Biobased Polyisocyanates from Plant Oil Triglycerides: Synthesis, Polymerization, and Characterization

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ABSTRACT: In this study, an easy and efficient synthesis of unsaturated plant oil triglycerides having isocyanate groups is reported. In the first step of the synthesis, the triglyceride was brominated at the allylic positions by a reaction with N-bromosuccinimide, and in the second step, these brominated species were reacted with AgNCO to convert them to isocyanate-containing triglycerides. At the end of the reaction, approximately 60–70% of the bromine was replaced by NCO groups, and the double bonds of the triglyceride were not consumed. When the amount of AgNCO was increased, the yield also increased. The final products were characterized with IR and ^{1}H-NMR, and polyurethanes and polyureas were obtained from these fatty isocyanates with alcohols and amines, respectively. The polymers were characterized by differential scanning calorimetry and thermogravimetric analysis. Differential scanning calorimetry curves showed that glycerin polyurethane showed a glass-transition temperature at 19°C, castor oil polyurethane showed two glass-transition temperatures at −43 and 36°C, and triethylene tetraamine polyurea showed a glass-transition temperature at 31°C. Some properties of the polymers, such as the tensile strength and swelling ratios, were also determined. The swelling rate of glycerin polyurethane was higher than that of castor oil polyurethane in dichloromethane. The equilibrium swelling ratio was highest for the castor oil polyurethane. The polyurethanes synthesized in this study had a Young's modulus around 50 kPa and a tensile strength around 0.01 N/mm^2 (100 kPa). The tensile strength of glycerin polyurethane was higher than that of castor oil polyurethane. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2948–2955, 2008

Key words: biomaterials; biopolymers; mechanical properties; polycondensation; polyurethanes

INTRODUCTION

Isocyanates are valuable compounds that are used widely in many application areas in the polymer industry. The most important area of use for isocyanates is the synthesis of polyurethanes and polyureas. Important isocyanates used in polyurethane manufacturing include 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4′-diphenyl methane diisocyanate, 1,6-hexamethyl diisocyanate, xylene diisocyanate, and isophorone diisocyanate, all of which are petroleum derived.[1–3]

Isocyanates can be synthesized in many ways. The Curtius, Hoffman, and Lossen rearrangements, which may involve the nitrene as an intermediate, are not successful for large-scale operations (Fig. 1). The use of azides is hazardous, and the utility of the Hoffman and Lossen rearrangements is limited to the preparation of aliphatic isocyanates. Tertiary butyl hypochloride can be used for nonaqueous Hoffman rearrangements, but this reagent is expensive. Phosgenation of primary amines and dehydrohalogenation of the resulting carbamoyl chloride are important commercially, despite the known toxicity of phosgene (Fig. 2).[4]

The synthetic route used in this study was the substitution of the allylic bromides of plant oil triglycerides with AgNCO. Methyl oleate was chosen as a model compound to optimize the reaction conditions and to serve as a structure determination aid. Then, the reaction was carried out on soybean oil triglycerides, as shown in Figure 3.

A literature search revealed a number of publications on the synthesis of biobased polyurethanes. In almost all of them, castor oil was used as a polyol source, and petroleum-based isocyanates were used as the isocyanate.[5–12] There were no examples where the isocyanate was biobased. With the simple synthesis described in this study, it was possible to obtain polyurethanes where both the isocyanate and polyol were biobased.

EXPERIMENTAL

Materials and methods

AgNO$_3$ was purchased from Horasan Kimya (Istanbul, Turkey). NaOCN, silica gel 60, N-bromosuccini-
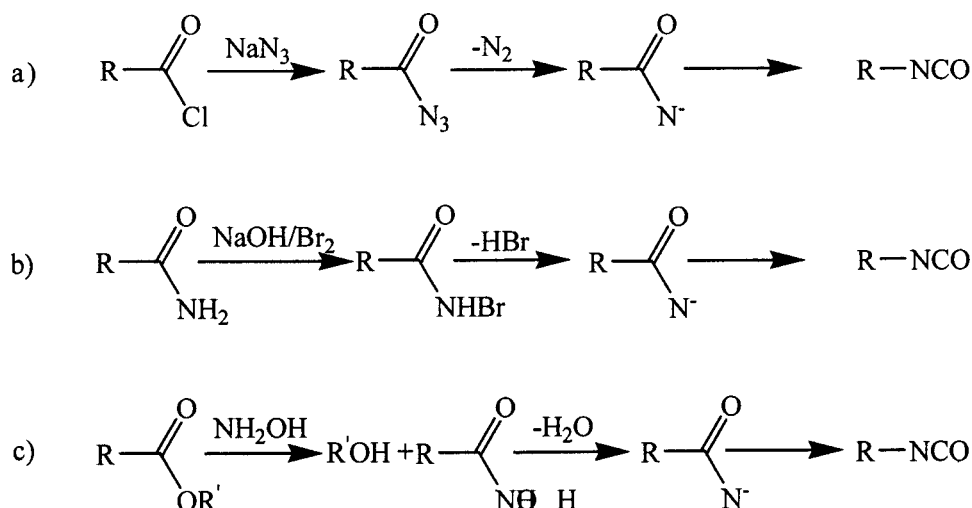
Figure 1 Laboratory-scale synthesis of isocyanates: (a) Curtius, (b) Hoffman, and (c) Lossen rearrangements.

mide (NBS), glycerin, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) were purchased from Merck (Darmstadt, Germany). Tetrahydrofuran (THF) was purchased from J. T. Baker (Deventer, Holland). Triethylene tetraamine (TETA) was purchased from Aldrich (Milwaukee, WI). $CDCl_3$ was supplied by Aldrich, and it was used for NMR characterization. Soybean oil was supplied by Marsa (Adana, Turkey). AgNCO was prepared from NaOCN, and $AgNO_3$ was prepared by a conventional method.[13]

IR characterization of the compounds was performed by PerkinElmer (Waltham, MA) FTIR 1600 series instrument. 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 protons. Differential scanning calorimetry (DSC) characterization was performed by a Thermal Analyses Q 200 instrument (New Castle, DE) at a 10°C/min heating rate. Thermogravimetric analysis (TGA) characterization was performed by Thermal Analyses Q 50 instrument with a 10°C/min heating rate. The swelling behaviors of the polymers were tested in CH_2Cl_2 with a Gaertner (Skokie, IL) 7109-46 traveling microscope. The strain test was performed by a Zwick Material Prüfung (Ulm, Germany) 1446 model tester with a 20-mm/min elongation rate.

Allylic bromination of methyl oleate [allylic brominated methyl oleate (ABMO)]

Dry methyl oleate (29.0 g, 0.1 mol) and NBS (17.8 g, 0.1 mol) were mixed in 150 mL of freshly distilled CCl_4. The mixture was refluxed for 4.5 h. The mixture was protected from light, kept overnight at room temperature, and then filtered. CCl_4 was evaporated at 30°C *in vacuo*. An orange oil (37.0 g)

was obtained. The desired monoallylic bromide was obtained at 80% yield. The crude product was purified by column chromatography (28 cm × 2 cm) on silica gel 60 (Merck, 70–230 mesh) with *n*-pentane/$CHCl_3$ (8.5:1.5) as an eluent to produce 29.6 g (80% yield) of ABMO.

IR (cm^{-1}): 3008 (=CH); 2928, 2853 (C—H); 1659 (C=C cis); 1463, 1435 (CH_2 scissoring); 1247, 1196, 1170 (C—O); 965 (CH=CH—CHBr); (C—H) 723 (C—Br); 646. ^{1}H-NMR (ppm): 0.9 (—CH_3), 1.2–1.3 (—CH_2—), 1.6–1.7 (—CH_2—CH_2—$COOCH_3$), 1.85 (CH=CH—CHBr—CH_2), 1.95 (—CH_2—CHBr—CH=CH—CHBr—CH_2—), 2 (CH=CH—CH_2—), 2.15 (CHBr—CH_2—), 2.25–2.3 (triplet, —CH_2—$COOCH_3$), 3.65–3.7 (singlet, —OCH_3), 4.2 (simple alkyl bromide proton, —CHBr—), 4.4 (monoallylic bromide proton, —CH=CH—CHBr—), 4.8 ppm (double allylic bromide protons, —CHBr—CH=CH—CHBr), 5.4 (—CH=CH—CHBr), 5.6 (—CH=CH—CHBr), 5.8 (—CHBr—CH=CH—CHBr).

Methyl oleate isocyanate (MONCO)

ABMO (5 g) was dissolved in 20 mL of dried THF. AgNCO slurry (6 g) in 60 mL of THF was added in three portions with 1 h intervals at room temperature. Stirring was continued for 4 more hours, and the flask was kept overnight at room temperature. During the reaction, the apparatus was covered with aluminum foil to prevent light ingress, and all glass-
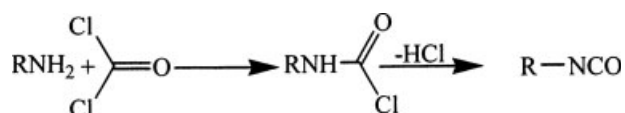

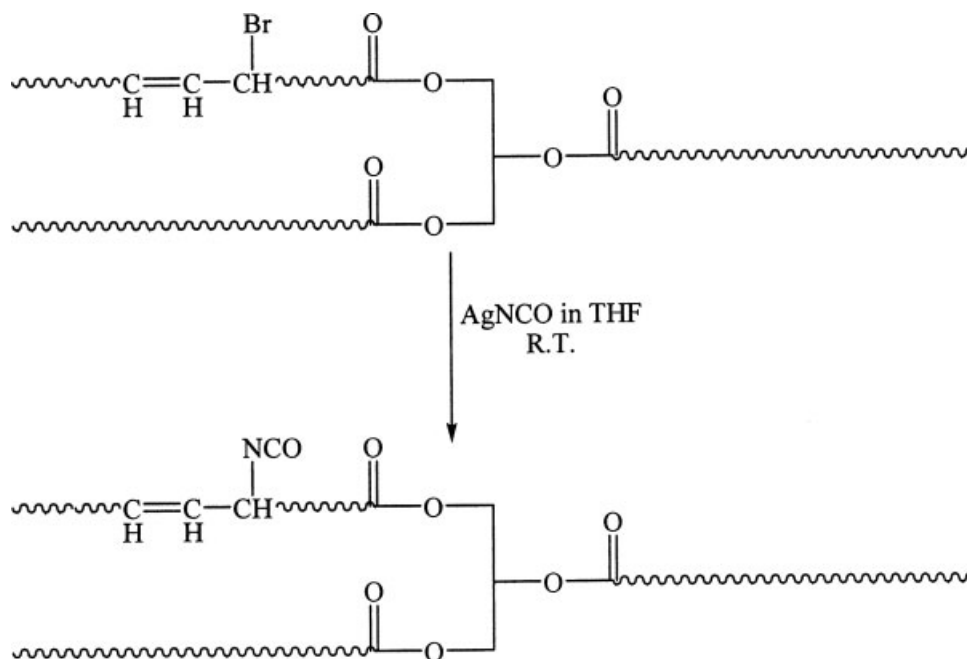**Figure 2** Industrial synthesis of isocyanates with phosgene.

Figure 3 Schematic synthesis of SONCO (positional isomers are not shown; R.T. = room temperature).

ware was dry. In the IR spectrum, a new peak appeared at 2258 cm^{-1} (N=C=O; Fig. 4).

^{1}H-NMR (ppm): 1.5 (O=C=NCH—CH$_{2}$—), 3.8–3.9 (CH=CH—CHN=C=O), 4–4.1 (O=C= NCHCH=CH—CHN=C=O), 5.4 (CH=CH—CHN= C=O), 5.6 (**CH=CH—CHN=C=O**), 6.1 (O=C= NCH—CH=CH—CHN=C=O). [These are the peaks that differed from those of ABMO; also, ABMO peaks at 4.2–4.4 and 4.8 disappeared (Fig. 5).]

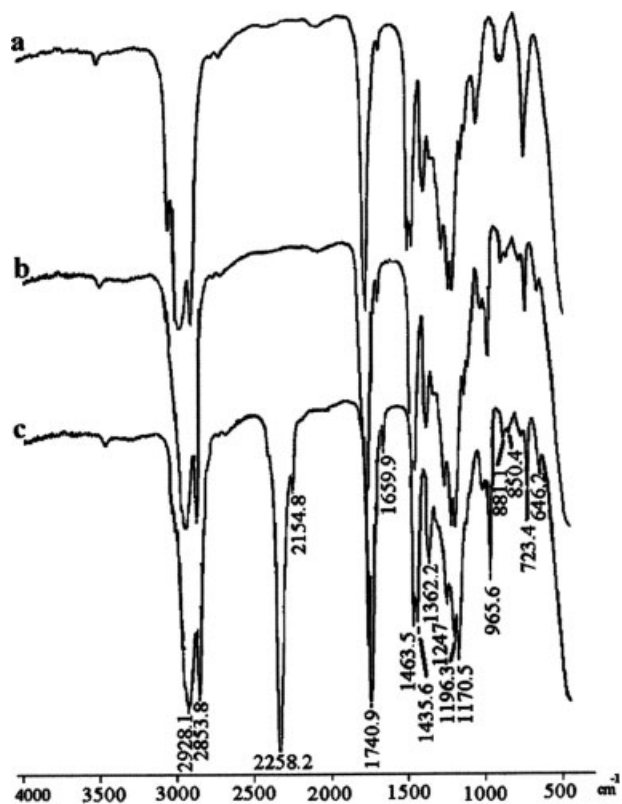## Methyl carbamate of isocyanated methyl oleate

Isocyanated methyl oleate (2 g) was mixed with 50 mL of methanol. The mixture was refluxed overnight. Methanol was evaporated, and the product was characterized by IR and ^{1}H-NMR techniques. In the IR peaks, the 1742 carbonyl group was characteristic for the urethane group. At 1560 cm^{-1}, a peak was observed because of C—N stretching (Fig. 6).
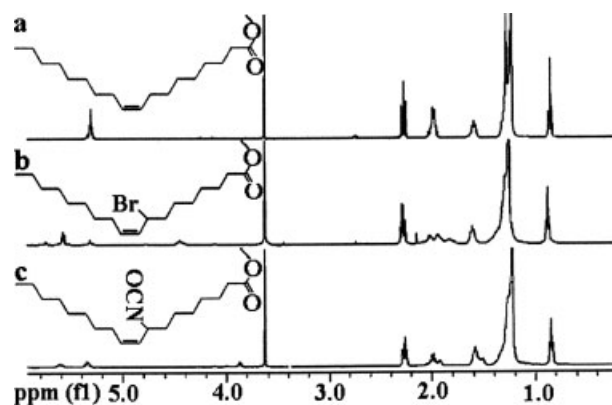

Figure 4 IR peaks of (a) methyl oleate, (b) ABMO, and (c) MONCO.

Figure 5 ^{1}H-NMR spectra of (a) methyl oleate, (b) ABMO, and (c) MONCO.
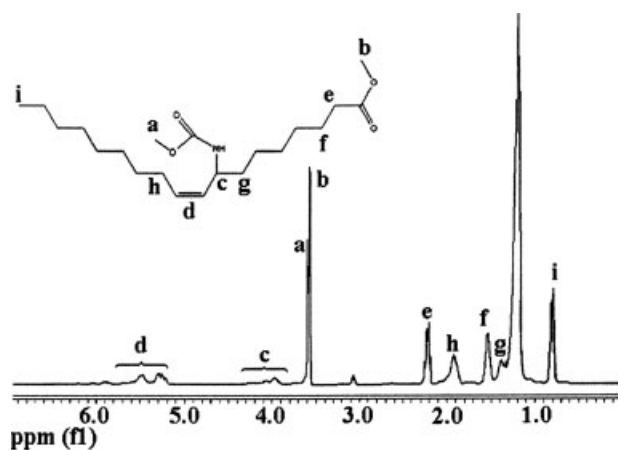
Figure 6 ^{1}H-NMR spectrum of methyl carbamate of MONCO.

^{1}H-NMR (ppm): 3.63 (carbamate ester, $CH_3OC=ONH-$), 4.2 (CH=CH—CH—NH), 1.53 (—C=ONH—CH—CH_2—; Fig. 7).

Allylic bromination of soybean oil [allylic brominated soybean oil (ABSO)]

Twenty grams of dried soybean oil and 25 g of NBS were mixed in 150 mL of CCl_4. The mixture was refluxed for 4.5 h. At the end of the reflux, the mixture was kept overnight in the dark at room temperature and then filtered. An orange solution was obtained. The solvent was evaporated under reduced pressure at 30°C. Approximately 30 g of ABSO was obtained. Unlike methyl oleate, this compound was used in the next steps without purification because all of the products and side products were reactive alkyl halides toward the AgNCO, and the separation of all of the positional isomers was not possible by any separation technique.

IR (cm^{-1}): 3010 (=CH); 2925, 2853 (C—H); 1654 (C=C cis); 1235, 1155, 1102 (triplet characteristic for triglycerides, C—O); 967 (CH=CH—CHBr); 725

(C—H); 640 (C—Br). ^{1}H-NMR (ppm): 0.8 (—CH_3), 1 (triplet, —CH=CH—CH_2—CH_3), 1.2–1.4 (—CH_2—), 1.6 (β to carbonyl group, —CH_2—CH_2—$COOCH_2$—), 2 (—CH=CH—CH_2—), 2.25 (α to carbonyl group, —CH_2—$COOCH_2$—), 2.75 (double allylic position, —CH=CH—CH_2—CH=CH—), 4.1 and 4.3 [multiplet (glycerin protons), O—CH_2—], 4.5 (broad, —CH=CH—CHBr—), 4.8 (—CH=CH—CHBr—CH=CH—), 5.25 (center proton of glycerin, —OCH_2—CHO—CH_2O—), 5.4 (—CH=CH—CH_2—CH=CH—CHBr—), 5.6 (—CH=CH—CH_2—CH=CH—CHBr—), 5.8 (—CH=CH—CHBr—CH=CH—).

Synthesis of soybean oil isocyanate (SONCO)

Crude ABSO (8 g) was dissolved in 20 mL of dried THF. AgNCO slurry (6 g) in 60 mL of THF was added in three portions with 1 h intervals at room temperature. Stirring was continued for 4 more hours, and the flask was kept overnight at room temperature. During the whole operation, the apparatus was covered with aluminum foil and was dry. The IR spectrum was very similar to the spectrum of ABSO, but a new peak was observed at 2250 cm^{-1}, the peak at 965 cm^{-1} was shifted to 967 cm^{-1}, and the peak at 1742 cm^{-1} was broadened (Fig. 8). The ^{1}H-NMR spectrum was also similar to the ABSO spectrum. A small new peak was observed around 3.9 ppm (—CH=CH—CH—NCO; Fig. 9).

Synthesis of glycerin polyurethane

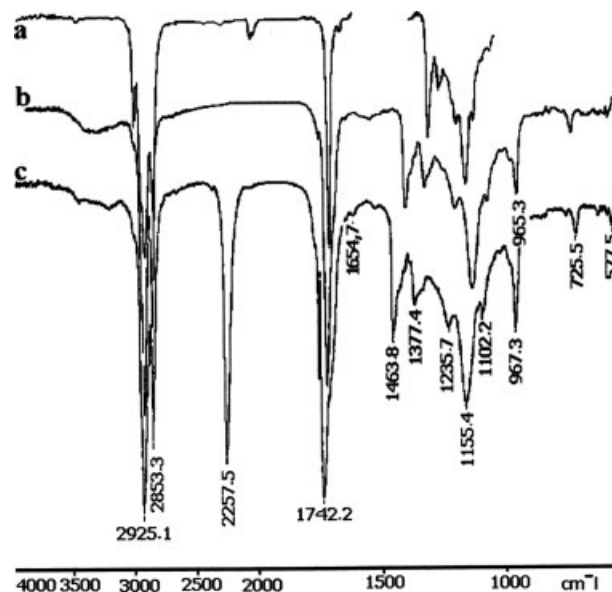SONCO (2.5 g, 1.78 mmol) was mixed well with 0.2464 g of glycerin (2.678 mmol). The mixture was

Figure 7 IR spectrum of methyl carbamate of MONCO.

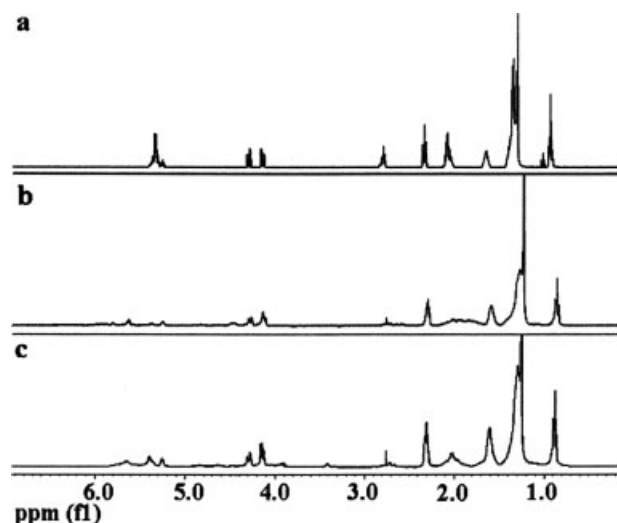**Figure 8** IR peaks of (a) soybean oil, (b) ABSO, and (c) SONCO.

Figure 9 ¹H-NMR spectra of (a) soybean oil, (b) ABSO, and (c) SONCO.

poured into a Teflon mold and heated to 110°C for 5 h. At the end of the reaction, a semisoft rubbery polymer was obtained.

Synthesis of castor oil polyurethane

SONCO (2.5 g, 1.78 mmol) was mixed well with 2.1 g of castor oil (2.21 mmol, with the generally accepted molecular weight of 932 g assumed). The mixture was poured into a Teflon mold and heated to 120°C for 5 h. A soft, very flexible rubbery solid was obtained.

Synthesis of TETA polyurea

SONCO (2.5 g, 1.78 mmol) was mixed well with 0.13 g of TETA at room temperature. The mixture started to solidify suddenly, and heat was released. At the end of the reaction, a hard polymer was obtained.

RESULTS AND DISCUSSION

Synthesis of the monomers

In the literature, no reference was found on the synthesis of isocyanate-containing plant oil triglycerides. The synthesis of iodoisocyanates of fatty esters has been reported,[14,15] but in these reactions, double bonds were consumed, the presence of the neighboring iodine made the isocyanate group unreactive, and during the polymerization reactions, unpredictable side reactions were likely. In this study, allylic isocyanates were synthesized in 60–70% yields. The yields increased with increasing amounts of AgNCO. We determined this easily by ¹H-NMR by following the allylic proton signal. When equimolar AgNCO and ABSO were reacted, the yield was almost 30%.

If 3 equiv of AgNCO was used, the yield increased to 70%. We calculated the yields by simply measuring the integration ratios between the peaks at 3.9 ppm (—**CH**—NCO) and 2.25 ppm (α to carbonyl peaks) in the ¹H-NMR spectrum of the products. We easily monitored the substitution of the bromine with isocyanate by observing the changes in the peaks of ABSO in the IR spectrum. A peak that appeared around 965 cm^{-1} was attributed to allylic —HC=CH**CH**Br stretching, and a peak around 640 cm^{-1} was attributed to C—Br deformation. When isocyanate addition occurred, a new peak around 2250 cm^{-1} was observed, and the allylic bromine peak at 965 shifted to 970 cm^{-1}. Compared with the other isocyanate synthesis methods, allylic bromination and the subsequent substitution reactions were simple reactions. Allylic bromination was completed in 4–5 h, and the substitution reaction was completed in 4 h. Purification was not required during synthesis. Although the reactivity ratios were different, the main product and the side products were all alkyl halides, and they readily reacted with AgNCO. We found the average number of isocyanate groups per triglyceride to be 2.1 by measuring the intensity ratio of the geminal H on the same C atom as the NCO group to the H of carbon α to ester groups. The average functionality of typical commercial polyisocyanates is around 2–2.8. The synthesis, however, suffered from the use of an expensive reagent, AgNCO. Unfortunately, AgNCO was unique for this reaction because Ag^{+} modified the nature of the intermediate. In the presence of Ag^{+} ion, OCN^{-} attacked through the nitrogen end instead of the oxygen end.[16,17] Isocyanates are sensitive to water. Thus, all of the apparatus had to be protected from humidity during the synthesis.

Synthesis and properties of the polymers

The polymerization of SONCO with glycerin and castor oil was completed in 5 h at 120°C. SONCO reacted very fast with TETA even at room temperature. Thus, the gel time of the mixture was too short to allow the production of samples for mechanical testing. The IR spectrum of polyurethanes and TETA polyurea are shown in Figure 10. At 1742 cm^{-1}, broad carbonyl peaks were unique for polyurethanes, and at 1530 cm^{-1}, a urethane N—H deformation was observed.

The physical properties of commercial polyurethanes may vary, depending on the application areas. Polyurethanes are generally copolymers of (AB)n type consisting of an alternating block of relatively long, flexible soft segments and another block of highly polar, rather stiff chains, or hard segments. The unique physical and mechanical properties of polyurethanes are determined by their two-phase
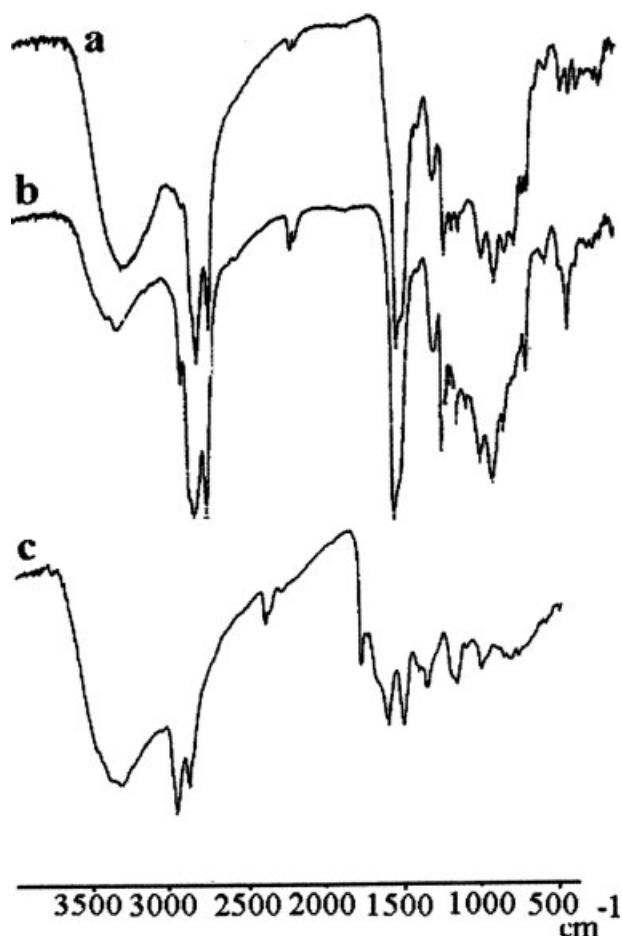
Figure 10 IR spectra of (a) glycerin polyurethane, (b) castor oil polyurethane, and (c) TETA polyurea of SONCO.

domain structure. The cohesion energy and hydrogen bonds in the hard domains are higher than in the soft domains. Hence, the role of hard domains is to improve the mechanical properties, such as the strength and hardness, of the polymer. On the other hand, elasticity is provided mainly by the soft segments.[18–21] The polyurethanes that were synthesized in this study had aliphatic and soft segments only. Thus, a higher elasticity and lower strength was expected.

The polyurethanes synthesized had a Young's modulus of around 50 kPa and a tensile strength of around 0.01 N/mm^2 (100 kPa). The tensile strength of glycerin polyurethane was higher than that of castor oil polyurethane. Although both materials had low ultimate tensile strengths and moduli, they showed excellent elongation and recovery. The elongation of castor oil polyurethane was higher than that of glycerin polyurethane. The strains at break were about 353% for glycerin polyurethane and 410% for castor oil polyurethane. This is typical rubbery behavior (Fig. 11).

The swelling behavior of the products in CH$_2$Cl$_2$ was determined by a traveling microscope. The sam-
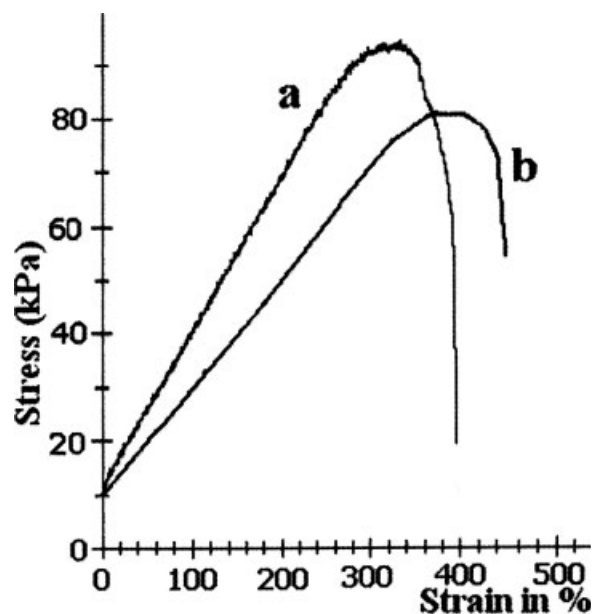

Figure 11 Stress–strain curves of (a) glycerin and (b) castor oil polyurethanes with SONCO.

ples were put in a closed container, and the experiment was continued until the solvent uptake ceased. The swelling ratio was expressed as follows:

$$\text{Swelling ratio} = (V/V_0) = (L/L_0)^3$$

where V_0 and V are the volumes and L_0 and L are the lengths of the unswollen and swollen polymer samples, respectively. Figure 12 shows the swelling behavior of the samples. It was very interesting that although glycerin polyurethane had a higher modulus than castor oil polyurethane, the swelling rate of glycerin polyurethane was higher than that of castor oil polyurethane in CH$_2$Cl$_2$. The equilibrium swelling ratio was highest for the castor oil polyurethane (Fig. 12).
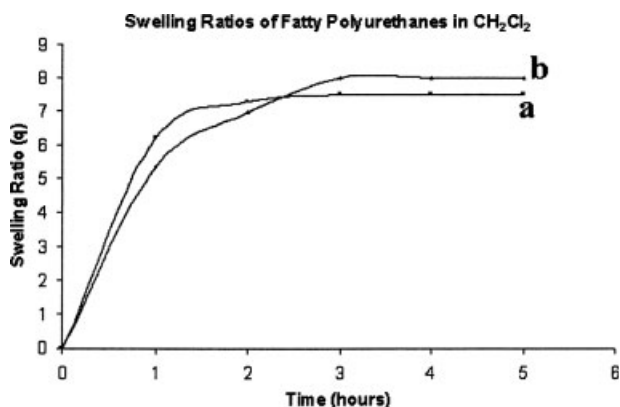

Figure 12 Swelling ratios of (a) glycerine polyurethanes and (b) castor oil polyurethane.
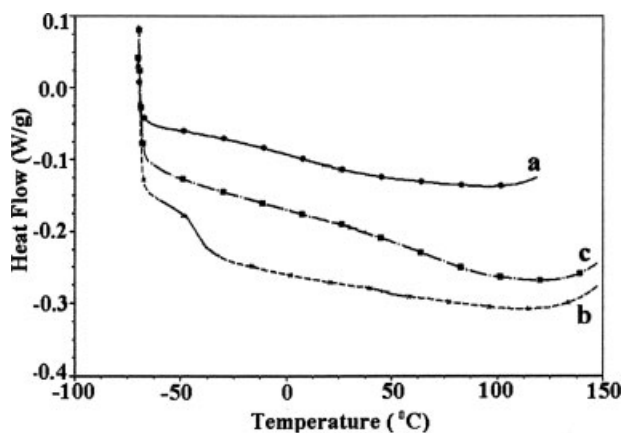
Figure 13 DSC traces of (a) glycerin, (b) castor oil polyurethanes, and (c) TETA polyurea with SONCO.

Figure 15 Derivative TGA traces of (a) glycerin, (b) castor oil polyurethanes, and (c) TETA polyurea with SONCO.

The thermal properties of the materials were monitored by DSC. DSC curves showed that glycerin urethane showed a glass-transition temperature (T_g) at 19°C. This polymer may be suitable for rigid foam applications. Castor oil polyurethane showed T_g's at −43 and 36°C, which agreed with the rubbery behavior of this polymer. Commercial polyurethanes generally have an average T_g around −20°C to room temperature.[6] TETA polyurea showed a T_g at 31°C (Fig. 13).

For the evaluation of thermal stability, TGA is the most favored technique. Because of the urethane and urea linkages, polyurethanes and polyureas have low thermal stability.[22,23] The thermal stabilities of the polymers synthesized in this study were monitored by a Thermal Analyses Q-50 instrument (Figs. 14 and 15). TETA polyurea started to decompose at temperatures as low as 50°C. The polyurethanes were relatively more stable: they started to decompose near 200°C. The 5% weight losses were observed at 56, 149, and 194°C for TETA polyurea,
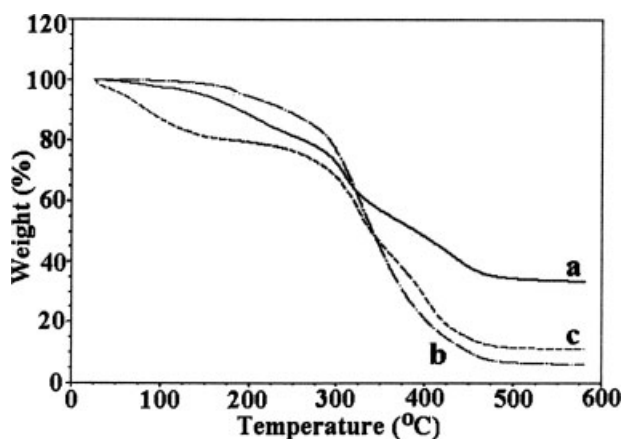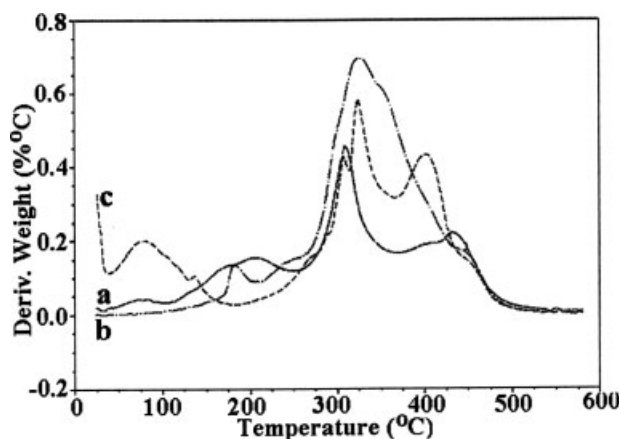
glycerin polyurethane, and castor oil polyurethane, respectively. Glycerin polyurethane gave the highest char yield of 30%. TETA polyurea and castor oil polyurethane gave similar char yields of 10% under N_2. The main weight loss was observed around 300°C. Generally, aliphatic urethanes, similar to those synthesized in this study, have thermal stabilities around 250°C; when both substituents on the urethane group are aryl groups, the thermal stability drops to around 120°C.[4]

CONCLUSIONS

Isocyanate-containing soybean oil was synthesized at 60–70% yield in two steps. This isocyanate-containing plant oil triglyceride is the first example of a plant-based isocyanate.

SONCO was reacted with castor oil and glycerin to give polyurethanes and with triethylenetetramine to give polyurea. These new polymers were characterized. Although expensive AgNCO was used to synthesize the isocyanate-containing triglycerides, at the end of the reaction, the AgBr byproduct was fully recovered and could then be used for the regeneration of AgNCO.

The polyurethanes and polyurea showed low mechanical strengths and high elongations. All of the polyurethanes had high swelling ratios. These polyurethanes can be used for applications where high mechanical properties are not needed, for example, as polyurethane foams.

Figure 14 TGA traces of (a) glycerin, (b) castor oil polyurethanes, and (c) TETA polyurea with SONCO.

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