

Thermoelastic Properties of Urethane Elastomers

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Synopsis

Several polyurethanes based on poly(ethylene adipate), 4,4'-diphenylmethane diisocyanate, 1,4-butanediol, and 3,3'-dichloro-4,4'-diaminodiphenylmethane were prepared. The thermoelastic properties of these polyurethanes depend on compositional variables and are interpreted in terms of the extent and stability of microphase separation.

INTRODUCTION

It is well known that force-temperature measurements at constant length and volume allow calculation of the energetic, f_u , and entropic, f_s , components of the retractive force f of a stretched elastomer. The thermodynamic quantities are given¹ by the equation:

$$f = (\partial U / \partial L)_{T,V} - T(\partial S / \partial L)_{T,V} = f_u + f_s \quad (1)$$

where

$$(\partial S / \partial L)_{T,V} = -(\partial f / \partial T)_{V,L} \quad (2)$$

The symbols U , S , L , T , and V stand for the internal energy, entropy, length, absolute temperature, and volume of the sample, respectively. From the Gaussian theory of rubber elasticity it also follows that the relative contribution f_u/f is related to the temperature coefficient of the unperturbed dimensions of the macromolecular coils, thus making possible the study of molecular processes.

Such measurements have been performed for almost all known elastomers,² but only a few studies³⁻⁵ have dealt with the thermoelastic properties of polyurethanes. These polymers certainly deserve more attention since they offer a great variety of structures. In a general sense urethane elastomers may be considered block copolymers of the $(AB)_n$ type. They are composed of relatively short urethane or urea hard segments and longer, flexible polyester or polyether blocks. The polar nature of the hard segments and their ability to form hydrogen bonds may result in microphase separation or domain formation.⁶ It seemed therefore worthwhile to study thermoelastic properties of some polyurethanes to show how such a structure may influence the properties.

EXPERIMENTAL

Materials

The polyurethanes investigated in this work were prepared in a two-step process. The prepolymer was formed from poly(ethylene adipate) glycol (PEA) marketed by Zachem under the trade name of Poles 60/20, having a number-average molecular weight of 2000, and 4,4'-diphenylmethane diisocyanate (MDI), Desmodur 44, Bayer. The diol was heated to 385 K and degassed for 2 hr at 2–3 mm Hg to remove water and dissolved gas. Then the diisocyanate was added and the polymeric diol–diisocyanate mixture was reacted at 395 K to give the prepolymer which consisted of excess uncombined diisocyanate and diisocyanate-terminated polymeric diol. The prepolymer was mixed either with 1,4-butanediol (BDO) or 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) and poured into a centrifuge equipped with a heating system. After 10–15 min the film had sufficient strength to be removed, and the curing reaction was completed in an oven (24 hr, 395 K). The molar composition of the investigated polyurethanes are given in Table I.

Force–Temperature Measurements

From the obtained films, $100 \times 10 \times 1$ mm bands were cut. The thermoelastic curves were obtained by means of an Instron extensometer adapted for temperature control with an accuracy of 0.5 K. The accuracy of the force readings was 0.05 N. The relative extension varied from 1.0 to 1.5, and the equilibrium stress-versus-temperature relationship was investigated in the temperature interval of 313–380 K. For every extension a separate band was used. The length of the samples was determined by measuring the distance between ink marks with a cathetometer. An accuracy of 0.05 mm was possible. The equilibrium forces required to maintain the length constant were taken at progressively increasing temperatures. Some measurements were repeated at decreasing temperatures. It was found that the stress–temperature relationships were reversible. Thus, the necessary conditions for the thermodynamic relations were fulfilled.

The experimentally found coefficients of $(\partial f/\partial T)_{p,\lambda}$ (λ is the relative extension, i.e., $\lambda = L/L_0$) required a correction factor to be transformed to $(\partial f/\partial T)_{V,L}$. The

TABLE I
Compositions of Investigated Polymers

Polymer	PEA/MDI/BDO	PEA/MDI/MOCA	w_h^a
PU-2	1.00/2.75/1.43		0.29
PU-3	1.00/3.50/2.08		0.35
PU-4	1.00/4.25/2.56		0.39
PU-5	1.00/5.00/3.57		0.44
PU-11		1.00/2.00/0.81	0.26
PU-12		1.00/2.75/1.35	0.34
PU-15		1.00/5.00/3.45	0.52

^a Weight fraction of hard segments.

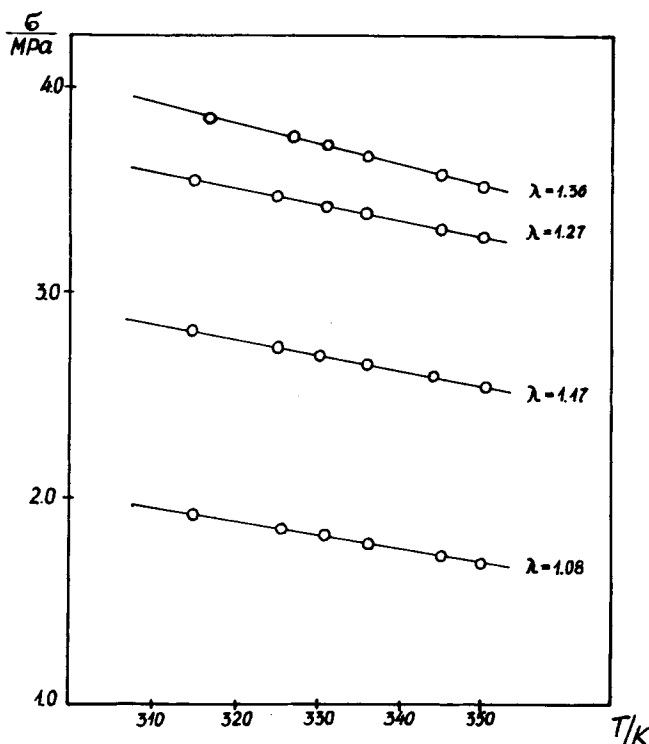


Fig. 1. Dependence of equilibrium stress σ on temperature for PU-4 at different extensions.

correction was calculated from the coefficient of longitudinal thermal expansion according to the formula⁷

$$(\partial f/\partial T)_{P,\lambda} = (\partial f/\partial T)_{V,L} + f\beta \quad (3)$$

where $\beta = (\partial L/\partial T)_P L^{-1}$. The thermal expansion coefficients were obtained from length-temperature measurements data at zero force. They varied from 0.8×10^{-4} to $1.16 \times 10^{-4} \text{ deg}^{-1}$ for MOCA extended polyurethanes and from 1.8×10^{-4} to $3.1 \times 10^{-4} \text{ deg}^{-1}$ for BDO extended polyurethanes.

RESULTS AND DISCUSSION

Typical results of force-temperature measurements obtained in this work are presented in Figure 1. They differ markedly from the results obtained for natural rubber and other elastomers in that the slopes of the lines are negative even for large extensions. The mechanical properties of the investigated polyurethanes are typical of other elastomeric products. Stretching the chains of such products is accompanied by a decrease in the entropy of the materials. As a result of this decrease, $(\partial f/\partial T)_L$ should be positive, eq. (2), which can be predicted theoretically. The theory of elasticity of homogeneous polymer networks leads to the well-known relation between force f and extension ratio λ :

$$f = NkTL_0^{-1}Q(\lambda - \lambda^{-2}) \quad (4)$$

where N is the total number of active network chains in the crosslinked rubber, k is the Boltzmann constant, and Q is the ratio of the mean square end-to-end

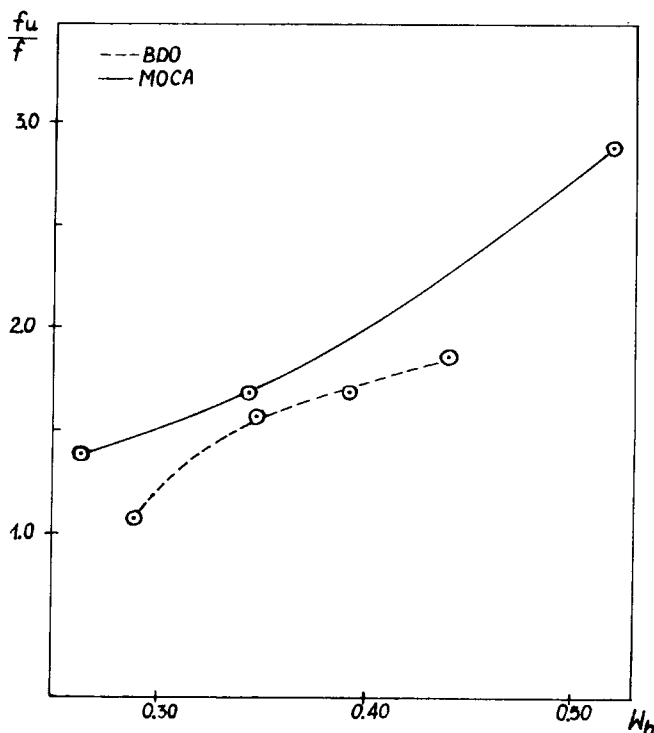


Fig. 2. Relative energy contribution f_u/f vs weight fraction of hard segments, w_h , at $\lambda = 1.3$: (---) BDO; (—) MOCA.

distance of the polymer chains in the undeformed network to that of random coils of the same length. If eq. (4) is differentiated with respect to T while L and P are kept constant (L_0 , however, is temperature dependent) and the temperature variation of Q is ignored, one obtains

$$(\partial f/\partial T)_{L,P} = NkL_0^{-1}Q [\lambda(1 - 2T\beta) - \lambda^{-2}(1 + T\beta)] \quad (5)$$

where β is the coefficient of longitudinal expansion. The values are of the same order for all rubberlike materials⁸ and close to the values found in this work. For the investigated polyurethanes, β is on average $2 \times 10^{-4} \text{ deg}^{-1}$. Thus, at $T = 300 \text{ K}$ the critical value of extension is about 1.06. Below this value one could expect the $(\partial f/\partial T)_L$ coefficient to be negative. This expectation is in satisfactory agreement with the results obtained for rubberlike materials,⁹ but is not confirmed by the results of this work. In other words, the behavior of the polyurethanes deviates much more from the behavior of the ideal networks than does the behavior of other elastomers. Such drastic deviations cannot be explained in the usual fashion, i.e., by network defects such as closed loops, free chain ends, or entanglements. It is much more reasonable to consider the deviations as a reflection of inhomogeneity of the network. On the basis of DTA measurements,¹⁰ however, we exclude crystallinity as a cause of the inhomogeneity. Thus, only microphase separation in the sense of domain formation can explain the observed deviations from the predictions of the statistical theory of rubber elasticity. As a result of these deviations the already mentioned relationship between the temperature coefficient of the unperturbed dimensions and the

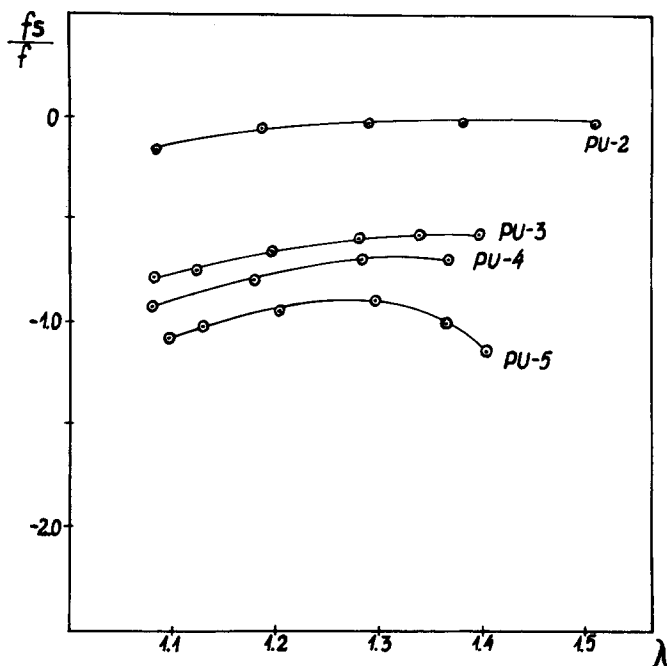


Fig. 3. Dependence of relative entropy contribution f_s/f on extension λ for BDO-extended polyurethanes.

energetic component of the retractive force is totally inapplicable to the systems studied.

A deeper insight into the structure of the investigated polymers can be obtained by analyzing the changes in the energetic and entropic components of the retractive force (Figs. 2, 3, and 4). As is seen from Figure 2, relatively high positive values of f_u have been found which increase while the weight fraction of hard segments, w_h , is increased. The unusual f_u values most probably result from the strain of hard domains during elongation. To the energetic component values correspond equally unusual f_s values (Figs. 3 and 4). To find an explanation of these values it is reasonable to assume that elongation in block polyurethanes probably involves two types of processes. Firstly, flexible polyester chains become more oriented and on further extension a restructuring of hard blocks in new arrangements takes place in the way described by Bonart.¹¹ This gives rise to a decrease in the entropy of the system and to positive f_s values. Secondly, elongation may lead to disruption of the hard regions of block copolymer structure. The latter process is accompanied by an increase in the entropy of the system and negative f_s values. Since f_s values found in this work are always negative, one has to conclude that the orientation effects are more than counterbalanced by the disruption effects. However, there are some differences between BDO- and MOCA-extended polyurethanes. For MOCA-extended polymers, f_s/f values are always more negative. These differences may be ascribed to differences in the extent of microphase segregation. When a diamine is employed as extender, the introduction of urea linkages which enter into strong hydrogen-bonded interactions leads to a higher degree of segregation than it does in the case of diol extended polyurethanes. Thus the volume of material aggregated into domains of hard segments is smaller for BDO extended

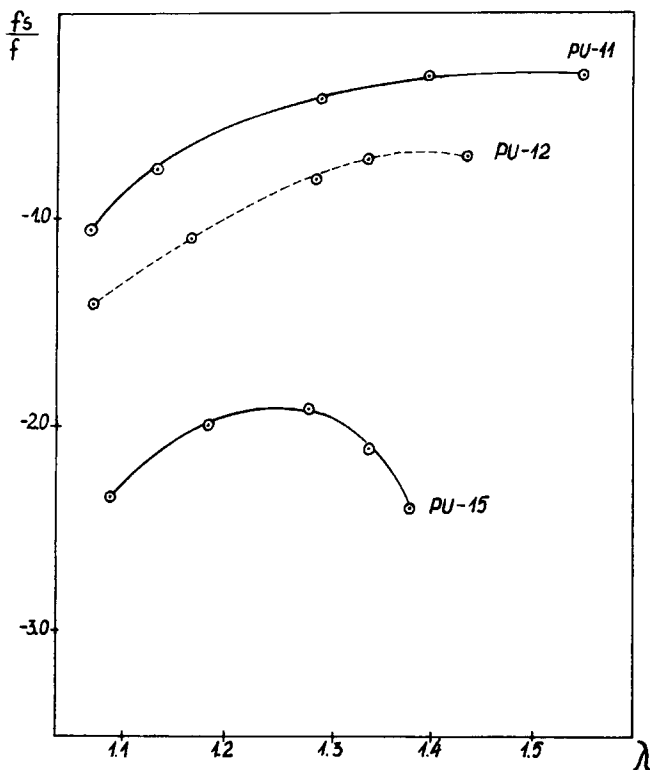


Fig. 4. Dependence of relative entropy contribution f_s/f on extension λ for MOCA-extended polyurethanes.

polyurethanes and the disruption effects contribute to a lesser degree to the equilibrium stress than they do in the case of MOCA-extended polymers.

Both for PU-5 and PU-15 a rapid increase in entropy can be noted when elongation is about 1.3. From the preparation scheme used in this work it should be clear that these two polymers have the lowest weight fraction of soft segment and the longest hard segment lengths. Thus, it may be reasonable to assume that at this extension the flexible chains are stretched to the maximum possible value and further accommodation to extension forces means the rapid disruption of the hard domain structure. For lower values of the weight fraction of hard segments such effects can probably also be observed, but at higher extensions. This conclusion is reinforced by more difficult attainability of equilibrium and by yielding and drawing processes which become manifest at $\lambda = 1.4$.

From comparison of PU-2, PU-3, and PU-4 with PU-11 and PU-12, it follows that the dependence of f_s/f on the relative extension λ is more pronounced for MOCA-extended polyurethanes. It may mean that the increase in the entropy of the systems during extension would be greater for BDO polyurethanes if the extent of microphase separation were the same for both types of polyurethanes in question. It is one more reflection of greater stability of hard urea domains resulting in higher levels of other physical properties of these systems.

Though the obtained data are not complete enough to draw too far-reaching conclusions, the picture emerging from the thermoelastic data is consistent with a variety of other studies on these polymers.

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