38 ± 0.9	423 ± 1.8	3.07 × 10 ³	3.6 × 10 ²	47 ± 2.7	52	380 ± 5.0
	16.5	16.5	49 ± 1.6	625 ± 3.1	2.72 × 10 ³	4.0 × 10 ²	—	62	—
	10	23	60 ± 2.4	690 ± 10.1	2.45 × 10 ³	4.5 × 10 ²	—	70	—
	0	33	71 ± 0.7	1084 ± 9.2	2.09 × 10 ³	5.3 × 10 ²	78 ± 0.9	84	940 ± 1.9
MAESO	33	0	41 ± 0.3	270 ± 4.2	4.22 × 10 ³	2.6 × 10 ²	48 ± 2.2	49	230 ± 10.4
	15	15	59 ± 5.1	1100 ± 40.2	3.99 × 10 ³	2.7 × 10 ²	74 ± 4.2	72	940 ± 9.9
	0	33	91 ± 0.6	1700 ± 10.3	3.69 × 10 ³	3.0 × 10 ²	99 ± 1.7	100	1620 ± 34.5
SOMG/MA	35	0	50 ± 2.4	302 ± 7.5	2.39 × 10 ³	4.6 × 10 ²	—	69	—
	17.5	17.5	84 ± 1.5	911 ± 8.1	1.99 × 10 ³	5.5 × 10 ²	89 ± 9.2	100	800 ± 10.7
	10	25	96 ± 0.8	1100 ± 5.2	1.45 × 10 ³	7.6 × 10 ²	—	113	—
	0	35	112 ± 7.2	1800 ± 31.2	1.27 × 10 ³	8.7 × 10 ²	118 ± 11.1	130	1710 ± 50.2
COMG/MA	35	0	62 ± 3.5	420 ± 6.2	2.27 × 10 ³	4.8 × 10 ²	—	70	—
	17.5	17.5	89 ± 0.4	1020 ± 5.5	2.01 × 10 ³	5.5 × 10 ²	99 ± 1.1	101	950 ± 9.9
	10	25	101 ± 6.4	1550 ± 41.4	1.91 × 10 ³	5.8 × 10 ²	106 ± 4.3	114	1420 ± 20.8
	0	35	121 ± 7.1	1955 ± 60.4	1.72 × 10 ³	6.4 × 10 ²	129 ± 5.7	132	1820 ± 30.4

^a At 25°C.

^b At 30°C.

^c Addition of 5 wt % of butyrate lignin respect to the total content of resin.

^d Values predicted employing the Fox equation.

linearly as the styrene content increased. The maximum loss value decreased as the styrene content decreased. Conversely, tan delta peak broadened and decreased in high as MLA content increased. This is expected due to the replacement of the rigid structure by the flexible long alkyl chain of MLA that increased the free volume of the polymeric matrix; but, mainly, because polystyrene has a T_g of $\sim 100^\circ\text{C}$ ^{1,9} whereas MLA homopolymers have a T_g of approximately -34°C .⁴¹

The cross-link density and Mc were estimated from experimental data using the rubber elasticity theory [eq. (8)] to be able to explain the effects of comonomers on the mechanical properties. The molecular weight due to cross-linking increased with increasing styrene content as shown in Table III. All resins with similar comonomer concentration (35 wt % diluent of styrene and MLA), exhibited increasing molar diluent content as styrene concentrations in the resin increased because MLA monomers have molecular weights 3.3 times higher than of styrene, as already shown in La Scala et al.^{9,10} Therefore an increase in the styrene content resulted in lower cross-link densities and higher Mc values (Table III). The cross-link density ratio between styrene and MLA for all the triglyceride cross-linkers was ~ 0.68 , and the ratio for Mc was approximately 1.49. The Mc decreased with the addition of MLA because the fatty acid chains increased the free volume of the polymeric matrix acting as a plasticizer. Mc decreased with MLA content because of the higher molecular weight and thus lower molar ratio of reactive diluent relative to styrene. Increasing the MLA content has the advantage

of reducing the HAP/VOC emissions, but the disadvantage of reducing the mechanical properties (e.g. T_g and modulus). These results show that using blends of COMG/MA or SOMG/MA with 10 wt % of MLA and 25 wt % of styrene can reduce the overall styrene content, with acceptable mechanical properties (storage modulus at 30°C was ~ 1220 MPa and the $T_g \sim 100^\circ\text{C}$), while reducing the HAP/VOC emissions.

The Fox equation [represented in eq. (10)] was employed to predict T_g values for this multi-component polymer mixtures, taking into account the respect values for each component of the system.

$$\frac{1}{T_{g,\text{system}}} = \left(\frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} + \dots + \frac{w_n}{T_{g,n}} \right) \quad (10)$$

where $T_{g,\text{system}}$ is the glass transition of the polymeric matrix, $T_{g,i}$ is the glass transition of component i in the system and w_i is the weight fraction of component i in the matrix. The values of T_g (determined as tan delta peak) employed in this work are: 100°C for styrene,¹⁻⁹ -27°C for MLA, 58°C for AESO,^{1,4} 80°C for MAESO,^{1,3} 117°C for SOMG/MA, and 124°C for COMG/MA.^{6,7,42} This model, can be used to predict the T_g for all polymeric bio-based systems studied in this manuscript. As shown in Figure 4, the experimental results are in good agreement with this model.

Thermo-mechanical properties of bio-based polymers with the addition of butyrate kraft lignin

Resins prepared from chemically modified vegetable oils were copolymerized with MLA and/or styrene

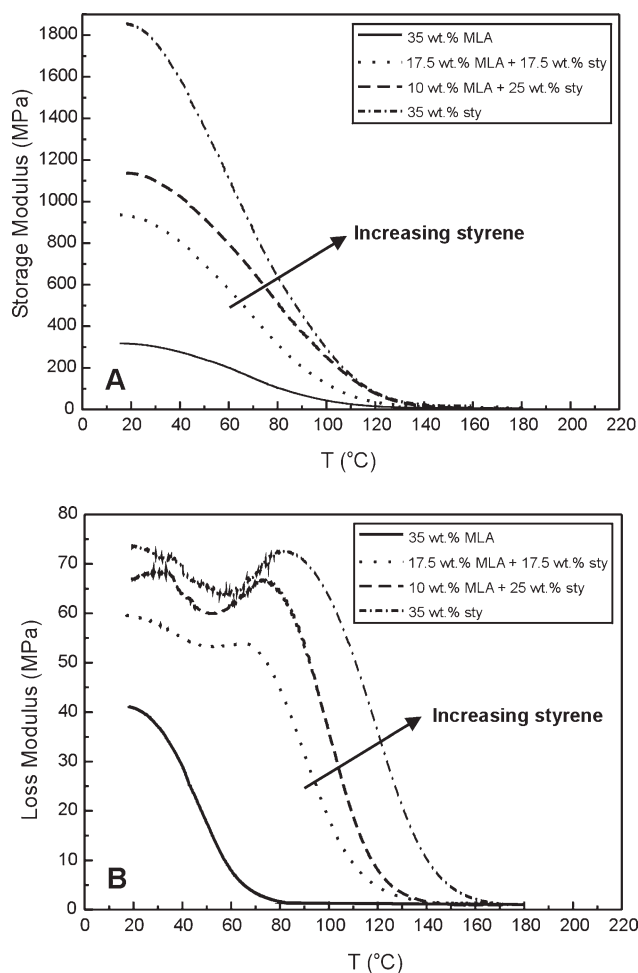


Figure 3 (A) Storage and (B) Loss Modulus as a function of styrene content employing 65 wt % of SOMG/MA and 33 wt % of comonomer (MLA and styrene).

and a chemically modified lignin (butyrate kraft lignin), and the T_g and modulus were evaluated for each material. As can be observed in Table III, the addition of butyrate kraft lignin has an effect in the polymer properties. There is an increase in T_g because the lignin has a high T_g of about 142 °C.¹⁶ In fact, as shown in Table III, the Fox equation [eq. (10)] prediction does a good job of predicting the T_g increase for modified lignin samples.

Lignin does not have double bonds that participate in the free radical polymerization so E' at 30 °C decreases when it is incorporated to the matrix (Table III). This was also found by Thielemans et al.^{16–18} Resins viscosity increased significantly by the addition of butyrate lignin. For example, at room temperature an AESO/MLA has a viscosity of 2.24 Pa.s compared with 4.93 Pa.s for AESO/MLA with lignin. The viscosity is more than doubled when the resin does not contain lignin. This large increase in viscosity has a negative effect on the ability of the resin to flow during the liquid molding process and voids may occur in the composite part.

CONCLUSIONS

The viscosities of the bio-based cross-linkers employing MLA as a comonomer are considerably high and will become problematic during the resins injection into the mold. Therefore blends of MLA and styrene can be used as a comonomer to fit the composites industry requirements; or alternative MLA can be used without the styrene at higher temperatures to achieve a processable low viscosity.

The results of this studies showed that triglyceride-based cross-linkers resins using MLA as a reactive diluent have relatively low polymer properties and high viscosities, so blends of MLA and styrene are required. The T_g and stiffness of the copolymers of styrene, MLA, and triglyceride-derived cross-linkers decreased as the fatty acid monomer fraction increased.

Triglyceride-based cross-linkers resins, especially SOMG/MA and COMG/MA, employing 10 wt % of MLA and 25 wt % of styrene were produced with acceptable viscosities (~ 0.6 Pa.s) and polymer properties (storage modulus at 30 °C was ~ 1220 MPa and the $T_g \sim 100$ °C) comparable with petroleum-based commercial resins. So modified fatty acids can be employed to reduce styrene concentration, reducing VOC emissions, health and environmental risk. Bio-based resins made from SOMG/MA and COMG/MA are advantageous for having lower viscosities and higher mechanical properties. They both require glycerol for their manufacture and due to the large production of biodiesel in the world, high amounts of low cost glycerol (by-product) are produced.

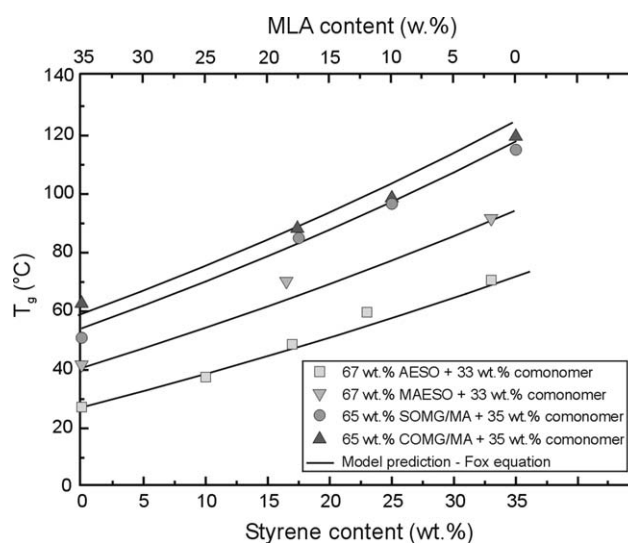


Figure 4 Glass transition temperature as a function of the temperature for AESO, MAESO, SOMG/MA, and COMG/MA copolymerized with MLA or/and styrene; the symbols indicates experimental data obtained with DMA, whereas the continuous lines stand for model predictions employing the Fox equation.

Also, it was found that butyrate kraft lignin can be added to the matrix leading to an increase in the T_g (for example for COMG/MA with 10 wt % of MLA and 25 wt % of styrene the T_g was equal to 106°C) and increasing the renewable content of the polymers. But, has the disadvantage that the viscosity of the resin with the addition of modified lignin doubles its value compared to the resin without the lignin, and the modulus decreased. This increasing of the viscosity is an issue when using liquid molding techniques to manufacture composite parts.

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