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DEFORMATION CALORIMETRY OF POLYURETHANE BLOCK-COPOLYMERS

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A thermodynamic analysis of the uniaxial stretching of polyurethanes of various compositions and mechanical histories was carried out by using deformation calorimetry. The initial small strain deformations were found to result from the volume elasticity of the hard phase. The intramolecular energy contributions of the soft blocks were estimated. The hard block contributions were shown to depend on their content and on the degree of sample stretching. The predominant role of the soft component is proved to be manifested only in softened samples with a hard block content not exceeding 30%. The thermodynamics of the softening and hysteresis phenomena were studied. The dependence of the deformation mechanism on the hard block content and mechanical history is discussed.

Keywords: block-copolymers, deformation calorimetry, polyurethane

Introduction

Within the last two decades, great success has been achieved in the synthesis of block-copolymers (BCP). Attention has been attracted to BCP which consist of alternative soft and hard blocks. At the optimum sample composition (30–50% of hard block), up to the temperature of hard component softening such BCP possess unique mechanical properties: a combination of high rubbery deformability and rigid plastic tensile strength. These materials are referred to as thermoelastoplastics (TEP). Segmented polyurethanes are typical TEP. Their components are segregated on a micro level due to valence bonds between blocks. A strong intermolecular interaction is a specific feature of polyurethanes. It is determined by the block polarity and crystallizability and depends on temperature and stress. All these factors offer difficulties in ascertaining the deformation behavior of such systems. In spite of numerous investigation [1–4], there is no clear view of the individual block contributions to the deformation mechanism of TEP. In our opinion, this problem can be settled by comparing the properties of polyurethanes whose soft block differ in polarity and crystallizability, using a thermodynamic

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approach. This approach is based on the simultaneous registration of the stress-strain curves and thermal effects resulting from the tensile behavior [5]. It consists in an analysis of the entropy and energy effects of deformation. The method proved to be useful and promising in characterizing the elasticity of both homopolymers [6, 7] and a heterogeneous polymer system [8].

Experimental

Samples

The polybutadiene polyurethanes (PBU) with various percentages of hard block were obtained by reacting oligobutadienediol (OB, MM = 2000), chain extender and diisocyanate, the NCO/OH ratio being kept at 1. Triazine containing diol was used as an extender [9]. The content of the hard block in the samples varied from 24 to 79%. The polyesterurethanes (PEU) were produced from polyethylene/butylene glycol adipate (MM = 1940) and diphenylmethane diisocyanate with butanediol. The hard block content was 11–58%.

Method

The thermomechanical behavior was studied at 20°C with the aid of a deformation microcalorimeter in uniaxial extension, at rates of 1.7 and 10 mm/min [10]. Three experimental techniques were applied 1) the extension-contraction mode with an intermediate pause, 2) gradual extension with stepwise elongations of 10–50%, and 3) an extension-contraction cycle without the pause. The values of the mechanical work (*W*) and thermal effects (*Q*) at a given deformation were determined as the areas under the corresponding curves whose shapes are shown in Fig. 1.

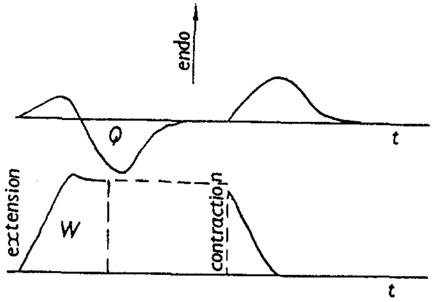


Fig. 1 Thermal and mechanical effects during deformation

The device has two units: the microcalorimeter proper and the deformation unit. The calorimeter function is based on the Tian-Calvet method [11]. The heat fluxes were measured via copper-constantan thermocouples, containing 810 differential junctions prepared by electrolyte deposition. At room temperature, the maximum sensitivity of this calorimeter was ca. 2×10^{-7} J/sec. The time constant was 30 sec. The force was measured with an automatic bridge type dynamometer which had a sensitivity of 0.5 g/mm. The accuracy of measurements of the thermal effects and work was 3%.

For analysis of the soft block energy contribution to the elasticity of BCP, the following expression was used:

$$(\Delta U / W)_{V,T} = (\Delta U / W)_{P,T} - 2\alpha T(\lambda^2 + \lambda - 2)\ [5] \qquad (1)$$

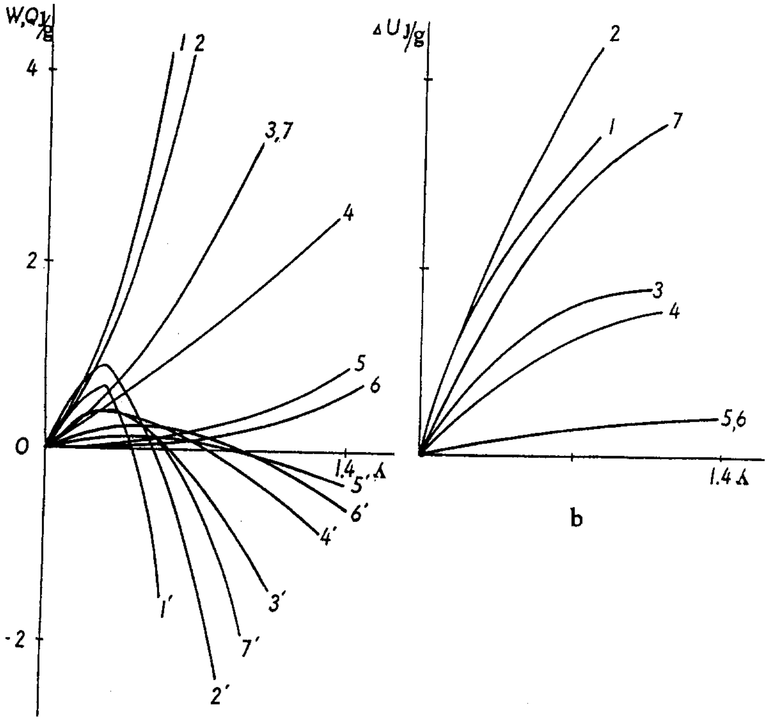
where α is the thermal expansion coefficient, and λ is the elongation.

Results and discussion

DSC analysis has shown that the PBU systems are completely phase segregated, and the PEU are heterogeneous, but the phases are mixed [12].

The small strain deformations up to 7–8% for PBU and 3% for PEU are reversible and homogeneous. They are accompanied by the absorption of heat, increasing with hard phase content and elongation (Fig. 2). The positive changes in the internal energy are similarly dependent on these parameters (Fig. 2b). Similar entropy and energy effects were observed on the small strain deformation of plastics, unfilled and filled rubbers. However, in rubbers the effects are two orders of magnitude lower [6]. In BCP containing more than 20% hard component, the values of the effects are typical for solid polymers [7], and hence the deformation behavior results from the properties of the hard phase. The effect can be explained by the hard phase continuity. It is known that for some BCP this feature can be achieved if the hard block content reaches 20–30% [13, 14]. The BCP containing less than 20% of hard blocks behave as rubber.

The increasing elongation results in neck formation and its propagation. The evolution of heat was observed during the process, so inversion of the thermal effect sign occurs (Fig. 2). In all samples, the mechanical work considerably exceeds the amount of dissipated heat. Abrupt changes in the deformation dependences of the positive energy effect are absent. The values of the observed effects depend substantially on the hard block content and resemble those for the cold drawing of solid polymers [7]. The main difference for the thermomechanical effects of second stretching is the heat evolution during the initial small strain deformation (Fig. 3). A similar heat inversion has been observed for solid polymers [7] after their orientation, and for SBS BCP after stress-softening [15]. However, the reasons for the inversions are quite different. In the solid polymers, it results from the change of the positive thermal expansion coefficient to a negative one. In the SBS samples, this effect is connected with the breakdown of the initially continuous hard domain phase (which was proved by the X-ray method) and the appearance of rubber elasticity in stress-softened samples [15]. The latter conclusion is also true for polyurethanes and is supported by the correlation of the initial endo-effect enhancement and domain dimensions in PBU on increase of the hard block content.



a

b

Fig. 2 PU first loading deformation plots a) W and Q b) ΔU with hard block content for PBU 1–63, 2–79, 3–50, 4–42, 5–24, and PEU 7–58, 6–33 wh.%

The following stretching (at the second mode of deformation) leads to a separation of all samples into two groups. One group consists of polyurethanes containing hard blocks up to 50%: the internal energy of these samples decreases at large deformations. Such behavior is similar to that of conventional filled rubbers and SBS TEP. The samples containing more than 50% of hard block display heat and energy effects which are similar to those of the original samples. However, their absolute values are considerably higher. Note that an increase of the hard block content in such samples leads to a decrease in deformability. Such behavior is close to that of oriented crystalline polymers. Thus, the stress-softening of the polyurethanes of this group can be considered similar to the cold drawing of crystalline polymers. This conclusion is supported by the high energy changes on cycle testing, which accompany hysteresis effects.

An energy balance over the first cycle (Fig. 4) shows that only part of the hysteresis loop is dissipated as heat, as for filled rubbers. Energy is also spent on the changing of the internal energy of the system. It can be seen from Fig. 4 that the energy is stored for all samples except PBU-24, and it increases with hard block content up to that for the solid polymer.

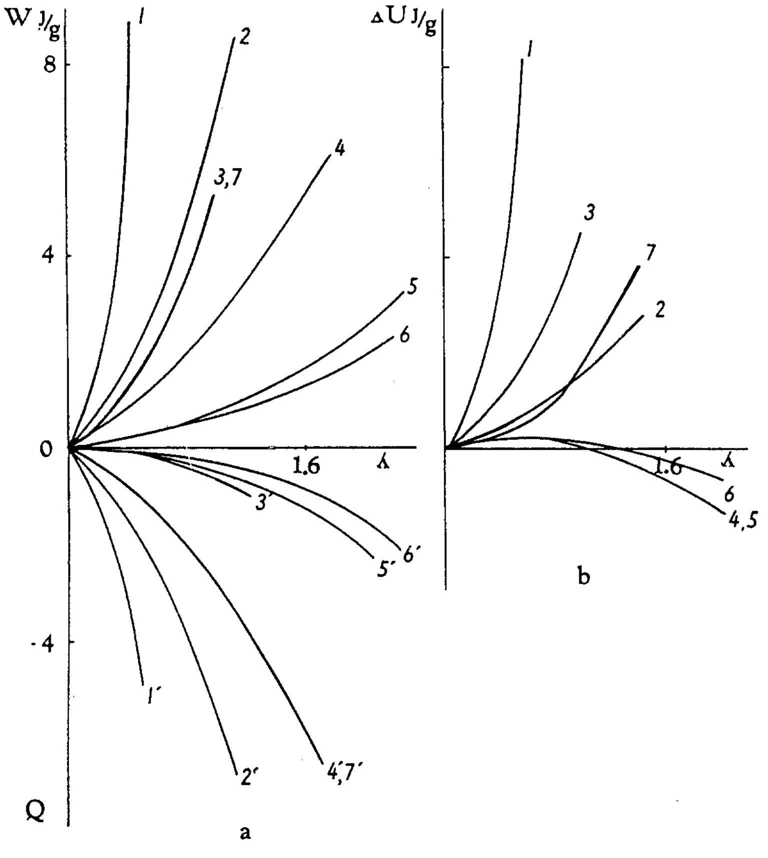


Fig. 3 PU second loading deformation plots a) *W* and *Q* b) ΔU with hard block content for PBU 1–63, 2–50, 3–79, 4–42, 5–24, and PEU 7–58, 6–24

The relative hysteresis parameters (Fig. 5) indicate that the total hysteresis losses depend sharply on the hard block content, but not on the chemical nature of the polyurethanes. They can reach 90% of the work spent on the first loading. The proportion of stored energy is enhanced up to 0.35. The smallest hysteresis is observed for PEU containing 20% of hard blocks. Here, the bulk of the work is dissipated as heat; the energy changes are small. Increasing hysteresis effects for

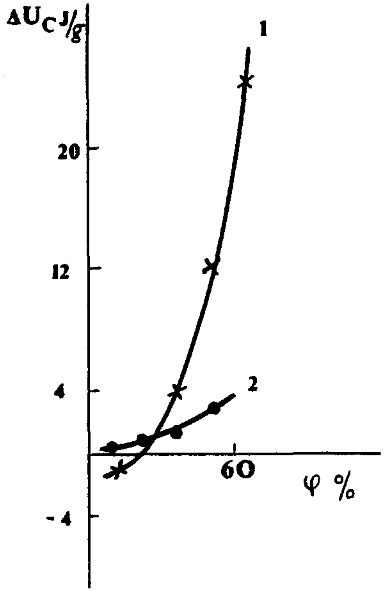


Fig. 4 Internal energy changes *vs.* concentration for PBU (1) an PEU (2)

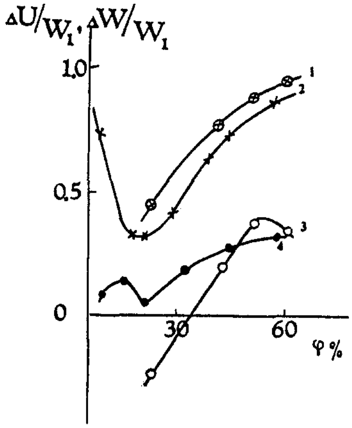


Fig. 5 The relative hysteresis parameters *vs.* concentration $\Delta W/\Delta W_1$ (1, 2) and $\Delta U/\Delta W_1$ (3, 4) for PBU (1, 3) and PEU (2, 4)

PEU-11 should be explained by its homogeneity and by the absence of physical cross-links. The deformation dependence of the stored energy parameters (Fig. 6) indicates that there are slight reductions for the PBU system. This demonstrates that the distortion of hard domains in PBU takes place over the whole elongation region and not merely in the initial one, as for SBS [15]. These parameters of the

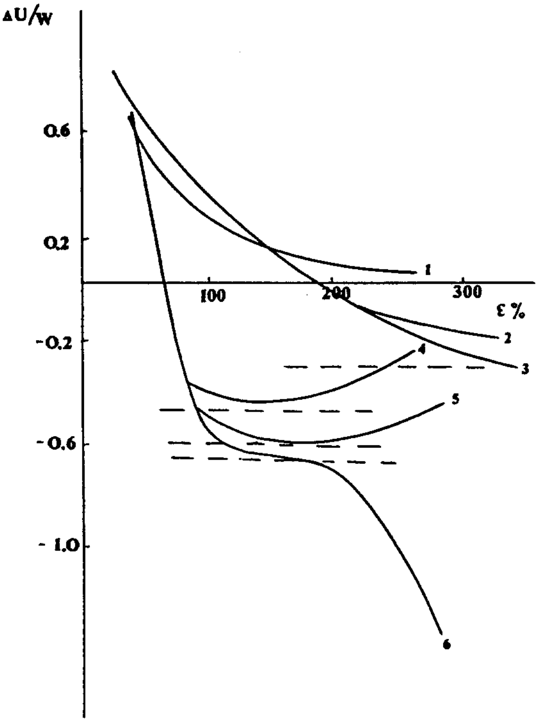


Fig. 6 The relative stored energy parameters *vs*. elongation for PBU-50 (1), 42 (2) and PEU-45 (3), 33 (4), 18 (5)

PEU system vary in a complicated way. Such an effect can be caused by a higher restoring rate of hard phase continuity after stress-softening [16].

To estimate the contribution of soft block elasticity to the total energy changes, the conformation (intramolecular) energy contribution was calculated (Eq. (1)). Softened samples PBU-24, PEU-18, PEU-23 and PEU-33 in test mode '1' were used for this purpose. The results are shown in Fig. 7. It can be seen that the relative energetic parameters can depend on the prior deformation and contraction extents. For instance, the greater the deformation during the stress-softening of PBU-24, the more the internal energy changes, and thus the energy fraction of mechanical work becomes negative. This fraction reaches a minimum (–0.3 for PBU-24 and 0.4 for PEU-33) when reversion of the sample to the original state is restricted. The minimum is rather low, as for the polybutadiene and polyester matrix: only 100% cis-butadiene rubber has such a value of energy contribution [17]; that for polytetramethyleneoxide is –0.65 [18]. Obviously, the difference is caused by the hard block influence. The sharp decrease $(\Delta U/\Delta W)_{P,T}$ for PEU-23 after 200% elongation is explained by soft matrix crystallization, which is supported by the X-ray data.

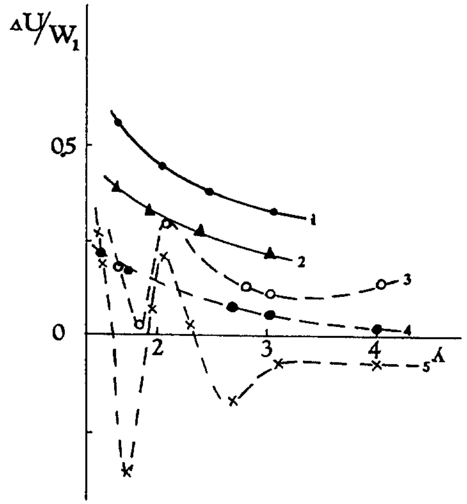


Fig. 7 Deformation dependences of relation $\Delta U/W$ for PBU-24 stress-softened up to 200% (1), 300% (2) and 350% with incomplete contraction (3) and for PEU33 (4), 18 (5), 23 (6) with complete contraction contraction, $(\Delta U / W)_{P,T}$ - straight lines, $(\Delta U / W)_{V,T}$ - dotted lines

Conclusions

The calorimetric investigation results presented show that the hard block play an important role in the deformation behavior of polyurethanes. Heat absorption and the internal energy increase during the initial stretching suggest that their deformation behavior is similar to that of solid polymers. Considerable positive energy effects accompanying the further stretching, and their strong dependence on the hard block content, demonstrate essential intermolecular changes. Under first loading, the rubber elasticity does not predominate, even if the sample matrix consists of the soft phase (its intramolecular energy contributions are negative). The energy effects result from processes taking place within hard domains, such as rearrangement of H-bonds and the hard domain structure under strain. They are responsible for the stress-softening and hysteresis losses.

The hard block content plays the important role in stress-softened samples. If the hard block content is below 50%, the disruption of hard block continuity under first loading results in a plastic-to-rubber transition. After this, the soft phase is decisive as concerns the deformation, although intermolecular parameters reflect the effect of hard domains. The first stretching of samples containing 50% or more of hard blocks is similar to crystalline polymer cold drawing. After this, the soft phase is blocked and its ability of rubber-like deformation is not realized in the pure form.

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Zusammenfassung — Mittels Deformationskalorimetrie wurde eine thermodynamische Analyse der einachsigen Dehnung von Polyurethanen verschiedener Zusammensetzung und mechanischer Vorgeschichte durchgeführt. Für die anfänglichen geringen Stauchungsverformungen wurde festgestellt, daß sie der Volumenelastizität der Hartphase entstammen. Es wurde der intramolekulare Energiebeitrag der Soft-Blöcke geschätzt. Der Beitrag der Hart-Blöcke hängt von ihrem Gehalt und vom Dehnungsgrad der Probe ab. Die dominierende Rolle der Soft-Komponente macht sich ausschließlich in weichgemachten Proben mit einem Hart-Blockgehalt von weniger als 30% bemerkbar. Weiterhin wurde die Thermodynamik des Weichmachens und Hysterese-Erscheinungen untersucht.

Es erfolgt eine Besprechung der Abhängigkeit des Deformationsmechanismus vom Hart-Block-Gehalt und der mechanischen Vorgeschichte.