

Rheological and Mechanical Properties of Polyurethane Modified by BHET

CHEN-CHONG LIN* and BIN-ZW YANG, *Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan*

Synopsis

The chemical structure of polyurethane modified by BHET is correlated with its mechanical and dynamic mechanical properties. Evaluation of this amorphous elastomer by means of stress-strain tests and transition temperature measurements reveals that incorporation of the BHET structure into the soft polyester segment affects the domain structure and, in turn, the entire mechanical behavior of polyurethane. It is also shown that polyurethane has a wide range of T_g and secondary transition temperature by varying the ratio of BHET to EG as well as the ratio of TDI to polyester polyol.

INTRODUCTION

The polyester used as polyols in urethane elastomers has been previously investigated. Urethane elastomers usually consist 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. 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.^{1,2} The effect of the hydrogen bonding was studied by several workers from a segmental point of view.^{3,4} Studies have also been made on the effect of crosslinking on the thermomechanical properties of these materials.^{5,6} An attempt to modify the properties of this elastomer by the incorporation of BHET in the polyester polyol segment was reported.⁷ The polyester is prepared by reacting adipic acid and BHET or BHET/EG mixtures. The resulted polyester polyol is then reacted with TDI in the presence of NaCN to form a chemically crosslinked polyurethane. Some mechanical properties of this elastomer are

TABLE I
Characteristics of Polyesters^a

Code	[BHET]:[EG], mole	[OH]:[COOH], mole	Acid No.	P^b	\overline{DP}	\overline{M}_n
A	100:0	1.482	0.8521	0.9961	5.104	1000
B	75:25	1.398	0.6533	0.9975	6.019	1000
C	50:50	1.319	0.8975	0.9972	7.275	1000
D	25:75	1.247	0.7633	0.9980	9.081	1000
E	0:100	1.84	0.5608	0.9989	11.892	1000

^a By reacting under 180–185°C for 80 hr.

^b Extent of reaction.

* Visiting professor (1979–1980), Department of Chemical Engineering, Louisiana State University.

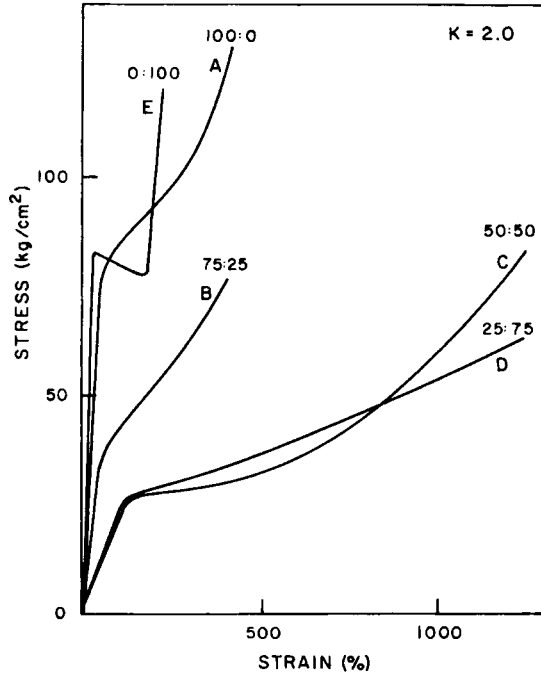


Fig. 1. Stress-strain curves of polyurethanes with $k = 2.0$.

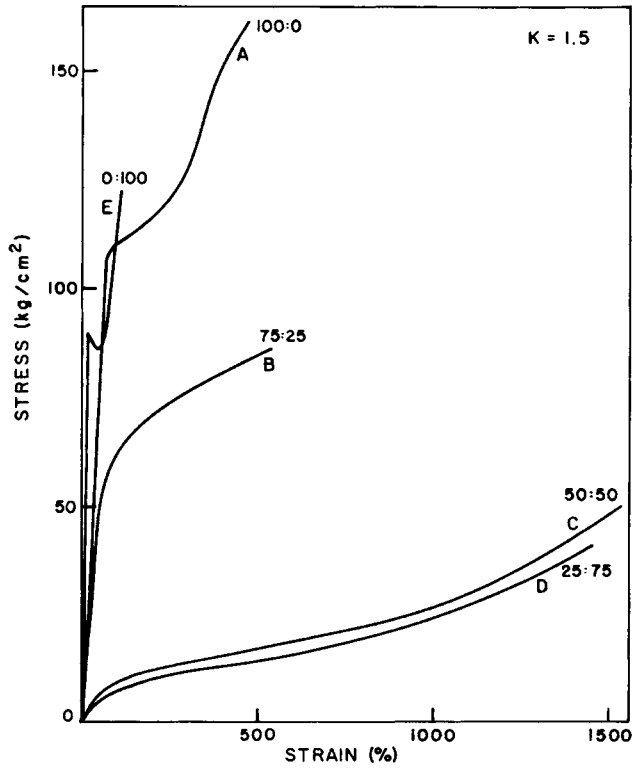


Fig. 2. Stress-strain curves of polyurethanes with $k = 1.5$.

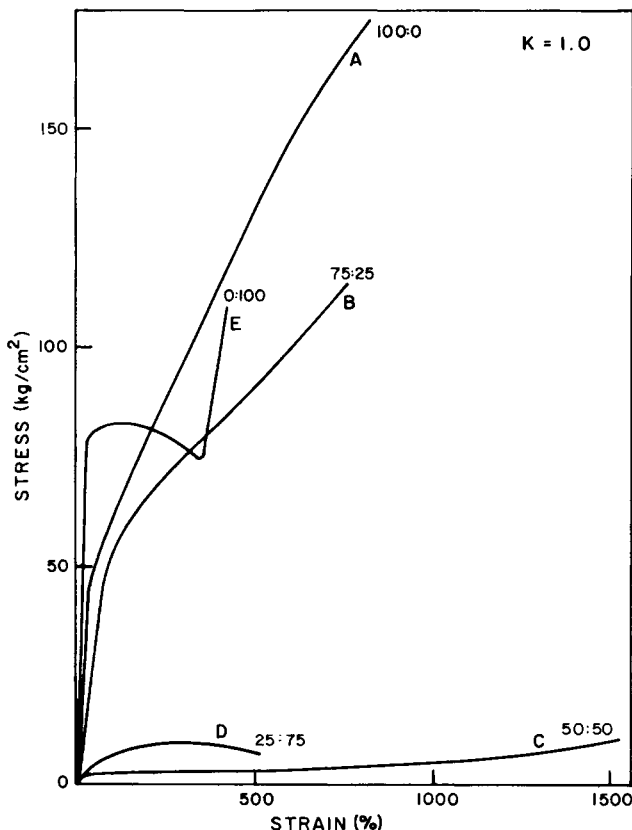


Fig. 3. Stress-strain curves of polyurethanes with $k = 1.0$.

correlated with their dynamic mechanical properties and discussed in the light of the morphology.

EXPERIMENTAL

Preparation of Polyurethanes

The polyester polyols were prepared by reacting adipic acid and either bis(B-hydroxyethyl terephthalate) (BHET) or BHET/ethylene glycol (EG) mixture. Polyurethane was obtained by reacting these polyester polyols with toluene diisocyanate (TDI) in the presence of a NaCN catalyst to form isocyanurate ring crosslinking in accordance with Sasaki's method.⁸ The apparatus and procedure are the same as those reported previously.⁷

The characterization of polyester polyols synthesized is shown in Table I, where five types of polyurethanes are classified according to the different ratios of BHET to EG in the polyester segment.

By varying the $[\text{NCO}]/[\text{OH}]$ ratio denoted by k value, one obtains prepolymers having different degrees of polymerization but the same number-average molecular weights. Therefore, k values also represent the crosslinking densities of these polyurethanes. Stress-strain curves were obtained by using an Instron tester with 500 mm/min extension rate at room temperature. Dynamic me-

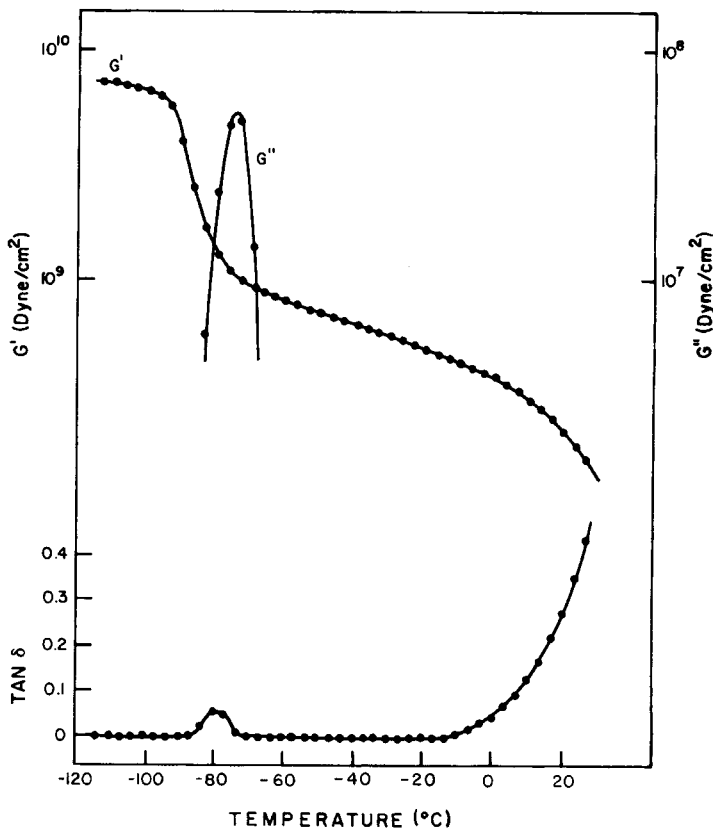


Fig. 4. Dynamical mechanical properties for type A polyurethane with $k = 2.0$.

chanical measurements were achieved by a direct reading dynamical viscoelastomer (Reovibron) in the temperature range of -150 to 20°C . A constant heating rate of $2^\circ\text{C}/\text{min}$ was used in all experiments, and data were taken at 3°C intervals.

RESULTS AND DISCUSSION

Stress-strain curves of the samples with different crosslinking densities of $k = 2.0$, 1.5 , and 1.0 are shown in Figures 1, 2 and 3, respectively. The chemistry of crosslinking reaction might be very complex; the profound effect of crosslinking, however, is evident. Samples A, B, and C exhibit satisfactory elastomer characteristics, but sample E tends to be more plasticlike. Samples C and D show weak strength when the crosslinking density is low (i.e., $k = 1.0$). Sample C, with higher crosslinking density, has the combination of high modulus and good tensile strength, which are of great practical importance. Polyurethane polymers can be modified to either flexible or rigid form, depending on the BHET composition in the polyester segments.

For sample A with $k = 2.0$, the elastic segment is too short and hard to exhibit elastic characteristics. The structure blocks the crystalline part in the soft segment, even when stretched. In fact, the secondary transition temperature

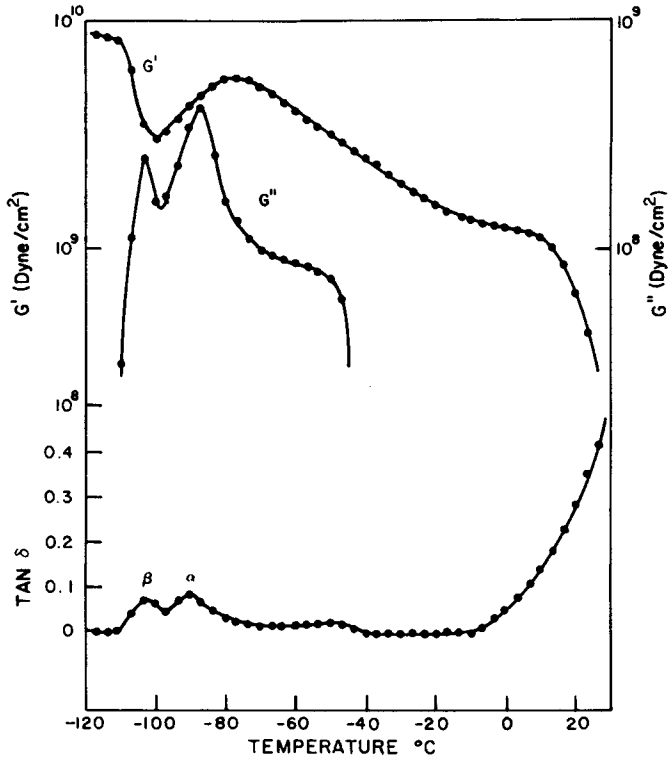


Fig. 5. Dynamical mechanical properties for type A polyurethane with $k = 1.5$.

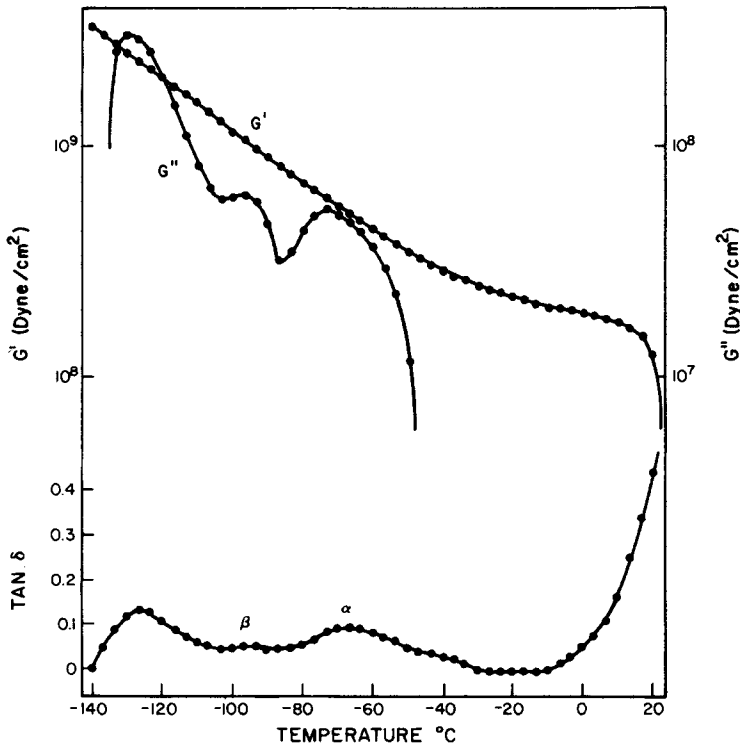


Fig. 6. Dynamical mechanical properties for type A polyurethane with $k = 1.0$.

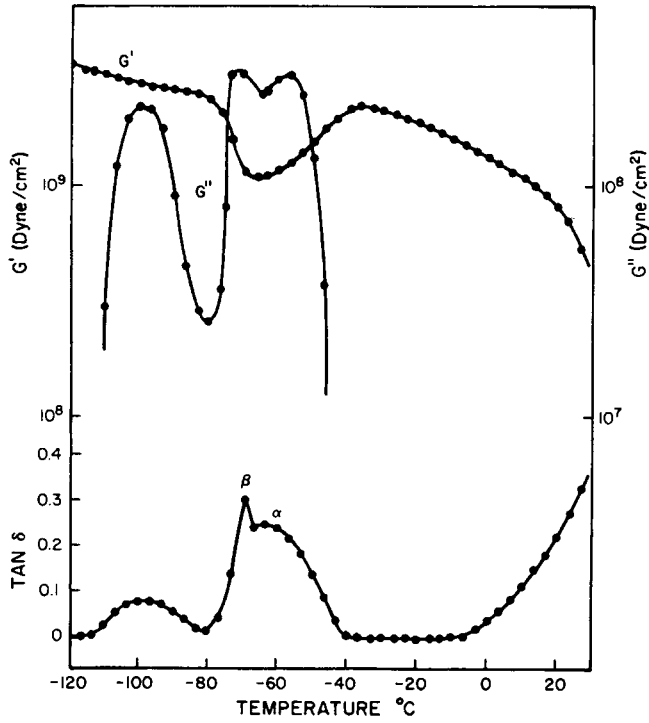


Fig. 7. Dynamical mechanical properties for type B polyurethane with $k = 2.0$.

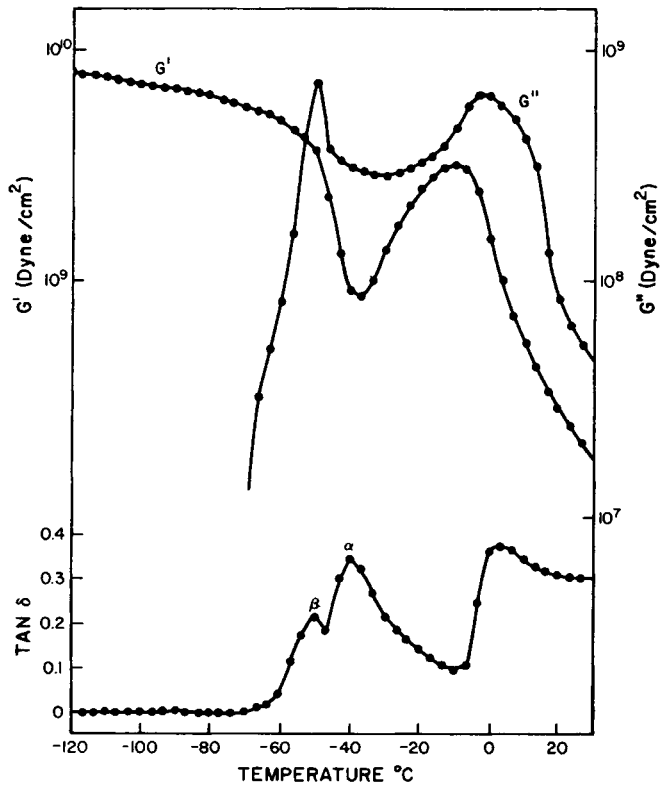


Fig. 8. Dynamical mechanical properties for type C polyurethane with $k = 2.0$.

TABLE II
 T_g and Secondary Transition of Polyurethane

Type	A	B	C	D		
k	2.0	1.5	1.0	2.0	2.0	2.0
T_g ($^{\circ}\text{C}$)	-80	-88	-70	-60	-40	-5
β ($^{\circ}\text{C}$)	—	-105	-95	-70	-50	-40

is missing with a lower glass transition of -80°C (Fig. 4). If one decreases the crosslinking density and, in turn, increases the length of the soft segment by depressing k value of sample A, the β peak appears with a lower glass transition of -88°C (see Fig. 5). With further decrease in k value (i.e., $k = 1.0$), the crosslinking point becomes essentially zero and the material weakens. The α peak shifts to a higher temperature (-70°C). A γ transition appears, indicating the domain formation and the high local segmental mobility (see Fig. 6).

Sample B with $k = 2.0$ exhibits α and β peaks which are almost superimposed because of the combined effects of the two phenomena (Fig. 7). For sample C with $k = 2.0$, the hindrance caused by the benzene ring structure diminishes and the crystalline part becomes easier to grow. A higher glass transition of -5°C is indicated (Fig. 8). Sample E has a transition above room temperature and is no longer a rubberlike material. These transitions are summarized in Table II. Incorporation of BHET in polyester soft segments causes the decrease in

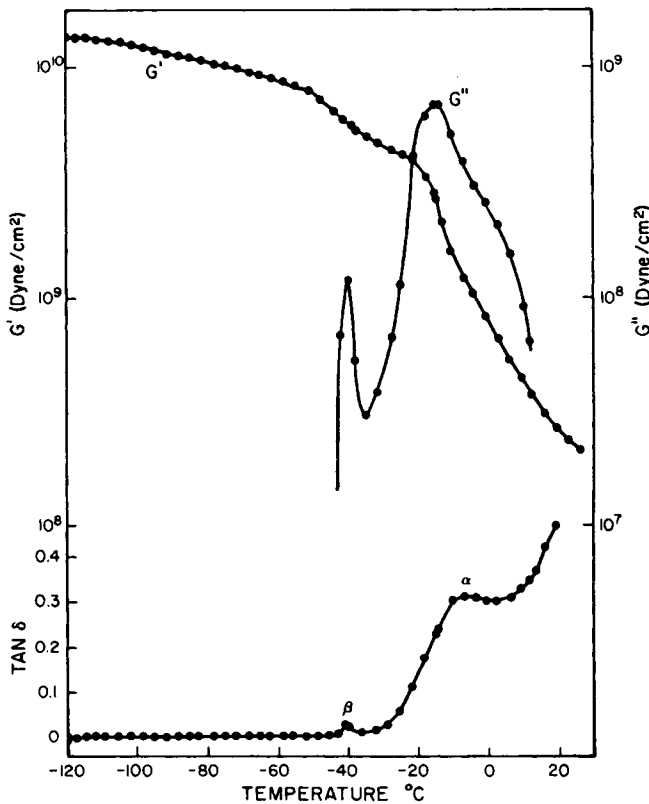


Fig. 9. Dynamical mechanical properties for type D polyurethane with $k = 2.0$.

transition temperature. The combination of high crosslinking density and bulky benzene ring would restrain the long-range movement of polyurethane but leave local segmental mobility. From a domain structure point of view, the incorporation of BHET may prevent crystalline segments from growing, thus resulting in lower transition temperature and mechanical strength. The phenomena observed are consistent with this morphological explanation.

References

1. T. L. Smith, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 1825 (1974).
2. R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
3. G. L. Wilkes, S. Bagrodia, W. Hemphries, and R. Wildnauer, *J. Polym. Sci. Polym. Lett. Ed.*, **13**, 321 (1975).
4. G. L. Wilkes and R. Wildnauer, *J. Appl. Phys.*, **46**, 4148 (1975).
5. T. Nishi, *Appl. Polym. Symp.*, **20**, 353 (1973).
6. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **11**, 1361 (1967).
7. C. C. Lin, P. C. Yu, and L. C. Huang, *J. Appl. Polym. Sci.*, **24**, 1169 (1979).
8. N. Sasaki, T. Yokoyana, and T. Tanada, *J. Polym. Sci.*, **11**, 1765 (1973).

Received February 11, 1980

Accepted March 10, 1980