

Photolytic and Free-Radical Polymerization of Monomethyl Maleate Esters of Epoxidized Plant Oil Triglycerides

Hüseyin Esen,¹ Selim Küsefoğlu,¹ Richard Wool²

¹Department of Chemistry and Polymer Research Center, Boğaziçi University, Bebek, Istanbul, 34342, Turkey

²Center of Composite Materials, University of Delaware, Newark, Delaware 19716

Received 13 August 2005; accepted 24 July 2006

DOI 10.1002/app.25155

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Epoxidized soybean oil (ESO) was reacted with monomethyl maleate with AMC-2 catalyst. Monomethyl maleate was found to react with 65% of the available epoxy groups to give the monomethyl maleic esters of ESO (MESO). ¹H-NMR, ¹³C-NMR, and IR spectra of the new derivative confirmed the proposed structure. The NMR spectra revealed that the average number of monomethyl maleate groups per triglyceride molecule was 2.6. MESO was photopolymerized with ultraviolet light and was free radically homopolymerized and copolymerized with styrene (STY), vinyl acetate (VA), and methylmethacrylate (MMA). MESO was also reacted with maleic anhy-

dride at the newly formed hydroxyl groups to give maleinized MESO, (MESOMA), which now contained 4.9 maleate unsaturations per triglyceride. Dynamic mechanical analysis revealed the dynamic modulus for styrene copolymers of MESO and maleinized MESO as 105 and 140 MPa, respectively. Both of these plant oil derived monomers are good candidates for a practical and economical liquid molding resin. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 626–633, 2007

Key words: maleate esters; epoxidized plant oil; composites; renewable resources; thermosets

INTRODUCTION

Epoxidized plant oil triglycerides can be found in naturally occurring oils such as vernonia oil and are easily synthesized from the more common unsaturated oils such as linseed, sunflower, and soybean oils by standard epoxidation reactions.¹ Recently, soybean oil has been epoxidized by enzymatic pathways with above 90% conversion.² Numerous commercial efforts to produce genetically modified soybean plants containing higher amounts of oil and higher amounts of oleic acid in their triglycerides have been disclosed. These make epoxidized soybean oil, (ESO), an attractive raw material for the synthesis of successful thermoset resins. ESO has been used as a safe plasticizer for PVC and has been successfully polymerized by photocationic ring opening polymerization with onium salts.^{3,4} We had earlier converted ESO to its acrylate ester by reaction with acrylic acid, which was free radically polymerized or copolymerized with reactive diluents such as styrene to give thermoset resins with mechanical properties that are similar to commercially successful polyester and vinyl ester resins.^{5,6}

We have examined soybean oil and epoxidized soybean oil chemistry at some depth and reported our results in earlier publications.^{6–8} We have also reported the synthesis, photopolymerization, and free-radical polymerizations of cinnamate esters of ESO.⁹ Rheological properties of ESO and acrylic acid product were also identified.¹⁰ ESO was utilized as a raw material for polyurethane reaction after it was converted to diol form.¹¹ There are other efforts to utilize epoxidized soybean oil in composite field with different fabrication methods. These results were published by Erhan and Wool separately.^{12,13}

In our continuing efforts to synthesize new rigid and load bearing thermosetting polymers from renewable resources that are suitable for structural composites, we decided to synthesize monomethyl maleate esters of epoxidized soybean oil (MESO). To further increase free radically polymerizable unsaturation on the molecule, maleinization of the newly formed hydroxyl groups of MESO gave the maleated MESO, (MESOMA). Homo- and copolymers of these monomers were synthesized and examined. The reactions are shown in Schemes 1 and 2.

Correspondence to: S. H. Küsefoğlu (kusef@boun.edu.tr).

Contract grant sponsor: DPT; contract grant number: 03K120250.

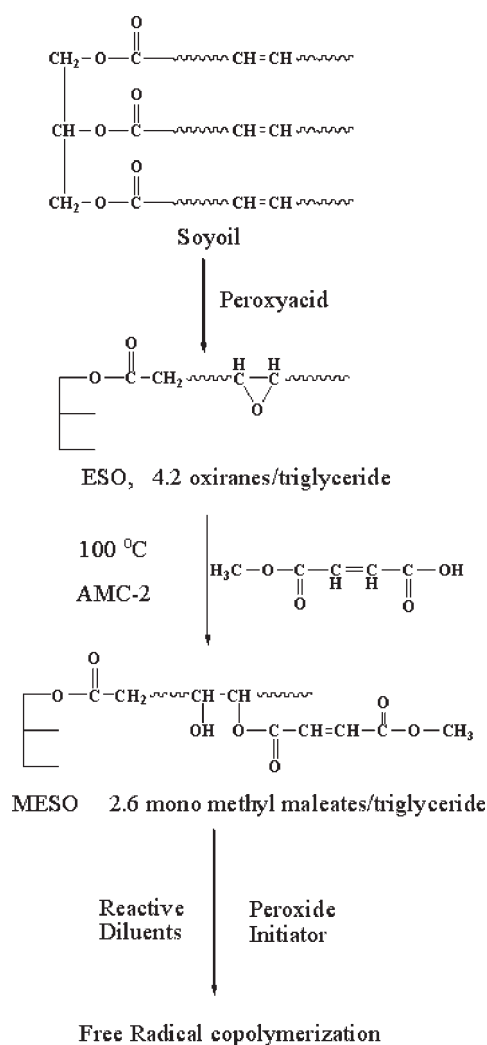
EXPERIMENTAL

Materials

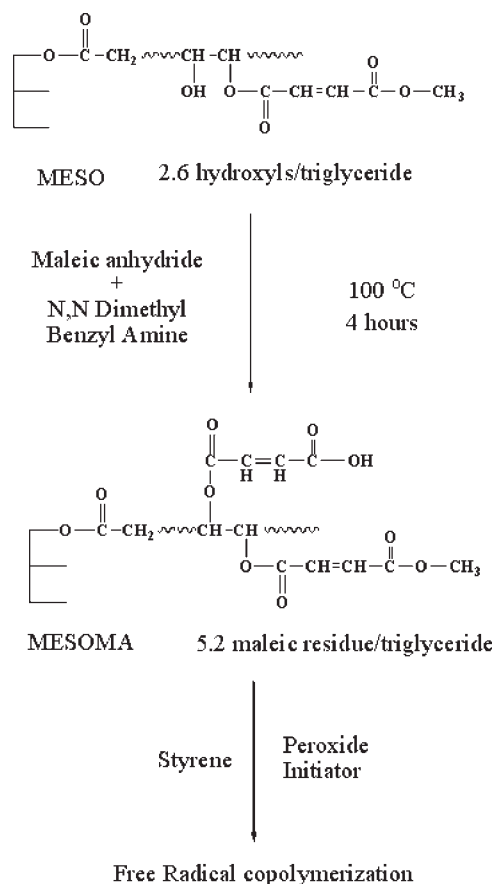
Monomethyl maleate was acquired from TCI America (Portland, OR). Calcium chloride, sodium bicarbonate,

Journal of Applied Polymer Science, Vol. 103, 626–633 (2007)
© 2006 Wiley Periodicals, Inc.

diethyl ether, and carbon tetrachloride were purchased from Merck (Darmstadt, Germany). Styrene (STY), methyl methacrylate (MMA), and vinyl acetate (VA) were obtained from Fluka (Busch, Switzerland). Epoxidized soybean oil (ESO) was purchased from Cargill (Minneapolis, MN). An average molecular weight of 950 was assumed for ESO and it had 4.2 epoxy groups per triglyceride molecule. Maleic anhydride and *N,N* dimethyl benzyl amine were acquired from Aldrich (Milwaukee, WI) and were used as received. AMC-2 catalyst, supplied by Aerojet Chemicals (Rancho Cordova, CA), was used as received. The material data safety sheets of AMC-2 indicate that it is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters. The photoinitiator used, 2,2-dimethoxy-2-phenyl-acetophenone (DMPA), was obtained from Aldrich (Milwaukee, WI). The technical grade AIBN, 2,2'-azobis(isobutyronitrile), was obtained from Fluka (Busch, Switzerland) and was recrystallized from warm methanol before use. The radical initiator methyl ethyl ketone peroxide (MEKP,



Scheme 1 Synthesis and copolymerization of MESO.



Scheme 2 Synthesis and copolymerization of MESOMA.

Lucidol) was also used without further purification as was cobalt naphthanate accelerator.

Instrumentation and characterization

All ^1H - and ^{13}C -NMR spectra were taken on Varian 400-MHz NMR spectrometer (Varian Associates, Palo Alto, CA) operating at a frequency of 399.986 MHz for proton and 100.587 MHz for carbon in CDCl_3 (Aldrich, Milwaukee, WI), and all data are reported as chemical shifts (δ) with respect to tetramethylsilane. All IR spectra were obtained with KBr or NaCl windows on a Genesis II Fourier transform infrared spectrometer (New Castle, DE). The glass transition temperature (T_g) for homo- and copolymers were evaluated using differential scanning calorimetry (DSC). DSC measurements were carried out for the polymers at temperatures from -60 to 200°C using modulated differential scanning calorimetry with a TA Instrument Universal (Giancarlo Scientific, Pittsburgh, PA) V2-5H system at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Photopolymerization was done under a UV SL-25 ultraviolet lamp operating at 366 nm, placed 20 cm from the sample. TGA were performed with Netzsch STA 449C Jupiter system (Selb, Germany) at $20^\circ\text{C}/\text{min}$ in an Al_2O_3 pan

under N₂ atmosphere of flow rate 50 mL/min. Dynamic viscosity was measured with a Haake rotating cup viscometer. The dynamic mechanical thermal analysis of the sample was performed with a Polymer Laboratories dynamic mechanical thermal analyzer (Amherst, MA). Samples with dimensions of 20 mm × 10 mm × 2 mm were scanned at a frequency of 1 Hz and at a heating rate of 5°C/min under nitrogen atmosphere.

Synthesis of monomethyl maleate adduct of epoxidized soybean oil

To ESO (12.11 g, 12.7 mmol, assuming an average molecular weight of 950 for ESO), monomethyl maleate (3.32 g, 25.5 mmol) and AMC-2 catalyst (0.1 g) were added and the mixture was magnetically stirred in a round-bottom flask. The flask was placed in an oil bath at 90°C. After 4 h, the mixture was cooled to room temperature. The reaction product was dissolved in diethyl ether and extracted three times with 10% (aqueous) sodium bicarbonate for the removal of unreacted monomethyl maleate. Aqueous salt solution was added to each mixture to facilitate the phase separation. The ether layer was dried with anhydrous sodium sulfate and evaporated to dryness in vacuum at room temperature. The product was a viscous liquid weighing 9.3 g.

¹H-NMR (CDCl₃, δ): 0.9 (—CH₃ of fatty acids), 1.2–1.4 (—CH₂— of fatty acids), 2.3 (—CH₂CO—), 3.8 (—COOCH₃), 4.2 (—COCH₂— of glycerol), 6.2 (—CH=CH—). IR (KBr): 3452, 1741, 1733, 1724, and 1641 cm⁻¹. Integration of the ¹H-NMR signals indicated that the average number of maleate esters per triglyceride was 2.6.

Synthesis of maleinized MESO, MESOMA

MESO (10 g, 7.75 mmol, based on the assumption of molecular weight of 1290 and the hydroxyl functionality of 2.6), maleic anhydride (1.97 g, 20.1 mmol), *N,N* dimethyl benzyl amine (1% w/of maleic anhydride, 0.0197 g, 0.16 mmol), and hydroquinone (0.002 g) were mixed in a round-bottom flask and placed in an oil bath at 100°C and magnetically stirred. Aliquots were removed every hour to check the final conversion and the viscosity of the resin. The product was a viscous, tacky liquid, weighing 11.02 g. It was soluble in organic solvents.

¹H-NMR (CDCl₃, δ): 10.3 (—OH of carboxylic acid of monomethyl maleate), 0.9 (—CH₃ of fatty acids), 1.2–1.4 (—CH₂— of fatty acids), 2.3 (—CH₂CO—), 3.8 (—COCH₃ of monomethyl maleate), 3.9 (—COCH₃ of monomethyl fumarate), 4.2 (—COCH₂— of glycerol), 6.2 (—CH=CH— of monomethyl maleate). Integration of the ¹H-NMR signals indicated that a total of 4.9 maleate groups were attached to each glyceride.

Homopolymerization of MESO

MESO (2.00 g, 1.6 mmol, based on the assumption of an average molecular weight of 1290 g/mol for MESO with 2.6 monomethyl maleate groups per triglyceride) was mixed with 2% AIBN (0.02 g, 0.12 mmol), purged with nitrogen for 5 min and heated at 80°C for 24 h and at 100°C for an additional 24 h. The product was a viscous liquid soluble in polar organic solvents.

Copolymerization of MESO with methyl methacrylate

MESO (2.00 g, 1.6 mmol) and methyl methacrylate (1.077 g, 10.7 mmol) were mixed to give a molar feed ratio of 59.9% MESO and 40.1% MMA. Methyl ethyl ketone peroxide (0.092 g, 0.87 mmol) and cobalt naphthanate (0.008 g, 0.04 mmol) were added and the mixture was purged with nitrogen and sealed. After 24 h at room temperature, the crude product was extracted with chloroform twice to remove unreacted monomers and homopolymers of MESO and MMA. Extraction resulted in 48% weight loss. This unusually high value was obtained in three separate experiments. The ¹H-NMR of the extract of the sample revealed the poly(methylmethacrylate) protons and olefinic protons of monomethyl maleate. ¹H-NMR of the copolymer shows the expected peaks for PMMA and polyMESO segments. The copolymer molar composition analysis could not be performed due to the broadened and overlapped peaks in NMR spectrum of swollen sample.

Copolymerization of MESO with vinyl acetate

MESO (2.00 g, 1.6 mmol) and VA (1.077 g, 8.1 mmol) were mixed to give a feed molar ratio of 11.3% MESO and 88.6% VA. Methyl ethyl ketone peroxide (0.092 g, 0.87 mmol) and cobalt naphthanate (0.008 g, 0.04 mol) were added and dissolved. The mixture was purged with nitrogen and sealed. After 24 h at room temperature, the copolymer was obtained as an opaque and insoluble solid weighing 2.3 g and was extracted with chloroform twice to remove the unreacted monomers and homopolymers of MESO and VA, if any. A weight loss of 9% was observed. The extracted material had IR peaks mostly coinciding with poly(vinyl acetate). The copolymer molar composition was 45% MESO and 55% VA according to ¹H-NMR analysis. The ¹H-NMR of the extract of the sample revealed the olefinic protons of monomethyl maleate and vinyl acetate at 6.2 and 7.4–7.6 ppm, respectively.

Copolymerization of MESO with styrene

MESO (2.00 g, 1.6 mmol) and styrene (1.077 g, 10.3 mmol) were mixed to give a feed molar ratio of 13.4% MESO and 86.6% styrene. The resulting solution had a viscos-

ity of 275 cp at 30°C. Methyl ethyl ketone peroxide (0.092 g, 0.87 mmol) and cobalt naphthanate (0.008 g, 0.04 mmol) were added and dissolved. The mixture was purged with nitrogen and sealed. After 24 h at room temperature, the copolymer was obtained as a transparent and insoluble solid weighing 2.6 g and was extracted with chloroform twice to remove the unreacted monomers and homopolymers of MESO and styrene. A weight loss of 24% was observed. The extracted material had IR peaks coinciding with poly (styrene). The copolymer molar composition was 38.8% MESO and 61.2% STRY according to $^1\text{H-NMR}$ analysis. The $^1\text{H-NMR}$ of the extract of the sample revealed the olefinic protons of monomethyl maleate and styrene at 6.2 and 7.4–7.6 ppm, respectively.

Photopolymerization of MESO

MESO (2.00 g, 1.6 mmol) was mixed with styrene (1.077 g, 10.3 mmol, 35% w/total weight) and photoinitiator, DMPA (1% of total weight, 0.0307 g, and 0.12 mmol). The mixture was divided into two equal weight parts and placed in petri dishes. One of the petri dishes was masked with aluminum foil and both were placed over ice filled supports under the UV lamp. After 40 min of irradiation, both of the samples were rinsed with CCl_4 . The sample in the unmasked petri dish did not dissolve, whereas the sample in the masked petri dish dissolved. The photopolymerization yielded 1.5 g of insoluble solid. The solidified sample was triturated with chloroform twice. IR (KBr): 3597, 1742, 1697, and 1644 cm^{-1} .

Copolymerization of MESOMA with styrene

MESOMA (2.00 g, 1.2 mmol) was mixed with styrene (1.077 g, 10.3 mmol) and methyl ethyl ketone peroxide (0.092 g, 0.87 mmol) and cobalt naphthanate (0.008 g, 0.04 mmol) was added and dissolved. The mixture was purged with nitrogen and sealed. After 24 h at room temperature, 2.6 g opaque and insoluble polymer was obtained and was extracted with chloroform twice to remove the unreacted monomers and homopolymers of MESOMA and styrene. The product showed a weight loss of 5% after extraction of monomers.

RESULTS AND DISCUSSION

Synthesis and characterization of MESO

Previous work with maleic anhydride modified epoxidized vegetable oils done in our group indicates that when maleate groups react at both ends, undesirable gelations occur. When they react at one end, the unreacted carboxylic acid end of the maleate reduces the styrene solubility of the product. This reduced

solubility is not desirable for the production (preparation) of liquid molding resins. To solve both of these problems, reaction of epoxidized soybean oil with monomethyl maleate was chosen so that the product cannot gel and is soluble in most reactive diluents. The average functionality, which is the average number of epoxy groups per triglyceride, of epoxidized soybean oil (ESO) used in this work, is 4.2. This is the number specified by the manufacturer as the percent epoxy oxygen and was also determined by epoxy equivalent analysis experimentally. Thus, this is the average number of monomethyl maleate groups that will be attached to one epoxidized triglyceride molecule if all epoxides reacted. Terminal epoxides react with carboxylic acids at ambient temperatures, but internal epoxides need somewhat higher temperature because they are less reactive.¹⁴ Sometimes, catalysts are also needed to obtain high yields. A competing reaction is the ring opening polymerization of the intermediate alkoxide ion, which may cause an increase in the molecular weight of the adduct. This has the drawback of consuming epoxide groups without introducing the monomethyl maleate groups, thereby reducing the free radically polymerizable functionality. The best synthetic procedure for the synthesis of MESO was found to be heating ESO and monomethyl maleate in the presence of AMC-2 catalyst at around 100°C for 3 h. The catalyst, AMC-2, was designed as a specific catalyst for an acid-epoxy reaction. Detailed information regarding its composition is not available because of the proprietary nature of the catalyst. However, this catalyst minimizes undesirable side reactions such as homopolymerization of epoxy groups.¹⁵ The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum of MESO are shown in Figure 1. The $^1\text{H-NMR}$ spectrum of MESO indicates that there is no ester interchange reaction of the fatty acids with monomethyl maleate. In the $^1\text{H-NMR}$ spectrum, maleate double bonds appeared at 6.2 ppm together with a very small peak

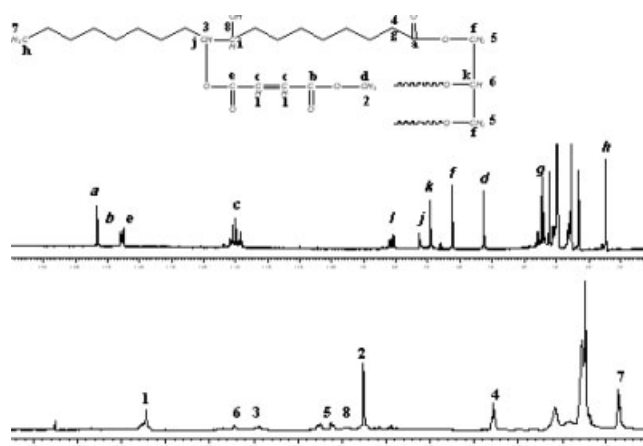


Figure 1 The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum of monomethyl maleate adduct of epoxidized soybean oil, MESO.

of fumarate at 6.82 ppm, which is produced by isomerization of the maleate during the reaction. Integration of maleate vinyl protons, together with the fumarate protons, revealed that 62% of epoxy groups were converted to ester groups having polymerizable double bonds. The rest are either consumed by ring opening polymerization or remain unreacted. Similar loss of epoxy functionality was also observed in the reaction of ESO with acrylic acid in our earlier work.⁶ That is, the functionality of the new monomer is 2.6 maleates per triglycerides. The methyl ester protons of monomethyl maleate appeared at 3.75 ppm and could be used for calculating functionality. Protons at carbons bearing hydroxyl group and monomethyl maleate groups appeared at 3.95 and 4.9 ppm, respectively. This and the absence of epoxy peaks in ¹H-NMR spectrum indicate that the rest of epoxy groups are also consumed by ring opening polymerization.

Unfortunately, the epoxy peak in the infrared spectrum at 833 and 831 cm⁻¹ was obscured by the monomethyl maleate double bond stretching peak at 830 cm⁻¹ and could not be used to follow the reaction. However, disappearance of monomethyl maleate acid peak at 1716 cm⁻¹ and appearance of new ester peak at 1724 cm⁻¹ and the methyl ester and glycerol ester peaks at 1733 and 1741 cm⁻¹, respectively, indicates the attachment of monomethyl maleate groups to the triglycerol. Also, a conjugated carbon-carbon double bond stretching peak appeared at 1641 cm⁻¹.

¹³C-NMR also indicates the expected structure. Peaks at 172.8, 173.2, and 173.3 ppm are associated with the peaks of glycerol esters of epoxidized soybean oil.¹⁶ The alpha beta unsaturated carboxylic acid and ester carbons appeared between 164 and 166 ppm. Also, the vinyl carbons of the maleate appeared between 128.5 and 131.7 ppm. Glycerol peaks appeared at 62.4 and 69.2 ppm and methyl carbon of the maleate ester appeared at 52 ppm. The carbon bearing hydroxyl group and the carbon bearing the maleate group appeared at 72 and 82 ppm, respectively. The methyl carbon of fatty acid chain ends also appeared at 14.5 ppm. Disappearance of epoxy carbons at 56–57 ppm is an indication that all epoxy groups are reacted.¹⁶

Free-radical initiated homopolymerization and copolymerization of MESO

Homopolymerization of MESO with AIBN free radical initiator resulted in the consumption of only 10% of the maleate double bonds and a viscous liquid was obtained. This is a typical behavior of 1–2 disubstituted alkenes. The 10% loss of monomethyl maleate double bond of MESO is observed from the difference in integration ratio of vinyl proton signals to the hydrogens alpha to the carbonyl group in ¹H-NMR spectrums before and after the reaction. The con-

sumption of these double bonds is not sufficient to produce a polymer with a high connectivity to give a hard solid. In fact, the product is not crosslinked enough to be insoluble.

Although monomethyl maleate is a poor monomer in homopolymerization, it will readily undergo copolymerization with other alkene monomers, especially with those that have electron deficient double bonds. As the MESO mixture has a very high viscosity, the use of reactive diluent to bring the viscosity to the industrially acceptable value of 300–400 cP is also required. Therefore copolymers of MESO with STY, MMA, and VA with different comonomer ratios were made.

The copolymer of MESO with 35% (w/total weight) VA gave a clear infusible and insoluble polymer. Extraction of the product with chloroform gave a 9% weight loss. The feed molar ratios used for this reaction are 11.7% and 88.6% for MESO and VA, respectively. The reactivity coefficients of diethyl maleate (as a model compound) and vinyl acetate are 0.043 and 0.17, respectively.¹⁷ Using these literature figures, the theoretical copolymer molar composition for diethyl maleate and vinyl acetate should be 46 and 54 mol %, when the same feed molar ratios are used for MESO instead of diethyl maleate and VA, respectively. The ¹H-NMR spectrum of monomer free MESO-VA copolymer obtained as CDCl₃-swollen sample indicates a copolymer molar composition of 45 mol % MESO and 55 mol % VA. This result is in good agreement with the theoretical value. The DSC spectrum of this copolymer shown in Figure 2 displayed a low temperature transition around -15°C and a recognizable T_g around 55°C. These results are sufficiently different from PVA homopolymer and therefore indicate the formation of a copolymer.

The copolymer with 35% (w/total weight) STY was insoluble infusible, hard, and transparent. Extraction with chloroform to remove unreacted monomers and

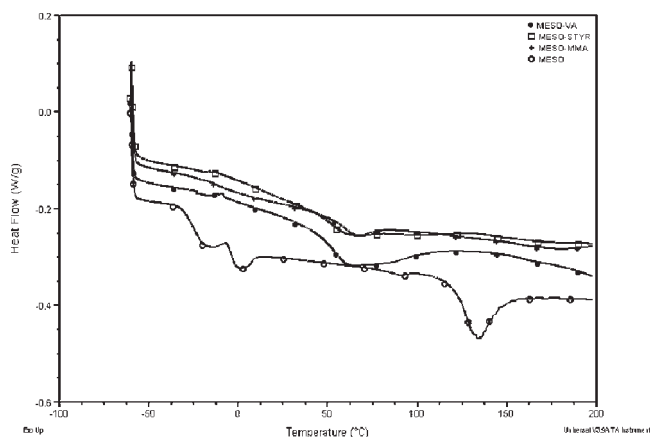


Figure 2 DSC spectra of copolymers and homopolymer of MESO.

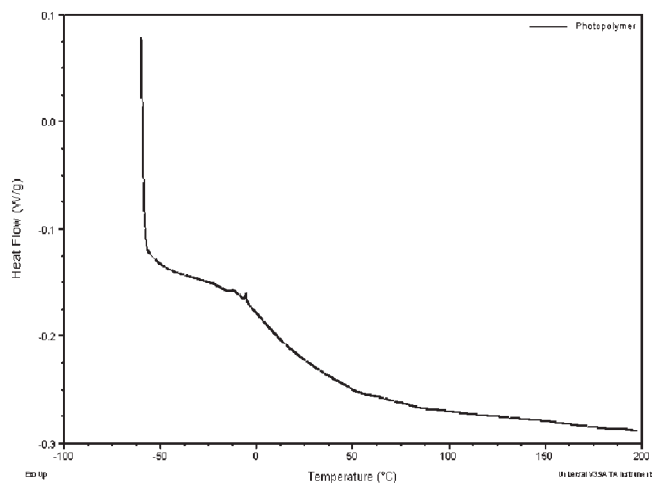


Figure 3 DSC spectrum of the monomer-free photopolymer.

homopolymers of MESO and styrene resulted in a 24% weight loss. The IR spectrum of the copolymer shows the characteristic peaks of MESO together with the typical peaks of aromatic ring at 1633 and 1566 cm^{-1} . Feed molar ratio for MESO is 13.4 mol % and for styrene, it is 86.6 mol %. The reactivity coefficients of diethyl maleate (as a model compound) and styrene are 0.01 and 6.52, respectively.¹⁶ Assuming similar reactivity ratios for styrene and MESO, theoretical copolymer molar compositions for MESO and styrene as 2.3 and 97.7 mol %, respectively, should be obtained. The $^1\text{H-NMR}$ spectrum of triturated sample of MESO-STY copolymer indicates a molar copolymer composition of 38.8 mol % MESO and 61.2 mol % styrene. The difference between the actual and the theoretical values of copolymer molar composition values may be the result of solubility and reactivity differences between diethyl maleate and MESO. The DSC spectrum of the MESO-STY copolymer, shown in Figure 2, shows a typical low temperature range transition due to the side chain relaxations and a T_g at around 60°C due to the crosslinked regions. The DSC spectrum is vastly different from that of polystyrene, indicating that a copolymer is formed.

The copolymer with 35% (w/total weight) MMA also gave insoluble infusible but soft and opaque solid. Extraction of the sample with chloroform indicated a 48% weight loss. This unusually high value was obtained repeatedly and may indicate the formation of large amounts of PMMA. The opaqueness of the solid is probably due to the formation of PMMA. The IR spectrum of swollen sample could not reveal the formation of copolymer because the new ester peak coming from the methyl methacrylate coincided with the methyl ester of polymerized monomethyl maleate. Also, the proton NMR spectrum of swollen sample did not yield enough information due to the broadened and overlapped peaks, thus copolymer

composition analysis could not be performed. However, the DSC spectrum of the monomer and PMMA free sample of MESO-MMA showed a single transition around 60°C , other than the usual β -relaxation of free pendant chain groups, indicating a copolymer. The increased transparency of the dried solid indicates that there is no phase separation due to the similar natures of both components. DSC spectra of MESO-STY, MESO-MMA, and MESO-VA copolymers and the homopolymer MESO are shown in Figure 2.

Photopolymerization of MESO

To prevent thermal polymerization, reaction was performed in a nitrogen ventilated glove box over ice filled supports. After 40 min of irradiation, the product solidified to a transparent, insoluble, and infusible film. A similar sample that was masked did not polymerize. The $^1\text{H-NMR}$ of the monomer free CDCl_3 -swollen sample revealed the aromatic benzene ring protons of the comonomer, styrene, and other details could not be observed due to the low quality of the spectrum. The disappearance of the double bond in infrared spectrum could not be observed due to the overlapping of the olefin band with the aromatic band. The DSC spectrum of the monomer free photopolymer, shown in Figure 3, did not reveal any glass transition temperature. This may be due to the highly crosslinked structure of the photopolymerized sample. Photopolymerization in a thin film gave a polymer with much higher crosslink density than bulk free radical polymerization. Photopolymerized sample was insoluble in all common solvents.

Synthesis and characterization of MESOMA

Generally higher connectivity leads to more rigid polymers. This can be achieved by increasing the number of polymerizable functionalities per triglyceride. In

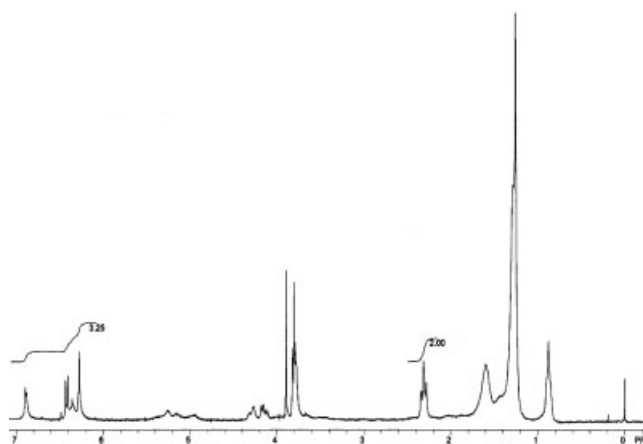


Figure 4 The $^1\text{H-NMR}$ spectrum of the MESOMA.

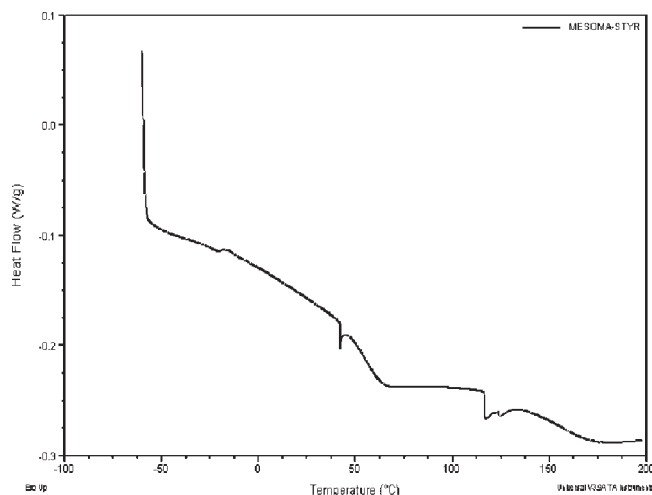


Figure 5 The DSC spectrum of MESOMA-STY.

this work, we achieved this goal by the reaction of the newly formed hydroxyl groups of MESO, with maleic anhydride as shown in Scheme 2. This is a desirable strategy since the maleinization reaction does not produce any by-products, propagates under mild conditions and is accomplished in short time.¹⁸ Theoretically, the polymerizable functionality of this new resin should be doubled to 5.2, based on the assumption of complete consumption of hydroxyl groups. Maleinization of primary hydroxyl groups proceeds in excellent yield at room temperature. Secondary hydroxyl groups require higher temperatures.¹⁷ In our case, essentially complete maleinization was achieved. The maximum ratio of olefinic protons to protons on the carbon- α to the triglyceride carbonyl was achieved within 4 h at 100°C and the absence of hydroxyl absorption, ($-\text{CH}(\text{OH})-$), at 3.95 ppm in $^1\text{H-NMR}$ showed that all hydroxyl groups were consumed. The average molecular weight of this new resin designated as MESOMA is approximately 1625 and should have functionality of 5.2. The $^1\text{H-NMR}$ of the MESOMA is shown in Figure 4. However, integration of vinyl protons of all types of maleates indicates that there are 4.9 maleate groups per triglyceride, thus giving corrected molecular weight of 1550.

Free-radical initiated copolymerization of MESOMA with styrene

The copolymer of MESOMA with 35% (w/total weight) styrene was insoluble, infusible, hard, and transparent solid. Extraction with chloroform indicated a 5% weight loss. The extract contained unreacted maleate residues but no styrene. The DSC spectrum of this monomer-free sample yielded an extra transition at around 125°C when compared with MESO-STY copolymer as shown in Figure 5. The increased effective concentration of the reactive double

bond (resulted from ring opening reaction of epoxy group and then maleinization of formed hydroxyl group) may result in higher crosslink density region, which appeared as an extra transition at around 125°C. MESOMA is very similar to unsaturated polyesters in terms of its molecular weight and presence of maleate unsaturation. Unlike MESO, MESOMA now has free carboxylic acid groups formed by the second maleinization reaction and this should lead to better adherence to glass fibers when reinforced parts are made. When cured in the presence of styrene, this highly crosslinked polymer is an excellent candidate for a liquid molding resin and the mechanical properties of the composites made from MESOMA are under investigation.

Dynamic mechanical and thermogravimetric analysis of copolymers

DMA traces of styrene copolymers of MESO and MESOMA are shown in Figure 6. Large relaxation windows together with the $\tan \delta$ peaks are obvious and glass transition temperatures for MESO-STY and MESOMA-STY were found to be 55 and 90°C, respectively. Having both high $\tan \delta$ value and broad peak also indicates that the materials have quite acceptable damping capacities at relatively broad temperature range. This indicates that copolymers rather than blends are obtained.

TGA traces of some new polymers are shown in Figure 7. In all cases, a general trend was observed. However, copolymer of MESO with VA revealed an earlier and continuous decomposition trend when compared with the other copolymers, which were stable up to 300°C. The copolymer of MESO with styrene showed the latest decomposition around 400°C. Also, the copolymer of MESOMA with styrene revealed 21% char yield at 500°C.

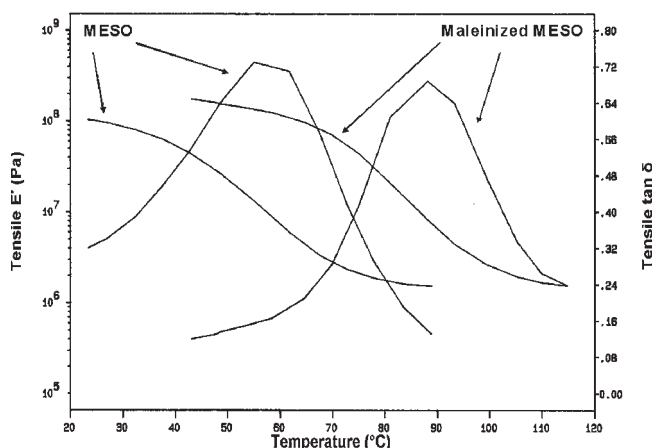


Figure 6 DMA spectra of styrene copolymers of MESO and MASOMA.

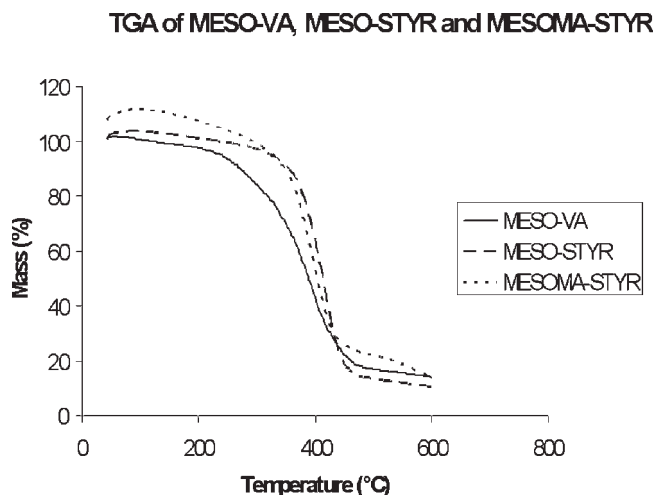


Figure 7 TGA of MESO-VA, MESO-STY, and MESOMA-STY.

CONCLUSIONS

Attachment of a monomethyl maleate ester to epoxidized triglyceride gives an entry to inherently photopolymerizable derivatives of plant oils whose functionalization can be further increased. These can be homo- or copolymerized at convenient wavelengths with the addition of photo sensitizers. Depending on the amount and the nature of the comonomer, structurally rigid copolymers can be obtained by free-radical copolymerization of the monomethyl maleate derivative with different alkene type monomers. These polymers are excellent candidates for new liquid molding resins. In this study, ESO was reacted with monomethyl maleate to give a resin (MESO) that

can be copolymerized with different reactive diluents. MESO was also reacted with maleic acid (maleinized) to have a higher functionality MESOMA. MESOMA has superior physical properties compared with MESO due to higher connectivity.

References

- Eckwert, K.; Jeremin, L.; Meffert, A.; Peukert, E.; Gutsche, B. U.S. Pat. 4,647,678 (1987).
- Biermann, U.; Friedt, W.; Lang, S.; Lühs, W.; Machmüller, G.; Metzger, J. O.; Klaas, M. R.; Schäfer, H. J.; Schneider, M. P. *Angew Chem Int Ed* 2000, 39, 2206.
- Wypych, J. *Polyvinyl Chloride Stabilization*; Elsevier: Amsterdam, 1986.
- Crivello, J. V. *J Polym Sci Part A: Polym Chem* 1999, 37, 4241.
- Hodakowski, L. E.; Osborn, C. L.; Harris, E. B. U.S. Pat. 4,119,640 (1978).
- Wool, R.; Kusefoglu, S.; Palmese, G.; Khot, S.; Zhao, R. U.S. Pat. 6,121,398 (2000).
- Can, E.; Kusefoglu, S. H.; Wool, R. P. *J Appl Polym Sci* 2001, 81, 69.
- Can, E.; Kusefoglu, S. H.; Wool, R. P. *J Appl Polym Sci* 2002, 83, 972.
- Esen, H.; Kusefoglu, S. H. *J Appl Polym Sci* 2003, 89, 3882.
- La Scala, J.; Wool, R. P. *J Appl Polym Sci* 2005, 95, 774.
- Javni, I.; Zhang, W.; Petrovic, Z. *J Appl Polym Sci* 2003, 88, 2912.
- Liu, Z. S.; Erhan, S. Z.; Xu, Y.; Calvert, P. D. *J Appl Polym Sci* 2002, 85, 2100.
- Hong, C. K.; Wool, R. P. *J Appl Polym Sci* 2005, 95, 1524.
- Kakiuchi, H.; Tanaka, Y. *J Org Chem* 1966, 31, 1559.
- Aerojet Fine Chemicals Product Bulletin for AMC-2 Accelerator; 1999.
- Gunstone, F. D. *J Am Oil Chem Soc* 1993, 70, 1139.
- Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1975.
- Siegel, E. F.; Moran, M. K. *J Am Chem Soc* 1947, 69, 1457.