Domain Structure and Time-Dependent Properties of a Crosslinked Urethane Elastomer*

R. R. LAGASSE, *Polymer Research and Development, Division 5813, Sandia Laboratories, Albuquerque, New Mexico 87115*

Synopsis

The morphology of a chemically crosslinked urethane elastomer is correlated with its time-dependent mechanical properties. Evaluation of this amorphous elastomer by electron microscopy and small-angle x-ray scattering reveals that incompatible chain segments cluster into separate microphases having a periodicity in electron density of about 90 Å. This observed domain structure is similar to that seen previously in uncrosslinked, thermoplastic urethane elastomers. As in earlier studies on such linear systems, thermal pretreatment of the crosslinked elastomer causes a time-dependent change in its room temperature modulus. However, the magnitude of this modulus change (about 20%) is generally less than observed previously with the linear systems. Another contrast with previous findings is that this time-dependent phenomenon is apparently not caused by thermally activated changes in microphase segregation. Rather, the observed time dependence in modulus is believed to be caused by molecular relaxation resulting in densification of amorphous packing within the hard-segment domains. The validity of this proposed mechanism is supported by differential scanning calorimetry experiments showing evidence of enthalpy relaxation during room-temperature aging of the elastomer. This relaxation is qualitatively similar to that observed previously during sub-T_g annealing of single-phase glassy polymers.

INTRODUCTION

Over the past ten years, considerable progress has been made in understanding the mechanical properties of the linear segmented urethane elastomers. The molecular backbone of these thermoplastic elastomers usually consists of long polyether or polyester chains, referred to as the *soft* segments, linked together by relatively short, *hard* segments consisting of aromatic diisocyanates reacted with diols or diamines. Many studies of the morphology of these hard–soft segmented systems have demonstrated that the two kinds of chain segments can preferentially cluster into separate microphases.[1–6] On the basis of these morphologic studies, it has become quite clear that the high strength and modulus of these elastomers arise from physical crosslinking or reinforcement caused by the hard-segment domains dispersed in a soft-segment matrix.[7,8]

In these segmented systems, hydrogen bonding can be established in two different ways: (1) between urethane groups in the hard segments themselves, and (2) between these urethane groups and ether or ester groups in the soft

segments.[9]   Although hydrogen bonding probably does not directly influence mechanical properties to any great extent, the balance between hard–hard and hard–soft hydrogen bonding may exert a secondary effect by modulating the degree of microphase separation between hard and soft segments.[8,9]   In fact, a model based on changes in the perfection of microphase separation has been recently developed to explain thermal history dependence in the modulus of these materials.[10,11]

In contrast with the extensive studies that have been carried out on the linear systems, relatively little attention has been directed at the chemically crosslinked urethane elastomers.   These materials have important technological applications as liquid castable resins for encapsulation, coating, and adhesive applications. Previously, the results of creep experiments on a crosslinked casting system were interpreted to suggest the existence of domain structure.[12]   On the other hand, it is quite reasonable to expect that the presence of crosslinks in a segmented system could restrain the chains from achieving those configurations necessary for phase separation.   This hypothesis is supported by the results of Cooper and Tobolsky[13] who modified linear thermoplastic elastomers by adding various crosslinking agents.   On the basis of observed changes in thermomechanical spectra, these workers inferred that the domain structure initially present in the linear systems could be either maintained or destroyed when crosslinking was introduced, depending on the number and location of the crosslinks in the segmented copolymer chains.   In fact, in the only direct study of the morphology of a crosslinked urethane elastomer small-angle x-ray scattering measurements showed no immediate evidence of any domain structure.[2]   Thus, although the mechanical properties of urethane network polymers have suggested that microphase segregation may be present in some cases, neither characterization of the inferred domain structure nor development of correlations between this morphology and mechanical properties appears to have been carried out.

This paper reports the results of a detailed morphologic study of a chemically crosslinked urethane elastomer having polybutadiene soft segments.   Besides chemical crosslinking, another significant feature of the material studied is the restriction of hydrogen bonding to the hard segments only.   Obviously, the nonpolar nature of polybutadiene precludes hydrogen bonding between hard and soft segments.

Techniques utilized to characterize this material are small-angle and wide-angle x-ray diffraction, transmission electron microscopy, and differential scanning calorimetry.   In addition, some mechanical properties of the elastomer, including their thermal history dependence, are discussed in light of the observed morphology.   The results presented lead to new insights with regard to the origin of time-dependent phenomena in both crosslinked and linear segmented elastomers.

EXPERIMENTAL

Materials

The system chosen for study is a two-part liquid castable urethane elastomer; its composition has been described previously.[14]   (This castable elastomer is marketed by CONAP, Inc., under the trade name EN-7.)   The first component

is a mixture of 2,4-toluene diisocyanate plus a multifunctional polybutadiene endcapped with the same diisocyanate, the mix having 9.0 wt-% unreacted isocyanate (NCO). The polybutadiene in this prepolymer has a number-average functionality[15] of about 2.3 and a number-average molecular weight[16] of about 2700. The second component, or curing agent, of the casting system consists of 55 wt-% 2-ethyl-1,3-hexanediol, 45 wt-% N,N-bis(2-hydroxypropyl)aniline, and 45 ppm of a catalyst.

Bulk samples of the elastomer for mechanical testing and x-ray characterization were prepared by mixing the two components in stoichiometric proportions and curing in a steel mold at 80°C for 16 hr. Specimens were stored in a desiccator at room temperature prior to testing.

Very thin electron microscopy specimens of the crosslinked elastomer were prepared by a modified solvent casting technique. Stoichiometric amounts of the two reactive components were dissolved separately in toluene to form a 3 wt-% solution. A drop of this diluted mixture of prepolymer and curative was cast onto a clean mercury surface. The solvent evaporated instantaneously to leave a film of the reactive components with estimated thickness 400 Å. Films cast in this way were cured at room temperature for time periods of up to 47 days. In order for complete reaction to occur under these conditions, it was necessary to increase the catalyst concentration in the diol curing agent. This room-temperature cure schedule and the previously described 80°C cure yield elastomers having approximately the same mechanical properties.[17] Accordingly, the solvent-cast films were assumed to be representative of the 80°C cured bulk samples. Additional evidence supporting this assumption is given in the results section.

Samples of the cured film were mounted directly from the mercury surface onto 200-mesh electron microscopy grids. Some grid-mounted specimens were stained in the vapor above a 1 wt-% aqueous solution of osmium tetroxide.

Curing of this urethane elastomer consists of the reaction of the two diols with the toluene diisocyanate to form hard segments which interconnect the polybutadiene soft segments. The chemical crosslinks in the system arise from the multifunctionality (>2) of the polybutadiene prepolymer. It can be shown that stoichiometric mixing of the two reactive components produces a crosslinked elastomer composed of about 31 wt-% of the hard segments.

Characterization Methods

X-Ray diffraction patterns were obtained at both small and wide angles by means of a Warhus camera mounted on a Norelco unit which generated nickel-filtered CuKα radiation. Sample thicknesses were 1.1 mm for small-angle exposures and 0.51 mm for wide-angle exposures. Microdensitometer scans on the diffraction patterns were performed with an Optronics S-2000 instrument. In addition, electron micrographs were taken with a Philips EM-200 operated at an accelerating voltage of 100 kV. Differential scanning calorimetry was carried out with a Perkin-Elmer DSC-2; polymer samples weighing about 14 mg were scanned at 10°C/min with a synthetic sapphire reference material.

Dynamic mechanical measurements were made at 0.1 and 3.5 Hz using a Rheometrics mechanical spectrometer in the forced torsion pendulum mode and a Rheovibron DDV-II in the tensile mode, respectively. Finally, softening
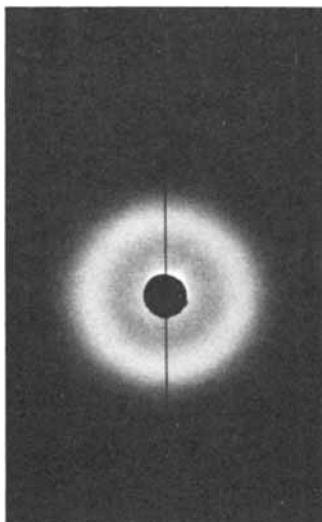
Fig. 1. Small-angle x-ray scattering pattern from the crosslinked urethane elastomer.

temperatures were determined by means of a Perkin-Elmer TMS-1 ther-momechanical analyzer operated in the penetrometer mode.

RESULTS

Morphologic Characterization

The small-angle x-ray scattering pattern obtained from the crosslinked elas-tomer is shown in Figure 1. It consists of a dark area around the beam stop and a broad, but distinct, halo at larger scattering angles. The radial microdensi-tometer scan of this x-ray exposure clearly shows the maximum in scattered in-tensity (Fig. 2). This is indicative of a quasi-periodic fluctuation in electron density within the material.[18] A semiquantitative characterization of the pe-riodicity can be given by the Bragg spacing corresponding to the scattering angle at peak intensity[19]; the computed d-spacing is 93 ± 1 Å. In polymer systems such an electron density fluctuation can be caused by microphase segregation of incompatible chain segments or by a crystal-amorphous texture.[19]

The chemical structures shown in Figure 3 suggest that crystallinity is unlikely to be present in the subject material. The polybutadiene soft segment, being a random copolymer of about 20% cis isomer, 60% trans isomer, and 20% vinyl isomer, is expected to be noncrystalline.[20] Furthermore, the presence of two different diols and the lack of symmetry in both the aliphatic diol and the di-isocyanate would seem to preclude crystallinity in the hard segment.

Wide-angle x-ray diffraction experiments on this material revealed only a single diffuse halo, rather than sharp diffraction rings (Figs. 4 and 5). These results verify that no appreciable crystallinity exists in the elastomer. Ac-cordingly, the small-angle scattering peak shown in Figure 2 is believed to be caused by clustering of the hard and soft segments into separate microphases.

The presence of domain structure in this crosslinked urethane elastomer is confirmed by transmission electron microscopy examination of solvent-cast films.
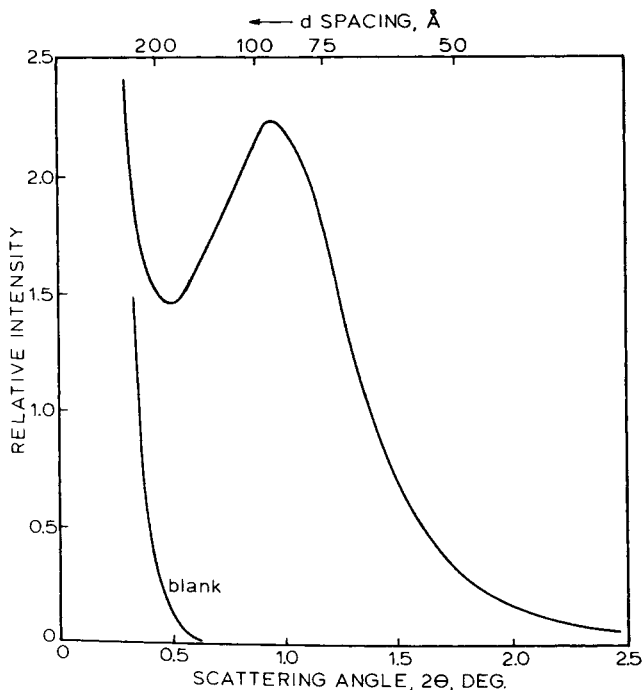
Fig. 2. Microdensitometer scan of the small-angle x-ray scattering pattern.

POLYBUTADIENE

2,4-TOLUENE DIISOCYANATE

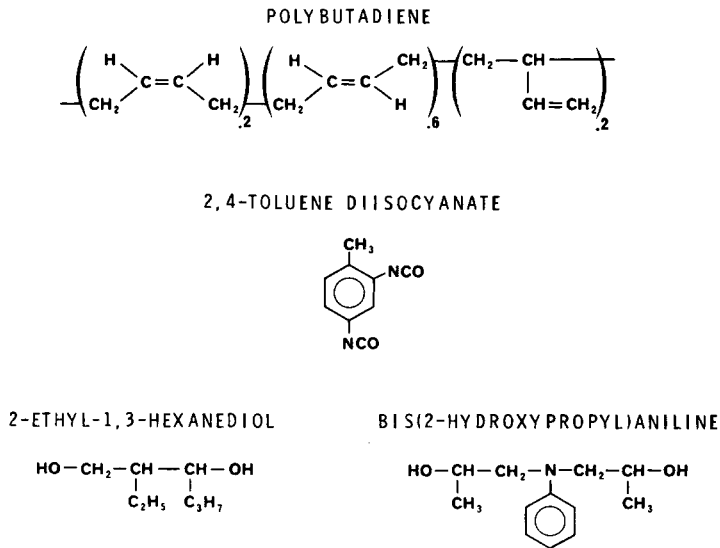2-ETHYL-1,3-HEXANEDIOL   BIS(2-HYDROXYPROPYL)ANILINE

Fig. 3. Chemical structures of constituents of the urethane elastomer.

An electron micrograph of the unstained elastomer vaguely suggests a pebbly texture of high and low electron-density regions (Fig. 6a). If this texture indeed represents microphase segregation of incompatible chain segments, then treating the film with osmium tetroxide should enhance the contrast. The reason is that the high electron density stain preferentially attaches to the double bonds in the
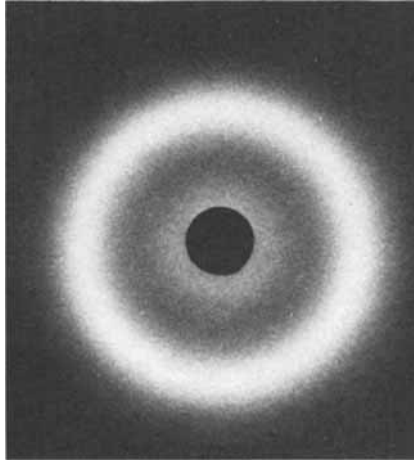
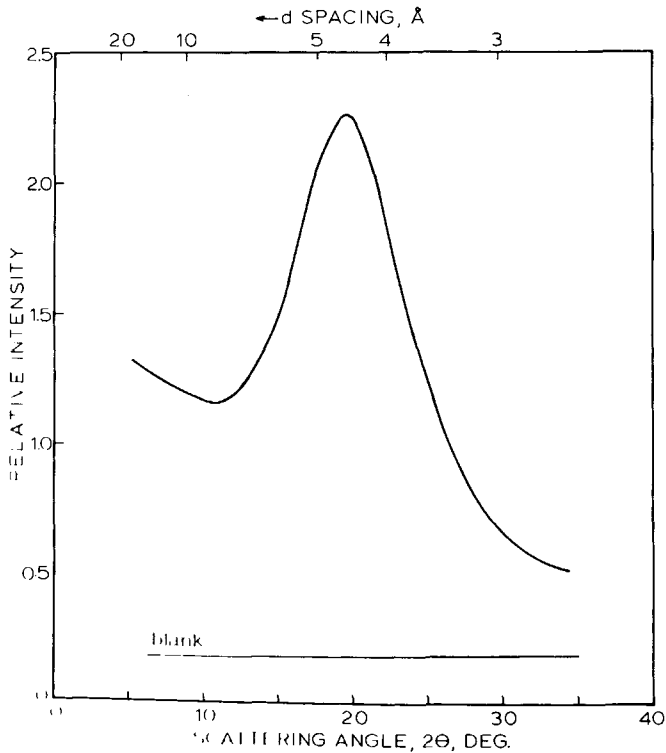Fig. 4. Wide-angle x-ray diffraction pattern from the urethane elastomer.

Fig. 5. Microdensitometer scan of the wide-angle x-ray diffraction pattern.

polybutadiene soft segment.[21]   The electron micrograph of stained elastomer
shows greatly enhanced contrast and therefore demonstrates the presence of
domain structure (Fig. 6b).   (The micrographs in Figure 6 were taken after 12
days of room-temperature cure, but these are representative of domain structure
observed after longer cure times, up to the maximum of 47 days.)   It should be
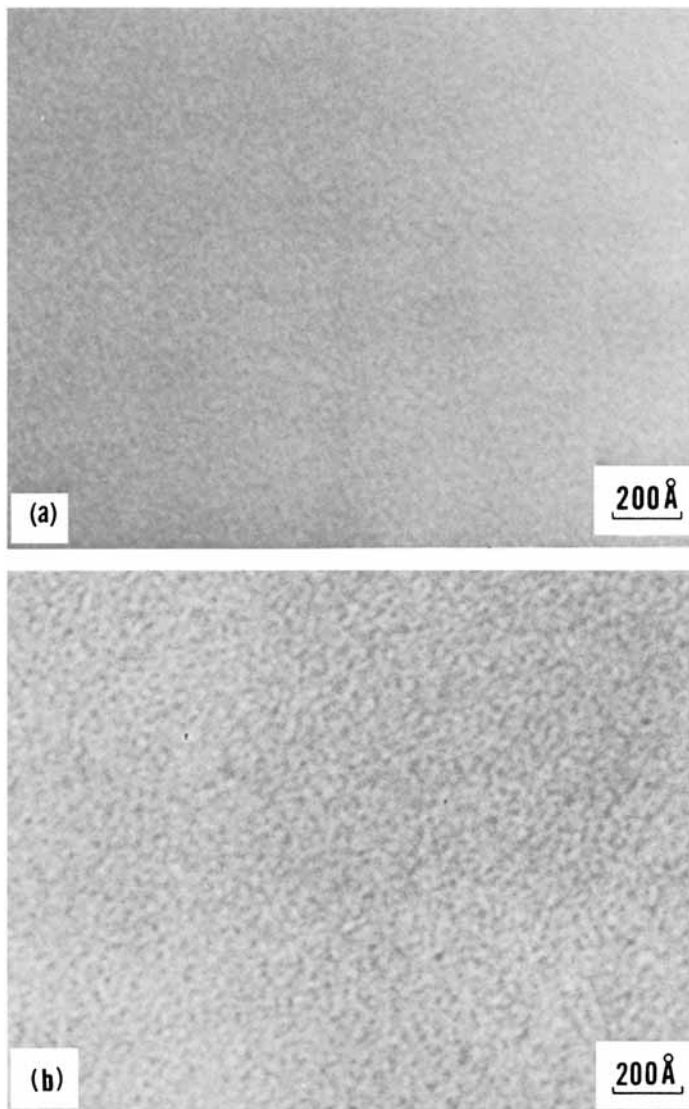emphasized that the same result was obtained when the casting solvent was

Fig. 6. Transmission electron micrographs of thin films of the urethane elastomer: (a) unstained; (b) OsO$_4$ stained.

changed from relatively nonpolar toluene to polar tetrahydrofuran and when the casting surface was changed from mercury to carbon. Thus, it is believed that the domain structure shown in Figure 6b is genuine and not an artifact of the method used to prepare the thin films.

Mechanical Properties

A characterization of the crosslinked urethane elastomer by means of the forced torsion pendulum is shown in Figure 7, as a plot of the in-phase shear modulus versus temperature. By analogy with previous work on the linear segmented systems, the two major transitions centered at about −80° and +50°C
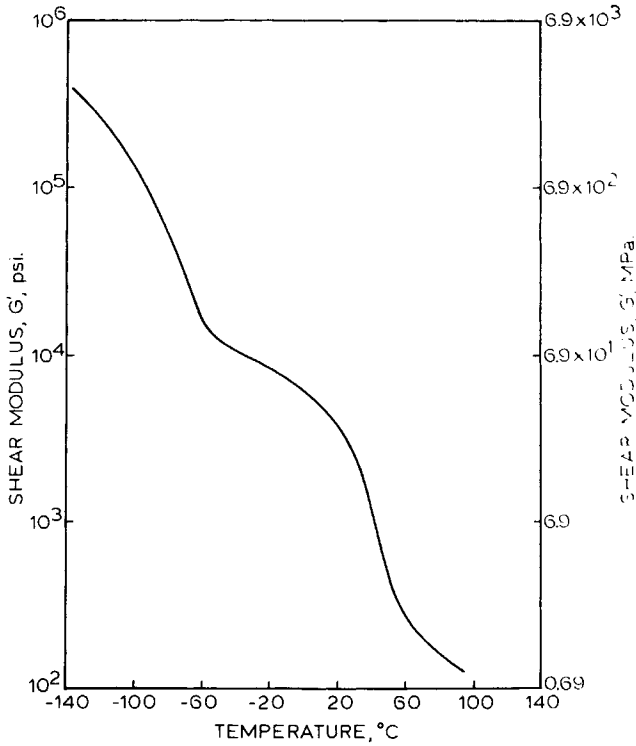
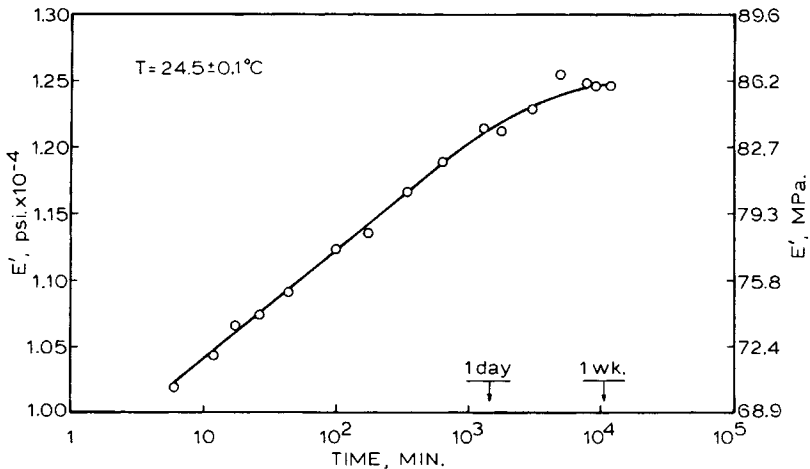Fig. 7. Dynamic mechanical spectrum of the urethane elastomer at 0.1 Hz.

Fig. 8. Time dependence of the 3.5-Hz tensile modulus of the urethane elastomer after quenching to room temperature from 80°C.

can be assigned to the soft-segment (polybutadiene) phase and the hard-segment phase, respectively. In the range of temperatures between these two glass transitions, a region of enhanced rubbery modulus evidently arises from *physical* crosslinking by the glassy hard-segment domains. It appears that at temperatures above the hard-segment transition, the modulus asymptotically approaches
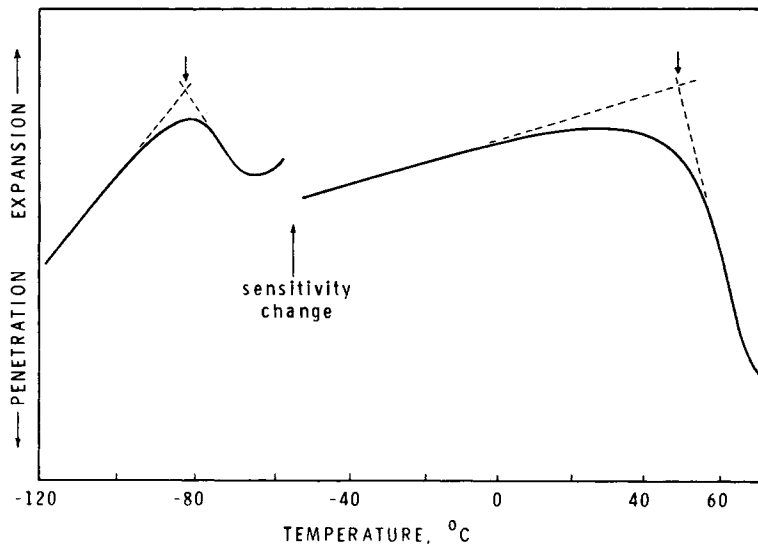
Fig. 9. Thermomechanical analyzer characterization of a well-aged sample of urethane elastomer: penetration of a weighted probe during a 5°C/min scan.

a low value, which would be dependent solely on the degree of *chemical* crosslinking in the elastomer.

Thermal history dependence in the enhanced rubbery modulus of this material was investigated by heating a well-aged sample through the upper transition to 80°C for 5 min and then quenching to room temperature between highly conductive steel blocks. Then, the in-phase tensile modulus was monitored by means of the Rheovibron during aging at room temperature to produce the results shown in Figure 8. It is seen that at 3.5 Hz frequency, the room temperature modulus gradually increased over a period of a week to an equilibrium value more than 20% above the initial value. A similar time dependence in room-temperature modulus was observed when the measurement frequency was raised to 110 Hz, except that the magnitude of the effect was smaller. That is, while the 3.5-Hz modulus increased by 21.7% during room-temperature aging, the 110-Hz modulus increased by only 13.5%. It is to be emphasized that in either case, this time dependence in room-temperature modulus was found to be a reversible phenomenon; repeating the thermal cycle on the same sample again caused the modulus to drop and then gradually recover with aging.

In order to understand the origin of this time-dependent phenomenon in the crosslinked elastomer, the effect of 80°C thermal treatment on its room-temperature morphology was studied. Small-angle x-ray scattering experiments indicated that the thermal pretreatment caused a slight reduction of less than 10–15% in scattered intensity near the interference peak (only). However, direct observation of the domain structure by electron microscopy revealed no detectable change in microphase separation between hard and soft segments due to thermal cycling.

The effect of thermal cycling on the glass transition temperatures of the crosslinked elastomer was also determined. The relatively rapid time scale of the process would have made it difficult to precisely measure true thermomechanical transition temperatures by means of the usual dynamic mechanical
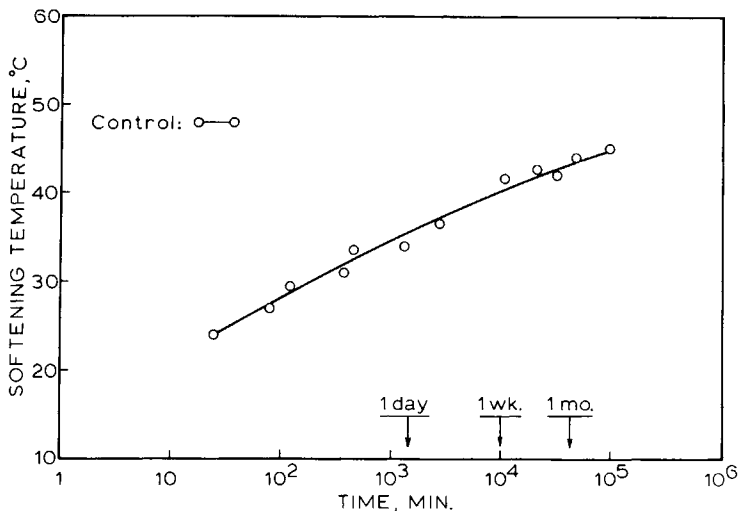
Fig. 10. Time dependence of the upper level softening temperature of the urethane elastomer after quenching to room temperature from 80°C. Control sample: aged six months at room temperature.

instruments (e.g., the Rheovibron). Thus, it was deemed necessary to settle for more qualitative softening temperatures determined by the thermomechanical analyzer.

An example of the results obtained with this instrument is given in Figure 9; this shows the displacement of a weighted penetrometer as a well-aged sample of the elastomer was heated at 5°C/min. Thermal expansion of the sample causes upward motion of the penetrometer, whereas softening of the sample causes indentation, or downward motion, of the penetrometer. The two main softening transitions, attributed to the soft- and hard-segment phases, are characterized by initial penetration temperatures of −83° and +48°C. Replicated penetrometer scans gave softening temperatures in agreement to within ±1°C.

By analogy with the time-dependent experiments described above, a well-aged elastomer sample was cycled to 80°C and then tested intermittently with the thermomechanical analyzer during aging at room temperature. Thermal cycling to 80°C caused no change whatsoever in the lower softening temperature of the elastomer. On the other hand, the upper softening temperature initially dropped by more than 20°C and then gradually recovered during room-temperature aging (Fig. 10). As with the modulus, the thermal history dependence of the upper transition was found to be completely reversible: the phenomenon could be reproduced by repeat thermal cycling on the same sample.

The thermal history dependence of the transitions in the urethane elastomer was further studied by means of differential scanning calorimetry. The thermoanalytical results revealed the presence of a second-order transition at about −70°C; this was the usual broad step change in specific heat characteristic of transitions in amorphous polymers. This lower transition, which can undoubtedly be attributed to the soft-segment phase, was found to be exactly the same in both a virgin sample of the elastomer and one which had been thermally cycled to 80°C. This lack of thermal history dependence in the glass transition
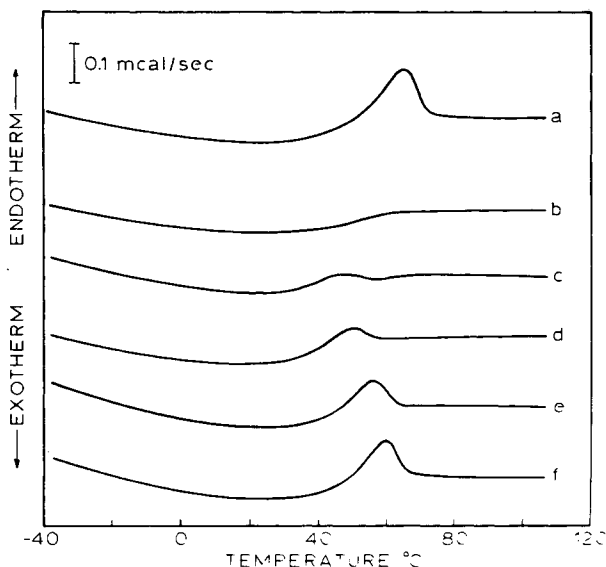
Fig. 11. Differential scanning calorimetry at 10°C/min on urethane elastomer samples: (a) aged six months at room temperature (R.T.); (b) quenched from 80°C to −50°C; (c) quenched from 80°C to R.T., then aged for 80 min; (d) quenched from 80°C to R.T., then aged for 8.5 hr; (e) quenched from 80°C to R.T., then aged for four days; (f) quenched from 80°C to R.T., then aged for 27 days. A new sample was used for each of the six thermograms, which have been vertically shifted for purposes of clarity.

of the soft matrix confirms the thermomechanical analyzer results described above.

The glass transition of the hard domains in the subject material showed considerably more complex thermal behavior. Fixing attention on the top thermogram in Figure 11, one sees that in a well-aged sample, this upper transition consisted of a distinct endothermic peak superimposed on a very broad step change in specific heat. The next thermogram (b) was obtained on a sample which had been heated to 80°C for 5 min, quenched to −50°C within 5 min, and then immediately scanned. It is seen that the upper glass transition in this quenched sample was accompanied by only the step change in specific heat. The remaining thermograms in Figure 11 show that aging a thermally cycled sample at room temperature caused the superimposed endothermic peak to gradually increase in size and move upward in temperature, thereby approaching the appearance of the peak characteristic of the well-aged sample (a).

The results in Figures 10 and 11 suggest that the reversible thermal history dependence in the mechanical properties of the urethane elastomer is related to physical changes within the hard-segment domains rather than the soft-segment matrix. The possibility that these physical changes are caused by ordering phenomena within the hard domains was checked by means of wide-angle x-ray diffraction and infrared spectroscopy. Evaluation of room-temperature samples by these two techniques revealed that pretreatment at 80°C caused no reduction in either the degree of interchain ordering or the extent of hydrogen bonding between hard segments. (Methods of detecting changes in the degree of hydrogen bonding by means of infrared spectroscopy are described in refs. 8 and

9.) Further analysis of the experimental results in the next section leads to a more plausible explanation of these time-dependent phenomena.

DISCUSSION

As stated above, the urethane elastomer studied in this investigation has two features distinguishing it from the materials that have been studied previously: (1) the absence of hydrogen bonding between hard and soft segments, and (2) the presence of chemical crosslinks. In spite of the crosslinking, microphase segregation of hard and soft segments definitely exists in this material. In fact, the periodicity in electron density estimated from the small-angle x-ray scattering peak, 94 Å, is quite similar to values observed before in linear polyether- and polyester-based segmented elastomers.[4,6,22]

Another similarity between the results of this and previous work is the detection of a reversible thermal history dependence in the room-temperature modulus. Time dependence in modulus has been previously noted for a number of thermoplastic urethane elastomers when these were thermally cycled to temperatures in the vicinity of the hard-segment transition interval.[10,11] This phenomenon has been attributed by Wilkes and co-workers to thermally activated disruption of domain structure which results in increased mixing of hard segments in the soft matrix. The time dependence in room-temperature modulus then arises from a finite rate of phase separation between hard and soft segments. Support for this hard–soft mixing model comes from the observation of parallel changes in the glass transition temperature of the soft matrix: differential scanning calorimetry experiments showed that the rise in modulus following thermal cycling is accompanied by a reduction in the lower transition temperature.[10,11] (It should be noted that these thermoanalytical experiments also demonstrated thermal history dependence in the hard-segment transition, but this phenomenon was not featured in the proposed model.)

The time-dependent change in modulus observed in the present work (~20%) is less than that observed previously with linear polyester-based elastomers, but about the same as observed with a linear polyether-based material.[11] However, the phenomenon presently observed with the polybutadiene-based system is markedly different in that it is not accompanied by any measurable change in the lower transition temperature, as described above. This difference between the linear materials studied previously and the crosslinked material with regard to the response of the soft matrix to thermal cycling has been confirmed by pulsed NMR experiments carried out in this laboratory.[23] In terms of the model discussed above, these observations mean that there may not be any significant thermally activated mixing of hard segments in the soft matrix with the present material. This behavior could be caused either by the presence of chemical crosslinks or by the absence of hydrogen bonding between hard and soft segments.

Thus, it is clear that time dependence in the mechanical properties of hard–soft segmented elastomers need not necessarily be accompanied by changes in the glass transition temperature of the soft matrix. Also, wide-angle x-ray diffraction and infrared spectroscopy experiments showed that the time-dependent effects observed with the crosslinked elastomer are not accompanied by any measurable changes in the extent of interchain ordering within the hard-segment domains.

Accordingly, it is believed that the observed phenomena are not at all related to morphologic changes, but rather to relaxation effects occurring within the hard domains at room temperature. Support for this view comes from recognizing the similarity between the phenomena observed in this work and the behavior of a single-phase amorphous polymer when it is annealed slightly below its glass transition temperature.

Recent studies have shown that when a single-phase amorphous polymer is quenched from the liquid state to a temperature 10–30°C below its glass transition, a time dependence in mechanical properties is observed during annealing at that temperature. For example, when quenched atactic polystyrene is annealed at 13°C below T_g, its dynamic, in-phase modulus (0.6 Hz) at the annealing temperature gradually rises by about 20%.[24] Furthermore, this time-dependent change in modulus during sub-T_g annealing is accompanied by a reduction in the enthalpy of the glass. This enthalpy relaxation process is made evident in scanning calorimetry experiments by the development of an endothermic peak superimposed on the usual step change in specific heat over the glass transition interval.[24,25] The peak both grows in size and shifts upward in temperature with increased annealing time at a given temperature. The magnitude of this endotherm gives a measure of the enthalpy reduction during annealing, which can become sufficiently large that the endotherm becomes the dominant feature of the thermogram in the transition interval.[26] A similar time dependence in mechanical properties accompanied by growth and upward shift of an endotherm during sub-T_g annealing has been observed by many other workers and with at least one material other than polystyrene.[27–29]

These time-dependent changes in the thermal and mechanical properties of annealed glasses are believed to be caused by structural relaxation resulting in simple densification of amorphous packing rather than by molecular ordering.[24,26,30] In fact, direct measurement of the collapse of free volume during annealing below T_g has been used to interpret thermal history dependence in the viscoelastic behavior of various polymeric glasses: poly(vinyl acetate),[31] poly(butyl methacrylate),[32] and polystyrene.[33] Furthermore, it has been concluded[33] that the magnitude of the change in mechanical properties observed during annealing of glassy polymers depends on the effective time scale of the viscoelastic experiment: for example, in a dynamic mechanical test, a lower measurement frequency results in a larger thermal history dependence. (This frequency dependence of the thermal history effect is related to the fact that viscoelastic data obtained at various annealing times can be superimposed by horizontal shifts along the frequency axis.[31,32])

It seems likely that similar sub-T_g annealing effects could take place within a separate microphase of a segmented or block copolymer. In fact, preliminary experiments have already indicated that such annealing effects can occur in styrene–butadiene block copolymers having well-defined domain structure.[34] In the subject material of this investigation, the glass transition interval of the hard-segment domains is centered about 15–25°C above room temperature (Fig. 7). Thus, time-dependent changes in its modulus observed during room-temperature aging could very well be caused by slow collapse of free volume within the amorphous, hard domains after quenching from above their T_g. This proposed mechanism is consistent with the observed reversibility of the time-dependent phenomenon, as well as the absence of any significant morphologic

changes within the elastomer. Additional strong support for this model comes from observation of the same phenomena that occur during annealing of glassy polymers: first, the growth and upward shift in the superimposed endothermic peak (Fig. 11); and second, the increase in the thermal history dependence of the in-phase modulus when the measurement frequency is decreased from 110 to 3.5 Hz. (It is anticipated that additional data will be obtained to strengthen this second point.)

It should be noted that assignment of an endothermic peak in the thermogram of a segmented elastomer to enthalpy relaxation has not been proposed before. One or more endotherms have often been detected in the hard-segment transition interval of thermoplastic urethane elastomers,[10,11,35] but these have generally been attributed to thermally activated disruption of various kinds of molecular order within the hard-segment domains.[8] The presence of incipient, paracrystalline-like order[2,5,36] is quite reasonable for those cases in which the hard segment is regular in structure and therefore crystallizable.[8,35,37] However, as was pointed out earlier, the hard segment in the subject material of this investigation has a very irregular chemical structure and accordingly is considered to be noncrystallizable. On the basis of this plus the analogies with glassy systems described above, it is believed that the observed endothermic behavior of the crosslinked urethane elastomer is caused by enthalpy relaxation within the amorphous hard-segment domains rather than an ordering process. In order to further confirm the distinction between these two sources of an endothermic peak, the influence of different heating and cooling rates on the calorimetric results can be evaluated.[26,30,38]

Finally, it should be pointed out that, although this study has been directly concerned with a chemically crosslinked segmented elastomer, the results reported herein may have significance for a wider class of materials. In particular, it seems reasonable that the same sub-T_g annealing effect could contribute to the thermomechanical behavior of linear, uncrosslinked segmented copolymers if these also contained some amorphous hard segments.

SUMMARY

The morphology of a chemically crosslinked urethane elastomer was characterized in some detail. No crystalline structure could be detected in this material by means of wide-angle x-ray diffraction. On the other hand, a domain structure due to microphase separation of incompatible chain segments was detected by both small-angle x-ray scattering and transmission electron microscopy. To the author's knowledge, this work represents the first successful effort to detect and characterize such a domain structure in a chemically crosslinked urethane elastomer. It is, therefore, concluded that the presence of crosslinks in a segmented elastomer does not necessarily prevent microphase separation between the so-called hard and soft chain segments, in agreement with an earlier study of Cooper and Tobolsky.[13]

In addition, some mechanical properties of the crosslinked elastomer were correlated with the observed morphology. Of particular importance was the detection of time dependence in the room-temperature modulus after thermal treatment. In contrast with previous findings on linear systems, this time dependence in the crosslinked elastomer was not accompanied by any measurable change in the T_g of the soft-segment phase. Rather, the results of differential

scanning calorimetry experiments suggested that the room-temperature aging phenomenon was caused by sub-T_g annealing effects within the glassy hard-segment phase. Accordingly, it is believed that such relaxation of amorphous packing may contribute to the thermal history sensitivity of both crosslinked and linear segmented elastomers, along with previously discussed morphologic changes in the domain structure.

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