

Interdependence of Structure and Properties in Segmented Polyurethanes

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Synopsis

On the basis of Clough and Schneider's studies, who investigated segmented polyurethanes with the use of DSC, we assumed that warming may lead to morphological changes in these compounds. We warmed polymers for 10 h in argon atmosphere at 130°. Morphological changes occurring in polyurethanes at a modified temperature were confirmed with an electron microscope and were found to affect to a high degree the mechanical properties of the polymer investigated.

INTRODUCTION

The interdependence of morphology and properties has been discussed in a number of reports.^{1,2} In segmented polyurethanes (PU), which have particularly rich morphological forms,³ this interdependence should be clearly noticeable. The study of physical structure can be facilitated by the use of an electron microscope, which also permits work with a small amount of substance. If a relationship could be detected between the electron-microscopic image of a polymer and its macroscopic properties, then its initial evaluation might be made by means of an electron microscope, particularly when the amount of polymer is small.

EXPERIMENTAL

Polyurethane was obtained by the prepolymer method from adipic acid and ethylene glycol polyester of ca. 2000 molecular weight, *p,p'*-diphenylmethyl diisocyanate (MDI), and 1,4-butanediol at the ratio polyester:MDI:But = 1:3.5:2.5. The synthesis of PU-1 was conducted at 70° and of PU-2 at 125°.

Heating was performed at 130° in argon atmosphere for 10 h. Substances for electron-microscope studies were prepared by two-stage replica from the surface of the fragile polymer fracture.

DISCUSSION OF RESULTS

In our previous studies on the submolecular structure of polyurethanes it was found that certain morphologies determine some polymer properties. To find out what properties and structures were interrelated, it was necessary to individualize the physical structure in samples of identical chemical structures. We based our further work on Clough and Schneider's reports who had observed three transition temperatures in thermoplastic PU.⁴ Samuels and Wilkes⁵ and Seymour and Cooper⁶ had ascribed them to local melting temperatures, leading,

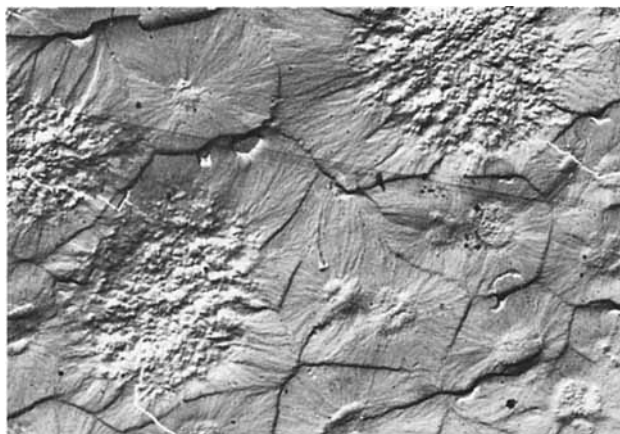


Fig. 1. Transmission electron micrograph of the two-stage replica of PV-1 after the synthesis.

as they supposed, to structures of lower energy. Assuming that these structures are visible in an electron microscope, we heated the sample to obtain various morphological forms for one and the same polymer. The desired effect for the PU investigated was obtained at 130° .⁷ When unheated, the sample was characterized by the morphology shown in Figure 1. The structure is distinctly spherulitic in the polymer volume. Spherulites of the order of $3\ \mu\text{m}$ had a fine-grained structure in their central part. The remaining are radial elements. A characteristic element is grains of various size of the order of spherulites. They differed from the central part of spherulites by somewhat chaotic packing.

After heating, the same polymer was characterized by a supermolecular structure, with two interpenetrating phases (Fig. 2), very similar to that of glass. The granular elements alone remained unchanged. Results of mechanical studies of samples with these structures are summarized in Table I.

We studied not only the structure of the sample here discussed, designated PU-1, but also that of polymer PU-2, whose synthesis was performed with similar raw materials, but under different conditions. Both polymers had a similar spherulitic structure after the synthesis. After heating, both samples had the structure of "interpenetrating phases." Polymers which had been heated are



Fig. 2. Transmission electron micrograph of the two-stage replica annealing in argon atmosphere at 130°C .

TABLE I
Mechanical Studies

Polymer	PU-1	PU-1 ₁₃₀	PU-2	PU-2 ₁₃₀
Modulus M_{100} , MPa	7.0	4.3	3.8	3.2
Tensile strength MPa	40.3	27.4	29.6	7.7
Tear strength, KN/m	8.8	4.1	5.6	4.3
Elongation at break, %	462	550	540	380
Resilience, %	7	24	24	60
Alternating extending strength ^a	77	880	—	—

^a The samples were extended about 50% with frequency of 5 Hz.

denoted by the index 130 accompanying their symbols in table. The change of properties brought about by morphological changes in polymers PU-1 and PU-2 had a similar course.

We included these polymers into the group of block copolymers. Their chains comprise the so-called hard segments formed with diisocyanate and micro-molecular diol and soft segments obtained from polydiol. The interaction of these segments may lead to phase separation and give the domain structure to which the good mechanical properties of the PU are attributed.⁸⁻¹² The domains of hard segments act as network nodule and as an active filler, while the matrix of soft segments imparts greater elasticity to the material. These findings show that the resistance and elasticity of the sample are considerably altered by the elements of the superstructure, which are larger than are the domains. The polymer spherulitic structure observed with electron microscopy is responsible for a reinforcing effect on some strength properties. The mutually penetrating structures slightly lower the modulus M_{100} , the tensile strength, and the tear strength but considerably enhances the alternating extending strength.

Only two of the morphological forms obtained are here discussed. It can be assumed that the properties of polymers may also depend on other elements of their physical structure (their shape and size). Therefore, when the conditions under which these elements are formed are known, the properties of the polymers can be modified in a desired direction.

References

1. L. Holliday and W. A. Holmes-Walker, *J. Appl. Polym. Sci.*, **16**, 139 (1971).
2. N. W. Michajlow, W. I. Maiboroda, et al., *Vysok. Sojed.*, **8**, 2077 (1966).
3. J. Foks, *Polymer*, to appear.
4. S. B. Clough and N. S. Schneider, *J. Macromol. Sci.-Phys.*, **B2**(4), 443 (1968).
5. S. L. Samuels and G. L. Wilkes, *J. Polym. Sci., Part A-2*, **11**, 807 (1973).
6. R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
7. J. Foks and H. Janik, *Proc. 5th Conference on Electron Microscopy in Solid State*, Polish Academy of Science, Warsaw, September 1975.
8. R. K. Bonart, L. Morbitzer, and G. Henze, *J. Macromol. Sci.*, **B-3**, 337 (1969).
9. J. A. Koutsky, N. V. Hien, and S. L. Cooper, *J. Polym. Sci.*, **8**, 353 (1970).
10. J. L. Illinger, N. S. Schneider, and F. E. Karasz, *Polym. Eng. Sci.*, **12**, 25 (1972).
11. S. L. Aggarwal, *Polymer*, **17**, 938 (1976).
12. B. Bonart, *Angew. Makromol. Chem.*, **58/59**, 259 (1977).

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