Rigid, Thermosetting Liquid Molding Resins From Renewable Resources. I. Synthesis and Polymerization of Soy Oil Monoglyceride Maleates

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ABSTRACT: In this study, rigid thermoset polymers were prepared from radical copolymerization of the soybean oil monoglyceride maleates with styrene. In the first part of the study, soybean oil monoglycerides (SOMGs) were obtained from the reaction of soybean oil with glycerol at 220–240°C with an optimization of the reaction to maximize the monoglyceride yield. In the following step, SOMG were reacted with maleic anhydride at temperatures around 100°C to produce the SOMG maleate half esters. Different catalysts and different reaction conditions were examined to increase the maleate half esters' yields. The reactions were followed by IR and ^{1}H NMR, and the products were characterized by mass spectrometry. In the final step, the radical initiated copolymerization of the SOMG maleates with styrene produced rigid, thermoset polymers. The emulsion copolymerization of the SOMG maleates with styrene was also carried out successfully without the addition of an emulsifier. The obtained polymers were characterized by IR and the crosslinked network structure of the copolymers was examined with the swelling behavior in different solvents. Mechanical properties of the cured resin such as T_g, dynamic flexural modulus, and surface hardness were also determined. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 69–77, 2001

Key words: soybean oil; soybean oil monoglyceride; soybean oil monoglyceride maleates; liquid molding resins

INTRODUCTION

Thermosetting liquid molding resins such as polyesters and vinyl esters have enjoyed a long period of industrial success. They lend themselves to relatively easy and cheap processing, and are extremely versatile. They are also synthesized entirely from petroleum-based chemicals.

Our overall goal in this research is to synthesize liquid thermosetting resins that

1. are suitable for reinforcement with glass, carbon or kevlar fibers;
2. are capable of being processed by the established methods such as hand lay-up, resin transfer, spray-up, filament winding, pultrusion, etc.;
3. have the same mechanical properties as unsaturated polyester or vinyl ester resins;
4. use renewable resources as raw materials.

As a part of this effort, we report here the synthesis and polymerization of maleate half es-
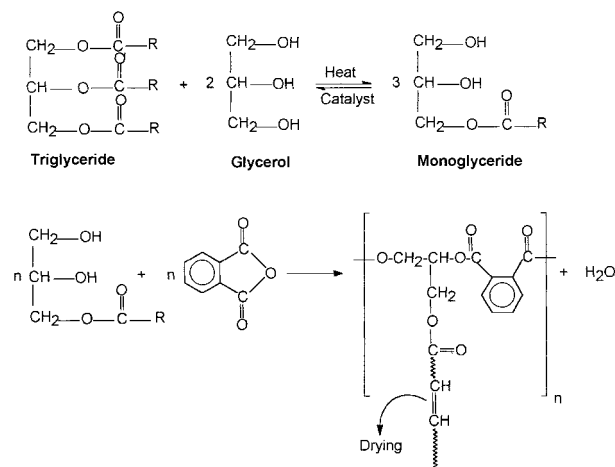
Figure 1 Idealized structure of an alkyd obtained from the glycerolysis process. Alkyd resin components: triglyceride, glycerol, phthalic anhydride.

ters of fatty acid monoglycerides derived from soybean oil. Conversion of plant oil triglycerides to monoglycerides by the well-known glycerolysis reaction[1] and the use of the resulting monoglycerides as the diol component in polyesterification reactions with various diacids and anhydrides is the basis of alkyd resin manufacture.[2] The products are used as binders in paints and varnishes, and are made to "dry" by air-mediated peroxidative crosslinking in the presence of drying agents through the fatty acid unsaturation.[3] This necessarily requires intimate contact with air, and such materials can only be used as thin films with no structural strength. This chemistry is shown in Figure 1. It is also well known that fatty acid double bonds are incapable of homopolymerization due to the facile chain transfer to the many allylic positions in the molecule.[4]

If the monoglycerides derived from plant oil triglycerides were esterified with maleic anhydride to half esters and the resulting polyfunctional monomer was free radically copolymerized with a reactive diluent such as styrene, a network with a high degree of connectivity and hopefully high mechanical strength should be formed. This strategy makes no attempt to produce a polyester, and the half ester formation is expected to proceed at low temperatures and without any by products. Radical initiated copolymerization of the half esters with the reactive diluent should proceed through the maleate unsaturation and this fast polymerization is known to be insensitive to chain transfer. This chemistry is shown in Figure 2.

Literature search indicates that Friedman and Garti[5] have synthesized monoesters of maleic acid using monoglyceride mixtures derived from tallow oil. These products were then sulfonated and used as wetting agents and surfactants, but no effort was made to maximize maleinization yield or to use the reactive maleate unsaturation in a radical initiated polymerization. While polyesters derived from fatty acid monoglycerides with phthalic and maleic acids is known,[3] simple half esters of maleic acid with monoglycerides and the free radical polymerization of the product in presence of reactive diluents such as styrene is new.[6]

EXPERIMENTAL

Reagents and Instruments

The soybean oil (Marsa) used was food grade and was used without further purification. Glycerol (Atabay) was preheated to 220–250°C under N_2 atmosphere for 2 h before the glycerolysis reaction to remove trace amounts of water. The commercially available Haci Sakir soap was used as the emulsifier catalyst for the glycerolysis reaction. Maleic anhydride from Fluka was used without further purification. The catalysts used in the maleinization reactions, their suppliers and puri-
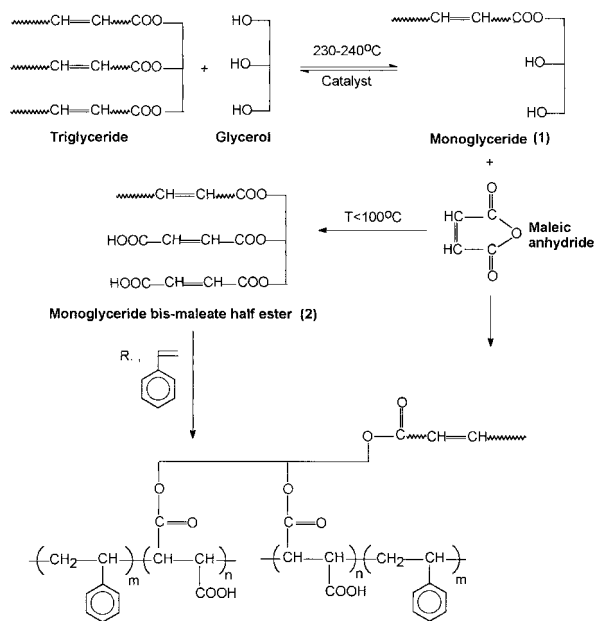

Figure 2 Synthesis and polymerization of soy oil monoglyceride maleates.

ties are as follows; 2-methyl imidazole (Aldrich), 99%; *N,N*-dimethyl aniline (Fisher), reagent grade; p-toluene sulfonic acid (Fisher); sulfuric acid (Akkimya), 98%; NaOH (Hanover), pure. CDCl$_3$ used for ^{1}H NMR analysis was from Aldrich and was spectrometric grade, D$_2$O was from Merck and its purity was 99.75%. The radical initiators benzoyl peroxide (Fisher) and MEKP (Lucidol) were also used without further purification.

The IR analysis was performed on a Perkin Elmer 1600FT-IR spectrometer using KBr windows. ^{1}H NMR spectra were obtained on a Varian T-60A NMR spectrometer. Mass spectra were obtained on a Du Pont 1200 quadruple mass spectrometer operated in secondary ion (SIMS) mode. High performance liquide chromatography (HPLC) analyses were made on a Buchi 688 chromatograph with UV detector.

Glycerolysis of Soybean Oil

The amount of 175 g (1.90 mole) glycerol was placed in a 1 L three necked round-bottom flask, equipped with a mechanical stirrer and a N$_2$ gas inlet, and connected to a downward condenser. Glycerol was then heated to about 220–230°C under N$_2$ atmosphere and kept at this temperature for 2 h during which time 3 mL of water and glycerol mixture was distilled. Then 3.5 g of commercial soap and 350 g soybean oil (0.40 mole, assuming an average molecular weight of 875 for soybean oil triglycerides) was added in five portions in 1 h intervals. The solution was heated for 5.5 h at 220–240°C with mechanical stirring and nitrogen gas sparging. At the end of this time, the reaction flask was cooled with an ice and salt mixture, and the solution was rapidly cooled to room temperature. When cooled to 15°C, some of the excess glycerol in the product separated as a lower layer that was removed and found to weigh 45 g. The amount of 476 g soy oil monoglyceride mixture SOMG (1) was obtained as a viscous oil. IR and NMR data were in good agreement with the structure shown in Figure 2.

Maleinization of SOMG

Ten grams of SOMG was placed in a 50 mL round-bottom flask equipped with a thermometer and a magnetic stirrer, and heated to 80°C. The amount of 6.67 g (0.068 mole) maleic anhydride, 0.1 g 2-methyl imidazole, and 0.1 g of hydroquinone were added to the mixture. The color of the solution changed from yellow to orange. Both IR and NMR data showed that maleic anhydride was totally consumed in 5.5 h at 80°C. The product obtained at the end of reaction, SOMG maleates (2), weighed 15.6 g. Maleic anhydride sublimation on the walls of the flask was observed throughout the reaction. The reaction product was a red-orange viscous liquid that crystallizes during storage at room temperature.

Radical Copolymerization of the SOMG Maleates with Styrene

Bulk Polymerization

The polymerizations were run either in a closed vial or in a teflon mold closed with a microscope slide. SOMG maleate mixture was mixed with 30% of its own weight of styrene to give a straw-colored transparent solution. The viscosity of the solution was 475 cps. One percent benzoyl peroxide was added, the mixture was purged with N$_2$ for 30 min and heated in an oil bath at 90°C until the polymerization was complete. The same reaction could be run with methyl ethyl ketone peroxide/cobalt naphthenate initiator system at room temperature with similar results.

Emulsion Polymerization

The amount of 2.55 g of the SOMG maleates mixture was added with stirring to 10 mL 5% NaOH dropwise, forming a slightly acidic, yellowish emulsion with a pH of 6.9. The amount of 0.90 g styrene was then added with stirring and the yellow color of the emulsion changed into milky white. The emulsion was oil in water type and stable for days with no additional emulsifier used. The emulsion was then placed in a 50 mL round-bottom flask equipped with a condenser and magnetic stirrer and was heated to 80°C. The amount of 0.037 g K$_2$S$_2$O$_8$ dissolved in 3 mL water was added drop by drop to this emulsion. At the end of 2.5 h at 75–85°C with magnetic stirring, a light yellow color suspension separated as an upper layer from the emulsion. The upper layer was removed, washed with water and dried at 100°C in air to give a solid polymeric mass.

Swelling Tests

Rectangular pieces of dimensions about 2 × 5 × 10 mm were cut from the solid samples. The samples were weighed and placed in a closed container containing the solvent. The samples were

Table I   Fatty Acid Weight Composition of Soybean Oil Determined by HPLC Analysis

Fatty Acid	Formula	Weight %
16:0	$C_{16}H_{32}O_2$	10.99
18:0	$C_{18}H_{36}O_2$	3.91
18:1	$C_{18}H_{34}O_2$	31.23
18:2	$C_{18}H_{32}O_2$	52.19
20:0	$C_{20}H_{40}O_2$	0.20
20:1	$C_{20}H_{38}O_2$	0.26

then reweighed at certain time intervals and the weight of the swollen polymer was recorded. The procedure was continued until the polymer was fragmented or the solvent uptake ceased. Determination of water absorption were done according to ISO 62 1980 standard.

RESULTS AND DISCUSSION

Glycerolysis of Soybean Oil

The glycerolysis of triglycerides is an ester interchange reaction and therefore reversible. To increase the yield of maleate half esters it is necessary to maximize the yield of the monoglyceride and minimize diglycerides and unreacted triglycerides. The latter are especially undesirable as they are incapable of radical polymerization and act as plasticizer in the final product. To increase the yield of monoglyceride the use of excess glycerol is indicated, but this is limited by the solubility of glycerol in the triglyceride. To provide intimate contact between the triglyceride and glycerol phases, glycerol can be emulsified in the triglyceride by using a suitable surfactant. Simple soaps seem to be ideal emulsifiers.[7]

While the equilibrium is favorable for monoglyceride formation at high temperature, diglyceride formation becomes significant at low temperatures. So, to prevent reversion at the end of the reaction, the mixture must either be rapidly cooled to a temperature where all transesterification reactions have a negligible rate, or the catalyst must be first destroyed at the high temperature and the mixture subsequently cooled to room temperature. We found that rapid cooling of the mixture with high speed stirring allowed the best yield of soy oil monoglyceride.

The presence of excess glycerol is not detrimental to the overall scheme as it will also be maleinized at the next step and this product can be radically polymerized. But to avoid consuming excess glycerol and to increase the soy oil content of the final product, a method was developed whereby the excess glycerol could be removed as a bottom layer when the mixture was cooled to about 15°C. With these improvements we could show by pentane extraction that the glycerolysis mixture contained no unreacted triglyceride at the end of the reaction.

The SOMG product is a very complicated mixture of positional isomers and glycerol esters of different fatty acids that naturally occur in soybean oil. The HPLC analysis of the fatty acids found in the soybean oil used in this work is summarized in Table I and shows that linoleic acid (18:2) is the most abundant fatty acid. No attempt was made to separate or purify these products as the goal of the research was to demonstrate the suitability of soy oil for the planned syntheses as its naturally occurring mixture. However, NMR and IR analysis of the mixture gives a very good idea about the constituents of the SOMG mixture. In the IR spectrum of the SOMG, the peak at 3384 cm^{-1} belongs to primary and secondary OH groups, and the strong absorption at 1738 cm^{-1} is indicative of the ester functional group. In the NMR spectrum additional peaks in the monoglyceride mixture at 3.7 ppm are indicative of C<u>H</u>—OH and C<u>H</u>$_2$— OH protons. Peaks between 3.5 and 4.5 ppm belong to O<u>H</u> protons as they can be made to disappear upon D$_2$O exchange. Characteristic NMR peak positions for soy oil and its monoglyceride are given in Table II.

Maleinization of SOMG

Maleinization of SOMG mixture with maleic anhydride was tried under various conditions, using

Table II   Chemical Shifts for Different Types of Hydrogen Nuclei in Soybean Oil Monoglycerides

Type of Protons	Chemical Shift (ppm)
—CH$_3$ (terminal)	0.9
—CH$_2$—	1.3
—CH$_2$—CH=CH—	2.0
—C<u>H</u>$_2$—(C=O)—O—	2.3
—C<u>H</u>=CH—C<u>H</u>$_2$—CH=CH—	2.8
—C<u>H</u>—OH, —C<u>H</u>$_2$—OH	3.7
—C<u>H</u>$_2$—O—(C̲=O)—/\/\/\/\	4.2
—C<u>H</u>—O—(C=O)—/\/\/\/\	5.1
—C<u>H</u>=C<u>H</u>—	5.3

Table III Reaction Conditions and Maleinization Efficiency for SOMG + MA System[a]

Run No.	SOMG:MA (Weight Ratio)	Catalyst	T (°C)	Duration (Time Spent Out After MA Addition)	N_m/N_{fa}	N_f/N_{fa}
1	2.34:1	NaOH	80–100	10 min	0.370	—
				5 h	0.388	—
2	1.76:1	NaOH	80–100	1 h	0.357	—
				6 h	0.588	—
3	1.50:1	NaOH	80–100	15 min	0.625	—
				6.5 h	0.625	—
4	1.19:1	NaOH	80–100	50 min	0.500	—
				12.5 h	0.300	0.150
5	1.50:1	H$_2$SO$_4$	50–70	2 h	0.317	—
6	1.50:1	p-toluene sulfonic acid	50–60	15 min	0.322	—
				6 h	0.330	—
7	1.50:1	N,N-dimethyl aniline	60–75	1 h	0.550	—
				6.5 h	0.660	—
8	1.50:1	2-methyl imidazole	80–100	3.5 h	0.650	—
				5.5 h	0.600	—
9[b]	1.50:1	2-methyl imidazole	80–100	35 min	0.800	—
				5 h	0.853	—
10[c]	1.50:1	Heat	180–200	10 min	0.216	0.810

[a] N_m, N_f, N_{fa} refer respectively to NMR signal intensity for maleate, fumurate, and fatty acid vinylic protons.
[b] Reactions carried out in presence of trace amount of hydroquinone.
[c] The product obtained at the end of reaction is insoluble in styrene.

different catalysts, and feed ratios without a solvent. Table III gives the summary of our results. In all cases, except run 10, the reaction temperature was kept below 100°C so that no polyesterification took place. A good indication of the success of this reaction is to follow the signal intensity ratio of maleate vinyl protons to fatty acid vinyl protons in the NMR spectrum (N_m/N_{fa}). Maximizing this ratio will provide a monomer capable of high connectivity when polymerized. In some runs, the amount of maleate unsaturation in the product was found to be lower than predicted based on maleic anhydride consumed. This led us to search for undesirable side reactions that consume maleate unsaturation during the reaction. Literature indicates that some alcohols are capable of Michael addition to α,β-unsaturated esters under basic conditions[8] as shown in Figure 3. Cristobal has shown that a number of diols such as ethylene glycol, 1,4-butylene glycol, and 1,6-hexanediol will add to maleic anhydride in the Michael sense.[9–11] Temperatures where this reaction becomes significant is about 190–200°C and we found that the rate of this reaction could be reduced to negligible at low temperatures.

Homopolymerization of maleic anhydride is not known, but radical-induced dimerization is known. A reaction between the maleate double bonds that goes through a radical mechanism for unsaturated polyesters prepared from maleic anhydride and different glycols has also been mentioned by Cristobal.[11] It has also been stated that the fumarates are more reactive in this reaction. Therefore, the use of a free radical inhibitor such as hydroquinone was indicated and this increased maleate unsaturation ratio in the product from 0.60 to 0.85 (Run Nos. 8 and 9). Another reaction that may consume maleate unsaturation is ene reaction between the fatty ester allylic position and maleic anhydride. In fact, maleinized oils synthesized by this reaction are commercial products.[12] Other work done in our laboratory[13] indicates that, unless Lewis acid catalysts are used or unless the fatty esters have previously been con-
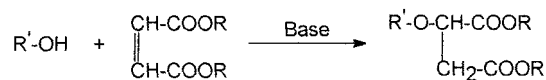
Figure 3 The Michael-type addition of an alcohol to esters of maleic anhydride.

Table IV   Peak Intensities in the Mass Spectra of SOMG + MA Reaction Products with Increasing Maleic Anhydride Feed Ratio[a]

Assigned MWs for SOMG: MA Reaction Products ⇒	SOMG:MA Weight Ratios			
	SOMG:MA 1:1	SOMG:MA 1:1.5	SOMG:MA 1:2	SOMG:MA 1:2.5
338 (Mg—18)	39	15	5	2
356 (Mg)	30	16	8	—
387 (Glyceroltrismaleate)	—	9	25	2
436 (Mgmonomaleate—18)	162	157	139	89
454 (Mgmonomaleate)	62	87	126	10
552 (Mgbismaleate)	16	50	147	84
717 (Dgmonomaleate)	1	4	28	12

[a] Mg = Monoglyceride, Dg = Diglyceride.

verted to conjugated dienes, this reaction requires at least 200°C to be observable. Thus, the choice of low temperatures and the use of radical scavengers was found to increase the yield of the desired maleate half esters and the reaction was optimized in terms of reaction conditions.

While the exact composition of the SOMG mixture is not known, its hydroxyl equivalent is known. The total number of moles of hydroxyl groups in the mixture must be equal to three times the number of moles of glycerol actually used in the reaction, regardless of the position of the equilibrium. Therefore, the maleinization reaction can also be optimized in terms of feed ratio for any given SOMG mixture. To affect this optimization, maleinization of SOMG was tried with different feed ratios of SOMG and maleic anhydride. The product composition was followed by mass spectrometry and the results are shown in Table IV. As expected, increasing maleic anhydride feed ratio decreases the intensity of the SOMG peak (m/e = 356) and increases SOMG monomaleate (m/e = 454), SOMG bis maleate (m/e = 552), diglyceridemonomaleate (m/e = 717), and glycerol tris-maleate (m/e = 387) peaks. The mass spectrum of maleinization product (SOMG:MA = 1:2) is given in Figure 4 and structures assigned to various mass numbers are given in Figure 5. Multiplicity seen in the mass spectra near the intense peaks is due to the natural abundance of various fatty acids in the soy oil.

In terms of the optimization of maleinization catalyst, we found that the best results were obtained with amines. *N,N*-dimethylaniline and diazobicyclooctane (DABCO) gave good results while 2-methylimidazole gave excellent results.

Acidic catalysts such as H_2SO_4 and p-toluenesulfonic acid led to hydrolysis of maleic anhydride, and were therefore not used.

When the maleinization reaction was followed by NMR, it was found that the reaction proceeds very fast initially but slows down towards the end. Thus N_m/N_{fa} ratio reaches 0.8 in only 30 minutes (Run No. 9) but requires another 4.5 h to reach 0.85. We believe that the initial fast reaction is one between the primary hydroxyls of SOMG and maleic anhydride while the slower reaction that takes place afterward is between the secondary hydroxyls and maleic anhydride. As our aim was to maximize the maleate ester yield, longer reaction durations were chosen.

Maleate to fumarate (*cis* to *trans*) isomerization is known to occur on extended heating. This isomerization was also observed in our reactions when the reaction times were extended. (Run No. 4). In terms of radical copolymerization with styrene, fumarates have a higher reactivity than maleates so any fumarate that may have formed is not detrimental to the overall goals of this synthesis.

The best procedure for the maleinization reaction was found to be an 80°C reaction temperature with a 1.5:1 weight ratio of SOMG to maleic anhydride with 1.0% 2-methylimidazole catalyst based on SOMG and 5 h reaction time. These conditions give a combined yield of 93% of all hydroxyl containing compounds as a yellow viscous liquid at room temperature. IR spectroscopy shows the 1779 and 1849 cm^{-1} peaks of the cyclic anhydride diminish as the broad COOH peak between 2500 and 3600 cm^{-1} increases. NMR spectroscopy shows the disappearance of the sharp anhydride vinyl protons
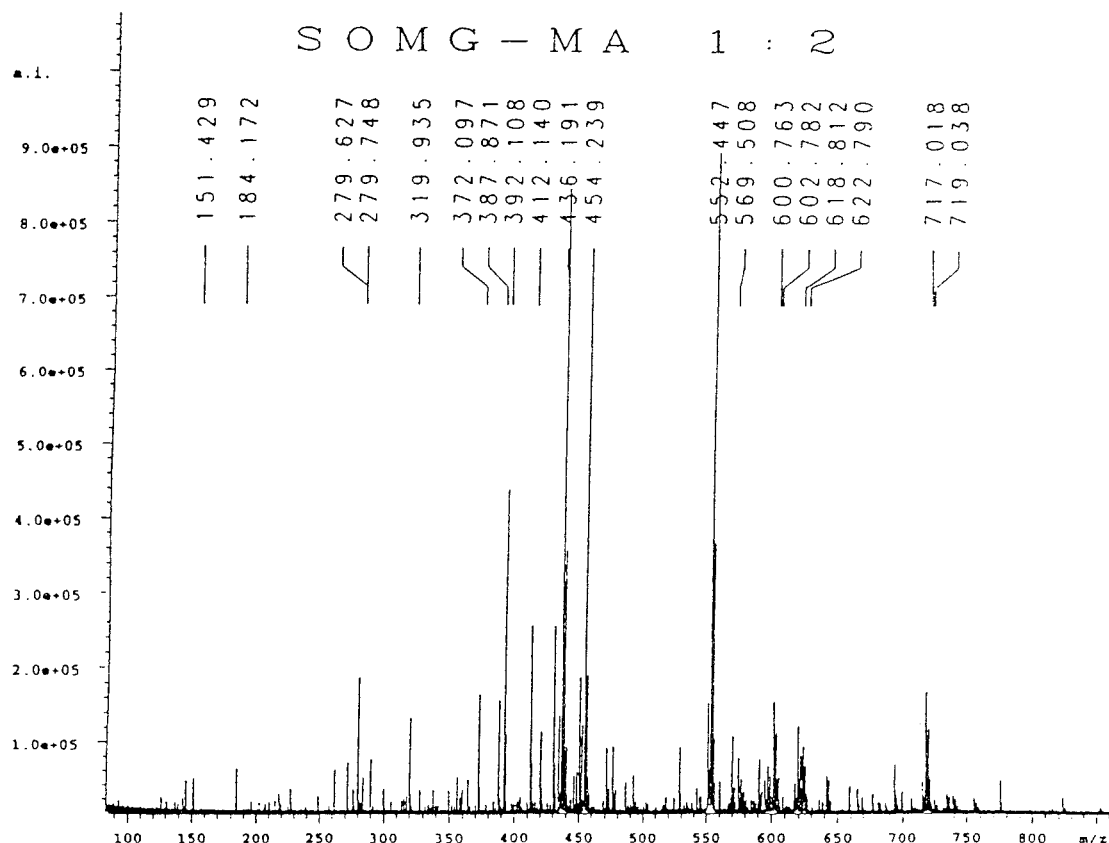
Figure 4 The mass spectrum of the SOMG/MA reaction product (SOMG:MA = 1:2).

at 7.1 ppm, and appearance of maleate and later fumarate ester vinyl protons at 6.35 and 6.90 ppm, respectively. The disappearance of the 3.7 ppm peak due to the C<u>H</u>—OH protons and appearance of COO<u>H</u> protons at 8.95 ppm are additional clues for the formation of maleate half esters. The chemical shifts we observe are in excellent agreement with Grobelney's work[14] on the chemical shifts of maleate and fumarate esters with various alcohols.

Free Radical Initiated Copolymerization of SOMG Maleates with Styrene

All SOMG maleates with the exception of those purposefully heated to 200°C to effect polyesterification, (Run No. 10), were soluble in styrene. Depending on the reaction conditions and stoichiometry of the maleinization reaction, about 30% styrene addition to the viscous liquid maleates gave resins mixtures that have viscosities around 475 cps, a value that is accepted by manufacturers. It was found that the viscosity of the final resin system could be easily adjusted by small changes in styrene content.

The mixture could be polymerized at room temperature or at higher temperatures using the well-established catalyst systems MEKP/Co naphthenate or benzoyl peroxide. The cured product was a straw-colored, clear, rigid solid. Solvent extraction and swelling experiments proved the crosslinked nature of the product. Chloroform and dimethylsulfoxide solvents swelled and fragmented the sample, but did not extract any unreacted monomers or oligomers.

Carbon tetrachloride gave a uniformly swollen but unfragmented sample. The swelling behavior of the sample in carbon tetrachloride is shown in Figure 6.

Water absorption of thermosetting resins is an important parameter as water absorption is usually the first step of premature biodegradation. Water absorption values at room temperature upon 24 h of immersion was 1.05% and at 100°C upon 30 min of immersion was 4.7%. Both of these values compare very favorably with commercial polyester and vinyl ester resins.

The polymerization was followed by IR spectroscopy but the decrease in the intensity of the
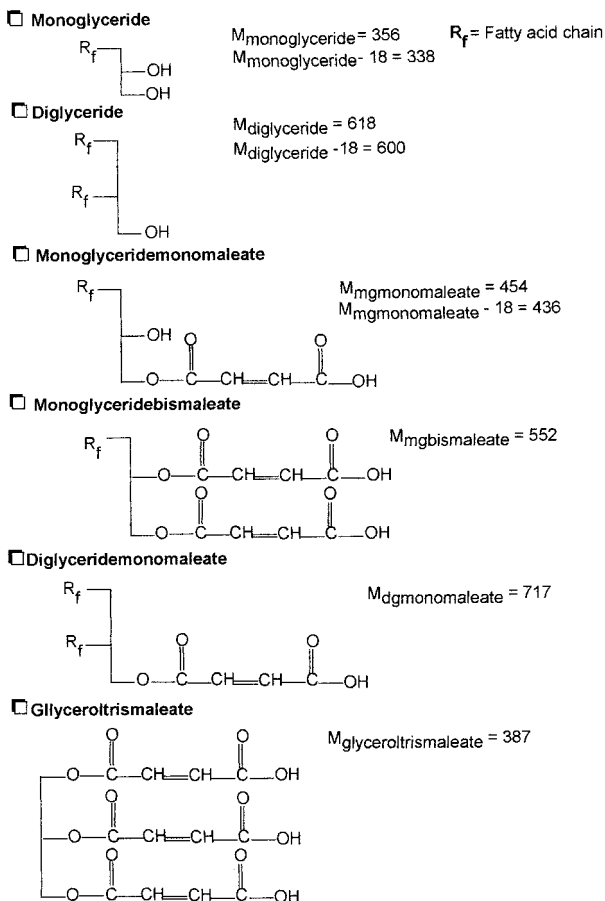
□ Monoglyceride

$M_{monoglyceride} = 356$ R_f = Fatty acid chain
$M_{monoglyceride} - 18 = 338$

□ Diglyceride

$M_{diglyceride} = 618$
$M_{diglyceride} - 18 = 600$

□ Monoglyceridemonomaleate

$M_{mgmonomaleate} = 454$
$M_{mgmonomaleate} - 18 = 436$

□ Monoglyceridebismaleate

$M_{mgbismaleate} = 552$

□ Diglyceridemonomaleate

$M_{dgmonomaleate} = 717$

□ Gllyceroltrismaleate

$M_{glyceroltrismaleate} = 387$

Figure 5 Mass numbers of probable structures expected in the SOMG/MA system.

1640 cm^{-1} unsaturation peak could not be observed due to the overlap of benzene ring absorptions. Carboxyl group and benzene ring absorp-

tions at $2500-3700 \text{ cm}^{-1}$ were observed. Mechanical properties of the cured resin are being examined in detail now, but preliminary tests gave very promising results: T_g determined by differential scanning calorimetry (DSC) is unexpectedly high at 135°C, dynamic flexural modulus as determined by dynamic mechanical analyzer (DMA) is 645 MPa and surface hardness is 72 Shore (D). There is also a good indication that, due to the presence of polar carboxyl groups on the monomer, the final resin shows excellent interfacial adhesion to glass fibers. The properties of various composites made from the new resin are under investigation. There is also clear evidence of participation of the fatty acid unsaturation in the maleate–styrene copolymerization reaction. The nature of this participation and the use of other plant oils with varying degrees of unsaturation in resin preparation is also under study.

Conclusion

The preparation of the styrene-diluted SOMG maleates as final products can be carried out conveniently in one pot. The steps involve glycerolysis of the soy oil, cooling, removal of excess glycerol as a bottom layer for recycle, addition of maleic anhydride to the resulting mixture, maleinization under mild conditions with no byproducts, cooling, and styrene dilution. These steps are all easily carried out with no gaseous or liquid effluents, and in one reactor. The reactor does not require an efficient condenser and there is no need for vacuum application. Therefore, the
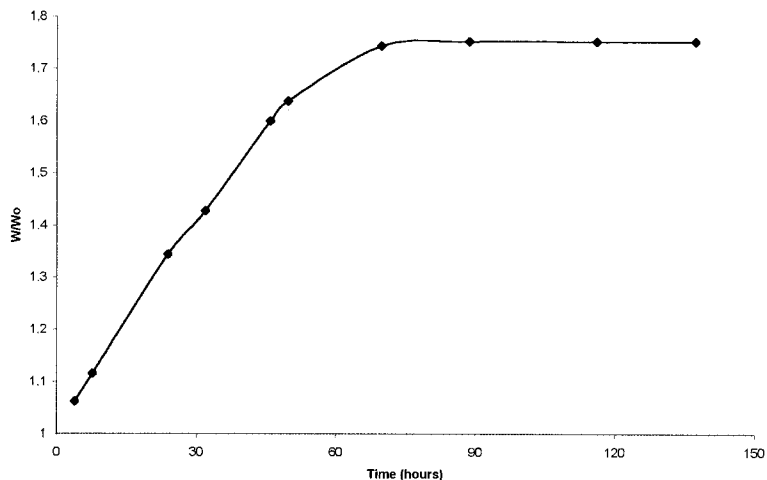
Figure 6 W/W_o vs time graph of the SOMG maleate–styrene copolymer in CCl_4. (W: Weight of the swollen polymer; W_o = weight of the dry polymer.)

overall synthesis is environmentally friendly, cheap, and very suitable for scale-up. Upon free radical initiated cure, the final resin mixture solidifies to a rigid solid that has mechanical properties similar to commercially successful polyesters and vinylesters.

REFERENCES

1. Sonntag, N. O. V. JAOCS 1982, 59, 795.
2. Bailey, A. E. Bailey's Industrial Oil and Fat Products; Wiley: New York, 1985.
3. Solomon, D. H. The Chemistry of Organic Film Formers; Wiley: New York, 1967.
4. Harrison, S. A.; Tolberg, W. E. JAOCS 1953, 30, 114.
5. Friedman, M.; Garti, N. JAOCS 1983, 60, 1134.
6. Wool, R. P.; Palmese, G.; Khot, S.; Küsefoğlu, S. U.S. Patent 6,121,398, September 19, 2000.
7. Edeler, A.; Richardson, A. S. U.S. Patent, 2206167-8, 1940.
8. Trivedi, B. C. Maleic Anhydride; Plenum Press: New York and London, 1982.
9. Cristobal, L. V.; Gilberto, P. M. Polym Bull 1989, 22, 513.
10. Cristobal, L. V.; Gilberto, P. M. J Appl Polym Sci 1991, 43, 1605.
11. Cristobal, L. V.; Gilberto, P. M. J Appl Polym Sci 1993, 47, 121.
12. Metzger, O. J.; Bierman, U. Fat Science and Technology 1994, 96, 321.
13. Küsefoğlu, S.; Eren, T. Unpublished work.
14. Grobelny, J. Polymer 1995, 36, 4215.