

Mechanical and Dynamic Mechanical Properties of Polyurethane and Polyurethane/Polyurea Elastomers Based on 4,4'-Diisocyanatodicyclohexyl Methane

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ABSTRACT: The physical and thermal properties of hand-cast polyurethane and polyurethane/polyurea elastomers prepared from prepolymers of 20 and 97% *trans,trans*-4,4'-diisocyanatodicyclohexyl methane (*t,t*-rMDI) and C₃- and C₄-polyethers chain extended with either 1,4-butanediol (XB) or a commercial mixture of diethyl toluenediamine isomers (DETDA) were determined. The influence of the distribution of geometric isomers of the diisocyanate and of the chain-extender building blocks on these properties is significant. Urethane/ureas are harder and have higher modulus than polyurethanes formed from the same prepolymer. The polyurethane/polyurea elastomers all have somewhat high compression set. Dynamic Mechanical Analysis (DMA) suggests that DETDA extended systems based on 20% *t,t*-rMDI are phase separated, as illustrated by extended rubbery plateau regions and significantly higher softening points than the corresponding XB extended ones. Uniquely, these elastomers are transparent rather than opaque as typical with most other phase-segregated elastomers. Polyurethanes based on 97% *t,t*-rMDI are harder and have higher modulus than those based on 20% *t,t*-rMDI (Desmodur[®] W). They have good phase separation and high softening points but they are opaque. Surprisingly, there is not much difference between the physical or thermal properties of polyurethane/polyureas and polyurethanes based on 97% *t,t*-rMDI. Replacing XB with DETDA gives only moderate improvement in properties, but it does make the elastomers optically clear. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 957-970, 1997

Key words: aliphatic diisocyanate; cast elastomers; 4,4'-diisocyanatodicyclohexyl methane; polyether-urethane/urea

INTRODUCTION

Cast polyurethane (PUR) elastomers are prepared by combining linear high molecular weight polyols and low molecular weight diols (chain ex-

tenders) with diisocyanates. From a morphological standpoint, they consist of crystalline or glassy hard domains of the segregated polyurethane so-called hard segments in an elastic matrix of the so-called soft segments. Many of the physical properties of these elastomers are due to this microphase separation.¹⁻⁵ The hard domains function as multifunctional crosslinks and as reinforcing fillers in a relatively fluid, less polar polyether or polyester soft segment phase. Physical properties of thermoplastic PUR elastomers are directly

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related to the morphology and constitution of these copolymers and especially to the hard segment structure and amount of it that is dispersed in the soft phase.

Most commercial cast PUR elastomers are prepared using the "prepolymer process." The soft segment polyol is incorporated into an isocyanate-terminated oligomer (prepolymer) in a first step by reacting with excess diisocyanate. In a second step, this prepolymer is subsequently chain extended by the molders to form the elastomer. Prepolymers typically contain from about 4 to about 10 wt % available residual isocyanate groups. The commonly used aromatic diisocyanates are 2,4- and 2,6-toluene diisocyanate mixtures (TDI) and 4,4'-diisocyanatodiphenyl methane (MDI), which are combined with polyester or C₃- or C₄-polyether polyols to form commercially available prepolymers.

MDI-based prepolymers are typically chain extended with 1,4-butanediol (XB) to form PUR elastomers containing almost exclusively urethane linkages. TDI-based prepolymers are usually chain extended with aromatic diamines to form PUR elastomers that contain both urethane (from polyol in the prepolymer) and urea (from diamine) linkages. MDI prepolymers are not normally extended with diamines due to their higher reactivity compared to TDI-based ones, even when the deactivated diamine chain extender, methylene bis(*ortho*-chloro aniline) (MBOCA) is used. Prepolymers based on the cycloaliphatic 4,4'-diisocyanato dicyclohexylmethane (rMDI) have lower reactivity than those based on either TDI or MDI. They react sufficiently slowly to be easily chain extended in hand-casting operations with aromatic diamines as well as with diols.

Because rMDI is prepared by the hydrogenation of 4,4'-diaminodiphenyl methane (MDA) and subsequent phosgenation of the 4,4'-diaminodicyclohexyl methane (rMDA), the phosgenated, hydrogenated material is a mixture of three geometrical isomers: *trans,trans*-, *cis,trans*-, and *cis,cis*-rMDI (Fig. 1).⁶⁻⁸ The properties of the rMDI-based polyurethanes are strongly dependent on the *trans,trans*-isomer content of the rMDI.⁹⁻¹²

PUR elastomers based on 4,4'-diisocyanato dicyclohexylmethane (rMDI) are known for their excellent light stability and hydrolysis resistance.⁶ PUR elastomers made from Desmodur[™] W (consisting of ca. 20% *trans,trans*-, 50% *cis,trans*-, and 30% *cis,cis*-rMDI commercially available from Bayer Corporation, see Fig. 1) are opti-

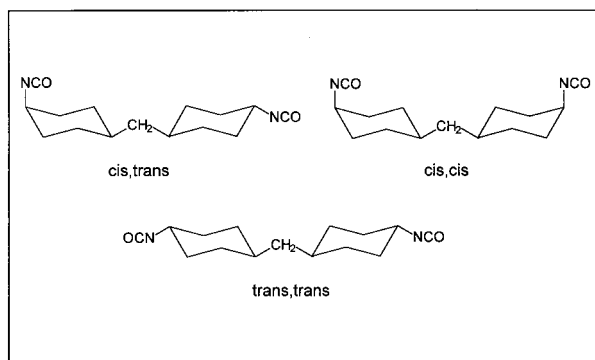


Figure 1 Structures of the geometrical isomers of 4,4'-diisocyanatodicyclohexyl methane.

cally clear. The PUR elastomers based on isomerically pure *trans,trans*-rMDI (100% *t,t*-rMDI) show superior mechanical properties and resistance to solvents as well as improved high temperature performance. As an illustration, dynamic mechanical analysis (DMA) of elastomers prepared from 100% *t,t*-rMDI, 2000 MW C₄-polyether, and XB (40% hard segment content, prepared by chain extending an 8.4% NCO prepolymer) shows an at least 70°C higher hard segment melting point and an elastomeric plateau that is significantly extended compared to analogous polymers prepared with commercial Desmodur[™] W.⁹ These PUR elastomers based on pure *t,t*-rMDI are opaque, possibly indicating that they have improved microphase separation and higher hard domain crystallinity. The improved phase separation also leads to a higher modulus in the elastic plateau region (Fig. 2).

Our goal was to investigate if polyether-urethane/urea elastomers based on 97% *t,t*-rMDI also had superior mechanical and dynamic mechanical properties compared to those based on 20% *t,t*-rMDI. The soft segments in the elastomers investigated were either 2000 MW C₃- or C₄-polyethers. Prepolymers were made with both diisocyanates and both polyethers. The chain extenders were 1,4-butanediol (XB) in the case of polyether-urethanes, and diethyl toluenediamine (isomeric mixture, DETDA) in the case of polyether-urethane/ureas.

EXPERIMENTAL

Materials

The 20% *trans,trans*-4,4'-diisocyanatodicyclohexyl methane (20% *t,t*-rMDI Desmodur[™] W, Bayer

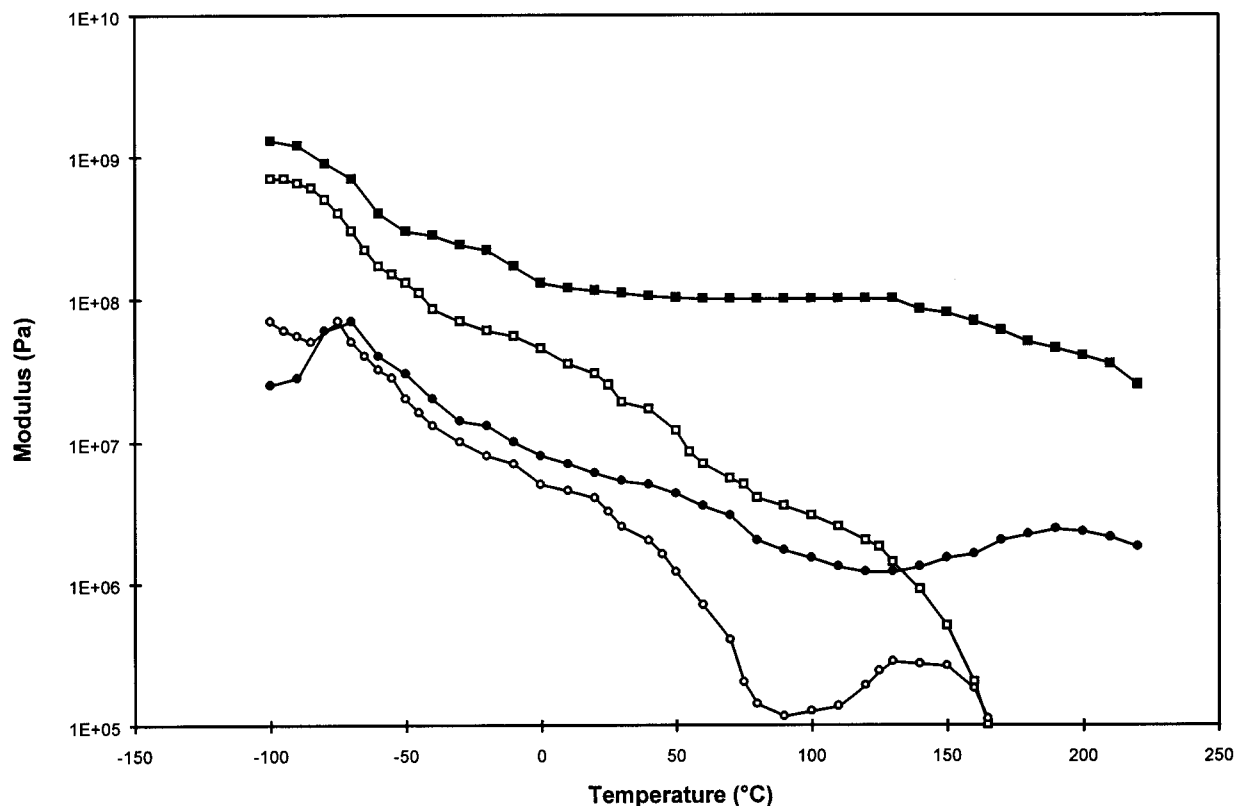


Figure 2 Shear storage modulus (G') and shear loss modulus (G'') versus temperature of PUR elastomers based on 100% t,t -rMDI (G' : shaded squares, G'' : shaded circles) and 20% t,t -rMDI (G' : open squares; G'' : open circles).⁶

Corporation) had a hydrolyzable chloride content of less than 2 ppm and was used without further purification. The actual 4,4'-isomer distribution was 22.7% *trans,trans*, 49.3% *cis,trans*, and 28.0% *cis,cis*, as determined by gas chromatography.

An intermediate, 50% t,t -rMDI, was prepared by crystallizing the *trans,trans* isomer from Desmodur[™] W by cooling to 0°C. The 97% t,t -rMDI was obtained by melt crystallizing the 50% t,t -rMDI at 15°C,¹³ decanting the liquid phase, and then solvent washing the crystals using cyclohexane. The crystals were vacuum filtered and residual solvent was removed by vacuum distillation. The 4,4'-isomer distribution was 96.8% *trans,trans*, 2.3% *cis,trans* and 0.9% *cis,cis*. The hydrolyzable chloride content was less than 2 ppm.

The same lots of all raw materials were used in this study. The 2000 MW polytetramethylene glycol (Polymeg[™] 2000, Quaker Oats), 2000 MW polypropylene glycol (Multranol[™] 3600, Bayer Corporation), and 1,4-butanediol (BDO, ARCO Chemical Corp.) all contained less than 0.01 wt % water and were used as received. Dibutyltin

dilaurate catalyst (DBTDL, Dabco[™] T-12, Air Products, Inc.) was also used without purification.

Diethyl toluenediamine (DETDA) was obtained commercially from Ethyl (now Albemarle) Corporation as a mixture of isomers, the main constituents of which are the 2,4- and 2,6-diaminotoluenes substituted in the 3,5-positions on the ring with on the average two ethyl groups per molecule. The material also contained less than 0.01 wt % water and was used as received. Both chain extenders were stored over molecular sieves.

Processing

The elastomers were prepared using the prepolymer process. Isocyanate-terminated prepolymers were synthesized by reacting one equivalent (1/2 mol) of the polyol, either 2000 MW C_4 -polyether or 2000 MW C_3 -polyether, with 3.5 equivalents (1.75 mol) of rMDI. DBTDL was added to the polyols at 25 ppm using 97% t,t -rMDI and at 50 ppm using 20% t,t -rMDI to form the respective

Table I Temperature/Viscosity Relationship of rMDI-Based Prepolymers (7% NCO)

Prepolymer Based on	Viscosity [Pa s]					
	25°C	55°C	60°C	73°C	80°C	90°C
C ₄ -ether	10–25	3–5	2–3	1.5–2	1–1.5	0.5–1
C ₃ -ether	2–6	0.7–0.9	0.5–0.7	0.3–0.5	0.2–0.4	0.1–0.3

prepolymers. The mixtures were stirred under vacuum at 90°C for about 3 h until the reactions were completed, as determined by titration with *n*-butyl amine according to ASTM D-4666 (ca. 7% NCO content at completion). Table I lists representative viscosity ranges of prepolymers at different temperatures. Most prepolymers containing the 97% isomer were slightly more viscous than those based on 20% *t,t*-rMDI.

The elastomers were formulated with an NCO to active H ratio of about 1.05. Prepolymers were degassed (entrapped air was removed) at 90°C under vacuum at 0.1 mmHg for 20 min. To prepare castings, the preheated prepolymers and the respective chain extenders were weighed into dried glass jars and stirred thoroughly for about 30 s, being careful to avoid whipping air into the mixtures. The prepolymer temperatures were held at either 80–90°C when butanediol was used as chain extender or at 55–65°C with DETDA. Potlives (i.e., the working times before the viscosity became too high to cast) of the polyurethane mixtures were 2–4 min.

The mixtures were poured into closed preheated molds (100–110°C) to produce $6 \times 6 \times \frac{1}{8}$ " plaques and approximately 0.5" high \times 1.2" diameter cylindrical (button) samples for each polymer. After 30–60 min at 110°C, depending on the time necessary for the polymers to solidify (demold times), the elastomers were removed from the molds, the samples were postcured for 22 h at 110°C, and then conditioned at room temperature and humidity for at least 2 weeks prior to testing.

All polyurethane/ureas were optically clear but had light brown color caused by the deeply brown-colored diamine. The color did not become darker during the conditions of curing in this study, but may increase when materials are postcured at higher temperatures. All polyurethanes were colorless and either clear in the case of elastomers based on 20% *t,t*-rMDI or opaque when using 97% *t,t*-rMDI.

Because the materials were prepared using the same levels of raw materials and the same pro-

cessing conditions, we assumed that the reactions went to the same degrees of completion and that the molecular weights of the materials were approximately the same. The molecular weights of the individual elastomers could not be determined due to insolubility of all of the polyurethane/ureas, but they should be greater than about 100,000 atomic mass units.¹⁴

Analysis

The stress–strain properties of the elastomers were determined according to ASTM D-412–87 using a standard Instron testing machine. The samples were cut using a standard die (Die C) and tested at room temperature using a crosshead speed of 20 inches/min. The Shore hardness was determined according to ASTM D-2240; the resilience was determined according to ASTM D-2632; and the compression set was determined according to ASTM D-395.

The dynamic-mechanical properties of the elastomer samples were determined with a Rheometrics Dynamic Spectrometer (Model 7700). Rectangular samples ($2\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$ ") were torsionally stressed at 1 Hz, with strains between 0.04 and 1.5%. The storage modulus (G') and loss modulus (G'') were determined as a function of temperature between –80°C and 220°C in 5°C increments with 2-min equilibration intervals. T_g values in this study were determined from the local maximum of the Tan δ (loss tangent) curves. For purpose of clarity in making the comparisons between the various elastomers, only the storage modulus curves are included in the figures.

RESULTS AND DISCUSSION

Mechanical properties of the elastomers are tabulated in Tables II and III. The same behavior as observed by Seneker et al.⁹ was again found for the C₄-ether based polyurethanes; i.e., almost all physical property levels are improved by replac-

Table II Physical Properties of C₄-Ether-Based Polymers

Physical Property	20% <i>t,t</i> -rMDI		97% <i>t,t</i> -rMDI	
	XB	DETDA	XB	DETDA
Shore D hardness	26	47	41	47
Resilience (%)	39	53	58	57
100% modulus (psi)	814	1765	1380	1539
300% modulus (psi)	1848	4396	1580	3181
Tensile strength (psi)	2676	4410	3686	4412
Ultimate elongation (%)	368	312	720	382
Die C tear (pli)	345	506	741	590
Compression set (%)	42	50	27	55

Polymers prepared by chain extending 7% NCO prepolymers.

ing 20% *t,t*-rMDI with 97% *t,t*-rMDI. The same effect, albeit less pronounced, was observed in this study with the C₃-ether based polyurethanes. Urethanes based on the purer isomer are harder, more resilient, and are tougher than the corresponding systems based on the 20% *t,t*-isomer. The polyurethanes based on the purer isomer are both opaque while those based on the isomer mixture are clear.

This large difference seen comparing properties of the polyurethanes with varying isomer content of the diisocyanate does not extend itself into those of the polyurethane/ureas. The properties of the polyurethane/ureas based on the 20% *t,t*-rMDI are superior to those of the analogous polyurethanes, but the polyurethane/urea elastomers based on 97% *t,t*-rMDI are not greatly different from those based on the 20% *t,t*-rMDI containing isomer regardless of the type of polyether. All of the urea containing elastomers are transparent.

C₄-ether based polyurethanes are harder, have higher tear strengths and smaller compression sets

compared to analogous C₃-ether based polymers. Polyurethane/ureas with both polyethers have very similar physical properties except for compression set, which is significantly higher in the C₃-ether based polymers. This may be due to the higher fluidity of the C₃-ether matrix, which is plausible, given the difference in the viscosity of the C₃- and C₄-polyether prepolymers used (see Table I).

This higher fluidity or increased tendency towards plastic slippage¹⁴ could allow the hard segments to realign more easily when the samples are compressed at 70°C.

The shapes of the stress-strain curves of polyurethanes and polyurethane/ureas in both polyether systems were very similar for either 20 or 97% *t,t*-rMDI. The obvious differences are the effects of soft segment crystallization in the C₄-based materials and the magnitude of the strain values in both polyether systems. Stress induced crystallization can occur in the C₄-ether soft segments but not in the C₃-ether based ones. The stress-strain curves of the polyurethanes based

Table III Physical Properties of C₃-Ether-Based Polymers

Physical Property	20% <i>t,t</i> -rMDI		97% <i>t,t</i> -rMDI	
	XB	DETDA	XB	DETDA
Shore D hardness	21	42	38	49
Resilience (%)	41	47	51	54
100% modulus (psi)	762	1427	1335	1406
300% modulus (psi)	1190	2646	1360	2640
Tensile strength (psi)	1939	4522	1557	3294
Ultimate elongation (%)	697	459	762	370
Die C tear (pli)	389	502	475	510
Compression set (%)	57	78	32	72

Polymers prepared by chain extending 7% NCO prepolymers.

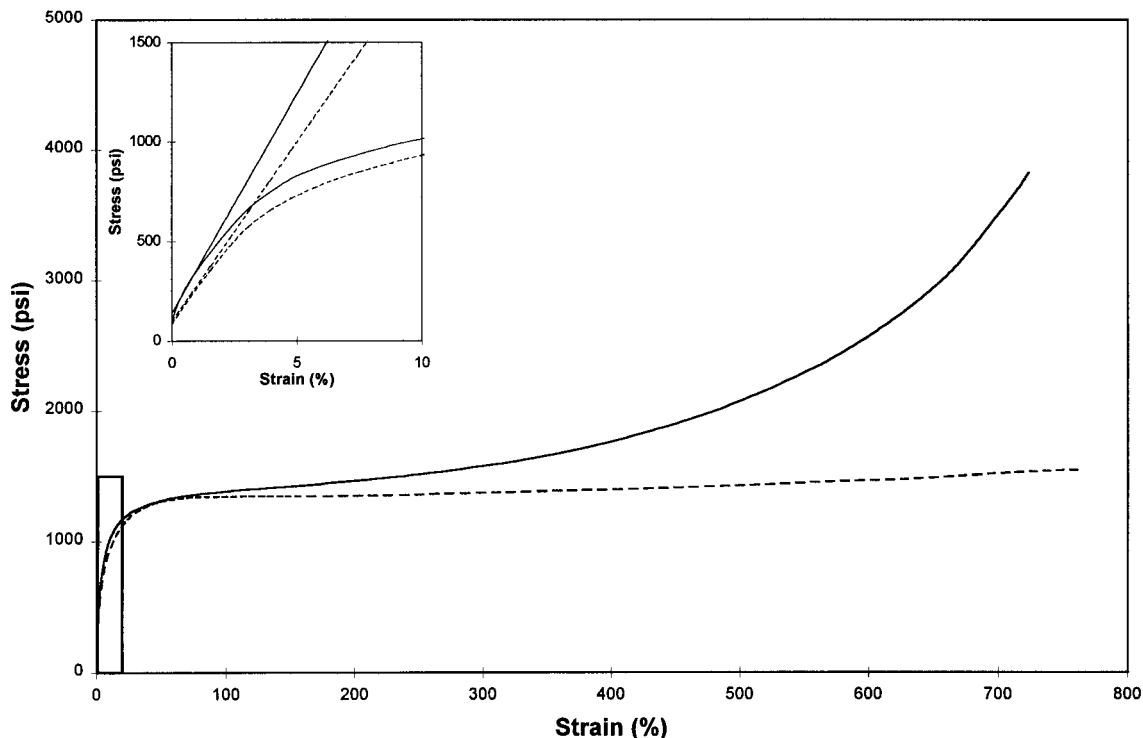


Figure 3 Stress-strain curves of polyurethanes based on 97% *t,t*-rMDI and either C_4 -ether (—) or C_3 -ether (---); 7% NCO prepolymers, chain extended with XB (25–50 ppm of T-12). Inset is the Young's modulus: 22,000 psi for C_4 -ether and 18,000 psi for C_3 -ether.

on 97% *t,t*-rMDI with both soft segments are depicted in Figure 3.

The polyurethane with C_4 -ether as soft segment has a higher modulus at every elongation than those based on C_3 -ether. The differences in the stress-strain curves at low elongation, the Young's or yield modulus, are smaller than at higher ones. At low elongation the moduli are primarily defined by the micromorphology of the polymer. Because both have comparable hard domain sizes and contents, one would not expect a great difference in the yield modulus of the two polyether urethanes. However, the modulus at higher elongations increases sharply in C_4 -ether based polyurethanes. Poly(tetramethylene glycol) is a semicrystalline polymer. At high elongations, the soft segment chains in the elastic matrix order parallel to each other and crystallize. The stress-induced crystallization causes a strengthening of the material that results in an increase of the modulus. On the other hand, C_3 -based ethers form a noncrystallizable amorphous elastic matrix in which the modulus remains almost constant until the polymer fails.

Differences in the stress-strain behavior be-

tween polyurethanes and polyurethane/ureas are evident above 100% strain and become dramatic with higher elongation. The stress-strain curves of the 97% *t,t*-rMDI/ C_3 -ether prepolymers chain extended with XB and DETDA are shown in Figure 4. Irrespective of the type of polyether polyol, the DETDA chain-extended system is characterized by a higher stress at a given strain, this difference increasing with increasing strain. However, the elongation to break is lower for the polyurethane/ureas. In other words, the ductility of the polyurethanes is higher.

Ureas form stronger secondary bonds than urethanes because two NH groups are available for hydrogen bonding. The resulting stronger intermolecular interactions lead to increased interchain attractions of the polyureas in the hard segments and thus, a higher mechanical stability of the hard domains. At high elongations (greater than about 200% in this case) the differences in stress are quite evident due to these hard segment interchain attractions. The forces necessary to break these secondary bonds are quite high. On the other hand, the Young's modulus, which is the slope of the stress-strain curve at low elongations

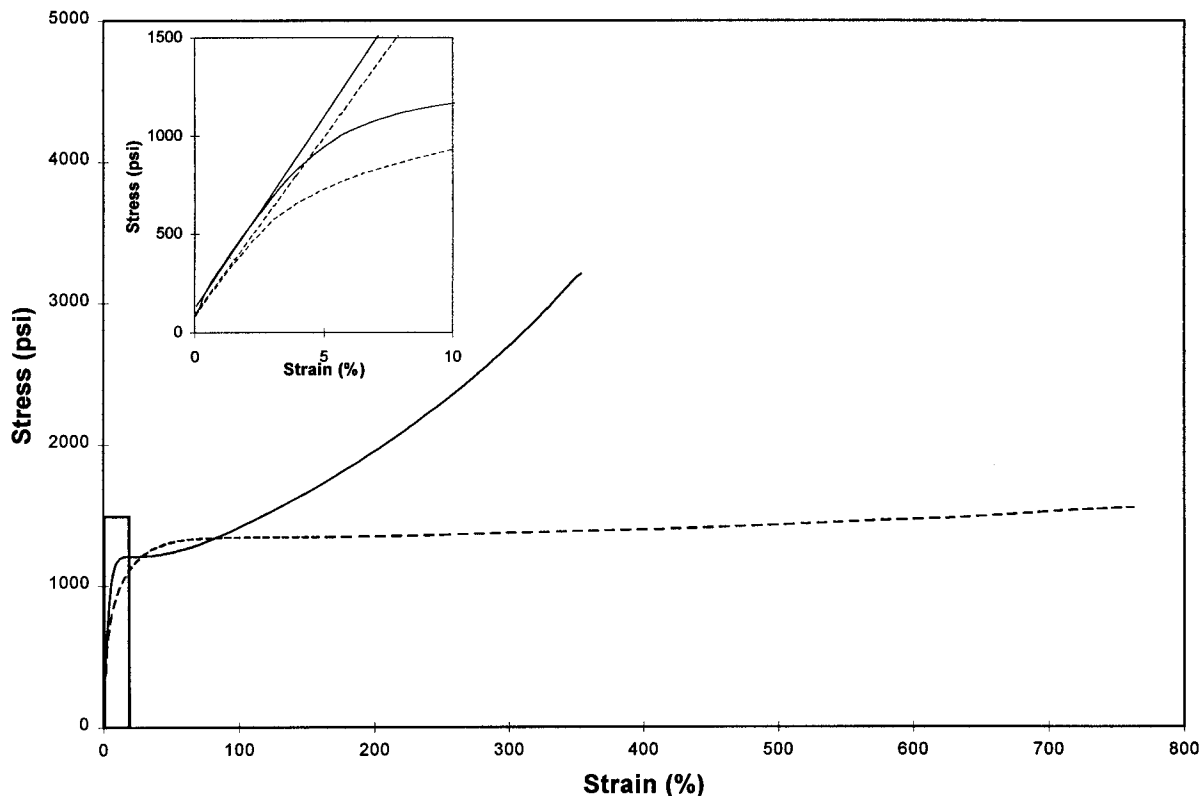


Figure 4 Stress-strain curves of polymers based on 97% *t,t*-rMDI and C₃-ether chain extended either with XB (---) or DETDA (—). Young's modulus: 18,000 psi for XB and 19,500 psi for DETDA.

(less than 5%), is about the same for the urea-containing elastomers as for the all urethane elastomers. Modulus at low elongation is dictated by microdomain interconnectivity. It is a measure of the force required to begin to move the hard domains through the relatively fluid soft segment matrix. Although the urethane and urea hard domains are very different, their content is about the same. Thus, the modulus at low elongations is proportional to the entropy elasticity of the network. The polyether segments, the elastic chains, are the same in both cases.

Polyurethane/ureas based on 20% *t,t*-rMDI have dramatically improved property levels compared to the corresponding polyurethanes. For example, at relatively high strain levels, modulus is nearly double in the urea-containing elastomers. The increases in moduli are less pronounced when comparing 97% *t,t*-rMDI polyurethane/ureas to the corresponding polyurethanes at intermediate elongations (between about 10 and 200%). Above 200% elongation, differences begin to appear. Here the type of polyether plays a more prominent role. At this point, the hard segments are still

intact and soft segment crystallization dictates these differences. At elongations greater than 300%, forces necessary to break the bonds from the hard segment interchain attractions are only about as high as in the 20% *t,t*-rMDI system.

The question of why we do not see the same tremendous increase in the middle portions of the modulus curve when replacing the diol extender with the diamine in the 97%-isomer systems as in the 20%-isomer ones can be answered by considering: (1) the effect of the rMDI isomeric purity on the hard segment packing order in the hard domains, and (2) the hydrogen bond-forming possibilities of the urethane and urea groups. DETDA is an isomeric mixture of diamines. Consequently, the hard segment also consists of a mixture of isomers that cannot form the highly ordered crystal structure reported for the XB chain extended analogue¹⁵ in the 97% *t,t*-rMDI-based polyurethane. On the other hand, the stabilizing effect of hydrogen bond formation on hard segment interaction is more pronounced in the DETDA-extended systems (urea linkages) than in the XB-extended ones (urethane linkages).

Table IV Physical Properties of C₃-Ether/
20% *t,t*-rMDI-Based Polyurethane/Ureas

Physical Property	%NCO		
	4.4	8.7	13.6
Hard block content (%)	30	45	60
Shore D hardness	31	55	71
Resilience (%)	47	52	57
100% modulus (psi)	670	1970	NA
300% modulus (psi)	1240	3245	NA
Tensile strength (psi)	2840	3995	4450
Ultimate elongation (%)	600	375	66
Die C tear (pli)	360	535	ND ^a
Compression set (%)	77	87	ND ^a

^a These properties could not be determined because the samples were too hard and brittle.

Thus, the urea linkages are decisive in the 20% *t,t*-rMDI-based elastomers because the better hydrogen bond formation compensates for the limitations in hard segment packing due to the rMDI isomeric mixture.

In all cases, the polyurethane/ureas are harder than the polyurethanes but have significantly higher compression sets. When a load is applied at the relatively high temperature (70°C) of the test method, the urea hard segment units realign themselves and then retain these new positions in the soft segment matrices after the load is removed. The breaking and formation of new hydrogen bonds at this elevated temperature would be consistent with this behavior. In the case of the polyurethanes based on the purer isomer, compression set is better because these crystalline hard segments would not be expected to melt at this temperature. The set values for most of these urea systems based on rMDI are considerably higher than those of elastomers based on aromatic isocyanates, which typically fall in the range 10–30%.

Although all polymers were prepared with 7% NCO prepolymers, the hard segment content (defined as weight percent of diisocyanate plus chain extender) of the polyurethane/ureas (40%) is always higher than that of the polyurethanes (36%) because the molecular weight of DETDA is higher than that of XB. The increased hard segment con-

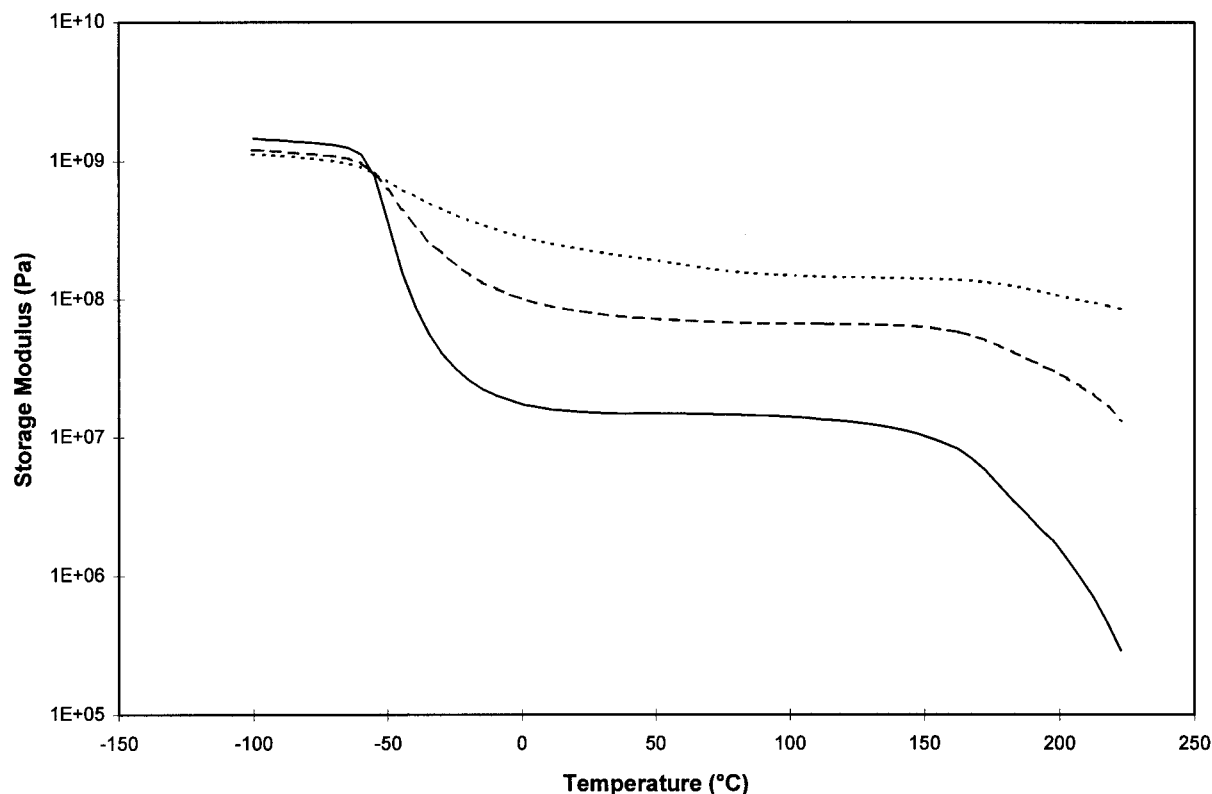


Figure 5 Comparison of polyurethane-ureas based on 20% *t,t*-rMDI/C₃-ether prepolymers with varying isocyanate content: (—) 4.4% NCO, (---) 8.7% NCO, (···) 13.6% NCO.

Table V Thermal Properties of r-MDI-Based Polymers

rMDI Elastomer	Thermal Event (°C)			
	T_g	ΔT_g^a	$T_{\text{softening}}$	ΔT_m^b
C ₄ -ether based				
20% <i>t,t</i> /XB	-74	11	145	120
20% <i>t,t</i> /DETDA	-77	8	178	125
97% <i>t,t</i> /XB	-75	10	195	70
97% <i>t,t</i> /DETDA	-75	10	205	98
C ₃ -ether based				
20% <i>t,t</i> /XB	-51	14	130	135
20% <i>t,t</i> /DETDA	-52	13	180	123
97% <i>t,t</i> /XB	-56	9	189	76
97% <i>t,t</i> /DETDA	-56	9	215	88

^a ΔT_g was calculated by subtracting the glass transition temperature (ca. -65°C) of 2000 MW poly(propylene glycol) or of 2000 MW poly(tetramethylene glycol) as reported in ref. 10 (-85°C) from the T_g of the elastomer.

^b ΔT_m was calculated by subtracting softening temperature of the elastomer from the T_m of the urethane hard block (265°C) as reported in ref. 9 or from the T_m of the 20% *t,t*-rMDI/DETDA urea hard block (ca. 303°C) as determined by the same method as reported in ref. 9.

tent may also contribute to the higher hardness and modulus.

This increase in modulus and hardness coincidental with increasing the hard segment content is consistent with the behavior of polyurethanes⁶ and polyurethane/ureas. As an example of the latter, the physical properties of polyurethane/ureas obtained from C₃-polyether (2000 MW) prepolymers based on 20% *t,t*-rMDI with varying isocyanate content chain extended with DETDA are included in Table IV.

As is normally the case, the tensile strength increases and the ultimate elongation decreases with increasing hard segment content. This is consistent with the results of Wang et al.,¹⁶ which compared the analogous all polyurethane series (XB extended) based on Desmodur[™] W to ones based on MDI.

Thermal Properties

As an illustration to explain how physical properties of these polyurethane and polyurethane/ureas shown in Table IV are interrelated to their thermal properties, the discussion now focuses on the DMA curves of this series of polyurethane/urea elastomers prepared from the C₃-ether/20% *t,t*-rMDI prepolymers with varying isocyanate content shown in Figure 5.

The storage modulus (G') increases with increasing hard segment content. This is consistent with the higher moduli at room temperature seen

in Table IV. Also, there is a well defined "rubbery plateau" region for the DETDA extended polyurethane/ureas, which is in sharp contrast to that of the XB-extended polyurethane materials based on the 20% *t,t*-rMDI prepolymer (8.7% NCO) shown in Figure 2. This not only results in the much better physical properties of the polyurethane/ureas at room temperature, but also makes the glass transition temperature (T_g) of the soft segment and the melting point of the crystalline hard segment (T_m) much easier to recognize.

Due to high melting points of the hard segments of the elastomers in this study and the temperature limitations of our DMA test method, we have used an arbitrary value, $T_{\text{softening}}$, in place of T_m . We define $T_{\text{softening}}$ as the temperature at which the storage modulus G' value falls to one-half of the value for G' at 100°C. The reasoning for this becomes quite evident upon close examination of the G' curve for the 13.6% NCO prepolymer chain extended with DETDA. T_m is somewhat higher than the reliable limit of our instrument, ca. 220°C.

The curve for the extremely hard material (13.6% NCO prepolymer chain extended with DETDA) is much flatter with a change of less than one order of magnitude in the storage modulus from -100 to 220°C. At this high hard segment content, the material no longer behaves like an elastomer with a discreet soft segment T_g and hard segment T_m , but becomes hard and more brittle like an amorphous plastic. Notice also that the glass transition of this urea is less easy to

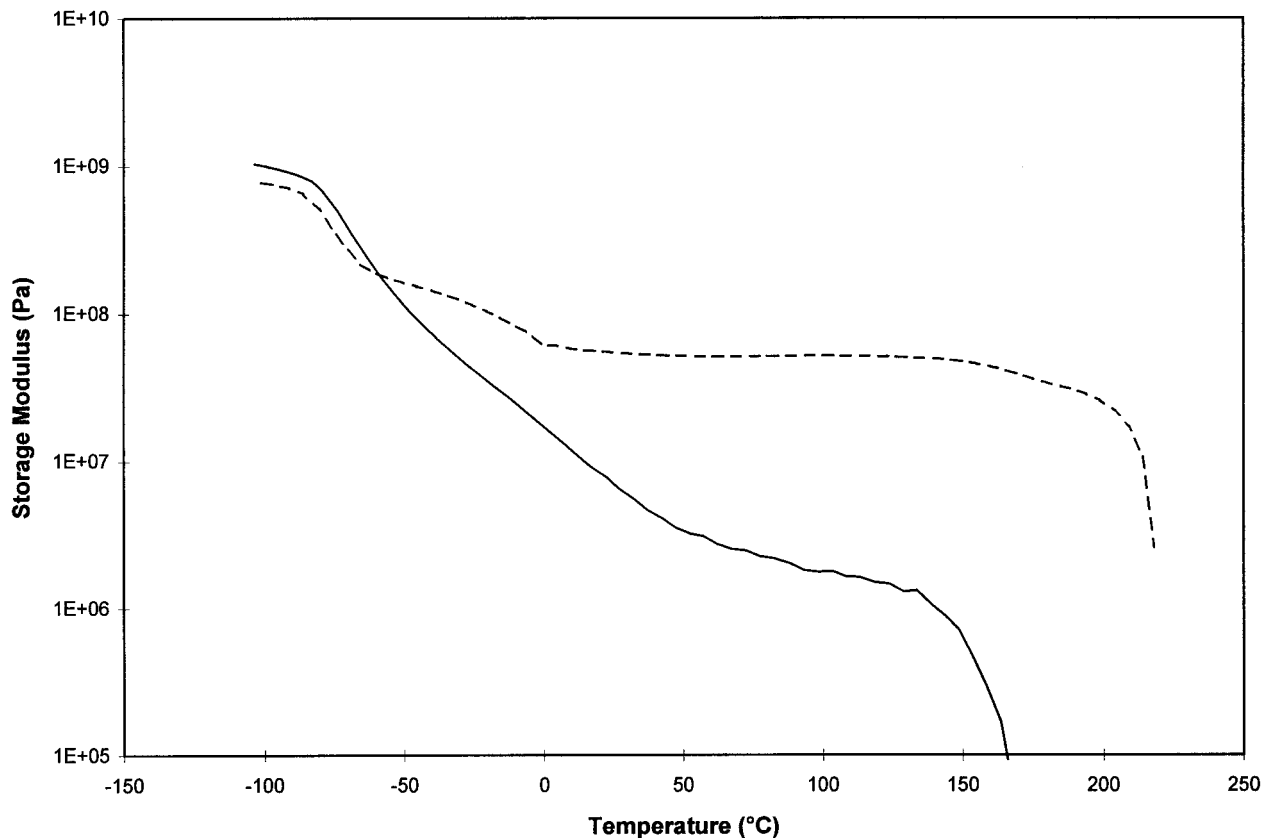


Figure 6 Comparison of C₄-ether polyurethanes based on (—) 20% *t,t*-rMDI/XB or (---) 97% *t,t*-rMDI/XB.

recognize and occurs at a higher temperature than that of the other two elastomeric polymers.

Ideally, the perfectly segregated two phase elastomer would have the T_g of the pure polyol soft segment and the T_m of the pure crystalline hard block with the storage modulus remaining nearly constant as an extended "rubbery plateau" between these two temperatures. Industrial elastomer applications have confirmed that larger temperature spans of the rubbery plateau coincide with wider use temperature ranges for the polymers. As expected, the elastomers in this study all have T_g somewhat higher than the T_g of the pure soft segment and $T_{\text{softening}}$ somewhat lower than the T_m of the "pure crystalline" or "semicrystalline" hard block. For comparison purposes we have used the following conventions to quantify these phenomena:

$$\Delta T_g = \text{polymer } T_g - \text{pure polyol } T_g$$

$$\Delta T_m = \text{pure hard segment } T_m - \text{polymer } T_{\text{softening}}$$

The magnitude of these differences should give some qualitative indication as to the extent of phase mixing. Lower relative values of ΔT_g would indicate that there is less hard segment mixed into the soft segment polyol matrix.¹⁷ Although the T_m of the hard segment depends largely on the size of the crystalline domains and the packing of these crystals, it is also affected by impurities (in this case, soft segment polyol) that lower the melting point. Lower values of ΔT_m could suggest that less soft segment polyol is mixed into the "crystalline" or "semicrystalline" hard segment domain. The result is a lower degree of freezing point depression of the pure hard segment contaminated with smaller amounts of soft segment.

The thermal-mechanical properties of the elastomers are tabulated in Table V. The relatively low and approximately equal values for ΔT_g for all of the elastomers suggests that there is probably little mixing of the hard segments in the soft segment matrixes of the polymers. Much larger differences are observed in the ΔT_m values, suggesting that more contamination of the hard do-

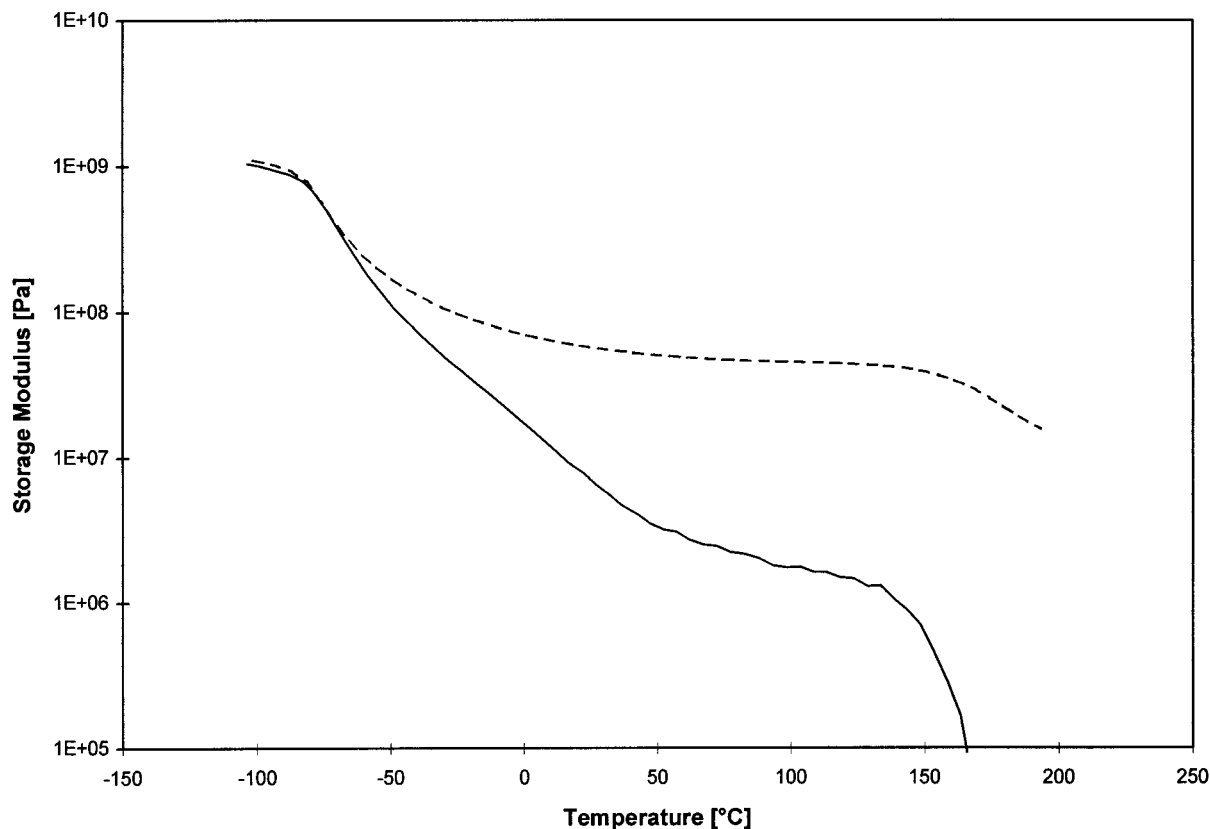


Figure 7 Comparison of polyurethane and polyurethane-urea based on 20% *t,t*-rMDI/C₄-ether cured with (—) XB or (---) DETDA.

mains by soft segments is occurring. Also, there is much greater differences between these values for the individual elastomers.

Assigning the value for $T_{\text{softening}}$ as we have defined it may skew the quantitative values for ΔT_m , making the 20% *t,t*-rMDI-based polyurethanes appear to have a better property spectrum than they actually do, but the qualitative trends are very clear. Here, the softening points of the polymers based on the purer isomer are at least 50 to 60°C higher than those based on the diisocyanate mixture. The crystalline hard segment melting endotherms in DSC scans of butanediol/r-MDI hard segments¹⁸ do parallel our DMA results for $T_{\text{softening}}$. That is, the melting endotherms of the crystalline hard segment from urethanes based on the pure *t,t*-isomer are generally 50 to 60°C higher than those containing *c,t*-isomer.

Figure 6 illustrates the very large advantage in thermal mechanical properties that polyurethanes based on the purer *t,t*-isomer have over 20% *t,t*-rMDI based ones. Quite noticeable is the broad rubbery plateau observed in the purer isomer that is virtually absent with the 20% *t,t*-rMDI

based materials. Also, the transition at about -30°C with the purer isomer is probably due to the combined effects of crystallinity of the C₄-polyether and less hard segment/soft segment phase mixing in this elastomer.

Replacing the diol with the diamine has a significant positive effect in the 20% *t,t*-rMDI-based systems, as illustrated in Figure 7. The polyurethane-ureas have superior thermal mechanical properties to those of the polyurethanes. As with the urethanes based on the purer isomer, a broad rubbery plateau is observed in the urea containing elastomers that is absent with the all urethane ones. The softening temperature of the urea containing elastomers is also at least 30 to 50°C higher. In fact, the softening temperatures of these polyurethane/urea elastomers approach those of the polyurethanes based on the purer diisocyanate isomer. There is not much difference between the polyurethane-ureas based on 20% *t,t*-rMDI and the two polyethers. As expected, the T_g of the C₄-ether system is lower than that of the C₃-based one. $T_{\text{softening}}$ is virtually the same.

The advantage that the amine-extended 20%

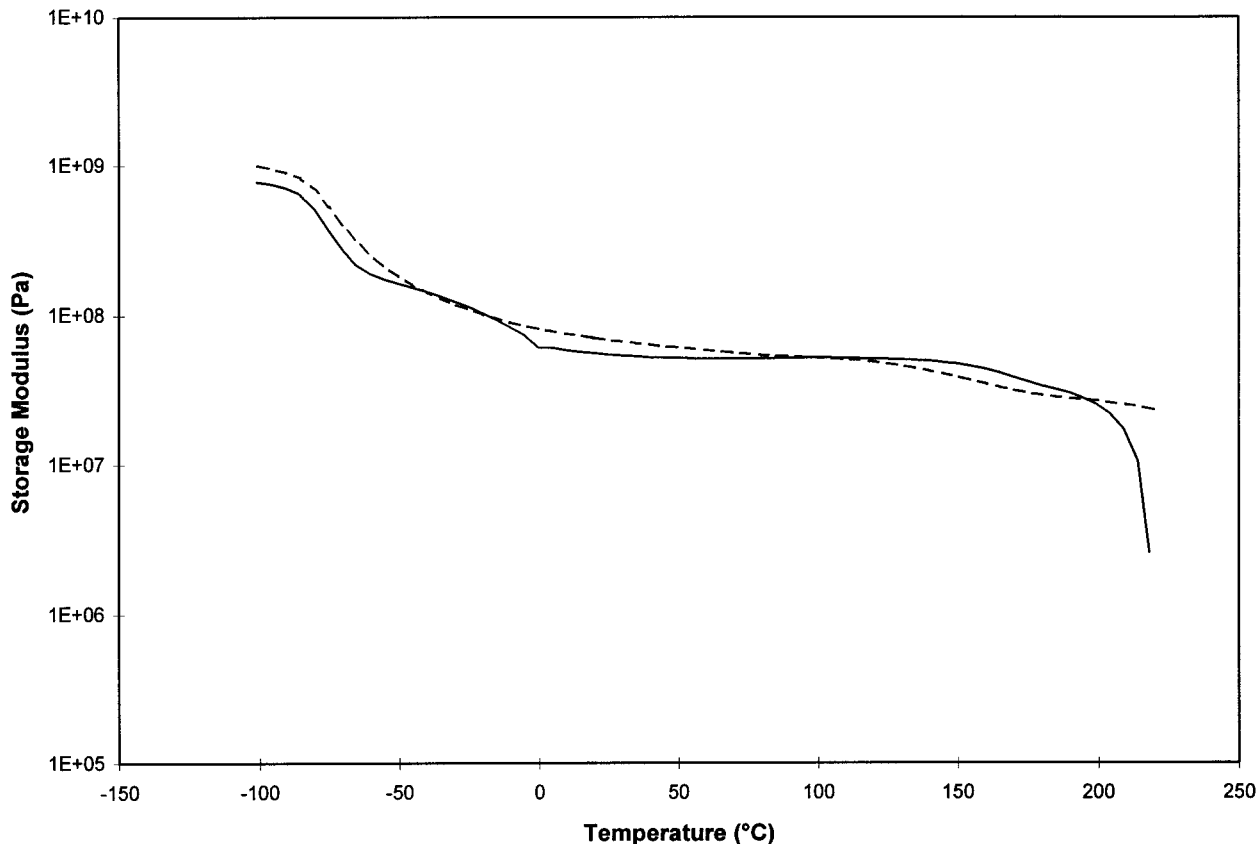


Figure 8 Comparison of polyurethane and polyurethane-urea based on 97% *t,t*-rMDI/ C_4 -ether cured with (—) XB or (---) DETDA.

t,t-rMDI-based systems have in thermal mechanical properties does not manifest itself to the same degree in the systems based on the purer diisocyanate isomer. Aside from the fact that the polyurethane/ureas are clear, the main advantage that one can observe in the 97% *t,t*-rMDI system is that the softening temperatures of the them are 10 to 25°C higher than the urethanes. However, this increase is less than half as much as was the case with the 20% *t,t*-rMDI system. Figure 8 compares the 97% isomer/ C_4 -ether urethane to urethane/urea. Notice also that the transition at around -30°C disappears, indicating that soft segment crystallization is also somewhat suppressed in these urethane/ureas. As with the less purer diisocyanate isomer, the T_g of these C_4 -ether systems are lower than that of the C_3 -based ones. $T_{softening}$ is slightly higher in the C_4 -ether system.

Urea containing elastomers based on both the mixture of isomers and on the purer diisocyanate have relatively high softening temperatures. The

97% *t,t*-rMDI systems have softening temperatures of the urethane/urea that are 25–35°C higher than the ones based on the mixture of isomers. Otherwise, there is not much difference between the polyurethane/ureas based on the two diisocyanate isomers, as illustrated in Figure 9.

The elastomeric properties of polyurethanes and polyurethane/ureas arise from the phase separation of the hard domains from the continuous soft segment matrixes. The DMA curves of the materials suggest that both the urethanes based on the purer isomer and the urethane/ureas based on either the mixture of isomers or the purer isomer have improved phase separation compared to the polyurethanes based on the mixture of isomers. The driving force for this phase separation, however, appears to be different for the two cases. Otherwise, the ureas of the purer isomer would be expected to have an even higher level of properties.

The driving force for phase separation in the case of the urethanes based on the purer isomer

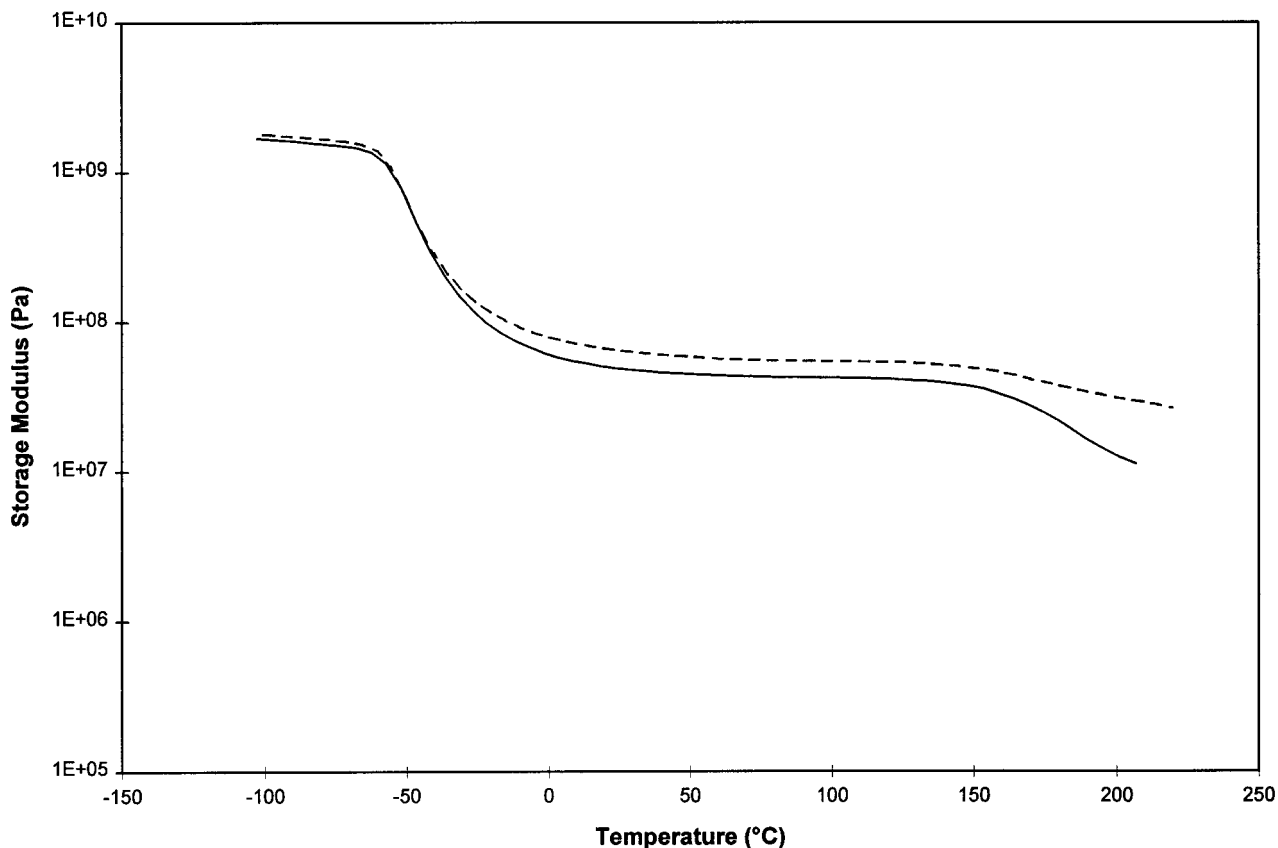


Figure 9 Comparison of 20% *t,t*-rMDI (—) to 97% *t,t*-rMDI (---) polyurethane-urea in C₃-ether cured with DETDA.

is crystallization of these highly symmetrical urethane blocks within the hard domain. X-ray analysis of both model compounds¹⁵ and elastomers containing this butanediol/rMDI urethane¹⁹ have determined that this adduct is highly crystalline.

The driving force for phase separation in the case of the urethane/ureas cannot solely be the effect of crystallinity. DETDA is a mixture of isomers so the urea hard segment blocks also consist of a mixture of isomers with reduced degree of crystallinity. Hydrogen bond formation is more pronounced in the urea systems compared to the urethane ones. This better hydrogen bond formation compensates for the limitations in hard segment packing due to the rMDI isomeric mixture of the 20% *t,t*-rMDI. But when the more isomerically pure 97% *t,t*-rMDI was employed, the structural irregularities of the urea hard blocks due to the isomeric composition of DETDA cancel the otherwise expected increased hard domain stability. Thus, the individual chains cannot orient them-

selves for the urea groups to align to provide the optimal packing observed with the crystalline polyurethane hard segments.

CONCLUSIONS

Changing the chain extender from a symmetrical diol to an aromatic diamine dramatically improves the elastomer properties of 20% *t,t*-rMDI/polyether prepolymer based polymers. Both physical and thermal mechanical properties are significantly higher while the polymers remain clear (slightly yellowish-brown tint) and transparent. These polyurethane/ureas can approach most of the high property levels achieved by the opaque polyurethanes based on 97% *t,t*-rMDI except for low compression set. Polymer properties of the polyurethane/ureas seem to be less affected by the choice of C₃- or C₄-ether than in the case of the polyurethanes.

Polyurethanes based on the 97% *t,t*-rMDI are

superior to the analogous 20% *t,t*-rMDI ones. These same improvements are not carried over into the polyurethane/urea series; i.e., the urethane/ureas are not dramatically improved compared to the 97% *t,t*-rMDI-based polyurethanes. This may be due to less efficient crystalline packing of the urea hard segments based on the mixture of DETDA isomers. The two advantages that replacing the symmetrical diol chain extender with the aromatic diamine achieve are higher polymer softening temperatures and clarity of the polyurethane/ureas.

Polyurethane/ureas based on 20% *t,t*-rMDI may be an attractive cost-effective alternative to polyurethanes based on the purer diisocyanate isomer in applications where good dynamic properties and high use temperatures are not requirements and where transparency of the polymer is desirable.

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