Synthesis and Characterization of Polymers from Soybean Oil and *p*-Dinitrosobenzene

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ABSTRACT: In this study, rubbery, bio-based thermoset polymers were synthesized from soybean oil (SO) and *p*-dinitrosobenzene (DNB) via an *ene* reaction. Polymeric *p*-dinitrosobenzene (PDNB) was synthesized from *p*-quinone dioxime and was thermally depolymerized in the presence of SO. SO/PDNB polymers were synthesized by a two-stage polymerization. During the reaction, the role of different parameters such as mol ratio of SO and PDNB, preheating temperature of SO, polymerization time, and temperature were examined. Polymerization was followed by IR spectroscopy, and the polymers obtained were characterized by dynamic mechanical analysis, thermogravimetric analysis, and differential scanning calorimetry. The polymers have glass transition temperature ranging from $-51.5°C$ to $-46.3°C$, whereas their storage moduli are between 430 and 210 MPa at $-60°C$. Thermogravimetric analysis reveals that all of the polymers have temperatures of maximum degradation around $500°C$. The crosslinked network structure of the polymers was investigated by swelling behavior and surface hardness test. Methyl oleate was used as a model compound to examine the chemical structure of the products. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1925–1934, 2009

Key words: renewable resources; biomaterials; biopolymers; elastomers; vulcanization

INTRODUCTION

The use of renewable resources such as starch, cellulose, and vegetable oils to produce polymeric materials aims to reduce our dependence on petroleum-based raw materials.[1] Vegetable oils are particularly interesting, since they are raw materials obtained from renewable resources throughout the world at a relatively low cost. Moreover, vegetable oils present numerous reactive sites such as ester groups, double bonds, allylic positions, and the α-position to ester groups, where it is possible either to introduce polymerizable groups or to polymerize the oils directly, thus obtaining biodegradable, bio-based materials.[2] The reactivity of the internal double bonds of unsaturated triglycerides is similar to that of polybutadiene, and the doubly allylic hydrogens found in polyunsaturated triglycerides are more reactive than allylic ones. Thus the vulcanization methods using sulfur, peroxide, phenolics, and quinoids, which have been successful in rubbers, seem to be good candidates for the polymerization of unsaturated triglycerides.[3]

In fact, sulfur polymerization of oils to factice is known.[4–7] Also, peroxide curing of unsaturated oils leading to soft rubbers and reactions of soybean oil with amine and diethyl azodicarboxylate (DEAD) at high temperatures have been reported.[1,8–11] Furthermore, Cayli has investigated the phenolic-resin cure of different plant oils.[12] However, a literature search revealed that there is no reference related to the polymerization of a triglyceride molecule using *p*-dinitrosobenzene (PDNB).

p-Dinitrosobenzene (DNB) is a finely crystalline, green substance that is sparingly soluble in dimethyl formamide, alcohol, hot xylene, and water. This compound exists as an amorphous polymeric solid (PDNB) at room temperature, and the monomeric DNB can be obtained by fast heating in xylene or by sublimation in vacuum onto a surface cooled by liquid nitrogen.[13] The relative stabilities of monomeric, dimeric *cis*, and *trans* structures of DNB are dependent on the physical state, the temperature, and the solvent properties (Fig. 1).[14] DNB has been successfully used for crosslinking rubbers to give chemically resistant vulcanizates but has now been surpassed by newer and more user-friendly vulcanizing agents.

Polymeric DNB (PDNB) undergoes transformations upon heating from cryogenic temperatures (Fig. 2).[15]

During the depolymerization of PDNB, the free monomeric nitroso compounds obtained are in a gaseous state and are very labile. The polar N=O
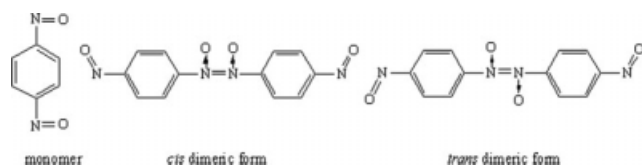
Figure 1 Monomeric, *cis*, and *trans* dimeric forms of DNB, respectively.

Figure 3 Transformations of the nitroso group.[16]

bond results in a susceptibility to additions of nucleophiles and free electron pair on nitrogen renders the compound nucleophilic. Furthermore, the N=O group can be easily oxidized to a nitro group or reduced to hydroxylamine or even to an amino group by disproportionation (Fig. 3).[16] Therefore, dinitrosobenzene is a substance that is difficult to handle experimentally.

In this work we wish to report the synthesis and characterization of novel bio-based polymers prepared by the polymerization of soybean oil (SO) with polymeric PDNB via an *ene* reaction.

EXPERIMENTAL

Materials

1,4-Benzoquinone dioxime (QDO, 97%) was purchased from Aldrich (Steinheim, Germany) and was used as obtained. Hydrogen peroxide (30%) was supplied by Riedel-de Haën Fine Chemicals (Seelze, Germany) and was used as received. Hydrochloric acid (37%) was obtained from Tekkim Lab. SO supplied by Marsa (Adana, Turkey) was food grade and used without further purification. Petroleum ether (boiling range 40–60°C) was purchased from Prolabo (Paris, France) and used as obtained. CDCl$_3$, purchased from Aldrich (Milwaukee, WI) was used for ^{1}H-NMR analysis. Dichloromethane was supplied by Cakir Kimya (Istanbul, Turkey). Methyl oleate was synthesized according to the procedure described by Cayli and Kusefoglu.[17]

Synthesis of PDNB

PDNB was synthesized according to Vladykin and Trakhtenberg by oxidation of QDO in an aqueous suspension using hydrogen peroxide as an oxidizing agent in the presence of hydrochloric acid as a catalyst.[18] Pure PDNB was obtained as green powder in around 94% yield.

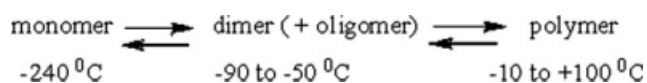IR (cm^{-1}): 3110 (m), 1485 (s, *trans* —N=N—O, Asym.), 1417 (s, N=N), 1306 (m, C$_{aromatic}$—N), 1258 (s, *trans* N—O), 1104 (s, N—N for aromatic structures), 1012 (s, N—N for aromatic structures), 858 (s, C—H for *para* substituted aromatic structures), 775 (s), 570 (s) and 482 (s, out-of-plane ring deformation. IR spectrum coincides with the spectrum given in the literature.[15]

Polymerization of SO with PDNB

In a typical example, 0.351 g (0.00258 mol, 136 g/mol) of PDNB was added to 1.727 g (0.00199 mol, 867 g/mol) SO preheated to 120°C in a round-bottom flask equipped with a magnetic stirrer. N$_2$ gas was passed through the flask to remove any residual moisture and oxygen. The dispersion was stirred at 90°C under N$_2$ atmosphere for 11 min. A temperature increase was observed; the dispersion became milky brown colored and then dark brown and finally black. The dispersion became very thick, viscous, and tacky. The viscous pre-polymer (Stage A) was poured into a silicone mold and the sample was postcured under vacuum (Stage B) for ~ 100 min at 120°C. The nomenclature used throughout the manuscript is as follows: a sample containing 1 mol of SO preheated at 120°C and 1 mol of PDNB is denoted as SO/PDNB-1/1-120.

Model compound polymerization

In an N$_2$-purged, 25-mL, round-bottom flask, 0.1894 g (0.00139 mol, 136 g/mol) PDNB and 0.5397 g (0.00181 mol, 297 g/mol) methyl oleate (MO) were mixed. The curing process was done under N$_2$ atmosphere to remove any moisture and oxygen present in the medium. Polymerization was carried out at 80°C for 60 min, then at 90°C for 60 min, and finally at 120°C for 2 h. Black-colored, sticky, rubber-like material was obtained. The reaction was followed by FTIR spectroscopy.

Characterization

Before instrumental analysis, the unreacted SO was removed from the samples by extraction with petroleum ether. The IR analysis was performed on a PerkinElmer 1600 FTIR spectrometer (Waltham, MA) using KBr windows and on a Nicolet 380 FTIR with

Figure 2 Transformations of PDNB upon heating.[15]

TABLE I
Reaction Conditions and Mol Ratios of SO-PDNB

Sample code	SO/PDNB mol ratio	Preheating temp. of SO (°C)	Curing temp. of Stage A (°C)	Curing time of A Stage (min)	Postcuring temp. (°C)	Curing time of B Stage (min)
SO/PDNB-1/1-120	1/1	120	90	35	120	130
SO/PDNB-1/1-80	1/1	80	90	45	120	180
SO/PDNB-1/1	1/1	Not preheated	90	60	120	No curing
SO/PDNB-1/1.3-120	1/1.3	120	90	11	120	100
SO/PDNB-1/1.3-80	1/1.3	80	90	18	120	120
SO/PDNB-1/1.3	1/1.3	Not preheated	90	30	120	190
SO/PDNB-1/1.5-120	1/1.5	120	90	4	120	60
SO/PDNB-1/1.5-80	1/1.5	80	90	12	120	80
SO/PDNB-1/1.5	1/1.5	Not preheated	90	20	120	120

Smart Diamond ATR (Waltham, MA). All the ^{1}H-NMR spectra were recorded on Varian 400-MHz and Varian 60-MHz NMR spectrometers (Waltham, MA). The thermal gravimetric analysis (TGA) of polymer samples was done with TA Instrument TGA Q50 (New Castle, DE). Temperature scans were performed from room temperature to 600°C with a heating rate of 10°C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed with a TA Q 100 instrument (New Castle, DE) at a 10°C/min heating rate, from −75 to 150°C, under nitrogen atmosphere. For each sample, two runs were done, and approximately the same T_g value was observed in both runs. Dynamic Mechanical Analysis (DMA) was performed using a TA Instruments Q800 (New Castle, DE) equipped with a liquid-nitrogen cooling apparatus in the single cantilever mode. The polymer samples for dynamic mechanical analysis were prepared to dimensions of 25 mm × 5 mm × 0.5 mm. Temperature scans were run from −70 to 130°C at a heating rate of 5°C/min with a frequency of 1 Hz and strain of 0.01%. The viscoelastic properties, namely, the storage modulus (E′) and mechanical loss (damping) factor (tan δ), were recorded as a function of temperature. Glass-transition temperatures (T_gs) for the polymers were obtained from the peaks of the tan δ curves. The swelling behavior of the polymers was tested in CH_2Cl_2 with a Gaertner 7109-46 traveling microscope (Skokie, IL). The samples were placed in a closed container and the experiment was continued until the solvent uptake ceased. The Zwick/Roell Durometer (Ulm, Germany) was used to determine the surface hardness of polymer samples; the test was performed according to ASTM D 2240 standard test.

RESULTS AND DISCUSSION

Polymerization and crosslinking of SO with PDNB

The reaction between PDNB and SO is believed to be an *ene* reaction. Although *ene* reactions usually need high temperatures, catalyst, and long reaction times, in our work the reactions went in a comparatively short time and at lower temperatures. The polymerization reactions of SO and PDNB were carried out by mixing the reactants in a given ratio without solvent in a dry N_2 atmosphere (Table I). It has been reported that the PDNB has the potential to behave as a living polymer in the presence of air.[19] PDNB is a difficult material to disperse in any liquid, and it tends to agglomerate in SO. The mixing of PDNB and SO should be thorough enough to provide a reasonably homogenous mixture. Agglomerated PDNB particles caused heterogenous polymerization, and nonhomogenous polymer samples were obtained. Furthermore, sometimes PDNB particles clustered together and caused sudden expansion, probably due to sudden depolymerization. These obstacles were overcome by applying continuous stirring during synthesis of the A stage of the polymer. After a sufficient time, the highly viscous prepolymer can be poured into a suitable mold for postcuring.

The TGA trace of PDNB shown in Figure 4 indicates that the depolymerization starts at 90°C; therefore the reaction temperature of the A Stage was adjusted to 90°C.
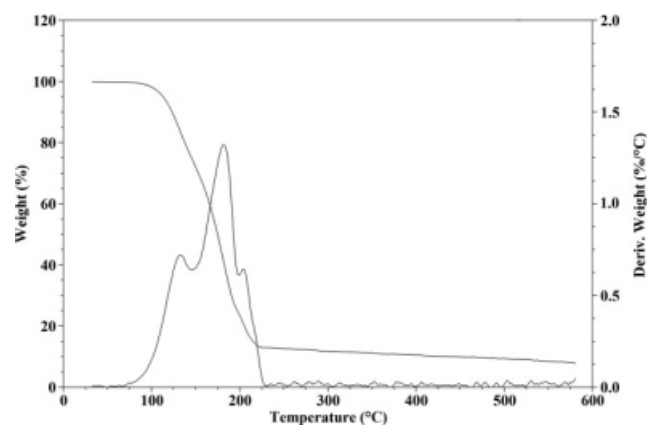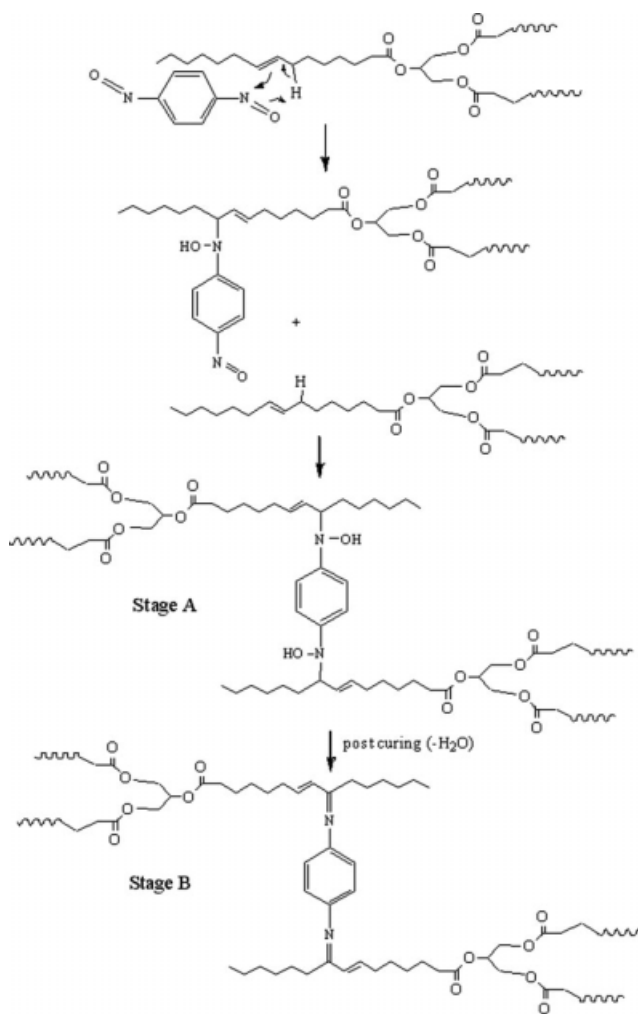

Figure 4 TGA and DTGA traces of PDNB.

Figure 5 Polymerization of SO with PDNB in two stages.

At the end of the A Stage, tacky, viscous, black-colored products were obtained (Fig. 5). Characterization of the products was performed by IR spectroscopy. NMR spectroscopy was not useful because samples were insoluble in NMR solvents. This suggests that a crosslinked structure is formed. However, the data obtained from the IR spectra were not enough to determine the exact structure of the product of Stage A. Considering the references about the vulcanization of rubber with PDNB and the pathway of *ene* reaction, we proposed the chemical structure in Figure 8 as the most favorable structure for the crosslinking of the pre-polymer.[20–27]

In the IR spectrum of the unreacted SO/PDNB mixture [Fig. 6(a)], the peaks corresponding to the triglyceride molecule of SO and PDNB are clearly observed. 3109.8, 1484, 1416.6, 1305.9, 1261.1, 1101.8, 1010.2, 858.4, and 774.4 cm^{-1} are attributed to PDNB[15]; 3008.4, 2922.2, 2852.9, 1746, 1461, 1159.1, and 720.9 cm^{-1} belong to SO, respectively. The spectrum of the SO and PDNB mixture after a 5-min

reaction at 90°C [Fig. 6(b)] differs from that of the spectrum of unreacted SO and PDNB mixture. The disappearance of the peaks corresponding to the polymeric DNB is clearly observed. Since there is no peak related to PDNB, we assumed that at 5 min of the reaction, there is no polymeric DNB. A broad and intense band in the region of 3182–2731 cm^{-1} is attributed to the O—H vibrations of —N—O—H bond, and the new band at 1599 cm^{-1} can be assigned to —C=C— stretching frequency of the aromatic structure. The small band at 1498 cm^{-1} may arise from the nitroso (—N=O) that might be present as a pendant group. The absorption band at 1415 cm^{-1} is most likely to be associated with the —N=N— stretching of dimeric dinitrosobenzene, which suggests the existence of the azoxy type crosslink structure as a side reaction (Fig. 7).

The rather strong and diffuse absorption band around 990 cm^{-1} may be attributed to the N—O vibrations of —N—O—H bond. The IR spectrum at 5 min of the reaction reveals the disappearance of the band at 1499 cm^{-1} and the formation of a new
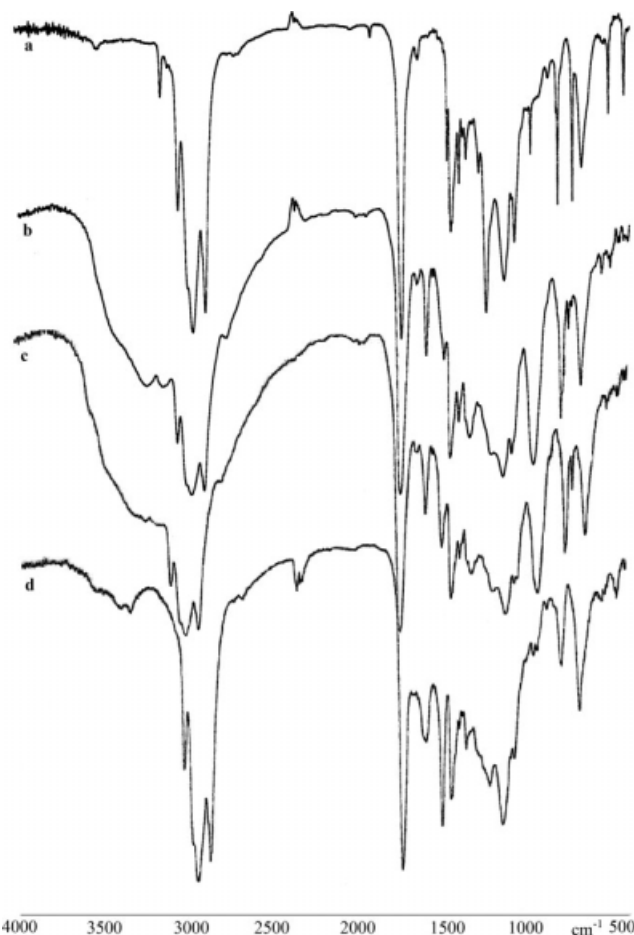

Figure 6 IR spectra of (a) unreacted SO/PDNB mixture, (b) 5 min of reaction, (c) A Stage product, and (d) B Stage product.
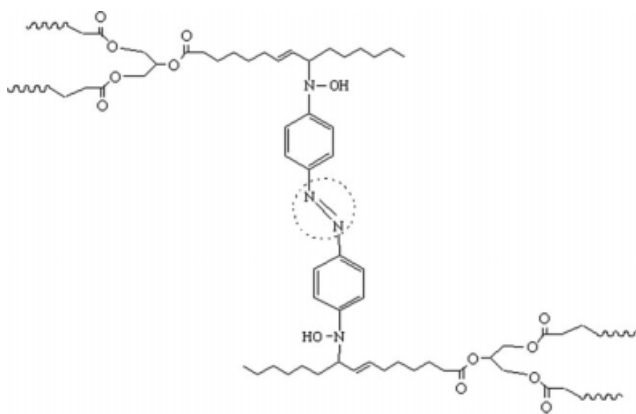
Figure 7 Azoxy type crosslink structure.

absorption band around 1514 cm^{-1}, which can be attributed to —C=N—, suggesting that the dehydration process shown in Figure 5 is taking place.

The products resulting from the postcuring of the A Stage are black-colored, rubbery, and tacky thermoset polymers. Striking facts in the spectrum of the postcured polymer in Figure 6(d) are the disappearance of the broad peak around 3182–2731 cm^{-1}, the decrease in the intensity of the peak at 990 cm^{-1}, and the increase of the intensity of the peak at 1514 cm^{-1}. The spectra in Figure 6(a,c,d) show the shift of absorption band at 1599–1608 cm^{-1}, which implies the conjugation of —C=C— aromatic bonds with —C=N— anil bond. Despite all effects for degassing the starting material, the final products still contain minor voids. This suggests that a volatile by-product is being formed in the B Stage of the polymerization. Our conclusion is that the by-product is water.

Effects of SO/PDNB mol ratio and preheating temperature of soybean oil

Since the exact number of free nitroso groups created during the depolymerization of PDNB is not known, the stoichiometry of the reaction cannot be predicted. The first trial was to react PDNB with excess SO; however, the reaction rate was slower and considerable amount of SO remained unreacted. SO/PDNB ratios of 1/1, 1/1.3, and 1/1.5 were chosen.[20–27]

Preheating of SO facilitates the dispersion and faster dissociation of the PDNB and thus provides shorter polymerization time and lower polymerization temperature. Table I indicates that for a given temperature and a given SO/PDNB mol ratio, the time of polymer formation depends on the preheating temperature of SO. It was evident from the results that as the PDNB content increases, the polymer changes from a tacky, sticky, semi-fluid mass to a firmer, less tacky, rubber-like mass. It is obvious also that as the ratio of the crosslinking agent is

increased, the crosslinking formation sets in before the mixing operation can be completed so the optimum state of cure is reached in a very short time at a relatively low temperature. In such samples, the separation of the polymerization into two steps was impossible and samples could not be molded. Furthermore, as the ratio of PDNB is increased, DNB is produced at a rate faster than its consumption, and some DNB is lost due to evaporation. This causes incomplete polymerization and the polymer obtained has more of a crumbly character and reduced elasticity. Moreover, too high a PDNB content tends to produce an odor in the finished product.

With regard to the results of the reactions in the Table I, it was decided that the best SO/PDNB mol ratio is 1/1.3 and most efficient preheating temperature of SO is 120°C. This ratio and this temperature gave the products with the best properties and in the shortest time.

Model compound polymerization

To obtain more reliable spectral data and better insight into the polymerization mechanisms, methyl oleate, which has only one double bond, was used as a model for SO triglyceride. Methyl oleate was reacted with PDNB in the same manner as SO. The final products were tacky and viscous liquids. Surprisingly, they were also crosslinked and insoluble. The unsaturation in MO presents two allylic positions on either side. Separate reactions of these sites probably give crosslinked structures. Thus, an examination by NMR was impossible, and the characterization of the products was performed only by using IR spectroscopy. Figure 8 shows the overlayed IR
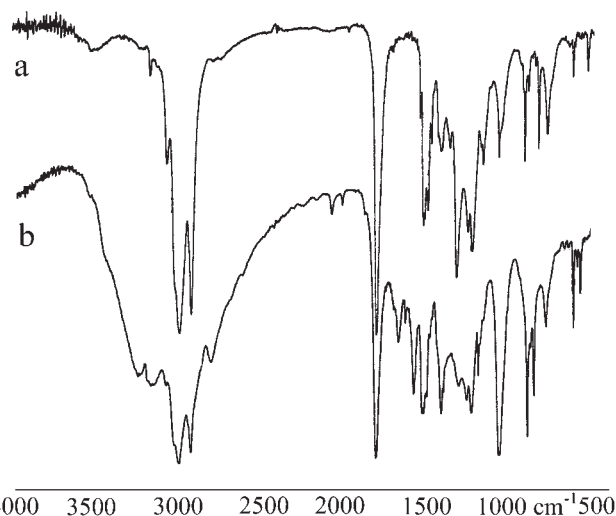

Figure 8 IR spectra of (a) unreacted MO/PDNB mixture and (b) final product of MO/PDNB.

TABLE II
Soluble Portions (wt %) of the Polymers After Extraction

Sample code	Soluble portion (wt %)
SO/PDNB-1/1-120	25
SO/PDNB-1/1-80	29
SO/PDNB-1/1.3-120	10
SO/PDNB-1/1.3-80	17
SO/PDNB-1/1.5-120	17
SO/PDNB-1/1.5-80	16

spectrum of unreacted MO/PDNB mixture and the final product of MO/PDNB.

In the IR spectrum of the unreacted MO/PDNB mixture in Figure 8(a), the peaks corresponding to the triglyceride molecule of MO and PDNB are clearly observed. 3109.8, 1484, 1416.6, 1305.9, 1261.1, 1101.8, 1010.2, 858.4, and 774.4 cm^{-1} are attributed to PDNB[15]; 3011.4, 2922.2, 2852.9, 1741, 1463, 1435, 1168.1 and 722.9 cm^{-1} belong to MO,[17] respectively. In the spectrum (b) in Figure 8, the disappearance of the peaks corresponding to the polymeric DNB appearance of an absorption band around 3200 and 2780 cm^{-1} suggests the O—H vibrations of —N—O—H bond.

A new absorption band is seen around 1512 cm^{-1} that can be attributed to the conjugation of —C=C— of the aromatic system with —C=N—. This suggests the structures shown in Figures 10 and 11 as products of the MO/PDNB reaction. Insolubility of the
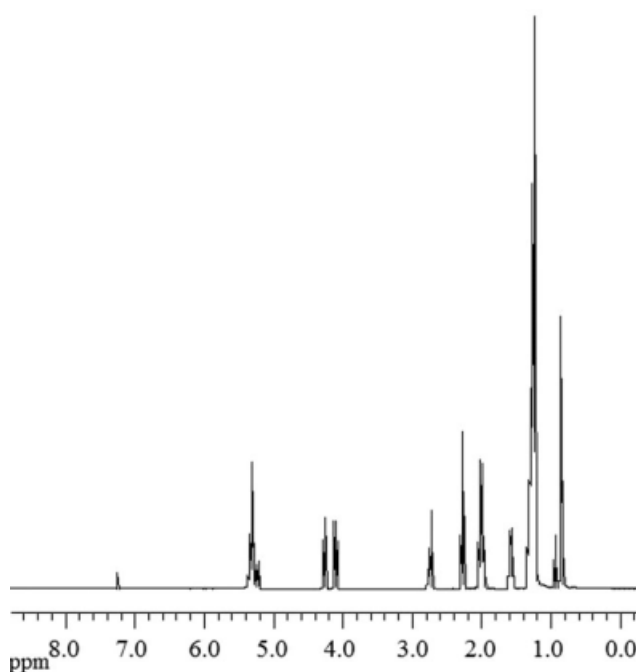

Figure 9 ^{1}H-NMR spectrum of the soluble substances.
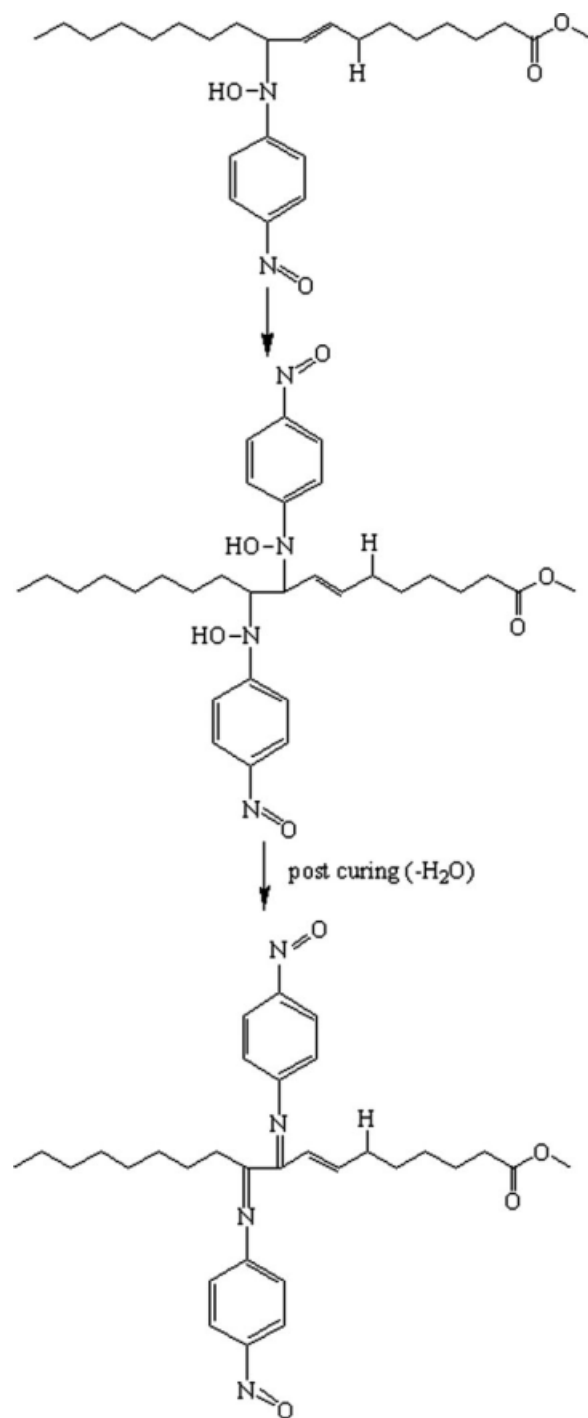
Figure 10   MO/PDNB product structures.

material in common solvents supports the proposed structure.

Determination of unreacted soybean oil

Since the unreacted monomers plastify polymer and reduce their rigidity, determination of the amount and extraction of unreacted SO in the product becomes important. Table II shows the percentages of the soluble portion of different SO/PDNB mol
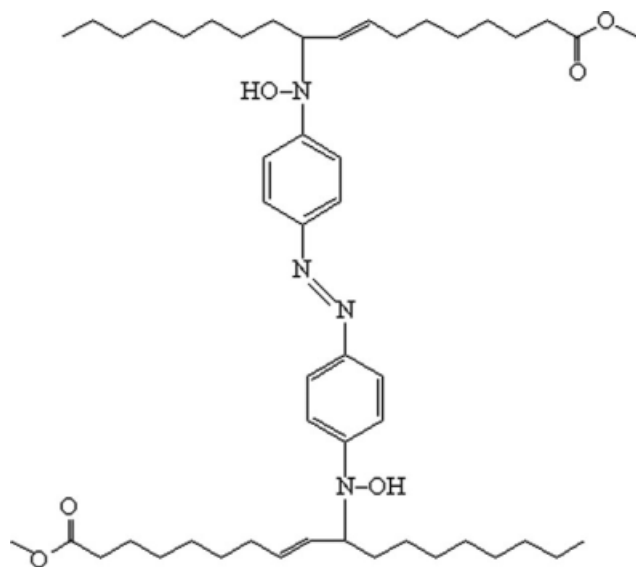
Figure 11 MO/PDNB azoxy-type product structure.

Figure 12 Storage modulus data for (a) SO/PDNB-1/1.5-120, (b) SO/PDNB-1/1.3-120, and (c) SO/PDNB-1/1-120 polymer samples, respectively.

ratio polymers after repeated petroleum ether extractions.

The soluble substances of the all samples proved to be unreacted SO. No aromatic protons are evident in the ^{1}H-NMR spectrum of the soluble substances (Fig. 9); hence no molecules with DNB reacted only at one end are produced, as shown in Figure 10(a), which shows the products of the model compound polymerization. The fact that unreacted triglycerides still exist in the products even when stoichiometrically sufficient PDNB is used indicates that the depolymerization PDNB is not as complete as desired. Structures corresponding to structures in Figure 11 are also obtained. The insoluble substances are crosslinked polymers that are not soluble but are swellable in common solvents such as THF, CCl$_4$, DMSO, and CH$_2$Cl$_2$.

  i. The materials are composed of crosslinked polymer networks plasticized by about 10% of unreacted free oil.
 ii. About 90% of the SO has participated in polymerization and has been incorporated into the crosslinked polymer network.
iii. The polymer structure is determined by the preheating temperature of SO and the stoichiometry.

Dynamic mechanical analysis

Figures 12 and 13 show the temperature dependence of the storage modulus E' and the loss factor tan δ for the various compositions of SO/PDNB polymers.

Within the temperature range tested, the storage modulus E' for all polymers in Figure 12 shows a sharp drop followed by a plateau as the temperature increased. The appearance of a plateau above the
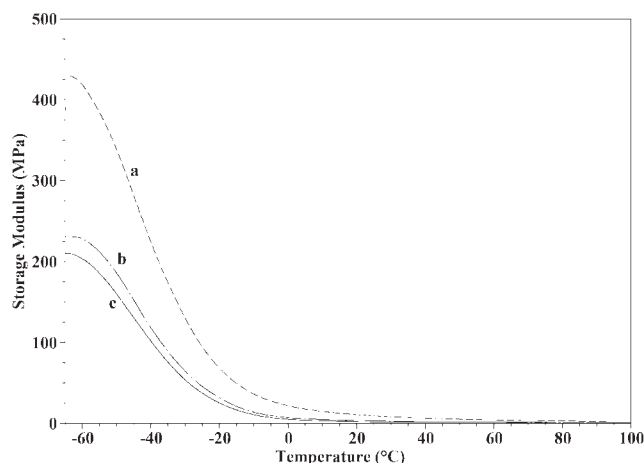
glass transition of the polymers indicates that a stable crosslinked network exists in these polymers. The sample with the highest PDNB ratio (SO/PDNB-1/1.5-120) has the highest storage modulus—approximately 430 MPa at −60°C. This sample also has the highest modulus over the whole temperature range compared with the other two samples with lower PDNB ratios.

The tan δ, the ratio of the storage modulus over the loss modulus (E''/E'), can be used to measure T_g and is taken as the temperature corresponding to the maximum of the tan δ peak (Fig. 13). The glass transition values are −17.8, −16.4, and −15.1°C, for SO/PDNB-1/1-120, SO/PDNB-1/1.3-120, and SO/PDNB-1/1.5-120, respectively. The T_g regions are fairly broad, with the broadest region for the sample with highest ratio of PDNB, and SO/PDNB-1/1.3-120 and SO/PDNB-1/1.5-120 polymers possess
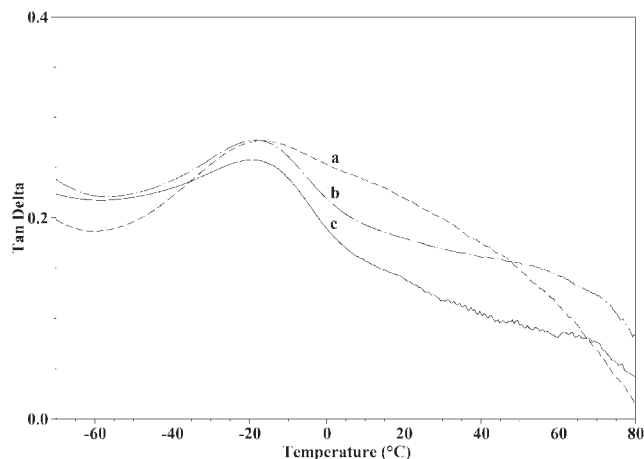

Figure 13 Tan δ data for (a) SO/PDNB-1/1.5-120, (b) SO/PDNB-1/1.3-120, and (c) SO/PDNB-1/1-120 polymer samples, respectively.
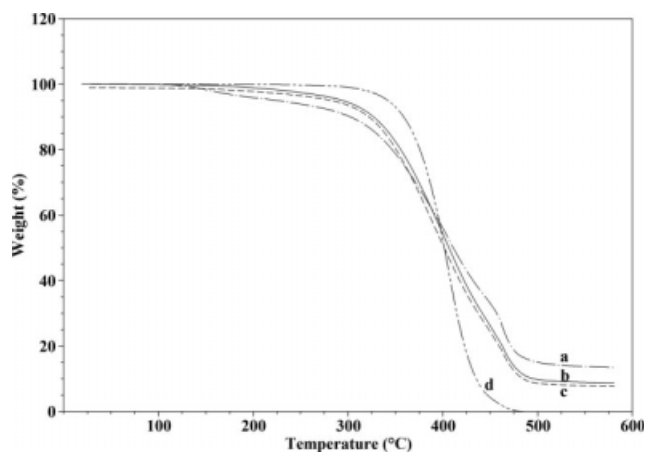
Figure 14 TGA traces for (a) SO/PDNB-1/1.5-120, (b) SO/PDNB-1/1.3-120, (c) SO/PDNB-1/1-120 polymer samples, and (d) SO, respectively.

Figure 15 DTGA traces for (a) SO/PDNB-1/1.5-120, (b) SO/PDNB-1/1.3-120 and (c) SO/PDNB-1/1-120 polymer samples, and (d) SO, respectively.

single tan δ curves, indicating no phase separation. However, the SO/PDNB-1/1-120 sample shows slightly smaller second maxima, which emphasizes heterogenous phase formation. Despite this, the broader peaks indicate that there is a wider distribution of chain lengths between the crosslink points.

Thermal analysis

Figures 14 and 15 show the overlayed results for the TGA and DTGA data for SO/PDNB-1/1-120, SO/PDNB-1/1.3-120, and SO/PDNB-1/1.5-120, respectively, with thermogram of pure SO included in this graph for comparison purposes. All the polymers were extracted and the unreacted SO was removed before TGA analysis.

The TGA and their derivative (DTGA) thermograms, together with Table III, which shows the percentages of weight loss of the polymers at different temperatures, point out that SO-based polymers appear to be relatively thermally stable at temperatures lower than 200°C under N_2 atmosphere. These thermosetting materials typically show three-stage thermal degradation at 200–300°C (Stage I), 300–500°C (Stage II), and >500°C (Stage III), with the second stage being the fastest. The first stage of degradation can be attributed to the evaporation of the
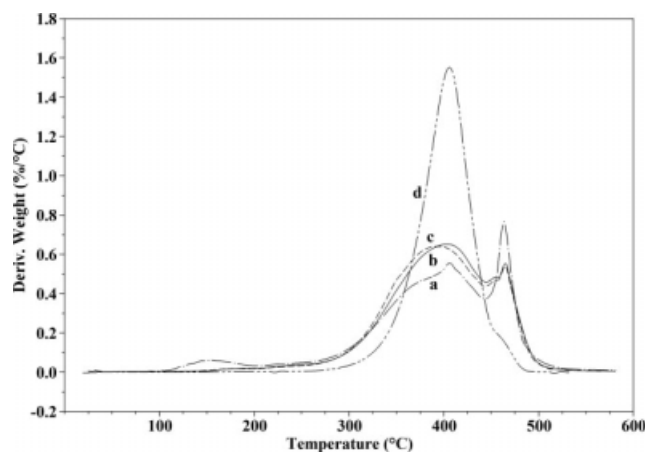
water obtained during the dehydration of the residual intermediate. The second step probably corresponds to degradation and char formation of the crosslinked polymer structure and the decomposition of the fatty acid incorporated in the polymer network.

The glass transition temperatures (T_g) of the SO/PDNB polymers range from –51.5 to –46.3°C (Fig. 16). The kink observed at around −10°C in the second-scan DSC curves arises probably due to water produced during the dehydration of the residual intermediate. Because this kink is also observed in the second DSC scan, we are led to believe that the dehydration of the residual intermediate is still taking place during the DSC run. It is obvious that all polymers have T_gs that are below ambient temperature and therefore are in their rubbery state. The glass transition temperatures of all polymers gradually decrease with increasing amounts of SO in the initial composition. This is mainly due to higher incorporation of the more flexible triglyceride molecules into the crosslinked polymer structure with increasing amounts of oil in the initial polymer composition. It is noted that the T_g values produced by the DMA are higher than those produced by DSC—a situation that is usually observed in crosslinked samples.

TABLE III
Percentage of Weight Loss at Various Temperatures

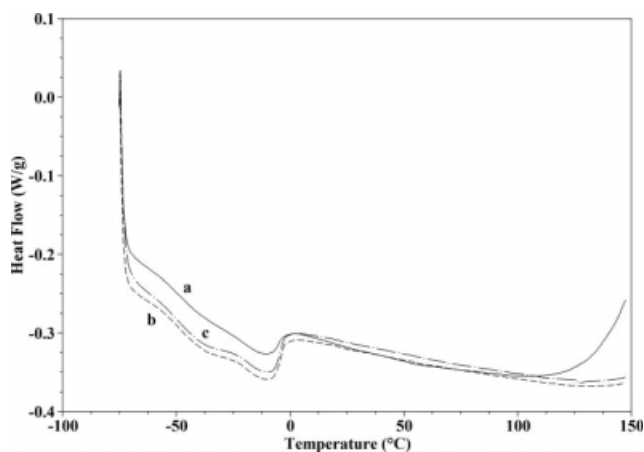| Chemical compound	Percentage of weight loss (%) at various temperatures (°C)					
	100	200	300	350	400	500
SO/PDNB-1/1-120	0.13	1.14	5.4	18.64	48.18	90.24
SO/PDNB-1/1.3-120	0.13	1.14	5.6	17.62	45.92	90.23
SO/PDNB-1/1.5-120	0.13	4.1	9.7	21.3	44.1	85

Figure 16 DSC traces for (a) SO/PDNB-1/1.5-120, (b) SO/PDNB-1/1.3-120, and (c) SO/PDNB-1/1-120 polymer samples, respectively.

Swelling test

The useful parameter that may be obtained from a swelling test is the linear equilibrium swelling ratio (*q*), reported as $V/V_0 = (L/L_0)^3$, where V_0 and V are the volumes of unswollen and swollen polymer samples, respectively; and L_0 and L are the unswollen and swollen lengths of the samples, respectively. This ratio depends on the molar volume of the solvent, the crosslink density, and crosslink segment length of the polymer.

The swelling behavior of the polymers in CH_2Cl_2 was examined by using a traveling microscope. $q = (L/L_0)^3$ versus a time graph for the polymers shows that the polymer with higher concentration of the crosslinking agent swelled less, due to increased crosslink density. It can be concluded that the equilibrium swelling ratio was highest for SO/PDNB-1/1-120 (Fig. 17).
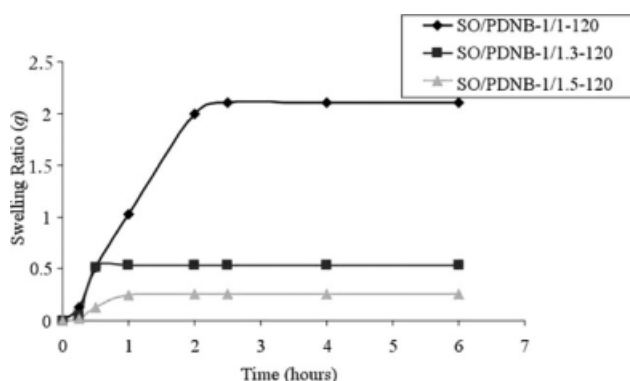

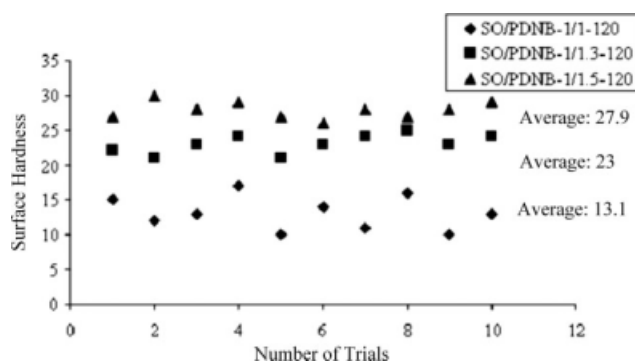**Figure 17** Swelling behavior of polymers based on different SO/PDNB mol ratios.

Figure 18 Shore test results for different SO/PDNB polymer samples.

Surface hardness test

The surface hardness test is a measure of the indentation resistance of elastomeric or soft plastic materials based on the depth of penetration of a conical indentor. Hardness values range from 0 for full penetration to 100 for no penetration.

The polymer samples were cut 1-mm thick and were protected from any possible mechanical stress before testing. To obtain a reliable analysis data, the samples were tested at least from 10 different points on the same surface. Results from the test are presented in Figure 18.

Our results reveal that as the crosslinking agent ratio increases, there is an increase in the surface hardness. Decreasing the mol ratio of PDNB causes fluctuations on the surface hardness of the polymer samples, which can be attributed to the uneven crosslinking causing soft segments in the polymer network. This result is in agreement with the results of DMA analysis.

CONCLUSION

New bio-based, thermoset polymers from SO and PDNB were synthesized by a two-stage polymerization. The SO/PDNB polymers were rubbery, highly crosslinked colored materials.

It was observed that as PDNB ratio increases, an increase in the storage modulus and T_g was observed. However, beyond a certain ratio and with longer reaction times, a crumbly, factice-like material is obtained. In TGA, all polymers were thermally stable at temperatures lower than 200°C under N_2 atmosphere, showing three-stage thermal degradation with the fastest one being in the 300–500°C range. Regardless of the sample composition, it was observed that all of the polymers totally decomposed at 500°C, yielding ~ 10% char. The effects of various fillers such as mica and carbon black on the properties of these materials are under investigation.

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