A Simple One-Step Synthesis and Polymerization of Plant Oil Triglyceride Iodo Isocyanates

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ABSTRACT: In this study, a novel and simple route for the synthesis of the iodine isocyanate (INCO) adduct of soybean oil triglycerides is described. Soybean oil iodo isocyanate (ISONCO) was synthesized by the reaction of iodine isocyanate and soybean oil at room temperature. ISONCO was then polymerized with polyols, such as, castor oil, pentamethylene glycol, and glycerol to give the corresponding polyurethanes and with polyamines, such as, ethylene diamine, hexamethylene diamine, and triethylene tetramine to give corresponding polyureas. The structures of the monomer and the polymers were determined by FTIR and ^{1}H-NMR analyses. Thermal properties of the polymers were determined by DSC and TGA. Thermal degradation of the polyurethanes started at 150°C. Stability of the polyureas was higher than polyurethanes. Almost all polymers showed a T_g around −50°C. The mechanical properties of the polymers were determined by tensile tests. Among the polymers synthesized, castor oil polyurethane showed the highest elongation at break and the lowest tensile strength of 140 KPa. The highest tensile strength of 900 KPa was observed in the pentamethylene glycol polyurethanes. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2433–2440, 2010

Key words: soybean oil; polyurethanes; polyureas; biopolymers; iodine isocyanate

INTRODUCTION

Plant oil based polyurethanes have been synthesized with various petroleum based isocyanates and plant oil based polyols.[1] We have recently reported the first example of a triglyceride based polyisocyanate (SONCO) and its polyurethanes with plant oil based polyols.[2] This was the first example of a polyurethane whose isocyanate and polyol components were both plant oil based. As a continuation of this work, we also worked on iodine isocyanate derivatives of soy oil triglycerides.

The reaction of iodine isocyanate with olefinic compounds has received considerable attention for many years.[3] The pioneering work of Birckenbach and Linhard[4,5] showed that iodine isocyanate adds to olefinic double bonds in a manner typical of pseudo-halogens. Drefahl and Ponsold[6,7] showed that the isocyanate group attaches to the more alkyl or aryl substituted olefinic bonds. Addition reactions of iodine isocyanate to alkenes occur in a stereospecific trans manner and it was suggested that an iodonium ion is involved as an intermediate. The diaxially trans positions of iodine and isocyanate groups in the rigid and fused cyclohexane ring was demonstrated by Hassner and Heathcock.[8] The vicinal iodo isocyanates are useful intermediates in the preparation of carbamates, aziridines and ureas, 2-oxazolidines, and β-iodoamines. There is a report on the synthesis of aziridine derivatives of the fatty acid methyl esters from iodoisocyanates.[9]

Addition of iodine isocyanate to plant oil triglycerides should give valuable intermediates. One mole unsaturated plant oil triglyceride can bind around three moles of iodine isocyanate (Fig. 1) but many positional isomers should be obtained. The product would be a valuable intermediate for the synthesis of polyurethanes and polyureas.

In this study, soybean oil triglycerides double bonds were reacted with iodine isocyanate to give soybean oil iodo isocyanate (ISONCO). Compared to plant oil isocyanate derivative (SONCO) reported earlier, ISONCO synthesis is quite simple. SONCO synthesis involved allylic bromination of the triglyceride and then substitution of the bromide with isocyanate. Silver isocyanate was used as the nucleophile. In this work, simple one step synthesis of plant oil iodo isocyanates by the addition of Iodoisocyanate to the triglyceride double bonds is described. Unile SONCO, ISONCO is olefinicly saturated, which constitutes an advantage in terms of the oxidative stability of the polymers synthesized. Synthesis of different type of polyurethanes and ureas by using various polyols and polyamines was demonstrated. Characterization of the monomer and

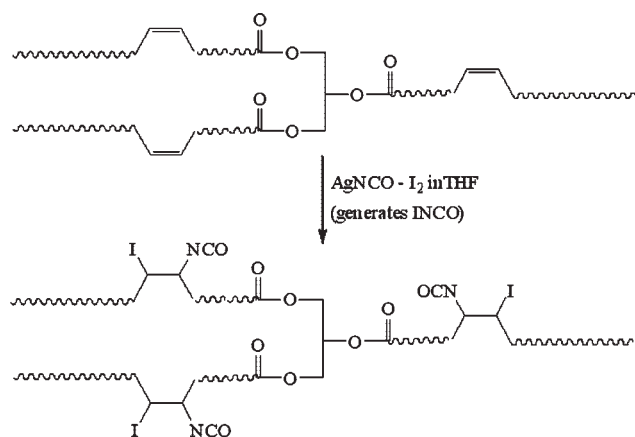*Correspondence to:* S. Küsefoğlu (kusef@boun.edu.tr).

Figure 1 Addition of 3 mol of iodine isocyanate to plant oil triglycerides.

thermal and mechanical properties of the polyurethanes and polyureas synthesized with this monomer was also carried out.

EXPERIMENTAL

Apparatus

IR characterization of compounds was performed by PerkinElmer FTIR 1600 (Waltham, MA) series spectrometer using KBr windows. Surface characterization of the polymers synthesized were performed by Thermo Nicolet, FTIR 380 spectrometer (Waltham, MA), using the diamond ATR accessory. The ^{1}H-NMR and ^{13}C-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 and 100.587 MHz for carbon. The spectra were recorded as ppm (δ) with CDCl$_3$ as a solvent. DSC characterizations were performed by "Thermal Analyses" Q 200 instrument (New Castle, DE) with a heating rate 10°C/min under nitrogen atmosphere from −70 to 120°C. 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. Tensile strength tests were performed by Devotrans DVG 32 Model tester with a 20 mm/min elongation rate.

Synthesis of ISONCO

In a 250 mL round bottom flask, which was covered with aluminum foil, 19.8 g of freshly prepared AgNCO (0.13 mol) was mixed with 200 mL of THF. This slurry was cooled to −30°C. To this cold mixture 25.4 g of I$_2$ (0.1 mol) was added and stirred for 2 h. Then to this mixture, 20 g of dry soybean oil (0.022 mol) was added. Mixture was kept at room temperature for approximately 2 h. At the end of the

reaction, the red color of the solution disappeared. The slurry was filtered and resulting yellow colored solution was evaporated. The product was yellow viscous oil.

IR spectrum

Peaks were observed at 2920, 2850 cm^{-1} (strong) C—H aliphatic stretching, 2250 cm^{-1} (strong) NCO group, a triplet at 1235, 1160, 1100 cm^{-1} (Medium) C—O stretching of ester moiety. A peak at 575 cm^{-1} (medium) belonging to C—I bond and at 1742 cm^{-1} belonging to the ester groups of triglyceride were observed (Fig. 2).

^{1}H-NMR spectrum

Peaks were observed at 0.8 ppm (—CH$_3$, the methyl hydrogens of the fatty acid moieties), 1.2 ppm (—CH$_2$— methylene hydrogens of fatty acids), 1.6 ppm (—CH$_2$— methylene hydrogens β to carbonyl), 2.0 ppm (mono allylic hydrogens), 2.2 ppm (—CH$_2$— methylene hydrogens α to carbonyl), 2.7 ppm (double allylic hydrogens), 2.8 (—HC—NCO geminal hydrogen to isocyanate group), 4–4.2 ppm (hydrogens of glycerol moiety), 4.1 (—CH—I geminal hydrogen to iodine atom), 5.2 ppm (hydrogen of glycerol moiety), 5.3 ppm (double bond hydrogens of triglyceride) (Fig. 3).

Synthesis of ISONCO methyl carbamate

ISONCO (1 g, 0.7 mmol) was dissolved in 25 mL of dry methanol. To this solution one drop of pyridine was added and the mixture was refluxed overnight. Then excess methanol removed by evaporation. The crude material was dissolved in 25 mL of dichloromethane. Dichloromethane phase was extracted with 25 mL 5% HCl solution then dried over Na$_2$SO$_4$ and evaporated. Methyl carbamate of ISONCO was obtained as orange oil.

Synthesis of ISONCO urea

ISONCO (1 g, 0.7 mmol) was dissolved in 50 mL of 7 N NH$_3$ in methanol solution. The solution was stirred for 5 h at room temperature then the methanol solvent was evaporated. Urea of ISONCO was obtained as yellow oil.

Synthesis of polyurethanes

A typical procedure for polyurethane synthesis involves mixing the diol and ISONCO in such amounts that the moles of isocyanate and hydroxyl groups are the same in a teflon mold, addition of 0,5 % of pyridine based on the amount of ISONCO

TABLE I
Typical Conditions for Polyurethane Synthesis

Polyurethane	ISONCO amount (g)	Polyol amount (g)	Synthesis temperature	Reaction time	Triglyceride % in the product
Castor oil	5.0	3.32	70°C	24 h	100
Glycerol	5.0	0.33	70°C	24 h	94
1,5- pentanediol	5.0	0.32	70°C	24 h	94

and keeping at 70°C for 24 h. Table I shows the amounts used.

Synthesis of polyureas

A typical procedure for polyurea synthesis involves mixing the diamine and ISONCO in such amounts that the moles of isocyanate and amino groups are the same in a Teflon mold at 5°C and keeping at room temperature for 4 h. Table II shows the amounts used.

RESULTS AND DISCUSSIONS

Synthesis and characterization of monomers

Soybean oil was reacted with iodine isocyanate in THF at 0°C and in 2 h. At the end of the reaction, ISONCO were obtained as positional isomers in nearly 100% yield. Isocyanate number per triglyceride was found to be 3.1 by calculating the integration ratios of the H geminal to the NCO group and the methylene protons alpha to the carbonyl group in the ^{1}H-NMR spectrum. Theoretically, soybean oil may bind approximately 5 mol of iodine isocyanate based on the iodine value of 143; however, it was found impossible to increase the number of isocyanate groups beyond 3.1 per triglyceride even when using excess iodine isocyanate reagent. This result is also consistent with literature.[8]

Product was characterized by IR and ^{1}H-NMR. IR spectrum showed a broad and strong peak at 2258 cm^{-1} due to isocyanate group and a new peak at 577 cm^{-1} due to C—I bond. Residual unsaturation of the soybean oil was also observed by peaks at 3006 and 1635 cm^{-1}. When reactions were repeated with excess amount of iodine isocyanate (INCO) reagent, peaks in this region did not disappear completely (Fig. 2).

^{1}H-NMR spectrum showed a peak at 2.9 ppm due to —CH—NCO proton. And a peak due to the proton geminal to iodine appeared at 4.0–4.2 ppm. This peak coincides with the glycerol protons (Fig. 3) and accurate peak integration is impossible.

Characterization of ISONCO methyl carbamate and ISONCO urea

IR and ^{1}H-NMR techniques were used to characterize these model compounds. Carbamates (urethanes) and ureas show characteristic peaks in IR spectrum. For carbamates usually, amide I band falls in the 1736–1700 cm^{-1}. Amide II band appears at around 1618 cm^{-1} and NH stretching absorption appears in the 3300–3250 cm^{-1} region. IR spectra of the ureas are more complex than those of urethanes but generally C=O absorption appears near 1660 cm^{-1} in mono and disubstituted ureas. At 1634 cm^{-1}, NH$_2$ deformation is observed.

Methyl carbamate of the ISONCO showed strong absorption at 1729 cm^{-1} due to the carbonyl group of the carbamate group (Amide I band), medium absorption at 3330 cm^{-1} due to NH stretching. There were no peaks observed at 1618 cm^{-1} but material showed strong absorption at 1509 cm^{-1} (Amide II band) (Fig. 4). ^{1}H-NMR also gave valuable information about the structure of the methyl carbamate. Peak at 2.9 ppm disappeared and new peak was obtained at 3.6 ppm due to methoxide group of carbamate ester (Fig. 5).

Urea of the ISONCO showed a strong absorption at 1738 and 1690 cm^{-1} due to the C=O stretching of ester group of the triglyceride and carbonyl group of the urea group. A strong peak at 1530 cm^{-1} was also observed due to the C—N stretching (Amide II band). At 731 cm^{-1} a medium peak was observed due to the NH deformation and at 3180 cm^{-1} NH stretching of the urea group was observed (Fig. 4).

TABLE II
Typical Conditions for Polyurea Synthesis

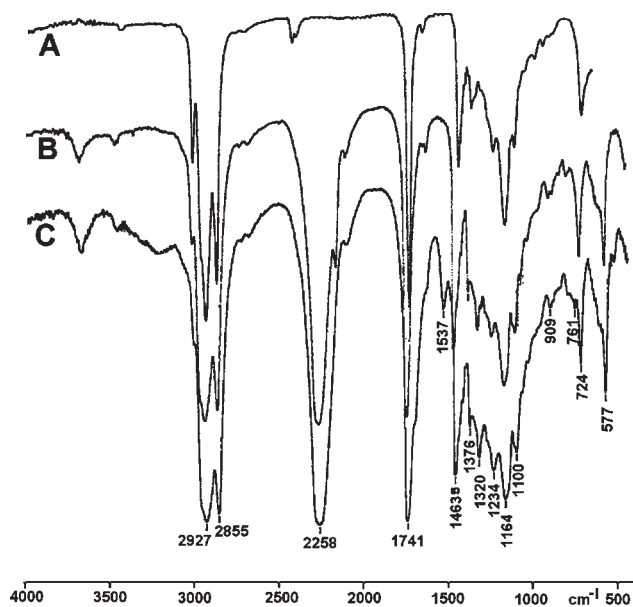| Polyurea	ISONCO amount (g)	Amine amount (g)	Synthesis temperature	Reaction time	Triglyceride % in the product
Ethylene diamine	5.0	0.32	5°C	4 h	94
Hexamethylene diamine	5.0	0.55	5°C	4 h	90
Triethylene tetra amine	5.0	0.39	5°C	4 h	93

Figure 2 IR spectra of (A) Soybean oil, (B) ISONCO synthesized with a 2.5 mol of INCO, and (C) ISONCO synthesized with a 5 mol of INCO.

In the NMR spectrum, the peaks at 2.9 and 4.2 ppm disappeared and new peaks were observed at 5.6 ppm due to the amine groups of urea, and at 2.5 ppm due to H geminal to NH group of urea (Fig. 5).

Synthesis and characterization of ISONCO based polymers

ISONCO was reacted with different alcohols and amines to give polyurethanes and ureas. Aliphatic isocyanates are less reactive than aromatic ones. Thus, synthesis of polyurethanes required longer
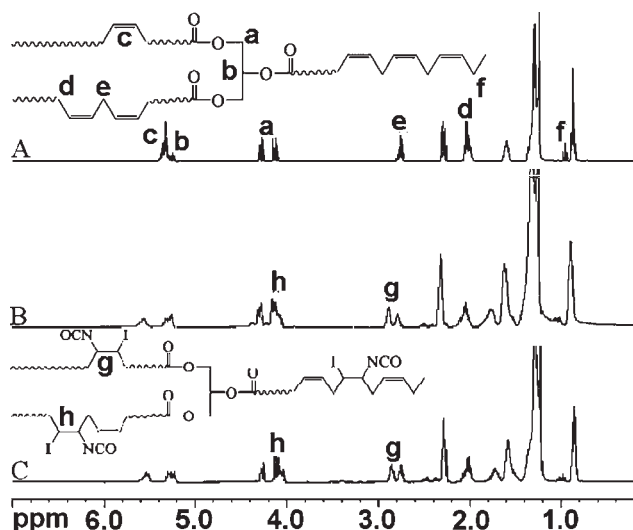
Figure 3 ¹H-NMR's of (A) Soybean oil, (B) ISONCO synthesized with an equivalent amount of INCO, and (C) ISONCO synthesized with an excess of INCO.
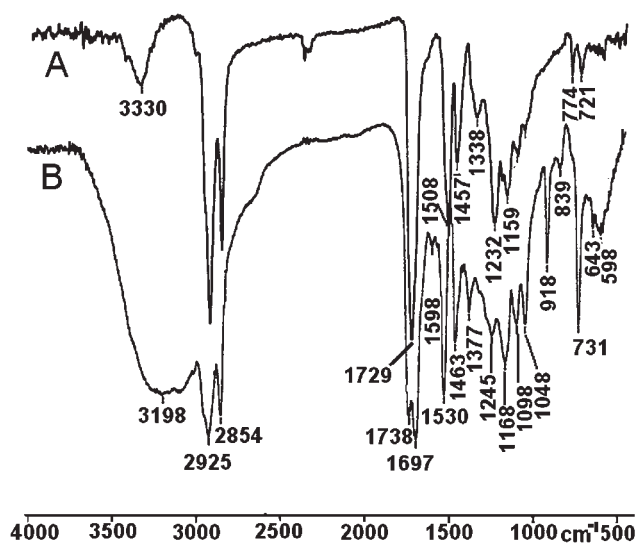
Figure 4 IR spectra of (A) ISONCO methyl carbamate and (B) ISONCO ammonia urea.

reaction times and required around 24 h for completion. By using catalysts, such as tin compounds the reaction rate may be accelerated. On the other hand, amines are strong nucleophilic compounds and they do not need any catalyst during polymerization and they are not affected by the structure of the isocyanates. Thus fast polymerization reaction was observed at room temperature.

Spectral characterization of the polymers was performed by ATR-IR spectroscopy due to the cross-
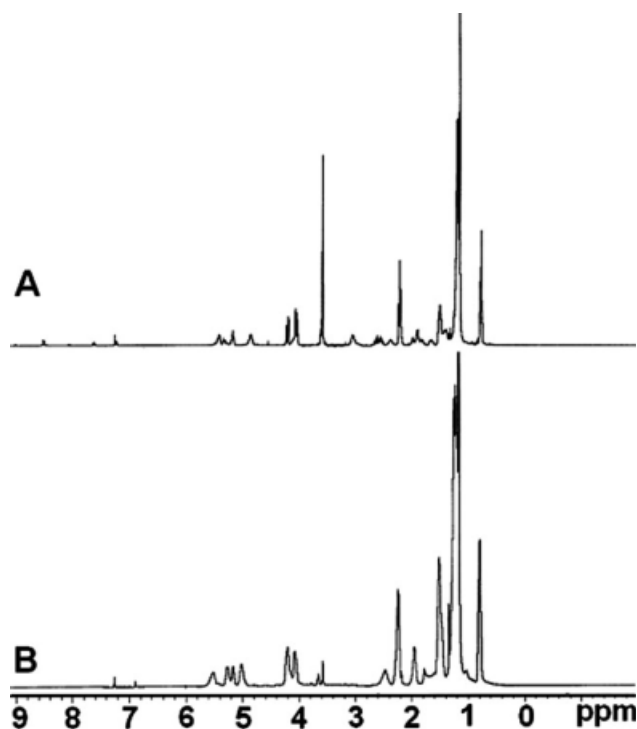

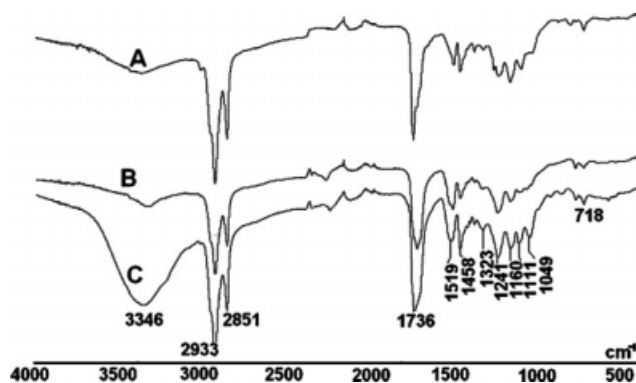**Figure 5** ¹H-NMR spectra of (A) ISONCO methyl carbamate and (B) ISONCO ammonia urea.

Figure 6 IR Spectra of ISONCO polyurethanes with (A) castor oil, (B) pentamethylene glycol, and (C) glycerol.

Figure 7 IR spectra of ISONCO polyureas with (A) ethylene diamine, (B) hexamethylene diamine, and (C) tetra ethylene diamine.

linked nature of the materials synthesized. IR spectra of the polyurethanes showed an ester carbonyl peak at 1742 cm^{-1} and a urethane carbonyl peak at 1695 cm^{-1}. Two new peaks were observed at 1519 cm^{-1} due to C—N stretching and at 1042 cm^{-1} due to C—O stretching of the urethane group (Fig. 6).

In the polyureas, a peak was observed at 1691 cm^{-1} in addition to the ester carbonyl. Other sets of peaks were found at 1650 cm^{-1} and 1550 cm^{-1} due to the C—N stretching and at 3400 cm^{-1} due to N—H stretching of the urea groups (Fig. 7).

Mechanical properties of the polymers Synthesized

Mechanical and thermal properties of the polymers are summarized in Table III. Structures of polyisocyanates, polyols, and polyamines have strong effect on the morphology and strength of polyurethanes and polyureas. Introducing aromatic segments to polyurethanes and ureas often causes improvements mechanical and thermal properties. Symmetric and aromatic polyisocyanates produce higher-strength materials, which show good packing ability and orientation.[10] Pandya et al.[11] have studied the effect of the isocyanates on the mechanical properties of polyurethanes and reported that highest mechanical strength was obtained with toluene diisocyanate polyurethanes.
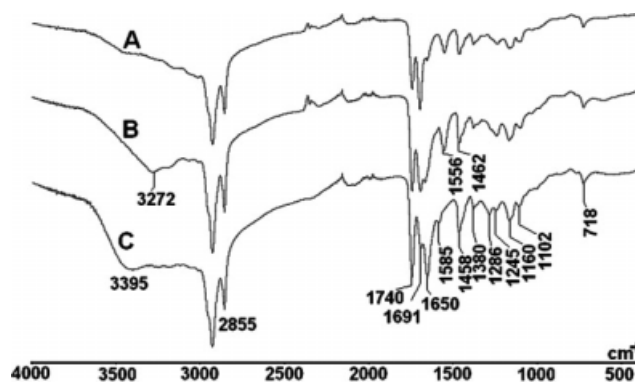
ISONCO and all polyols and amines used in this work are aliphatic compounds. Thus higher mechanical and thermal properties were not expected. The highest tensile strengths were observed in the 1,5 pentamethylene glycol and glycerol polyurethanes. Besides the structure of polyols and polyamines, three reasons can be cited to explain low tensile strengths of polymers synthesized. First reason is the structure of the plant oil triglycerides: the long alkyl chains of the triglycerides may act as internal lubricants and this causes a decrease in the mechanical strength of the materials. Second important factor is the position of isocyanate groups, in the middle of the fatty acid moiety, which would lower the reactivity of the isocyanate group. Similar trend was also observed epoxidized soybean oil (ESO). Due to the internal epoxide groups, ESO is not as reactive as terminal epoxide resins and shows lower mechanical properties. The last, may be the most important reason, is the random distribution of the fatty acids in the triglyceride. Depending on the conditions, under which the soy plant is grown, fatty acid composition may vary. Some triglyceride molecules are rich in saturated fatty acids and these inert fatty acids reduce the connectivity in the sample and act as a lubricant.

Structures of the polyols and polyamines also affect mechanical and thermal properties of polyurethanes and ureas. The literature shows that with

TABLE III
Mechanical and Thermal Properties of Polyureas and Polyurethanes Synthesized

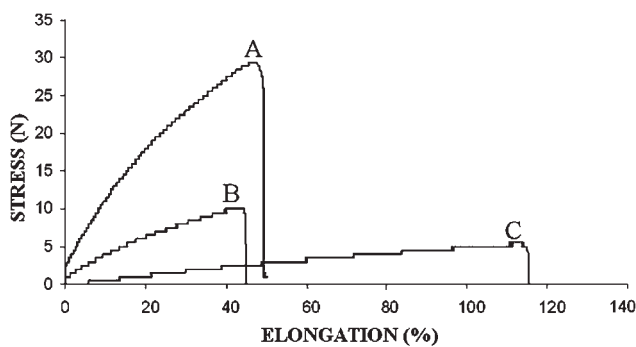| POLYMER	Stres at break (KPa)	T_g's (°C)	5 % Weight lost temperature (°C)
ISONCO-1,5 pentanediol polyurethane	900	−50, −15	157
ISONCO-Glycerol polyurethane	270	−53, 4, 92	165
ISONCO-Castor oil polyurethane	140	−45, 40	206
ISONCO-Ethylene diamine polyurea	95	−50, 35, 80	206
ISONCO-hexamethylene diamine polyurea	NA	−50, 28, 80	230
ISONCO-Triethylene tetra amine polyurea	NA	−52, 37, 72	219

Figure 8 Stress-elongation graphs of ISONCO polyurethanes with (A) pentamethylene glycol, (B) glycerol, and (C) castor oil.

common isicyanates and diols, tensile strength decreases in the following order 1,4 butanediol > ethylene diol > 1,5 pentane diol > 1,6 hexamethylene diol > 1,3 propanediol.[12] Among the polymers synthesized castor oil polyurethane showed the highest elongation at break and the lowest tensile strength of 140 KPa. The highest tensile strength was observed in the pentamethylene glycol polyurethanes at a value of 900 KPa (Fig. 8). An interesting behavior was observed in glycerol polyurethane: when the samples were kept for 2 weeks at room temperature mechanical properties improved. Tensile strength increased from 270 to 950 KPa and elongation at break of the sample was reduced. This may be due to oxygen mediated 'drying' of the residual double bond of ISONCO. We have previously observed increased reactivity towards oxygen due to the conjugation of the polyunsaturated fats. The polyurethanes synthesized contained more than 90% of plant oil triglyceride and showed reasonably high tensile strengths. If reinforced with glass or carbon fibers we think these polyurethanes would be excel-
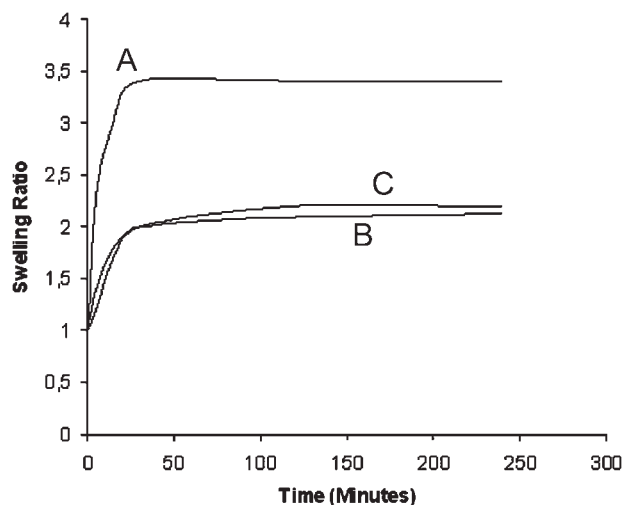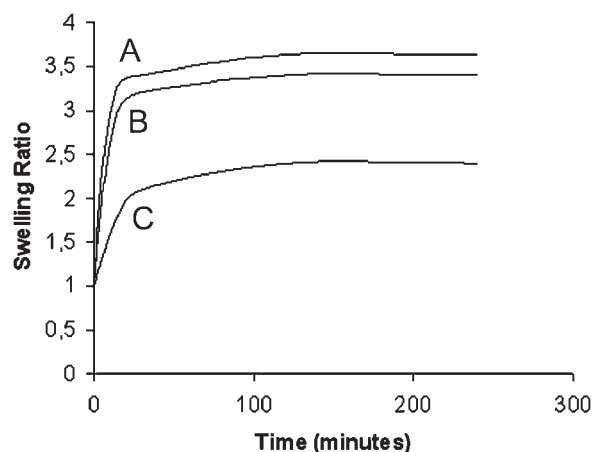

Figure 10 Swelling ratios of (A) hexamethylene daimine, (B) ethylene daimine, (C) triethylene tetraamine polyureas.

lent candidates for the Reaction injection molding (RIM) process.

Preparation of mechanical test samples with ISONCO and diamines was difficult due to the very fast reactions observed. Many samples had defects and voids due to gas evolution and were discarded. Only ethylene diamine polyureas could be molded satisfactorily and these gave lower tensile strength than the polyurethanes.

Swelling properties of the materials synthesized were characterized by using diethyl ether as solvent. Generally polyureas showed a higher swelling ratio than polyurethanes and, as expected, when the connectivity increased, swelling ratio decreased. Thus it was no surprise that glycerol polyurethane and triethylene tetra amine polyurea showed the lowest swelling ratios. The highest swelling ratios were observed in castor oil polyurethane and hexamethylene diamine polyurea (Figs. 9 and 10).
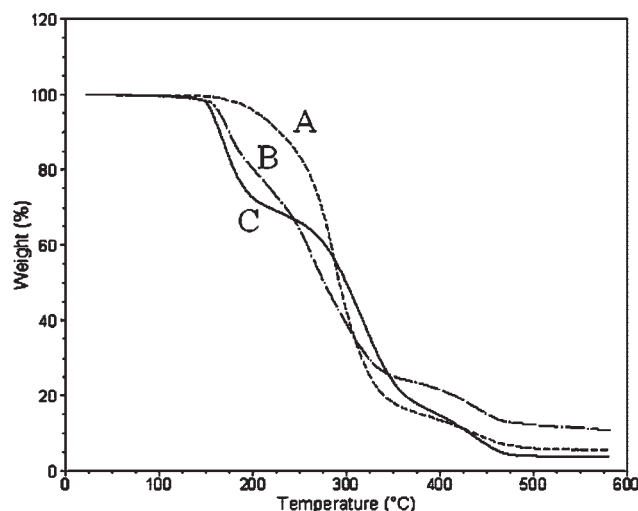

Figure 9 Swelling ratios of (A) castor oil polyurethane, (B) glycerol polyurethane, and (C) pentane 1,5 diol polyurethane of ISONCO.

Figure 11 TGA curves of polyurethanes of ISONCO with (A) castor oil, (B) glycerol, and (C) pentamethylene glycol.
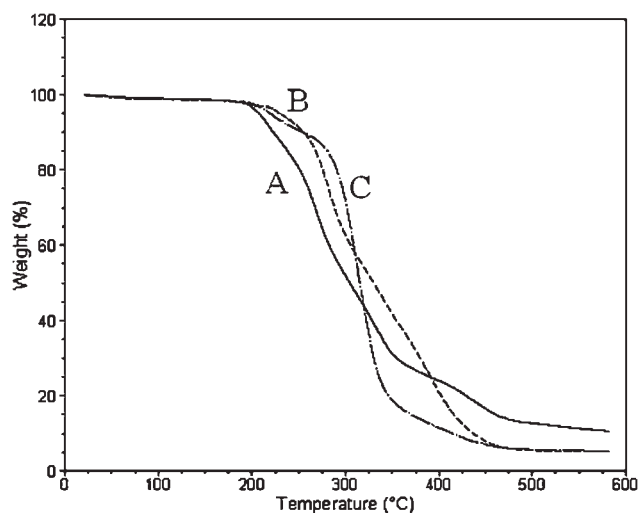
Figure 12 TGA curves of polyureas of ISONCO with (A) ethylene diamine, (B) hexamethylene diamine, and (C) triethylene tetraamine.

Thermal properties of the polymers synthesized

Thermal properties of the materials were also interesting. The temperature, at which 5% weight loss was observed, was evaluated as an indication of thermal stability. Thermal degradation of the polyurethanes synthesized started at around 150°C, which was lower than SONCO polyurethanes reported earlier[2] (Fig. 11). The highest thermal stability was shown by castor oil polyurethane at 206°C and surprisingly the stability of the polyureas were higher than that of polyurethanes (Fig. 12). The lowest thermal stability of polyureas was shown by ethylene diamine polyurea at 206°C. Low thermal stability of polyurethanes can be explained by HI evolution from the compounds. This strong acid can easily hydrolyze ester, urethane, and urea bonds. In the polyureas free
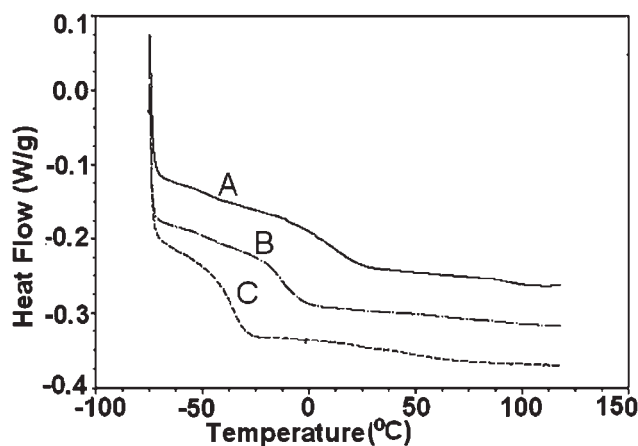

Figure 13 DSC Traces of polyureas of ISONCO with (A) glycerol, (B) 1,5 pentane diol, and (C) castor oil polyurethanes.
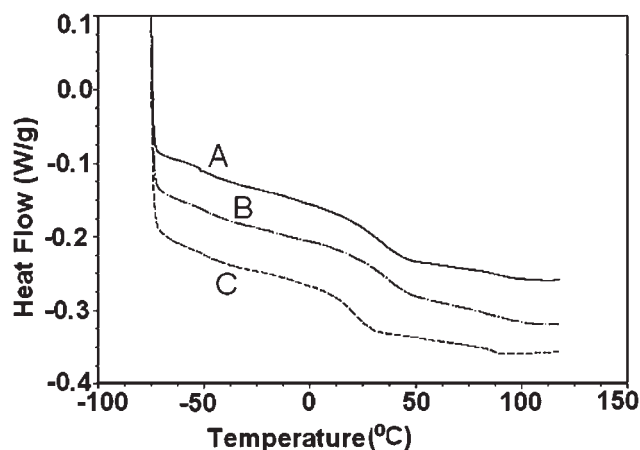

Figure 14 DSC traces of ISONCO with (A) Ethylene diamine, (B) hexamethylene diamine, and (C) triethylene tetra amine polyureas.

amino groups may neutralize HI evolved and this would give them extra thermal stability.

Thermal properties of all materials are summarized in Table III. DSC traces of the polymers revealed that all materials showed a T_g at around −50°C probably due to the gyrations of the long alkyl chains of the triglyceride moiety. All polyurethanes and polyureas showed more than one T_g and when the functionality of alcohol or amine and therefore the crosslink density of the network polymers was increased, T_g of the materials also increased (Figs. 13 and 14). Increasing functionality of the reacting monomers would cause different type of amorphous domains that would cause multiple T_g.

CONCLUSIONS

Iodine isocyanate derivative of soy oil triglycerides were synthesized by direct and easy addition of iodine isocyanate to double bonds. The number of the isocyanate groups per triglyceride was found to be approximately three. Reaction of the ISONCOs with different type of polyols and polyamines gave the corresponding

polyurethanes and polyureas. Due to the high functionality of the ISONCO, mechanical properties of the polyurethanes synthesized were higher than the polyurethanes, which were synthesized from allylic isocyanates. ISONCO was soluble in polyols with low polarity such as castor oil and homogenous products were obtained. Curing with polyols should be conducted at low temperatures to minimize isocyanurate and allophanate formation. At high temperatures HI evolution occurs and this acid might hydrolyze the polyurethane and ester bonds. ISONCO gave a fast reaction with poly amines even at

0°C. Thus shaped specimens could not be prepared. The iodine isocyanate derivative of plant oil triglycerides promises to be suitable for a fast RIM process.

References

1. Dwan'isa, J. P. L.; Mohanty, A. K.; Misra, M.; Drzal, L. T. In Natural Fibers, Biopolymers and Biocomposites, Mohanty, A. K.; Misra, M.; Drzal, L. T., Eds.; CRC Press: Boca Raton, FL, 2005.
2. Çaylı, G.; Küsefoğlu, S. J Appl Polym Sci 2008, 109, 2948.
3. Hassner, A.; Lorber, M. E.; Heathcock, C. H. J Org Chem 1967, 32, 540.
4. Birckenbach, L.; Linhard, M. Ber Dtsch Chem Ges B 1930, 63, 2544.
5. Birckenbach, L.; Linhard, M. Ber Dtsch Chem Ges B 1931, 64, 961.
6. Drefahl, G.; Ponsold, K. Chem Ber 1960, 93, 519.
7. Drefahl, G.; Ponsold, K.; Koellner, G. J Prakt Chem 1964, 23, 136.
8. Hassner, A.; Heathcock, C. C. Tetrahedron Lett 1964, 19, 1125.
9. Metzger, J. O.; Fuermeier, S. Eur J Org Chem 1999, 3, 661.
10. Ansari, F. H.; Osman, S. M. Indian J Chem 1973, 111, 10179.
11. Pandya, M. V.; Desphande, D. D.; Hundiwale, D. G. J Appl Polym Sci 1986, 32, 4959.
12. Szycher, M. Szycher's Handbook of Polyurethanes; CRC press: Boca Raton, FL, 1999.