Polymerization of Acrylated Epoxidized Soybean Oil with Phenol Furfural Resins via Repeated Forward and Retro Diels–Alder Reactions

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ABSTRACT: In this work, the Diels–Alder reaction between the acrylate groups of acrylated epoxidized soybean oil and the furan rings of p-tertiary butyl phenol furfural resin (TBPF) is described. The reaction was carried out at 110°C in presence of $FeCl_3$ catalyst, and tough polymers were obtained in 1 h. Surprisingly, samples that were heated and cooled 5, 10, and 20 times to 140°C and room temperature had better mechanical properties than samples that were kept at 140°C for the same total duration. This unexpected behavior is attributed to a series of forward and retro Diels–Alder reactions between the functional groups. To prove this hypothesis, a model reaction between TBPF and n-butyl acrylate was studied. At 100°C, ^{1}H-nuclear magnetic resonance signals of the furan ring protons disappeared, only to reappear at 140°C. Thermogravimetric analysis of the adduct showed a weight loss at 140–150°C, which was in quantitative agreement with the amount of butyl acrylate. Infrared analysis showed that furan rings were not completely consumed by extended heating at 110°C. After five heating and cooling cycles of much shorter duration at 140°C, the furan absorption in the infrared disappeared. The storage modulus of acrylated epoxidized soybean oil-TBPF samples after 20 heating cycles was 1.15 GPa. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1707–1712, 2011

Key words: biodegradable; cross-linking; Diels–Alder polymers, renewable resources, thermosets

INTRODUCTION

Phenolic resins are one of the oldest polymers. Bakelite, introduced in 1907, is a trade name of the thermosetting phenol–formaldehyde resin. Although it has now been replaced by more modern thermosets as an industrial manufacturing material, in the past, Bakelite was used in myriad applications.[1–3] The largest market segment for phenolic resins is wood adhesives. After cure, the phenolic resins give high modulus, high T_g, and high cross-link density polymers. Phenolic resins also show good heat, moisture, solvent, and electrical resistance. These resins are generally cheap, and these factors make them valuable materials for many applications.[4,5] Unfortunately, phenolic resins are not environmentally friendly materials because of the toxicity of formaldehyde, and this is the main drawback of these groups of materials. If one substitutes formaldehyde with other aldehydes, these polymers can be used instead of phenol–formaldehyde resins. Different aldehydes and ketones such as furfural, acetaldehyde, and chloral can be used instead of formaldehyde. Furfural is one of the most successful candidates as the aldehyde component for use in the synthesis of phenolic resins. Furfural has the advantage that it can be produced from renewable resources (corn cobs) and has a high boiling point, and is less toxic compared with formaldehyde. However, it is not stable in acidic medium and is also susceptible to oxygen. Because of resonance, electron density in the furan ring increases at the second and fifth positions. This makes the furan ring of furfural unstable in acidic medium. Thus, condensation reaction of phenol and furfural cannot be carried out by acid catalysts.[6–8] In acidic medium, phenol–furfural resins readily undergo a cationic polymerization reaction to give black infusible materials. When using basic catalysts, the ratio of furfural to phenol is generally smaller than 1; thus, the resin obtained is actually a novolac-type resin. Although they are made with less than 1 mol of furfural per mol of phenol, these resins are not as stable and fusible as formaldehyde novolacs. Phenol–furfural resins are stable under neutral and alkaline medium and have been successfully used as binders for fiberboard.
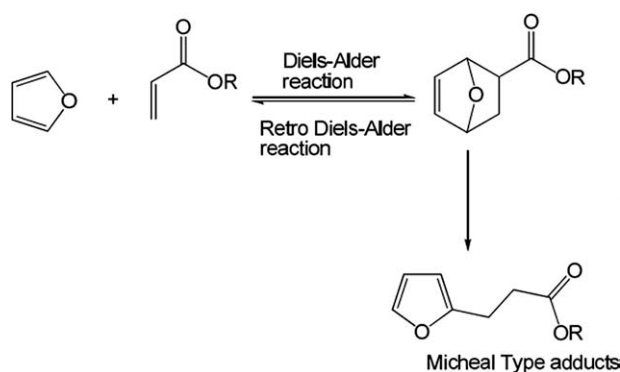
Figure 1 Reaction of furan with acrylates.

An interesting property of the furan ring is the possibility of Diels–Alder reaction. Furan ring is an aromatic ring and has the lowest resonance energy among the other aromatic five-membered rings such as thiophene and pyrrole. Furan ring can act as a diene and reacts readily with suitable dienophile such as, acrylates, maleates, and acetylenes to give valuable six-membered rings. These rings are not stable at elevated temperatures and readily decompose back to furan and unsaturated compounds.[9,10] The retro Diels–Alder reaction does not give a perfect reversal, and, at the end of the reaction, Michael-type adducts can also be observed (Fig. 1).[11] The Diels–Alder product and the Michael addition product can be distinguished easily by the presence of the typical furan aromatic hydrogens in [1]H-nuclear magnetic resonance (NMR).

One of the most important plant oil triglyceride-based monomers is acrylated epoxidized soybean oil (AESO).[12] AESO is obtained from renewable resources, and soil burial experiments of the polymers of this compound showed that it is environmentally friendly compared with other acrylate polymers.[13]

In this study, we report the synthesis of the Diels–Alder network polymer of AESO with p-tertiary butyl phenol furfural resin (TBPF) resin (Fig. 2). Because of the multifunctional nature of the monomers, cross-linked polymers with good mechanical and thermal properties are obtained.

EXPERIMENTAL

Materials and methods

AESO was obtained from Sartomer Co. (Exton, PA) and was used as obtained. Chloroform, furfural, p-tertiary butyl phenol, potassium carbonate, sodium hydroxide, and toluene were purchased from Merck (Darmstadt, Germany) and were used as received. n-Butyl acrylate was obtained from Fluka (Buchs, Switzerland), and it was passed from a basic alumina column before use.

Fourier transform infrared spectroscopy characterization of compounds was performed by Nicolet 380

series ATR spectrometer using diamond window. The ^{1}H-NMR spectra were 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 CDCl$_3$ as a solvent. Thermogravimetric analysis (TGA) characterizations were performed by Thermal Analyses 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 dynamic mechanical analysis (DMA) experiments were prepared with a microtome into rectangular shapes having the average dimensions of $12 \times 35 \times 3$ mm^3. Strain tests were performed by Devotrans DVG 32 Model tester with a 20 mm/min elongation rate.

Synthesis of TBPF resin

Literature methods were used with some modifications.[14] 37.5 g of p-tertiary butyl phenol (0.25 mol) was mixed with 37.5 g of water. 3.75 g of NaOH
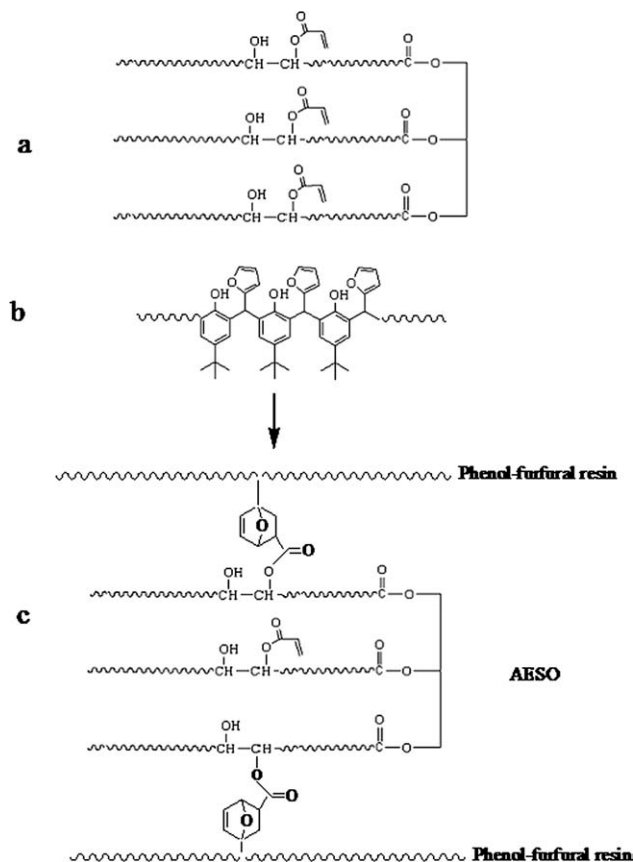
Figure 2 Structures of (a) AESO, (b) TBPF resin, and (c) the Diels–Alder adduct of (a) and (b).

(0.093 mol) and 70 mL of toluene were added, and this mixture was heated to 60°C. Then, 48 g (0.5 mol) of furfural was added dropwise in 30 min. Then, temperature was increased and allowed to reach reflux. Reflux was continued for 2 h, and the mixture was cooled. At the end of the reaction, the residual toluene and water was removed on a rotary evaporator at 95°C. Then, the crude product was dissolved in 100 mL of diethyl ether, and ether layer was extracted with concentrated salt solution four times. Then, the ether layer was dried over sodium sulfate, and ether was evaporated. The gel permeation chromatography result indicated that the molecular weight of the polymer was 1800.

Model reaction with n-butyl acrylate

In a round-bottom flask, 1 g of TBPF resin was dissolved in 2 mL of n-butyl acrylate. Then, 0.02 g of dry $FeCl_3$ (2% of phenolic resin by weight) was added to this mixture, and N_2 was introduced to the system. Mixture was stirred to obtain a clear transparent solution, and the temperature was raised to 100°C and stirred at this temperature for 1 h. Then, the mixture was cooled, and the excess n-butyl acrylate was removed with N_2 purging. A brittle solid was obtained with dark red color. For the retro Diels–Alder reaction, the material was heated at 140°C with N_2 purging for 1 h. A black material was obtained. This material was not completely soluble in chloroform. The weight loss on heating was determined by thermogravimetry.

Polymerization of TBPF resin with AESO

TBPF resin, 15.0 g (0.059 mol furan), and 20.6 g of AESO (0.059 mol acrylate) were mixed in 50 mL dry $CHCl_3$. To this mixture, 0.36 g $FeCl_3$ (2% of phenolic resin by weight) solution in 20 mL $CHCl_3$ was added. Stirring was continued until all materials were dissolved. Then, this homogenous solution was poured into a Teflon mold, and $CHCl_3$ was removed at 50°C in a vacuum oven. Dark red-colored creamy mixture was obtained, and, then, this mixture was cured at 110°C for 1 h under N_2 atmosphere. Flexible, tough, and strong polymers were obtained.

RESULTS AND DISCUSSIONS

Characterization of *TBPF* resin and *AESO* polymer

Characterization of the TBPF resins was performed with infrared (IR) and ^{1}H-NMR spectroscopy techniques. The IR spectra of TBPF, AESO, and Diels–Alder products of TBPF and AESO are shown in Figure 3. IR spectra of TBPF showed a broad peak at 3370 cm^{-1} due to OH functionality. Peaks at 2960, 2900,
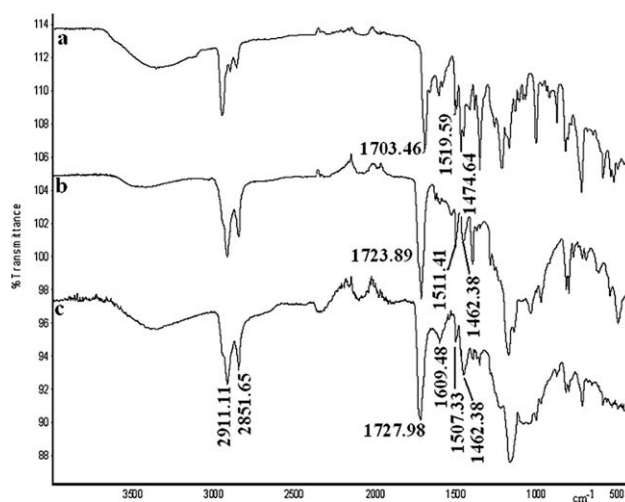

Figure 3 IR spectrum of (a) TBPF resin, (b) AESO, and (c) Diels–Alder product of AESO and TBPF resin.

and 2860 cm^{-1} belong to aliphatic C—H stretching of the tertiary butyl group. A triplet was observed at 1270, 1229, and 1180 cm^{-1} due to C—O stretching of the furan ring. The characteristic IR peaks of AESO are at 3300 cm^{-1} due to the-OH groups, at 1723 cm^{-1} due to the acrylate ester carbonyl, and multiple peaks lie between 1300 and 1000 cm^{-1} due to the presence of C—O stretching of ester groups. Unfortunately, when TBPF resin was reacted with AESO, the change in the intensity of the peaks at 1270, 1229, and 1180 cm^{-1} could not be easily observed. But, disappearance of the peaks at 1703, 1519, and 1474 cm^{-1} was easily followed, and the change of the peaks at 1609 cm^{-1} was also observed. These findings indicate that the Diels–Alder reaction went.

^{1}H-NMR spectrum showed —CH$_3$ protons of the p-tertiary butyl group at 1 ppm. Proton vicinal to furan ring was observed at 4.5 ppm as a broad peak. Protons of the furan moiety were observed at 5.8, 6.4, and 6.8 ppm. Aromatic protons of the phenyl ring were observed at 7 ppm (Fig. 4).

TBPF resin was synthesized by the condensation reaction of p-tertiary butyl phenol and furfural in the presence of NaOH catalyst. Polymerization was performed by azeotropic distillation with toluene for 2 h. Earlier work in our group had shown that phenolic resins are soluble in plant oil derivatives only if the phenol has a large *para* substituent such as p-tertiary butyl, p-ethyl, p-phenyl, etc.[15] Among such groups, *para* tertiary butyl phenol was chosen in this study because of its solubility in AESO and its simple NMR spectrum. The gel permeation chromatography gave an M_n of 1800 and polydispersity index of 1.08, which indicated that the number of the repeating units is 7.

AESO is synthesized by the acrylation of epoxidized soybean oil (ESO).[12] This material has been used and studied in our group earlier. It was found
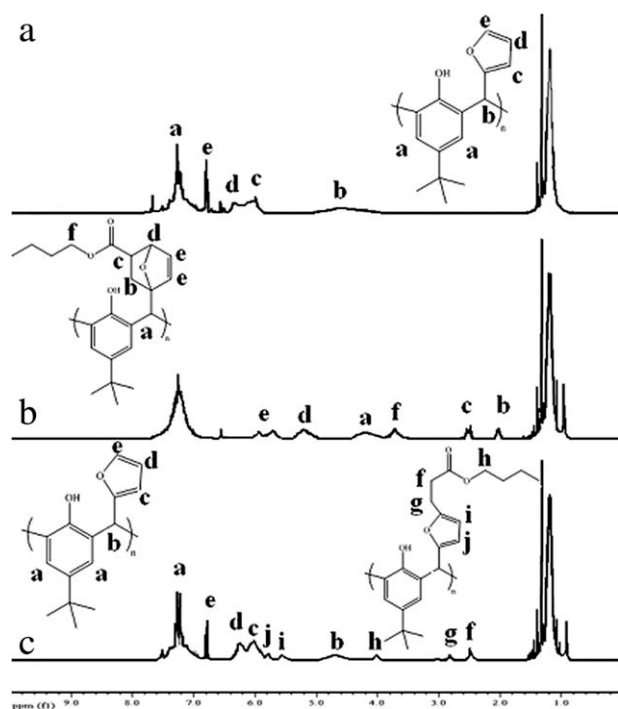
Figure 4 ¹H-NMR spectrum of (a) TBPF polymer, (b) Diels–Alder product of TBPF polymer and *n*-butyl acrylate, and (c) products of retro Diels–Alder reaction of TBPF resin and *n*-butyl acrylate.

to have, on the average, 3.2 acrylate groups per triglyceride and a molecular weight of 2200. This fact indicates that some dimerization due to epoxy ring opening takes place during acrylation of ESO.

Evidences of Diels–Alder and retro Diels–Alder reactions

To prove the Diels–Alder reaction and retro Diels–Alder reaction, model reactions were carried out. For this purpose, TBPF resin was reacted with *n*-butyl acrylate in the presence of a Lewis acid catalyst.

Diels–Alder reaction was followed by ¹H-NMR and TGA instruments. ¹H-NMR spectrum showed the disappearance of the furan protons and appearance of the protons of the new double bonds at the end of the Diels–Alder reaction. ¹H-NMR spectrum of the TBPF resin, Diels–Alder reaction product of the resin with *n*-butyl acrylate, and Michael adduct of the nonperfect retro Diels–Alder reaction are shown in Figure 4. We note that furan aromatic hydrogens are absent in the ¹H-NMR of the product. This indicates that the Michael addition product is either absent or present in too small an amount to be detectable by ¹H-NMR.

When Diels–Alder product was heated to 140°C for 1 h, furan ring protons were again observed with low intensity. The yield of the retro Diels–Alder reaction was found to be around 35%. The yield was calculated by the NMR signal ratio between the

proton geminal to furan ring (1H) and aromatic protons of the phenyl ring (2H). At the beginning of the reaction, the integration ratio was 1 : 2, as expected, but after the retro Diels–Alder reaction, it was found to be 0.35 : 2 (Fig. 4).

Similar observations were also obtained by TGA instrument. For this purpose, derivative of the TGA traces were analyzed. TGA of the TBPF resin showed weight lost at 100°C, which probably corresponds to loss of water produced by chain extension by further condensation of the polymer, and at 300°C, which is probably associated with the loss of furan. The amount of the weight loss was 24%, which was exactly the percentage of the furan rings in the TBPF resin. When derivative TGA of the Diels–Alder product of TBPF resin and *n*-butyl acrylate was examined, a broad weight loss peak between 100°C and 200°C was observed. This is probably due to both chain extension of the phenolic resin and retro Diels–Alder reaction. The retro Diels–Alder reaction yield was found to be 30% by measuring the amount of the weight lost (Fig. 5). This result was so close to the ¹H-NMR findings.

Polymerization reaction

TBPF resin was a very hard and brittle solid and was not easily soluble in AESO. Thus, all monomers mixed in the minimum amount of CHCl₃ and FeCl₃ solution was added to the mixture. Because of the presence of phenol, color of the mixture turned to greenish-blue. CHCl₃ was evaporated, and a homogenous mixture was obtained. At low temperatures, Diels–Alder reaction was not observed. Heating this homogenous mixture at 110°C under N₂ atmosphere gave a tough and elastic material in 1 h. When the material was cooled to room temperature, it hardened. It is interesting to note that normally AESO
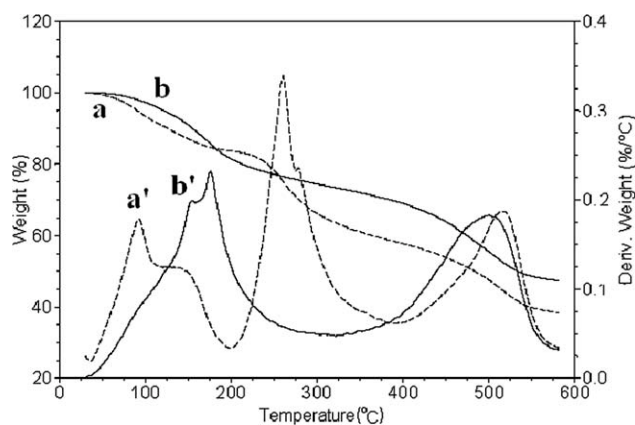
Figure 5 TGAs of (a) TBPF resin and (b) Diels–Alder product of TBPF polymer and *n*-butyl acrylate, and derivative TGAs of (a′) TBPF resin and (b′) Diels–Alder product of TBPF polymer and *n*-butyl acrylate.
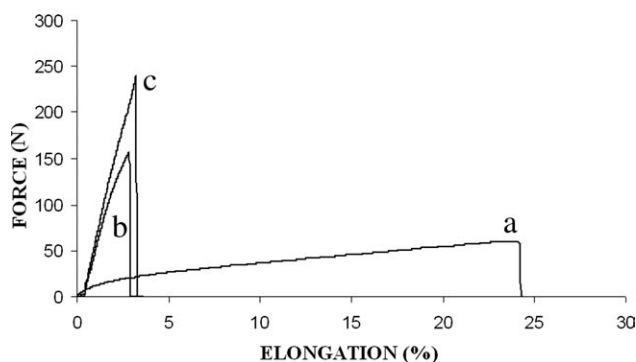
needs to be protected against prolonged heating by the use of a free-radical inhibitor. In this case, there was no need for an inhibitor because the phenols in the phenolic resin are known to act as excellent inhibitors.[16] When the Diels–Alder reaction was attempted without any catalyst, much higher temperatures were used, but in each case AESO survived under this reaction conditions without thermally homopolymerizing. These facts lead us to believe that the Diels–Alder cross-linking reaction is the only reaction that operates under these conditions.

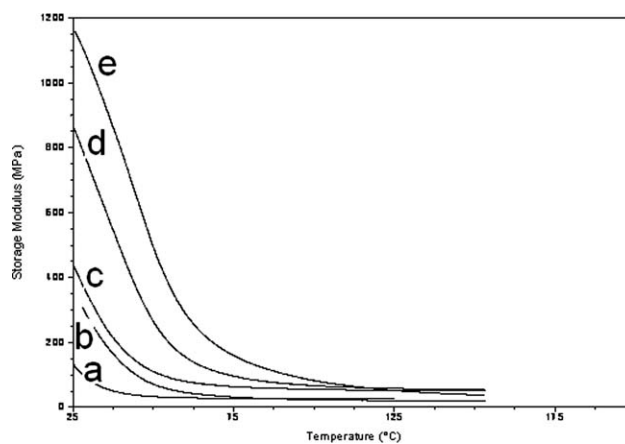## Mechanical properties of the polymers synthesized

The product is a tough and flexible material and had a maximum tensile strength of 1.6 MPa at break. Surprisingly, the product got harder and harder after repeated heating and cooling cycles between 140°C and room temperature, and the hardness reached a plateau after 10 cycles.

After 10 such heating cycles, maximum tensile strength reached 7.2 MPa, which corresponds to a 4.5-fold increase. When the sample was kept at 140°C for the same amount of total heating time, the highest tensile strength was found to increase only to 4.1 MPa, which corresponds to a 2.5-fold increase (Fig. 6). This result suggests that a series of forward and retro Diels–Alder reactions are taking place. When the retro reaction takes place, the cross-link density is reduced, the polymer chains can change their conformation, and more and more furan and acrylate pairs can assume the rigid requirements of the Diels–Alder transition state.

DMA is another technique, which gives better information about the mechanical properties of the synthesized material. The DMA plot of the polymers is shown in Figure 7. Material that was heated and cooled for 10 times showed a storage modulus at around 1 GPa. This value is close to the values of industrial thermoset resins and is one of the best

Figure 7 DMA-obtained storage modulus of TBPF-AESO polymers, which were exposed to different heat treatments. (a) Thermoset polymer without heat treatment; (b) thermoset polymer heated for 300 min at 140°C; (c) thermoset polymer exposed to five heating and re-cooling cycles; and thermoset polymer exposed to (d) 10 and (e) 20 heating and re-cooling cycles between 140°C and room temperature.

results obtained from a plant oil-based polymer synthesized by our research group.[17–20] Neat polymer showed a tan δ maximum at 35°C, whereas the material that was heat cycled 20 times showed a maximum at 58°C. This result is an evidence of the increasing cross-link density. Another piece of information was obtained from the heights of the tan δ peaks. The maxima of the peaks decreased after thermal cycling, indicating an increase in toughness. After 20 heating and cooling cycle, the value of maximum of tan δ peak was the lowest, and this could be accepted as an indication of the increasing elastic character of the polymer (Fig. 8).
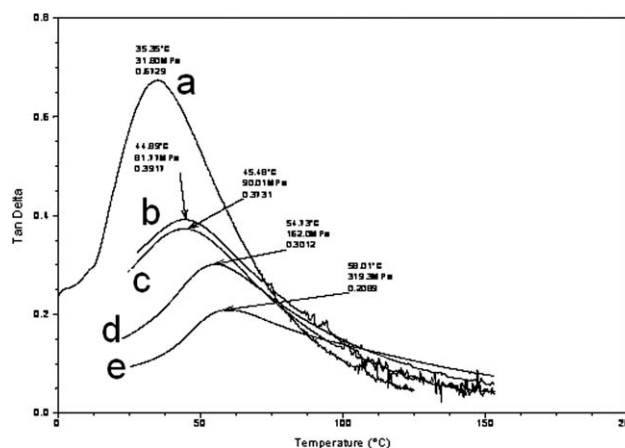

Figure 6 Stress-elongation graphs of (a) TBPF-AESO polymer, (b) TBPF-AESO after 300 min heat treatment at 140°C, and (c) TBPF-AESO polymer after 10 heating and cooling cycles between 140°C and room temperature.
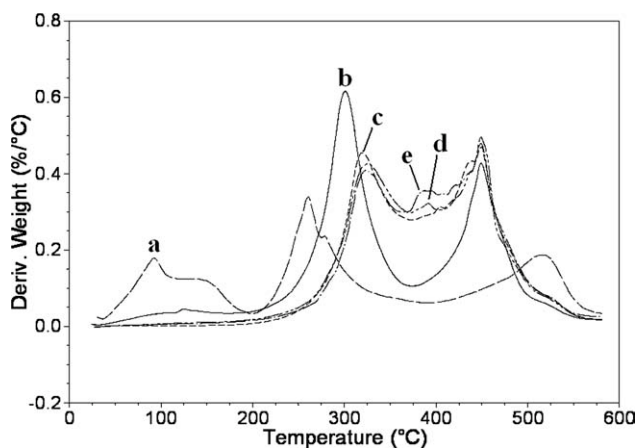

Figure 8 Tan δ values of TBPF-AESO polymers, which were exposed to different heat treatments. (a) Thermoset polymer without heat treatment; (b) thermoset polymer heated for 300 min; and thermoset polymer exposed to (c) 5, (d) 10, and (e) 20 heating and cooling cycles between 140°C and room temperature.
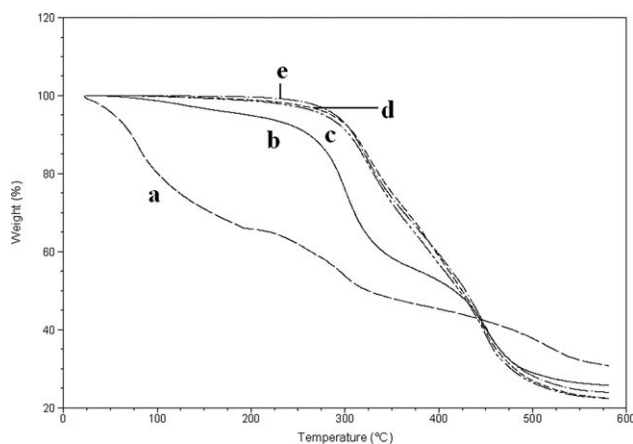
Figure 9 TGA graphs of TBPF-AESO polymers, which were exposed to different heat treatments. (a) TBPF resin, (b) thermoset polymer without heat treatment, (c) thermoset polymer heated for 300 min, and thermoset polymer exposed to (d) 5 and (e) 10 heating and re-cooling cycles between 140°C and room temperature.

Thermal properties of the polymers synthesized

Thermal decomposition of the materials was followed by TGA. In Figure 9, TGA curves show that the TBPF resin showed three plateaus, which means that three fragments were sequentially lost when the heat was applied to the material. When the furfural resin was polymerized with AESO, the shape of the curves shifted to higher temperatures. There was almost no difference between the curves of (e) and (d) (Figs. 9 and 10). Derivative TGA curves also gave valuable data. All TBPF-AESO polymers that were exposed to different heat treatments showed two maxima, one at 310°C and the other at 450°C. When the number of heating cycles was increased, maxima at 310°C decreased and the maxima at

Figure 10 Derivative TGA graphs of TBPF-AESO polymers, which were exposed to different heat treatments. (a) TBPF resin, (b) thermoset polymer without heat treatment, (c) thermoset polymer heated for 300 min, and thermoset polymer exposed to (d) 5 and (e) 10 heating and re-cooling cycles between 140°C and room temperature.

450°C increased. This is another indication that the retro Diels–Alder reaction does not proceed cleanly.

CONCLUSIONS

Acrylate groups on the soybean oil gave Diels–Alder reaction with furan rings on the phenolic resin. A dark red-colored polymer was obtained at 110°C in 1 h. This polymer had a unique behavior in that it was hardened on heating and re-cooling numerous times. This is attributed to repeated Diels–Alder and retro Diels–Alder reactions. Polymers with good thermal and mechanical properties were obtained. After 10 heating and cooling cycles, storage modulus of the polymers approached to 1 GPa, which is close to the storage modulus of many industrial polymers. Polymers synthesized contain approximately 60% of plant oil triglyceride and 40% of phenolic resin. If one considers the fact that furfural is also obtained from plant-based materials, the finished polymer has 70% renewable raw material content. The high renewable content and very good mechanical properties make the polymers synthesized in this work unique. Phenols that are substituted by alkyl groups other than tertiary butyl can also be used in similar syntheses, and these are currently under investigation.

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