

Soybean and Castor Oil Based Monomers: Synthesis and Copolymerization with Styrene

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ABSTRACT: In this study, castor oil was alcoholized with both aliphatic alcohols, such as glycerol and pentaerythritol, and an aromatic alcohol, bisphenol A propoxylate. The resulting alcoholysis products were then malinated and cured in the presence of styrene. Soybean oil pentaerythritol glyceride maleates were also prepared for a direct comparison of the properties of the castor oil and soybean oil based resins. Castor oil was directly malinated as well to see the effect of the alcoholysis step on the properties of the castor oil based resins. The monomers synthesized were characterized by ¹H-NMR spectroscopy, and the styrenated resin liquid

properties, such as viscosity and surface energy values, were determined. The conversion of polymerization was determined using time resolved FTIR analysis for the styrenated soybean oil pentaerythritol glyceride maleates, castor oil maleates, and castor oil pentaerythritol glyceride maleates. The effect of monomer identity and styrene content on the conversion of polymerization was explored. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2433–2447, 2006

Key words: thermosets; FTIR; renewable resources; resins; radical polymerization

INTRODUCTION

Polymers have a range of applications that far exceeds any class of material available to man. Today, the majority of polymeric materials are derived from petroleum feed stocks, which will be depleted in the next 50 years. The limitation of the petroleum resources and their environmental disadvantages combined with the huge demand for polymers make the use of an alternative renewable resource for these materials quite attractive. Plant oils are suitable starting materials for polymers because of their abundance, the rich chemistry that their triglyceride structure provides, and their potential biodegradability. Although the use of plant oils in the polymer field as coatings is very old and well studied,^{1,2} the research in the preparation of structural plastics from plant oils is rather new. Li et al. recently prepared thermosetting polymers by cationic polymerization of a variety of oils, including fish, tung, and soybean oil, with petroleum-based comonomers such as styrene, divinyl benzene and dicyclopentadiene in the presence of boron trifluoride diethyl etherate as the initiator.^{3–5} Polymers ranging from rubbers to hard plastics were obtained. Crivello et al. prepared fiberglass-reinforced composites fabri-

cated by ultraviolet and visible irradiation of epoxidized vegetable oils in the presence of cationic initiators.⁶ Another approach to making plant oil based polymers is to introduce polymerizable functional groups onto the triglyceride structure using the reactive sites readily available. Our group has developed a broad range of chemical routes to utilize plant oils to make polymers and composite materials that can be used in structural applications.^{7,8}

As a part of this research project, we previously reported the preparation of rigid thermoset polymers from soybean oil triglycerides using the alcoholysis of the oil with glycerol.⁹ The glycerolysis product of soybean oil was reacted with maleic anhydride to form maleate half esters (SOMGMA) and cured in the presence of styrene. Copolymers of the SOMGMA with the maleate half esters of more rigid diols such as neopentyl glycol and bisphenol A exhibited increased modulus and glass transition temperature (T_g) values compared to those of the SOMGMA polymer.¹⁰ The fatty acids present in the above-mentioned soybean oil based monomers do not participate in polymerization; therefore, these fatty acids act in the same manner as a plasticizer, reducing the overall modulus and strength of the resulting polymers. To reduce this plasticizing effect in this study, castor oil, a specialty oil containing hydroxyls on the fatty acid chains, was used instead of soybean oil in alcoholysis reactions with various polyols and then malinated. Castor oil is obtained from the

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seeds of the castor oil plant *Ricinus communis*. It consists of ~ 87% ricinoleic acid (12-hydroxy *cis*-9-octadecenoic acid).¹ Because of the wide range of reactions it affords, it has multifarious applications in cosmetics, paints, adhesives, plastics, rubbers, and pharmaceuticals. Castor oil's main use in the polymer field has been in the preparation of polyurethanes using various aromatic and aliphatic diisocyanates and the interpenetrating polymer networks^{11–14} and semi-interpenetrating polymer networks^{15–17} based on these polyurethanes. In this study, castor oil was alcoholized with both aliphatic alcohols, such as glycerol and pentaerythritol, and an aromatic alcohol bisphenol A propoxylate. The resulting alcoholysis products were then malinated and cured in the presence of styrene. Castor oil was directly malinated and copolymerized with styrene as well to see the effect of the alcoholysis step on the properties of the resins. Soybean oil pentaerythritol glyceride maleates were also prepared for a direct comparison of the properties of the castor oil and soybean oil based resins. The monomers synthesized were characterized by ¹H NMR spectroscopy. The styrenated resin liquid properties such as viscosity and surface energy values were determined. The conversion of polymerization of the maleates and styrene and the total conversion were explored using time resolved FTIR analysis for the styrenated soybean oil pentaerythritol glyceride maleates (SOPERMA), castor oil maleates (COMA), and castor oil pentaerythritol glyceride maleates (COPERMA). The effect of monomer identity and styrene content on the conversion of polymerization was explored. The mechanical properties of these polymers will be presented in a following article.

EXPERIMENTAL

Materials

The soybean oil, castor oil, pentaerythritol (98%), and glycerol (99.5%) used were all supplied by Aldrich Chemicals. Maleic anhydride (99%), supplied by Aldrich Chemicals, was in the form of briquettes and powdered before use. The bisphenol A propoxylate used, which was also obtained from Aldrich Chemicals, has a number-average molecular weight of (M_n) 344 g/mol. All the catalysts used, calcium hydroxide (95% ACS reagent), *N,N*-dimethyl benzyl amine (99+%), *tert*-butyl peroxy benzoate (98%), and the radical inhibitor hydroquinone (99%), were also obtained from Aldrich Chemicals.

Soybean oil pentaerythritol alcoholysis and malination reaction (SO : PER : MA mole ratio = 1 : 3 : 7.62)

About 400 g of soybean oil (0.457 mol) was mixed with 186.51 g (1.371 mol) pentaerythritol and 5.87 g

Ca(OH)₂ in a three-necked 1 L round bottom flask equipped with a mechanical stirrer, thermometer, a nitrogen gas inlet, and a calcium drier. The flask was placed in a heating mantle. The reaction mixture was heated to 230–240°C and agitated under N₂ atmosphere for 2 h at this temperature. Soap formation on the solution was observed at the beginning of the reaction. Ca(OH)₂ reacts with the free fatty acids in the oil to form soaps, which promotes the reaction, at least in part, by increasing the solubility of the polyol in the fat phases. At the end of 2 h, the product was cooled to room temperature and the reaction flask was placed in an oil bath. The reaction product at room temperature was a light brown viscous liquid. For the malination reaction, 341.27 g (3.482 mol) of maleic anhydride and 0.934 g of hydroquinone were added to the alcoholysis product and the reaction mixture was heated to 90°C. Hydroquinone was used in the formulation to avoid radical side reactions that may consume maleate double bonds. The mixture was agitated at this temperature until the maleic anhydride melted and mixed with the soybean oil pentaerythritol alcoholysis product. Then 9.34 g *N,N*-dimethyl benzylamine was added and the reaction mixture was heated to 98°C. The mixture was agitated at this temperature for 2 h. The product at room temperature was a light brown solid. Both the infrared (IR) and the proton nuclear magnetic resonance (¹H NMR) spectra of the product confirmed the consumption of maleic anhydride and the formation of maleate half esters. The SOPERMA (1 : 3 : 12) and SOPERMA (1 : 2 : 8) products were prepared in a similar manner changing the molar ratios of the reactants in the formulation. The idealized structures of both the reactants and the products are shown in Figure 1.

Castor oil pentaerythritol alcoholysis and malination reactions (CO : PER : MA mole ratio = 1 : 2 : 10.7)

About 120 g of castor oil (0.13 mol), 35.33 g (0.26 mol) pentaerythritol, and 0.778 g Ca(OH)₂ were weighed in a four-necked 500 mL round bottom flask. The flask, equipped with a mechanical stirrer, thermometer, a nitrogen gas inlet, and a calcium drier, was placed in a heating mantle. The reaction mixture was heated to 230–240°C and agitated under N₂ atmosphere for 2 h at this temperature. At the end of this time, the product was cooled to room temperature and placed in an oil bath. The reaction product at room temperature was a light brown viscous liquid. For the malination reaction, 178.99 g (1.826 mol) maleic anhydride and 0.335 g hydroquinone were added to the alcoholysis product and the reaction mixture was heated to 90°C. The mixture was stirred at this temperature until maleic anhydride melted and mixed with the castor oil

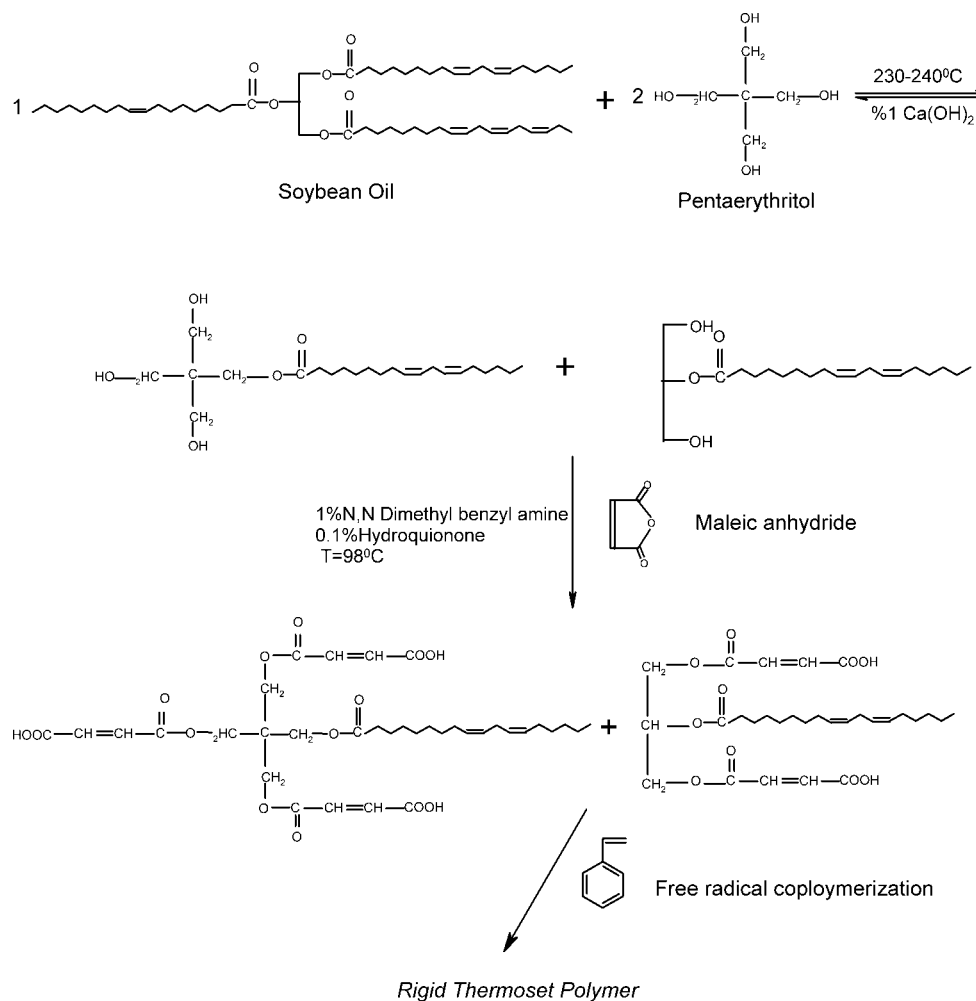


Figure 1 The idealized reaction scheme for the synthesis of SOPERMA.

pentaerythritol alcoholysis product. Then 3.35 g *N,N*-dimethyl benzylamine was added and the reaction temperature was stabilized at 98°C. The mixture was agitated at this temperature for 5 h. The product obtained was a light brown solid at room temperature. Both the IR and ¹H NMR spectra of the product confirmed the consumption of maleic anhydride and the formation of maleate half esters. The idealized structures of both the reactants and the products are shown in Figure 2.

Castor oil glycerolysis and malination reactions (CO : GLY : MA mole ratio = 1 : 2.2 : 9.3)

About 100 g of castor oil (0.108 mol), 21.905 g (0.238 mol) glycerol, and 1.22 g Ca(OH)₂ were reacted according to the procedure described for the castor oil pentaerythritol alcoholysis. The castor oil glycerolysis product at room temperature was an orange colored viscous liquid. This product was reacted with 98.08 g (1 mol) of maleic anhydride in the presence of 3.18 g *N,N*-dimethyl benzylamine and 0.318 g

of hydroquinone in the same procedure described for the malination of the castor oil pentaerythritol alcoholysis product. The product obtained was a light brown solid at room temperature. The idealized structure of the reactants and products are shown in Figure 3.

Castor oil bisphenol A propoxylate alcoholysis and malination reaction (CO : BPAPR : MA mole ratio = 1 : 2 : 6.7)

About 89.65 g of Castor oil (0.0970 mol) was alcoholized with 66.75 g (0.194 mol) bisphenol A propoxylate in the presence of 0.782 g Ca(OH)₂ in the procedure described for the castor oil glycerolysis and pentaerythritol alcoholysis reactions. The alcoholysis reaction was carried out for 5 h. The alcoholysis product at room temperature was a light brown viscous liquid. For the malination reaction, the alcoholysis product was reacted with 63.7 g (0.65 mol) of maleic anhydride in presence of 2.21 g *N,N*-dimethyl benzylamine and 0.221 g of hydroquinone according to the procedure described above. The product

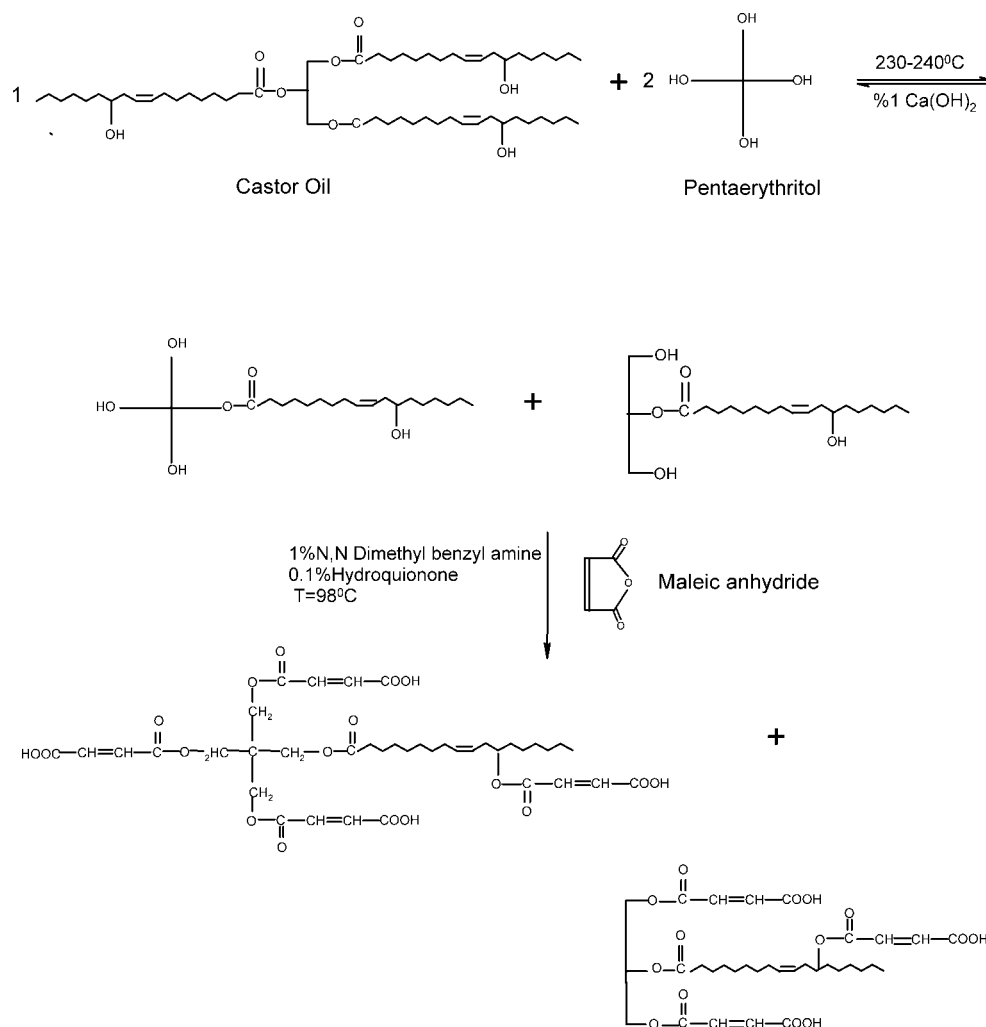


Figure 2 The idealized reaction scheme for the synthesis of COPERMA.

obtained was a light brown solid at room temperature. The idealized structure of the reactants and products are shown in Figure 4.

Malination of castor oil (CO : MA mole ratio = 1 : 3)

About 100 g of castor oil (0.1082 mol), 31.82 g (0.3247 mol) of maleic anhydride, and 0.132 g of hydroquinone were placed in a 250 mL round bottom flask equipped with a thermometer and a mechanical stirrer. The reaction flask was then placed in an oil bath and the mixture was heated to 90°C. When the maleic anhydride melted, 1.32 g of *N,N*-dimethyl benzylamine was added to the reaction mixture and the reaction temperature was stabilized at 98°C. The mixture was agitated at this temperature for 5 h. The product obtained was a light yellow, viscous liquid at room temperature. Both the IR and ^1H NMR spectra of the product confirmed the formation of castor oil maleate half esters.

Characterizations

The IR analysis of the monomer mixtures was performed on an ATI Mattson FTIR spectrometer using KBr windows. All the ^1H NMR spectra were recorded in CDCl_3 using a Bruker AM250 spectrometer, which has a magnetic field strength of 250 MHz. The viscosities of the styrenated resins were measured using a Brookfield II+ viscometer with an S31 type of spindle. The surface energies were measured on a Kruss K10T model digital surface tensiometer.

Determination of conversion of polymerization

For all the maleic anhydride-modified soybean and castor oil based resins, a similar curing procedure was employed. The maleic anhydride-modified oil was first heated to a temperature around 60–70°C to reduce the viscosity and then mixed with the specified amount of styrene. The styrene used was obtained from Aldrich Chemicals and was 98% pure. After completely mixing, *tert*-butyl peroxy benzoate

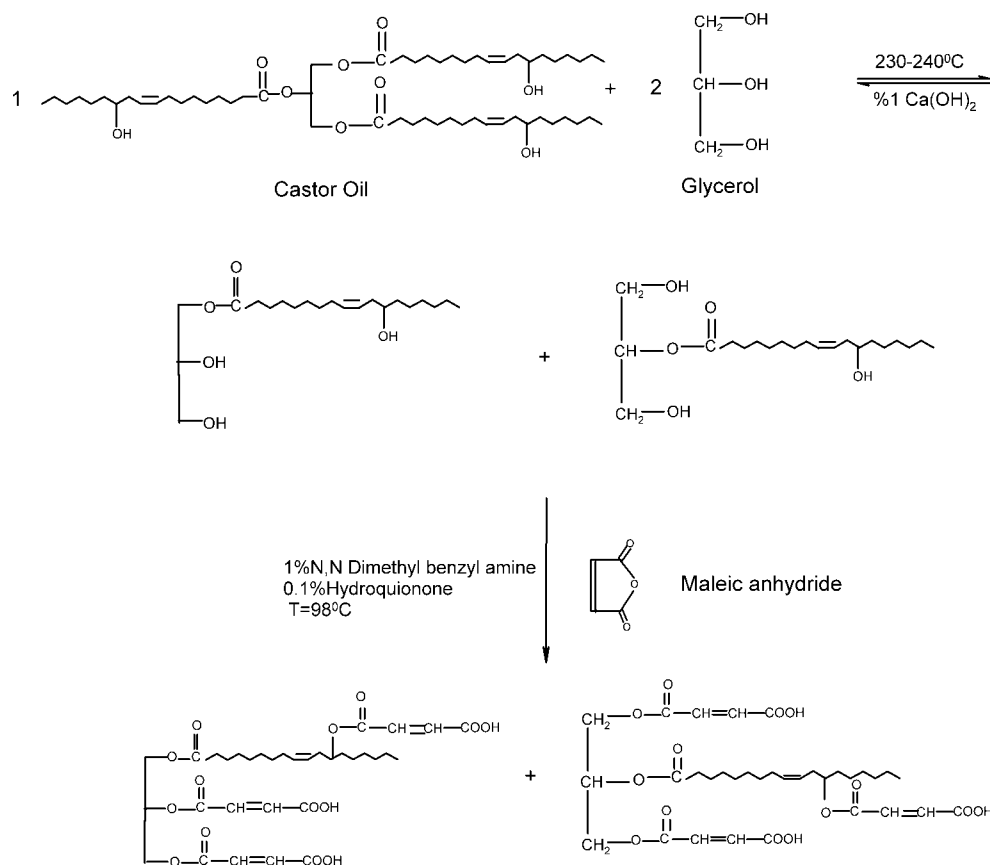


Figure 3 The idealized reaction scheme for the synthesis of COGLYCMA.

was added as initiator. The amount of initiator used was 2% of the total resin weight for the SOPERMA and COMA resins and 1.5% for the COPERMA resin.

The resins were purged with nitrogen gas for 2 min before the experiment to remove free oxygen. A drop of the resin was sandwiched between two 25 mm diameter NaCl disks (International Crystal Labs) separated by a 0.025 mm thick Teflon™ spacer (International Crystal Labs). One NaCl disk was 2 mm thick while the other was 4 mm thick. An aluminum holder was used to clamp the two FTIR NaCl cells. The holder was placed in an aluminum heating block with two 100 W cartridge heaters. A PID temperature controller from Omega Engineering, model CN76030, connected to the heating block with a thermocouple and also connected to the cartridge heaters, kept the temperature within 0.5°C of the desired temperature. The NaCl disk temperature was independently checked with an external thermocouple. The IR cells were heated to the desired temperature and a background was taken. The cells containing the sample were then loaded into the heating block and immediately placed in the IR beam.

A Nicolet Magna 860 FTIR operating in transmission mode with 4 cm⁻¹ resolution was used. The deuterated triglycine sulfate detector gives a linear

response between absorbance and concentration for measured absorbance less than two, according to Beer's Law. Eight scans were taken (acquisition time 18 s) per spectrum with a delay between spectra of 40 s. The cure of all resins was carried out at 120°C for 3 h for comparison of the conversion of polymerization in different resins. The SOPERMA and COPERMA resins were also postcured at 160°C for 1 h after 2 h at 120°C.

RESULTS AND DISCUSSION

Structural analysis of soybean and castor oil based monomers

The alcoholysis and malination reaction products can be characterized using both IR and ¹H NMR spectroscopic techniques. The alcoholysis products of the oil with polyols carry the characteristic features of both the alcohol and the glyceride structure. The IR spectra of the alcoholysis products are characterized by the broad hydroxyl band at around 3500 cm⁻¹ as well as the strong ester carbonyl peak of the glycerides at ~ 1740 cm⁻¹. The malination reaction of the alcoholysis products can be followed by IR with the decrease in the maleic anhydride characteristic peaks. These peaks are the 1779 and 1849 cm⁻¹ peaks that belong to

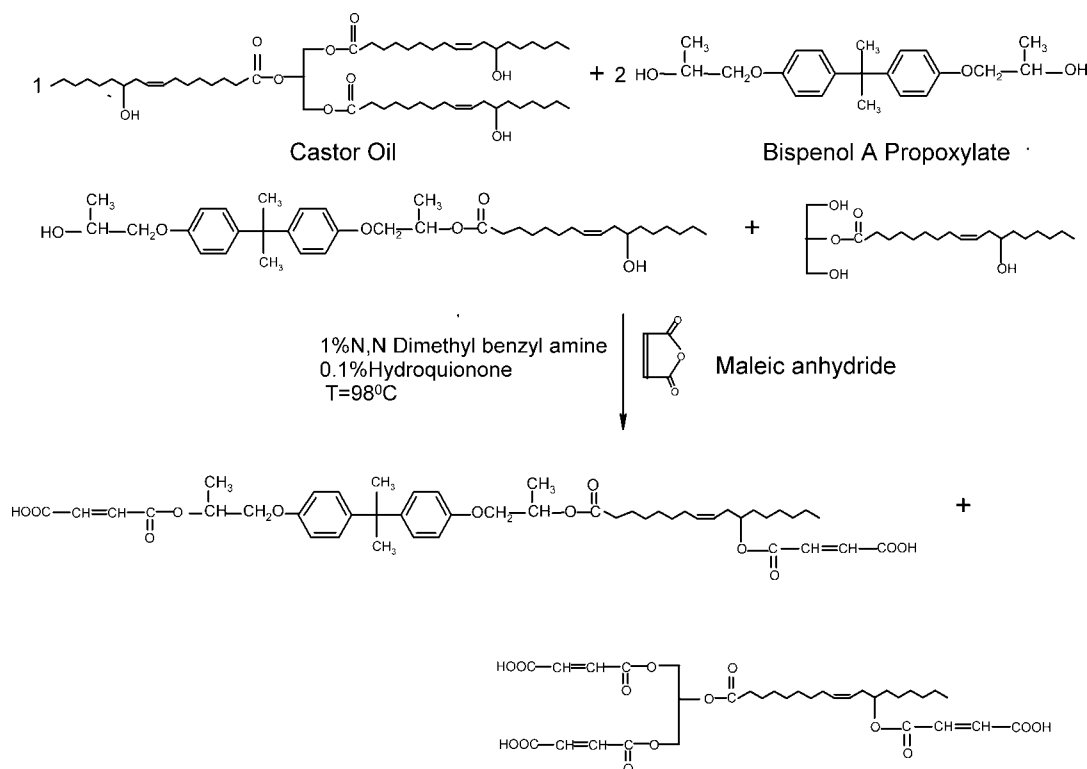


Figure 4 The idealized reaction scheme for the synthesis of COBPAPRMA.

the carbonyl ($C=O$) asymmetric and symmetric stretching vibrations, respectively. The hydroxyl band of the alcoholysis product, at 3500 cm^{-1} is replaced by the broad acid band of the maleate half esters ($2500\text{--}3400\text{ cm}^{-1}$) as the reaction progresses.⁹

The ^1H NMR spectrum of the soybean oil pentaerythritol alcoholysis product shown in Figure 5(a) contains multiplet peaks in the 3.4–3.8 ppm region that show the methylene and methine protons that are connected to the hydroxyls in addition to the characteristic peaks of the triglycerides. The ^1H NMR spectrum of the SOPERMA shown in Figure 5(b) is characterized with the maleate vinyl protons' peak at 6.35 ppm as well as the peak of the acid protons that appears around 9.65 ppm. The fumarate (trans isomer of the maleate) peak appears with a very low intensity at 6.9 ppm, since the maleate–fumarate isomerization favors higher temperatures than the temperature, in which this addition reaction is carried out at (98°C). The maleate–fumarate isomerization occurs to a greater extent in polyesterification reactions with maleic anhydride, which usually require temperatures above 160°C .¹⁸ The disappearance of the multiplet peaks in the 3.4–3.8 ppm region that belong to the methylene protons attached to the hydroxyls ($\text{CH}_2\text{—OH}$) present in the alcoholysis product confirms the formation of the maleate half esters.

For the alcoholysis of soybean oil with pentaerythritol, molar ratios of oil to pentaerythritol of 1 : 2 and 1 : 3 have been employed. The alcoholysis reaction is com-

pleted in 2 h at $230\text{--}240^\circ\text{C}$ in the presence of 1% $\text{Ca}(\text{OH})_2$ as a catalyst. Longer reaction times decrease the hydroxyl content of the alcoholysis products as observed from the ^1H NMR analysis, due to polyetherification of pentaerythritol, which occurs as a side reaction during the alcoholysis.¹⁹ For the malination of the alcoholysis products, maleic anhydride was in a 1 : 1M ratio with the number of hydroxyls on pentaerythritol used in the alcoholysis reaction, thus molar ratios of SO : PER : MA = 1 : 2 : 8 and 1 : 3 : 12 were employed. A good way to follow the maleate yield in these reactions is to take the 5.3 ppm peak as reference. In ^1H NMR analysis; the integral of this peak should show 10 protons per triglyceride assuming that soybean oil contains 4.5 double bonds per triglyceride and taking into account the methine proton of the glycerol backbone attached to ester functionality, which shows its peak in the same region. The ^1H NMR analysis of these malinated products (SO : PER : MA = 1 : 2 : 8) and (SO : PER : MA = 1 : 3 : 12), with reference to the 5.35 ppm peak, showed that the products contain 1 mol and 4.4 mol of unreacted maleic anhydride per triglyceride respectively, although all $\text{CH}_2\text{—OH}$ protons are consumed. The presence of excess maleic anhydride in each of the malinated products can be explained via diester formation between the carboxylic acid of the maleate half esters and the available hydroxyls. The diester formation leads to the consumption of two hydroxyls per maleic anhydride thus

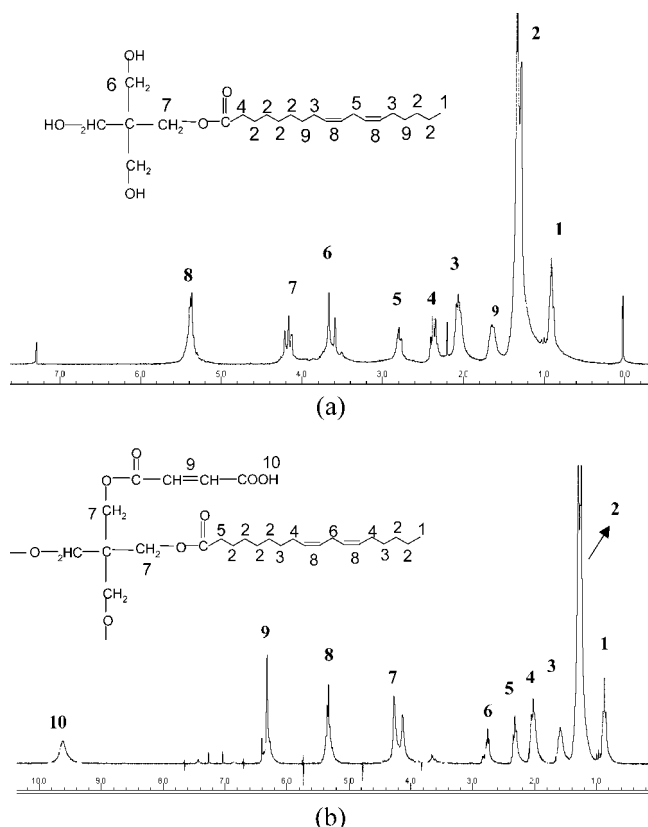


Figure 5 The ^1H NMR spectra of (a) SOPER alcoholysis and (b) SOPERMA products.

results in the presence of excess maleic anhydride in these reactions. Maleyl diesters of monoglycerides were reported to be formed as by-products during the malination of monoglycerides of saturated fatty acids at a temperature of 100°C .²⁰ The Michael type addition of the alcohols to the maleate unsaturation is another side reaction that may consume the hydroxyls as well as the maleate double bonds during malination. This reaction has been reported as a side reaction in the preparation of unsaturated polyesters from diols and maleic anhydride.^{21,22} The maleate yield as determined from the intensity of the maleate vinyl protons peak was 4.55 maleates per triglyceride for the (SO : PER : MA = 1 : 2 : 8) product and 5.77 maleates per triglyceride for the (SO : PER : MA = 1 : 3 : 12) product. Since the SO : PER : MA 1 : 3 : 12 product contains a large amount of excess maleic anhydride, the reaction was carried out in a molar ratio of SO : PER : MA = 1 : 3 : 7.62 by subtracting the amount of excess maleic anhydride in the original formulation. The maleate yield of this product was similar to that of SOPERMA (1 : 3 : 12): ~ 5.60 maleates and 0.11 fumarates per triglyceride. Since the use of excess maleic anhydride decreases the triglyceride content of the resin and also a higher maleate content per triglyceride, which would result in a higher crosslink density for the resulting polymers, was needed, and the (SO : PER : MA = 1 : 3 : 7.62)

formulation was taken as the optimized formulation for the alcoholysis of soybean oil with pentaerythritol and the malination reactions. Table I shows the maleate, fumarate, and excess maleic anhydride content of the products of each reaction carried out at different molar ratios.

The ^1H NMR spectrum of castor oil shown in Figure 6(a) with the peak assignments is different from that of other triglycerides with an additional multiplet peak at around 3.62 ppm that is characteristic of the methine protons that are connected to the hydroxyls ($\text{CH}-\text{OH}$). The integral of the 3.62 ppm peak shows around 2.7 methine protons α to hydroxyls per molecule of castor oil, which corresponds to 2.7 OH's per triglyceride. The molar ratio of castor oil to maleic anhydride was 1 : 3 for malination of castor oil; therefore, the reaction was carried out in an excess of maleic anhydride. Throughout the malination of castor oil, the 3.62 ppm peak disappears whereas a new peak at 5.05 ppm appears showing the methine protons ($\text{CH}-\text{O}-\text{CO}$) of fatty acids connected to maleate functionality. The ^1H NMR spectrum of this product, shown in Figure 6(b), indicates that about 92.6% of the fatty acid hydroxyls were converted to maleate half esters with reference to the integral of this peak. The maleate, fumarate, and maleic anhydride content of this product with reference to the 4.1–4.3 ppm peak, which shows the methylene protons of the glycerol backbone of castor oil ($\text{CH}_2-\text{O}-(\text{C}=\text{O})-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{CH}=\text{CH}-\text{COOH}$) and the 6.3, 6.9, and 7.1 ppm peaks showing the maleate, fumarate, and maleic anhydride vinyl protons respectively, are listed in Table II. The integral of the 4.1–4.3 ppm peak does not change throughout the malination reaction, since the triglyceride structure is preserved during malination of the oil.

The ^1H NMR spectra of the castor oil alcoholysis products show peaks that belong to hydroxyl functional methylene or methine protons of the polyol in the 3.4–3.8 ppm region. The castor oil hydroxy methine protons also show a multiplet peak in the same region as shown in Figure 6(a). For malination of the alcoholysis products of castor oil, maleic anhydride was used in an equimolar ratio with the number of hydroxyls on castor oil and the polyols used in the alcoholysis reactions. The ^1H NMR spectra of the

TABLE I
The Maleate, Fumarate, and Maleic Anhydride Content (N moles/mole SO) of the SO : PER : MA Reaction Products

(SO : PER : MA) (mole ratio)	$N_{\text{maleates}}/$ mole SO	$N_{\text{fumarates}}/$ mole SO	$N_{\text{MA}}/$ mole SO
1 : 2 : 8	4.55	0.21	1.0
1 : 3 : 12	5.77	0.1	4.4
1 : 3 : 7.6	5.60	0.1	0.9

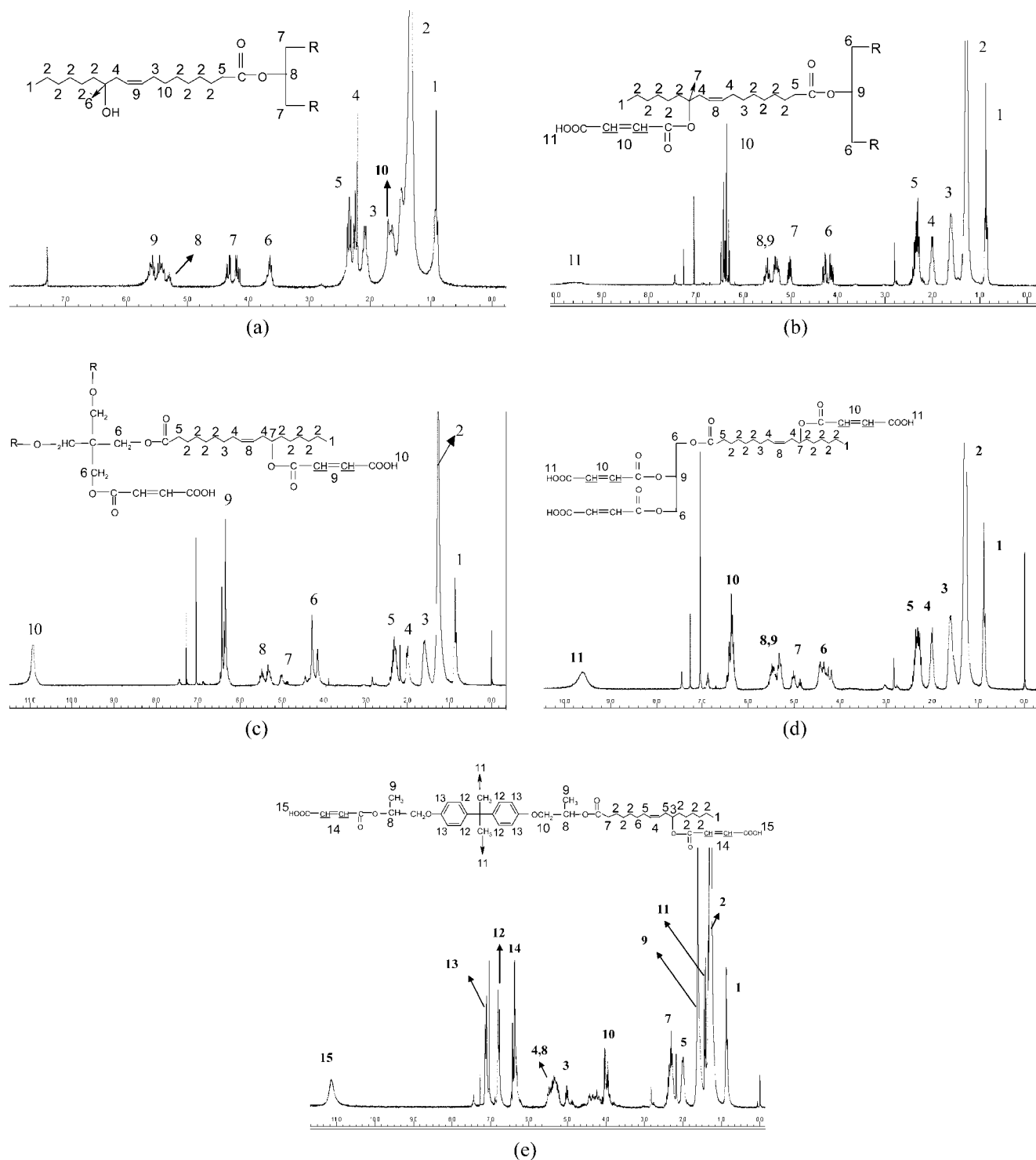


Figure 6 The $^1\text{H-NMR}$ spectra of (a) castor oil, (b) COMA, (c) COPERMA, (d) COGLYCMA, and (e) COBPAPRMA products.

malinated castor oil alcoholysis products COPERMA, COGLYCMA, COBPAPRMA with the peak assignments are shown in Figure 6(c–e), respectively. As can be seen, for all the malinated products, the peaks in the 3.4–3.8 ppm region are totally consumed, showing the conversion of both the castor oil and polyol

hydroxyls to maleate functionality. These spectra are also characterized by the 5.05 ppm peak showing the methine protons (CH-O-CO) of fatty acids connected to maleate functionality, the 6.35 ppm maleate, the 6.9 ppm fumarate, and the acid proton's peak at 9–10 ppm region, in addition to the characteristic

TABLE II
The Maleate, Fumarate, and Unreacted Maleic Anhydride Content of Malinated Castor Oil Alcoholysis Products

Reaction	$N_{\text{maleate}}/\text{mole CO}$	$N_{\text{fumarate}}/\text{mole CO}$	$N_{\text{MA}}/\text{mole CO}$	% Conversion of CO hydroxyls
CO : MA (1 : 3)	2.5	—	0.23	92.6
CO : PER : MA (1 : 2 : 10.7)	7.8	0.15	0.47	96.3
CO : GLYC : MA (1 : 2.2 : 9.3)	5.2	0.4	0.94	85.2
CO : BPAPR : MA (1 : 2 : 6.7)	6.2	0.05	0.50	83

The percent conversions of castor oil hydroxyls to maleates are also listed.

peaks of the castor oil backbone. The ^1H NMR spectrum of the COBPAPRMA product is further complicated by peaks that belong to the bisphenol A propoxy-late moiety as shown in Figure 6(e). For the ^1H NMR analysis of the castor oil based monomers, the 0.9 ppm peak showing the terminal methyl protons of fatty acids ($-\text{CH}_3$) was taken as reference, since the intensity of this peak should not be altered throughout the alcoholysis and the malination reactions. The integral of this peak should show 9 protons per three fatty acids, which corresponds to one mole of castor oil in the original formulation. The maleate, fumarate, and maleic anhydride content of each product with reference to the 0.9 ppm reference peak and the 6.3, 6.9, and 7.1 ppm peaks is shown in Table II. The percent of conversion of castor oil hydroxyls to maleates with reference to the peak at 5.05 ppm that shows the methine protons ($\text{CH}-\text{O}-\text{CO}$) of fatty acids connected to maleate functionality and the 0.9 ppm reference peak are also listed in Table II. The peak that appears at 7.28 ppm in each spectrum represents the residual protons of CDCl_3 . The peak at 7.45 ppm that appears in the ^1H NMR spectra of the malinated products on the other hand shows the aromatic protons of N,N' -dimethyl benzyl amine used as a catalyst for the malination reaction.

The ^1H NMR spectra of the malinated castor oil alcoholysis products show that the conversion of the castor oil hydroxyls to maleate half esters is lower than a complete conversion in all of the products. This may be explained by the dehydration of ricinoleic acid chains that may occur as a side reaction during the alcoholysis of the oil and the malination reaction. The dehydration of ricinoleic acid leads to the formation of 9,12-octa decadienoic and 9,11-octa decadienoic acids.¹⁹ The appearance of the 2.8 ppm peak that is characteristic of the methylene protons between two double bonds ($-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$) in the ^1H NMR spectra of the malinated products confirms the conversion of ricinoleic acid chains of the glycerides to 9,11-octa decadienoic acid chains as a side reaction. Thus, the presence of excess maleic anhydride in the malinated castor alcoholysis products can be attributed both to the loss of castor oil hydroxyls via dehydration during the alcoholysis reaction and to diester formation that may occur during the malination reaction.

Styrenated liquid resin properties

The soybean and castor oil based resins prepared in this study are intended to be used as liquid molding resins. A liquid molding resin should have properties within a certain operating range to be successfully used in molding processes.²³ Possibly the most stringent requirement is the resin's viscosity, which must range between 200 and 1000 cP. At viscosities lower than 200 cP, air pockets will remain in the mold after injection. At viscosities greater than 1000 cP, voids may occur in the part, the time required for injection increases and there can be problems with fiber wetting during composite preparation. Apart from the malinated castor oil, which is a viscous liquid, all the malinated alcoholized oils are solid at room temperature with melting points in the 60–70°C ranges. Thus, they cannot be used without a diluent in a liquid molding process. Additionally the maleates are unreactive in homopolymerization but very reactive in copolymerization with styrene. Styrene is the most commonly used reactive diluent in unsaturated polyester (UP) resins due to its low viscosity, low cost, and reactivity with the unsaturated sites of polyesters. Thus, styrene is used in the formulations to make the resins more processable and to ensure the polymerization of the maleate reactive groups. Table III shows the specific gravity, viscosity (η), and surface energy values for the plant oil based resins containing 33% styrene by weight. As can be seen from Table III, apart from the COMA resin, these resins show viscosities that are in a range that is suitable for liquid molding processes. Although the COMA resin shows a low viscosity, decreasing the amount of the styrene diluent can easily increase the viscosity of the resin. The surface free energy of a liquid, also referred to as surface tension, determines most of the surface and interfacial properties such as wetting, adhesion, and adsorption.²⁴ Surface tension results from an imbalance of molecular forces in a liquid. At the surface of the liquid, the liquid molecules are attracted to each other and exert a net force pulling themselves together. High values of the surface tension means the molecules tend to interact strongly; thus, polar materials show high surface energy values. The surface energy of a liquid molding resin may be especially important

TABLE III
The Specific Gravity, Viscosity (η), and Surface Energy Values for the Plant Oil Based Resins (33 wt % Styrene)

Resin	Specific gravity (g/mL)	Viscosity η (cP)	Surface energy (mN/m)
SOPERMA	0.94	343	27.38
COPERMA	1.06	363	28.84
COGLYCMA	1.04	213	26.36
COBPAPRMA	0.98	183	27.2
COMA	0.90	92	26.02

for reinforcement of the resins by fibers. The wetting of a fiber with a liquid resin can be judged by the difference between the surface energies of the fiber and the resin. For the most desirable condition, proper wetting and spreading in resin transfer molding processes, the surface energy of the fiber should be high, while the surface energy of the resin should be low.

The surface energy values of these resins are in the range of 26–28 mN/m and are significantly lower than those of vinyl ester resins (32–34 mN/m), which may have difficulty in wetting fiber substrates.²⁴ Among the malinated resins, the surface free energy value is highest for the COPERMA resin and the lowest for the COMA resin in proportion with the maleate content of the resins. Higher maleate content should result in a higher polarity and a higher surface free energy.

Phase separation of the malinated glycerides in styrene

All the malinated triglyceride based resins mentioned above showed phase separation in styrene in the microscale. Figure 7 shows the optical microscopic pictures of the SOPERMA–styrene mixtures at decreasing SOPERMA concentrations at 500 \times magnification. The SOPERMA forms nonuniform droplets in the continuous styrene matrix in the 1–5 μ m size range. As can be seen in Figure 7, these droplets become less dense and more uniform in size as the concentration of SOPERMA decreases from 80 to 20 wt %. The optical microscopic analysis of all the other malinated castor oil based resins showed similar phase separation behavior in styrene.

The incompatibility of the malinated plant oil based resins in styrene can be attributed to the abundance of the acid groups of the maleate half esters. The acid number of all the malinated glyceride based resins was found to be above 200 mg KOH/g. This value is much higher than that of the general purpose UP resins (30–35 mg KOH/g). The molecular species present in the malinated glyceride based resins are highly polar compared to styrene, and the strong interactions of these molecules, via hydrogen bonding between the acid groups, result in the incomplete solubility of the malinated glycerides in styrene.²⁵

Polymerization: Determination of conversion

The unsaturation present on the malinated triglycerides is very sluggish in homopolymerization. The reactivity ratio of styrene and maleic/fumaric acid esters is about zero, indicating that this system has a tendency to form alternating copolymers.^{18,26} Since the malinated plant oil based resins were found to be insoluble in styrene at room temperature, it was especially important for us to determine the conversion of polymerization for the maleate and styrene monomers.

The polymerization reaction conversion can be followed by differential scanning calorimetry DSC,^{27–31} and time-resolved FTIR.^{32–36} The cure reaction is an exothermic process, thus the polymerization reaction advancement is directly proportional to the rate of heat generation, and the ultimate extent of conversion is proportional to the total heat that the system is capable of liberating, which can be measured by DSC. While DSC gives information on the average degree of polymerization or the extent of cure, it does not provide information concerning the rate of reaction or degree of conversion of individual species, while FTIR does. Time-resolved FTIR has the advantage of directly determining the concentration of carbon–carbon double bonds (C=C) of different monomers. By following the absorbance peaks of the C=C bonds, one can determine the conversion of different species as well as the total conversion. Thus, the time-resolved FTIR was used here for its ability to determine the conversion of individual monomer species.

Figure 8 shows a sequence of FTIR spectra of a resin mixture of the SOPERMA and styrene taken over the course of polymerization. The important peak assignments are also shown. The peak at 826 cm^{-1} represents the CH=C–H out of plane bending vibrations of the maleate esters. The peak at 910 cm^{-1} represents the CH=C–H out of plane bending vibrations of styrene.³⁷ The C=C stretching vibrations of both the maleate and styrene double bonds show a peak at 1635 cm^{-1} , but this peak developed a shoulder during the cure reaction, and thus was not used in analysis. As these groups polymerized, these peaks reduced in height until the polymerization stopped or the reaction ended. Beer's Law can relate the change in absorbance to the concentration of functional groups. The IR detector response is generally linear for absorbance values less than 2.0, resulting in a direct relationship between concentration and absorbance. To account for differences in absorbance due to evaporation, changing sample thickness, and external factors, internal standards were used, and relative peak heights were used in the calculation of the conversion. For the malinated glycerides, the signal at 1744 cm^{-1} represents the ester carbonyl groups of both the glycerides and the maleate esters. The absorbance signal at 700 cm^{-1} represents the aromatic C–H stretching

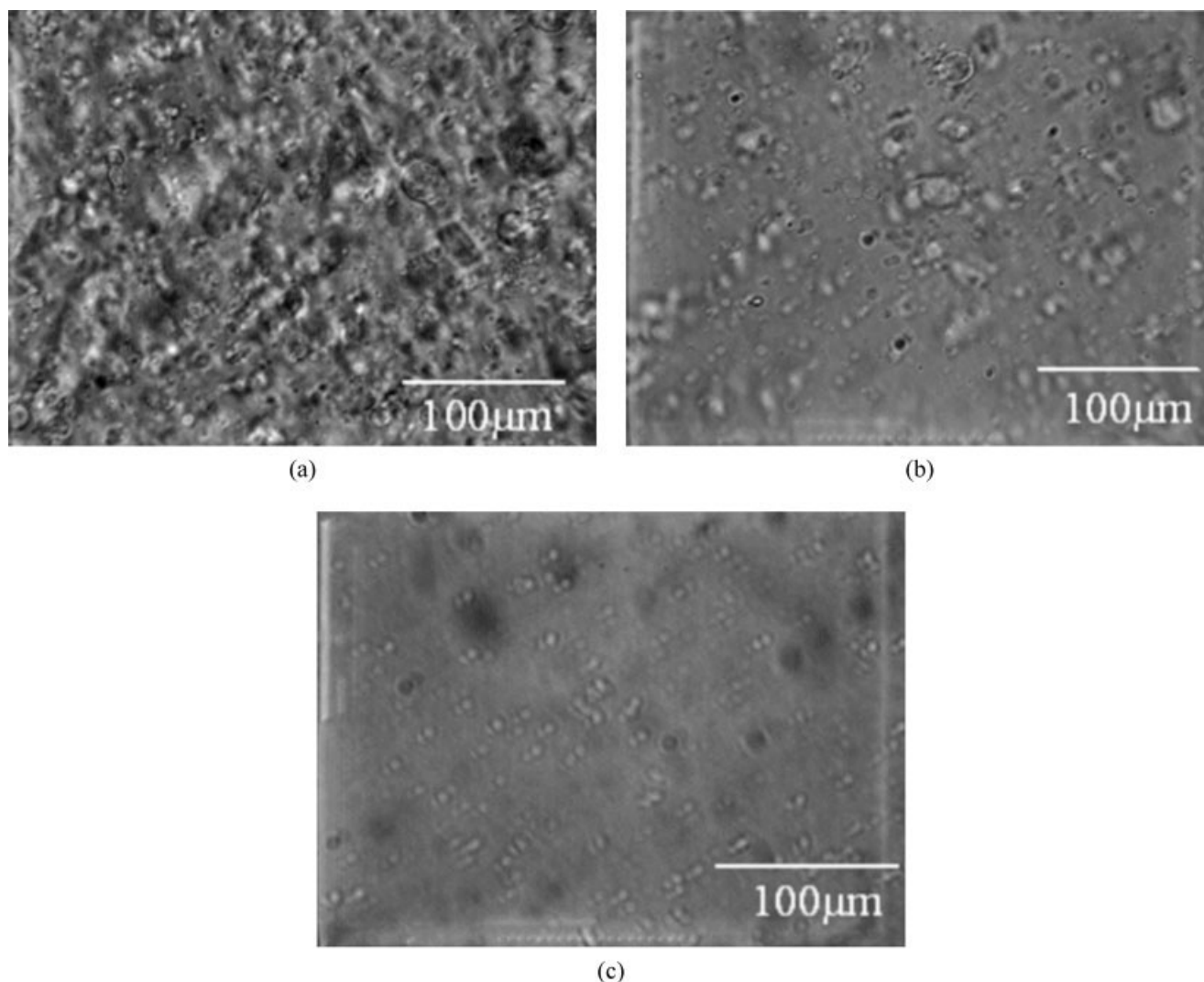


Figure 7 Optical microscopic pictures of the SOPERMA–styrene mixtures (500×): (a) 80 wt %, (b) 60 wt %, and (c) 20 wt % SOPERMA.

vibrations of styrene. Both of these groups are unaffected by the polymerization reaction and act as internal standards. The conversion, (α), can be calculated from the FTIR peak absorption measurements (ABS) as a function of time. The conversion of maleate double bonds, α_{ma} , can be calculated as

$$\alpha_{ma} = 1 - \left(\frac{ABS(t)_{826\text{ cm}^{-1}}}{ABS(t=0)_{826\text{ cm}^{-1}}} \right) \left(\frac{ABS(t=0)_{1744\text{ cm}^{-1}}}{ABS(t)_{1744\text{ cm}^{-1}}} \right) \quad (1)$$

The conversion of styrene double bonds, α_{st} can be similarly calculated as

$$\alpha_{st} = 1 - \left(\frac{ABS(t)_{910\text{ cm}^{-1}}}{ABS(t=0)_{910\text{ cm}^{-1}}} \right) \left(\frac{ABS(t=0)_{700\text{ cm}^{-1}}}{ABS(t)_{700\text{ cm}^{-1}}} \right) \quad (2)$$

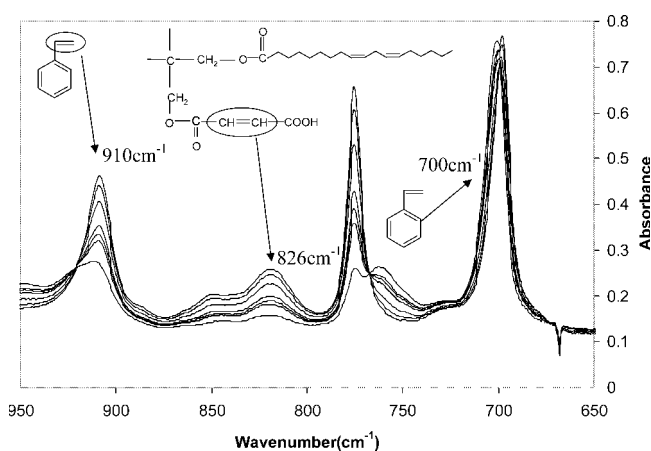


Figure 8 The sequence of FTIR spectra of a resin mixture of the SOPERMA and styrene taken over the course of polymerization.

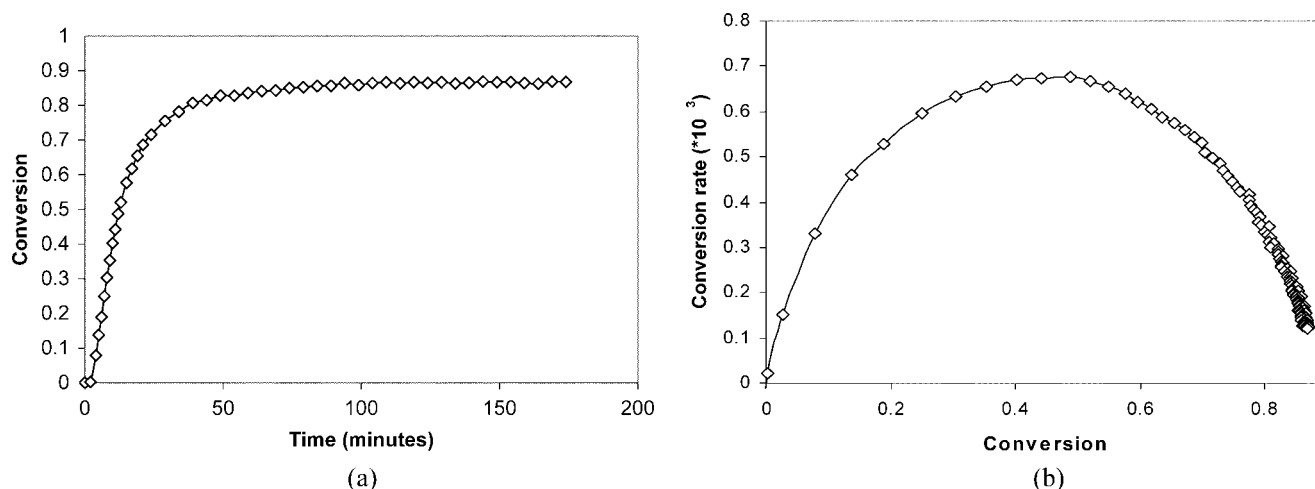


Figure 9 (a) The conversion (α) versus time and (b) conversion rate ($d\alpha/dt$) versus conversion (α) profiles for the SOPERMA resin cured at 120°C for 3 h.

The overall conversion can be calculated from the maleate and styrene conversion according to the following equation:

$$\alpha_t = \phi_{st}\alpha_{st} + \phi_{ma}\alpha_{ma} \quad (3)$$

where ϕ_{st} and ϕ_{ma} are the mole fractions of vinyl groups on styrene and the maleates, respectively, such that their sum equals 1. The FTIR spectra of the styrenated COMA and COPERMA resins showed the same characteristic peaks, and the same equations are used in determination of conversion of polymerization for the COMA and COPERMA resins.

Results of FTIR analysis

The conversions of maleate, styrene, and total carbon-carbon double bonds were tracked using FTIR as a function of reaction time and calculated using eqs. (1)–(3) for the SOPERMA, COMA, and COPERMA resins. The conversion versus time ($\alpha - t$) and cure rate versus conversion ($d\alpha/dt - \alpha$) profiles for the SOPERMA resin cured at 120°C for 3 h are shown in Figure 9(a, b), respectively. All the other resins showed similar profiles. A clear inhibition period, at very low times was not observed during the cure of the resins, since no additional amount of inhibitor was added to the resins apart from the hydroquinone used in the malination reaction (0.1% of the malinated resin weight). At the beginning of the cure process, the rate of polymerization increased drastically, as is expected from an autocatalytic process. The rate of polymerization then decreased at higher conversions due to reduced monomer concentrations and diffusive constraints on the movement of monomers.

The conversion of maleates (α_{ma}) and styrene (α_{st}) as a function of time for the SOPERMA resin are shown in Figure 10. The COMA and the COPERMA

resins showed similar conversion versus time profiles. The maleate conversion was higher than the styrene conversion for all of the resins. It was observed for the SOPERMA and COPERMA resins that after the autocatalytic process, when the polymerization became diffusion controlled, the maleate conversion increased slowly, whereas there was no noticeable increase in styrene conversion. As discussed earlier, during the synthesis of the SOPERMA and COPERMA resins, the maleate half-ester formation is accompanied with maleate diester formation. The maleate half esters or mono-alkyl maleates are especially resistant to homopolymerization, although they are reactive in copolymerization with styrene. The maleate diesters, on the other hand, do homopolymerize. The maleate diesters are reported to yield soft tacky thermoplastics in presence of free radical initiators.²⁶ When considering the phase separation of the malinated glycerides in styrene as well as the resistance of maleate half-esters to homopolymerization and their reactivity through

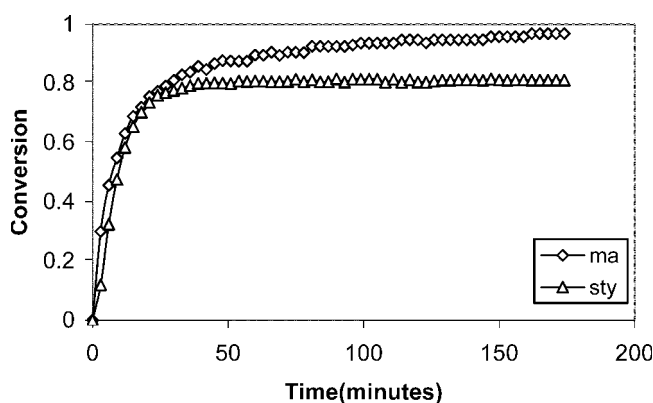


Figure 10 The conversion of maleates, (α_{ma}), and styrene (α_{st}), as a function of time for the SOPERMA resin cured at 120°C.

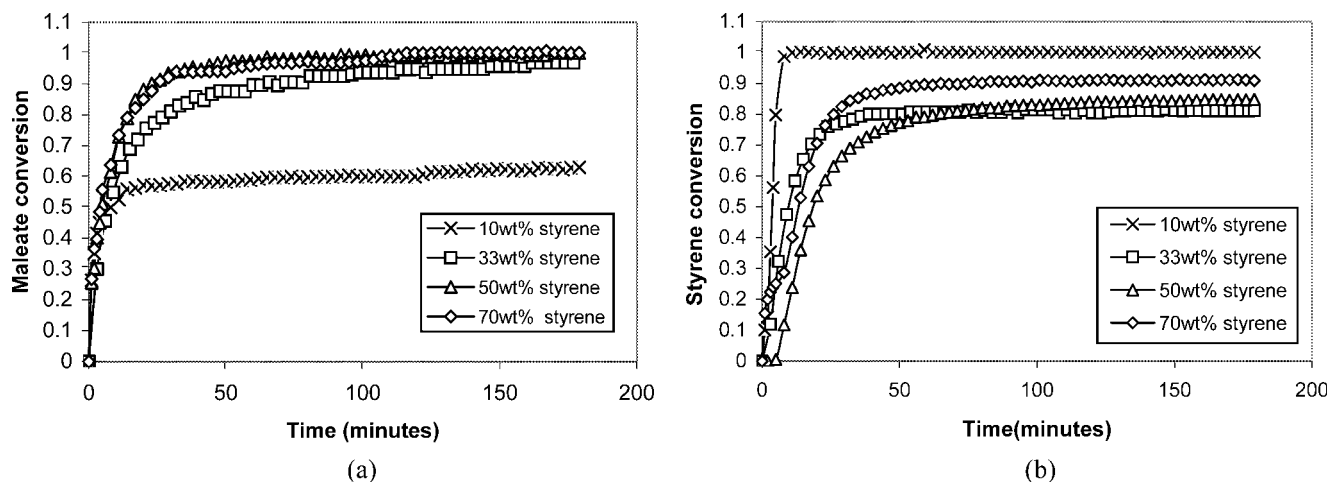


Figure 11 (a) The maleate (α_{ma}) and (b) styrene (α_{st}) conversion versus time profiles at increasing styrene concentrations for the SOPERMA resin cured at 120°C.

copolymerization with styrene, it can be postulated that the maleate half-ester styrene copolymerization took place in the initial stages of the curing process, forming a highly crosslinked system. In fact, maleate half-esters are reported to be used as copolymerizable surfactants.²⁶ In the later stage, the maleate diester double bonds buried inside the glyceride phase homopolymerized, slowly increasing the conversion of maleates.

The effect of styrene concentration on the conversion of maleates and styrene during an isothermal cure of the SOPERMA resin under the same conditions was also explored. Figure 11(a and b) shows the maleate (α_{ma}) and styrene (α_{st}) conversion versus time profiles at increasing styrene concentrations. The total conversion (α) versus time profiles at increasing styrene concentrations are given in Figure 12. As can be seen in Figure 11(a), the maleate conversion significantly increases as the styrene concentration increases. At 10% styrene, ($N_{styrene(C=C)}/N_{maleate(C=C)} = 0.432$) the total maleate conversion reaches only 62% conversion, since there is no sufficient amount of styrene to react with all the maleates in the system, and due to diffusion constraints of the highly crosslinked system. The maleate conversion significantly increases at higher concentrations of styrene and reaches unity at the end of the cure process for 50% ($N_{styrene(C=C)}/N_{maleate(C=C)} = 4.444$) and 70% ($N_{styrene(C=C)}/N_{maleate(C=C)} = 12.5$) styrene. The significant increase in maleate conversion with increasing styrene concentrations can be attributed to both the better solubilization of the malinated glycerides by styrene, and also to the decrease in diffusion limitations with the decreasing crosslink density of the system. The styrene conversion, on the other hand, reaches unity at the very beginning of the cure process at 10% styrene, showing all the available styrene reacts with the maleate half-esters present in

the system. At higher concentrations of styrene, the final styrene conversion is lower than 90% and increases with increasing styrene concentrations. As a result, the total conversion increases with increasing styrene concentration as shown in Figure 12. The increase in the conversion of individual monomers and total conversion with increasing styrene concentrations is a result of better solubilization of the malinated glycerides in styrene, and the decrease in crosslink density both of which should decrease the diffusion limitations on polymerization.

Although all the resins showed similar conversion versus time profiles during the isothermal cure, the final conversion values were different for each resin. Table IV lists the total conversion (α), the conversion of maleates (α_{ma}), and styrene (α_{st}), for the SOPERMA, COMA, and COPERMA resins (33 wt % styrene) at the end of 3 h at 120°C, as well as the ratio of styrene double bonds to maleate double bonds for the

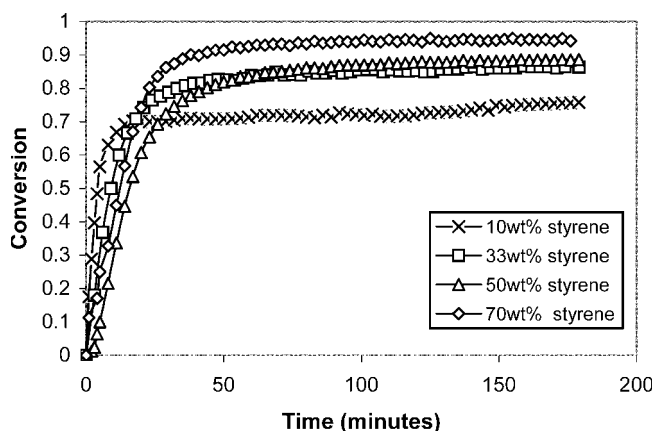


Figure 12 Total conversion versus time profiles at increasing styrene concentrations for the SOPERMA resin cured at 120°C.

starting resins. As can be seen, the final maleate conversion decreases as the maleate content of the resin increases from COMA to COPERMA. The styrene conversion, and thus the total conversion, is also considerably lower for the SOPERMA and COPERMA resins than the COMA resin. It is expected that the molecular mobility of the resin decreases as the crosslink density increases, resulting in lower total conversion. As a result, styrene monomer, as well as some resin, can be trapped in the network and cannot participate in polymerization.³¹ However, although the COPERMA resin has a higher maleate content, therefore a higher crosslink density than the SOPERMA resin, the styrene and thus the final conversions for the SOPERMA and COPERMA resins do not show a significant difference. The cure rate of the resins may play an important role at this point. The diffusion limitations caused by higher crosslink density in the COPERMA resin may be compensated by a significantly higher rate of the cure of this resin compared to the SOPERMA resin.

The maleate conversion was higher than styrene conversion for all of the resins. Ramis et al.³⁰ similarly reported, for the room temperature cure of an UP resin based on propylene glycol, phthalic anhydride and maleic anhydride, that the final conversion of UP double bonds was higher than styrene conversion. The styrene concentration was 31 wt % (mole styrene/mol UP (C=C) = 2.11). The conversion values were as follows, polyester unsaturation conversion $\alpha_p = 0.95$, styrene conversion $\alpha_s = 0.80$, and total conversion $\alpha = 0.85$.

The total ultimate conversion of UPs range from 0.75 to 0.9, and increase with increasing temperatures.³¹ Similarly, the final conversions for the isothermal cure of the plant oil based resins were lower than a complete conversion. During an isothermal cure, when the increasing glass transition temperature of the resin reaches the reaction temperature and the material evolves from the rubbery state to glassy state, the rate of propagation becomes diffusion controlled. This process, referred to as vitrification, may virtually cease the polymerization, limiting the conversion that can be reached isothermally.²⁹

TABLE IV
The Total Conversion (α), Maleate Conversion (α_{ma}), and Styrene Conversion (α_{st}) for the COMA, SOPERMA, and COPERMA Resins (33 wt % styrene) at the End of 3 h at 120°C

Resin	$N_{styrene(C=C)}/N_{maleate(C=C)}$	α_{ma}	α_{st}	α
COMA	1.852	0.998	0.921	0.948
SOPERMA	1.587	0.979	0.828	0.886
COPERMA	1.324	0.952	0.835	0.885

The mole ratio of styrene double bonds to maleate double bonds of the resins before polymerization is also listed.

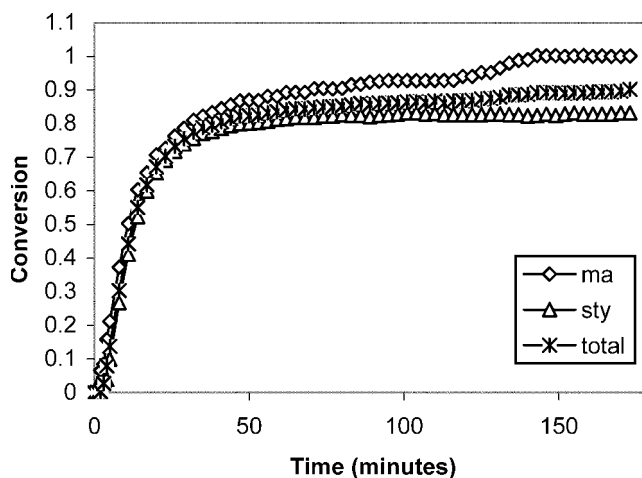


Figure 13 The conversion (α) versus time profiles for the SOPERMA resin cured at 120°C for 2 h and postcured at 160°C for 1 h.

This was especially true for the SOPERMA and COPERMA resins which possess glass transition temperatures (T_g) of 139 and 146°C, respectively, when fully cured. A postcure was necessary for these systems to increase the conversion. Figure 13 shows the conversion versus time profiles for the SOPERMA resin cured at 120°C for 2 h and postcured at 160°C for 1 h. The COPERMA resin cured at 120°C for 2 h and postcured at 160°C showed a similar profile. Figure 13 indicates that the increase of the cure temperature above the glass transition temperature of the system results in a complete conversion for the maleates, whereas no significant effect on styrene conversion is observed. The total conversion (α) at the end of 2 h at 120°C was 0.87 and 0.86 for the SOPERMA and COPERMA resins, respectively. At the end of the postcure process, the total conversion increased to around 0.90 for both of the resins. This result indicates that the postcure process has a significant effect on the total conversion, and thus the crosslink density, which would in turn determine the mechanical properties of the resulting polymers.

CONCLUSIONS

Triglyceride-based monomers were prepared via the malination of the alcoholysis products of soybean and castor oil with various polyols such as pentaerythritol, glycerol, and bisphenol A propoxylate. COMAs were also prepared via direct malination of castor oil. The malinated alcoholized triglycerides were solid at room temperature and diluted with styrene before polymerization. The styrenated, malinated triglyceride based resins showed phase separation in the microscale, which was attributed to the highly polar structure of the maleate half esters compared to the less polar styrene. These resins showed

viscosities that are suitable for use in liquid molding processes at 33 wt % styrene. Time resolved FTIR analysis was used to determine the conversion of polymerization. The maleate conversion was found to be higher than styrene conversion and the maleate conversion continued to increase after the autocatalytic process, although no significant increase in styrene conversion was observed. Since the maleate half-esters are known to be extremely unreactive in homopolymerization, and maleate conversions were as high as 0.9 at the end of the autocatalytic process, it was concluded that the styrene maleate copolymerization took place in the initial stages of the polymerization. The maleate, styrene, and total conversion of polymerization all increased with increasing styrene concentration. This increase in conversion with the increase in styrene content was attributed to the decrease in diffusion limitations with decreasing crosslink density and better solubility of the malinated glycerides in styrene. The thermal and mechanical properties of these polymers will be presented in a following article.

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