

Polymerization Reactions of Epoxidized Soybean Oil and Maleate Esters of Oil-Soluble Resoles

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ABSTRACT: In this study, the polymerization reactions of epoxidized soybean oil (ESO) with the maleate half-esters of oil-soluble resoles and the properties of the final products were demonstrated. The maleate half-esters of the dimeric oil-soluble resoles were obtained by the esterification reaction of maleic anhydride with a *p*-tertiary butyl phenol (*p*-TBP) resole and *p*-nonyl phenol resole resins in the first step. The monomers were characterized by IR and ¹H-NMR techniques. Then, the oil-soluble resole maleates were polymerized with ESO to obtain tough and load-bearing thermoset materials. The thermal and mechanical properties of the materials were determined by dynamic mechanical analysis, differential scanning calorimetry, thermogravimetric analysis, and tensile strength testing. The tensile strengths and storage moduli of the crosslinked polymers varied between 0.17 and 13 MPa and 10 and 1088 MPa, respectively. The elongation percentages of the materials were between 1 and 128%. The thermal resistance of the thermosets was measured as the 5% weight loss temperature. The reaction product of the ESO and maleate ester of *p*-TBP showed the highest 5% weight loss at 247°C. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41457.

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INTRODUCTION

Petroleum is one of the most important resources in today's world. Unfortunately, because of the depletion of petroleum reserves, high prices, and environmental concerns, too much effort has been spent by many research groups to develop new materials that can be manufactured in environmentally acceptable ways that involve a minimum consumption of energy and petroleum-based raw materials and still maintain as favorable an ecological balance as possible.¹ For those reasons, vegetable oils seem to be one of the most important renewable feedstocks for industry.² A wide variety of chemicals and polymers can be synthesized from plant oils, and the mechanical properties of the synthesized materials can be adjusted with different types of plant oils and petroleum-based compounds.³ With the reactive parts of plant oil triglycerides, one can polymerize plant oil triglycerides into thermoset materials directly.⁴

One of the most important derivatives of plant oils is epoxidized soybean oil (ESO), which is obtained by the epoxidation of the double bonds of soybean oil.⁵ Despite their availability and industrial acceptance, the main drawback of ESO-based polymers is their poor mechanical properties compared to those of petroleum-based polymers.^{6,7} To improve the mechanical properties of ESO polymers, ESO can generally be mixed with

various types of petroleum-based resins, such as polyester resins, amino resins, and phenolic resins, or comonomers, such as carboxylic acids, amines, and phenols. Usually, ESO polymers that are prepared with aromatic reagents show better thermal and mechanical properties than polymers are obtained from aliphatic reagents.⁸

One of the most used petroleum-based liquid resins that have aromatic moieties is the phenolic resin. When one considers the price and ease of synthesis, phenolic resins are one of the most promising materials. They generally show high mechanical and thermal strengths and solvent resistance, but they are tacky and show no flexibility. To improve the flexibility of phenolic resins, ESO has been used as a reactive lubricating additive.^{9,10}

In this study, the polymerization reaction of the maleate half-esters of oil-soluble resoles with ESO was demonstrated. The aim of this study was to synthesize industrially applicable thermoset polymers from cheap starting materials with a minimum amount of petroleum-based chemicals.

EXPERIMENTAL

Materials and Methods

ESO was kindly donated by Hall Star Co. (Chicago, IL). Diethyl ether, tetrahydrofuran (THF), sodium sulfate, *p*-tertiary butyl

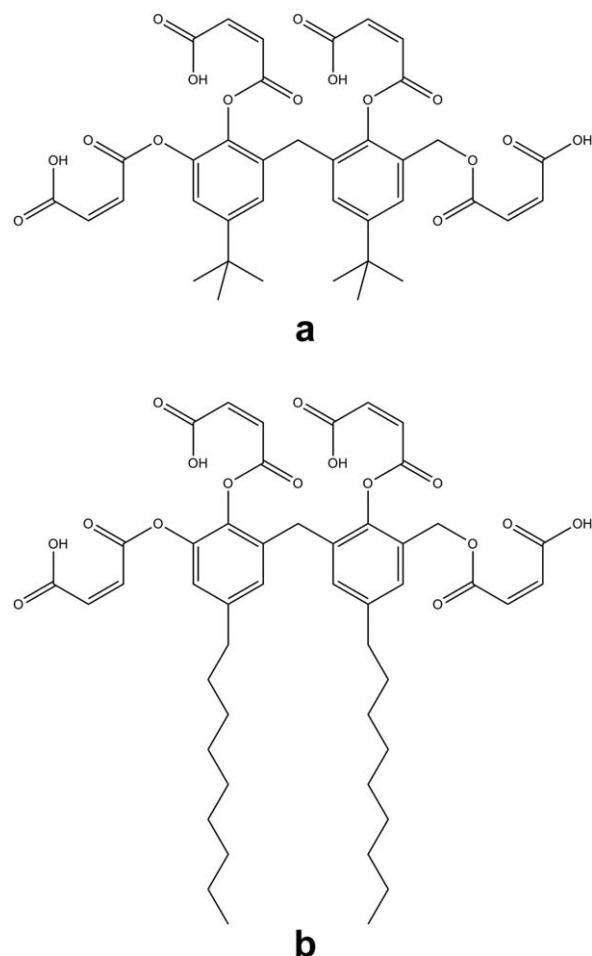


Figure 1. Maleate half-esters of (a) *p*-TBP and (b) *p*-NP.

phenol (*p*-TBP), *p*-nonyl phenol (*p*-NP) resole, a 37% formaldehyde solution, and maleic anhydride (MA) were purchased from Merck (Darmstadt, Germany).

The IR characterization of the compounds and polymers was done with a Nicolet 380 Fourier transform infrared (FTIR) spectrometer with smart diamond attenuated total reflectance. The $^1\text{H-NMR}$ spectra were recorded on a Varian 400-MHz NMR instrument operating at a frequency of 399.986 MHz for protons. The thermal stabilities of the material was characterized by a Thermal Analyses Q 50 model thermogravimetric analysis (TGA) instrument with a $10^\circ\text{C}/\text{min}$ heating rate under a nitrogen atmosphere. The dynamic mechanical properties of the suitable polymers were measured with a dynamic mechanical analyzer (DMA Q800) in single-cantilever mode at a frequency of 1 Hz and a heating rate of $3^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The samples for the dynamic mechanical analysis (DMA) experiments were prepared with a microtome into rectangular shapes having average dimensions of $12 \times 35 \times 3 \text{ mm}^3$.

Synthesis of *p*-Substituted Oil-Soluble Resoles

In a typical procedure, 1 mol of oil-soluble phenol was mixed with 37% formalin, which contained 1.5 mol of formaldehyde and 0.15 mol of NaOH. The mixture was reacted at 90°C for

1 h. Then, the product was dissolved in 150 mL of diethyl ether and washed with 100 mL of distilled water three times. The ether solution was dried with Na_2SO_4 overnight, and the ether was finally evaporated. The product was used without any further purification.

Synthesis of the Maleate Half-Esters of the Resoles

In a typical procedure, 0.1 mol of each resole was refluxed with 0.4 mol of MA in 100 mL of THF for 4 h and mixed overnight under N_2 . Then, THF was evaporated by a rotevaporator, and the product was used without purification.

Polymerization of the Maleate Half-Esters with ESO

In a typical procedure, 0.1 mol of the resole maleate half ester was mixed with 0.095 mol of ESO (weight-average molecular weight $\approx 952 \text{ g/mol}$). This mixture was poured into a Teflon mold and heated to 90°C under N_2 . After 2 h, the mixture became a light yellow homogeneous and viscous liquid. Then, the mixture was further cured at 150°C for 2 h and 190°C for another 2 h. The final material was a yellowish, transparent, tough, and strong solid.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Maleate Esters of the Resoles

The synthesized *p*-TBP and *p*-NP resoles were mainly in dimeric forms, and we accepted that 1 mol of the resins contained approximately 4 mol of hydroxyl groups. We observed that when the molar ratio of phenolic resins to MA was adjusted to 1:4, free hydroxyl group were not detected after the esterification reaction. The maleate half-esters of the oil-soluble phenolic resins that were used in this study are shown in Figure 1. The characterizations of these maleic-modified resoles were performed with $^1\text{H-NMR}$ and FTIR spectroscopic techniques.

The $^1\text{H-NMR}$ spectra of the monomers and starting materials are shown in Figure 2 and the integration ratios of hydrogens are given in Table I. The $^1\text{H-NMR}$ of the *p*-TBP resin in CDCl_3 showed an intense peak at 4.8 ppm due to methylol group protons (phenyl- $\text{CH}_2\text{-OH}$). The peak at 1.3 ppm indicated tertiary butyl hydrogens. Aromatic hydrogens were observed around 7.0 ppm. A small and broad peak at 3.5 ppm corresponded to the -OH hydrogens. The peak at 4.0 ppm showed the presence of double benzylic hydrogens. The integration ratio of double benzylic hydrogens was accepted as 1.0. The ratio of methylol hydrogens to double benzylic hydrogens was 2; this indicated that all of the resoles were mainly in dimeric forms. If the ratio of methylol hydrogens to double benzylic hydrogens was 1, one could assume that almost all of the resole resin was composed of trimers.

In the $^1\text{H-NMR}$ of the *p*-tertiary butyl phenol resole-maleate (*p*-TBPMA) resin in CDCl_3 , the peak corresponding to methylol groups at 4.8 ppm was shielded to 5.1 ppm; this proved the change in the environment of methylol groups during the reaction. The double-bond hydrogens were also shielded, and they appeared around 4.6 ppm. The hydrogens of the maleate groups were observed as two single peaks at 6.2 and 7.4 ppm. There was no single sharp peak at 7 ppm, and this finding supported the fact that all of the MA was completely reacted with the hydroxyl groups of the *p*-TBP.

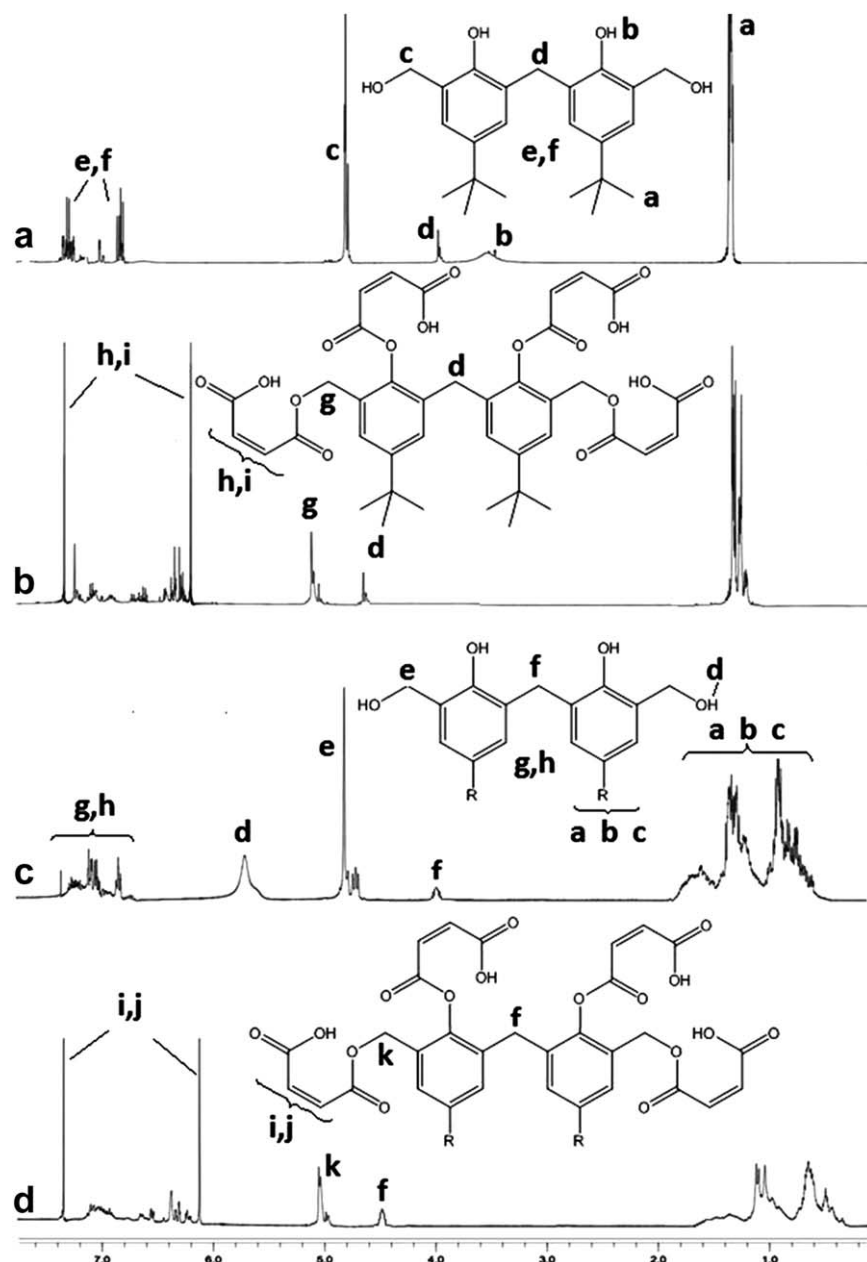


Figure 2. $^1\text{H-NMR}$ spectra of the phenolic resoles and their maleate half-esters: (a) *p*-TBP, (b) *p*-TBPMA, (c) *p*-NP, and (d) *p*-NPMA.

The same findings were also determined in the $^1\text{H-NMR}$ of the *p*-NP resin in CDCl_3 . A broad peak at 5.7 ppm corresponded to the $-\text{OH}$ hydrogens. The peak at 4.8 ppm was due to the methylol groups (phenyl- CH_2-OH), and the double benzylic hydrogens appeared 4.0 ppm. The peaks appearing at 0.8, 1.3, and 1.6 ppm, respectively, belonged to the $\text{CH}_3-\text{CH}_2-\text{CH}_2-$ hydrogens of the nonyl groups. The ratio of methylol hydrogens to double benzylic hydrogens was 4:2; this also indicated that the *p*-NP resole was mainly in dimeric form.

In the $^1\text{H-NMR}$ spectra of the *p*-nonyl phenol resole-maleate (*p*-NPMA) resin, we observed that the peak corresponding to the methylol groups at 4.7 ppm was shielded to 5.05 ppm; this indi-

cated the esterification of the methylol groups. The double-bond hydrogens of the maleate group appeared at 6.2 and 7.4 ppm.

Figure 3 shows the FTIR spectra of the *p*-TBP and *p*-TBPMA resins and the ESO-*p*-TBPMA polymer. The IR spectrum of the *p*-TBP resole showed a peak around 3300 cm^{-1} that indicated the presence of $-\text{OH}$ groups. The peak at 1612 cm^{-1} corresponded to the $\text{C}=\text{C}$ stretching of the aromatic rings. The peak, which was observed at 1008 cm^{-1} indicated the methylol group. When *p*-TBP reacted with the MA, the $-\text{OH}$ peaks at 3300 cm^{-1} disappeared, and two new carbonyl peaks appeared at 1777 and 1720 cm^{-1} ; these belonged to acid carbonyl and ester carbonyl, respectively. The broad peak in the

Table I. Integration Ratios of the Hydrogens of the Synthesized Monomers

Monomer synthesized	Hydrogens in the functional groups/Integration ratio ^a				
<i>p</i> -TBP	CH ₃ —/9.0	Phenyl—CH ₂ —phenyl/1.0	Phenyl—CH ₂ —OH/2.0	—OH/2.0	Aromatic hydrogens/2.0
<i>p</i> -TBPMA	CH ₃ —/9.0	Phenyl—CH ₂ —phenyl/1.0	Phenyl—CH ₂ —OH/2.0		Aromatic hydrogens/2.0 Maleate hydrogens/4.0
<i>p</i> -NP	Aliphatic hydrogens/19.3	Phenyl—CH ₂ —phenyl/1.0	Phenyl—CH ₂ —OH/2.02	—OH/1.97	Aromatic hydrogens/2.0
<i>p</i> -NPMA	Aliphatic hydrogens/19.3	Phenyl—CH ₂ —phenyl/1.0	Phenyl—CH ₂ —OH/1.98		Aromatic hydrogens/2.0 Maleate hydrogens/3.9

^aThe integration ratio of double benzylic hydrogens was accepted as 1.0.

3000–3500-cm⁻¹ region indicated the presence of the hydroxyl stretching of free acid (—COOH) groups formed after the esterification reaction.

The FTIR spectra of the *p*-NP and *p*-NPMA resins also showed the same trend, and this is demonstrated in Figure 4(a,b). The peaks of the acid and new ester carbonyl at 1778 and 1705 cm⁻¹ were observed when *p*-NP was reacted with MA. No peak was observed at 1850 cm⁻¹; this indicated that there was no unreacted MA in the *p*-NPMA resin.

Additionally, because of the C—O bond formation, which was another indication of ester formation, new peaks appeared in the 1300–100-cm⁻¹ region in the IR spectrum of the maleate esters of the resoles.

Synthesis and Characterization of the ESO-Maleinized Phenolic Resole Polymers

Both the *p*-TBPMA and *p*-NPMA resoles contained approximately 4 mol of maleic acid end groups, which were available to

react with 4.2 mol of epoxy groups from the ESO. The maleic acid could react with ESO through a ring-opening reaction.^{11,12}

Although NMR characterization could not be performed because of the crosslinked nature of the polymers, valuable information was obtained by FTIR spectroscopy. The FTIR spectra of the polymeric materials are shown in Figures 3(c) and 4(c). The strong and sharp carbonyl peaks at 1777 cm⁻¹ and the broad peaks at 300–3500 cm⁻¹ disappeared in both spectra; this proved the addition reaction between the carboxyl groups of the resole esters and the oxirane rings of ESO. At the end of the addition reaction, new carbonyl peaks were observed at 1730 and 1738 cm⁻¹. The presence of the oxirane groups of ESO was easily followed by the peak at 830 cm⁻¹. Unfortunately, because of the conjunction of C—O stretching vibrations of different functional groups, the consumption of oxirane groups could not be followed by the IR technique.

Mechanical Properties of the Synthesized Polymers

Wool, Lenox, and coworkers^{13–15} reported the mechanical properties of several polymer derived from ESO. With the incorporation of different type of compounds, including anhydrides and acids, the properties of ESO-based polymers improved greatly but were still often below the values of traditional synthetic polymers. The tensile strength values of the ESO-based polymers showed great distribution from small values, such as 0.6

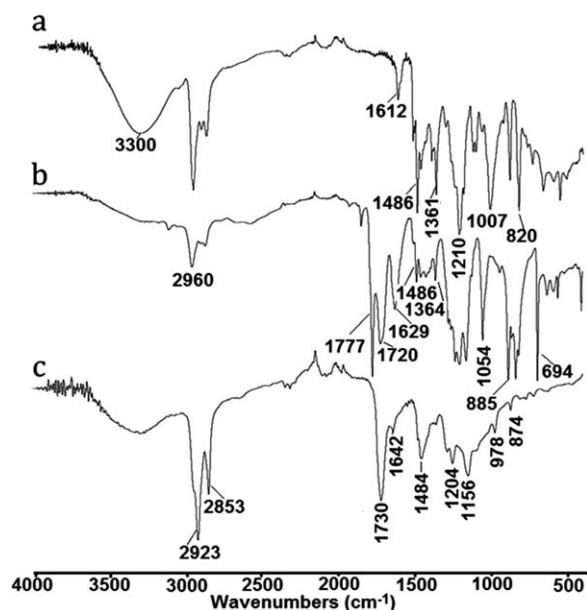


Figure 3. FTIR spectra of (a) *p*-TBP, (b) *p*-TBPMA, and (c) ESO-*p*-TBPMA.

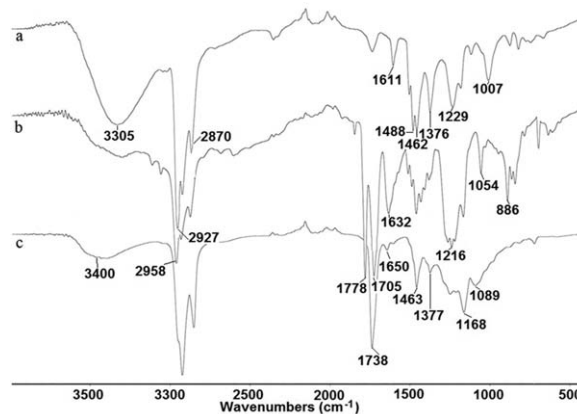


Figure 4. FTIR spectra of (a) *p*-NP, (b) *p*-NPMA, and (c) ESO-*p*-NPMA.

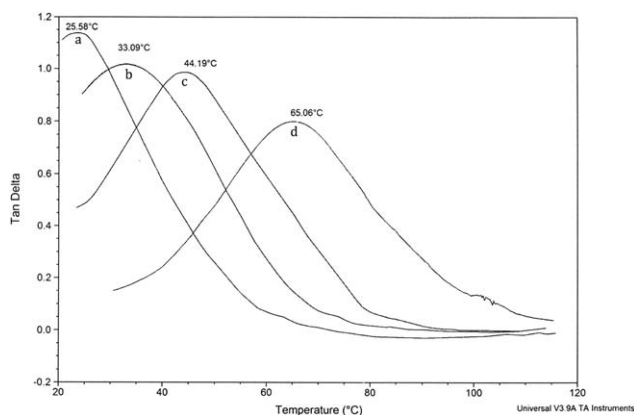
Table II. Mechanical and Thermal Properties of the Synthesized Polymers

Synthesized polymer	Elongation (%)	Stress at break (MPa)	Storage modulus at 30°C (MPa)	Tan δ temperature (°C)	5% weight loss temperature (°C)	50% weight loss temperature (°C)
ESO- <i>p</i> -TBPMA-150	34	4	40	33	164	385
ESO- <i>p</i> -NPMA-150	128	1,5	10	25	187	390
ESO- <i>p</i> -TBPMA-190	20	12	1088	65	247	389
ESO- <i>p</i> -NPMA-190	48	13	180	45	220	390

MPa, to higher values, such as 20–30 MPa, with different elongation percentages. The maximum storage moduli of those polymers appeared in the range 1–2 GPa. According to the Situ et al.,¹⁶ the addition of ESO to phenolic resins increased the flexibility of the phenolics, and they found that the ESO-phenolic resin matrix was a cheap matrix with excellent properties.⁹ There was no literature about the polymerization reaction and mechanical properties of ESO and maleate esters of the oil-soluble phenolic resin.

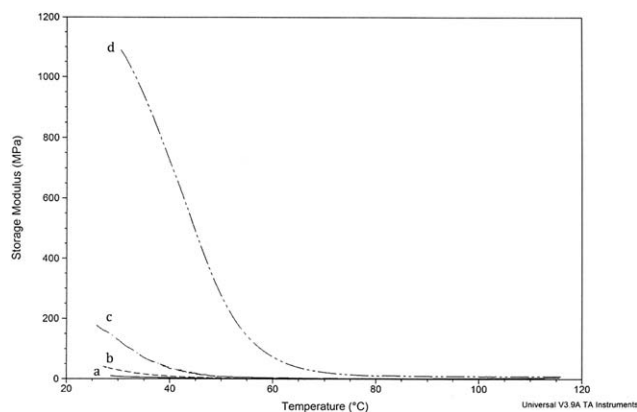
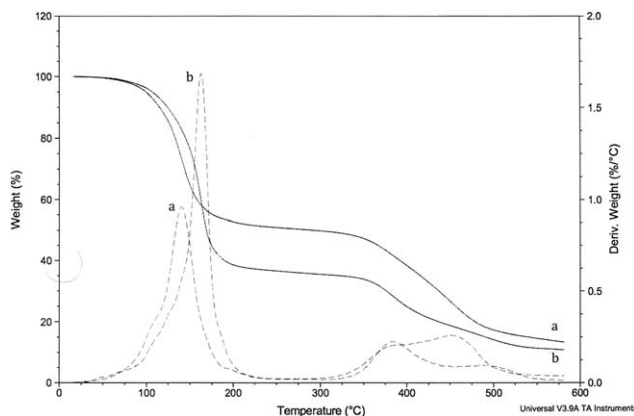
The mechanical and thermal properties of the materials synthesized in this study are summarized in Table II. For the evaluation of the polymers, stress-strain testing and DMA were applied. The highest tensile strength at break values were observed to be 12 and 13 MPa for the ESO-*p*-TBPMA-190 (ESO-*p*-TBPMA polymer cured at 190°C) and ESO-*p*-NPMA-190 (ESO-*p*-NPMA polymer cured at 190°C) resins, respectively. On the other hand, the ESO-*p*-NPMA-150 (ESO-*p*-NPMA polymer cured at 150°C) resin showed the lowest tensile strength of 1.5 MPa. This result was probably caused by the presence of long nonyl groups that acted as an internal plasticizer. The highest elongation at break value was obtained for the ESO-*p*-NPMA-150 resin and was 128%. When the alkyl chain at the para position of the phenolic resin was a tertiary butyl, the lowest elongation was observed at 20%.

The storage moduli of the samples were determined by the DMA technique. The storage moduli of the polymers synthesized at 190°C was higher than those of the polymers synthesized at 150°C. The highest storage modulus was obtained from

**Figure 6.** Tan δ traces of the polymers: (a) ESO-*p*-NPMA-150, (b) ESO-*p*-TBPMA-150, (c) ESO-*p*-NPMA-190, and (d) ESO-*p*-TBPMA-190.

the ESO-*p*-TBPMA-190 polymer at 1088 MPa. However, the ESO-*p*-NPMA-150 polymer showed a 10-MPa storage modulus; it was the lowest one among the others (Figure 5 and Table II).

Because of the thermosetting nature of the materials, the glass-transition temperatures could not be determined by the differential scanning calorimetry method. Instead of differential scanning calorimetry, the DMA technique was used. These values were obtained as tan δ temperatures. The highest tan δ temperature was measured for the ESO-*p*-TBPMA-190 polymer at 65°C, and the lowest one belonged to ESO-*p*-NPMA-150 at 25°C. The height of the tan δ peak also gave an idea about the

**Figure 5.** Storage moduli of the polymers: (a) ESO-*p*-NPMA-150, (b) ESO-*p*-TBPMA-150, (c) ESO-*p*-NPMA-190, and (d) ESO-*p*-TBPMA-190.**Figure 7.** TGA and derivative TGA traces of the maleate half-esters of the phenolic resins: (a) *p*-TBP and (b) *p*-NP.

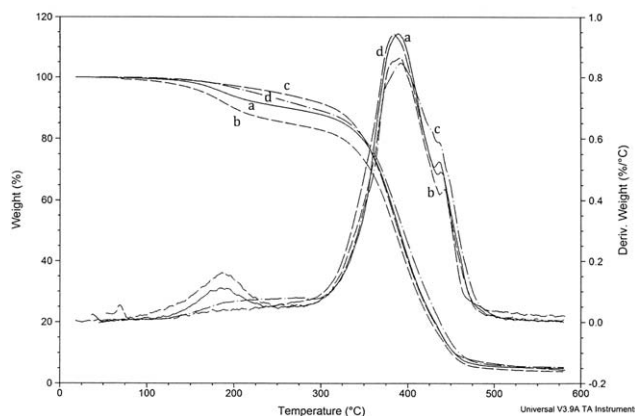


Figure 8. TGA and derivative TGA traces of the polymers of (a) ESO-*p*-NPMA-150, (b) ESO-*p*-TBPMA-150, (c) ESO-*p*-NPMA-190, and (d) ESO-*p*-TBPMA-190.

viscoelastic nature of the materials. The reduction of the height of the $\tan \delta$ peaks indicated the increment of the elastic nature of the resulting polymers. When the material was cured at low temperature and included a longer alkyl chain in the phenolic content, the resulting thermoset polymers showed the highest $\tan \delta$ peaks; this indicated a more viscous character (Figure 6).

Thermal Properties of the Synthesized Polymers

For the evaluation of the thermal resistance of the polymers, the TGA technique was used. TGA and derivative TGA traces of the maleate esters of the phenolic resins are shown in Figure 7. The parasubstituted resoles gave three segmental losses around 150, 375, and 500°C, respectively, and this observation was consistent with the literature.¹⁷ The amount of the weight loss was around 30% for each transition. It was found that the TGA traces of the maleate esters of the oil-soluble resoles showed two plateaus instead of three. The first one ended around 75°C, and the second transition appeared between 200 and 350°C. The maleate group amount was 60% in the *p*-TBP resole ester and 50% in the *p*-NP resole ester resins. The same weight loss was observed in the TGA traces. According to this result, the first weight loss probably occurred because of the disruption of ester bonds.

For the thermal resistance of the materials, the 5% weight loss temperatures were used as indicators. The 5% weight loss temperatures were also investigated by TGA. ESO-*p*-TBPMA-190 showed the highest 5% weight loss temperature at 247°C. The lowest 5% weight loss temperature belonged to ESO-*p*-TBPMA-150 at 164°C. Although they not as important as the 5% weight loss temperature, the 50% weight loss temperatures also gave us an idea about the thermal resistivity of polymers. The 50% weight loss temperatures of all of the polymers were observed around 390°C (Figure 8). Those values could be accepted as the limit of commercial polymers.

CONCLUSIONS

With cheap starting materials, including ESO and the maleate esters of oil-soluble resoles, tough and load-bearing polymeric

materials were synthesized. These materials could replace petroleum-based resins. The neat phenolic resins generally showed tensile strengths between 10 and 70 MPa and low elongation. Although the tensile strength of the synthesized polymers was not as high as 70 MPa, the materials showed generally acceptable tensile strength values. The ESO-*p*-TBPMA-190 and ESO-*p*-NPMA-190 polymers showed 12–13-MPa tensile strengths. Moreover, the synthesized materials showed more than 20% elongation, and that is higher than the elongation of nonpliable phenolic resins. At the end of the synthesis, the materials still contained reactive maleate double bonds that made the materials suitable comonomers for styrene or another olefinic reactive monomer in radical polymerization reactions. The synthesized polymers could be swelled with those comonomers and polymerized *in situ*. This subject is also under investigation.

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