

Polymerization of Linseed Oil with Phenolic Resins

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ABSTRACT: In this study, linseed oil was directly polymerized with different oil soluble resoles. *p*-Ethyl (PEP), *p*-tertiary butyl (PTB), *p*-tertiary octyl (PTO), and *p*-phenyl (PPP) phenols were separately reacted with formaldehyde to give linseed oil soluble resoles. These were then reacted with linseed oil to give transparent rubbery polymers. A model reaction was performed with methyl oleate and PTB phenol resole to clarify the reaction mechanism. Reaction products were characterized with $^1\text{H-NMR}$ and IR techniques. Spectral examination of the model reaction showed that polymerization reaction proceeded via ene reaction of the quinone methide formed at the end group of the resole with the allylic positions of the fatty ester. Rubbery polymers were obtained with linseed oil using 10 to 40% of the different resoles. Hard, load bearing and tough materials were obtained at 40% phenolic resin loading. Mechanical properties of the materials were character-

ized by dynamic mechanical analyzer (DMA) and stress-strain tests. The best mechanical and thermal properties were obtained with PEP resole which showed a storage modulus of 350 MPa and a $\tan \delta$ peak at 65°C. Storage moduli of 275, 250, and 30 were obtained for PPP, PTB, and PTO resoles-linseed oil polymers, respectively. At the same phenolic resin loading, elongation at break and swelling ratios in CH_2Cl_2 increased with the longer alkyl substitution on the resole resins. The highest thermal stability was observed by PEP resole-linseed oil polymer which has a 5% weight loss temperature of 340°C as determined by TGA. The lowest thermal stability was observed for PTB resole-linseed oil polymer at 220°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 849–856, 2010

Key words: renewable resources; elastomers; mechanical properties; vulcanization

INTRODUCTION

Petroleum is still the most important natural resource for the polymer industry. Unfortunately, these resources are nonrenewable and are getting more expensive. Moreover, widespread use of petroleum-based nonbiodegradable polymers cause environmental problems with increasing social price. There is a major effort to find suitable renewable resources to replace petroleum. At this point, vegetable oils offer one of the most important renewable feedstock for the chemical industry.^{1,2}

Use of the plant oils in chemical industry has three main advantages. Plant oil triglycerides are renewable, can be used as poly reactive monomers and they usually lead to biodegradable polymers. By using suitable functionalization these fine chemicals can be easily converted to wide variety of soft, strong or load bearing polymers. The mechanical properties of these polymers can be easily adjusted by using different types of plant oil based chemicals

together with small amounts of petroleum based chemicals.^{3–5} Parts made from such polymers are usually biodegradable and the carbon dioxide produced during biodegradation or combustion is reused by the next year's crop via photosynthesis. Thus plant oil based polymers can be made to be carbon neutral.

Plant oil double bonds resemble those of natural rubber in terms of structure. They are nonconjugated and in the *cis* configuration. Thus, any chemical reaction or polymerization reaction which is suitable for crosslinking rubbers is also a good candidate for polymerizing plant oil triglycerides.⁴

In the past we and other research groups have used suitably functionalized triglycerides to obtain monomers that can be easily polymerized.^{5–7} In each case, this preliminary functionalization step involves an additional reaction such as epoxidation, maleinization, halogenation etc. There are very few examples in the literature of the use of the triglyceride in its natural and cheapest form directly as a monomer. Using rubber vulcanization reactions allows one to use the triglyceride molecules directly without prior functionalization and therefore promises to be a cheaper and industrially a more acceptable method. Many type of vulcanizing agents have been used for rubber vulcanization and excellent reviews of the subject exist.^{8–11} These classical vulcanization

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methods can be classified into 5 groups: (i) Sulphur containing vulcanizing agents; (ii) Oxygen containing vulcanizing agents; (iii) Phenolic type vulcanizing agents; (iv) Maleimide containing vulcanizing agents; (v) Nitroso containing vulcanizing agents.

The reactions between plant oil triglycerides and some of the vulcanizing agents mentioned earlier have been studied well. For example, reaction product of sulfur and plant oils is known as "factice" and is used commercially as additives for rubbers. Linoleum is also another commercial product obtained from oxygen mediated vulcanization of plant oils. Vulcanization of plant oil triglycerides with maleimides is also possible, but due to the poor solubility of maleimides in plant oils, this reaction did not find much success. Dinitrobenzene vulcanization which is an older method has been successfully used in our group to polymerize soybean oil.¹²

Among the vulcanizing agents, phenolic resins are still of great interest in the rubber industry due to the low cost of starting materials and excellent mechanical properties of the vulcanizates obtained. There are no examples of the use of phenolic resins in plant oil polymerizations in the literature. There are some references to the use of phenolic cross linkers with plant oils in patents,^{13–18} but these works do not examine the reaction pathway or the products obtained and the chemical reactions that take place are not at all clear. The reaction pathway between phenolic resins and rubbers is not simple and it is proposed that the reaction occurs by Diels-Alder pathway or an ene pathway. In this study, by using methyl oleate as a model compound the mechanism was clarified and rubbery polymers made from different type phenolic resins and linseed oil were synthesized and fully characterized.

EXPERIMENTAL

Chemicals and apparatus

Linseed oil was obtained from Yeni Turan (Istanbul, Turkey) and used without any further treatment. Aqueous formaldehyde solution, *p*-ethyl (PEP), *p*-tertiary butyl (PTB), *p*-tertiary octyl (PTO), *p*-phenyl phenols (PPP), sodium hydroxide, and sodium sulphate were purchased from Merck (Darmstadt, Germany) and they were used as received.

IR characterization of compounds was performed by Perkin-Elmer FTIR 1600 series spectrometer using KBr windows. The ¹H-NMR spectra was recorded on a Varian 400-MHz NMR instrument (Varian Associates, Palo Alto, CA) operating at a frequency of 399.986 MHz for proton. The spectra were recorded as ppm (δ) with CDCl₃ as a solvent. TGA characterizations were performed by "Thermal Anal-

yses" Q 50 instrument (New Castle, DE) with a heating rate 10°C/min under nitrogen atmosphere from room temperature to 600°C. The dynamic mechanical properties of the suitable polymers were measured with a dynamic mechanical analyzer [(DMA) Q800, TA Instruments, New Castle, DE] in the single-cantilever mode at a frequency of 1 Hz and a heating rate of 3°C/min under nitrogen atmosphere. The samples for the DMA experiments were shaped with a microtome into rectangular shapes having the average dimensions of 12 × 35 × 3 mm. The swelling behaviors of the polymers were tested in CH₂Cl₂ by using a Gartner 7109-46 traveling microscope. Strain tests were performed Devotrans DVG 32 Model tester (İstanbul, Turkey) with a 20 mm/min elongation rate using the methods given in ISO 8256.

Synthesis of PEP resole

Para ethyl phenol, 43.65 g (0.36 mol), was mixed with 2.21 g (0.055 mol) of NaOH and 43.54 g (0.55 mol of formaldehyde) of 37% formalin solution. The mixture was then heated to 90–92°C for 1 h. The crude red colored product was dissolved in diethyl ether and washed several times with distilled water then was dried over Na₂SO₄ and the solvent was removed by distillation in a rotavaporator.

Synthesis of PTB resole

Para tertiary butyl phenol, 54.24 g (0.36 mol) was mixed with 2.21 g (0.055) of NaOH and 43.54 g (0.55 mol of formaldehyde) of 37% formalin solution. The mixture was heated to 90–92°C for 1 h. Then the crude product was dissolved in diethyl ether and washed with distilled water several times and dried over Na₂SO₄. Ether was removed by distillation in a rotavaporator.

Synthesis of PTO phenol resole

Para tertiary octyl phenol, 37.24 g (0.18 mol) was mixed with 1.105 g (0.027) of NaOH and 22 g (0.27 mol of formaldehyde) of 37% formalin solution. This mixture was heated to 90–92°C for 1 h. The product was dissolved in diethyl ether and washed several times with tap water then dried over Na₂SO₄. Ether was removed by distillation in a rotavaporator.

Synthesis of PPP resole

Para phenyl phenol, 30 g (0.17 mol) was mixed with 1.056 g of NaOH (0.027 mol) and 21.5 g (0.27 mol of formaldehyde) of 37% formalin solution. The mixture was heated to 92°C for 1 h. Crude product was dissolved in diethyl ether and washed with water

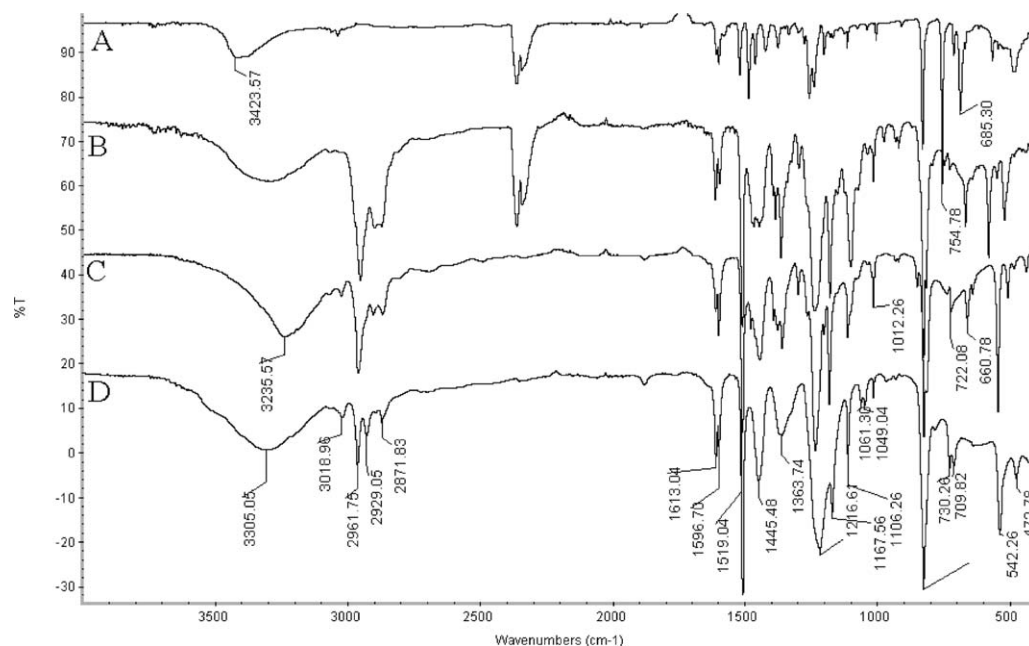


Figure 1 IR spectra of (A) *p*-phenyl phenol (B) *p*-tertiary octyl (C) *p*-tertiary butyl (D) *p*-ethyl phenols.

several times then dried over Na_2SO_4 . Ether was removed by distillation in a rotavaporator.

Polymerization of resoles with linseed oil

In a typical procedure, mixtures of linseed oil and resoles containing 10–40% resoles were prepared. To these mixtures maleic acid (3% of phenolic resin) was added. Mixture was preheated to 80°C in vacuum oven for half an hour at 1 mm to remove any volatile component. Then these mixtures were poured into Teflon molds and the temperature was raised to 145°C . All polymerization reactions were performed for 24 h.

RESULTS AND DISCUSSIONS

IR and $^1\text{H-NMR}$ characterizations of phenolic resins

Four different types of *p*-substituted alkyl and aryl phenols were used in this study. The reason why *p*-alkyl substituted phenols were used is that phenol itself gives phenol-formaldehyde resins that are insoluble in plant oils. IR spectra of the phenols are shown in Figure 1. The OH peaks are observed at around 3500 cm^{-1} . At 1610 and 1590 cm^{-1} the $\text{C}=\text{C}$ stretching, and at 800 cm^{-1} para substituted aromatic peaks are observed. By changing the para substituents, peaks which appear at 1000 – 1500 cm^{-1} are also changed. In case of PEP a unique peak is observed at 754 cm^{-1} probably due to the second phenyl ring.

The IR spectra of the oil soluble resoles are shown in Figure 2. The peak at 1012 cm^{-1} indicates the methylol group and cluster of peaks at 874 and 816 cm^{-1} are attributed to tetra substituted aromatic ring.

The $^1\text{H-NMR}$ spectra of the resoles is shown in Figure 3. An intense peak at 4.7 ppm is due to the methylol group (phenyl- CH_2 -OH). At 7 ppm aromatic hydrogens are observed. The OH hydrogens have variable chemical shifts but are generally observed at 3.4 ppm. There is small amount of hydrogen atoms of methylene group linking two phenyl rings which appears at 4.0 ppm. The ratio of these hydrogens to methylol hydrogens allows one to calculate the molecular weight of the resoles. The ratio indicates that the average degree of polymerization of the resoles synthesized in this work is 2. As the reactive groups of the resoles are the end groups, with shorter resoles more reactive end groups are available per unit weight of the resole. This allows lower weight percentage of resoles to be used with linseed oil.

Model reaction of methyl oleate with oil soluble resoles

Literature has a lot of conflicting information about the reaction of phenolic vulcanizing agents with rubbers. Two mechanisms are proposed for the vulcanization of rubbers by phenolic resins. Due to the resemblance of the rubber and plant oil triglyceride double bonds, we assume that these proposals are also valid for the reaction between phenolic resins and plant oil triglycerides.

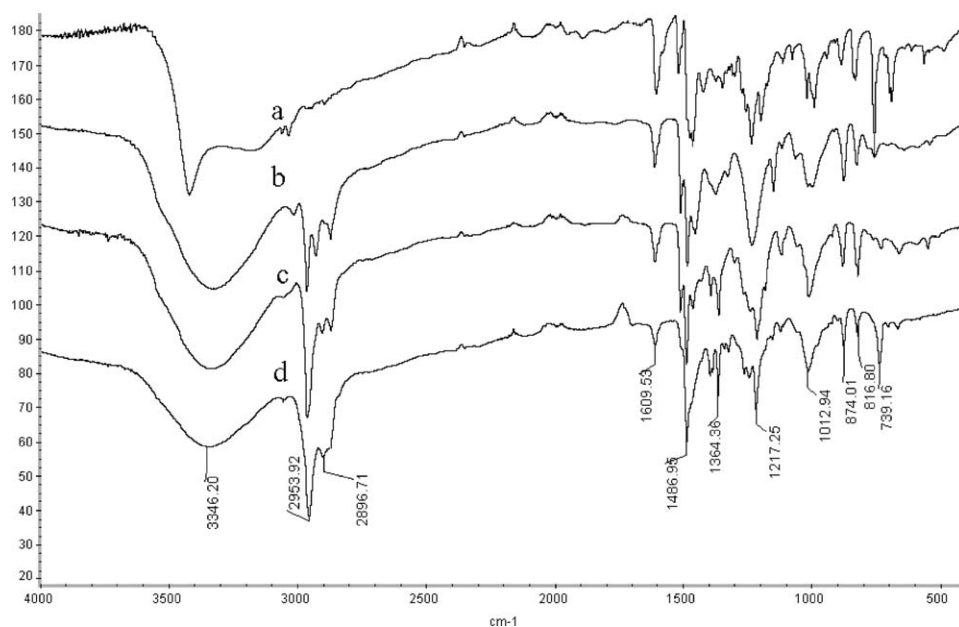


Figure 2 IR spectra of (a) *p*-phenyl phenol (b) *p*-ethyl phenol (c) *p*-tertiary butyl phenyl (d) *p*-tertiary octyl phenol resoles.

It is proposed that, at elevated temperatures methylophenols lose 1 mole of water and quinone methide intermediate is obtained. These reactive species react directly with the double bonds via

Diels-Alder reaction pathway or react with allylic hydrogens via ene reaction pathway (Fig. 4). Both reaction pathways are $4n+2$ type electro-cyclic reactions and are thermally allowed. The driving force

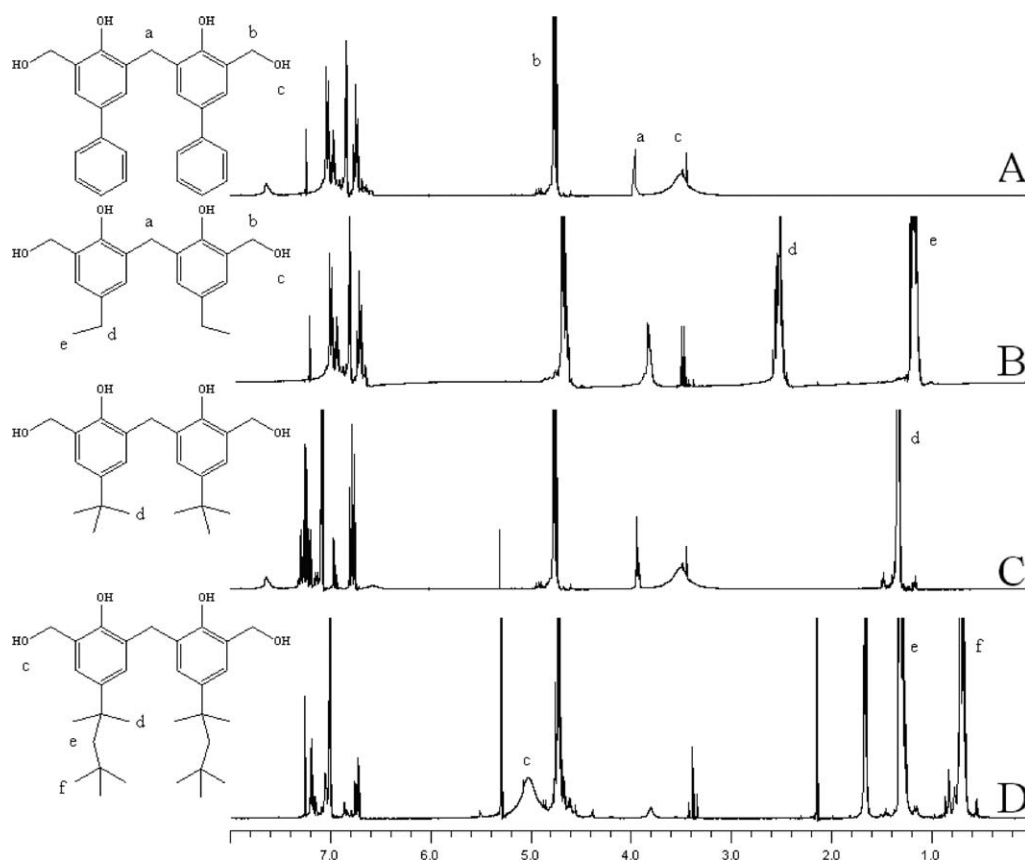


Figure 3 $^1\text{H-NMR}$ spectra of (a) *p*-phenyl phenol (b) *p*-ethyl phenol (c) *p*-tertiary butyl phenyl (d) *p*-tertiary octyl phenol.

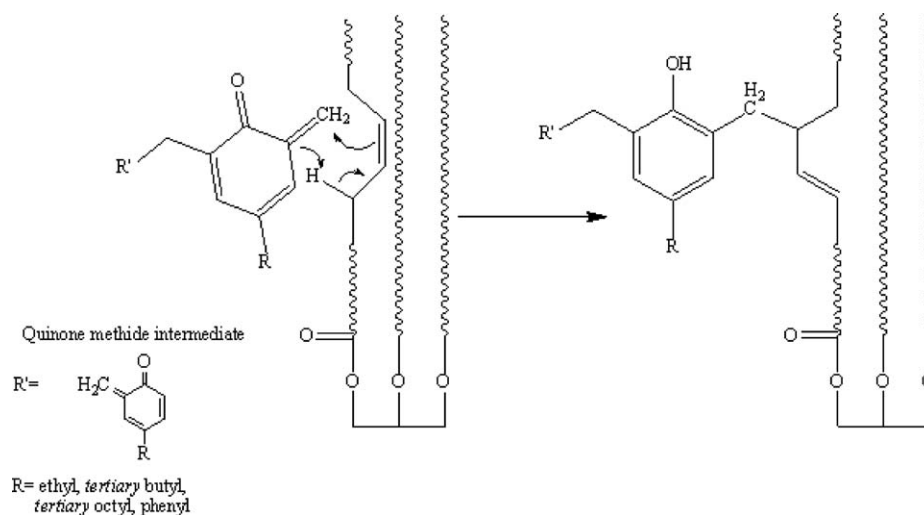


Figure 4 Reaction of the quinone methide intermediate with double bonds of plant oil triglycerides by ene pathway.

for the ene reaction is re-aromatization of the benzene ring. We note that while the Diels-Alder route consumes the triglyceride unsaturation, the ene route merely shifts its position.

Methyl oleate and PTB resole were used as model compounds to elucidate the reaction mechanism. Our previous work shows that polyunsaturated fatty esters are unsuitable as model compounds in such reactions as they undergo a number of self-dimerization reactions which complicates the results. An equimolar mixture of the two compounds was heated to 190°C without adding any catalyst. After 10 min, viscosity of the mixture increased. Gas and formaldehyde evolution was also observed. $^1\text{H-NMR}$ samples were taken at 10 min intervals and the reaction was complete in 60 min. In the $^1\text{H-NMR}$ spectra, disappearance of the hydrogens of the methylol groups was easily followed. The peak at 4.8 ppm was reduced and disappeared in 60 min. At 4.0 ppm a peak was also observed due to the presence of the hydrogen atoms of methylene group linking two phenyl rings of the resole. At 2.9 and 2.6 ppm new peaks appeared due to the allylic-benzylic and homoallylic-benzylic hydrogens. During the reaction the intensity and the ratios of the peaks assigned at 4.0, 2.9, and 2.6 increased (Fig. 5). This finding implies that there were two competitive reactions. These reactions are (i) Self-condensation polymerization of resole and (ii) Ene reaction between quinone methide intermediate and allylic hydrogens of the methyl oleate.

The ratio between the hydrogen atoms of methylene group linking two phenyl rings and the hydrogens of the methylol groups are ~ 0.5 at the beginning of the reaction and increase as the reaction progresses. This indicates that the self condensation between resoles is also taking place. This increase in resole molecular weight is undesirable as it decreases the number of available reactive methylol

end groups. Therefore higher temperatures are not suitable for this reaction. The intensity ratio of the aromatic hydrogens to the methoxy hydrogens or alpha hydrogens of the fatty ester remains the same. The intensity of the fatty ester double bond hydrogens remains essentially the same (Fig. 5). If the reaction between quinone methide intermediate and allylic hydrogens of methyl oleate went via Diels-Alder reaction pathway, one would observe a reduction in the intensity of the fatty ester double bond absorption. Therefore we conclude that the reaction proceeds through an ene pathway.

To suppress the side reactions and increase the probability of the ene reaction, reaction temperature was reduced to 145°C, but, at lower temperatures, longer reaction times were required to complete the

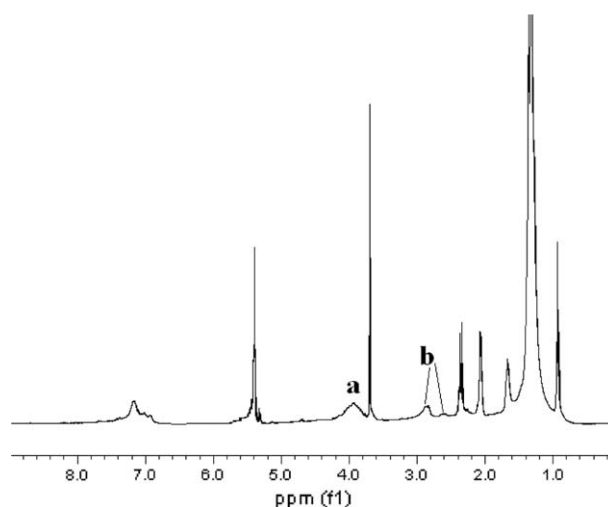


Figure 5 $^1\text{H-NMR}$ of the reaction mixture of methyl oleate and *p*-tertiary butyl phenol resole after 60 min at 190°C. Characteristic peaks of the competitive reactions are labeled as (a) for self-condensation and (b) for ene reactions.

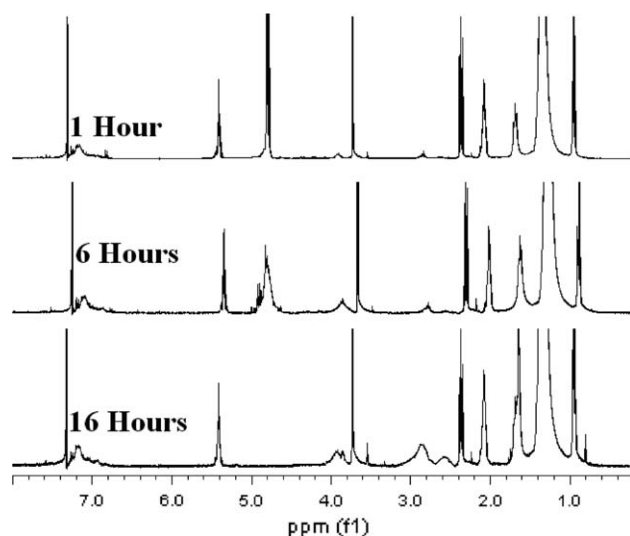


Figure 6 $^1\text{H-NMRs}$ of the reaction mixture of methyl oleate and *p*-tertiary butyl phenol resole with maleic acid catalyst at 145°C .

reaction. It was observed that reaction could not be completed even in 36 h without addition of any catalyst. Therefore maleic acid was used as an ene catalyst and the reaction was completed in 16 h at 145°C . Peaks at 2.9 and 2.5 ppm were observed with relatively high intensity when compared the peak at 4.0 ppm (Fig. 6). In the IR spectrum, the peak at 1654 cm^{-1} whose intensity increased with time is due to self condensation products of PTB resole. Diminishing of the peaks at 1123, 1066, 1017 cm^{-1} due to the loss of methylol groups and observation of a new peak at 976 cm^{-1} due to the allylic groups also agrees with the ene mechanism (Fig. 7).

Properties of polymers synthesized

Reaction of phenolic resins with plant oils may be accelerated at higher temperatures but in this case undesirable self condensations of the phenolic resins also take place. At higher temperatures such as 190°C gas evolution due to the decomposition of phenol formaldehyde resins was observed and the samples always contained gas bubbles. Therefore, lower temperatures were used in the polymerization step. The lowest optimum temperature for this reaction was found to be 145°C by using maleic acid catalyst. Materials were kept for 24 h, under nitrogen, at 145°C to complete the polymerization. Reaction of oil soluble resoles with linseed oil triglycerides gave orange colored rubbery solids samples containing from 10% to 40% of phenolic resin. At 50% phenolic resins loading very hard and strong materials were obtained.

Mechanical properties of the polymers

Stress-strain measurements on a universal testing instrument indicated that the highest tensile strength of 1.25 MPa was obtained with the PEP resole. PPP, PTB and finally PTO showed lower tensile strengths. When the amount of the PTB resin was increased, the stress at break values also increased from 83 to 1125 KPa (Table I). If the *p*-substituent of the resole was smaller, the elongation at break values were also smaller. PEP resole had the smallest *p*-substituent and the reaction product of this resole with linseed oil showed the lowest elongation at break values. Longer *p*-alkyl substituents acted as internal

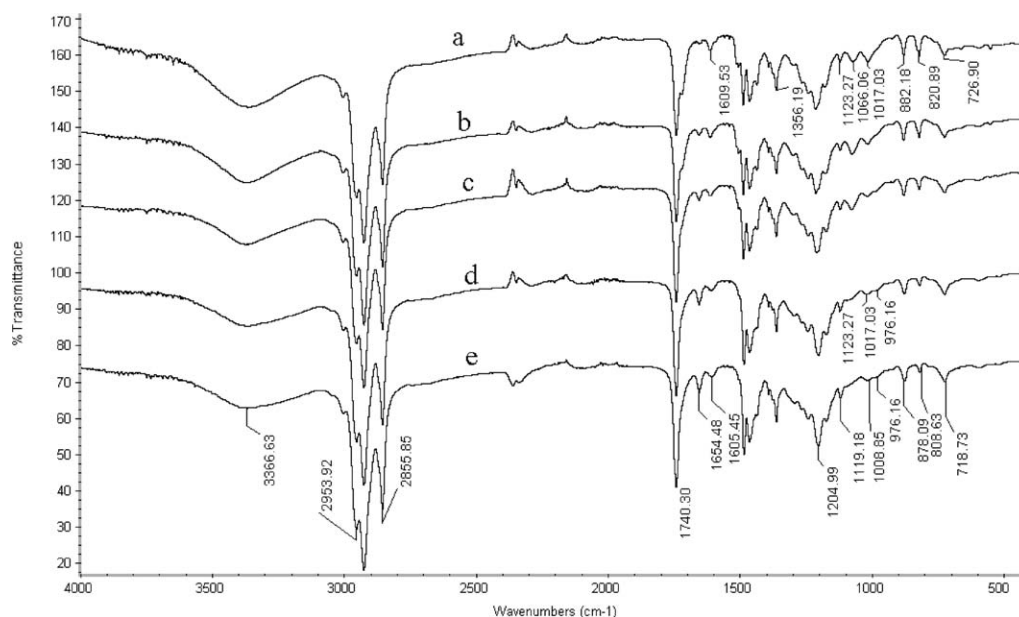


Figure 7 IR spectra of methyl oleate and *p*-tertiary butyl phenol resoles (a) at starting, after (b) 1 h (c) 2 h (d) 6 h, and (e) 16 h at 145°C .

TABLE I
Stress at Break and % Elongation Values of the Polymers Synthesized

Code of polymer	Amount of the resole (%)	Stress at break (KPa)	Elongation (%)
PEP 10	10	277	1
PEP 20	20	502	2
PEP 30	30	750	1
PEP 40	40	1250	0.75
PPP 10	10	36	31
PPP 20	20	500	36
PPP 30	30	1125	28
PTB 10	10	27	13
PTB 20	20	83	16
PTB 30	30	152	23
PTB 40	40	700	39
PTO 10	10	27	16
PTO 20	20	40	18
PTO 30	30	55	19
PTO 40	40	125	23

plasticizer and they reduced the stress at break and increased the elongation at break values.

Similar interesting findings were also observed by Dynamic mechanical analysis of the polymers synthesized. By changing the *p*-substitution from ethyl to *tertiary* octyl group, storage modulus of the materials decreased from 400 MPa to 50 MPa. Similar trend can also be observed at $\tan \delta$ values (Fig. 8). With the increasing size of the alkyl substituent, maxima of $\tan \delta$ peaks increases which implies the viscous character of the material. Another observation is shifting of the peak maxima to lower temperatures with increasing size of alkyl substituents. By using *p*-ethyl phenol with linseed oil a storage modulus of 400 MPa was obtained and the $\tan \delta$ peak at observed at 65°C with a lowest maxima. This result implies the higher elastic nature of the linseed oil and PEP resoles polymers.

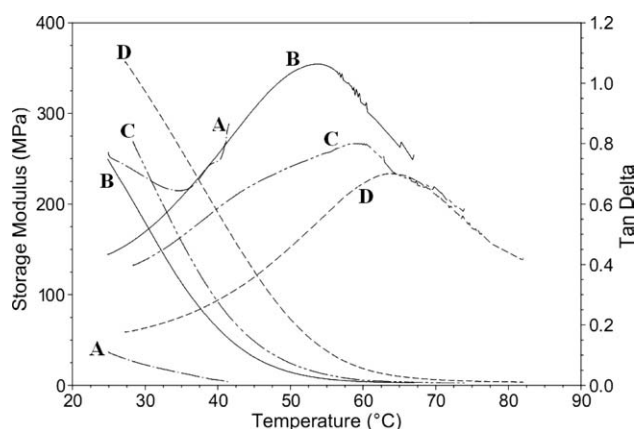


Figure 8 Storage modulus and tan delta values of polymers of linseed oil with 40% (A) PTIOP (B) PTBP (C) PPP (D) PEP resoles.

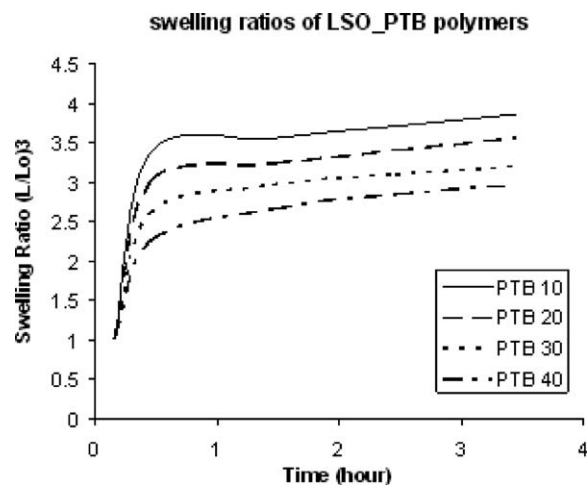


Figure 9 Swelling ratios of polymers which composed of linseed oil and different amount of *p*-*tertiary* butyl phenol (PTB) resoles.

To prove the cross linked structure of the polymers obtained, swelling ratios were measured in CH_2Cl_2 . It was found that when the amounts of the phenolic resin increased to 40%, the swelling ratios of the products were decreased (Fig. 9). Another relationship was also found between the length of the substituent of the phenolic resins and swelling. It was found that when the number of the carbon atoms of the alkyl substituent on the phenol increased, the swelling ratio of the polymer also increased. All polymers reach a plateau after 3 h. And the highest swelling ratio was observed in PTO resole (Fig. 10).

Thermal properties of polymers synthesized: TGA instrument also gave valuable information about thermal stability of the polymers synthesized. The most thermally stable resole was PPP resole. Almost all resoles showed 3 degradation plateaus in their

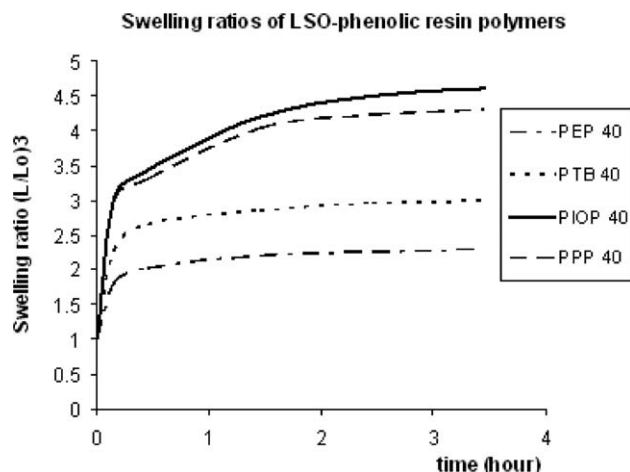


Figure 10 Swelling ratios of the polymers which composed of linseed oil and different type of oil soluble resoles.

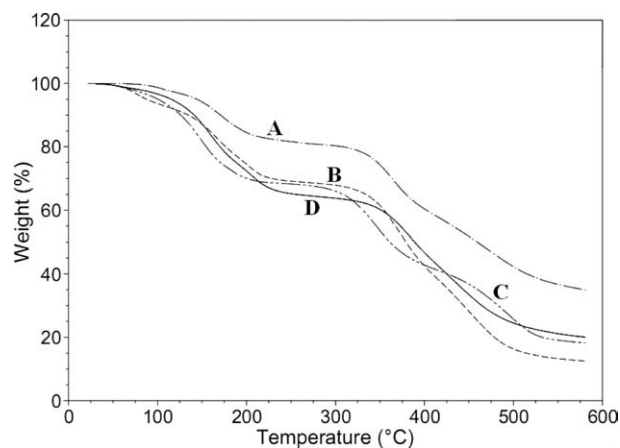


Figure 11 TGA curves of the synthesized resoles (A) *p*-phenyl phenol, (B) *p*-tertiary octyl phenol, (C) *p*-tertiary butyl phenol, (D) *p*-ethyl phenol resoles.

TGA curves (Fig. 11). These plateaus indicated three different decomposition modes. When the resoles were polymerized with linseed oil, thermal stability of the resultant polymers was improved compared to the resole itself. It seems that the resoles start decomposing at their end groups and when the end group is attached to a triglyceride this decomposition pathway is blocked. The highest thermal stability was observed at PEP resole–linseed polymers. This result was also surprising because thermal stability of the PEP resole and linseed oil polymers were expected to be highest due to the heat resistance properties of the aromatic compounds (Fig. 12).

CONCLUSIONS

Short chain resoles proved to be very convenient reagents for polymerizing polyunsaturated plant oils. Unlike the previously used strategies this method gives thermoset products without the need for any

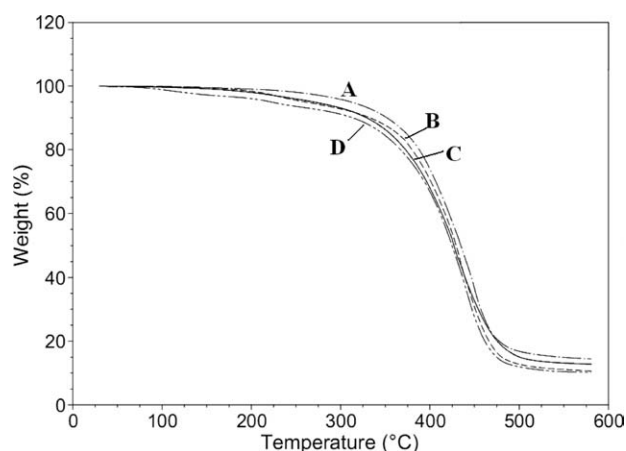


Figure 12 TGA curves of linseed oil polymers with (A) *p*-ethyl phenol, (B) *p*-phenyl phenol, (C) *p*-tertiary octyl phenol, (D) *p*-tertiary butyl phenol resoles.

preliminary functionalization of the plant oil. The oil can be used in its cheapest and most readily available natural state. The polymerization process allows the formation of lightly cross linked pre-polymers (A Stage) which can be molded and further polymerized to fully cross linked materials (B Stage). Polymerization of the linseed oil with different type of oil soluble resoles gave transparent, rubbery polymers with excellent rebound and different physical properties.

Linseed oil gave rubbery polymers when it was reacted with less than 40% of resoles. Above 40%, hard insoluble and infusible brown colored polymers were obtained. When the para substituents of the phenyl ring of the resoles were changed from ethyl to *tertiary* octyl group, thermal and mechanical properties of the product were lower. Long alkyl chains act as an internal plasticizer and this may be responsible for the observation of these changes. Linseed oil contains about 50% of linolenic acid and the availability of a high level of unsaturation allows the use of lower amounts of resoles. Among the resoles, PEP resoles gave the best mechanical properties: Apparently the alkyl chains of this resole were too small to act as a plasticizer. Almost all the polymers synthesized showed good mechanical properties and could be used as surface coatings, adhesives and rubbers.

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