

Polyurethanes from Soybean Oil, Aromatic, and Cycloaliphatic Diamines by Nonisocyanate Route

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ABSTRACT: Polyurethanes were prepared via a nonisocyanate route, by reacting carbonated soybean oil (CSBO) with aromatic and cycloaliphatic diamines. Nonisocyanate polyurethanes prepared from CSBO and aliphatic diamines have relatively low tensile strength and one of the possible ways to increase strength and rigidity is to use diamines with rigid aromatic or cyclic structure. The effect of amine structure and amine to carbonate ratio on polyurethane structure and mechanical, physical, and swelling properties was studied. *m*-xylylene diamine (*m*-XDA), *p*-xylylene diamine (*p*-XDA), and isophorone diamine were used as the reactants, with amine to carbonate ratios of 0.5 : 1, 1 : 1, and 1 : 2. All amines produced elastomeric polyurethanes with glass transitions between -6°C and 26°C , as measured by differential scanning calorimeter (DSC). T_g was primarily controlled by the amine-to-cyclic carbonate ratio, and to a lesser extent by the amine structure. The highest tensile strength was obtained for *p*-XDA and the lowest for *m*-XDA as a result of differences in hydrogen bonding. Tensile strength and hardness were higher than in aliphatic diamine-based polyurethanes. Swelling in toluene and water depended on the polarity of polyurethane networks that was dominantly controlled by the amine-to-cyclic carbonate ratio. Swelling in toluene was higher at the lower amine to carbonate ratio due to lower polarity of the polyurethane matrix. Swelling in water behaved quite the opposite, the degree of swelling for the more polar polyurethane matrix was higher. Reaction temperatures of $70\text{--}100^{\circ}\text{C}$ were high enough to promote ester group cleavage and along with urethanes, amide formation was always present. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: soy oil; non-isocyanate; polyurethane; diamine; aromatic

Received 3 January 2012; accepted 14 June 2012; published online

DOI: 10.1002/app.38215

INTRODUCTION

Nonisocyanate polyurethanes are new class of polymeric materials that can be prepared without toxic isocyanates, which are raw materials for standard polyurethanes. One of the possible synthetic methods is to use reaction of cyclic polycarbonates with amines.^{1–8} Soybean oil (SBO) is a viable renewable source that can be used for preparation of nonisocyanate polyurethanes by this route. Epoxidized SBO (ESBO) which is a commercial product, is used as a starting chemical that reacts with carbon dioxide in the presence of a catalyst to produce carbonated SBO (CSBO).^{9–13} The benefit of this technology is the utilization of carbon dioxide, an inexpensive and environmentally friendly monomer and circumventing the use of toxic isocyanates. Using CO_2 as a C1 feedstock is a direct route to its recycling and the reduction of carbon dioxide in atmosphere.

The reaction of a cyclic carbonate with an amine produces urethane and the hydroxyl group. Because of the presence of hydroxyls, these polyurethanes absorb water much more than isocyanate-based polyurethanes and may have applications where

water absorption and retention are desirable. The polyurethanes obtained from very hydrophobic vegetable oil by the nonisocyanate route can be easily made hydrophilic by selecting the amine type and amine to carbonate ratio. Water absorption makes these polymers unique among polyurethanes and their potential application is in different water gels and as water-borne materials. Hydrophilic properties of isocyanate-based polyurethanes are usually adjusted by using hydrophilic polyols (such as ethylene oxide based ones) or specific isocyanates. Nonisocyanate polyurethanes have better thermal stability than regular polyurethanes due to lack of thermally unstable biurets and allophanates.¹⁴

Nonisocyanate polyurethanes prepared from CSBO and aliphatic diamines had relatively low tensile strength in the range 0.5–6 MPa.^{15,16} One of the possible ways to increase strength and rigidity is to use diamines with rigid aromatic or cyclic structure. The objective of this work was to study the effect of aromatic and cycloaliphatic diamines on properties of SBO-based nonisocyanate polyurethanes. The formation of polyurethanes from the CSBO and diamines is illustrated in Figure 1.

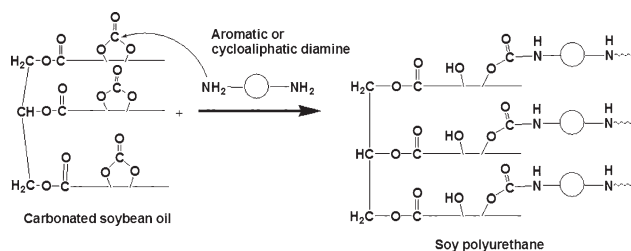


Figure 1. Poly(hydroxy urethane) formation from CSBO and diamines.

EXPERIMENTAL WORK

Materials

ESBO “Epoxol 7-4” with epoxy oxygen content (EOC) 7.1% was purchased from American Chemical Service, Griffith, IN. Tetrabutylammonium bromide (TBAB) was supplied by Fisher Scientific, Waltham, MA and *m*-xylylene diamine (*m*-XDA), *p*-xylylene diamine (*p*-XDA), and isophorone diamine (IPDA) were purchased from Aldrich, St. Louis, MO. Carbon dioxide was supplied by Airgas, Radnor, PA.

Synthesis

Preparation of CSBO. CSBO was prepared by reacting ESBO with carbon dioxide in presence of TBAB catalyst.¹⁶ ESBO (200 g) and the 0.025 mol TBAB catalyst per mol of epoxy groups were placed in a 500 mL reactor under 5.65 MPa (820 psi) pressure of carbon dioxide. The reaction was carried out for 22 h at 140°C with strong stirring. Conversion of epoxy groups to cyclic carbonate groups was 98% and residual EOC was low (0.15%). CSBO had four cyclic carbonate groups per soy oil molecule and a viscosity of 41.9 Pa s. The characteristic shift at ¹H nuclear magnetic resonance (NMR) spectra for cyclocarbonate protons was $\delta = 4.274$ and 4.477 ppm, Figure 2. The ratio of the cyclocarbonate proton peak area to the total number of proton peak area corresponded to the presence of four carbonate groups in CSBO molecule. FTIR spectra, Figure 3, showed that carbonate carbonyl absorption in CSBO at 1802 cm⁻¹ was stronger than ester carbonyl peak 1741 cm⁻¹ giving additional proof of the calculated cyclocarbonate content, (four groups per molecule), from epoxy group conversion.

Polyurethane Preparation. CSBO (25 g) was placed in a 100 mL Erlenmeyer flask with the amine and mixed thoroughly. The

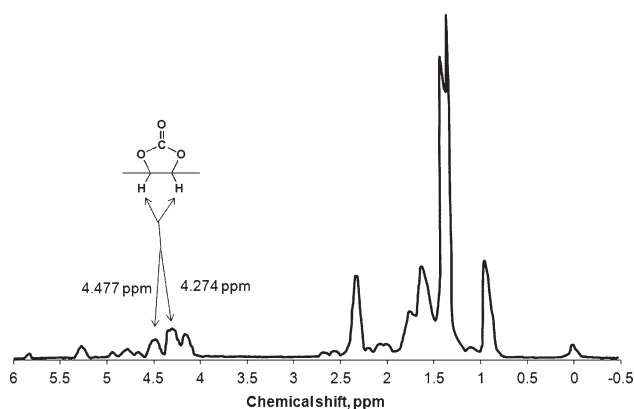


Figure 2. ¹H NMR of CSBO.

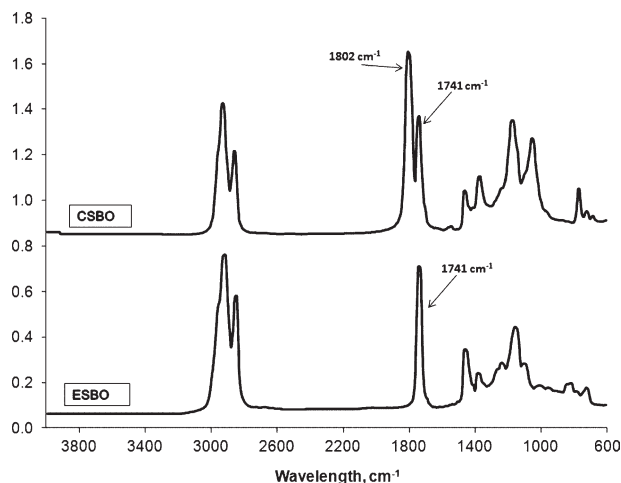


Figure 3. FTIR spectra of ESBO and CSBO.

viscous solution was poured into a mold and heated at 70°C for 6 h, and then for 15 h at 100°C.

Test Methods

Density was measured by immersion in water according to ASTM 792. A DSC model Q100 and dynamic mechanical analyzer (DMA), model DMA 2980 from TA Instruments, New Castle, DE, were used for thermal analysis of monomers and polymers. Measurements were performed in nitrogen atmosphere at a heating rate of 10°C/min. Tensile properties were measured on Qtest-2 Tensile Tester from MTS, Eden Prairie, MN, according to ASTM D882-97. FTIR spectra were recorded on a Perkin-Elmer FTIR spectrometer Spectrum 1000, Waltham, MA. The spectra were recorded by ATR (Attenuated Total Reflectance) technique from the solid plaques or by the smearing sol or gel samples on the NaCl-windows. Molecular weight distribution of the sol fraction was determined using gel permeation chromatography (GPC) (Waters Corporation, Milford, MA) consisting of a 510 pump, 410 differential refractometer, and data collection system. Tetrahydrofuran was used as the eluent at 1.00 mL/min at 30°C. Four Phenogel 5 μ m columns (50, 100, 1000, and 10,000 Å pore size) and a Phenogel guard column from Phenomenex (Torrance, CA), covering a MW range of 10² to 10⁶ were used. Swelling tests in toluene and water were carried out at room temperature at a solvent to sample weight ratio of 50 : 1. ¹H NMR spectra were recorded by Bruker 300 apparatus, Billerica, MA, at 300 MHz and CDCl₃ as a solvent.

RESULTS AND DISCUSSION

FTIR Spectra

FTIR spectra of *m*-XDA-based polyurethanes are presented in Figure 4 and similar spectra were obtained from the *p*-XDA and IPDA samples. The O—H and N—H absorption bands at 3300–3440 cm⁻¹ from hydroxyl and urethane groups were present in all samples. The peak at 1802 cm⁻¹ was assigned to the unreacted cyclic carbonate carbonyl and strong peak of ester carbonyl was at 1739 cm⁻¹. The absorption band of urethane group appeared between 1700 and 1730 cm⁻¹ and the amide group resulting from the ester group aminolysis was at 1640 cm⁻¹.

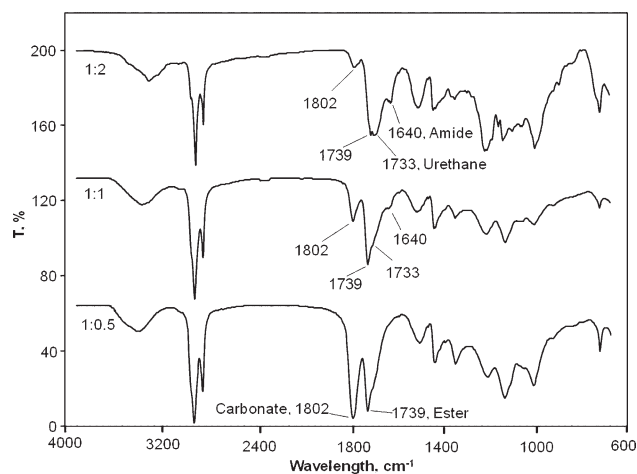


Figure 4. Effect of the carbonate-to-amine ratio on the FTIR spectra of the m-XDA-based samples.

The samples prepared with 1 : 0.5 carbonate-to-amine ratios had a significant amount of residual carbonate along with newly formed urethane. The urethane absorption band appeared as a shoulder on the ester carbonyl peak in the range of 1700–1730 cm^{-1} . The amide peak at about 1643 cm^{-1} was not noticeable, indicating that aminolysis of ester groups was not significant. The samples prepared with 1 : 1 carbonate-to-amine ratio displayed a smaller peak of the residual carbonate, a strong ester carbonyl peak with a shoulder of the urethane absorption band. The amide absorption band observed at 1643 cm^{-1} was a result of ester group aminolysis. At 1 : 2 carbonate to amine ratio aminolysis occurred to a larger extent as evidenced by the amide absorption peak. The urethane peak at 1714 cm^{-1} was the strongest as a result of urethane formation from carbonate. Carbonyl peak of the residual cyclic carbonate at 1802 cm^{-1} was small but still present suggesting that carbonate conversion to urethane was higher than at the higher carbonate to amine ratio, although not totally complete. IPDA, which has two amine groups of differing reactivity, reacted slower and residual carbonate peaks were stronger than in the case of m-XDA and p-XDA at the same ratios. Aminolysis was not present in the IPDA samples prepared at the 1 : 0.5 ratio, but at 1 : 1 and 1 : 2 ratios it was noticeable, as observed from FTIR spectra in Figure 5.

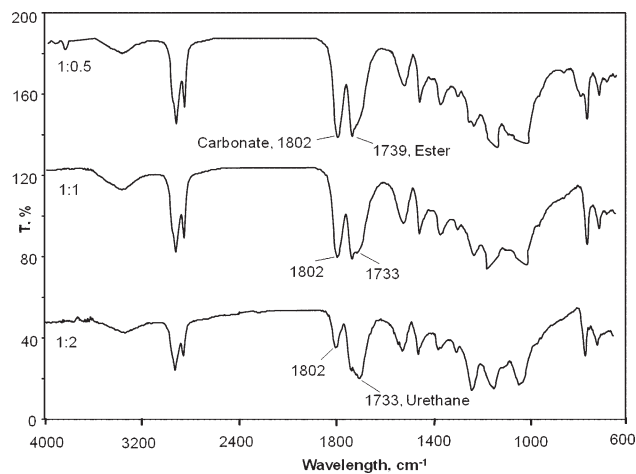


Figure 5. Effect of the amine to carbonate ratio on FTIR spectra of the IPDA-based samples.

Mechanical Properties and Glass Transition Temperature (T_g)

The samples were typically nontransparent yellow solid plaques. They displayed Shore A hardness in the range 4–98 units, tensile strength between 0.1 and 11.1 MPa, and elongation 3–433% (Table I). p-XDA and IPDA samples had much higher tensile strength than the samples based on 1,2-ethylenediamine, 1,4-butylenediamine, and 1,6-hexamethylenediamine (5.8, 4.7, and 3.8 MPa, respectively)¹⁶ at 1 : 1 carbonate to amine ratio. The higher strength of nonisocyanate polyurethanes based on aromatic and cycloaliphatic diamines than aliphatic diamines based ones can be assigned to the presence of rigid aromatic and cycloaliphatic structures that could be aligned under stress and increase intersegmental physical interactions. Mechanical properties of the polyurethanes depended on crosslinking density and hydrogen bonding between urethane, hydroxyl, and ester groups, which was controlled by the carbonate to amine ratio and the amine structure. At the carbonate to amine ratio 1 : 0.5, the crosslinking was incomplete, which was reflected in low hardness, T_g , and tensile strength and high elongation of all samples. At the carbonate to amine ratios 1 : 1, tensile strength was the highest for p-XDA samples prepared at 1 : 1 ratio, lower for IPDA, and the lowest for m-XDA. p-XDA with the linear molecular geometry produced polyurethane chains that

Table I. Glass Transition Temperature and Mechanical Properties of the PU Samples

Sample	Carbonate to amine ratio	Hardness, shore A	Tensile strength, MPa	Elongation at break, %	T_g (DSC), °C	T_g (DMA), °C
m-XDA-1 : 0.5	1 : 0.5	12	0.3	227	-5.6	18.1
m-XDA-1 : 1	1 : 1	80	5.5	154	20.7	40.7
m-XDA-1 : 2	1 : 2	75	2.3	70	18	32.5
p-XDA-1 : 0.5	1 : 0.5	18	0.5	269	-0.2	19.1
p-XDA-1 : 1	1 : 1	95	11.1	129	24.2	41.0
p-XDA-1 : 2	1 : 2	98	5.1	3	23.2	46.1
IPDA-1 : 0.5	1 : 0.5	4	0.1	433	-6.4	16.3
IPDA-1 : 1	1 : 1	98	7.1	150	26.1	44.6
IPDA-1 : 2	1 : 2	99	n/a	n/a	25.9	n/a (too brittle)

Table II. Relative Ratio of the Species in the Sol Fraction Determined by GPC

Sample	Sol fraction (%)	OLI	TRIG	DG	MG
mX-1 : 0.5	52.7	62	30	4	4
mX-1 : 1	18.6	34	29	22	15
mX-1 : 2	16.5	19	15	26	40
pX-1 : 0.5	53.1	60	32	6	2
pX-1 : 1	17.1	41	30	17	12
pX-1 : 2	15.4	10	10	27	53
IP-1 : 0.5	Dissolved completely	54	34	8	4
IP-1 : 1	36.5	50	33	14	3
IP-1 : 2	Dissolved completely	36	18	30	16

had good hydrogen bridging between urethane groups, which was reflected in higher hardness, T_g , and strength than the other samples (Table II). The m-XDA-based samples had lower hardness, T_g , and tensile strength than the p-XDA samples, probably due to the nonlinear molecular geometry with the amino groups placed at the bond angle of 120° . It made hydrogen bridging between urethane groups more difficult, decreasing the density of hydrogen bonding, which decreased the strength of the polymer. IPDA gave products of high hardness, T_g , and strength, probably due to the bulky cyclic ring that decreased segment mobility and increased rigidity and toughness of polymeric network.

Elongation at break was the highest for the samples based on carbonate to amine 1 : 0.5 ratio due to lower crosslinking density and plasticizing effect of residual CSBO. IPDA sample showed the highest elongation and this sample was completely soluble in toluene showing that polymeric network was not continuous and polymerization reached oligomeric level. The material was very soft plastic of low hardness (4 Shore A) and very low strength (0.1 MPa). Elongation at break for the samples prepared with ratio 1 : 1 was relatively similar, in the range 130–150%. The samples prepared with the ratio 1 : 2 had much lower elongation at break. Elongation at break decreased with the increased amine to carbonate ratio and the p-XDA and IPDA samples became brittle. At the increased amine to carbonate ratio, elongation is decreased due to the effect of rigid cyclic structures from amines. At excess of amine to carbonate ratio, amines react with ester groups giving amides and a free hydroxyl group. This behavior was quite opposite than elongation of aliphatic diamine-based soy nonisocyanate polyurethanes,¹⁶ which had elongation at break increased with the increased amine to carbonate ratio. Amides of fatty acids and aliphatic diamines are soft materials and acted as plasticizers for polyurethane network, which resulted in higher elongation. Fatty acid amides based on rigid aromatic or cycloaliphatic diamines are rigid structures that increased rigidity of polymeric matrix and decrease elongation at break.

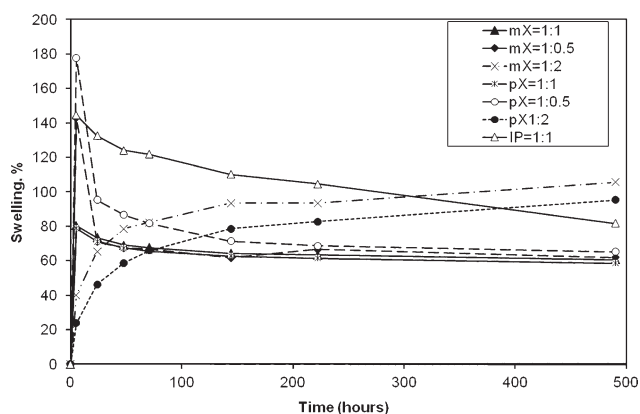
Glass transition temperature (T_g) was measured by DSC and DMA (Table II). T_g was the highest for the 1 : 1 carbonate to amine ratio, lower for the 1 : 2 ratio, and the lowest for the 1 : 0.5 ratio, irrespective of the amine type. At the ratio 1 : 0.5, the

network was insufficiently cured (proved by the highest sol fraction content) resulting in lower crosslinking density and residual cyclic carbonates that acted as plasticizers. At the ratio 1 : 2, the excess of amine reacted with ester groups forming amides. Amidation of the triglyceride (TRIG)-based network by bifunctional amines produces the network of lower crosslinking density, but presence of rigid aromatic and cycloaliphatic rings in the polymeric network increased T_g and made it close to the samples based on 1 : 1 ratio.

Swelling in Toluene

Swelling in solvents and the analysis of the extracted species gave additional information on the extent of the reactions. Swelling is affected by several parameters such as degree of crosslinking of the polymeric matrix and solubility parameters of the polymer and solvent. CSBO-based polyurethanes consisted of nonpolar hydrophobic fatty acid chains and polar urethane, ester, and hydroxyl groups. The samples with the carbonate to amine ratio 1 : 0.5 had the highest hydrophobic-to-hydrophilic ratio and a lower level of crosslinking density so they were the most susceptible to toluene penetration. They had an insufficiently-cured network, and part of the sample was dissolved, resulting in the weight loss, as shown in Figure 6. The IPDA samples at the carbonate to amine ratio 1 : 0.5 were dissolved completely, therefore, the polymeric network was not formed.

The samples at the ratio 1 : 1 had less residual carbonate and higher crosslinking density. The higher hydrophilicity along with higher crosslinking density contributed to lower sol fraction content and lower weight loss due to the partial dissolution in comparison to the samples prepared with 1 : 0.5 ratio. m-XDA- and p-XDA-based samples swelled much less than IPDA-based sample, probably due to more complete crosslinking. The m-XDA- and p-XDA-based samples with the 1 : 2 ratio were the most hydrophilic and the least sensitive to the toluene. They did not show significant partial network dissolution and the weight increase with time was continuous unlike with the IPDA sample that was dissolved completely. The amine to carbonate excess and the presence of a less reactive amine group contributed to a lower degree of crosslinking. The cyclic ring with three methyl groups made the sample more hydrophobic than the 1 :

**Figure 6.** Effect of the swelling time on the degree of swelling in toluene at room temperature.

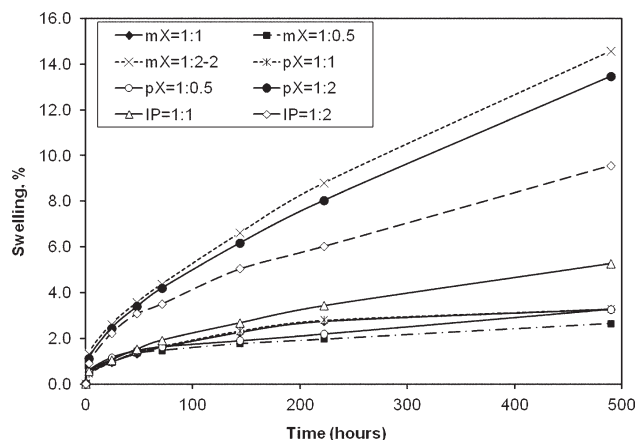


Figure 7. Effect of the swelling time on the degree of swelling in water at room temperature.

2 samples based on m-XDA and p-XDA and more soluble in toluene. The p-XDA sample swelled less than m-XDA, probably due to the better packing and stronger hydrogen bonding of the linear structure of p-XDA. Swelling in toluene was in the range of 60–110%, which was much higher than swelling of polyurethanes based on aliphatic diamines¹⁶ (10–70%), due to the higher hydrophobicity of polyurethane network and similarity of diamine structure with the structure of the solvent.

Swelling in Water

Presence of hydroxyl groups made these polyurethanes susceptible to the water absorption. Swelling in water did not reach equilibrium for the testing period of time of 500 h, Figure 7. The samples based on carbonate to amine ratio 1 : 2 displayed the highest swelling in water, ones at 1 : 1 ratio had lower swelling and the lowest was observed with the samples at the ratio 1 : 0.5. Higher amine-to-carbonate ratio gives better conversion of carbonate to polar urethanes and a free hydroxyl for every urethane linkage, also the excess of amine gave a lower degree of crosslinking and produced polyurethane chains terminated with amine groups. In addition, cleavage of TRIG and possible for-

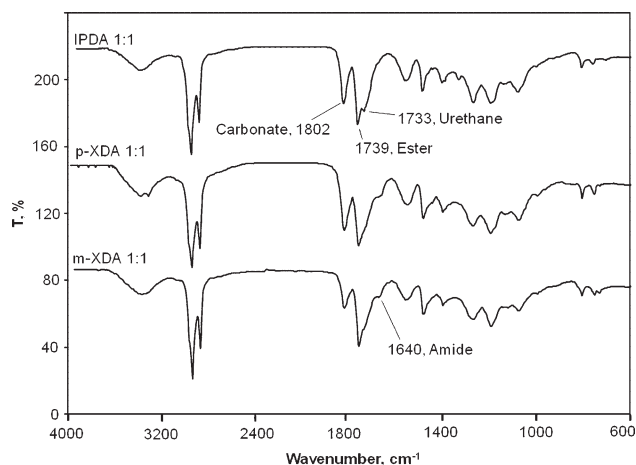


Figure 8. FTIR spectra of the sol fraction obtained from the samples prepared at the 1 : 1 carbonate to amine ratio.

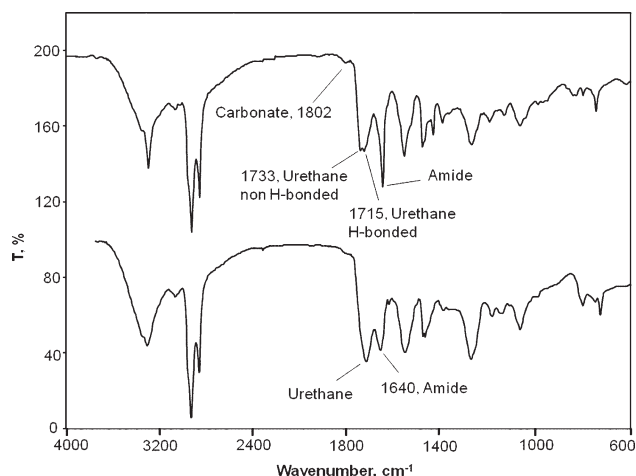


Figure 9. FTIR spectra of the sol fraction obtained from the samples prepared at the 1 : 2 carbonate to amine ratio.

mation of amide with free terminal amine groups, and glycerides with free hydroxyl groups, decreases crosslinking density and increases polarity of the polymeric matrix, enabling a higher water uptake. At the 1 : 2 ratio, the IPDA sample swelled less than m-XDA and p-XDA samples, probably because the ring substituted with three methyl groups made polyurethanes more hydrophobic than the 1 : 2 samples based on m-XDA and p-XDA. Samples based on 1 : 1 ratio m-XDA and p-XDA swelled practically identically. At the ratio 1 : 0.5, the IPDA sample after 12 h was too tacky, soft and further testing was impossible. Swelling in water was much lower (2–9% after 230 h) than swelling of polyurethanes based on aliphatic diamines,¹⁶ which was in the range 2–37% for the same period of time. Aromatic and cycloaliphatic diamines contributed to the higher hydrophobicity of the polymeric network that was less susceptible to water penetration.

Sol/Gel Analysis

The extraction of the soluble part from the samples was carried out in a Soxhlet apparatus with refluxing toluene for 6 h, followed by the GPC and FTIR analysis of the sol fraction and the FTIR analysis of the polymeric residue. The extract consisted of starting TRIG, oligomerized triglyceride (OLI), diglyceride (DG), and monoglyceride (MG), Table II. DG and MG were the products of TRIG decomposition and ester group cleavage by amines. The formed fatty acid amides and diamides were incorporated into the MG and DG fractions. The highest extractable content was around 50% for m-XDA and p-XDA samples prepared with the carbonate to amine ratio 1 : 0.5, as shown in Table II.

The samples based on IPDA were completely dissolved, and the dominant part of the sol fraction consisted of oligomers. With the amine to carbonate ratio 1 : 1, the TRIG content in the sol fraction dropped to 18.6% for m-XDA, 17.1% for p-XDA, and 36.5% for IPDA samples. A lower sol fraction was the result of a more complete reaction of carbonate groups and formation of crosslinked polyurethanes, what contributed to the higher molecular weight species formation, which could not be extracted by toluene. At the carbonate to amine ratio 1 : 2 extractable

parts for m-XDA and p-XDA was slightly decreased to 16.5 and 15.4% as result of more complete carbonate conversion to urethane. The ratio of DG and MG combined reached 66 and 80% respectively, showing that extractable parts were dominantly low-molecular weight ester group amidation products, but amidation of ester groups did not cause strong chain scission and formation of extractable parts to a larger degree than at the carbonate to amine ratio 1 : 1. The IPDA samples at the 1 : 2 ratio dissolved completely and dominant part of the dissolved sample were oligomers, resulting from the less reactive amine groups in IPDA. Sol content was about three times higher than the sol content of aliphatic amine-based urethanes¹⁶ due to the higher susceptibility to toluene penetration.

FTIR of the sol fractions showed the presence of carbonate, urethane, and ester groups with absorption bands at 1803, 1715, and 1741 cm^{-1} , respectively. The samples prepared at 1 : 1 ratio are presented in Figure 8. The peak at 3444 cm^{-1} showed the presence of hydroxyl groups formed simultaneously with urethane groups, and as a result of ester cleavage, producing MGs and DGs. Peak of amide at 1647 cm^{-1} was present as a small shoulder.

Table I shows that at the ratio 1 : 2, the dominant extraction part, based on the GPC traces, consisted of DG and MG. The extractable content at this carbonate to amine ratio was similar for m-XDA and p-XDA, the IPDA sample was completely dissolved. FTIR spectra of the extracts (Figure 9) showed that the amide peak in the range 1630–1650 cm^{-1} was much stronger than the similar peak for polyurethanes prepared at the carbonate to amine ratio 1 : 1, probably as result of the stronger transamidation of ester groups.

CONCLUSIONS

- Nonisocyanate polyurethanes based on aromatic and cycloaliphatic amines had higher tensile strength and elongation than similar polyurethanes based on aliphatic diamines. Structure of diamines affected properties in different ways. Tensile strength was the highest for p-XDA and lowest for m-XDA due to differences in ability of hydrogen bonding. The samples made with the carbonate to amine ratio 1 : 1 had the highest strength due to the highest crosslinking density of the polymeric network. At the lower or higher carbonate to amine ratio, strength was lower due to the lower network crosslinking density. Elongation at break was decreased with the increased amine to carbonate ratio due to increased rigidity of polymeric network caused by rigid aromatic or cycloaliphatic structures. This behavior was quite opposite than elongation of aliphatic diamines which had increase of elongation with the increased amine to carbonate ratio.
- T_g was similar for all three diamines and variations were within the range of experimental error. Glass transition temperature was the lowest for the samples prepared with the carbonate to amine ratio 1 : 0.5 due to incomplete crosslinking and higher for the 1 : 1 and 1 : 2 ratio caused by complete crosslinking and higher content of rigid aromatic or cycloaliphatic groups.
- Swelling in toluene was higher at the higher carbonate to amine ratio (1 : 0.5) due to less crosslinked and lower polarity of the polymeric matrix. Swelling in water behaved quite opposite, for more polar polyurethane matrix, the degree of swelling was higher. Swelling at the same ratio was similar for all three diamines and variations were within the range of experimental error.
- The sol fraction extracted by toluene consisted of oligomers, DGs, and monoglycrides as result of imperfectly crude polyurethane network or chain scission as result of the amine and ester group reaction.

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