Synthesis and Characterization of Rubber-Seed-Oil-Based Polyurethanes

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ABSTRACT: Novel biobased polyurethanes were synthesized from rubber seed oil (RSO), a renewable resource. The RSO monoglyceride, together with xylene and hexamethylene diisocyanate (HMDI), was employed to synthesize the desired urethane-based prepolymer with isocyanate (NCO)-terminated end groups followed by curing. The degrees of crosslinking of the polyurethane after curing were assessed with their swelling behavior. The properties of the resulting polyurethanes were found to be dependent on the type of diisocyanate and their molar ratios to the RSO monoglyceride. The network structures, which were assessed through swelling studies, showed that networks based on HMDI with an NCO/OH ratio of 1.50 were better crosslinked than with those toluene diisocyanate. The thermal properties of the samples analyzed by thermogravimetric analysis showed two and three decomposition stages in aliphatic- and aromatic-based RSO polyurethanes, respectively. The highest stability with initial decomposition temperature (253°C) and percentage residual at 500°C (11.4%) was achieved with an aliphatic-based RSO polyurethane. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3292–3301, 2008

Keywords: crosslinking; polyurethanes; renewable resources

INTRODUCTION

Polyurethane are materials widely used in coatings, medical applications, construction engineering applications, the automotive and consumers goods industries, and so on in the form of rigid and flexible plastics, elastomers, protective coatings, lacquers, and adhesives.[1,2] These polymers are synthesized by the reaction of diisocyanates (polyisocyanate) with polyols and a chain extender, which are usually low-molecular-weight diols or amines containing active hydrogen.[3] There is a wide range of commercially available polyisocyanates, polyols, and chain extenders, which has led to many varied formulation possibilities for polyurethanes. The molecular structures vary from rigid crosslinked polymers to linear, highly extensible elastomers, hence, their versatile applications.[2–5] These starting monomers are derived from fossil feed stocks. However, the continuous increase in crude oil prices and contemporary geopolitical and economical development has brought to mind the disadvantages of overdependence on known oil reserves. Hence, alternative renewable material resources have been intensively investigated.[6]

There has been growing interest in the use of renewable agricultural-based resources for the development of consumer products. These raw materials are generally low cost, inexhaustible, and highly biodegradable with favorable legislations in many countries.[7] Among products from agricultural resources, vegetable oils constitute raw materials useful in polymer synthesis. These oils are predominantly made of triglyceride molecules with varied fatty acid chains. The double bonds, allylic carbons, ester groups, and the carbon α to ester or olefinic groups on these acyl chains are good reactive sites for functionalizing the oil.[8]

Traditionally, triglycerol oils are used in coatings and printing inks, whereas their epoxidized derivatives are used as additives in thermoplastics to improve stability and flexibility.[9] These triglycerol-based materials have low molecular weight, are slightly crosslinked, and do not display networks with the necessary rigidity and strength required for engineering applications.[8] As a result, oil-based polymers have to be synthesized with unsaturated and/or acyl-functionalized derivatives to produce polymers with networks capable of offering the high stiffnesses achieved with high crosslinking densities.[10,11]

Castor oil has been extensively used as polyol precursor in polyurethane synthesis because of the

reactive hydroxyl functional groups (OH) contained in its molecule.[9,12] There have also been reports on polyurethanes derived from the hydroxylated epoxides of linseed, soybean, and rapeseed oils.[13,14] More recently, the preparation of polyurethanes from terminal-hydroxlated triglycerides of rapeseed oil was reported.[15]

Recent studies in our laboratory and elsewhere have shown that rubber seed oil (RSO) is a potential raw material for the production of alkyd resins used as binders for surface coatings,[16,17] processing aids for polymers,[18,19] diesel fuel substitutes,[20,21] and the production of liquid soaps.[22] Currently, RSO has no commercial value to the best of our knowledge. In this study, RSO-based urethane prepolymers terminated with isocyanate (NCO) groups were synthesized with RSO monoglyceride derived from the glycerolysis of the oil. The monoglyceride prepared was treated with diisocyanate having an NCO to hydroxyl (NCO/OH) ratio greater than one. The excess NCO group was further polymerized by reaction with urethane groups to form an allophanate linkage.[1] The type and distribution of acyl chains on the glycerol moiety determines the properties of the oil. Consequently, we characterized RSO and its functionalized products by spectroscopic methods and chemical analysis to gain insight into the structure and properties of the polyurethanes. The resulting polyurethanes were also characterized. The overall objective was to develop an alternative source of thermosetting polymer from bioresource materials.

EXPERIMENTAL

Materials

RSO was obtained from Murugesan and Sons (Tamil Nadu, India). Calcium oxide and glycerol were obtained from S.D. Fine Chemicals, Ltd. (Mumbai, India). Toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and dibutyl tin dilaurate (DBTD) were all obtained from Aldrich Chemicals. All of the chemicals were used without further purification.

Physicochemical properties

The physicochemical properties, including acid value, specific gravity, saponification value, monoglyceride content, and hydroxyl and iodine values, were determined by AOCS methods.[23]

Synthesis of RSO monoglyceride

RSO monoglyceride was prepared by an alcoholysis method. The reaction was carried out in a 100-mL flask fitted with a thermometer, reflux condenser, and nitrogen gas inlet tube to create an inert atmos-

phere in the reaction flask. RSO (1 mol), glycerol (3 mol), and 0.1% CaO (catalyst) were poured into the reaction flask. Heating was effected with a thermostated oil bath. The reaction temperature was raised and maintained at 230°C for about 3.5 h under nitrogen. The reaction was stopped when the sample of the alcoholysis product formed a clear solution in anhydrous methanol (1 : 3 w/v oil:methanol). After cooling, the unreacted glycerol was removed from the resulting glyceride mixture. The glyceride was dissolved in an equal mixture of *n*-hexane and diethyl ether. The product was washed with water and dried over sodium sulfate, and the solvent was removed *in vacuo*.

Synthesis of urethane from the RSO monoglyceride

A known quantity of diisocyanate was poured into a three-necked reaction flask fitted with a motorized stirrer and a water-cooled condenser with the recipe shown in Table I. The RSO monoglyceride with two drops of DBTD dissolved in xylene were degassed and added dropwise. The reaction temperature was maintained at 30°C in an inert atmosphere created by the bubbling of dry nitrogen gas into the reactor. The lower temperature was maintained to prevent tautomerization in the presence of DBTD, and dry gas was used to prevent other side reactions such as amine and substituted urea in addition to allophanate. Changes in the NCO value during the reaction were determined with a standard dibutylamine back-titration method (ASTM 2572). The reaction was stopped after 6 h, degassed, and poured into a tightly covered mold to keep out moisture. This prepolymer was subsequently allowed to cure at room temperature for about 8 h and, subsequently, at 70°C for another 24 h. The samples were taken to be cured when the NCO peak in the Fourier transform infrared (FTIR) spectra at 2270 cm^{-1} completely disappeared from the tested sample. Four RSO-based urethane networks with different diisocyanates, namely, TDI and HMDI, at various NCO/OH molar equivalents of 1.02 and 1.50 were prepared and coded as TDPU1.02, TDPU1.50, HMPU1.02, and HMPU1.50, respectively.

TABLE I
Recipe for the Formulation for Urethane Oil

| Code | Component (equiv mol) | | | NCO/OH ratio |
	Monoglyceride	TDI	HMDI	
TDPU1.02	0.0310	0.0316	—	1.02
TDPU1.50	0.0310	0.0466	—	1.50
HMPU1.02	0.0310	—	0.0316	1.02
HMPU1.50	0.0310	—	0.0466	1.50

Fatty acid composition

The fatty acid composition of RSO was determined by gas–liquid chromatography with its methyl ester derivates following AOCS method Ce2-66.[23] Fatty acid compositions were analyzed with a Hewlett Packard 5890 series II gas chromatograph with a flame-ionization detector (Avondale, PA). The injection and detection temperatures were maintained at 250 and 300°C, respectively. The flow rate of the carrier gas, nitrogen, was 20 mL/min. The oven temperature was programmed at 100–180°C at a rate of 5°C/min. Methyl esters of RSO were identified and quantified by comparison of the retention times and the areas under the peaks of the unknown with the standard methyl ester.

NMR spectroscopy

The ^{1}H-NMR spectra of RSO and its derivates were recorded with a Bruker 300-MHz NMR spectrophotometer (Bruker Instruments Inc., Karlsruhe, Germany) in CDCl$_3$ containing a small amount of tetra methyl silane (TMS) as an internal standard. About 25–30 mg of sample was dissolved in 1 mL of CDCl$_3$.

FTIR spectroscopy

Infrared spectra of the RSO and its derivates were recorded with an impact 400 D Nicolet FTIR spectrophotometer (Madison, WI). The samples were spread over NaCl cells, and their spectra were recorded. IR spectra were recorded in the range 4000–400 cm^{-1}.

Thermal analysis

The glass-transition temperatures (T_g's) of the polyurethane samples were determined by differential scanning calorimetry (DSC 7 PerkinElmer, Boston, MA). Three to eight milligrams of sample in a sealed pan was used at a heating rate of 5°C/min from −10 to 150°C under a nitrogen atmosphere purged at 10 mL/min. Thermogravimetric analysis was performed on Shimadzu TG 50 thermogravimetric analyzer (Japan). The rate of heating was 10°C/min in nitrogen from room temperature to 600°C.

Size exclusion chromatography (SEC)

The molecular weight averages of the RSO-based urethane prepolymers were measured by SEC with a Waters 510 high performance liquid chromatograph (HPLC) pump (Waters, Milford, MA) equipped with an HR-5E/4E/2/0.5 column a series and a Waters 2414 refractive-index detector. HPLC-grade tetrahydrofuran was used as an eluent at a flow rate 1.0 mL/min at 35°C. Polystyrene standards were used for calibrations.

Mechanical analysis

Mechanical properties of the samples where evaluated on an H5KS universal testing machine (Redhill, England) with ASTM D 882-97 at a speed of 10.00 mm/min and a gauge length of 40 mm. The average of five samples was used.

Swelling studies of the polyurethanes

The RSO-based polyurethane films, about 10 × 10 × 1.0 mm^3 in size, were swollen in toluene at room temperature for several days until an equilibrium state was achieved. The solvent uptake capacity (W_c) of each sample at equilibrium was determined. The swollen samples were wiped and weighed immediately after the surfaces were blotted on an electronic balance. The degree of swelling (W) and soluble fractions (S's) were calculated as follows:[24]

$$W_c(\%) = [(W_w - W_d)/W_d] \times 100 \quad (1)$$

S was calculated as follows:

$$S(\%) = [(W_d - W_{\text{des}})/W_d] \times 100 \quad (2)$$

where W_d and W_w are the weights of the polymer and the swollen sample at the equilibrium of solvent uptake, respectively; and W_{des} is the weight of the deswollen sample dried to a constant weight at 50°C. The averages of three values were recoded. The molecular weights of the network chains were obtained from the Flory–Rehner relations:[25]

$$M_c = -V_1 \rho_p \frac{(\phi^{1/3} - 2\phi/f)}{ln(1-\phi) + \phi + \chi_1 \phi^2} \quad (3)$$

where M_c is the average molecular weight of the chains between crosslinks, V_1 is the molar volume of the solvent, ρ_p is the density of the polymer, f is the functionality of the network branch points, and Φ is the volume fraction of the polymer in the swollen state calculated with the following equation:[26]

$$\frac{1}{\phi} = 1 + \frac{W_s \rho_p}{W_{\text{des}} \rho_p} \quad (4)$$

where W_s and W_{des} are the weights of solvent taken up by the polymer and deswollen polymer, respectively; ρ_s is the density of the solvent used; and χ_1 is the Flory–Huggins interaction parameter calculated by means of the following relationship:

$$\chi_1 = \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \quad (5)$$

where R is the gas constant, T is the temperature (K), and δ_1 and δ_2 are the solubility parameters of

Fatty acid		%	Property of RSO	Value
Saturated				
$C_{16:0}$	Palmitic acid	17.51	Color (Lovinbond)	22R, 23.2Y
$C_{18:0}$	Stearic acid	4.82	Specific gravity (30°C)	0.916
	Total	22.33	Acid value (mg of KOH/g)	43.62
Unsaturated			Free fatty acid	21.4
$C_{18:1}$	Oleic acid	25.33	Saponification value (mg of KOH/g)	202.91
$C_{18:2}$	Linoleic acid	37.50	Iodine value (g of I_2/100 g)	136.21
$C_{18:3}$	Linolenic acid	14.21		
	Total	77.04		
	Others	0.63		

the solvent and polymer samples, respectively. The solubility parameter and molar volume of toluene were taken to be 18.3 $J^{1/2}/cm^{3/2}$ and 106.8 cm^3/mol, respectively. The degree of crosslinking (V_c) and the number of chains per unit volume (N) were calculated for the samples with the relations:[25]

$$V_c = 1/2M_c \qquad (6)$$

$$N = \rho_p/M_c \qquad (7)$$

Gel determination

The gelation studies were measured with a gel timer (Techne, England). The same procedure described for the synthesis of urethane from RSO and the recipes described in Table I were used. The spindle of the gel timer was inserted into the reactor containing the diisocyanate. The complete addition of monoglycerides and two drops of DBTD dissolved in xylene to the diisocyanate was taken as start time for the gel timer (i.e., $t = 0$), which oscillated up and down in the reactor. The time at which the spindle became stationary

because of the high viscosity of the urethane prepolymer was recorded and taken as the gel time.

RESULTS AND DISCUSSION

Physicochemical analysis of RSO

The fatty acid composition of RSO is presented in Table II. The results show that the RSO was made up of about 22.33% saturation comprising mainly palmitic acid (17.51%) and stearic acid (4.82%) and about 77.04% unsaturation comprising essentially oleic acid (25.33%), linoleic acid (37.50%), and linolenic acid (14.21%). The main peaks of the FTIR analysis of the RSO and their assignments to functional groups are given in Table III. The results in Table III show that the functional groups present in the RSO were similar to other vegetable oils.[27]

The ^{1}H-NMR spectrum of RSO (Fig. 1) was comparable with most vegetable oils, which show between 9 and 10 different signals of significant intensity.[28,29] These signals of the spectrum were due to protons of the triglycerides and were assigned as presented in Figure 1. The methine proton of the β-glyceride

TABLE III
Main IR peaks and Their Corresponding Functional Groups of RSO

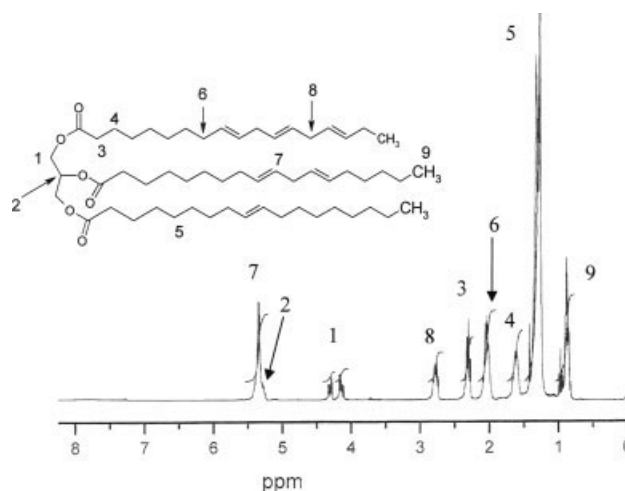| Frequency (cm^{-1})	Assignment	Remark
3009	C—H	Stretching frequency of nonconjugated unsaturation
2854	C—H	Stretching frequency of alkane
1745	C=O	Stretching frequency of ester
1654	C=C	Stretching frequency of alkene
1462	C—H	Bending frequency of unsaturated alkene
1165	C—O	Stretching frequency of ester
722	C—C	Bending frequency of saturated carbon atom

Figure 1 ^{1}H-NMR of RSO.
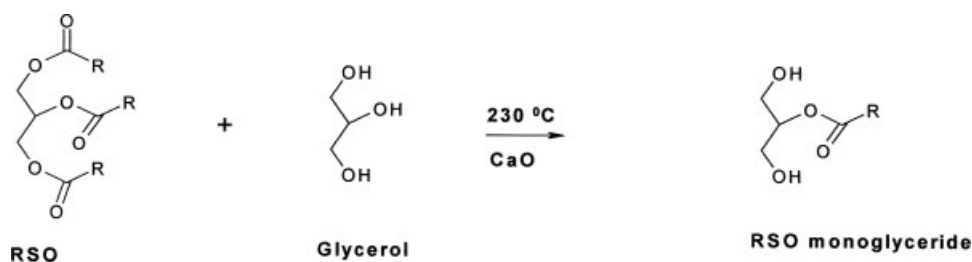
Scheme 1 Synthesis of the RSO monoglyceride (where R represents the fatty acyl chain).

backbone, represented as 2 in the triglyceride structure (Fig. 1), appeared at δ 5.29 ppm. This signal overlapped with the olefinic proton labeled 7 with δ = 5.33 ppm.

The levels of free fatty acid and the acid value showed that the RSO was highly acidic. This implied that large amounts of polyol would be required in the transesterification reaction before the polycondensation reaction, which would lead to the formation of the urethane prepolymer. From the iodine value of 136 g of $I_2/100$ g, we inferred that the RSO was a semidrying oil. This was further supported by the low polyunsaturated fatty acid content (Table II). These properties were similar to those of soybean and linseed oil, which are conventional oils used for technical applications.

Properties of RSO monoglyceride

The reaction scheme for the synthesis of seed oil monoglyceride is outlined in Scheme 1, where R represents the fatty acid of the starting oil. This reaction is a simplified chemical equation for glycerolysis because monoglyceride is the predominant product.

The properties of the monoglyceride are presented in Table IV. The acid value of the raw RSO (Table II) was much higher than the acid value of the RSO monoglyceride. The difference in acid value of about 31 mg of KOH/g could be attributed to the esterification reaction between the free fatty acid present in the RSO and glycerol during alcoholysis.

The percentage composition of the monoglyceride sample (alcoholysis product) was 48.30, 36.66, and 15.04% monoglycerides, diglycerides, and triglycerides, respectively (column chromatographic separation).[23] However, the titrimetric determination of monoglyceride revealed that periodic acid oxidation only gave 29.41% in that sample (Table IV). The difference must have been due to the presence of β-monoglyceride. Periodic acid only oxidizes α-monoglyceride,[3] and it is known that monoglycerides exist in two different structural modifications, namely, α-monoglyceride and β-monoglyceride.[27]

The ^{1}H-NMR spectra of the monoglyceride used for the preparation of the polyurethanes presented in Figure 2 had a characteristic chemical shift at δ = 3.74 ppm due to free OH protons, which was completely absent in the starting RSO. This indicated the presence of the hydroxyl group in the product. The IR spectrum of the monoglyceride product also showed a very broad absorption around 3370–3470 cm^{-1} (vO—H) due to the hydroxyl group. Some other notable features of the IR spectra included the bands at 3009 cm^{-1} (v C—H unsaturation), 2924 cm^{-1} (vC—H saturation), 1747 cm^{-1} (v C=O), 1249 and 1165 cm^{-1} (v C—O—C), and 1655 cm^{-1} (v CH=CH).

Synthesis of the RSO polyurethane

Polyurethanes can be synthesized by the reaction of a long-chain diol with an excess diisocyanate to

TABLE IV
Monoglyceride Content, Acid Value, Hydroxyl Value, and Glyceride Composition of the Alcoholysis Products

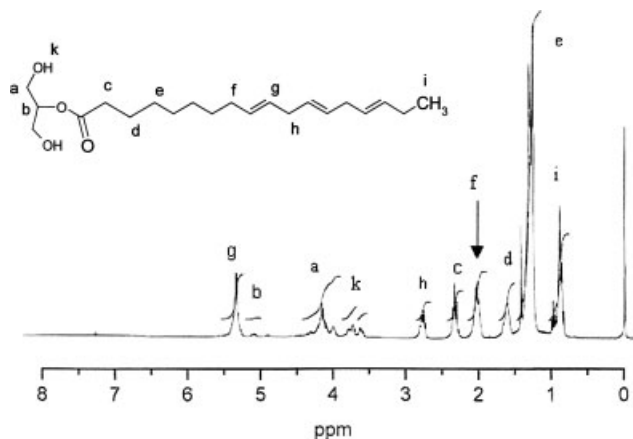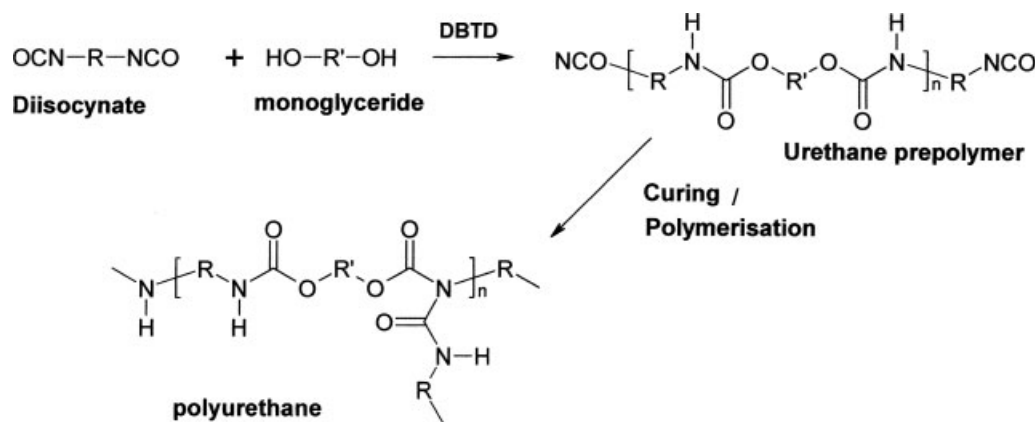| Alcoholysis sample	Value
α-Monoglyceride content (%)	29.41
Acid value (mg of KOH/g)	2.68
Hydroxyl value (mg of KOH/g)	183.15
Column chromatograph composition of the alcoholysis product	Value
Monoglyceride content	48.30
Diglyceride content	36.66
Triglyceride content	15.04
Total	100.00

Figure 2 ^{1}H-NMR of a typical monoglyceride.

Scheme 2 Synthesis of the RSO polyurethane (where R′ represents the glyceryl acyl chain and R represents hexamethylene or toluene).

obtain an NCO-terminated prepolymer. The prepolymer can subsequently react with a low-molecular-weight chain extender such as a diol or diamine.[1,4] In this method, we adopted the same strategy with a slight modification, as shown in Scheme 1. Four urethane prepolymers were synthesized by the reaction of HMDI or TDI with RSO monoglyceride with 1.02 and 1.50 equiv mol of NCO/OH. These prepolymers were cured further without any additional chain extender or crosslinker at room temperature to get polyurethane films resulting from allophanate formation between urethane N—H groups, and an NCO of excess diisocyanate (or other urethane prepolymer with NCO-terminated end groups) led to a crosslinked polymer,[4] as shown in Scheme 2.

Effect of the temperature on the gel time

The effect of temperature on the gel time of the RSO-based polyurethane system consisting of the
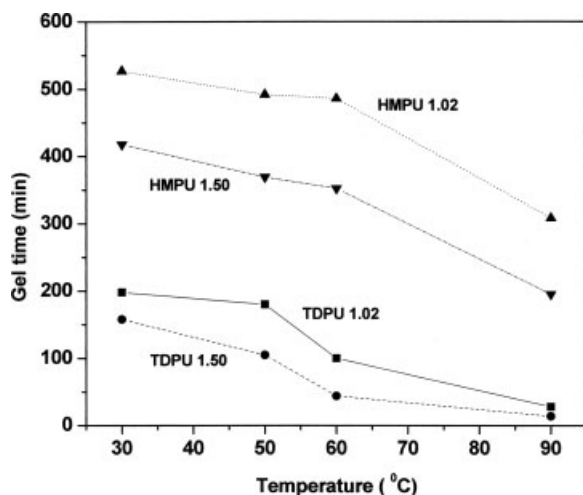
RSO monoglyceride and diisocyanate is shown in Figure 3. The results reveal that there was a decrease in gel time with an increase in reaction temperature. This trend was the same in both urethane systems; however, the gel time for the aliphatic system was higher than that of the aromatic system. The prediction of gel point conversion and network formation
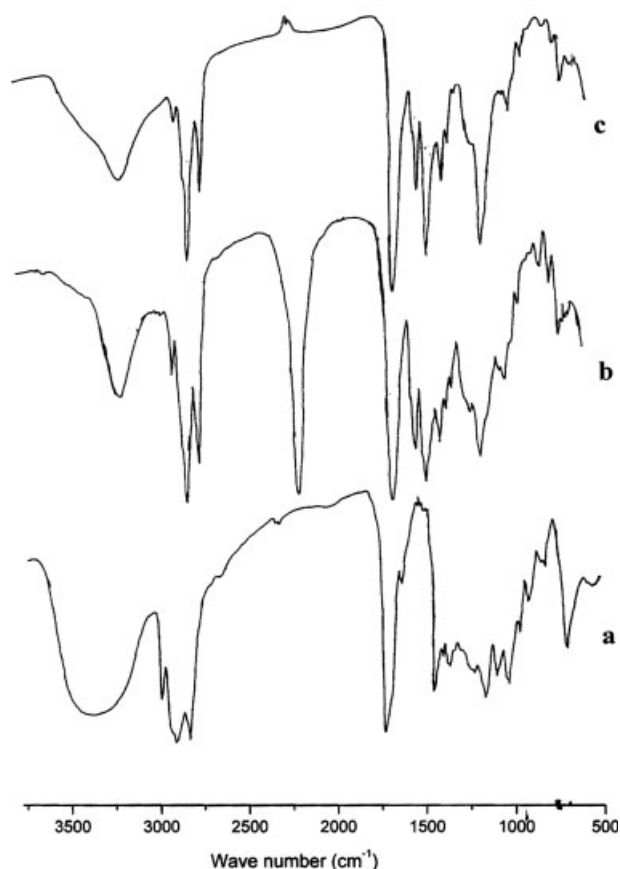

Figure 4 FTIR spectra of (a) a RSO monoglyceride, (b) a typical RSO-based urethane prepolymer, and (c) a typical RSO-based polyurethane film.

Figure 3 Effect of the temperature on the gel time of the urethane prepolymers.

TABLE V
Main IR Peaks and Their Corresponding Functional Groups of the RSO Urethane Prepolymers and the Corresponding Cured Films (Polyurethane)

Prepolymer frequency	Cured film	Assignment	Remark
3344	3331	—NH	NH stretching of the urethane group
3008	3008	C—H	Stretching nonconjugated unsaturation
2855/2927	2855/2929	C—H	Stretching frequency of alkane
2270	—	NCO	Stretching frequency of NCO
1731	1728	C=O	Stretching frequency of urethane carbonyl group
1532	1576	N—H	Deformation of NH

during synthesis and polymer processing enable estimates of the safe conversions for the reaction without gelation. Therefore, the aromatic-based urethane prepolymer of RSO could be prepared at lower temperatures ($\leq 50^\circ$C), whereas the aliphatic-based urethane prepolymer of RSO could be prepared at higher temperatures ($\leq 90^\circ$C).

FTIR spectra of the RSO-based urethanes

The FTIR spectra of the RSO prepolymers and their cured films for all four samples were similar. Therefore, the IR spectrum of a typical synthesized urethane prepolymer and the cured film from Figure 4 is presented in Table V.

The spectrum of the RSO prepolymer was compared with the spectra of the RSO monoglyceride and the cured polyurethane films (Fig. 4). The band due to the carbonyl stretching vibration (amide I band) of the prepolymer occurred at about 1728 cm^{-1}. The combination of N—H deformation and C—N stretching vibration (amide II bands) occurred at about 1532 and 1251 cm^{-1}, respectively. The N—H stretching vibration of urethanes appeared at 3331 cm^{-1} compared with the broad absorption band of the hydroxyl (—OH) stretching vibration between 3300 and 3500 cm^{-1} for the monoglyceride. This indicated that the entire hydroxyl group was used for urethane linkage. The —NCO band at approximately 2272 cm^{-1} in Figure 4(b) confirmed the NCO-terminated group of the prepolymer. This NCO group at 2272 cm^{-1} gave a prominent absorbance before curing but decreased to zero absorbance after curing, which

indicated that all of the NCO groups reacted during polymerization (curing) to form polyurethane. The disappearance of the NCO band may have been due to the crosslinking of urethane chains with NCO groups to form allophanate products.[1]

Network properties of the RSO-based polyurethanes

The NCO content of the urethane prepolymer determined with di-*n*-butylamine compared with the theoretical NCO is presented in Table VI. The NCO contents of the urethane prepolymers were generally lower than the theoretical NCO contents. The SEC results of the urethane prepolymer presented in Table VI show that the molecular weight averages and polydispersities of the TDPU samples were much higher compared to those of the HMPU samples. Previous reports have shown that the polymerization of urethane prepolymers is generally controlled by the rate of chemical reaction at the initial stage of the reaction because the chains are flexible because of their lower molecular weight.[30] After the gel point, the mobility of the reactive groups are hindered and restricted because of crosslinking and the formation of networks. The polymerization during this period becomes diffusion to control rather than chemical.

The crosslinking densities of the RSO-based polyurethanes were assessed from their swelling properties in toluene (Table VII). The two polyurethanes TDPU1.02 and HMPU1.02 with an NCO:OH ratio of 1.02 all dissolved after about 8 h. This indicated that there was no crosslinking in these two films. The correlations between the swelling ratio and swelling time of the samples (with NCO/OH = 1.50) are

TABLE VI
Properties of the Urethane Prepolymer

| | NCO content (%) | | | |
Sample	Determined	Theoretical	M_w	M_w/M_n
TDPU1.02	4.4	10.2	18,805	2.2
TDPU1.50	4.9	8.1	15,423	2.1
HMPU1.02	7.6	10.4	6,170	1.7
HMPU1.50	8.1	8.2	3,717	1.2

M_w = weight-average molecular weight; M_n = number-average molecular weight.

TABLE VII
Network Properties of the RSO-Based Polyurethane Films

Sample	Maximum swelling (%)	Crosslinking density	M_c	S (%)
TDPU1.02	Dissolved			
TDPU1.50	104.6	8.91×10^{-4}	1084	2.6
HMPU1.02	Dissolved			
HMPU1.50	56.32	3.87×10^{-3}	209	2.3
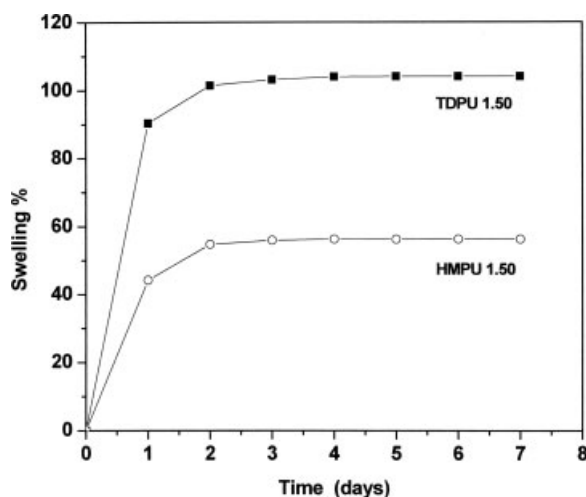
Figure 5 Effect of the diisocyanate type on the degree of swelling of the RSO-based polyurethane.

Figure 6 Typical stress–strain curve for the RSO-based polyurethane at 25°C.

shown in Figure 5. The swelling ratio increased with time at the initial stage for the two polyurethanes with an NCO/OH value of 1.50 until 72 h; thereafter, it became constant. The swelling ratio of the TDPU1.50 film was found to be higher than HMPU1.50. Also, HMPU with an NCO/OH ratio 1.50 had a higher crosslinking compared with TDPU1.50. These results (Table VII) show that HMPU1.50 was more efficiently crosslinked than TDPU1.50; hence, it had a higher crosslinking density and number of chains per unit volume. This probably resulted in the higher T_g observed in HMPU1.50 (Table VIII). The presence of sol, which indicated imperfect crosslinks, must have been due to residual triglyceride from alcoholysis products. On the other hand, the —OH group on the diglyceride could readily form urethane linkages with NCO; these urethane linkages could subsequently act as points of crosslinking to form allophanate compounds.

The stress–strain curves of the RSO-based polyurethane sample films are shown in Figure 6, and the mechanical property data are presented in Table VIII. The TDPU1.50 polyurethane exhibited brittle fracture and very low elongations at break compared with HMPU1.50, which was more flexible. The brittle nature of TDPU1.50 must have been due to the aromatic group within the polymer chain, which made the crosslinked film more rigid, which consequently reduced the chain flexibility as compared

with HMPU1.50, where the whole polymer chain was aliphatic. Also, the tensile strength of both polyurethane samples were close, although an unusual plateau was observed at about 2.0% strain. Generally, aromatic-based polyurethane networks are more rigid than aliphatic-based polyurethanes.[31] Also, higher swellings were obtained for networks with lower crosslinking densities and those in better solvents. It is, therefore, possible that toluene might have been a better swelling solvent for TDPU1.50 (an aromatic-based polyurethane) than for HMPU1.50 (an aliphatic-based polyurethane); this might have been responsible for the observed lower crosslinking density of TDPU1.50 determined from the swelling properties. The tensile strength obtained in this study was higher than the 0.67–1.11 MPa reported by Sekkar et al.[32] in synthetic polyurethane based on polybutadiene. These values were lower than those reported by Zlatanic et al.[11] (14.8–56.3 MPa) for other

TABLE VIII
Properties of the RSO-Based Polyurethane

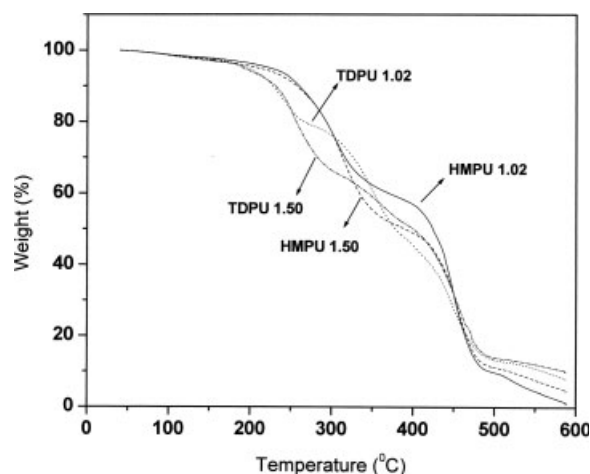| Sample	T_g (°C)	Elongation at yield (%)	Tensile strength (MPa)
TDPU1.50	35.4	2.878	4.99
HMPU1.50	46.9	42.226	5.15

Figure 7 Thermogravimetric analysis of the RSO polyurethane.

TABLE IX
Thermal Properties of the RSO-Based Polyurethanes

Sample	T_1	$T_{10\%}$	$T_{50\%}$	T_{max}	Residual weight at 500°C (%)
HMPU1.02	254	259	424	486	9.6
HMPU1.50	253	256	393	490	11.4
TDPU1.02	221	228	378	491	12.9
TDPU1.50	226	230	402	499	14.1

T_{max}, temperature at which maximum decomposition was attained.

vegetable-oil-based polyurethanes. The observed lower tensile strengths compared with those reported by Zlantanic et al.[11] must have been due to the lower functionality of the starting monoglyceride of about 2 versus a functionality of greater than 3 from the hydroxylated oils reported.

Thermal degradation of the RSO-based polyurethanes

The shapes of the weight loss curves of the polyurethanes prepared from the same diisocyanates were similar (Fig. 7). The HMPU-based polyurethanes degraded in two steps compared with TDPU-based polyurethanes, which degraded in three steps. The values of degradation temperature of the polyurethane samples from Figure 7 are presented in Table IX. The thermal behavior of the materials were determine from the initial decomposition temperature (T_1), the temperatures at which 10 and 50% weight loss of various polymer conversions were attained ($T_{10\%}$ and $T_{50\%}$, respectively), and the residual weight at 500°C. It is well known that polyurethanes decompose at temperatures between 200 and 300°C to give the either free NCO and alcohol or free amine, carbon dioxide, and oleines.[33] Generally, there are three main path ways for the degradation of the urethane linkages; dissociation to NCO and alcohol; dissociation to primary amines, olefins, and carbon dioxide; and the formation of a secondary amine with the elimination of carbon dioxide.[1,33]

The first-stage decomposition between 231 and 261°C has been reported to be due to breaking of urethane bonds.[34] However, the onset of second-stage and third-stage degradations in the HMPU and TDPU samples were about the same (422°C). It is possible that the second-stage decomposition in the TDPU1.02 and TDPU1.50, which was between 307 and 380°C, might have been due to the decomposition of aromatic moieties. The second- and third-stage decompositions in HMPU and TDPU, respectively, were in the range 419–490°C because the triglycerol oil molecules resulted in a faster rate of weight loss.[33] The observed sharp decomposition in polyurethane with an NCO/OH ratio of 1.5 (as reflected at about $T_{50\%}$) might have

been due to the decrosslinking of allophanates. This also eliminated possible crosslinking in the polyurethane with an NCO/OH ratio of 1.02, as previously shown by the swelling study (Table VII).

CONCLUSIONS

Novel biobased polyurethanes were synthesized from RSO, a renewable resource. The structures and properties of the RSO-based polyurethanes strongly depended on the NCO/OH ratio and the type of diisocyanate used. The thermal properties of aliphatic-based RSO polyurethanes were better than those of aromatic-based polyurethanes. The highest stability was achieved with an aliphatic-based RSO polyurethane with an NCO/OH ratio of 1.50.

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