

Properties of Linear Elastomeric Polyurethanes

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Synopsis

The viscoelastic properties of some polyester-urethanes are compared with the properties of other polymers. The behavior observed is anomalous in that these polyurethanes exhibit an unusually high value of modulus well above their T_g , unaccounted for by either crosslinking or crystallinity. Various experiments including incorporation of plasticizers of widely varying chemical composition have suggested interpretation of the system as a block copolymer, each block having its own T_g . Each of the two types of blocks seems to associate with similar blocks from other molecules.

INTRODUCTION

Elastomeric polyurethanes are of commercial importance in applications involving their use as adhesives, industrial fibers, and as elastomers. It is especially to the latter use that much recent literature has been devoted.¹⁻¹² Our interest has centered upon certain of these polyester-urethane elastomers that exhibit unusual viscoelastic behavior. This behavior is observed in systems that are apparently linear and noncrystalline yet possess substantial strength and high modulus at temperatures well above their major glass transition temperature T_g , where they would ordinarily be expected to be in the state of a viscous liquid.

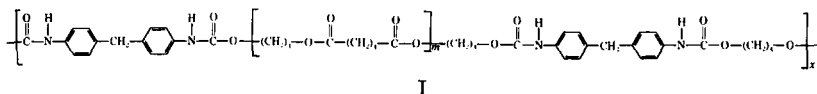
One well-defined polyester-urethane system, Estane,^{1-3,9b} has been the subject of this investigation. Evidence in the literature on similar systems^{4,5} suggests that the low-temperature glass transition in polyester-urethanes is determined by the nature of the flexible polyester, while the level of modulus above T_g is related to the influence of the aromatic diisocyanate used.

In this light we have been able to interpret Estane and similar polyester-urethanes as two-component block copolymers. Their unusual behavior can be attributed to intermolecular association of the aromatic segments producing a subsidiary high temperature T_g , with a similar association of the polyester segments producing a system with a major low temperature T_g .

EXPERIMENTAL

Material Used

The Estane system, a series of polyester-urethanes commercially available from B. F. Goodrich Chemical Company, was used in this study. Estane is made from 4,4'-diphenylmethane diisocyanate, (MDI), a low molecular weight polyester derived from adipic acid and 1,4-butanediol, and 1,4-butanediol. This polymer having the structure I, can be made with varying lengths of polyester and also varying lengths of aromatic blocks.



The two polymers used in this study were Estane 5740-070 and Estane 5740-100. The molecular structure of these two samples was determined by elemental analysis and comparison with published data on this system.¹ On the basis of the analyses shown in Table I, the calculated MDI content of these samples was 38% and 32% for 5740-070 and 5740-100, respectively.

TABLE I

Estane	C, %	H, %	N, %	O, % ^a
5740-070	63.39	7.08	4.29	25.24
5740-100	62.39	7.11	3.56	26.94

^a Oxygen analysis by difference.

Modulus Measurements

Samples were compression-molded from small pellets supplied directly by B. F. Goodrich Chemical Company. The temperature was kept at 330°F. for 5 min. at 40,000 psi. Molds of appropriate geometry were used to obtain samples for modulus-temperature and modulus-time experiments.

Modulus-temperature data were obtained at a constant time of 10 sec. by using both a Clash-Berg¹³ and Gehman^{14,15a} torsional testing apparatus. Silicone oil was used as the heat-transfer medium. The time dependence of modulus at different temperatures was measured by using a stress relaxation balance described elsewhere.^{15b} At values of modulus above 10⁹ dynes/cm.² creep measurements were used and converted to relaxation modulus by using an approximate conversion calculation.¹⁶

Incorporation of Plasticizer

Three different plasticizers, Carbowax 200, a polyethylene glycol of 200 molecular weight, Aroclor 1248, a chlorinated biphenyl, and dimethyl sulfoxide (DMSO) were used. These were added to a solution of approxi-

mately 5% polymer in tetrahydrofuran (THF). The THF was evaporated by gently heating the solution in a Teflon-coated tray. Subsequent heating was done in an oven at 75°C. for several hours to remove residual amounts of THF solvent. Samples were then molded as described above. Different concentrations of plasticizer were employed, ranging from 5 to 65% by weight of the polymer present.

RESULTS AND DISCUSSION

Modulus-Temperature Curves

The modulus-temperature behavior of most polymer systems can be classified according to one of the curves A-C appearing in Figure 1. A rubbery polymer that is not crosslinked or partially crystalline will show modulus-temperature behavior as depicted in curve A of Figure 1. The drop of 10^3 in modulus through T_g is typical in linear amorphous polymers. The rubbery plateau region (10^6 - 10^7 dynes/cm.²) is sensitive to molecular weight and can be extended to higher temperatures by crosslinking (curve B). Semicrystalline polymers, for which data are shown as curve C, generally have a very high "plateau modulus" above T_g and are usually tough

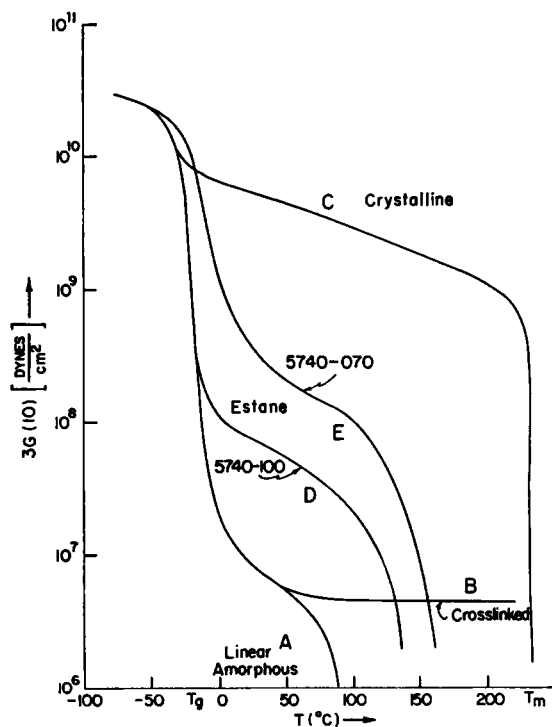


Fig. 1. Modulus-temperature curves: (A) linear amorphous polymer; (B) cross-linked polymer; (C) semicrystalline polymer; (D) Estane 5740-100; (E) Estane 5740-070.

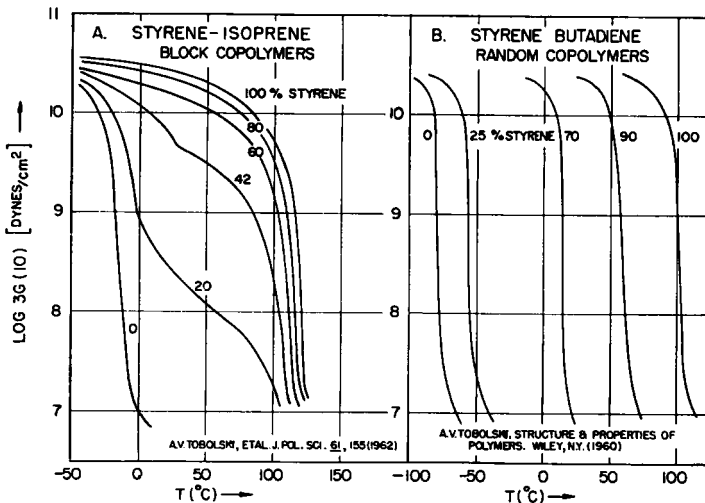


Fig. 2. Modulus-temperature curves: (A) styrene-isoprene block copolymers; (B) styrene-butadiene random copolymers.

and pliable, possessing good impact strength at a temperature between T_g and T_m , the melting point of the crystallites.

Elastomeric polyurethanes show an unusual viscoelastic response above T_g . The modulus-temperature curves of the two materials used in this investigation are shown as curves *D* and *E* of Figure 1. These materials possess a high value of modulus above T_g , which is unaccounted for by crystallinity or crosslinking due to primary chemical bonds.

Some insight into this behavior is afforded by comparison of modulus-temperature data of random and block copolymers of dienes (butadiene and isoprene) with styrene, shown in Figure 2. In the random copolymer, increasing amounts of styrene increase T_g , but not the shape of the modulus-temperature curve. On the other hand, in the block copolymer two T_g values are seen in the modulus-temperature curves, with a high "plateau modulus" between these regions. This is exactly the nature of the behavior one observes in elastomeric polyurethanes.

Modulus-Time Experiments

It is of interest to compare Estane with the well-characterized systems of polystyrene and polyethylene, representatives of completely amorphous and semicrystalline polymers, respectively. This is shown with relaxation modulus data appearing in Figure 3. In this figure, data recording modulus versus time at various temperatures are presented. The data on polystyrene and most other linear amorphous polymers can be transformed by shifting along the time axis so that the curves can be synthesized into a master curve.^{15b}

Empirically the shift factors for superposition in systems such as polystyrene can be represented by an equation first proposed by Williams,

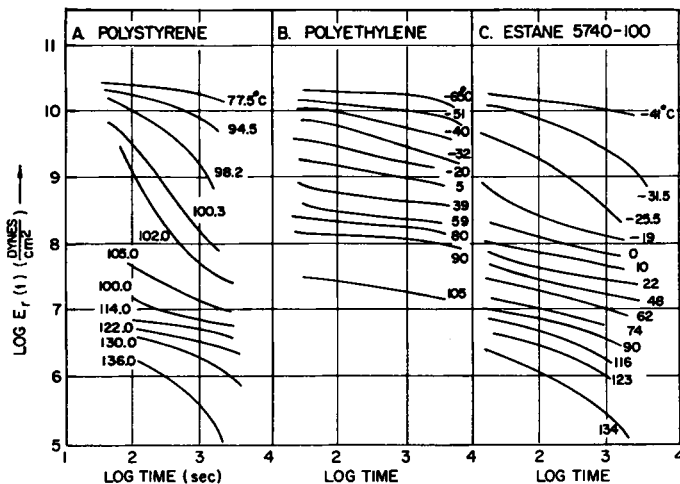


Fig. 3. Relaxation modulus curves: (A) polystyrene; (B) polyethylene; (C) Estane 5740-100.

Landel, and Ferry.¹⁷ We use a modification of this equation¹⁸ shown in eq. (1),

$$\log [K(T)/K(T_i)] = - [16.1(T - T_i)]/[56 + T - T_i] \quad (1)$$

where $K(T)$ is the time required at temperature T for $3G_r(T)$ to attain a value of 10^9 dyne/cm.² and T_i is the temperature for which $K(T)$ is 10 sec. In semicrystalline systems such as polyethylene this horizontal shift must be accompanied by a vertical shift in order to create a master curve.¹⁹ A somewhat intermediate situation exists in the Estane data as shown in Figure 3. Time-temperature superposition is possible, although through the rubbery plateau region the shift factors do not follow eq. (1).

Crystallinity

A reinforcement of structure which might account for the unusually high modulus and long rubbery plateau in Estane could be the presence of a crystalline phase. However, we find no experimental evidence of crystallinity existing in these systems. Estane is transparent, suggesting that no large areas of light-scattering crystallites are present, and x-ray diffraction shows a completely amorphous scattering diagram. The scattering is not affected in any marked fashion by annealing or orientation. Another observation is that the plateau modulus is independent of strain in the range of 2-40%. If it were possible to induce crystallinity by strain or if the structure was altered by the strain, this experiment would reveal a strain-dependent modulus.

Finally, the transition to a viscous liquid is different from that observed in crystalline polymers. The polymer gradually softens throughout the plateau region, finally passing through what appears to be a second second-

ary glass transition at about 120°C. This can be observed in Figure 1, curves *D* and *E*.

Plasticizer Incorporation

Three different plasticizing compounds were blended in Estane 5740-070. Samples were prepared with increasing amounts of plasticizer, and modulus-temperature curves were obtained shortly after preparation. Rapid testing (same day) was essential because none of the three plasticizers used, DMSO, Aroclor, and Carbowax, was completely compatible with Estane, and each had a tendency to diffuse out slowly. Nevertheless the data were reproducible if measurements were made within a day of preparation, and the effect of increasing plasticizer was consistent in each system.

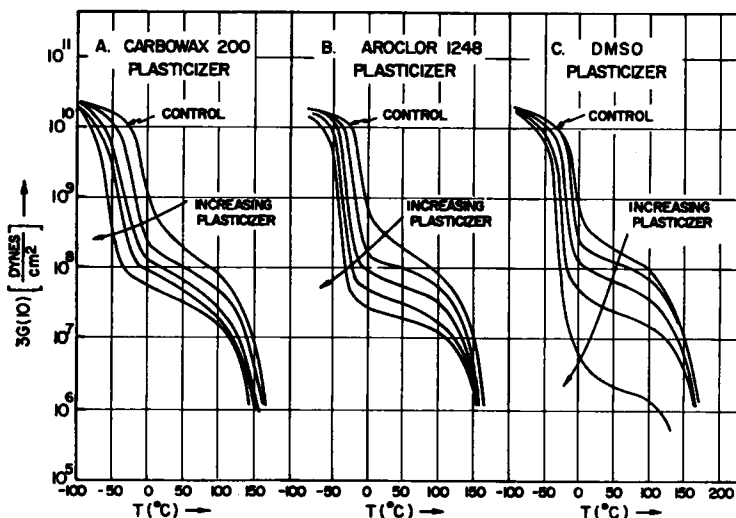


Fig. 4. Modulus-temperature curves of plasticized Estane 5740-070: (A) Carbowax 200; (B) Aroclor 1248; (C) DMSO.

The results presented in Figure 4 show that Estane is affected as a two-component system. The soft polyester segments seem preferentially plasticized by the Carbowax plasticizer, as shown by a marked shift in the T_g toward even lower temperatures. This effect is less marked with Aroclor and least in the DMSO blend. The order of increasing solubility parameter is very probably Carbowax, Aroclor, and DMSO.

The opposite effect is noticed in the influence of the plasticizer on the plateau modulus. The plateau modulus at a given value of $T - T_g$ is most affected by the DMSO and least by the Carbowax. These complementary results suggest that in linear segmented polyurethanes, regions of associated aromatic linkages and regions of associated aliphatic polyester exist which can be preferentially solvated. The above observations can be put

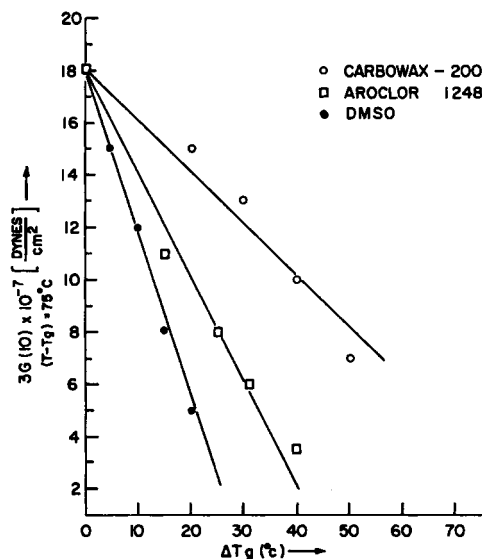


Fig. 5. Modulus vs. ΔT_g for plasticized Estane 5740-070. Modulus chosen at $T - T_g = 75^{\circ}\text{C}$.

on a semiquantitative basis if one plots the modulus at $T_g + 75^{\circ}\text{C}$. as a function of the change in T_g produced by varying amounts of the three plasticizers. For each of the plasticizers a nearly linear plot is obtained but the slopes differ widely, as shown in Figure 5.

Viscoelastic Model of Segmented Elastomeric Polyurethanes

Since the enhanced modulus observed in linear segmented elastomers can be ascribed to the glassy state of the hard blocks acting as "fillers" for the elastomeric blocks, it was thought that equations derived for predicting modulus in filled elastomer systems might be applicable. Previous treatments beginning with the work of Einstein,²⁰ Smallwood,²¹ and recently Kerner and others²²⁻²⁵ provide semiquantitative equations that could be tested. For modulus values of glassy and rubbery segments of 3×10^{10} dyne/cm 2 and 1×10^7 dyne/cm 2 , respectively, and reasonable values for the amount of hard phase, none of the treatments outlined above seemed to predict a high enough modulus enhancement to satisfy our data on the composite. This can be attributed in part to a relatively high concentration of the hard phase.

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Résumé

Les propriétés viscoélastiques de certains polyesteruréthanes sont comparées avec les propriétés d'autres polymères. Le comportement observé est anormal en ce sens que ces polyuréthanes manifestent une valeur anormalement élevée du module, bien au-dessus de leur transition vitreuse, et qui n'est pas due ni au pontage, ni à la cristallinité. Diverses expériences comportant l'incorporation de plastifiants de composition chimique très variée suggèrent que le système est un copolymère séquencé, chaque bloc ayant sa propre transition vitreuse. Chacun des deux types de blocs semblent s'associer à des blocs semblables appartenant aux autres molécules.

Zusammenfassung

Die viskoelastischen Eigenschaften einiger Polyester-Urethane werden mit denjenigen anderer Polymerer verglichen. Das beobachtete Verhalten ist insofern anomal, als diese Polyurethane einen ungewöhnlich hohen Modulwert weit oberhalb von T_g besitzen, der weder durch Vernetzung noch durch Kristallinität bedingt ist. Verschiedene Versuche, darunter solche mit Anwendung von Weichmachern sehr verschiedener chemischer Zusammensetzung, sprechen für einen Blockcopolymer-Aufbau des Systems, wobei jeder Block sein eigenes T_g besitzt. Jeder der beiden Blocktypen scheint sich mit ähnlichen Blöcken von anderen Molekülen zu assoziieren.

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