Soy-Based Polyurethanes by Nonisocyanate Route

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ABSTRACT: Polyurethanes by a nonisocyanate route were prepared by reacting carbonated soybean oil with different diamines. The effect of amine structure and carbonate to amine ratio on polyurethane structure and mechanical, physical, and swelling properties was studied. The reactants 1,2-ethylenediamine, 1,4-butylenediamine, and 1,6-hexamethylenediamine were used with the carbonate to amine ratio of 1 : 0.5, 1 : 1, and 1 : 2. It was found that along with urethane formation, the amine group reacted with ester groups to form amides. All amines produced elastomeric polyurethanes with glass transitions between 0 and 40°C and hardness between 40 and 90 Shore A. The reaction of epoxidized soybean oil with carbon dioxide was optimized resulting in complete conversion of epoxy to cyclic carbonate groups ending in polyurethanes with higher crosslinking density and much higher tensile strength than previously reported for similar polyurethanes. Swelling in toluene and water depended on crosslinking density and the polarity of polyurethane networks controlled by the cyclic carbonate-to-amine-ratio. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3867–3875, 2008

Key words: soy oil; nonisocyanate; polyurethane; structure; property

INTRODUCTION

Polyurethanes are reaction products of polyols and isocyanates. Isocyanates are very toxic compounds and their synthesis requires use of highly toxic substances such as phosgene. There is substantial interest to develop alternative, environmentally friendly methods for the preparation of polyurethanes, and one of the possible ways involves the reaction of cyclic polycarbonates with amines. Cyclic carbonates are excellent starting materials for new organic compounds,[1,2] plasticizers,[3] solvents,[4] fuel additives,[5] lubricants,[6] etc. Low-molecular cyclic carbonates have high boiling and flash points, low odor, evaporation rates and toxicity, good biodegradability, and high solvent power. The additional benefit of the carbonate route to urethanes is the utilization of carbon dioxide, an inexpensive and environmentally friendly monomer. Carbon dioxide is the cheapest and most abundant source of carbon, and using CO_2 as a C_1 feedstock is a direct route to carbon dioxide recycling and the reduction of carbon dioxide presence in the atmosphere. Synthesis of cyclic carbonates by older synthetic methods required the use of phosgene, as well as environmentally unfriendly solvents. The alternative synthesis uses an epoxide route with carbon dioxide to react with epoxy groups in the presence of a catalyst, thus producing cyclic carbonates. This method is very well suited for carbonate synthesis from epoxidized vegetable oils.

Cyclic carbonates react relatively easily with most hydrogen donor compounds. Aromatic hydrogen donor compounds, such as phenol and phenolic resins,[7] thiophenols,[8] aniline,[9] etc., produce alkylated aromatics. Aliphatic hydrogen donor compounds react differently than their aromatic analogues. Alcohols produce esters with cyclic carbonates.[10,11] Products of the reaction with carboxylic acids are mixtures of hydroxyalkyl esters and diesters.[12] Reaction with aliphatic diamines is utilized for the synthesis of polyurethanes by a nonisocyanate route.[13–17] This reaction also forms a hydroxyl group at the β-carbon atom of the polyurethane chain that is hydrogen bonded to the urethane carbonyl. Materials containing intramolecular hydrogen bonds display resistance to organic chemicals 1.5–2 times higher than the materials of the similar chemical structure without such bonds.[14] These materials have better thermal stability than regular polyurethanes because of the absence of thermally unstable biurets and allophanates. Because of the presence of hydroxyls, they absorb water much more than isocyanate-based polyurethanes and may have applications where water absorption and retention is desirable. Nonisocyanate polyurethanes derived from vegetable oils have ester groups and in a chemical sense they are polyester-polyurethane-polyhydroxyl compounds. It has been proven that soybean oil polyol-isocyanate-based polyurethanes can compete in many aspects with ones derived from petrochemical polyols.[18–21]

During formation of nonisocyanate polyurethanes derived from vegetable oils there is a possibility that

the amine reacts with the ester group, producing an amide. The published data did not give a clear answer on the course of the reaction at elevated temperatures that are commonly used for preparation of this type of polyurethane. Tamami et al.[22] investigated nonisocyanate polyurethanes based on carbonated vegetable oil and aliphatic diamines and found that ester groups did not react with diamines and the product of the reaction was urethane only. This was based on fourier transform infrared (FTIR) analysis of the model sample prepared in the solution at room temperature. We considered that the curing temperatures (70–100°C) could cause reactions between amines and esters, and besides the urethane, some amides could be formed. In order to clarify this we studied the reactions between carbonated soybean oil (CSBO) and aliphatic diamines and used different methods to analyze the samples cured in the mold. Nonisocyanate soy-based polyurethanes were prepared by reacting CSBO with 1,2-ethylenediamine (EDA), 1,4-butylenediamine (BDA), and 1,6-hexamethylenediamine (HMDA) with the carbonate to amine molar ratios of 1 : 0.5, 1 : 1, and 1 : 2. The polyurethane samples were analyzed by thermal, mechanical, swelling, and FTIR methods and results were expressed as a function of carbonate to amine ratio throughout the article. The sol fraction obtained by extraction with toluene was analyzed by FTIR and gel permeation chromatography (GPC).

Polyurethanes are known for the high level of mechanical properties yet the reported values[22] for tensile strengths of polyurethanes prepared via carbonate route from epoxidized soybean oil and EDA and 1,6-hexamethylene diamine were below 1 MPa, much lower than with isocyanate-based polyurethanes. One possible explanation is that there was incomplete carbonate formation from epoxidized soybean oil and thus lower crosslinking density of polyurethane networks. The reaction of carbon dioxide and epoxidized soybean oil was studied by varying the reaction temperatures, pressures, and the catalyst concentration. We were also searching for optimal reaction conditions for complete conversion of epoxy to carbonyl groups to avoid side reactions involving triglyceride ester groups, and to improve mechanical properties of new bio-based polyurethanes.

EXPERIMENTAL WORK

Materials

Epoxidized soybean "Flexol EPO," with the epoxy oxygen content (EOC) of 6.8% corresponding to 4.0 epoxy groups per triglyceride, was obtained from Dow Chemical. Carbon dioxide was supplied by Airgas.

Tetrabutylammonium bromide (TBAB) was supplied by Fisher Scientific, EDA, BDA, and HMDA were supplied by Aldrich.

Synthesis

#### Reaction of epoxidized soybean oil (ESBO) with carbon dioxide

ESBO (200 g) and the catalyst (ranging between 0.0125 and 0.0500 mol per mol of epoxy groups) were placed in a 500 mL reactor, stirred, and heated. The reactions were carried out from 110 to 180°C. The reaction pressure varied from atmospheric to 5.65 MPa (820 psi). The conversion of epoxy to carbonate was monitored by IR spectroscopy and the EOC was determined by titration of small aliquots taken in ∼ 3–5 h intervals. The number of carbonate groups per triglyceride was calculated from the initial and final EOC content, assuming no side reactions.

Polyurethane preparation

CBSO with residual EOC of 0.23% and a viscosity of 32 Pa s (25 g) was placed in a 100 mL Erlenmeyer flask followed by amine and mixed thoroughly. The viscous solution was poured into a mold and heated at 70°C for 10 h, and then for 3 h at 100°C.

Test methods

A thermal analysis system from TA Instruments, consisting of the Controller 3100 with DSC 2910 module and TGA 2050 Thermogravimetric Analyzer, was used to measure glass transition and thermal stability. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) tests were carried out at 10°C/min in a nitrogen atmosphere. Dynamic mechanical tests were carried out on DMA 2980 from TA Instruments with a heating rate of 3°C/min. DMA specimens were rectangular shaped and 1 mm × 10–12 mm × 15 mm. The testing was carried out in the tension mode in a nitrogen atmosphere at 15 μm amplitude and the frequency of 10 Hz. Tensile properties were measured on Qtest-2 Tensile Tester from MTS, according to ASTM D882-97. The test specimens were the strips of 100 mm length, uniform width (around 8 mm), and thickness (around 1 mm). The gap between the tester grips was 50 mm and the speed of testing was 50 mm/min. FTIR spectra were recorded on a Perkin-Elmer FTIR spectrometer Spectrum 1000. The spectra were recorded from the solid plaques using attenuated total reflectance (ATR) technique. The number of scans per one recording was 16 and the resolution 2 cm^{-1}. Viscosity data were obtained by Rheometric Scientific Dynamic Stress Rheometer SR
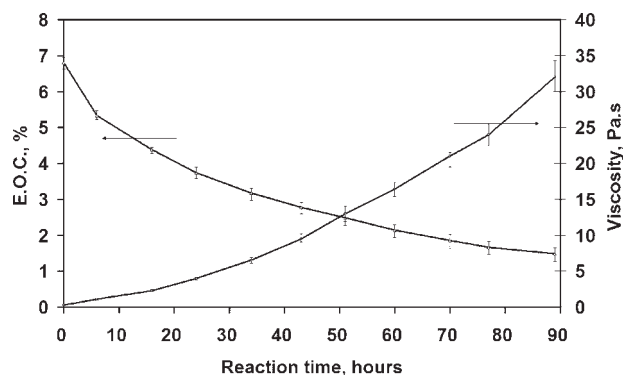
Figure 1 Variation of epoxy oxygen content and viscosity with time in the reaction of ESBO with carbon dioxide at 110°C, atmospheric pressure and TBAB concentration of 3.4 g/100 g ESBO.

500. Molecular weight distribution was obtained on the Waters GPC system consisting of the 510 pump and 410 Differential Refractometer at 40°C with tetrahydrofurane as a mobile phase and the flow rate of 1 mL/min.

## RESULTS AND DISCUSSION

Preparation of CSBO

CSBO was prepared from ESBO and carbon dioxide. Kinetics of conversion of epoxy groups to carbonate could be conveniently followed by measuring viscosity. Figure 1 shows the dependence of viscosity and conversion with time at 110°C and atmospheric pressure. Introduction of bulky carbonate groups increases viscosity by several orders of magnitude compared with epoxy groups. We monitored the progress of conversion of epoxy to carbonate groups by FTIR, GPC, viscosity, and EOC. FTIR spectra showed complete disappearance of epoxy bands at 823 and 845 cm^{-1} after 89 h at 110°C and atmospheric pressure, but EOC obtained by titration was 1.49% which corresponds to 22% of the starting epoxy groups (Fig. 1). The conversion rate determined by FTIR can be used for a rough assessment, but not as a precise parameter for calculating degree of conversion of epoxy to carbonate groups. Tamami et al.[22] used carbonated soybean oil with a viscosity of 13,200 mPa s at 25°C and according to our findings this corresponds to about 2.5% of residual EOC (see Fig. 1) or a conversion of epoxy to carbonate groups of around 63%, instead of the assumed 100%. This would explain the relatively low mechanical properties of polyurethanes (tensile strength was below 1 MPa) presented by the authors.

To find optimal conditions for preparation of CSBO with a high carbonate content and as low as possible residual epoxy content, the reaction parameters including the catalyst concentration, tempera-

ture, and pressure were varied. The literature reported a relatively high catalyst concentration (0.05 mol of the catalyst per 1 epoxy group or 6.8 g per 100 g of ESBO). We carried out the experiments with the same and less catalyst. At 140°C, 0.69 MPa (100 psi) and the catalyst concentration of 6.8 g/100 g ESBO, EOC dropped to 0.18% after 23 h. At the lower catalyst concentration of 3.4 g/100 g ESBO and the same reaction time and temperature, EOC was 0.91% after 23 h. The reaction with the lowest catalyst concentration of 0.0125 mol/epoxy (1.7 g/100 g ESBO) gave an EOC of 3.49%, but the reaction was considered too slow to be used for preparation of CSBO. Therefore, the rate of 0.025 mol or 3.4 g catalyst /100 g ESBO was considered acceptable and it was selected for further experiments. The following reactions were carried out at higher pressures, up to 5.65 MPa, and at the reaction temperatures of 110 and 140°C (Fig. 2). The slowest reaction was at atmospheric pressure and at 140°C. It was slower than the reaction at 110°C, probably due to decomposition and evaporation of the catalyst. The rate of the reaction was increased by increasing temperature and pressure, resulting in a low content of residual epoxy groups. The highest pressure used was 5.65 MPa and using a temperature of 140°C and 3.4 g catalyst /100 g ESBO, EOC dropped to 0.15% in 22 h. Viscosity of the product was 33 Pa s. The reactions at 0.69 MPa were also carried out at 160 and 180°C. At 160°C EOC was 0.56% after 23 h and at 180°C it was 3.79%, indicating that some side reactions deactivated the catalyst. The reaction rate at 140°C and 1.03 MPa was considered optimal and these conditions were selected for CSBO preparation. The EOC of CSBO prepared under these conditions was 0.23% and viscosity was 32 Pa s. This product was used for the polyurethane preparation. GPC of CSBO did not show any change in the shape of molecular weight distribution curves or the presence of new peaks as
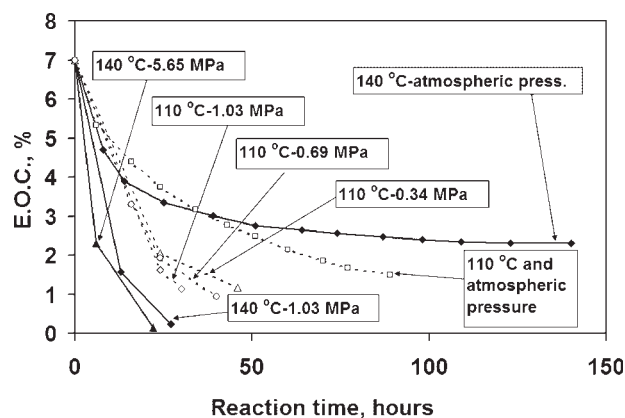
Figure 2 Effect of reaction time, pressure, and temperature on EOC during conversion of epoxy to carbonate groups.
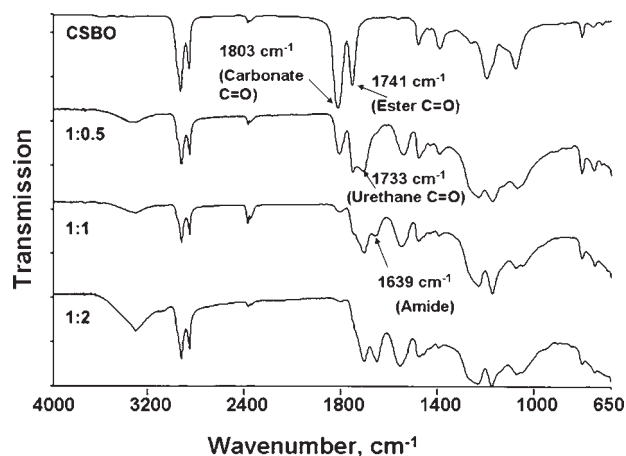
Figure 3 FTIR spectra of BDA-based polyurethanes at different carbonate to amine ratio.

a result of oligomerization or chain cleavage. However, a shift of the triglyceride monomer peak toward higher molecular weights due to the carbon dioxide attachment and molecular weight increase was observed. After the synthesis, CSBO was diluted in ethyl acetate, washed three times with equal quantities of water in order to remove the TBAB catalyst, and dried on a rotary evaporator at 100°C and high vacuum before use.

Preparation and properties of polyurethanes

The properties of polyurethanes derived form CSBO and amines depended strongly on the crosslinking density of the network. Crosslinking density is related to the functionality of CSBO and the degree of conversion of epoxy to carbonate groups. If conversion is not complete, crosslinking density of the derived PU network will be lower, since residual epoxy groups in CSBO will not react with amines under conditions for polyurethane preparation. To check this assumption, ESBO was reacted with equimolar ratios of EDA, BDA, and HMDA under the same conditions that were used for polyurethane preparation. The EOC was checked at the beginning and at the end of the reaction. The EOC was decreased by 14% in the reaction of ESBO with EDA, but change of EOC in the reaction with BDA and HMDA was very small, about 2%. The overall reaction of epoxy groups with amine was very small and it can be considered that residual epoxy groups in CSBO did not react with amines. Fatty acid chains with unreacted epoxy groups act as plasticizers decreasing glass transition temperature and modulus of the derived polyurethanes.

FTIR spectra

FTIR spectra of polyurethanes showed absorption bands at 3300–3440 cm^{-1} for O—H and N—H

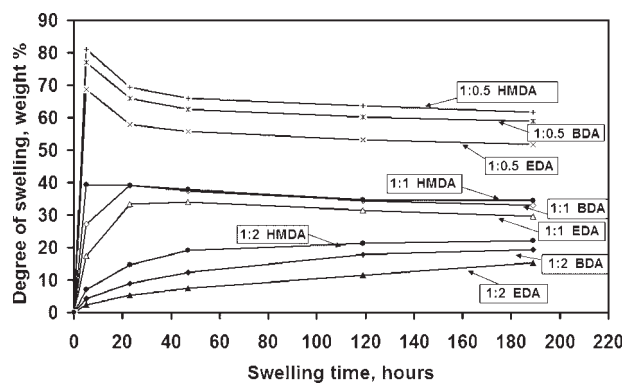stretching from hydroxyl and urethane groups. The band at 1803 cm^{-1} was assigned to the cyclic carbonate carbonyl and the ester carbonyl band of the soy oil was at 1741 cm^{-1}. The absorption band of the urethane group appears between 1700 and 1735 cm^{-1}, and absorption of the amide group was observed at 1636–1643 cm^{-1}. Figure 3 shows FTIR spectra of polyurethanes obtained using BDA with different carbonate-to-amine ratios designated on the spectra. Similar spectra were obtained from the EDA and HMDA samples. The samples formed at the 1 : 0.5 carbonate-to-amine ratio had significant amounts of residual carbonate and ester along with newly formed urethane at 1733 cm^{-1}. The amide peak at $\sim$ 1640 cm^{-1} was hardly noticeable as a shoulder.

Samples prepared with a 1 : 1 carbonate-to-amine ratio displayed a small peak of residual carbonate, a strong peak of urethane and a very clear amide absorption band. The ester absorption band was present as a shoulder. At 1 : 2 carbonate-to-amine ratio, the amide peak became as strong as the urethane peak. The ester peak at the carbonate-to-amine ratio 1 : 0.5 is as strong as the urethane peak, but at ratios 1 : 1 and 1 : 2 it is a small shoulder on the urethane peak due to conversion of the ester to amide. We concluded that the reaction of ester with amine resulting in amide goes simultaneously with the urethane formation as shown in the reaction scheme in Figure 4.

To check the possibility for the ester-amine reaction and the amide formation we reacted pure soybean oil with EDA at 70°C and the ester-to-amine ratio 1 : 1. The progress of the reaction between amine and ester group was monitored by FTIR. Soybean oil has three ester groups and no other groups that can react with amine under these reaction conditions. At the beginning of the reaction the starting concentration of ester groups was maximal and it was desig-
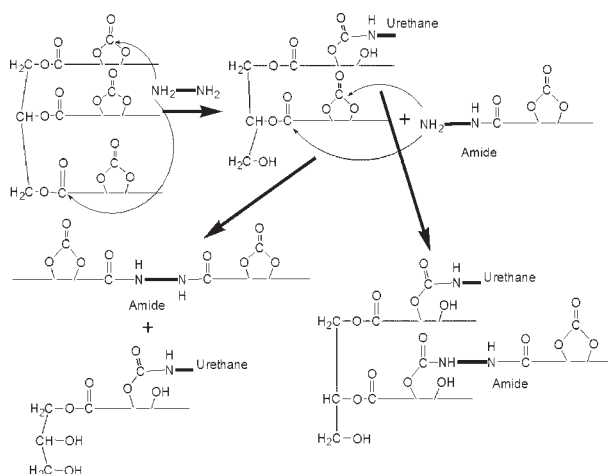
Figure 4 The scheme for the urethane and amide formation in the reaction of CSBO with diamines.

Figure 5 Effect of time on the degree of swelling in toluene at room temperature.

Figure 6 Effect of carbonate to amine ratio and the diamine type on the sol fraction content.
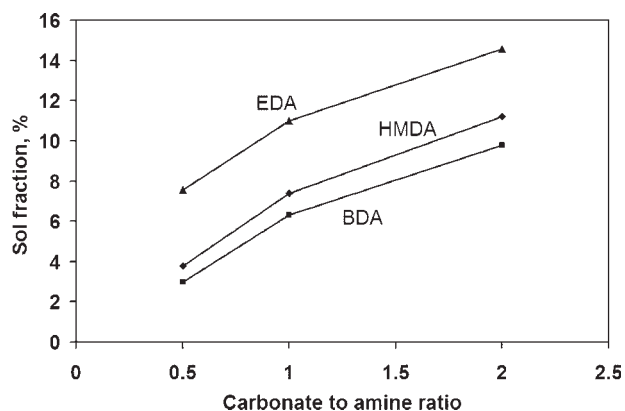
nated as 100% and the amide group concentration was 0%. After 2 h the concentration of ester groups decreased to 68% and amide group was increased to 32% of the maximal concentration. After 4 h, ester group concentration dropped to 48% from the starting value and amide group concentration was increased to 52% of the maximum. After 8 h, the ester group concentration was decreased to 25% and the amide was increased to 75% of their maximal concentrations. The end of the reaction was reached after 10 h when all ester groups were converted to amide.

Swelling in toluene

Crosslinking density of polymers is usually assessed by swelling in a solvent. Swelling in toluene showed strong dependence on the carbonate-to-amine ratio, as well as on the type of diamine. Surprisingly, the lowest degree of swelling of about 20% was obtained with the carbonate/amine ratio of 1 : 2, followed by the stoichiometric ratio (degree of swelling about 30%), while 1 : 0.5 ratio produced swelling of about 60%, as shown in Figure 5. Degree of swelling depends on crosslinking density and polymer/solvent interaction parameter, χ. Considering glass transition, hardness and mechanical properties of these polyurethanes, it appears that the samples with 1 : 2 carbonate to amine ratios do not have the highest crosslinking densities and the decisive factor for low swelling is the higher χ parameter. Longer chain amines produce a lower concentration of urethane and amide groups, resulting in higher swelling with samples based on HMDA, followed by BDA and EDA.

Sol–gel analysis

Measurement of the sol fraction by extraction with toluene in a Soxhlet apparatus indicated that the highest extractable content, between 9 and 15%, was
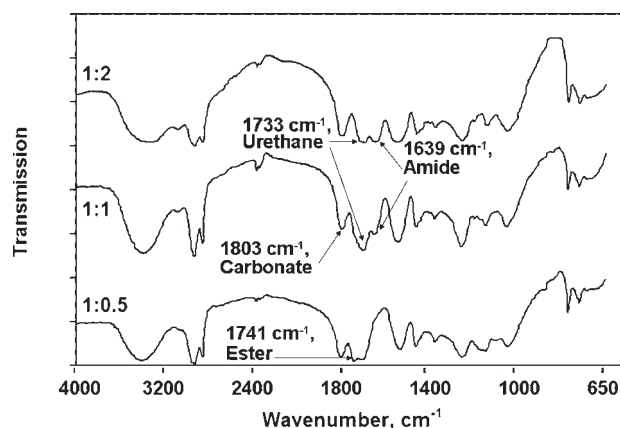
obtained from the specimens prepared with a deficiency of diamines, i.e., at the carbonate-to-amine ratio 1 : 0.5 (=2 as shown in Fig. 6). While differences between HMDA and BDA cured samples are within the experimental error, EDA cured samples displayed a higher sol fraction. This could be the consequence of the higher content of low-molecular fatty amid fractions as a result of the aminolysis with the strongest amine. FTIR spectra of the extract obtained from BDA samples, Figure 7, showed that the sol fraction at the carbonate to amine ratio 1 : 0.5 primarily consisted of nonreacted carbonated soybean oil characterized by absorption bands at 1803 and 1741 cm^{-1} from carbonate and ester carbonyls, respectively. The peak at 3444 cm^{-1} indicated the presence of hydroxyl groups as a result of carbonate and amine reactions, as well as ester cleavage, which produces mono- and diglycerides and possibly free glycerin. The sol fraction from the samples prepared at the 1 : 1 ratio had the peak of the carbonate group (1803 cm^{-1}) still present in the FTIR spectra, but the amide absorption band at 1639 cm^{-1}, was stronger
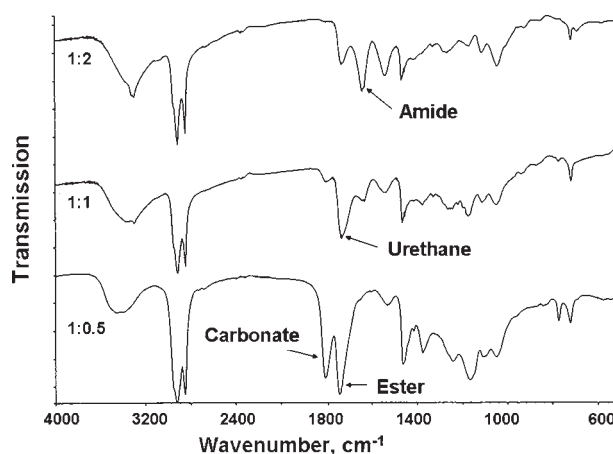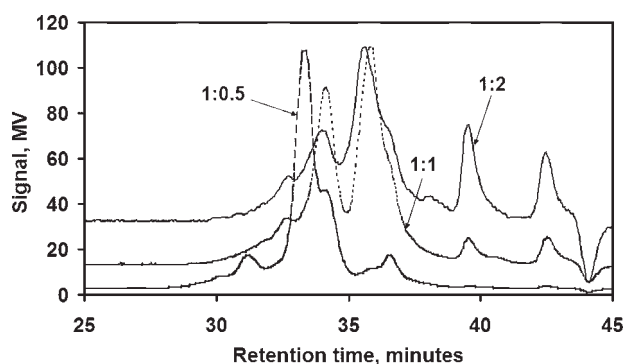

Figure 7 FTIR spectra of the sol fraction obtained from the BDA-based samples.

**Figure 8** FTIR of the gel fraction obtained from the BDA-based samples.

TABLE I
Relative Ratio of the Species in the Sol Fraction Determined by GPC

Sample	OLI	TRIG	DG	MG	Fatty amid	Glycerin	Diamine
EDA 1 : 0.5	16	55	18	12	0	0	0
EDA 1 : 1	9	10	27	26	28	5	5
EDA 1 : 2	4	6	21	33	20	15	2
BDA 1 : 0.5	12	56	18	14	0	0	0
BDA 1 : 1	5	8	33	32	17	4	1
BDA 1 : 2	2	7	21	37	20	9	4
HMDA 1 : 0.5	13	52	18	16	0	0	1
HMDA 1 : 1	4	6	33	25	15	4	3
HMDA 1 : 2	4	6	20	35	16	13	8

and the urethane peak at 1733 cm^{-1} was the strongest. The peak at 3299 cm^{-1}, assigned to the amine N—H stretching band, became as strong as and merged with the peak at 3440 cm^{-1} from the hydroxyl group. At 1 : 2 carbonate/amine ratio the amide peak at 1639 cm^{-1} was much stronger than the urethane peak at 1733 cm^{-1} and the carbonate carbonyl peak was not noticeable. Similar FTIR spectra of the gel component after extraction were obtained, Figure 8. The amide absorption band at 1639 cm^{-1} increased with decreasing carbonate to amine ratios from 1 : 0.5 to 1 : 2.

GPC traces of the sol fractions, shown in Figure 9, display the presence of a number of species such as oligomers (OLI) with the retention time (RT) 29–32.5 min, triglycerides (TRIG) displaying a peak with RT between 32.5 and 33.5 min, diglycerides (DG) between 33.5 and 35 min, monoglycerides (MG) from 35 to 37 min with the shoulder of fatty acid amides (fatty amid), free glycerin at 39.5 min and free diamines at 42.5 min. Their contents are given in Table I. With a decreasing carbonate-to-amine ratio, the triglyceride content in the sol fraction decreased, and the products of the ester group

decomposition (DG, MG, fatty amide, glycerin) increased from around 30 to about 80%.

The functional group ratio

The content of different functional groups in polyurethanes prepared at different amine to carbonate ratios for the system of CSBO/BDA was assessed from their FTIR spectra and displayed in Figure 10. The absorbance was measured from the peak height at 1803 cm^{-1} for carbonate, 1741 cm^{-1} for ester, 1700–1733 cm^{-1} for urethane and 1639 cm^{-1} for amide and compared with the absorbance of the internal reference at 2928 cm^{-1} for C—H stretching. The initial numbers of ester and carbonate groups were taken from the starting CSBO. This CSBO had three ester and four carbonate groups per one triglyceride molecule or 100% for each of these two groups and the initial urethane and amide content was 0%. At different amine to carbonate ratios the relative ratio of ester and carbonate groups to the reference at 2928 cm^{-1} varied since ester groups were consumed for the amide and the carbonate groups were used for the urethane formation. At any amine-to-carbonate ratio, ester and amide combined will give 100%

Figure 9 GPC of the sol fraction obtained from the BDA-based samples.
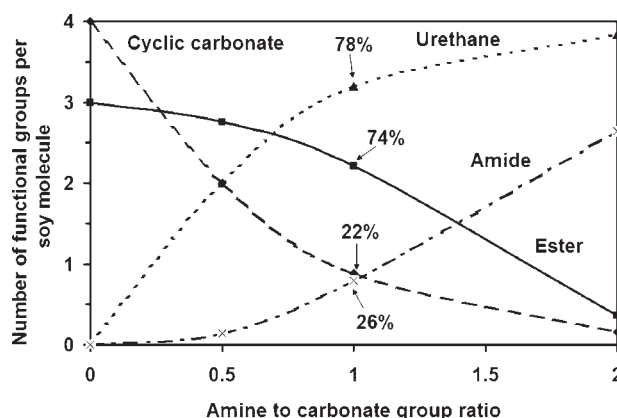
Figure 10 Effect of amine-to-carbonate ratio on the content of functional groups in the CSBO/BDA based polyurethane samples.

TABLE II
Glass Transition and Mechanical Properties of PU Samples

Sample	Carbonate to amine ratio	T_g (DSC) °C	T_g (DMA) °C	Hardness, shore A	Tensile strength (MPa)	Elongation at break (%)
EDA-1 : 0.5	1 : 0.5	7.8	15.6	41 (2.08)	0.49 (0.04)	72 (6.5)
EDA-1 : 1	1 : 1	22.0	38.0	83 (2.52)	5.77 (0.41)	90 (6.2)
EDA-1 : 2	1 : 2	18.2	22.4	50 (1.53)	1.75 (0.07)	198 (5.8)
BDA-1 : 0.5	1 : 0.5	2.3	15.2	40 (1.15)	0.84 (0.03)	87 (1.2)
BDA-1 : 1	1 : 1	19.3	40.1	59 (3.06)	4.71 (0.37)	131 (3.3)
BDA-1 : 2	1 : 2	16.7	40.0	47 (3.51)	3.28 (0.17)	219 (0.5)
HMDA-1 : 0.5	1 : 0.5	4.8	8.5	37 (2.00)	0.74 (0.06)	71 (5.5)
HMDA-1 : 1	1 : 1	22.5	35.3	47 (2.31)	3.80 (0.31)	189 (6.6)
HMDA-1 : 2	1 : 2	15.5	32.5	36 (1.00)	2.67 (0.14)	207 (3.3)

Numerical values in the brackets are standard deviations (S.D.).

and carbonate and urethane jointly will give 100%. None of the groups was present at the maximal, theoretical level. At amine/carbonate ratio 1 : 1, the urethane level reached 78% of the theoretical value, the ester group content decreased to 74% of the starting level because of the reaction with amine, and amide was formed at 26% of the possible concentration and residual, nonreacted carbonate was 22%. At the ratio 2, the residual cyclic carbonate was still present as a barely noticeable peak, but amide groups were present at about the same concentration as urethane groups. Amide formation resulted from the soy triglyceride cleavage, changing the structure of the crosslinked product and affecting its properties. These findings were contrary to the findings of other researchers[22] who found that the amine did not react with the ester and that no amides were formed. However, these authors did not use the same procedure for the preparation of polyurethane samples for FTIR and mechanical testing. Samples that they tested by FTIR were prepared at room temperature by reacting *n*-butylamine with CSBO dissolved in THF, unlike the samples in this study that were prepared in bulk and cured in the mold at 70°C and subsequently at 100°C. Endo and coworkers[17,23,24] came to the conclusion similar to Wilkes, based on the FTIR analysis of the samples prepared at room temperature in solution.

Physical and mechanical properties

Glass transition temperatures measured on our samples by DSC and DMA (Table II) were the highest for the samples with 1 : 1 carbonate to amine ratio, somewhat lower for the 1 : 2 ratio and much lower for the 1 : 0.5 ratio. At the carbonate-to-amine ratio 1 : 0.5, the network was insufficiently cured as observed from the highest sol fraction, resulting in lower crosslinking density and residual cyclic carbonates that acted as plasticizers. At the carbonate-to-

amine ratio 1 : 2, the excess amine reacted with ester groups to form amides. The fact that at lower carbonate to amine ratios amide groups are present in larger concentration and the sol fraction is the lowest, indicates that amidation of the triglyceride based network by difunctional amines produces a network of lower crosslinking density. This resulted in somewhat lower glass transition temperatures, hardness, and tensile strengths than in the polyurethanes with 1 : 1 carbonate-to-amine ratio, but the highest elongation, as shown in Table II. The EDA samples had the highest hardness and strengths as a result of higher crosslinking density and density of hydrogen bonds between polar groups than in the samples cured with BDA and HMDA. The highest elongation for HMDA and the lowest for EDA-based samples at the stoichiometric carbonate/amine ratio are the result of lower crosslinking density of the networks with longer diamines.

Swelling in water

The presence of hydroxyl groups made these polyurethanes susceptible to water absorption. Swelling in
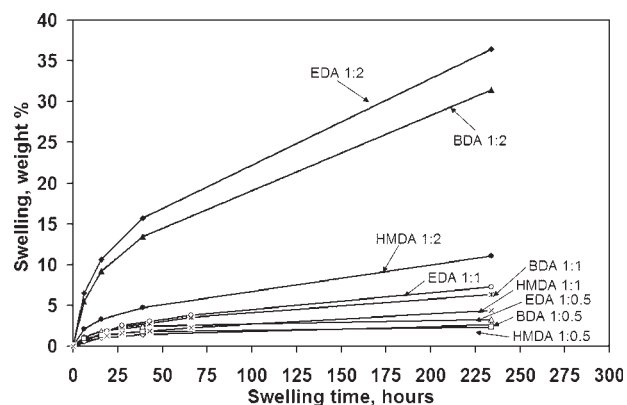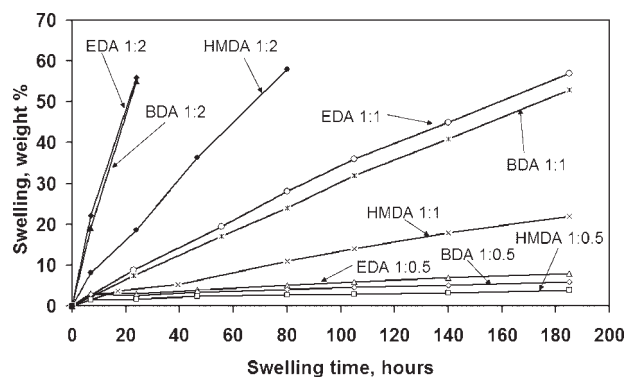
Figure 11 Effect of the swelling time on the degree of swelling in water at room temperature.

Figure 12 Effect of the swelling time on the degree of swelling in water at 70°C.

water had not reached equilibrium for the testing period both at room temperature and at 70°C as shown in Figures 11 and 12. Once the degree of swelling was over 50%, the samples became sticky and precise weight measurement was impossible. The samples based on carbonate-to-amine ratio 1 : 2 displayed the highest swelling in water, while samples at 1 : 1 ratio had lower swelling with the lowest swelling observed with the sample ratio of 1 : 0.5. Lower carbonate-to-amine ratios give better conversion of carbonate to polar urethanes and hydroxyls. Also, excess of amines results in some polyurethane chains being terminated with amine groups. Additionally, cleavage of triglycerides and possible amides with free terminal amine groups decreases crosslinking density and increases polarity of the material, causing a higher water uptake. Diamine molecular weights had an opposing effect on swelling in water as compared to the toluene results. EDA and BDA samples swelled in water much more than HMDA based ones. Shorter diamines produced polyurethanes with higher urethane and hydroxyl concentration contributing to the higher polarity of the networks and higher swelling in water. Water absorption makes these polymers unique among polyurethanes. Hydrophilic properties of isocyanate-based polyurethanes are usually adjusted by using hydrophilic polyols (usually ethylene oxide based ones) or specific isocyanates. The polyurethanes obtained by the nonisocyanate route based on very nonpolar vegetable oil can be easily made hydrophilic by selecting the type of amine and carbonate to amine ratio. Their potential application is in different water gels and in water containing materials.

CONCLUSIONS

- Amidation and ester group cleavage was always present and amides, along with urethanes and esters are always present at all amine to carbon-

ate ratios used. The urethane formation temperatures of 70–100°C promoted reactions between amine and ester groups.
- Reaction of ESBO with carbon dioxide under optimized conditions resulted in a high conversion and a low level of residual epoxy in CSBO. Polyurethanes with this CSBO reached tensile strengths close to 6 MPa.
- The stoichiometric carbonate-to-amine ratio produced the polymer networks of the highest density and the highest glass transition temperatures, hardness, and tensile strengths. Nonstoichiometric carbonate-to-amine ratios resulted in lower properties, except for elongation at break that was the highest for the samples prepared with an excess of diamines.
- Molecular weight of diamines affected properties in different ways. T_g variations in samples with three diamines were not large, but hardness and tensile strength were the highest for those with ethylene diamine and lowest for hexamethylene diamine due to differences in crosslinking density and hydrogen bonding.
- Swelling in toluene was higher at the higher carbonate-to-amine ratios due to lower polarity of the polyurethane matrix. The opposite relationship with higher carbonate-to-amine ratios having lower swelling was observed in water swelling data.
- These results indicate that when making polyurethanes using carbonated soybean oils and various diamines it is possible to produce a wide range of polyurethane products with varying mechanical, physical, and swelling properties useful for industrial applications. These results support the further explorations of safer and more environmentally friendly methods of producing polyurethanes.

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