

# Rigid Thermosetting Liquid Molding Resins from Renewable Resources. II. Copolymers of Soybean Oil Monoglyceride Maleates with Neopentyl Glycol and Bisphenol A Maleates

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**ABSTRACT:** Soybean oil monoglycerides (SOMG), obtained by the glycerolysis of soybean oil, were reacted with maleic anhydride to produce SOMG maleate half esters. The copolymers of the SOMG maleates with styrene produced rigid thermosetting polymers. The dynamic mechanical analysis (DMA) of this polymer showed a glass-transition temperature ( $T_g$ ) around 133°C and a storage modulus ( $E'$ ) value around 0.94 GPa at 35°C. The tensile tests performed on this polymer showed a tensile strength of 29.36 MPa and a tensile modulus of 0.84 GPa. Mixtures of SOMG with neopentyl glycol (NPG) and SOMG with bisphenol A (BPA) were also maleinized under the same reaction conditions and the resulting maleates were then copolymerized with styrene. The resulting polymers were analyzed for their mechanical properties. The  $T_g$  of the copolymers of the SOMG/NPG maleates with styrene was 145°C and the  $E'$  value at 35°C was 2 GPa. The tensile strength of this polymer as calculated from the stress-strain data was 15.65 MPa and the tensile modulus was 1.49 GPa. The  $T_g$  of the copolymers of SOMG/BPA maleates, on the other hand, was found to be around 131°C and the  $E'$  value was 1.34 GPa at 35°C. The changes observed in the mechanical properties of the resulting polymers with the introduction of NPG maleates and BPA maleates to the SOMG maleates can be explained by the structural changes on the polymer backbone. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 972–980, 2002

**Key words:** liquid resin; fatty acid monoglyceride; maleate half esters; free radical polymerization

## INTRODUCTION

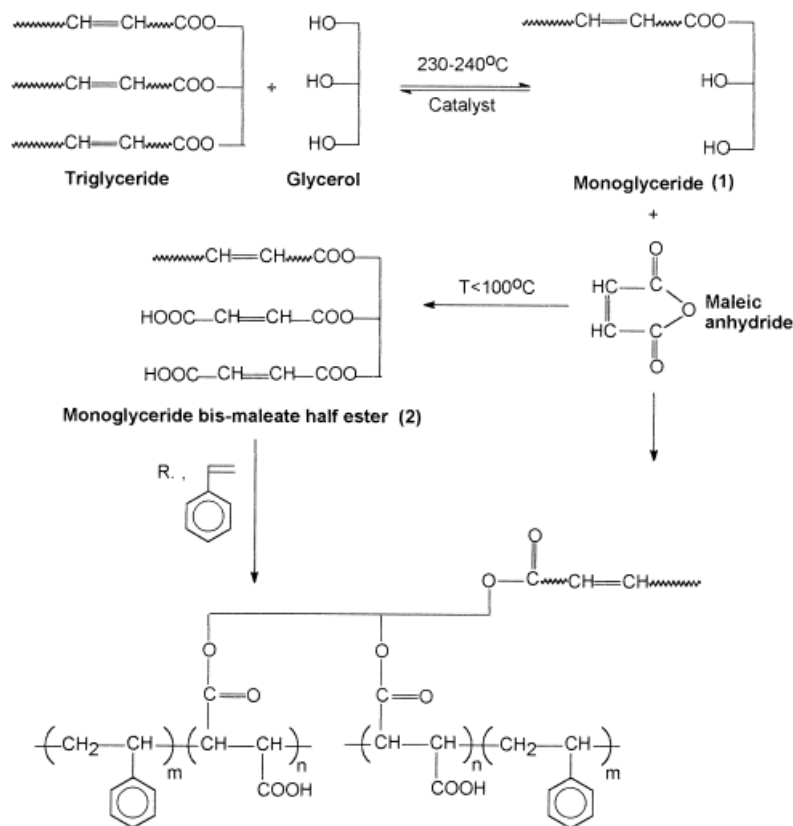
We previously reported our efforts on the synthesis of rigid thermosetting liquid molding resins from soybean oil triglycerides.<sup>1</sup> The successful strategy involved the treatment of soybean oil with glycerol

to produce soybean oil monoglycerides (SOMG), followed by maleinization of the monoglycerides to bismaleate half esters (SOMG/MA), as shown in Figure 1. Mixtures of SOMG/MA with a reactive diluent such as styrene can be free-radically copolymerized to give rigid, load-bearing resins containing up to 70% renewable resources.

In the present report, we describe the effect of adding other, more rigid diols to the maleinization mixture. Addition of neopentyl glycol (NPG)

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**Figure 1** The synthesis and polymerization of soybean oil monoglyceride maleate half esters.

and bisphenol A (BPA) to the maleinization mixture will reduce the renewable resource content of the final resin but should result in higher glass-transition ( $T_g$ ) values, given that both of these diols are known to produce rigid segments in the polymer backbone.

The reaction of a primary and secondary alcohol with maleic anhydride produces maleate half esters at temperatures around 100°C in the presence of either an acid or a base catalyst. Caryl<sup>2</sup> claims that he was able to form over 50 diesters, 50 half esters, and 1225 mixed esters from 50 different alcohols. Dialkyl maleates have often been used as reactants or monomers in place of maleic anhydride because they are liquids and thus are easier to handle.<sup>3</sup> Monoesters made from maleic anhydride and polyhydroxy alcohols (e.g., pentaerythritol, sorbitol, dipentaerythritol, and tripentaerythritol) have been claimed to be useful as detergent builders.

The esterification reaction between maleic anhydride and distilled monoglycerides from tallow and palm oil were investigated under controlled conditions by Friedman and Garti.<sup>4</sup> They ob-

tained maleate esters, which can be used as wetting and detergent agents by sulfonation with sodium bisulfite, to form sodium sulfosuccinic monoglyceryl esters. The present report investigates the effect of neopentyl glycol (NPG) and bisphenol A (BPA) addition to SOMG on the mechanical properties of the final polymers. For this purpose, mixtures of SOMG and NPG, and SOMG and BPA, prepared at the same weight ratio were maleinized and the copolymers of the resulting maleates with styrene were analyzed for their mechanical properties and compared to that of SOMG maleates (SOMG/MA). The synthesis of maleate half esters of organic polyols including NPG and BPA and the crosslinking of the resulting maleate half esters with a vinyl monomer such as styrene were previously reported in two patents.<sup>5,6</sup> The literature also abounds with examples of unsaturated polyesters prepared from NPG and maleic anhydride with some other polyols and diacids.<sup>7-10</sup> However, the copolymers of NPG and BPA bismaleate half esters with SOMG maleate half esters is new.

## EXPERIMENTAL

### Materials

The soybean oil used in the preparation of the SOMG was alkali refined, 100% pure, and supplied by Cargill Company. The glycerol used was 99.5% pure and was obtained from Aldrich Chemicals (Milwaukee, WI). Maleic anhydride used was in the form of briquettes and powdered before use; it was 99.5% pure and was obtained from Aldrich. The NPG and BPA used were both 99% pure and were supplied by Aldrich. The triphenyl antimony used as the catalyst for the maleinization reactions and *tert*-butyl peroxy benzoate used as the radical initiator were both obtained from Aldrich and were 99 and 98% pure, respectively. All the chemicals were used without further purification.

### Instrumentation

The IR analysis was performed on an ATI Mattson FTIR spectrometer using KBr windows. <sup>1</sup>H-NMR spectra were obtained on a Bruker AM 250 NMR spectrometer (Bruker Instruments, Billerica, MA).

### Preparation of Soybean Oil Monoglycerides (SOMG) by Glycerolysis of Soybean Oil

Glycerol (250 g, 2.717 mol) was placed in a 1-L three-neck round-bottom flask equipped with a N<sub>2</sub> gas inlet and a temperature controller, and was connected to a downward-distilling condenser. Glycerol was then heated to 220°C under N<sub>2</sub> atmosphere and kept at this temperature for 2 h, during which time 2 mL of water and glycerol mixture was distilled. Then white soap (5 g) and soybean oil (500 g, 0.5734 mol) were added to the glycerol in four portions at 1-h intervals. The solution was heated for 5.5 h at 220–240°C with mechanical stirring and N<sub>2</sub> gas sparging. At the end of this time, the reaction flask was rapidly cooled to room temperature (RT) with a salt ice bath. During the cooling of the solution, some of the excess glycerol in the product was separated as a lower layer and found to weigh 102 g. The remaining soybean oil monoglyceride mixture (636 g) was a viscous oil.

### Maleinization of Soybean Oil Monoglycerides (SOMG/MA)

SOMG (60 g) was heated to 100°C in a 250-mL round-bottom flask equipped with a temperature

controller and a magnetic stirrer. Maleic anhydride (40 g, 0.408 mol) and triphenyl antimony catalyst (0.6 g) were added. Hydroquinone radical inhibitor (0.01 g) was also added. The temperature was increased to 800°C and the maleic anhydride dissolved in the SOMG, forming a homogeneous solution. The reaction was then followed with IR for the decrease of maleic anhydride peaks. Both IR and NMR data showed that the consumption of maleic anhydride stopped at the end of 5.5 h at 80–100°C and the formation of the maleate half ester was confirmed by the appearance of the 6.3 ppm peak that shows the maleate vinyl protons and also by the appearance of the acid protons, which gave a signal at around 9 ppm in the NMR spectrum. Maleic anhydride sublimation on the walls of the flask was observed throughout the reaction. The product was a yellow colored viscous liquid (93 g) at RT.

### Maleinization of SOMG and NPG Mixture (SOMG/NPG/MA)

SOMG (45 g) was placed into a 250-mL round-bottom flask equipped with a temperature controller and a magnetic stirrer, and was heated to 125°C. NPG (15 g, 0.144 mol) was then added to SOMG and as NPG melted, maleic anhydride (58.3 g) was added. As the three compounds formed a homogeneous solution, triphenyl antimony catalyst (0.06 g) and hydroquinone (0.015 g) were added. The solution was stirred for 6.5 h at 120°C. The <sup>1</sup>H-NMR analysis of the product showed the formation of both the SOMG and NPG maleate and later fumarate vinyl protons at 6.35 and 6.9 ppm, respectively. The product was a light yellow colored viscous liquid (113 g) at RT.

### Maleinization of NPG (NPG/MA)

NPG/MA was synthesized by modifying the procedure given in U.S. Patent 3,784,586<sup>5</sup> in the following way: NPG (25 g, 0.24 mol) was placed into a 100-mL round-bottom flask equipped with a temperature controller and heated to 125°C. As it melted maleic anhydride (47.05 g, 0.48 mol) was added. Maleic anhydride dissolved and formed a colorless homogeneous solution. The reaction temperature was decreased to 115°C and triphenyl antimony (0.25 g) and hydroquinone (0.01 g) were added. The reaction was followed with IR for the decrease in maleic anhydride peaks and the solution was agitated for 5.5 h at 115°C. The <sup>1</sup>H-NMR analysis of the product confirmed the

formation of the maleate and fumarate half esters with the appearance of the signals at 6.35 and 6.9 ppm, respectively. The acid protons gave a signal at 9.05 ppm. The product was not a solid at RT, as indicated in the above-mentioned work, but a light yellow colored viscous liquid with a sweet odor.

#### Maleinization of SOMG and BPA Mixture (SOMG/BPA/MA)

The preparation of maleates of BPA and ethylene and propylene oxide adducts of BPA has been reported in Gardner's patent.<sup>6</sup> In the present work, SOMG and BPA were maleated as a mixture. SOMG (45 g) was placed into a 250-mL round-bottom flask equipped with a temperature controller and a magnetic stirrer and heated to 125°C. BPA (15 g, 0.0657 mol) was added to SOMG and as BPA dissolved, maleic anhydride (42.88 g, 0.4375 mol) was added. As the three compounds formed a homogeneous solution, triphenyl antimony (0.6 g) and hydroquinone (0.01 g) were also added. The solution was then stirred for 9 h at 125°C until maleic anhydride consumption was over. The <sup>1</sup>H-NMR analysis of the product showed the formation of both the SOMG and BPA maleate and later fumarate vinyl protons at 6.35 and 6.9 ppm, respectively. The reaction product was an orange colored viscous liquid (98 g) at RT.

#### Copolymerization of the Maleates with Styrene

The copolymerization of SOMG/MA, SOMG/NPG/MA, NPG/MA, and SOMG/BPA/MA with styrene were all run under the same conditions for comparison of the mechanical properties of the resulting polymers. For this purpose a certain weight ratio of the maleate mixture was mixed with 35% of its own weight of styrene in a closed vial. All the maleate products were found to be soluble in styrene. *tert*-Butyl peroxy benzoate radical initiator, 2% by weight of the total mixture, was added. N<sub>2</sub> gas sparging and vacuum degassing were carried out for 5 min. The solution was then transferred into a rectangular Teflon mold sandwiched between two steel plates. The resin-filled mold was placed in an oven at 30°C and the temperature was increased to 120°C at the rate of 5°C/min and the resin was cured at this temperature for 3.5 h and postcured at 150°C for 1 h. Samples were clear, homogeneous, and free from voids or gas bubbles. The polymer samples were then polished and prepared for DMA analysis.

#### Dynamic Mechanical Analysis (DMA)

The dynamic mechanical analysis of the samples was performed using an RSA II type spectrometer from Rheometrics. The dynamic temperature ramp default test was performed on samples with dimensions of 55 × 10 × 3 mm. Dynamic moduli (storage modulus  $E'$ , loss modulus  $E''$ ) and  $\tan \delta$  ( $E''/E'$ ) values were determined in a temperature range varying between 30 and 200°C with a heating rate of 5°C/min. The dynamic moduli ( $E'$ ,  $E''$ ) and  $\tan \delta$  versus temperature graph was then plotted and the glass-transition temperature ( $T_g$ ) values were determined with the maximum of the  $\tan \delta$  curve.

#### Tensile Testing

The tensile test was conducted in accordance with ASTM D 638-97. The specimens were 112 × 18 × 4 mm in dimension. The length of the narrow section was 35.6 mm. The test was conducted on an Instron Model 4484 testing machine at a constant crosshead speed of 5 mm/min. Force displacement graphs, plotted on a computer, were used to calculate the tensile strength and tensile modulus of the samples from the peak force and the initial straight line region of the force displacement graph. The following equations were used:

$$\sigma = P/WB \quad (1)$$

$$E = mL/WB \quad (2)$$

where  $\sigma$  is the tensile strength,  $E$  is the tensile modulus,  $m$  is the slope of the initial linear region of the force displacement graph,  $L$  is the gauge length,  $W$  is the specimen width, and  $B$  is the specimen thickness.

## RESULTS AND DISCUSSION

There is a close relationship between the structure of a polymer and its mechanical properties. Although the unsaturated fatty acids may form dimers or trimers in the presence of radical initiators,<sup>11</sup> there is no proof for the incorporation of the fatty acid unsaturation in the styrene-maleate copolymerization. The bulky, flexible fatty acid residues present in the SOMG maleate structure decrease the  $T_g$  of this polymer. The introduction of NPG maleates to the SOMG maleates

is designed to improve the mechanical properties (such as  $T_g$ , modulus, and tensile strength) resulting from the replacement of the flexible fatty acid chains by the rigid methyl and methine groups. The introduction of BPA maleates to the SOMG maleates, on the other hand, should work in the same direction because of the incorporation of the rigid benzene ring on the polymer backbone.

### SOMG Maleates (SOMG/MA)

In all the maleinization reactions the weight ratio of SOMG to maleic anhydride was 1.5 : 1, in which maleic anhydride was in a sufficient amount to maleinize all the hydroxyls present in the SOMG mixture. All the maleinization reactions were followed with IR. During the reaction, maleic anhydride characteristic peaks (1779, 1849, and  $696\text{ cm}^{-1}$ ) decrease, whereas the broad acid band between  $2500$  and  $3000\text{ cm}^{-1}$  increases in intensity. The IR spectra of the reaction mixture at both at the beginning and at the end of the reaction are shown in Figure 2. The  $^1\text{H-NMR}$  analysis of the product confirms maleate half ester and later a trace amount of fumarate half ester formation with the appearance of the 6.35 and 6.9 ppm peaks, respectively. The disappearance of the 3.7 ppm peak ascribed to the  $\text{CH-OH}$  protons of the starting material SOMG and the appearance of acid protons that signal at around 9 ppm are additional clues for the formation of half esters. At the end of each reaction both IR and  $^1\text{H-NMR}$  analyses show the presence of small amounts of unreacted maleic anhydride in the final product. This is not detrimental to our ultimate goal, given that maleic anhydride successfully copolymerizes with styrene.

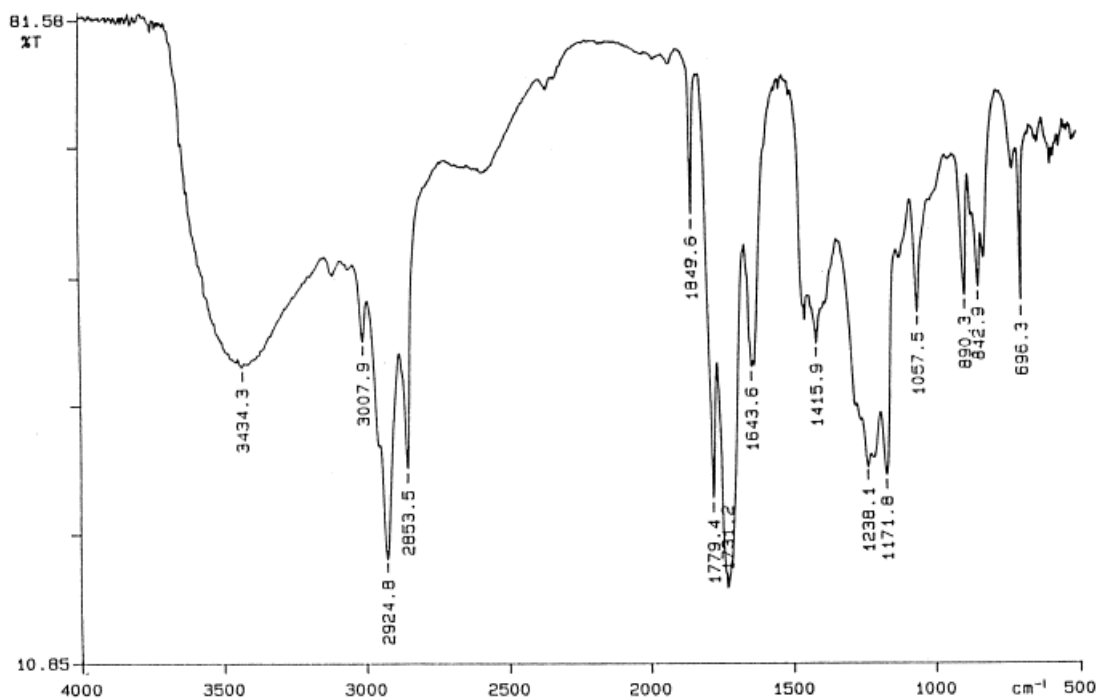
The SOMG maleate mixture was a transparent yellow liquid at RT and was completely soluble in 35% of its own weight of styrene. The cure of this resin at  $120^\circ\text{C}$  for 3.5 h and at  $150^\circ\text{C}$  for 1 h gave a rigid, thermoset polymer. The dynamic mechanical analysis of this polymer showed a  $T_g$  around  $133^\circ\text{C}$  and an  $E'$  value around 0.92 GPa at  $35^\circ\text{C}$ . The temperature versus  $\tan \delta$  curve is shown in Figure 3. The  $\tan \delta$  curve is rather a broad curve because of the broad MW distribution of the SOMG maleates. In fact, the formation of the soybean oil monoglyceride monomaleates, monoglyceride bismaleates, diglyceride monomaleates, and glycerol trismaleates was confirmed by the mass spectral analysis of the SOMG maleate mixture: the detailed information about the mass spectral analysis of this product was reported in a

previous publication.<sup>1</sup> The tensile tests performed on the copolymers of SOMG maleates with styrene showed a tensile strength of 29.36 MPa and a tensile modulus of 0.84 GPa, as calculated from the force displacement graph.

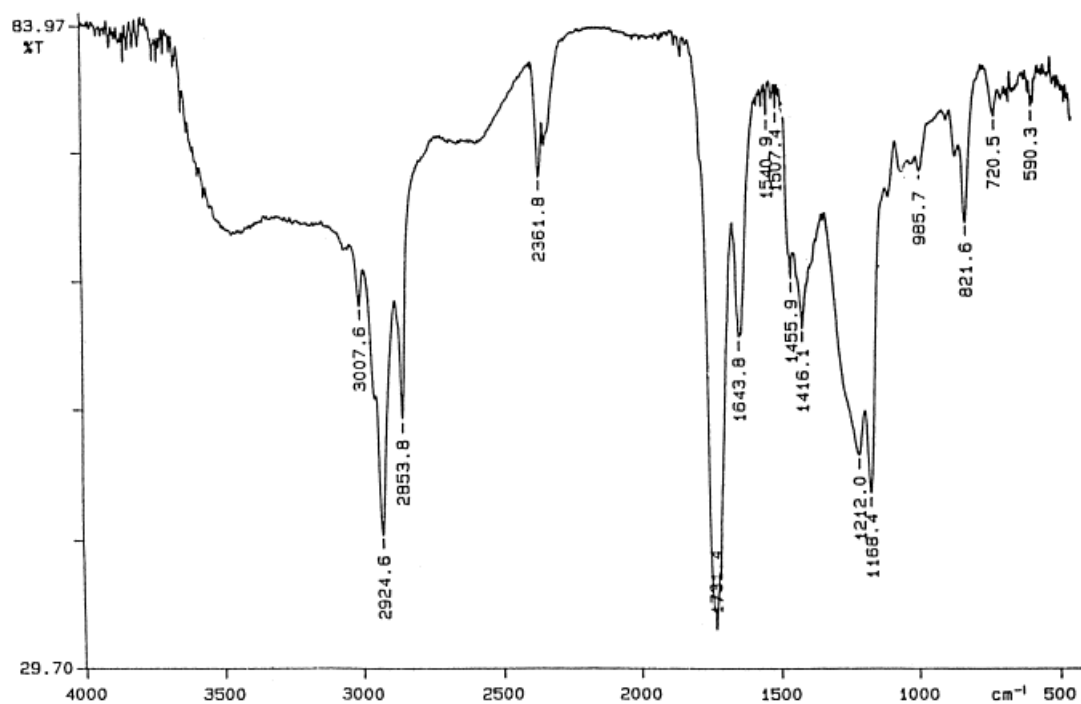
### SOMG/NPG Maleates (SOMG/NPG/MA)

The maleinization of the SOMG-NPG mixture was run in a similar manner to the maleinization of SOMG. The  $^1\text{H-NMR}$  analysis of this product was different from that of the SOMG maleates with the additional NPG's methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2\text{O-O-}$ ) protons' signal, respectively, at 1 and 4.05 ppm. The  $^1\text{H-NMR}$  of this product is shown in Figure 4. Both the SOMG and NPG maleate vinylic protons gave a signal at the same chemical shift value, 6.35 ppm. The acid protons' signal appeared further downfield at 10.3 ppm. At the end of the reaction 17% of the total unsaturation was found to be isomerized to the fumarate isomer, whose chemical shift is around 6.9 ppm. A good indication of the success of this reaction is to follow the signal intensity of the ratio of the maleate and fumarate vinyl protons to fatty acid vinyl protons in the NMR spectrum. The ratio of the total number of maleate and fumarate vinyl protons to that of fatty acid vinyl protons whose signal appears at 5.3 ppm was found to be 2.38, whereas the same ratio for the SOMG maleates was 0.9. This implies a high yield for the maleate half ester formation and therefore a high crosslinking density for this product. In fact the maleinization of pure NPG, under the same reaction conditions with the same catalyst, produces the NPG bismaleate half esters nearly by 97% yield as calculated from the  $^1\text{H-NMR}$  data. This is attributed to the presence of only primary hydroxyl groups on NPG, whereas SOMG has both primary and less-reactive secondary hydroxyls.

The SOMG/NPG maleate mixture was a light yellow colored viscous liquid at RT, and as the SOMG maleated, it was soluble in 35% of its own weight of styrene. The cure of this resin at  $120^\circ\text{C}$  for 3.5 h and at  $150^\circ\text{C}$  for 1 h gave a rigid, thermoset polymer. The dynamic mechanical analysis of this polymer showed a  $T_g$  around  $145^\circ\text{C}$  and an  $E'$  value of 2 GPa at  $35^\circ\text{C}$ . The tensile strength of the SOMG/NPG/MA samples, as calculated from the stress-strain data, was found to be 15.65 MPa, whereas the tensile modulus was found to be 1.49 GPa.



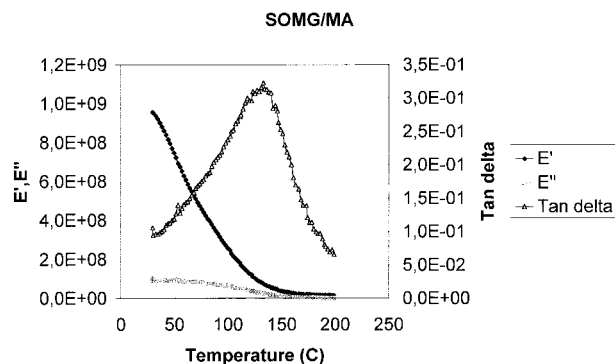
(a)



**Figure 2** IR spectrum of SOMG/MA: (a) at beginning of reaction; (b) at end of reaction.

The 12°C increase in the  $T_g$  and the considerable increase in the modulus of the copolymers of SOMG/NPG maleates with styrene compared to

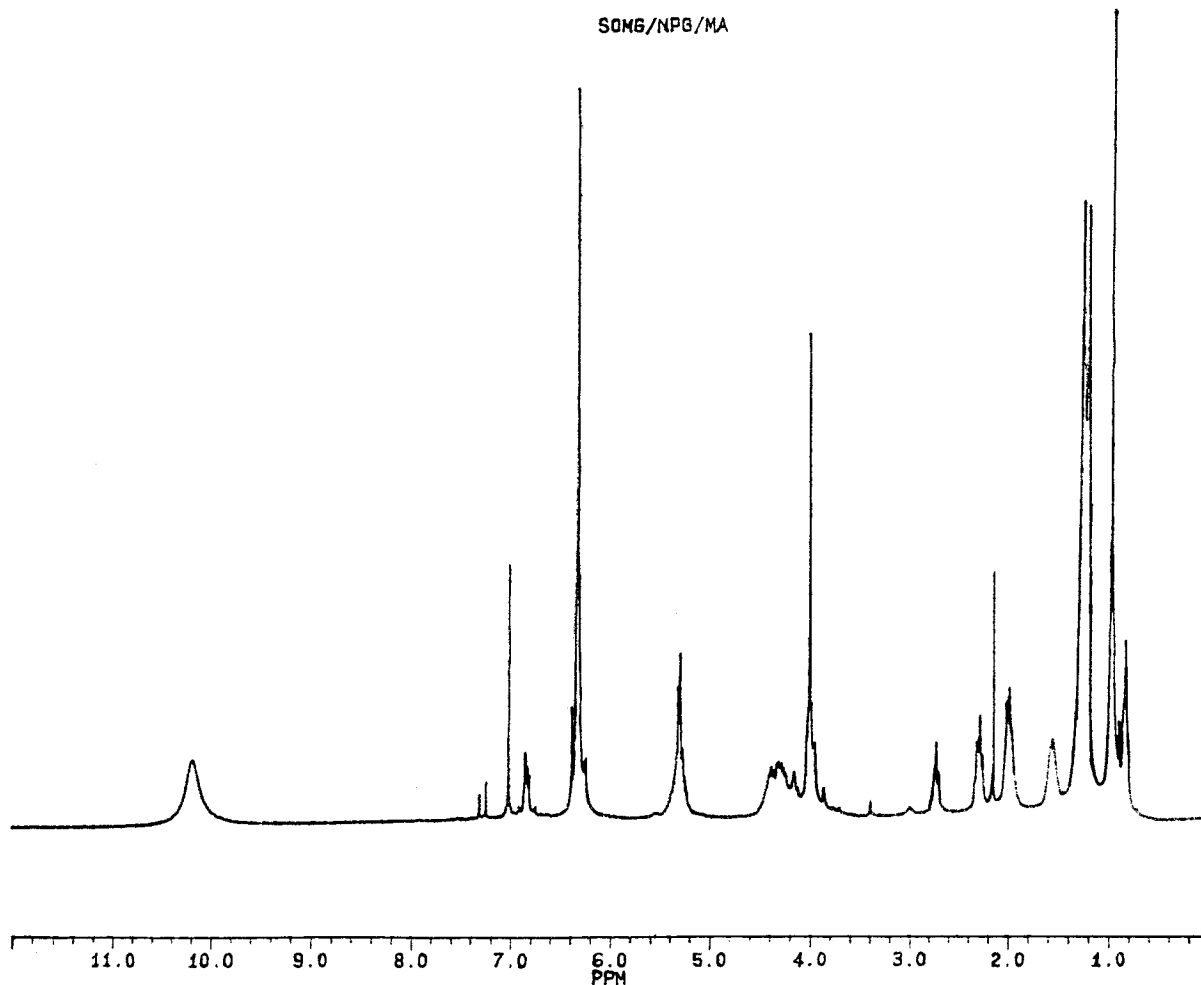
that of the SOMG maleates can be attributed to the replacement of the flexible fatty acid chains by the rigid methyl groups of NPG. The maleinization of



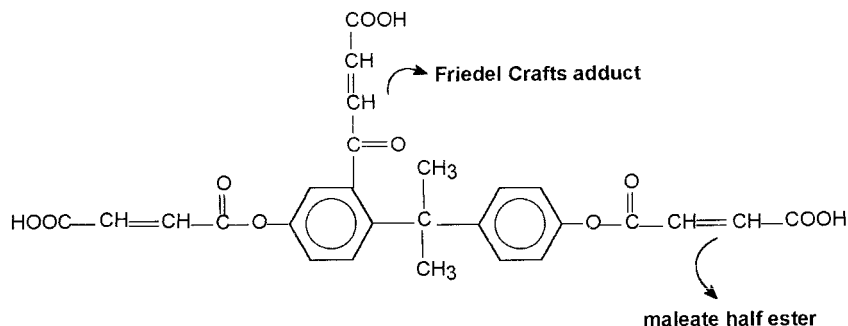
**Figure 3**  $E'$ ,  $E''$ ,  $\tan \delta$  versus temperature curves for the SOMG/MA–styrene copolymer.

pure NPG and the copolymerization of the resulting NPG bismaleates with styrene produced a rigid, thermoset polymer. This experiment was carried out to compare the resulting properties of this poly-

mer to those of the SOMG/NPG maleates. The DMA analysis of the copolymers of the NPG maleates with styrene showed a  $T_g$  around 103°C and an  $E'$  value around 2.27 GPa at 35°C. The high  $T_g$  value (145°C) observed for the SOMG/NPG/MA system should be a synergetic effect of both the NPG and SOMG together because the  $T_g$  value observed for the NPG/MA system (103°C) is much lower. This is probably a result of the incorporation of the fatty acid unsaturation into the polymer in the SOMG/NPG/MA system. The comparatively higher  $E'$  value observed for the NPG maleates, on the other hand, explains the increase in the  $E'$  observed for the SOMG/NPG/MA system compared to that of the SOMG/MA system. The decrease in tensile strength of the SOMG/NPG/MA system compared to that of SOMG/MA may be attributed to a broader MW distribution of this system compared to that of the SOMG maleates.



**Figure 4**  $^1\text{H}$ -NMR spectrum of the SOMG/NPG/MA product.



**Figure 5** The structure of Friedel–Crafts acylation side product for the BPA maleates.

### SOMG/BPA Maleates (SOMG/BPA/MA)

The maleinization of the SOMG and BPA mixtures was run in a similar manner to that of the SOMG–NPG mixture. The time of the reaction was longer and the mixture was agitated for 9 h at 125°C. The  $^1\text{H}$ -NMR analysis of this product was different from that of the SOMG maleates, with the additional peaks at 1.65, 6.7, and 7 ppm showing the methyl and the phenolic *meta*- and *ortho*-position protons of BPA, respectively. Both the SOMG and BPA maleates gave a signal at 6.35 ppm and fumarates at 6.9 ppm. The ratio of the total number of maleate and fumarate vinyl protons to the number of fatty acid vinyl protons was 0.87. This value is even lower than 0.9, the ratio obtained for the SOMG maleates prepared at the same SOMG maleic anhydride weight ratio. At the end of the reaction 22% of the total unsaturation was found to be isomerized to the fumarate *trans*-isomer. The  $^1\text{H}$ -NMR analysis of this product also showed that the integral of BPA's *ortho*- and *meta*-position protons' signals at 7.0 and 6.7 ppm, respectively, were not equal; considering the structure of the BPA bis-maleate half ester, they should have been the same. However, the integral of the *ortho*-position protons' signal was found to be higher than that of the *meta*-position protons' signal. This led us think that Friedel–Crafts acylation may also have taken place

as a side reaction with the maleate half ester formation. However, this acylation has no adverse effects on the final polymerization because this reaction also produces a reactive compound for the polymerization. The possible structure of this side product is shown in Figure 5. No further attempts were made for structure proof.

The SOMG–BPA maleate mixture was an orange colored viscous liquid at RT and, like the other maleate mixtures, it was soluble in 35% of its own weight of styrene. The cure of this resin at 120°C for 3.5 h and at 150°C for 1 h gave a rigid, thermoset polymer. The dynamic mechanical analysis of this polymer showed a  $T_g$  around 131°C and an  $E'$  value of 1.34 GPa at 35°C. The introduction of the rigid benzene ring on the polymer backbone caused a considerable increase on the modulus of the final polymer compared to that of the SOMG maleates. The  $T_g$  of this polymer, however, was found to be even lower than that of the SOMG maleates (133°C) as a result of a lower maleate yield of this reaction, as detected from the  $^1\text{H}$ -NMR data. Mechanical properties of the new polymers are summarized in Table I.

### CONCLUSIONS

SOMG maleates, obtained by the maleinization of soybean oil monoglycerides, were copolymerized

**Table I** Mechanical Properties of SOMG/MA, SOMG/NPG/MA, and SOMG/BPA/MA Resins

Type of Resin	$T_g$ (°C)	$E'$ (GPa) (35°C)	$E''$ (GPa) (35°C)	Tan $\delta$	Tensile Modulus (GPa)	Tensile Strength (MPa)
SOMG/MA	133	0.94	0.089	$3.23 \times 10^4$	0.84	29.36
SOMG/NPG/MA	145	2.01	0.152	$3.12 \times 10^{-1}$	1.49	15.65
SOMG/BPA/MA	131	1.34	0.122	$3.64 \times 10$	—	—



with styrene and the mechanical properties such as  $T_g$ ,  $E'$ , tensile strength, and tensile modulus of the resulting polymers were determined. The introduction of the NPG maleates to the SOMG maleates caused an increase in the  $T_g$  and modulus and a decrease in the tensile strength of the final polymers. The introduction of the BA maleates, on the other hand, did not lead to a considerable difference in the  $T_g$ , although a slight increase in the modulus of the resulting polymers was observed.

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