

Thermoplastic polyurethanes with isosorbide chain extender

Ivan Javni,¹ Olivera Bilić,¹ Nikola Bilić,¹ Zoran S. Petrović,¹ Eric A. Eastwood,²
Fan Zhang,³ Jan Ilavský⁴

¹Kansas Polymer Research Center, Pittsburg State University, Pittsburg, Kansas 66762

²Honeywell FM&T, LLC, Kansas City, Missouri

³Materials Measurement Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

⁴X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439

Correspondence to: Z. Petrovic (E-mail: zpetrovic@pittstate.edu)

ABSTRACT: Isosorbide, a renewable diol derived from starch, was used alone or in combination with butane diol (BD) as the chain extender in two series of thermoplastic polyurethanes (TPU) with 50 and 70% polytetramethylene ether glycol (PTMEG) soft segment concentration (SSC), respectively. In the synthesized TPUs, the hard segment composition was systematically varied in both series following BD/isosorbide molar ratios of 100:0; 75:25; 50:50; 25:75, and 0:100 to examine in detail the effect of chain extenders on properties of segmented polyurethane elastomers with different morphologies. We found that polyurethanes with 50% SSC were hard elastomers with Shore D hardness of around 50, which is consistent with assumed co-continuous morphology. Polymers with 70% SSC displayed lower Shore A hardness of 74–79 (Shore D around 25) as a result of globular hard domains dispersed in the soft matrix. Insertion of isosorbide increased rigidity, melting point and glass transition temperature of hard segments and tensile strength of elastomers with 50% SSC. These effects were weaker or non-existent in 70% SSC series due to the short hard segments and low content of isosorbide. We also found that the thermal stability was lowered by increasing isosorbide content in both series. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42830.

KEYWORDS: biopolymers & renewable polymers; elastomers; polyurethanes; structure-property relations

Received 19 May 2015; accepted 6 August 2015

DOI: 10.1002/app.42830

INTRODUCTION

Thermoplastic polyurethanes (TPU) are high value, linear block copolymers composed of alternating flexible soft segments and rigid hard segments.^{1–3} Rigid hard segments in TPUs usually form domain structures whose detailed morphology, size, shape, and concentration are closely correlated with their properties. In this phase-separation process, the miscibility between the hard and soft phases is important. Good phase separation is critical for the formation of two-phase structures but some degree of miscibility may improve interphase bonding and thus certain mechanical properties. In commercial TPUs, hard segments are usually formed by diphenylmethane diisocyanate (MDI) and butane diol (BD) because of their excellent material properties and favorable economics.

Recent developments of bio-based renewable materials have opened up new opportunities for improved, sustainable and environmentally friendly polymers. Isosorbide (ISO), a bicyclic diol, is such type of renewable material that can be synthesized from starch in a simple 3-step process. In the first step, glucose is pro-

duced in large quantities by hydrolysis of starch. Hydrogenation of glucose produces sorbitol, which in turn could be synthesized into isosorbide by double dehydration. Isosorbide is a rigid molecule with a high degree of thermal stability, atypical for sugar derived products. It is also biodegradable, non-toxic, non-mutagenic and soluble in water. As a renewable biomaterial, it has been used in epoxy and polycarbonates as replacement for bisphenol A, and in polyesters in place of ethylene glycol to increase glass transition.^{4,5} As shown in Figure 1, Isosorbide has two secondary hydroxyls, one of which is reactive (exo) and the other, internal and hydrogen bonded (endo-OH), is less based on steric consideration. This was proven in esterification reactions.^{4,6} However, endo OH groups were more reactive in phosgenation reactions catalyzed with pyridine⁷ and tosylation reaction.⁸ Reactivity of exo and endo hydroxyls with *p*-tolyl isocyanates in presence of a tin catalyst was found to be comparable.⁹ Our study of the kinetics of the reaction of isosorbide and phenyl isocyanate without catalyst demonstrated clear difference in reactivity of two groups, which was also higher than that with isomannide characterized by only endo hydroxyls.¹⁰

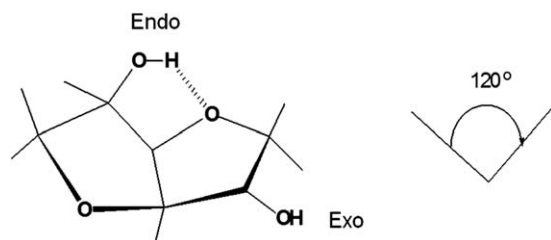


Figure 1. Structure of isosorbide.

Isosorbide, being a diol, invites significant research on synthesis of new bio-based polymers, including polyurethanes, for different applications. An excellent review of the applications of isosorbide and its isomers, isomannide and isoidide, in the synthesis of different polymers including polyurethanes was published relatively recently.¹¹ Such applications include those associated with biodegradable scaffolds and tissue engineering,^{12–14} as well as biocompatible polyurethanes.^{15,16} For example, polyurethanes synthesized from isosorbide and polyisocyanates that possess suitable physical properties for films, coating, molded articles and foams were revealed in a patent.¹⁷ A non-isocyanate route to polyurethanes using dicyclocarbonates from isosorbide and amines was also studied.¹⁸ A comparative study of polyurethanes from isosorbide and butane diol with two isocyanates showed that the presence of isosorbide increased glass transition temperature (T_g) and melting point (T_m), but was also responsible for an increased hydrolysis rate.¹⁹ In a related study, segmented polyurethanes were prepared from isosorbide or butane diol with MDI or hexamethylene diisocyanate (HDI) with polycaprolactone soft segments and their effect on polymerization rate and hydrolysis were analyzed.²⁰

Extensive studies on the synthesis of isosorbide-MDI hard segment and structure–property relationships in segmented polyurethanes based on isosorbide, MDI and polytetramethylene glycols (PTMEG) of different molecular weights were carried out by Cognet-Georjon et al.^{9,21} They varied molecular weights of PTMEG from 650 to 1000 and 2000 to make elastomers with hard segment concentration (HSC) of 35; 51 and 61 wt %. The synthesis in solution gave polymers with crystalline hard segments while polymers made in bulk had predominantly amorphous hard phase. As expected, phase separation was favored by longer soft segments.

In this study, we used MDI, butane diol and/or isosorbide and PTMEG of molecular weight 1400 to avoid crystallization of soft segments and systematically examined the effect of the structure and concentration of hard segments on the properties of TPUs. We prepared two series of polyurethanes having 50% and 70% SSC with varying molar ratio of BD/isosorbide in the hard segment in these steps: 100:0; 75:25; 50:50; 25:75, and 0:100, as illustrated in Figure 2. Thus, polyurethanes with 75:25, 50:50, and 25:75 BD/isosorbide ratios had mixed hard segment containing both chain extenders whereas the other two were made with a single chain extender.

MDI/BD and MDI/ISO hard segments of sufficient length have a tendency to crystallize, which yield blocks with melting points

that depend on their molecular weight. The morphology is also affected by the preparation protocol and was presented in a separate article.²² Standard polyurethane elastomers are prepared either by a prepolymer or a one-shot method. We used the prepolymer method in this work.

EXPERIMENTAL

Materials

Terathane 1400, obtained from Invista (Wilmington DE) is PTMEG of nominal molecular weight 1400 and hydroxyl number of 80.2 mg KOH/g. Rubinate 44 MDI, having isocyanate (NCO) content 33.5%, was kindly supplied by Huntsman. 1,4-Butanediol, 99%, and isosorbide (assay >98%) were purchased from Aldrich. While butane diol was distilled before use, isosorbide was used as delivered after drying.

Synthesis of Polyurethanes

One of the issues in synthesizing polyurethanes with isosorbide is low reactivity of secondary and particularly endo hydroxyl groups, which requires longer reaction times. The synthesis of polyurethanes was carried out in bulk by a two-step, prepolymer method. This method consisted of reacting PTMEG with excess MDI to obtain a quasi-prepolymer, which was then reacted with the chain extender in the second step to give the final product. In the case of mixed chain extenders, due to the low reactivity of the secondary isosorbide OH-groups, isosorbide was reacted first with the prepolymer for 2 h at 75°C and 1,4-BD was added later. This may lead to blocks of isosorbide/MDI units followed by blocks of BD/MDI units, but due to relatively low molecular weights of hard segments there were only few repeating units in the hard segments so the “blockiness” was not considered consequential.

Special measures were taken to prevent moisture contact with the reactants. Terathane 1400 was dried at 90°C at ≈ 133 Pa (1 mm Hg vacuum) for 2 h. MDI was distilled at 170°C under reduced pressure of ≈ 133 Pa, while 1,4-BD was distilled at atmospheric pressure. Isosorbide was dried at 120°C and reduced pressure of ≈ 133 Pa. Excess of isocyanate over the calculated requirement was 3%. Because of the difference in molecular weights of isosorbide and butane diol, in attempting to keep the molar ratio fixed, soft segment concentration departed slightly from the intended. The preparation procedure was as follows:

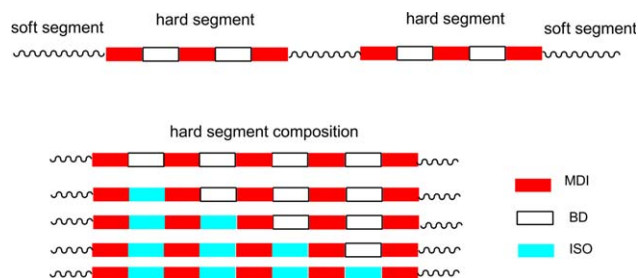


Figure 2. Schematic representation of segmented polyurethanes and the structure of hard segments with varying MDI/BD/Isosorbide composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

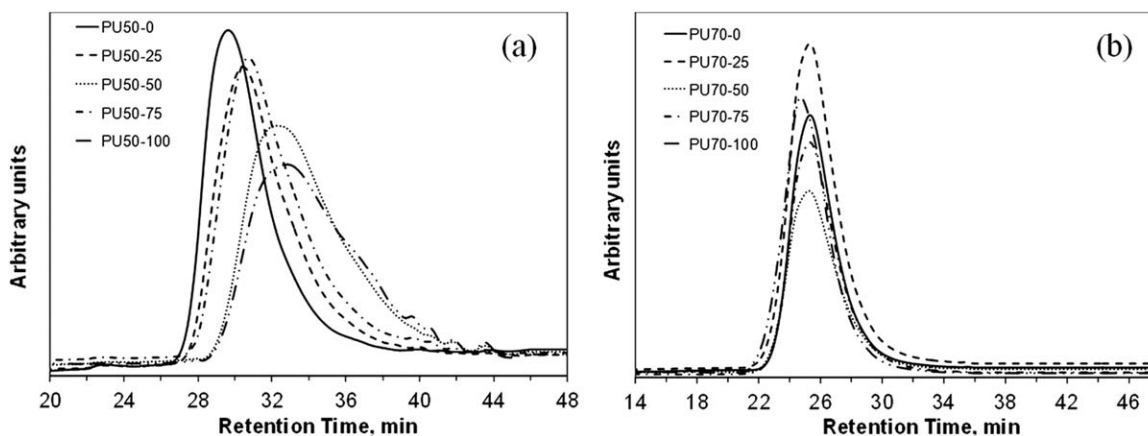


Figure 3. GPC curves of polyurethanes in DMF with 50% SSC (a) and 70% SSC run in THF (b). Sample identification is shown in Table I.

MDI was charged into a 125 ml Erlenmeyer flask, heated at 50–60°C and kept under low vacuum (~50 mm Hg) for several minutes. The polyol was added with strong stirring and heating. The reaction continued at ~75°C for 1 h. Isosorbide was then added and the reaction continued for 2 h. During this step, initially the reaction mixture exhibited low viscosity and was cloudy. We attribute this phenomenon to the fact that only one (exo) OH-group from isosorbide reacted immediately whereas the second (endo) OH group reacted later. After 2 h the reaction mixture became clear and more viscous. Additional reaction time did not change viscosity and we assumed that both OH-groups from isosorbide had been consumed. Butane diol was then added and the mixture was stirred for about 2 min and transferred into the mold, which was preheated to 120°C. The sample was cured overnight (16 h) at 120°C, cooled to room temperature and stored for a week in plastic bags before testing.

Polyurethanes in both series are soluble in dimethylformamide (DMF) and insoluble, but swell in acetone, toluene, ethyl acetate, chloroform, and dimethyl sulfoxide (DMSO). The series with 70% SSC was also soluble in tetrahydrofuran (THF).

Characterization

Size exclusion chromatography (SEC) was run on a Waters Model 2695 Separations Module with column oven option and Model 2414 RI Detector, using a set of four columns and DMF as the carrier solvent at 40°C. Polystyrene standards were used for calibration. The samples of the 70% SSC series in film form had difficulty to dissolve in DMF. After heating at the boiling point, the solutions eventually became clear. Molecular weights determined by SEC in DMF were in the million range and we assumed that some gel particles were present. Since polyurethanes with 70% SSC were soluble in THF, SEC on these samples after filtration was conducted with this solvent.

Tensile properties were measured on a Qtest-2 Tensile Tester from MTS, following protocols established by ASTM D882-97. DSC measurements were performed with differential scanning calorimeter model Q100, from TA Instruments (New Castle, DE, USA) in nitrogen atmosphere (50 mL/min. purge flow) at a heating rate of 10°C/min from –80°C to 200°C. Thermogravimetric analyzer (TGA) model Q50 (TA Instruments, New Castle, DE) was used for examining thermal stability. All TGA experiments were carried out under nitrogen (60 mL/min) with the heating rate of 10°C/min from room temperature to 600°C. Dynamic

Table I. Molecular Weights of Polyurethanes with 50% and 70% SSC and Different Ratios of Butane Diol/Isosorbide in the Hard Segment

Sample ID	BD/Isosorbide	M_n	M_w	D
50% SSC series				
PU50-0	100/0	57,240	108,080	1.89
PU50-25	75/25	40,130	78,370	1.95
PU50-50	50/50	21,800	36,030	1.69
PU50-75	25/75	34,220	65,370	1.91
PU50-100	0/100	19,320	33,750	1.75
70% SSC series				
PU70-0	100/0	22,480	36,711	1.63
PU70-25	75/25	19,280	36,000	1.87
PU70-50	50/50	20,960	36,050	1.72
PU70-75	25/75	21,900	36,160	1.65
PU70-100	0/100	25,880	40,230	1.55

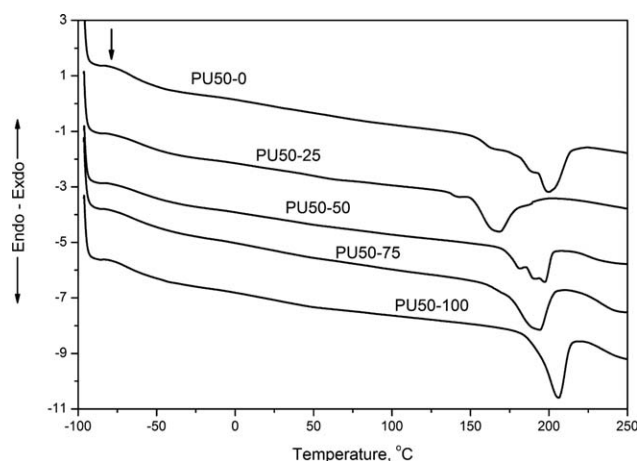


Figure 4. DSC curves for 50% SSC polyurethanes.

Mechanical Analysis (DMA) measurements were conducted using DMA 2980 from TA instruments (New Castle, DE) with a heating rate of 3°C/min from -80°C to 200°C at 10 Hz.

RESULTS AND DISCUSSION

Figure 3 illustrates the molecular weight distribution in the series with (a) 50% and (b) 70% SSC obtained by SEC. Sample ID consists of two numbers indicating SSC and mol % of isosorbide in BD/isosorbide mixture, respectively. Figure 3(a) shows that molecular weights generally decrease with increasing isosorbide content, except for the sample with 75% isosorbide. The lowest molecular weights were with pure isosorbide in the hard segment. Lower molecular weights are likely caused by incomplete reaction as a result of the endo-OH group's low reactivity. Polyurethanes in 70% SSC series had comparable molecular weights of around $M_w \sim 40,000$, as presented in Table I. The calculated polydispersity index (D) was close to 2 in all polymers. Generally, the observed molecular weights are sufficiently high so as not to influence material properties to a large degree.

Thermal Properties of Polyurethanes

Figure 4 shows the DSC curves of samples with 50% SSC. We found a melting peak, T_m , of the hard segment in all samples

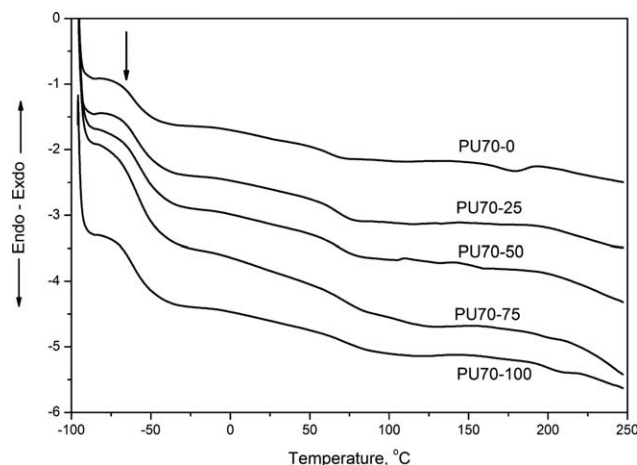


Figure 5. DSC curves for 70% SSC polyurethanes.

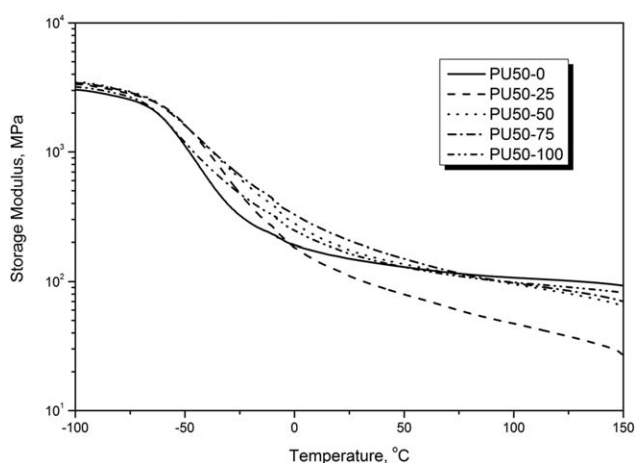


Figure 6. Storage modulus of polyurethanes with 50% SSC.

and the melting temperatures varied with the amount of isosorbide. The highest melting points were observed in TPU with pure isosorbide (at 206°C) and TPU with pure BD (at 201°C). The DSC curve of TPU with pure BD shows multiple and broad peaks, whereas the DSC curve of TPU with pure isosorbide shows a single, narrow peak. TPU with 75/25 BD/isosorbide has the lowest T_m at 168°C . Samples with 50/50 and 25/75 ratios also displayed multiple melting peaks with the highest melting temperature in the 195°C range. This fact indicates that isosorbide forms a very regular, rigid structure with MDI in spite of the bent rings of the former. Melting enthalpies of the hard segments decreased from 27.7 J/g for the BD/MDI hard segments to 16.9 J/g for the isosorbide/MDI hard segments as a consequence of lower crystallinity in the latter. Although the melting enthalpies of 100% crystalline isosorbide/MDI are unknown, considerably smaller enthalpy for the strained crystalline isosorbide/MDI hard segment is consistent with lower crystallinity obtained from x-ray diffraction experiments published separately.²²

MDI/isosorbide polymer of high molecular weight had a melting point at 236°C and T_g at 196°C . In comparison, Cognet-Georjon *et al.*⁹ found the melting point of model MDI/isosorbide hard segments at 236°C and T_g at $\sim 190^{\circ}\text{C}$. Hard segment

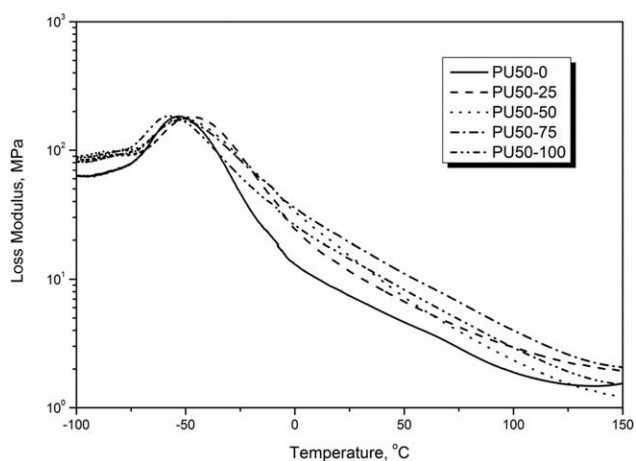


Figure 7. Loss modulus of polyurethanes with 50% SSC.

Table II. Transitions in 50% SSC and 70% SSC Series Measured by DSC and DMA

Sample ID	DSC T_g (°C)	T_m (°C)	Melting enthalpy, (J/g)	DMA ^a T_g (°C)	Sample ID	DSC T_{gSS} (°C)	DSC T_{gHS} (°C)	DMA ^a T_{gSS} (°C)
PU50-0	-62	201	27.7	-53	PU70-0	-59	63	-49
PU50-25	-62	168	20.4	-47	PU70-25	-57	68	-47
PU50-50	-59	197	14.0	-52	PU70-50	-56	69	-47
PU50-75	-64	194	16.5	-53	PU70-75	-57	72	-49
PU50-100	-64	206	16.9	-57	PU70-100	-59	73	-49

^aData acquired at 10 Hz.

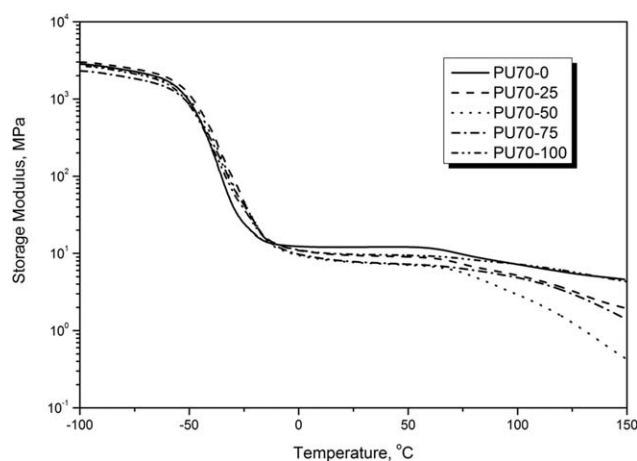
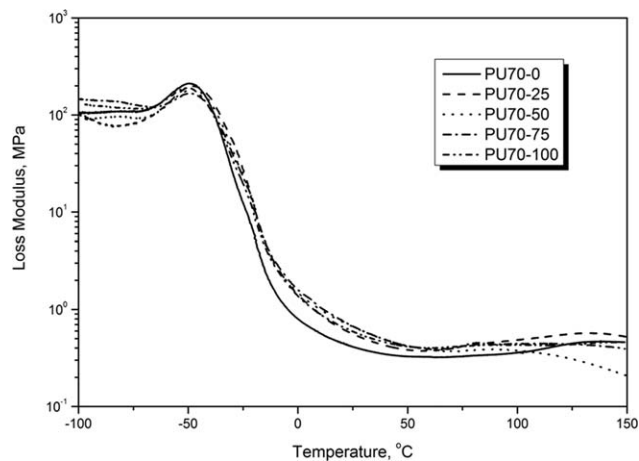
T_g in our samples with 50% SSC was not readily observable. Soft segment T_g was below -60°C and slightly decreased with increasing isororbide content, except for 50/50 sample which had T_g at -59°C , suggesting that isororbide causes slightly greater phase separation than BD.

Weak melting peaks of hard segments in the series with 70% SSC existed only in samples with 100% BD (at $\approx 169^\circ\text{C}$, melting enthalpy = 1.4 J/g) and 100% isororbide (at $\approx 200^\circ\text{C}$), as shown in Figure 5. The glass transition temperatures in samples with 70% SSC were surprisingly higher by a few degrees (around -59°C , and varied within experimental error) than their counterparts in the 50% SSC series. One reason for this observation may be the higher content of isolated MDI units in the soft segment as a result of the preparation method. Molecular weights of quasi-prepolymers at 70% SSC were higher and with more MDI units because the molar ratio of MDI and polyol was closer to stoichiometry than that in 50% SSC series. Another transition between 62°C and 73°C appeared in 70% SSC series, which increased with increasing isororbide content, and was tentatively assigned to the glass transition of the hard segment. It appears that hard segments in this series were predominantly amorphous, partly due to their low molecular weights.

Dynamic mechanical analysis reveals some features of the sample morphology as well. Polyurethanes with 50% SSC, whose co-continuous morphology was confirmed by scattering and imaging based techniques,²² display about one order of magni-

tude drop in storage modulus at the glass transition of the soft phase from ~ 3 GPa at -100°C to ~ 200 MPa at 0°C , and maintain relatively high modulus up to 150°C as shown in Figure 6. Only the sample with 25% isororbide in the hard segment showed faster loss to ~ 30 MPa at 150°C . Loss modulus curves as a function of temperature, shown in Figure 7, display a strong peak (α -transition) at about -50°C , associated with the glass transition of the soft segment and a shoulder at about -90°C , which existed only in samples with isororbide. The lowest temperature of the α -transition is found in the sample with 100% isororbide, as shown in Table II, due to a greater phase separation. Polyurethane with 100% BD had few degrees higher T_{max} , while all three polyurethanes with mixed diols in the hard segment had higher peak temperatures, indicating somewhat higher miscibility of hard and soft segments in the latter. Storage moduli of polyurethanes were consistently higher than that with pure BD up to $\sim 75^\circ\text{C}$, where T_g of the hard segment is located. The exception was the sample with PU50-25 where softening of the samples that began at lower temperature. Loss moduli of isororbide-rich samples were consistently higher, i.e., displayed higher energy dissipation.

In comparison, polyurethanes with 70% SSC exhibited a drop of storage modulus from ~ 1000 MPa to 10 MPa at the glass transition as shown in Figure 8. Rubbery modulus was stable from zero to around 60°C unlike in the 50% SSC series where a gradual decrease was caused by the softening of the continuous hard phase. Such behavior is consistent with the dispersed hard

**Figure 8.** Storage modulus by DMA for 70% SSC.**Figure 9.** Loss modulus by DMA for 70% SSC.

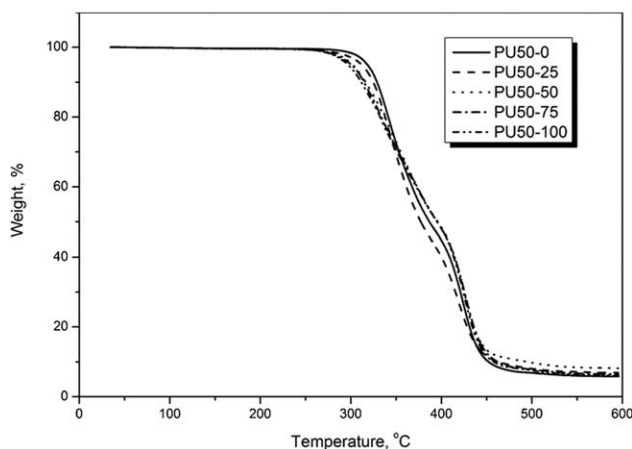


Figure 10. TGA curves of polyurethanes with 50% SSC.

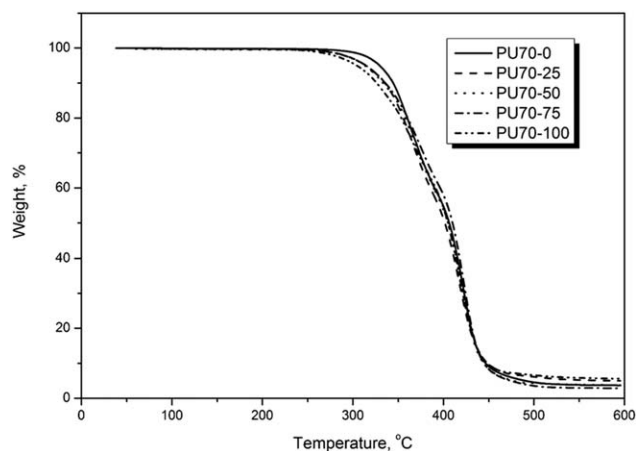


Figure 11. TGA curves of polyurethanes with 70% SSC.

phase in the soft matrix morphology, which again is confirmed in a separate morphological study.²² Loss modulus-temperature curves show the α -transition at -49°C which is not affected by the composition of the hard segment, as shown in both Figure 9 and Table II. A weak β -transition at -90°C was observed in samples with isosorbide containing hard segments.

Thermal Stability of Polyurethanes

The weakest points in the degradation of segmented polyurethanes are the urethane bonds. TGA curves of polyurethanes with 50% SSC, displayed in Figure 10, show that the TPU with BD-based hard segments has the highest onset of degradation

and the samples with the mixed BD/isosorbide hard segments the lowest onset. This tendency is even more pronounced in the 70% SSC series, Figure 11. Strained urethane bonds with secondary hydroxyls from isosorbide do not contribute to thermal stability.

Mechanical Properties

Hardness correlates with the modulus of elastomers and is determined by the content of the hard phase and its structure. Shore A and D hardness tests show that the series with 50% SSC are hard elastomers with Shore A values at the limit of the scale (about 90–99) and Shore D around 50, varying within

Table III. Summary of the Tensile Test Results for 50% and 70% SSC Series of Polyurethanes

Isosorbide/BD molar ratio in hard segment, %	50% SSC		70% SSC	
	Tensile strength, MPa	Elongation at break, %	Tensile strength, MPa	Elongation at break, %
0/100	27.0	375	12.9	465
25/75	29.2	414	11.0	538
50/50	30.3	264	11.0	588
75/25	36.4	321	16.0	668
100/0	32.1	308	10.9	516

Table IV. Elastic Recovery of Polyurethanes at 50%, 100%, and 200% Elongation

Isosorbide/BD molar ratio in Hard segment, %	50% SSC			70% SSC		
	Elongation, %					
	50	100	200	50	100	200
	Elastic recovery, %					
0/100	78	77	70	96	94	89
25/75	78	75	67	100	95	88
50/50	84	76	69	100	93	90
75/25	76	70	60	92	94	90
100/0	80	73	62	95	95	87

experimental error. Shore A hardness of the series with 70% SSC was 79 for BD containing hard segment and decreased to 74 with increasing isosorbide content, but Shore D was around 25 except for elastomers with pure BD in the hard segment at 29. Shore hardness is not a quantitative test and cannot be strictly correlated with the structure.

Stress-strain test results on both series of elastomers are shown in Table III. Tensile strength of 50% SSC elastomers varies from 27 to 36 MPa and increases with increasing isosorbide content. On the other hand, elongation generally decreases with increasing isosorbide content. In the 70% SSC series this trend does not exist and the tensile strengths vary from 11 to 13 MPa. The exception is elastomers with 75 molar percent of isosorbide which in both series displayed the highest values. Elongations varied from 260 to 410% for the series with 50% SSC and from 465 to 670% for elastomers with 70% SSC. Strength and elongation are strongly dependent on the molecular weight and sample preparation. At the same time, our observations do not appear to show systematic changes in both tensile strengths and elongations with the changes in the composition of hard segments. However, both properties were higher in samples with isosorbide than in TPU with BD as the sole chain extender.

Elastic Recovery

Elastic recovery is a measure of the extent to which an elastomer specimen regains its original dimensions after the release of an imposed strain. It was measured at 50%, 100%, and 200% of elongation. The results are shown in Table IV. Elastic recovery in samples with co-continuous morphology is usually lower than in those with dispersed hard domains in the soft matrix because continuous hard domains undergo plastic deformation or are broken at high elongations. Elastic recovery at 50% elongation is almost complete in 70% SSC series whereas it is around 80% in series with 50% SSC, which, in fact, is better than in polyurethanes with longer soft segments (and thus, longer hard segments at the same SSC). We also found that increasing elongation decreases elastic recovery. However, elastic recovery remains very high at around 90% even at 200% elongation for series with 70% SSC and 60–70% for series with 50% SSC. There is no clear effect of the isosorbide content in the hard segments on elastic properties of these polyurethanes.

Swelling, as measured by weight increase upon immersion in a solvent for 240 h, was tested in water and a range of organic solvents. Weight gain in water was observed only in samples with pure MDI/BD (10%) and pure MDI/isosorbide (10%) hard segments in series with 50% SSC. The only samples that showed weight gain in 70% SSC series were the one with pure isosorbide in the hard segments (9%) and one with 75:25 BD/isosorbide ratio (also 9%), but there was no systematic change of water absorption with BD/isosorbide ratio change. Swelling in methanol and isopropanol was considerably higher in both series ~20% in 50% SSC series and 30–40% in 70% SSC series.

CONCLUSION

Two series of polyurethane elastomers with renewable isosorbide chain extender were systematically synthesized and compared

with those with BD or mixture isosorbide/BD as chain extenders.

1. All samples in the 50% SSC series had crystalline hard domains, but only PU70-0 displayed a weak melting peak in DSC.
2. The sample with pure isosorbide displayed the highest melting point of 206°C vs. 201°C for pure BD.
3. Glass transitions of the soft segment were not affected by the structure of the hard segment but were lower in series with 50% SSC. Hard segment T_g in the 70% SSC series increased with increasing isosorbide content.
4. Initial (onset) thermal stability decreased with increasing isosorbide content in both series.
5. Tensile strength increased and elongation decreased in series with 50% SSC with increasing isosorbide content. Tensile strengths in 70% SSC series do not exhibit a strong dependence with isosorbide content but elongation generally increased with increasing isosorbide content.
6. Elastic recovery was high in 70% SSC series. It varied within experimental error with the composition of the hard segments in both series.
7. All sample displayed excellent elastic properties and are good candidates for applications where high repeated deformations and potential biocompatibility are required.

ACKNOWLEDGMENTS

The authors are indebted to Honeywell for the financial support. ChemMatCARS Sector 15 is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under grant number NSF/CHE-1346572. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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