

## TUNG OIL BASED MONOMER FOR THERMOSETTING POLYMERS: SYNTHESIS, CHARACTERIZATION, AND COPOLYMERIZATION WITH STYRENE

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A tung oil (TO) based monomer for rigid thermosetting polymer was synthesized, characterized, and copolymerized with styrene in this study. Tung oil was alcoholized with pentaerythritol (PER) to get tung oil pentaerythritol alcoholysis products (TOPER), and the optimized conditions were explored according to the yields of TOPER analyzed by gas chromatography-mass spectrometry (GC-MS). The resulting alcoholysis products were maleinated to form tung oil maleate half ester (TOPERMA), and the reaction conditions were determined by monitoring the reaction extents of TOPER and maleic anhydride (MA) with <sup>1</sup>HNMR spectroscopy. The TO alcoholysis and maleinization reaction products were characterized by IR, <sup>1</sup>HNMR, and electrospray ionization-mass spectrometry (ESI-MS) techniques. At last, the TOPERMA mixture was cured with styrene (St), and the initiator tert-butyl peroxy benzoate (TPB). Differential scanning calorimetry (DSC) was employed to characterize the curing process. Mechanical properties of the cured TOPERMA/St resin further confirmed the best procedure for the maleinization reaction. The loading of TO reached about 30% weight of the resulting thermosetting polymer. This promising material from renewable resources can be a potential substitution for petroleum products when used as sheet molding compounds.

*Keywords:* Polyester; Tung Oil; Monoglyceride; Thermosetting polymer; Sheet Molding Compound

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### INTRODUCTION

Petroleum-derived unsaturated polyester resin (UPR) is currently the most widely utilized thermosetting polymer because of its low cost, ease of handling, and good balance of mechanical, electrical, and chemical properties. The reinforced composite materials of UPR have been broadly employed in aerospace, automotive, marine, infrastructure, military, sports, and industrial fields. However, polymer materials derived from natural products have gained increased attention in recent years due to the threats of uncertain petroleum supply in the future and environmental pollution. These natural products include renewable substances, such as carbohydrates, proteins, and biological oils. Plant oils are suitable starting materials for polymers due to their abundance, the rich chemistry that their triglyceride structure provides, and their potential biodegradability.

As a result, development of bio-based UPR polymers from plant oils is being accelerated.

Although the use of plant oils in the polymer fields as coatings and films has been long studied, the research in the preparation of polymer matrixes from plant oils is relatively new. One approach to prepare plant oil-based UPR resin is to mix oils or derivatized oils with UPR polymers. For instance, Mehta et al. (2004) designed and engineered biocomposites from plant bio-fibres and a blend of UPR and derivatized vegetable oil, to replace existing glass fiber-polyester composites for use in housing applications; Haq et al. (2008, 2009a,b) prepared bio-based resins by a partial substitution of UPR with epoxidized soybean oil, and then reinforced them with natural fibers and nanoclays; Miyagawa et al. (2006, 2007) used UPR containing epoxidized methyl linseedate or soyate to prepare novel bio-based resins; Penczek et al. (2004) modified UPR with vegetable oil and dicyclopentadiene to improve mechanical and thermal properties of UPR. Another approach is to introduce polymerizable functional groups onto the triglyceride structure by using the reactive sites available. Unsaturated polyester-like resins can be obtained by functionalizing the oil triglyceride molecules. Actually, thermosets from oils can be obtained from the reaction of the C=C bonds in the fatty acid chains of triglyceride with other reactive vinyl monomers, through cationic, thermal, or free radical polymerization. For example, Crivello et al. (1997) prepared fiberglass-reinforced composites by ultraviolet and visible irradiation of epoxidized vegetable oils in the presence of cationic initiators; Larock et al. and their coauthors (Li et al. 2000; Li and Larock 2001, 2003; Andjelkovic et al. 2005; Lu and Larock 2006; Pfister et al. 2008; Sharma et al. 2010) developed new thermosetting resins by cationic polymerization of a series of oils, including soybean, corn, linseed, tung and fish oil, with petroleum-based comonomers such as styrene, divinyl benzene, and dicyclopentadiene. The inferior mechanical and thermo-physical properties of these new composites inspired other researchers to design new high-performance materials from plant oils. Wool et al. and their coauthors (Wool et al. 2000; Eren et al. 2003; Lu et al. 2005; Wool and Sun 2005; Can et al. 2006) have developed a broad range of chemical routes to utilize plant oils to make polymers and composite materials that can be used in structural applications. These methods of functionalizing plant oils have been adopted in others' work: Sen et al. (2010) synthesized polymeric nanocomposites from functionalized soybean-oil-based polymer matrix and montmorillonite clay using an in-situ free radical polymerization reaction; Fu et al. (2010) demonstrated acrylated epoxidized-soybean oil-based thermosets; Mosiewicki et al. (2005) made composites from derivatized linseed oil and woodflour. Besides, La Scala et al. (2004) and Can et al. (2007) have obtained some fatty acid-based monomers as styrene replacements from oleic acid to decrease the volatile organic compound emissions caused by styrene.

Tung oil is readily available as a major product from the seeds of tung trees, and China contributes to about 80% of the world TO production. The principal constituent of this oil is a glyceride composed of alpha-elaostearic acid (cis-9, trans-11, trans-13-octadecatrienoic acid). This highly unsaturated, conjugated triene system makes it an excellent drying oil at room temperature, used principally in the preparation of paints, varnishes, and related materials (Li et al. 2003). However, few publications have reported the preparation of a polymer matrix from TO, and usually the mechanical properties of the TO matrix cannot compete with the properties of a general-purpose UPR (Li et al.

2003; Pfister et al. 2008).

Our goal was to synthesize liquid thermosetting resins from TO. In this paper, we reported the synthesis and polymerization of a TO polymer matrix according to the route reported by Wool et al. (2000, 2006). Unsaturated polyester-like resins were obtained by functionalizing the TO triglyceride molecules in two basic steps: alcoholysis with PER to produce TOPER and reaction with MA to produce TOPERMA. The TOPERMA product was further blended with styrene, the reactive comonomer, and cured via a free-radical polymerization to get a crosslinked thermosetting polymer. The ideal reaction scheme is shown in Fig. 1. The aim of this work was to characterize the TOPER, TOPERMA products and optimize the reaction conditions for preparation of the TO polymer matrix.

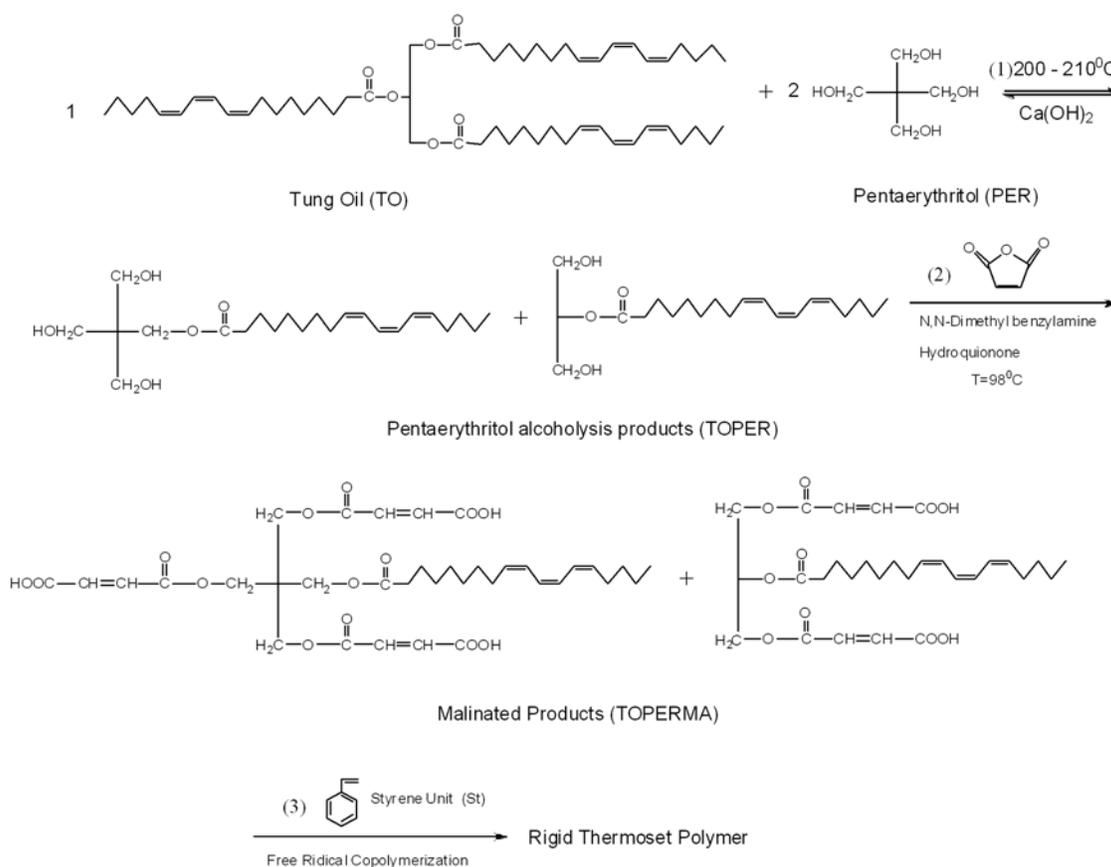


Fig. 1. Ideal reaction scheme for the synthesis of TOPERMA from TO triglyceride molecules

## EXPERIMENTAL

### Materials

The tung oil employed was a commercial product purchased from Jiangsu Donghu Bio-energy Plant Plantation (China). Tung oil has a yellow color and a specific gravity of 0.935-0.940 at  $25^\circ\text{C}$ . Pentaerythritol ( $\geq 98\%$ ) and Maleic anhydride ( $\geq 98\%$ )

in a solid state were obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd (China). Calcium hydroxide ( $\geq 98\%$ ) and *N, N*-dimethyl benzyl amine ( $\geq 98\%$ ) were obtained from Institute of Tianjing Chemical Reagent (China). Hydroquinone ( $\geq 98\%$ ) and styrene ( $\geq 98\%$ ) were obtained from Chengdu Kelong Chemical Reagent Co. Ltd (China). The initiator tert-butyl peroxy benzoate ( $\geq 98\%$ ) was obtained from Aladdin Chemistry Co. Ltd (Shanghai, China).

## Methods

### *Preparation of TOPER*

About 87.2 g (0.1 mol) of tung oil, 27.2 g (0.2 mol) pentaerythritol, and 1.14 g  $\text{Ca}(\text{OH})_2$  were placed together in a 250-mL four-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, a  $\text{N}_2$  gas inlet, and a refluxing condenser with a calcium drier. The flask was placed in a heating mantle with a temperature controller. The reaction mixture was heated to 200-210 °C and agitated under  $\text{N}_2$  atmosphere for 3 h at this temperature. Soap formation on the solution was observed during the reaction, especially at around 150 °C. At the end of 3 h, the product was cooled to room temperature. The reaction product TOPER at room temperature was a brown viscous liquid.

### *Maleinization of TOPER with MA*

For the maleinization reaction, 57.7 g alcoholysis product, 39.2 g (0.4 mol) of maleic anhydride, and 0.095 g of hydroquinone were added to the same reaction device used in the alcoholysis process. The mixture was heated to around 70 °C by an oil bath and agitated at this temperature for 0.5 h until the maleic anhydride melt and mixed with TOPER. Then 0.96 g *N, N*-dimethyl benzylamine was added and the reaction mixture was heated to 95 °C under  $\text{N}_2$  atmosphere. The mixture was agitated at this temperature for 5 h. The malinated product TOPERMA with a light yellow solid at room temperature was obtained. The acid value of TOPERMA resin was 211 mgKOH/g. At last, TOPERMA was mixed with 1/3 of its own weight of styrene to give a light brown transparent resin. The viscosity of the TOPERMA/33%St resin was 1050 cps.

### *Copolymerization of TOPERMA with St*

About 90 g of TOPERMA/33%St resin was mixed with TPB, the initiator, at a 1.5% of the resin weight. Thus, the loading of TO reached about 30% weight of the resulting thermoset polymer. The resins were purged with nitrogen gas for 20 min, and the residual oxygen was removed by pumping for 10 min. Then the resins were poured into home-made molds brushed with a mold release agent. The filled molds were placed in an oven at room temperature. The temperature was increased to 120 °C at a rate of 5 °C /min. The resins were cured at this temperature for 3h and postcured at 150 °C for 1h. The cured samples were polished slightly to avoid a surface defect in mechanical tests.

## Characterization

### *Instrumentation*

The IR analysis was performed on a Nicolet iS10 IR spectrometer. The  $^1\text{H}$ NMR spectra were obtained on a Bruker DRX-300 Advance NMR spectrometer. The mass

spectra were recorded on a WATERS Q-TOF Premier mass spectrometer using electrospray ionization (ESI).

The TOPER were analyzed using an Agilent 7890A/5975C GC-MS with a HP-5MS column (30m×250µm×0.25µm) under a helium flow of 1.54 mL/min. Samples were dissolved in toluene/ethanol mixture with a 1:1 volume ratio. The injection-port temperature was set at 290 °C. The oven-temperature program was initially set at 50 °C for 2 min and ramped to 290 °C at a heating rate 10 °C/min. The MS method contained multiple SIM functions overlapped by a m/z 50 to m/z 550 full-scan function. The mass spectrometer transfer line and ion source were heated to 280 °C.

A PerkinElmer Diamond DSC was used for the dynamic cure experiments under an argon flow of 20 mL/min and supported by a PerkinElmer computer for data acquisition/analysis. The dynamic (non-isothermal) DSC experiments were conducted at heating rates of 5, 10, 15, and 20 °C /min in a scanning temperature range from 25 to 220 °C.

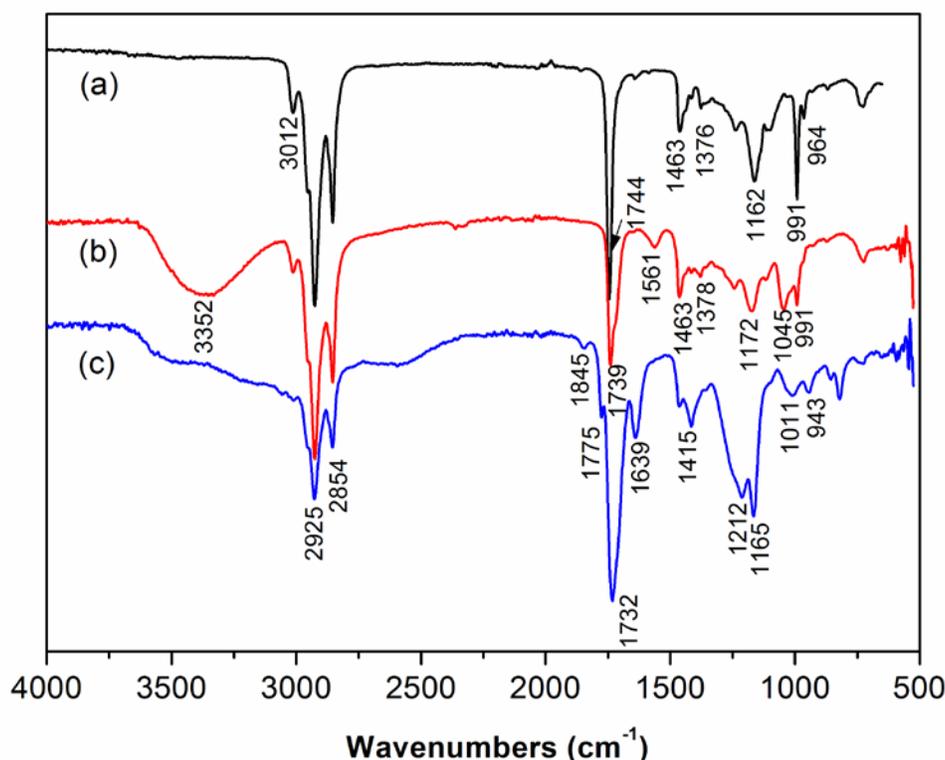
#### *Testing of Mechanical Properties*

The tensile and flexural tests of the matrix samples were evaluated using a SANS7 CMT-4304 universal tester (Shenzhen Xinsansi Jiliang Instrument Co. Ltd, China), following the procedure specified in the GBT 2567-2008 standard. Dumbbell specimens with a size of 50×10×4 mm<sup>3</sup> at the narrow middle part were conducted for the tensile tests at a constant draw speed of 5.0 mm/min. Cuboid specimens with a size of 100×15×4 mm<sup>3</sup> were performed for flexural tests at a constant crosshead speed of 10 mm/min.

## RESULTS AND DISCUSSION

### Characterization

The TO alcoholysis and maleinization reaction products were characterized by IR, <sup>1</sup>HNMR, and ESI-MS techniques. Figure 2 shows the FTIR spectra of TO, TOPER, and TOPERMA samples. The TO structure is characterized by the conjugated triene in TO molecules at 3012, 991, and 964 cm<sup>-1</sup> as well as the strong ester carbonyl peak of the glycerides at 1744 and 1050-1290 cm<sup>-1</sup>; the methylene and methyl of the TO glycerides were evident from the stretching at 2925 cm<sup>-1</sup> and 2854 cm<sup>-1</sup>, and bending at 1463 and 1376 cm<sup>-1</sup>. The alcoholysis products of the oil with polyols carry the characteristic features of both PER and the glyceride structure. The TOPER structure is characterized by a broad hydroxyl band at around 3352 cm<sup>-1</sup>, a strong ester carbonyl peak at 1739 cm<sup>-1</sup>, and the characteristic feature of the TO conjugated triene at 3012, 991, and 964 cm<sup>-1</sup>. The strong ester carbonyl peak of TOPER at 1739 cm<sup>-1</sup> is shifted from the peak of TO at 1744 cm<sup>-1</sup>, indicating the occurrence of the alcoholysis reaction. This ester carbonyl peak of TOPER has a shoulder compared with the single narrow peak of TO at 1744 cm<sup>-1</sup>, clearly showing that TOPER contains two kinds of ester carbonyl groups (Fig. 1). The primary alcohols of TOPER and residual PER bend apparently at 1045 cm<sup>-1</sup>. Ca(OH)<sub>2</sub> reacted with free fatty acids in the oil to form soaps, leading to the stretching absorbance of carboxylate at 1561 cm<sup>-1</sup>.



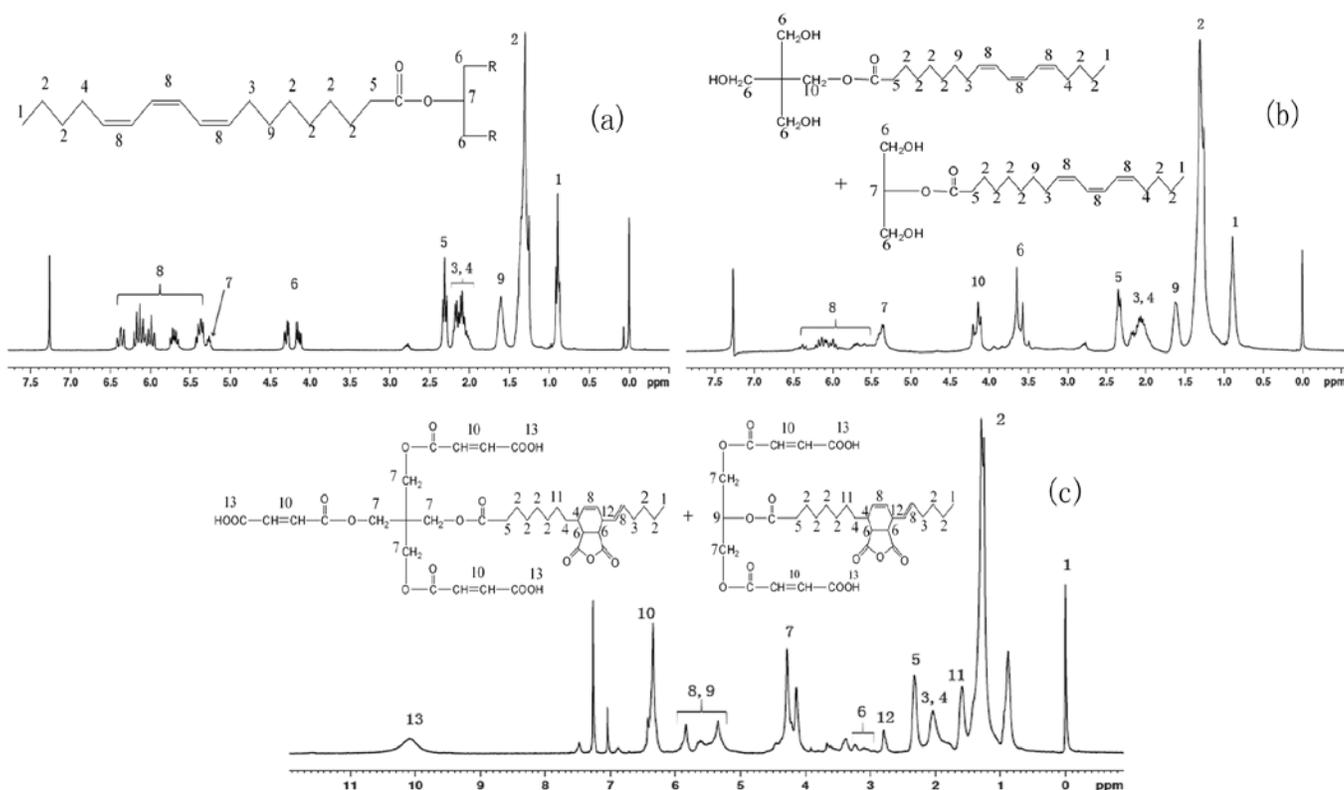
**Fig. 2.** FTIR spectra of (a) TO, (b) TOPER, and (c) TOPERMA

The hydroxyl band of the alcoholysis product at  $3352\text{ cm}^{-1}$  is replaced by a broad acid band of maleate half esters at  $2500\text{--}3400\text{ cm}^{-1}$  as the maleinization reaction proceeds. The strong ester carbonyl peak of TOPERMA at  $1732\text{ cm}^{-1}$  is shifted from the peak of TOPER at  $1739\text{ cm}^{-1}$ . This carbonyl peak of TOPERMA has a higher intensity than those of TO and TOPER when the peak intensity of methylene and methyl groups at around  $2925$  and  $2854\text{ cm}^{-1}$  is set as reference. The reason lies in the fact that more ester carbonyl groups have been formed in TOPERMA, as shown in Fig.1. The peaks at  $1639\text{ cm}^{-1}$  mainly denotes the carbon double bonds on the MA structure. All of these changes indicate the occurrence of the maleinization reaction. There are still some unreacted MA molecules, as evidenced by the carbonyl (C=O) asymmetric and symmetric stretching vibrations at  $1775$  and  $1845\text{ cm}^{-1}$ . The characteristic features of the TO conjugated triene at  $3012$ ,  $991$ , and  $964\text{ cm}^{-1}$  are undistinguishable, which may be attributed to that the MA unsaturation partially reacted with the conjugated triene in TOPER by Diels-Alder (D-A) reaction. The D-A reaction is an organic cycloaddition reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene system, which requires very little energy to create a cyclohexene ring (Nicolaou et al. 2003).

Figure 3(a) shows the  $^1\text{H-NMR}$  spectrum of TO. The peaks at  $4.0\text{--}4.4\text{ ppm}$  and  $5.2\text{--}5.3\text{ ppm}$  correspond to the protons of the glycerol backbone in a glyceride unit, indicating that the TO used in this study has a triglyceride structure. The multiple peaks in the  $5.3\text{--}6.5\text{ ppm}$  region show the protons of conjugated trienes in the triglyceride. For the  $^1\text{HNMR}$  analysis of the TO, TOPER, or TOPERMA mixtures, the peaks at around  $0.9\text{ ppm}$  showing the terminal methyl protons of fatty acids ( $-\text{CH}_3$ ) were always taken as

reference, because the intensity of these peaks should not be altered throughout the alcoholysis and the maleinization reaction. The integral of this peak should show 9 protons per three fatty acids, which corresponds to a TO molecule in the original formulation. As referenced by the terminal methyl protons at 0.9 ppm, we calculated that a single TO triglyceride has 15.6 protons in the structure of TO conjugated trienes, which means a conjugated triene in TO only has 2.6 carbon double bonds. TO is a triglyceride oil primarily composed of a fatty acid containing a conjugated triene, however, it also contains fatty acid side chains with non-conjugated double bonds, which is evidenced by the presence of a minor peak at 2.8 ppm corresponding to the protons in the methylene groups between two non-conjugated double bonds ( $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ ).

Figure 3(b) shows the  $^1\text{H-NMR}$  spectrum of TOPER. The multiplet peaks in the 3.3–3.8 ppm region belong to hydroxyl functional methylene protons of the polyol. The peaks at 4.0–4.4 ppm show the methylene protons of the polyols backbones connecting to the ester structure ( $-\text{CH}_2-\text{O}-(\text{C}=\text{O})-\text{CH}_2-$ ).



**Fig. 3.**  $^1\text{H-NMR}$  spectra of (a) TO, (b) TOPER, and (c) TOPERMA

Figure 3(c) shows the  $^1\text{H-NMR}$  spectrum of TOPERMA. The TOPERMA product is characterized by the maleate vinyl protons' peak at 6.3 ppm as well as the peak of the acid protons at around 10.1 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 a higher temperature than the reaction temperature (Can et al. 2000). The peaks at

6.3, 6.9, and 7.1 ppm, representing the maleate, fumarate, and MA vinyl protons respectively, can be used to determine the reaction extent of MA. The intensity of the peaks at 3.3–3.8 ppm is decreasing during the maleinization reaction, which can be used to monitor the reaction extent of TOPER. As the maleinization reaction of the alcoholysis product proceeds, the protons at 3.3–3.8 ppm are converted to those at 4.0–4.5 ppm, the methylene protons of the polyols backbones connecting to the ester structure. The intensity peaks at 2.8 ppm belonging to the protons in the  $-\text{CH}_2-$  groups between two nonconjugated  $\text{C}=\text{C}$  bonds becomes sharp, indicating the yield of a new structure like  $-\text{CH}=\text{CH}-\underline{\text{CH}_2}-\text{CH}=\text{CH}-$ . This can be interpreted that the D-A reaction

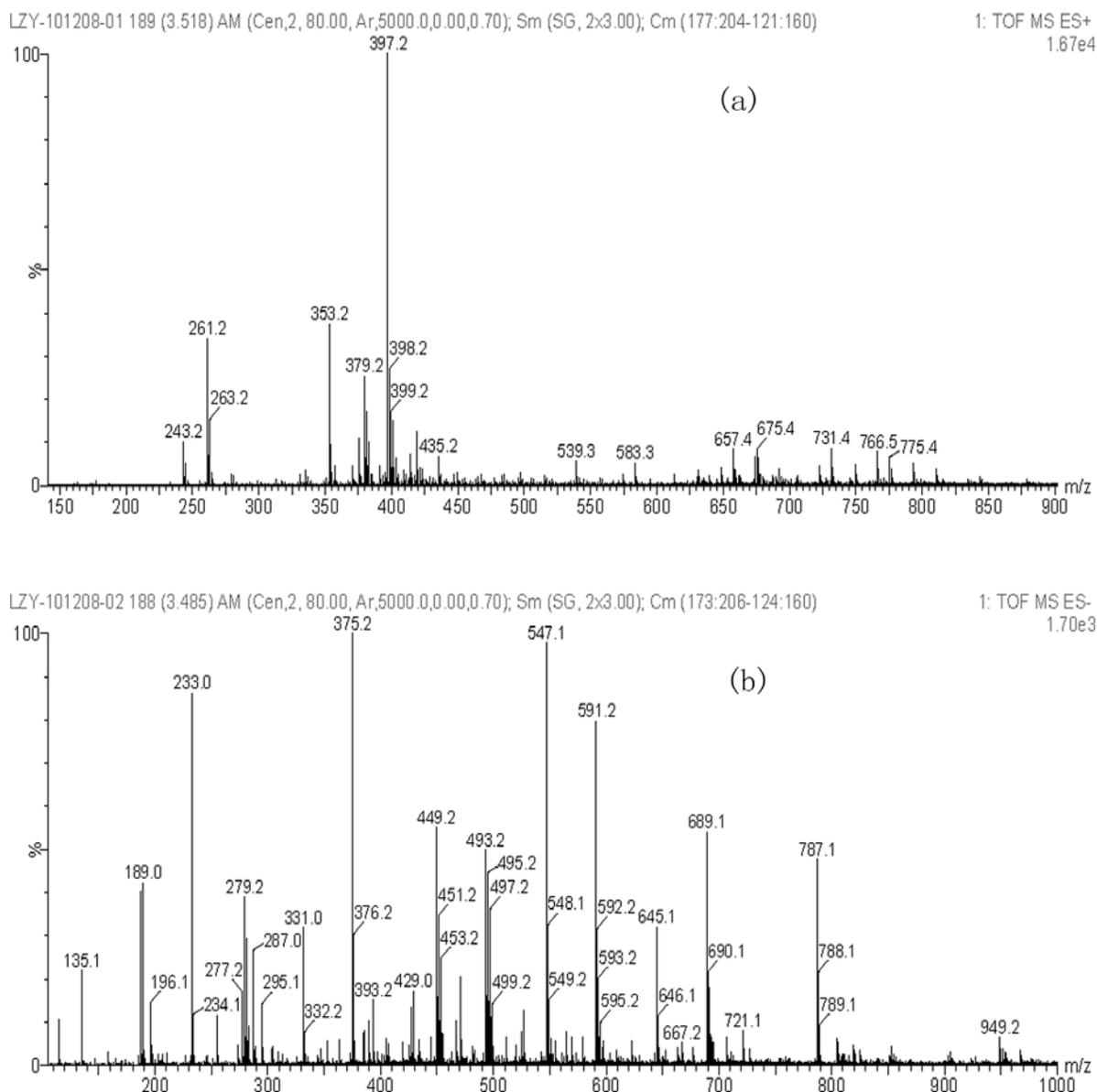
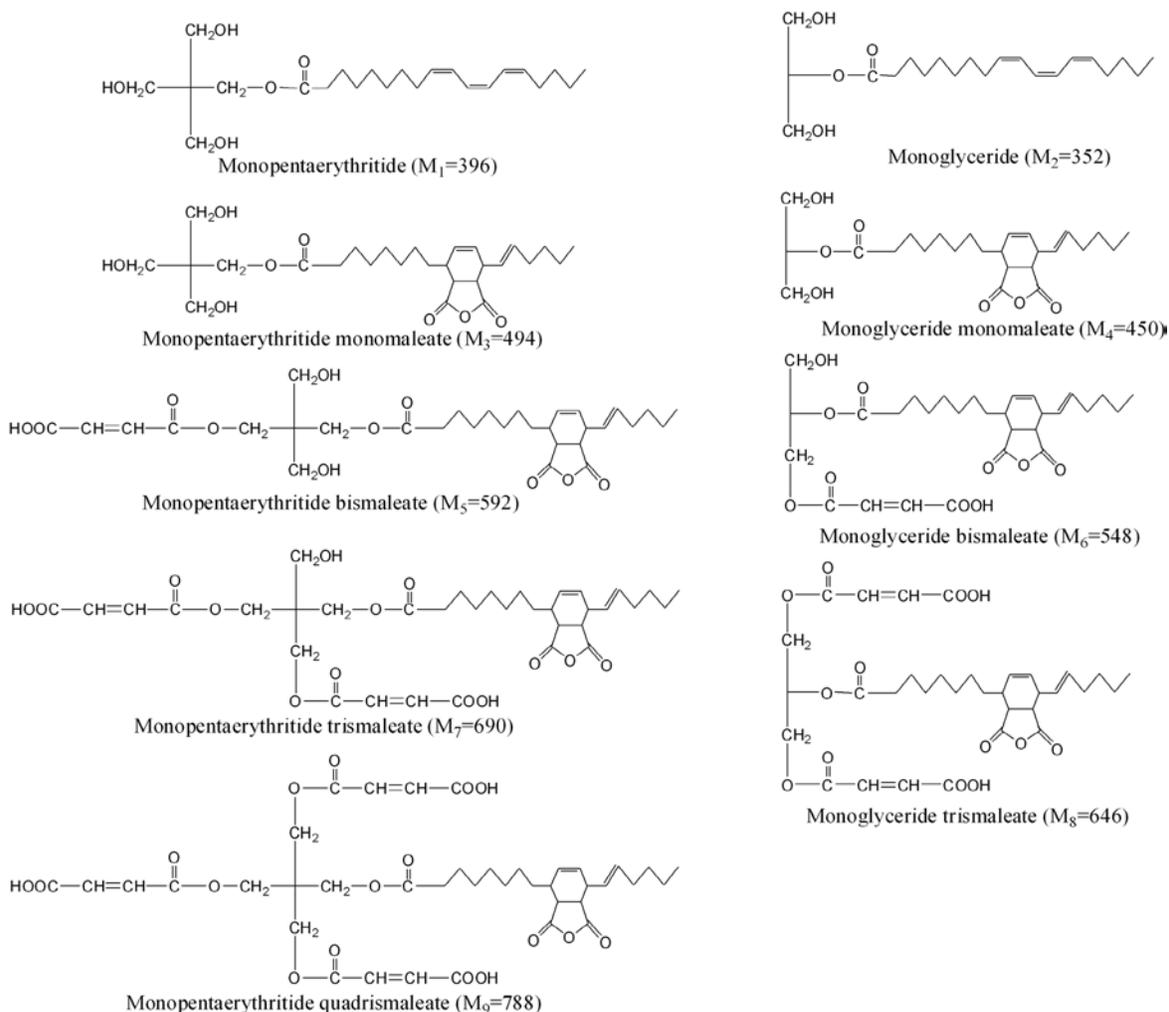


Fig. 4. ESI-MS spectra of (a) TOPER and (b) TOPERMA

between the TO conjugated triene with the double bond of MA yields the structure of  $-\text{CH}=\text{CH}-\underline{\text{CH}}-\text{CH}=\text{CH}-$ , as shown in Fig. 3(c). The peaks at 3.0-3.3 ppm are new, which thus can be attributed to the protons in the MA connecting to the conjugated triene. Hence, we can conclude that the malinated products shown in Fig. 1 are ideal structures of TOPERMA; the real products should contain by-products resulting from the D-A reaction. The peak that appears at 7.28 ppm in each spectrum represents the residual protons of  $\text{CDCl}_3$ . The peak at 7.45 ppm shows the aromatic protons of *N,N*-dimethyl benzyl amine used as a catalyst for the maleinization reaction.

Soft ionization combined with the inherent multiple charging mechanism of ESI has made MS an ideal tool for studying biopolymers and for accurately determining their molar masses. Figure 4 shows the ESI-MS spectra of TOPER and TOPERMA. The structures assigned to various mass numbers are given in Fig. 5. The peaks and the corresponding structures of TOPER were provided as MS (ESI)  $m/z$ :  $353.2[\text{M}_2+\text{H}]^+$ ,  $379.2[\text{M}_2+\text{Na}]^+$ ,  $397.2[\text{M}_1+\text{H}]^+$ , and  $435.2[\text{M}_1+\text{K}]^+$ , indicating the presence of monopentaerythritide and monoglyceride. The peaks and the corresponding structure of

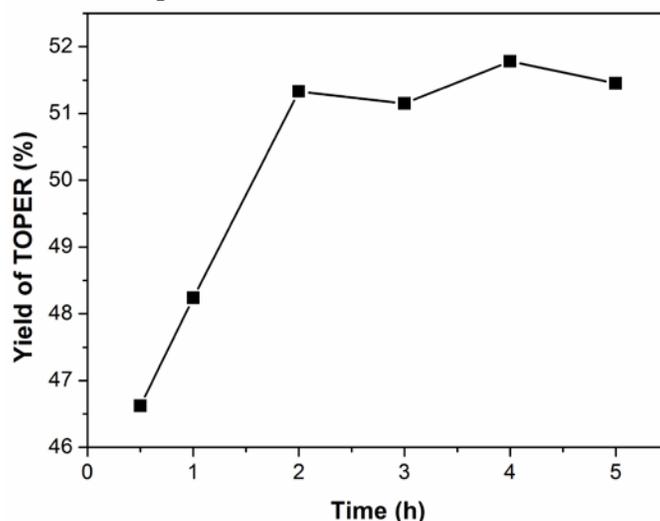


**Fig. 5.** Mass numbers of probable structures expected in the TOPERMA system

TOPERMA products were provided as MS (ESI)  $m/z$ : 449.2[M<sub>4</sub>-H]<sup>-</sup>, 493.2[M<sub>3</sub>-H]<sup>-</sup>, 547.1[M<sub>6</sub>-H]<sup>-</sup>, 591.2[M<sub>5</sub>-H]<sup>-</sup>, 645.1[M<sub>8</sub>-H]<sup>-</sup>, 689.2[M<sub>7</sub>-H]<sup>-</sup>, and 787.1[M<sub>9</sub>-H]<sup>-</sup>, which indicates that different kinds of maleate half esters had been formed. The peaks of 645.1[M<sub>8</sub>-H]<sup>-</sup> clearly reveal that the D-A adducts are in the TOPERMA mixture, because the monoglyceride cannot react with three MA if without the D-A reaction. The double bonds in the formed tetrahydrophthalate structure (Fig. 5) may participate in the copolymerization with styrene. Multiplicity seen in the mass spectra near the intense peaks is due to the natural abundance of various fatty acids in the TO mixtures.

### Alcoholysis Reaction of TO

The yield of maleate half ester is related to the yield of TOPER directly; thus it is important to maximize the TOPER yield. In this study, the yield of TOPER was taken as three times the content of monoglyceride (M=352) in the GC-MS chromatogram of TOPER. As we know, the alcoholysis of TO with PER is an ester interchange reaction and always reversible. As a consequence, the optimized experiment conditions need to be determined first for improving the yield. We here explored the conditions of reaction time and the concentration of catalyst Ca(OH)<sub>2</sub> under the feed ratio TO:PER=1:2 and reaction temperature 200-210 °C. Figure 6 demonstrates the effect of reaction time on the yield of TOPER at 1.0% Ca(OH)<sub>2</sub> concentration by weight. It can be seen that the yield of TOPER reaches the maximum value when the reaction time increases to about 2-3 h. Longer reaction times decrease the hydroxyl content of alcoholysis products, as observed from the <sup>1</sup>HNMR analysis, due to polyetherification of PER, which occurs as a side reaction during the alcoholysis. Figure 7 shows the effect of Ca(OH)<sub>2</sub> concentration on the yield of TOPER at the reaction time 3 h. The yield of TOPER increased with the increase of Ca(OH)<sub>2</sub> concentration. Too much Ca(OH)<sub>2</sub> will be detrimental to the maleinization reaction of TOPER, so we take 1.0% as the proper Ca(OH)<sub>2</sub> concentration for this reaction. Hence, the optimized procedure for the alcoholysis reaction was found to be 2-3 h reaction time with 1.0% Ca(OH)<sub>2</sub> concentration under the feed ratio TO:PER=1:2 and reaction temperature 200-210 °C.



**Fig. 6.** Yields of TOPER with the reaction time ( $t$ ) at 1.0% Ca(OH)<sub>2</sub> concentration and 200-210 °C

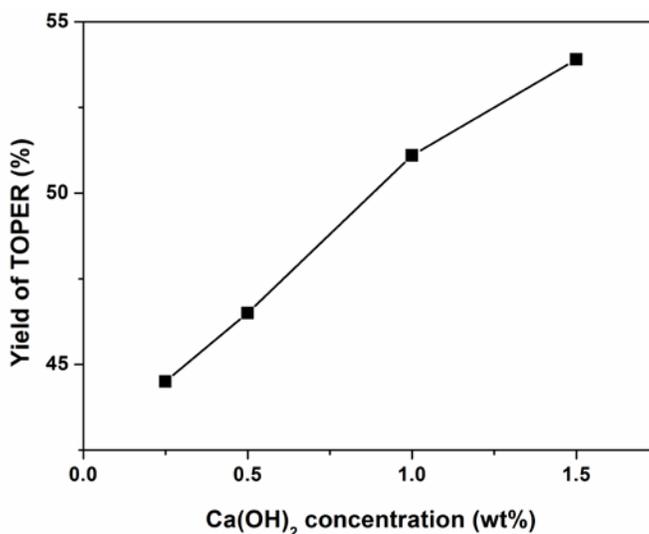


Fig. 7. Yields of TOPER with the Ca(OH)<sub>2</sub> concentration at  $t=3\text{h}$  and  $200\text{-}210\text{ }^{\circ}\text{C}$

### Maleinization Reaction of TOPER with MA

Maleinization of TOPER with MA by the catalyst *N,N*-dimethyl benzyl amine was monitored based on the reaction extents of TOPER and MA. According to the structural analysis from <sup>1</sup>HNMR spectra, the reaction extents of TOPER ( $\alpha_{\text{TOPER}}$ ), MA ( $\alpha_{\text{MA}}$ ) and unreacted MA ( $\alpha_{\text{un-MA}}$ ) can be calculated as,

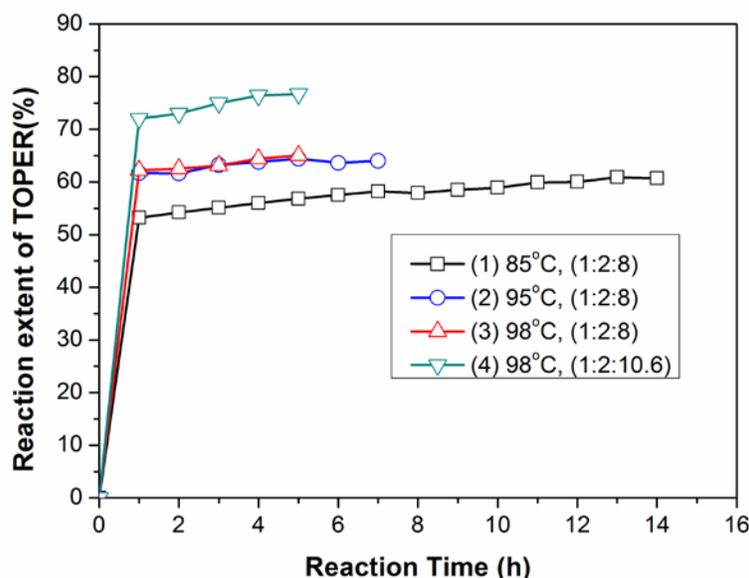
$$\alpha_{\text{TOPER}} = 1 - \frac{n_{\text{TOPERMA}(3.3-3.8\text{ ppm})}}{n_{\text{TOPER}(3.3-3.8\text{ ppm})}} \quad (1)$$

$$\alpha_{\text{MA}} = \frac{N_{\text{maleate}} + N_{\text{fumarate}}}{N_0} \quad (2)$$

$$\alpha_{\text{un-MA}} = \frac{N_{\text{MA}}}{N_0} \quad (3)$$

where  $n_{\text{TOPERMA}(3.3-3.8\text{ ppm})}$  and  $n_{\text{TOPER}(3.3-3.8\text{ ppm})}$  refer to the amounts of hydroxyl functional methylene protons of TOPERMA and TOPER at 3.3-3.8 ppm, as calculated with reference of the peaks at 0.9 ppm. The quantities  $N_{\text{maleate}}$ ,  $N_{\text{fumarate}}$ , and  $N_{\text{MA}}$  represent the amounts of maleate, fumarate, and MA with the vinyl protons at 6.3, 6.9, and 7.1 ppm, respectively;  $N_0$  is the feed amount of MA under different reaction conditions.

Four reaction conditions, including feed ratios (molar ratio), reaction temperature and reaction time, were chosen and first investigated by  $\alpha_{\text{TOPER}}$ , as shown in Fig. 8. The reaction temperature was kept below  $100\text{ }^{\circ}\text{C}$  so that no polyesterification took place. We first found that the reaction proceeds very fast initially but slows down towards the end. This effect has been interpreted by Can et al. (2000) to mean that the initial fast reaction is one between the primary hydroxyls of TOPER and MA, while the slower reaction that takes place afterward is between the secondary hydroxyls and MA. As our



**Fig. 8.** Reaction extents of TOPER with MA at different reaction conditions by analysis of the  $^1\text{H}$ NMR spectra

aim was to maximize the maleate ester yield, the proper reaction time for reactions (1), (2), (3), and (4) was chosen as long as 13 h, 5h, 4h, and 4h, respectively. Moreover, a higher reaction temperature leads to a higher final  $\alpha_{\text{TOPER}}$ , as shown in reactions (1)-(3) of Fig. 8. This may be due to the fact that a higher reaction temperature increases the collision chance of reactive functional groups on TOPER and MA. However, high reaction temperature will result in an increase of undesired D-A adducts rather than the desired maleate half esters.

At the feed ratio of TO:PER:MA=1:2:8 and temperature 98 °C, the  $\alpha_{\text{TOPER}}$  reaches a maximum value 65%, which means that about 35% of the TOPER hydroxyls are unconsumed. Thus, we improved the MA content at the feed ratio TO:PER:MA = 1:2:10.6, according to the hydroxyl content of PER and the conjugated triene content of TO triglyceride. It was seen that the maximum value of  $\alpha_{\text{TOPER}}$  at 98 °C increased to 77%. On the other hand, the maleate, fumarate, and unreacted MA content of malinated TO alcoholysis products are listed in Table 1 for different reaction conditions. The order of  $\alpha_{\text{MA}}$  can be listed as (2)>(1)>(3)>(4), and the  $\alpha_{\text{un-MA}}$  as (4)>(1)>(3)>(2). It was easily found that although the  $\alpha_{\text{TOPER}}$  value were improved by increasing the MA content from

**Table 1.** Reaction Extent of MA with TOPER at Different Experiment Conditions by Analysis of the  $^1\text{H}$ NMR Spectrum

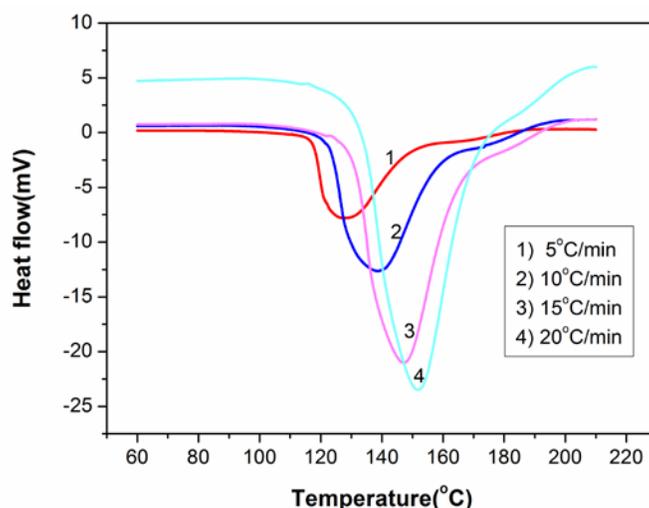
Run No.	Experiment conditions (temp., duration, feed ratio)	$N_{\text{maleates}}$ /mole TO	$N_{\text{fumarates}}$ /mole TO	$N_{\text{MA}}$ /mole TO	$\alpha_{\text{MA}}$ (%)	$\alpha_{\text{un-MA}}$ (%)
(1)	85 °C, 13h, (1:2:8)	4.13	0.21	0.51	54.2	6.4
(2)	95 °C, 5h, (1:2:8)	4.62	0.20	0.10	60.3	1.3
(3)	98 °C, 4h, (1:2:8)	3.64	0.32	0.45	49.5	5.6
(4)	98 °C, 4h, (1:2:10.6)	3.77	0.15	1.55	35.6	14.6

reaction (3) to (4), the  $\alpha_{MA}$  value decreased from 49.5% to 35.6% and the  $\alpha_{un-MA}$  value increased from 5.6% to 14.6%, which means that the efficiency of MA consumption decreased. The use of excess MA decreases the TOPERMA content, which will result in a lower crosslinking density of the resulting polymers, thus reducing the mechanical properties of the resin (Table 3). Another fact is that the reaction condition (2) has the highest  $\alpha_{MA}$  and the lowest  $\alpha_{un-MA}$ . Hence, the feed ratio of TO:PER:MA=1:2:8 can maintain a better balance of both  $\alpha_{TOPER}$  and  $\alpha_{MA}$  than of TO:PER:MA= 1:2:10.6. The best procedure for the maleinization reaction was found for a 95 °C reaction temperature, 5 h reaction time, and a feed ratio of TO:PER:MA = 1:2:8.

The sums of the amounts of maleate, fumarate, and unreacted MA were found to be lower than what was predicted based on maleic anhydride consumed. This is because some undesirable side reactions consume MA unsaturation during the reaction. One of the side reactions is the D-A addition reaction between the MA and the TO conjugated triene, which also lead to some residue of the TOPER hydroxyl at 3.3-3.8 ppm, as shown in Fig. 3(c). The D-A type addition during the maleinization of TOPER not only consumes the MA molecules, but also results in the transformation of the TO conjugated trienes into nonconjugated double bonds, which will affect the copolymerization with styrene. Other side reactions consuming the MA unsaturation were considered as the diester formation between the carboxylic acid of the maleate half esters and the available hydroxyls, the Michael addition to  $\alpha$ ,  $\beta$ -unsaturated esters under a basic condition, and so on (Can et al. 2000, 2006). The maleate to fumarate (cis to trans) isomerization known to occur on extended heating is not detrimental to the overall goals of this synthesis because fumarates have a higher reactivity than maleates (Can et al. 2000).

### Free Radical Initiated Copolymerization of TOPERMA

About 1/3 styrene by weight was mixed with the obtained TOPERMA maleates to obtain the TOPERMA/33%St resins. All TOPERMA maleates seemed soluble in styrene. The curing process was initiated by TPB with a 1.5% of the total resin weight. DSC technique is the most popular method in studying the curing reactions of thermoset resins; thereby it was employed to find out the optimized curing condition of TOPERMA with styrene. Dynamic DSC curves of resin mixtures curing at different heating rates for the reaction (2) are given in Fig. 9. The initial reaction temperature ( $T_i$ ), exothermal peak temperature ( $T_p$ ), final reaction temperature ( $T_f$ ), and total heat of reaction ( $\Delta H$ ) are listed in Table 2. It was pointed out that the three temperatures are dependent on test conditions, such as heat rates, sample shapes, initiator concentrations, and so on. In this paper the curing temperatures were determined only by the linear analysis between reaction temperatures and heating rates (Prime et al. 1973). By extrapolating the heating rate to zero, we deduced that the gel temperature, the peak temperature, and the final reaction temperature were 113 °C, 122 °C, and 145 °C, respectively. Therefore, the optimized curing procedure can be chosen as curing at 120 °C for 3 h, with postcuring at 150 °C for 1 h. This curing procedure meets the cure requirements for sheeting molding compounds (SMC).



**Fig. 9.** Dynamic DSC curves of the curing of TOPERMA/St resin mixture

**Table 2.** The Initial Reaction Temperature ( $T_i$ ), Exothermic Peak Temperature ( $T_p$ ), Final Reaction Temperature ( $T_f$ ) and Total Heat of Reaction ( $\Delta H$ ) of TOPERMA Resin at Different Heating Rates

Heating rate (°C/min)	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)	$\Delta H$ (J/g)
5	117.7	128.9	150.2	426.9
10	122.8	138.9	162.4	410.8
15	130.3	147.2	167.2	417.0
20	132.0	151.4	171.7	411.8

For all TOPERMA resins obtained by reactions (1) to (4), a similar curing procedure was employed. Partial mechanical properties of different TOPERMA maleates after being cured with styrene are presented in Table 3. Upon free radical initiated curing, the final resin mixture solidifies to a rigid solid that has mechanical properties similar to commercially successful polyesters and vinyl esters. According to the property analysis of the resins, the best procedure for the maleinization reaction was further verified as: a 95°C reaction temperature, 5 h reaction time, and a feed ratio of TO:PER:MA = 1:2:8.

**Table 3.** Mechanical Properties of TOPERMA Resin after Curing with Styrene

Run No.	Experiment conditions (temp., duration, feed ratio)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)
(1)	85°C, 13h, (1:2:8)	11.8(±0.4)	1.71(±0.06)	18.4(±0.9)	2.21(±0.07)
(2)	95°C, 5h, (1:2:8)	35.9(±1.2)	1.94(±0.09)	46.2(±2.3)	2.08(±0.09)
(3)	98°C, 4h, (1:2:8)	14.1(±0.9)	1.52(±0.05)	22.7(±1.2)	2.27(±0.06)
(4)	98°C, 4h, (1:2:10.6)	10.1(±0.8)	1.09(±0.05)	11.2(±0.7)	1.37(±0.05)

## CONCLUSIONS

1. A tung oil (TO) triglyceride-based monomer was prepared via the alcoholysis of TO with pentaerythritol (PER) to obtain the corresponding alcoholysis products (TOPER), followed by the maleinization reaction of TOPER to get the maleate half ester (TOPERMA). The optimized procedure for the alcoholysis reaction was found to be 2-3 h reaction time with 1.0% Ca(OH)<sub>2</sub> concentration under the feed ratio TO:PER=1:2, and reaction temperature 200-210°C. The best procedure for the maleinization reaction was found to involve a 95 °C reaction temperature, 5 h reaction time, and a feed ratio of TO:PER:MA = 1:2:8 under 1% dimethyl benzylamine and 0.1% hydroquinone. The copolymerization of TOPERMA with 33% styrene was cured at 120 °C for 3 h and postcured at 150 °C for 1 h.
2. By a structural analysis of the tung oil based monomer, we found that D-A products formed between MA and the TO conjugated triene. This not only consumes the MA molecules, but may also affect ultimate mechanical properties of the TOPERMA resin.
3. The polymer matrix gives very promising results of mechanical properties: tensile strength and modulus were 35.9 MPa and 1.94 GPa, whereas flexural strength and modulus were 46.2 MPa and 2.08 GPa. The properties of the polymer matrix will be discussed in a following article.
4. The overall synthesis is environmentally friendly, cheap, and very suitable for scale-up. The possible advantages of the TO polymer involve the low cost of their preparation from renewable natural resources and their presumed ability to biodegrade in an environmentally benign manner after service.

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## REFERENCES CITED

- Andjelkovic, D. D., Valverde, M., Henna, P., Li, F., and Larock, R. C. (2005). "Novel thermosets prepared by cationic copolymerization of various vegetable oils - Synthesis and their structure-property relationships," *Polymer* 46, 9674-9685.
- Can, E., Küseföglü, S., and Wool, R. P. (2000). "Rigid, thermosetting liquid molding resins from renewable resources. I. Synthesis and polymerization of soy oil monoglyceride maleates," *J. Appl. Polym. Sci.* 81, 69-77.
- Can, E., Scala, J. J. L., Sands, J. M., and Palmese G. R. (2007). "The synthesis of 9-10 dibromo stearic acid glycidyl methacrylate and its use in vinyl ester resins," *J. Appl. Polym. Sci.* 106, 3833-3842.

- Can, E., Wool, R. P., and Küseföglu, S. (2006). "Soybean and castor oil based monomers: Synthesis and copolymerization with styrene," *J. Appl. Polym. Sci.* 102, 2433-2447.
- Crivello, J. V., Narayan, R., and Sternstein, S. S. (1997). "Fabrication and mechanical characterization of glass fiber reinforced UV-cured composites from epoxidized vegetable oils," *J. Appl. Polym. Sci.* 64, 2073-2087.
- Eren, T., Kuseföglu, S. H., and Wool, R. P. (2003). "Polymerization of maleic anhydride-modified plant oils with polyols," *J. Appl. Polym. Sci.* 90, 197-202.
- Fu, L., Yang, L., Dai, C., Zhao, C., and Ma, L. (2010). "Thermal and mechanical properties of acrylated epoxidized-soybean oil-based thermosets," *J. Appl. Polym. Sci.* 117, 2220-2225.
- Haq, M., Burgueno, R., Mohanty, A. K., and Misra M. (2008). "Hybrid bio-based composites from blends of unsaturated polyester and soybean oil reinforced with nanoclay and natural fibers," *Compos. Sci. Technol.* 68, 3344-3351.
- Haq, M., Burgueno, R., Mohanty, A. K., and Misra, M. (2009). "Bio-based unsaturated polyester/layered silicate nanocomposites: Characterization and thermo-physical properties," *Compos. Part A-Appl. S.* 40, 540-547.
- Haq, M., R. Burgueno, Mohanty, A. K., and Misra, M. (2009). "Processing techniques for bio-based unsaturated-polyester/clay nanocomposites: Tensile properties, efficiency, and limits," *Compos. Part A-Appl. S.* 40, 394-403.
- Li, F., and Larock, R. C. (2001). "New soybean oil-styrene-divinylbenzene thermosetting copolymers. I. Synthesis and characterization," *J. Appl. Polym. Sci.* 80(4), 658-670.
- Li, F., and Larock, R. C. (2003). "Synthesis, structure and properties of new tung oil-styrene-divinylbenzene copolymers prepared by thermal polymerization," *Biomacromolecules* 4, 1018-1025.
- Li, F., Marks, D. W., Pacha, C. M., and Larock, R. C. (2000). "Fish oil thermosetting polymers: Synthesis, structure, properties and their relationships," *Polymer* 41, 7925-7939.
- Lu, J., Khot, S., and Wool, R. P. (2005). "New sheet molding compound resins from soybean oil. I. Synthesis and characterization," *Polymer* 46(1), 71-80.
- Lu, Y. S., and Larock, R. C. (2006). "Corn oil-based composites reinforced with continuous glass fibers: Fabrication and properties," *J. Appl. Polym. Sci.* 102, 3345-3353.
- Mehta, G., Mohanty, A. K., Misra, M., and Drzal, L. T. (2004). "Biobased resin as a toughening agent for biocomposites," *Green Chem.* 6, 254-258.
- Miyagawa, H., Mohanty, A. K., Burgueno, R., Drzal, L.Y., and Misra, M. (2006). "Development of biobased unsaturated polyester containing functionalized linseed oil," *Ind. Eng. Chem. Res.* 45(3), 1014-1018.
- Miyagawa, H., Mohanty, A. K., Burgueno, R., Drzal, L.Y., and Misra, M. (2007). "Novel biobased resins from blends of functionalized soybean oil and unsaturated polyester resin," *J. Polym. Sci. Part B-Polym. Phys.* 45(6), 698-704.
- Nicolaou, K.C., Snyder, S. A., Montagnon, T., and Vassilikogiannakis G. (2002). "The Diels-Alder reaction in total synthesis," *Angew. Chem. Int. Ed.* 41, 1668-1698.
- Penczek, P., Abramowicz, D., Rokicki, G., and Ostrysz, R. (2004). "Unsaturated polyester resins modified with vegetable oil and dicyclopentadiene," *Polimery*

- 49(11-12), 767-773.
- Pfister, D. P., Baker, J. R., Henna, P. H., Lu, Y. S., and Larock, R. C. (2008). "Preparation and properties of tung oil-based composites using spent germ as a natural filler," *J. Appl. Polym. Sci.* 108, 3618-3625.
- Prime, R. B. (1973). "Differential scanning calorimetry of epoxy cure reaction," *Polym. Eng. Sci.* 13(5), 365-371.
- Sen, S., and Cayli, G. (2010) "Synthesis of bio-based polymeric nanocomposites from acrylated epoxidized soybean oil and montmorillonite clay in the presence of a bio-based intercalant," *Polym. Int.* 59, 1122-1129.
- Sharma, V., Banait, J. S., Larock, R. C., and Kundu P. P. (2010). "Synthesis and characterization of linseed oil-based nanocomposites," *Polym. Compos.* 31, 630-637.
- Wool, R. P., Kusefoglu, S. H., Palmese, G., Khot, S., and Zhao, R. (2000). "High modulus polymers and composites from plant oils," *U.S. Patent* 6, 121, 398.
- Wool, R. P., and Sun, X. S. (2005). *Bio-based Polymers and Composites*, Elsevier: Burlington.
- Mosiewicki, M., Borrajo, J., and Aranguren, M. (2005). "Mechanical properties of woodflour/linseed oil resin composites," *Polym. Int.* 54, 829-836.
- Scala, J. J. L., Sands, J. M., Orlicki, J. A., Robinette, E. J., and Palmese, G. R. (2004). "Fatty acid-based monomers as styrene replacements for liquid molding resins," *Polymer* 45, 7729-7737.

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