Effect of Curative and Stoichiometry on the Hysteresis in Polyurethane-ureas

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ABSTRACT: Hysteresis in the fifth loading cycle has been measured for a series of polyurethane-ureas based on polytetramethylene glycol (PTMEG), toluene diisocyanate (TDI), and two different amine chain extenders/curatives, methylenebisortho chloroanaline (MBOCA) and a dimethylthio toluene diamine (Ethacure 300, Ethyl Corp.). Hysteresis was seen to increase with strain and temperature in all samples. However, the increase in hysteresis with strain was limited by crosslinking of the hard domains and these materials also showed decreased temperature dependence at higher temperatures. These results are discussed in terms of the structure of the polymers and possible mechanisms leading to hysteresis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 959–966, 1999

Key words: hysteresis; polyurethanes; curatives; stoichiometry

INTRODUCTION

Mechanical hysteresis of a polymer represents the fractional energy lost in a deformation cycle. As with other elastomers, it can occur in polyurethanes from a number of mechanisms such as internal friction as segments of the polymer molecules slide past each other as the molecules change their conformation during the deformation cycle, strain crystallization as aligned segments crystallize during loading, and delayed melting during unloading retards retraction of the molecules or in block copolymers such as polyurethanes, plastic deformation of the second phase domains. Many elastomers also show stress softening where on repeated loading of the polymer, the stress required to achieve a given strain decreases after the first cycle to that strain.

Trick[1] reported the first case of stress softening in polyurethanes. It was found that most of the softening took place during the loading to a given elongation with only small amounts of softening occurring in any subsequent cycle. This result was confirmed by Hicks et al.,[2] who studied polyurethane fibers and found little change in hysteresis after the fifth cycle and also noted permanent set at elongation above 200%, where rupture of tie points had occurred.

Hysteresis in polyurethanes was found to be sensitive to the morphology of the elastomer. Wang and Cooper[3] studied hysteresis in diphenylmethane diisocyanate (MDI)–ethylenediamine (ED) polyurethanes with different molecular weights of the soft-segment polytetramethylene ether glycol (PTMEG). They found that samples with a high hard-segment content had high hysteresis, which they attributed to hard domain interconnectivity, and plastic deformation in the hard domains which occurred at low strains due to the high degree-of-order in those domains. Samples with lower hard-segment contents or higher soft-segment molecular weight had a lower hysteresis because the hard domains were dispersed throughout the soft-segment matrix. These results are similar to those of Paik Sung et al.,[4] who observed the hysteresis of a 2,4-toluene diisocyanate (TDI)–ED–PTMEG series. For materi-

als with a soft-segment molecular weight of 1000 g mol^{-1} but with different urea content, hysteresis increased rapidly with strain at low strains but was independent of strain at high strains. These results were independent of urea content. However, increasing the molecular weight of the soft-segment PTMEG from 1000 g mol^{-1} to 2000 g mol^{-1} significantly decreased the hysteresis. The lower molecular weight soft-segment material also showed significantly higher permanent set. This result was explained on the basis of the work of Sequela and Prud'homme,[5] whose research on styrene-isoprene-styrene (SIS) and styrene-butadiene-styrene (SBS) block copolymers suggested that samples with discrete spherical microdomains show little stress softening, whereas specimens with interconnected domains show large degrees of stress softening. Using this model, Paik Sung et al. concluded that the TDI–ED–PTMEG 2000 materials were less interconnected than those materials with PTMEG 1000.

On the basis of a study on PTMEG–MDI–butanediol (BD) polymers with different hard-segment contents, Abouzahr et al.[6] suggested that hysteresis occurred due to different mechanisms at different strains. At strains below 50%, energy dissipation was associated with nonaffine deformation and orientation of the hard-segment domains. Between 50 and 500% extensions, disruption of hard domains and hard-segment backbone chain alignment occurred, whereas at higher extensions, hysteresis had little dependence on extension because the domains were already well disrupted. They considered that hysteresis here arose from chain slippage and the different viscoelastic responses of the hard and soft segments. With high hard-segment content, they found that domain disruption occurred at low elongation and hence the first of these mechanisms was not observed. At low hard-segment content, they argued that the hard segment in their system was largely solubilized in the soft domains and the lack of crosslinks allowed flow and high-energy dissipation during stress cycling. Gorce et al.[7] studied the hysteresis of a polyether–MDI–BD polyurethane thermoplastic elastomer as a function of temperature, percent strain, and deformation energy. Hysteresis values were found to remain small below the soft-segment T_g and remained small at higher temperatures, demonstrating the ability of the hard domains to act as physical crosslinks. At temperatures much higher than the hard-segment T_g, hysteresis began to increase as the hydrogen-bonded hard-segment domains weakened. Cooper et al.[8] reported a successful method for reducing hysteresis by crosslinking the polyure-

thane with a triol. The results suggest that hysteresis in thermoplastics was little affected by crosslinking unless the crosslinking disrupted the strong intermolecular bonding of the reinforcing domains. Similar results are obtained when vulcanization of rubber occurs. As crosslinking proceeds, hysteresis is lowered, but other properties such as tear strength, fatigue life, and toughness are first enhanced but are then reduced.

Most of these studies were concerned with the stress softening and hysteresis that occurred in the first stress cycle. This current study focuses on the hysteresis present during the fifth cycle where the effect of the mechanisms of stress softening might be expected to be reduced. Interest in repeated cycling grew out of a study on erosive wear of polyurethanes, where it was found that significant heating of the polymers occurred from repeated impacts of small particles during slurry erosion.

EXPERIMENTAL

Materials

The polyurethane materials used in this study were based on PTMEG and TDI. The following two aromatic chain extenders were used: 2,4-methylenebisortho chloroanaline (MBOCA) and a mononuclear aromatic diamine based on a isomeric 3,5-dimethylthio (80%, 2.4; 20%, 2.6) toluene diamine (Ethacure 300, Ethyl Corp.). Materials tested were prepared by ERA Polymers Pty. Ltd., Sydney, and had a hardness of 83 Shore A and 90 Shore A. The softer elastomer had a nominal soft-segment molecular weight of 2000 g mol^{-1}, whereas the harder material had a lower soft-segment nominal molecular weight of 1000 g mol^{-1}. The polyurethanes were prepared from commercial prepolymers and after degassing were cast into sheets approximately 2 mm thick between two glass plates.

The first series of materials were made to assess the effect of curative/chain extender on the properties and consisted of polymers made with a hardness 83 Shore A using 100% stoichiometry and materials of hardness 90 Shore A produced with 95% stoichiometry. Stoichiometry was defined as the ratio of the isocyanate to amine groups. The curing conditions for each hardness were slightly different. The 83 Shore A hardness materials were cured at 100°C for 1–2 h, followed by postcuring at 100°C for 16 h. 90 Shore A hard-

Figure 1   Load extension curves for the first five cycles for the 83 Shore A—MBOCA sample tested to 300% strain.

ness materials were cured initially at 100°C for 1 h followed by two postcuring stages, the first at 100°C for 3 h, whereas for the second stage, the temperature was lowered to 70°C for the remaining 13 h.

A second series of polymers were made using the Ethacure 300 curative and were made with a hardness of 83 Shore A but with stoichiometries of 95, 97, and 105%. The curing conditions for this batch were the same as for the softer materials in the first series.

Characterization

Thermal analysis of the polyurethanes was conducted on a Perkin–Elmer Differential Scanning Calorimeter (DSC 7, Norwalk, CT). Subambient scans were run over a temperature range of -100 to 40°C at a heating rate of 40°C/min. Upon completion of the first scan, the sample was cooled to -100°C at a rate of 200°C/min and the scan rerun.

An indication of the degree of crosslinking in the polymers was obtained by measuring the swell ratio. Weighed samples (~ 0.2–0.3 g) of the polyurethanes were placed in glass vials and swollen in dimethyl formamide (DMF) for a period of 24 h at room temperature. The swollen

samples were removed from the vial and reweighed after excess DMF had been removed. Those samples that had not dissolved were placed in a vacuum oven for 48 h at 50°C. The samples were reweighed and the swell ratio was calculated using the formula

$$Q = \frac{W_s}{W_{ds}} - 1 \qquad (1)$$

where W_s is the mass of the swollen material and W_{ds} is the mass of the deswollen material.

Mechanical Testing

Mechanical testing was conducted on tensile dumbbell specimens cut from the cast sheets. The gauge length of the sample was 15 mm and the gauge width was approximately 2 mm. All mechanical tests were completed on an Instron 5021 (U.K.) with a crosshead speed of 100 mm min^{-1} using wedge action grips. Room temperature tests were conducted in a temperature controlled room set at 22.5°C and a relative humidity of 40%. In all cases, hysteresis was calculated on the fifth cycle. The effect of extension was assessed by taking measurements on the fifth cycle at extensions of 50, 66, 100, 150, 200, and 300%.

Figure 2   Permanent set as a function of strain for the series 1 polymers.

Figure 3 Hysteresis on the fifth cycle as a function of extension for the series 1 polymers.

Hysteresis measurements were also completed at temperatures ranging from room temperature to 180°C in a constant temperature box. The materials tested were the softer 83 Shore A materials from both series. The crosshead speed was measured in millimeters per minute. Before testing, each sample was allowed to equilibrate at the set temperature for 20 min.

A final set of hysteresis experiments was conducted on samples of the polyurethanes that had been immersed in water at room temperature for 1 week before testing. A control series that had been stored at room temperature at 40% relative humidity was also tested.

RESULTS

Figure 1 shows the load extension curves for 83 Shore A MBOCA cured polyurethane-urea cycled to 300% extension. Similar features were observed with the other materials and at other extensions. The first cycle displayed a large hysteretic loop. The second to fifth cycles showed load extension curves of similar shape with the stress in the loading cycle being significantly less than that in the first cycle. The percent hysteresis, calculated as the area bounded by the loading and

unloading curve divided by the area under the loading curve for that cycle, decreased substantially from the first loading cycle to the second loading cycle but became approximately constant after the fifth cycle. These polyurethane elastomers also showed permanent set after the first cycle, but there was little increase in permanent set in subsequent cycles. Permanent set on the first cycle as a function of strain is shown in Figure 2 for the series 1 polymers.

Figures 3 and 4 show the hysteresis in the fifth cycle *versus* extension for the series 1 and 2 materials. All of the softer 83 Shore A materials showed a substantial increase in hysteresis with extension. For the series 1 elastomers, the 83 Shore A MBOCA material showed a slightly higher increase in hysteresis with strain than its Ethacure counterpart. Both of the harder elastomers had higher hysteresis at low strains than the softer polymers, but the MBOCA material showed only a small increase in hysteresis with strain, whereas the Ethacure material showed a substantial increase in hysteresis with strain. The series 2 polymers with different stoichiometry displayed very similar behavior to the 83 Shore A Ethacure polymer, although the 100% stoichiometry material (series 1) showed a slightly higher level of hysteresis at all strains.

Figure 4 Effect of stoichiometry on the strain dependence of hysteresis in the 83 Shore A–Ethacure materials.

Figure 5 Effect of temperature on the hysteresis of the series 1 polymers.

Figure 5 shows the hysteresis performance at 66% strain of 83 Shore A series 1 materials at different temperatures. The Ethacure 300 cured material displayed little temperature dependence below ~ 80°C, but above this temperature there was a continual increase in hysteresis with temperature. The MBOCA cured material showed only a minor increase in hysteresis with temperatures up to a plateau region at ~ 150°C.

Figure 6 shows the effect of stoichiometry on hysteresis as a function of temperature. The results are similar to the results presented earlier for the series 1 Ethacure material with a substantial rise in hysteresis above ~ 80°C. This rise in the hysteresis occurred at slightly higher temperatures as the stoichiometry decreased. The hysteresis of polymers immersed in water for 1 week showed a measurable decrease compared with those held at 40% relative humidity. This decrease was ~ 5% for the 83 Shore A polymers and ~ 10% for the harder polymers.

DISCUSSION

All of the materials tested in this work showed substantial stress softening in the first cycle with varying degrees of permanent set; both of these phenomena would lead to increased energy loss in the first cycle during stress cycling of these materials. It was reported previously,[1,2] and is confirmed in this article, that most of the stress softening in polyurethanes occurs in the first cycle and the amount of hysteresis in the first cycle is generally significantly higher than in later cycles. This work differs from many other studies on hysteresis in that it addresses hysteresis in the fifth stress cycle and consequently represents a condition that would largely be free of the mechanisms leading to stress softening, such as breakdown of the molecular network, orientation of the hard domains, and so forth.

It should be noted that there were differences in the permanent set on the first cycle among the materials (Fig. 2), with the Ethacure 300 materials showing a greater increase in permanent set with strain than the MBOCA cured materials. This can be related largely to the greater amount of crosslinking in the MBOCA system, which would restrict the plastic deformation of the hard domains. A qualitative measure of the amount of crosslinking in the elastomers was given by the swell ratios that are listed for the different materials in Table I. The 83 Shore A materials made with Ethacure 300 with stoichiometry of 100% (series 1) and 105% (series 2) dissolved completely, indicating a lack of crosslinks in these polymers. The MBOCA polymers showed sub-

Figure 6 Effect of stoichiometry on the temperature dependence on the 83 Shore A—Ethacure polymers.

Table I   Swell Ratios for the Different Polyurethanes Swollen in DMF for 24 h

Sample	Swell Ratio, Q
Series 1	
83 Shore A (MBOCA)	3.2
83 Shore A (Ethacure 300)	—
90 Shore A (MBOCA)	1.8
90 Shore A (Ethacure 300)	5.5
Series 1	
83 Shore A (Ethacure 300)—95%	4.9
83 Shore A (Ethacure 300)—97%	5.9
83 Shore A (Ethacure 300)—105%	—

stantially lower swell ratios and thus higher crosslinking than their Ethacure 300 counterparts correlating with the lower permanent set. For the series 2 polymers, the amount of crosslinking increased as the stoichiometry decreased, whereas the 95 and 97% stoichiometry samples, which contained crosslinks, had lower permanent set than the Ethacure 300 that dissolved completely.

Once the fifth cycle had been reached, the hysteresis results for all materials with a hardness of 83 Shore A and the higher molecular weight soft segments were quite similar. Both the materials with different curatives and different stoichiometry showed an increase in hysteresis with strain (Figs. 3 and 4). The results suggested that the hysteresis, at least at low strain, was largely independent of the nature of the hard domains and that the energy dissipation was a result, at least in part, of internal friction as molecular segments slid over each other in the soft domains. A reduction in hysteresis of 5–10% was found on immersion of these polyurethanes in water. Water would most likely be associated with the ether group of the PTMEG and act as a mild plasticizing agent for the soft domains that would reduce the internal friction.

The increase in hysteresis with strain for the softer materials may have resulted from increasing amounts of strain-induced crystallization. Figure 7 shows the subambient DSC curves for the series 1 polymers. Both materials with the higher soft-segment molecular weight showed the ability of the soft segments to crystallize. The slightly higher soft-segment crystallization observed in the MBOCA cured material may explain the slightly higher increase in hysteresis with strain for this material seen in Figure 3.

The hysteresis results for the 90 Shore A polymers with the lower soft-segment molecular weight were quite different to the softer materials. At low strains, hysteresis in both of the harder elastomers was higher than the softer materials. This is consistent with the results of Paik Sung et al.,[4] who on the basis of work on polytetramethylene oxide/TDI/polyethylene diamine systems with differing molecular weights of the polyether, suggested that the level of hysteresis was related to the degree of interconnectivity of the hard domains. They found that lower molecular weight in the soft segments produced a more interconnected hard domain structure that resulted in higher hysteresis, while higher molecular weight of the soft segments allowed more complete phase separation. The 90 and 83 Shore A polymers studied here were similar to those of Paik Sung et al. Moreover, mixing of hard segments in the soft domains would be expected to result in an increase in the soft-domain T_g and such an increase was observed for the 90 Shore A materials (Fig. 7). On the other hand, Cooper et al.[8] noted that polyurethanes with their domain structure disrupted by crosslinking showed lower hysteresis. The MBOCA cured 90 Shore A poly-

Figure 7 Subambient DSC curves for the series 1 polymers. (The curves have been displaced along the Y axis for clarity.)

mer showed substantially greater crosslinking than the Ethacure material. The hysteresis of the MBOCA cured 90 Shore A polymer at low strains was slightly less than the Ethacure material, whereas the hysteresis for both of the harder materials was higher than the softer materials, which contradicts the results of Cooper et al. Thus, the interconnectivity of the hard domains was probably the cause of the increase in hysteresis of the harder materials at low strains.

The main difference between the 83 and 90 Shore A hardness materials was that the 90 Shore A MBOCA cured material showed only a small increase in hysteresis with strain, whereas all the other materials showed a substantial increase in hysteresis with strain. The subambient DSC curves for both of the harder materials indicated little tendency for the soft domains to crystallize; this was consistent with other studies on these systems where decreased soft-segment crystallization was observed with decreasing molecular weight of the soft segments.[9] There may be a possibility that some strain-induced crystallization could still have occurred in the 90 Shore A materials, but it would be expected to be substantially less than in the softer elastomers.

A more plausible explanation of these results comes from the different crosslinking in the materials and the deformability of the hard domains. Abouzahr et al.,[6] in their study of polyether–MDI–butanediol polyurethanes suggested that with low molecular weight soft segments, hysteresis could result from deformation of the hard domains at relatively low strains. With low molecular weight, changes in conformation of the soft segments were limited and the stress was quickly transferred to the hard domains. In the Ethacure 90 Shore A polymer, the hard domains contain few crosslinks, so the domains would be relatively easy to mechanically disrupt. Although most of the deformation of the hard domains would have occurred in the first stress cycle, further deformation might have been possible in the fifth cycle. However, the MBOCA cured polymer contained substantial crosslinking and this would be expected to inhibit deformation of the hard domains. This may be the reason why the hysteresis in this material was relatively constant with strain.

It is possible that the different postcure temperatures in the harder elastomers may have affected the chemical structure of the polymers. The 90 Shore A materials were postcured at 100°C for a shorter period of time than the softer polymers and the remaining postcure was at 70°C. It is known that the reaction of isocyanate with urea groups occurs faster and at a lower temperature than the reaction with urethane groups,[10] and this may have caused differences to the nature of the crosslinking between the harder and the softer materials. However, all materials experienced temperatures of 100°C for at least 4 h; consequently, the effect of the change in cure conditions would be expected to be minor.

An alternative way of influencing the effect of the hard domains is to increase the temperature. The hard domains in polyurethane-ureas can contain both crosslinking, as discussed above, and a level of hydrogen bonding. The hydrogen bonding is known to dissociate at moderate temperatures of ~ 65°C, whereas the crosslinking would be stable to higher temperatures. Evidence for a decrease in the effect of hydrogen bonding with increasing temperature was reported in Fourier transform infrared spectroscopy studies conducted on TDI–BD–PTMEG polyurethanes by Senich and MacKnight[11] and by Brunette et al.[12] in TDI–BD and MDI–BD polyurethanes. Dynamic mechanical thermal analysis (DMTA) studies have shown that the hard-segment softening points were some 10–15°C higher in the crosslinked MBOCA systems than the Ethacure systems. As the hydrogen bonding weakens with increasing temperature, the hard domains would become more deformable and hysteresis increases. This was the observed result for all of the polymers with the possible exception of the 83 Shore A MBOCA polymer. This material showed a plateau in the hysteresis at ~ 150°C. For this material, the initial increase in hysteresis with temperature may have resulted from initial weakening of the hydrogen bonding but, because of its high crosslink density, softening of the hard domains does not continue above ~ 150°C, where the hydrogen bonding has fully dissociated. It is possible that at higher temperatures than those used here, the crosslinks will also dissociate and the hysteresis will also rise in this material.

CONCLUSIONS

The fifth cycle hysteresis observed in these polyurethane-ureas were consistent with three possible mechanisms. At low strains, internal friction was a contributing factor to hysteresis in all materials. The softer materials with the higher molecular weight soft segments showed soft-segment crystallization and the increase in hysteresis with

strain in these materials may have resulted from increasing amounts of strain-induced crystallization. At low strains, interconnectivity of the hard domains may have resulted in slightly higher hysteresis in the lower molecular weight soft-segment 90 Shore A materials leading to increased internal friction. The increase in hysteresis with strain in the harder materials was related to the deformability of the hard domains and was substantially reduced by increasing crosslinking in the hard domains.

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