

Microphase Separation and Properties of Urethane Elastomers

W. NIERZWICKI and E. WYSOCKA, *Technical University of Gdansk, Institute of Organic and Food Chemistry and Technology, 80-952 Gdansk, Poland*

Synopsis

Several polyurethanes were prepared from poly(ethylene adipate) glycol, 4,4'-diphenylmethane diisocyanate, 1,4-butanediol, or 3,3'-dichloro-4,4'-diaminodiphenylmethane. Thermomechanical curves were determined for all investigated systems, and the glass transitions found thereof formed the basis of subsequent analysis. The analysis showed that the investigated systems belonged to those polyurethanes that can undergo microphase separation. It was also shown that the separation in the diamine-extended elastomers was less sensitive to changes in chemical composition than in the diol-extended systems. The diamine-based polyurethanes were also closer to the ideal separation than the diol-extended elastomers. Examinations of elastomers of varying amount of chemical crosslinking revealed a joint action of the crosslinking and microphase separation in determining mechanical properties of the systems. Together with swelling measurements, the examinations showed that optimum mechanical properties were obtained while keeping a very careful balance between these two factors.

INTRODUCTION

In recent years there has been remarkable growth in interest in urethane elastomers. The interest is mainly because of the excellent physical characteristics of the urethane materials and has prompted extensive research activity on the nature of structure-property relations. From the data accumulated during the past 12 years, it follows that many polyurethanes may undergo microphase separation.¹⁻⁵ The polymers are composed of flexible polyester or polyether blocks and hard blocks consisting of aromatic diisocyanate reacted with low molecular diols or diamines. It is the incompatibility of the blocks that results in microphase separation with the hard segment domains dispersed in a soft matrix.

It is now generally accepted that such properties of block copolymers as stress-strain characteristics or strength are governed primarily by the microphase separation. Therefore, it seems worthwhile to study the effect of the type and level of isocyanate, chain extender, and polyol on the extent and perfection of the microphase separation. A great number of such studies have been carried out already, and some reviews^{6,7} of the results are available. In spite of the abundance of experimental findings, however, it is difficult so far to generalize and unify all the data concerning structure-property relations in polyurethane systems. The lack of complete generalization stems from the fact that not only chemical composition but also preparation techniques and processing histories may affect the domain structure. Thus, even the simplest contribution to the knowledge of microphase separation in urethane materials is valuable.

This paper belongs to a series of articles^{8,9} intended to show a correlation be-

tween chemical composition and the extent or perfection of microphase separation in urethane elastomers.

EXPERIMENTAL

Materials

The systems chosen for the study are urethane elastomers based on poly-(ethylene adipate) diol of MW 000 (PEA), 4,4'-diphenylmethane diisocyanate (MDI), and butanediol-1,4 (BDO) or 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA). The polyurethanes were prepared in a two-step process. The polyester was degassed and dried (385 K, 2 hr, 3 mm Hg), and prepolymerization was carried out at 395 K for 30 min. Chain extension was achieved by reaction with the low molecular diol or diamine at 395 K for 10–15 min and completed in an oven for 24 hr at 395 K.

Two different sets of samples were obtained. In the first, stoichiometry was adjusted so that the ratio of isocyanate to hydroxyl groups during chain extension was about 1.5. This set was designated the UBW and UMW series. In the second set, the NCO:OH ratio was allowed to change from 0.94 to 1.21. This set is identified as UB series. The figure following the symbols indicates the weight fraction of hard segments in percent, and B or M refers to butanediol or MOCA. The molar compositions of the investigated samples are given in Table I.

TABLE I
Molar Compositions of the Investigated Elastomers

Polymer	PEA	MDI	BDO or MOCA
UBW-22	1.00	2.00	0.82
UBW-25	1.00	2.35	1.14
UBW-29	1.00	2.75	1.43
UBW-35	1.00	3.50	2.08
UBW-39	1.00	4.25	2.76
UBW-44	1.00	5.00	3.57
UBW-47	1.00	5.30	3.82
UB-45.0	1.00	5.00	4.32
UB-44.4	1.00	5.00	4.01
UB-44.3	1.00	5.00	3.79
UB-44.1	1.00	5.00	3.69
UB-44.0	1.00	5.00	3.59
UB-43.8	1.00	5.00	3.46
UB-43.7	1.00	5.00	3.38
UB-43.3	1.00	5.00	3.12
UMW-26	1.00	2.00	0.82
UMW-33	1.00	2.31	1.09
UMW-36	1.00	2.59	1.36
UMW-42	1.00	3.01	1.72
UMW-45	1.00	3.48	2.08
UMW-49	1.00	4.00	2.63
UMW-52	1.00	5.00	3.50

Measurements

Thermomechanical analysis¹⁰⁻¹² was carried out in tension by means of a TMA-Politechnika Lodzka analyzer. The samples (about $35 \times 10 \times 1$ mm) were cut from uniform sheets and inserted in the clamps of the TMA instrument. Then they were cooled down to 180 K and loaded with a force of 1 N. The samples were subsequently heated at a rate of 2 K/min up to 460 K and their deformation under load was recorded. The measurements were performed with an accuracy of 0.5 K for temperature readings and of 0.25% for relative elongation. Typical thermomechanical curves of the investigated systems are shown in Figure 1. The glass temperatures of soft and hard phases were found at the intersection of a tangent drawn to the ascending branch of the curves with the abscissa axis (for high-temperature transition) or at the intersection of tangents drawn to the branches below and above transition (for low-temperature transition).

Ultimate tensile strength was measured on an tensile tester; the specimens were cut in dumbbell shapes of about 1 mm in thickness.

Swelling measurements were carried out by equilibrating the samples (0.5 g) for two days at room temperature in the following solvents: tetrahydrofuran (THF), dibutyl phtalate, and cyclohexanone. The samples were subsequently blotted and weighed in a closed vessel. The calculations of the swelling degree q , i.e., the ratio of the swollen volume to the dry one, were performed assuming additivity of polymer and solvent volumes. The densities of urethane elastomers were determined by hydrostatic weighing technique.

RESULTS AND DISCUSSION

For copolymers composed of compatible blocks, s and h , the following relationship derived by Fox¹³ may be applied:

$$1/T_g = (w_s/T_{g,s}) + (w_h/T_{g,h}) \quad (1)$$

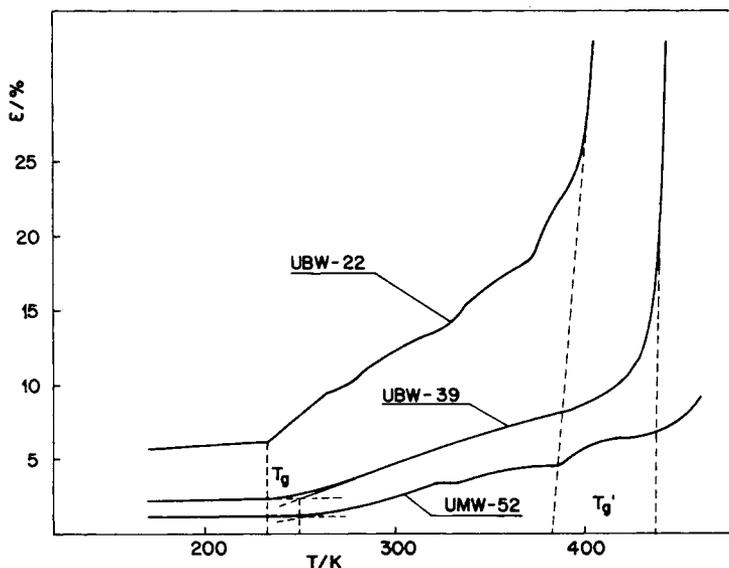


Fig. 1. Typical thermomechanical curves of the investigated systems.

where T_g is the glass transition temperature of the copolymer, w_s and w_h are the weight fractions of the blocks, and $T_{g,s}$ and $T_{g,h}$ are the glass transition temperatures of respective homopolymers. Since $w_s + w_h = 1$, the above equation can be transformed into

$$\frac{1}{T_g} = \frac{1}{T_{g,s}} + \left(\frac{1}{T_{g,h}} - \frac{1}{T_{g,s}} \right) w_h \quad (2)$$

If eq. (2) is applied to the glass transition temperatures of UBW and UMW elastomers, a plot as in Figure 2 is obtained. As seen, the glass transition temperatures may be approximated by straight lines, which leads to the conclusion that the investigated polyurethanes belong to the class of compatible block copolymers. This, however is not the case. Extrapolation to $w_h = 0$ gives $1/T_{g,s}$, which, for BDO-extended elastomers, results in $T_{g,s} = 227$ K, while for MOCA-based polyurethanes, $T_{g,s} = 235$ K is obtained. The tangents of the lines deliver the glass transition temperatures of the homopolymers formed by the hard segments. In this way $T_{g,h} = 289$ K for BDO-MDI homopolymer and $T_{g,h} = 272$ K for MOCA-MDI homopolymer are found. While the values determined for the soft-segment homopolymer, i.e., for poly(ethylene adipate), seem to be reasonable, the ones found for the hard-segment homopolymers are entirely unacceptable.

For poly(ethylene adipate) the glass transition is reported to be 225 K,⁶ and for BDO-MDI polyurethanes the transition was found experimentally to be about 400 K,¹⁴ that is, much higher than the value obtained from eq. (2). Furthermore, since MOCA molecules are more rigid than BDO ones, the glass transition of the hard polyurea segments should be definitely higher than that of BDO-MDI polyurethanes.

On the basis of the unreliable T_g values obtained from eq. (2) for the hard-

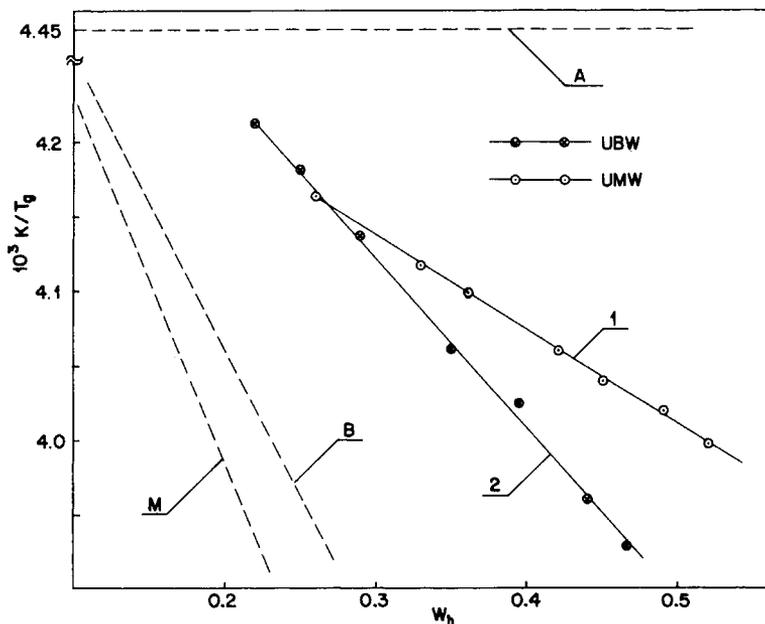


Fig. 2. Glass temperatures of the investigated systems.

segment polymers, it is concluded that the investigated polyurethanes cannot be considered compatible block copolymers. The apparent linearity of lines 1 and 2 in Figure 2 most probably stems from a too narrow range of w_h . It is, however, extremely difficult to prepare urethane elastomers of a broader range of w_h .

In the light of the well-known microphase separation in polyurethanes, the deviations from behavior predicted by eq. (2) may be treated safely as a reflection of the separation. Consequently, the rapid increase in deformation in the high-temperature region (Fig. 1) can be taken as the glass transition temperature of the hard-segment phase.

If the microphase separation in the investigated systems was perfect, the glass transition temperature would be independent of molecular composition and equal to the glass transition of pure PEA. Such a hypothetical situation is shown by line A in Figure 2. The line is consistent with $T_g = 225$ K found for PEA. For UBW elastomers—in the case of compatibility of the appropriate segments—the relation $1/T_g$ vs. w_h should follow line B. The line is drawn to yield $T_g = 400$ K for BDO-MDI homopolymer. Line M represents the UMW series of elastomers assuming compatibility of the soft and hard segments. It is drawn arbitrarily since the glass transition of MOCA-MDI homopolymers is not known to the authors. It provides, however, for the obvious fact that the transition is remarkably higher than that for BDO-MDI polyurethanes. From the thermomechanical curves of UMW elastomers (Fig. 1) it follows that the glass transition of the polyurea segments is at least 460 K.

From Figure 2 it is seen that an increase in w_h causes the glass transition temperature to raise. In other words, the perfection of microphase separation becomes poorer with increase in the amount of hard-segment material. It is also seen that T_g values for MOCA-extended elastomers are relatively stable when compared with the data for the diol-extended polyurethanes. It means that the perfection of microphase separation is more sensitive to changes in chemical composition for BDO-based systems. At the same time the fact reflects greater stability of the domain structure in MOCA-extended polymers. Furthermore, taking the state of ideal separation as a reference, the T_g dependence for UMW-type elastomers is seen to be much closer to the line of ideal separation than for UBW systems, which means that the microphase separation is more complete in the diamine-extended systems than in the diol-based ones. The conclusions are in line with considerations based on thermoelastic measurements⁸ and on partial molar enthalpy of dilution of a solvent⁹ for similar polyurethane systems.

It is well known that urethane elastomers are most often prepared with a molar deficiency of a chain extender. Thus, an overall excess of isocyanate groups remains, and a ratio of NCO:OH about 1:1 is usually preferred for optimum properties. The excess of isocyanate groups is able to take part in crosslinking reactions through formation of allophanate or biuret linkages. It is not, however, precisely clear why above and below the mentioned excess of NCO groups a weak elastomer is produced. Usually, the higher the crosslinking density, the better the values of such mechanical properties as tensile strength. The general relation does not hold in the case of polyurethanes,¹⁷ and below it is shown that the variation of mechanical properties of urethane elastomers with crosslinking density can be also related to the microphase separation.

In Figure 3 the dependence of the high-temperature glass transition, T'_g , together with the tensile strength is shown. It is easily seen that the optimum tensile strength properties correspond to the maximum in the T'_g curve. We base this part of the analysis on the high-temperature glass transition for two reasons. First, the chemical crosslinking in the urethane systems develops within the hard segments. Secondly, as pointed out by Work,¹⁵ the high-temperature glass transition is more sensitive to changes in microphase separation than the lower one.

From thermodynamic considerations¹⁶ it follows that microphase separation becomes easier as molecular weight of the block increases. During polyurethane formation the maximum molecular weight of hard segments is obtained when NCO:OH during the synthesis is exactly 1. Thus, for NCO:OH ratios below and above 1 the separation into soft and hard phases may be expected to be poorer. It obviously results in T'_g lowering. If only this effect operated in the investigated systems, one would obtain the T'_g dependence as given by curve 1 in Figure 4. The maximum of the curve is exactly at NCO:OH = 1. However, one has to take into account at least one more effect. The number of allophanate groups (crosslinks) certainly increases when the ratio NCO:OH is increased. The groups immobilize the hard segments causing the transition temperatures to increase. The contribution from crosslinking effects might be schematically presented by curve 2 in Figure 4. The net effect, with a shift of the maximum, is given by curve 3.

The joint action of the two factors can be also seen through swelling properties of the systems. In Figure 5 swelling degrees in three solvents are shown. Only in the case of tetrahydrofuran do they decrease monotonically with increasing NCO:OH ratio, i.e., the swelling behavior is governed by chemical composition in the usual fashion—the higher the crosslinking, the lower the swelling degree. This is not, however, the case when swelling is done with dibutyl phthalate or

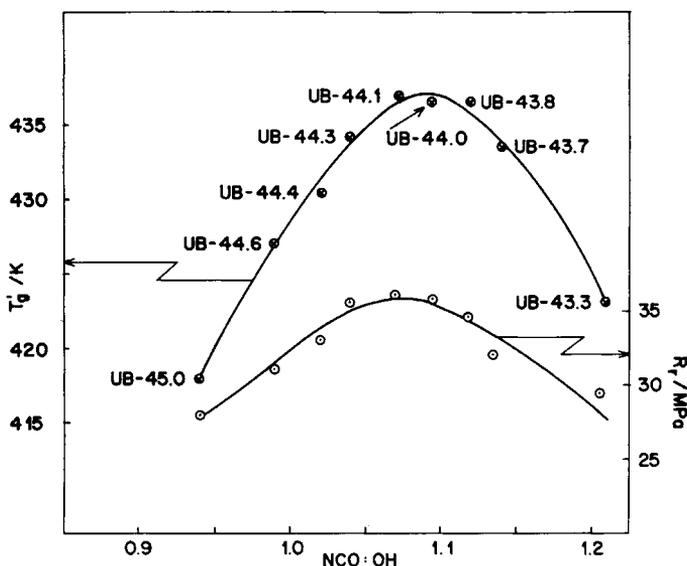


Fig. 3. Tensile strength and glass temperatures of UB elastomers. Temperatures refer to high-temperature transition.

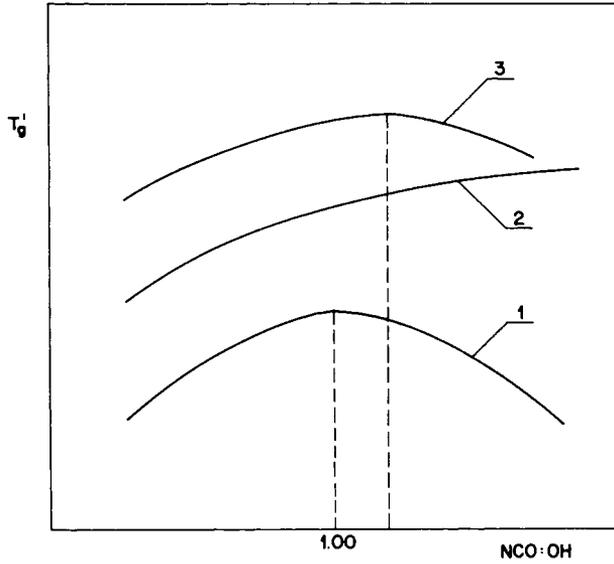


Fig. 4. Glass temperature in relation to microphase separation and crosslinking density.

cyclohexanone. For these two solvents, the swelling degree decreases with the crosslinking density up to $\text{NCO:OH} = 1.1$. For higher values of NCO:OH , the reverse trend in swelling is observed. The variations in swelling are one more reflection of the domain structure of the investigated systems. Apparently, tetrahydrofuran, as a good solvent (high swelling degrees), destroys the domain structure of the polymers so that only effects owing to chemical crosslinking can be detected. For poor solvents, such as dibutyl phthalate or cyclohexanone, the swelling is governed both by chemical and physical (i.e., domain type) crosslinking. From the swelling data it is seen that the contribution owing to mi-

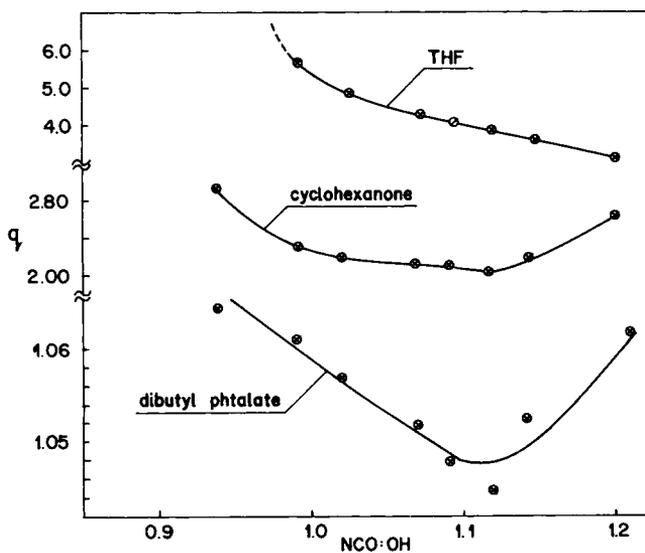


Fig. 5. Swelling behavior of UB polyurethanes.

crophase separation outweighs the effects originating from chemical crosslinking, as exemplified by the increase in swelling in the region of high values of the ratio NCO:OH, i.e., in the region where the average length of hard segments is decreasing with increasing NCO:OH ratio, thus leading to diminished microphase separation.

From comparison among Figures 3, 4, and 5 it follows directly that mechanical properties of urethane elastomers are governed not only by crosslinking density but also by microphase separation, and that optimum properties are obtained while keeping a very careful balance between these two factors.

The technical assistance of Mr. P. Buczkowski is greatly appreciated.

References

1. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1837 (1966).
2. S. B. Clough, N. S. Schneider, and A. O. King, *J. Macromol. Sci. Phys.*, **2**, 641 (1968).
3. R. Bonart, L. Morbitzer, and G. Hentze, *J. Macromol. Sci. Phys.*, **3**, 337 (1969).
4. S. L. Samuels and G. L. Wilkes, *J. Polym. Sci. Part C*, **43**, 149 (1973).
5. Y. P. Chang and G. L. Wilkes, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 455 (1975).
6. D. C. Allport and A. A. Mohajer, in *Block Copolymers*, D. C. Allport and W. H. Janes, Eds., Applied Science, London, 1973.
7. S. L. Cooper and J. C. West, in *Encyclopedia of Polymer Science and Technology*, Supplement, No. 1, Wiley, New York, 1978.
8. W. Nierzwicki and E. Szpilewicz, *J. Appl. Polym. Sci.*, **23**, 2147 (1979).
9. W. Nierzwicki and Z. Majewska, *J. Appl. Polym. Sci.*, **24**, 1089 (1979).
10. V. A. Kargin and G. L. Slonimsky, in *Encyclopedia of Polymer Science and Technology*, Vol. 8, Interscience, New York, 1968.
11. G. W. Miller and J. H. Saunders, *J. Appl. Polym. Sci.*, **13**, 1277 (1969).
12. G. W. Miller and J. H. Saunders, *J. Polym. Sci. Part A-1*, **8**, 1923 (1970).
13. T. G. Fox, *Bull. Am. Phys. Soc.*, **2**, 123 (1956).
14. J. L. Illinger, N. S. Schneider, and F. E. Karasz, *Polym. Eng. Sci.*, **12**, 15 (1972).
15. J. L. Work, *Macromolecules*, **9**, 759 (1976).
16. S. Krause, *Macromolecules*, **3**, 84 (1970).
17. J. H. Saunders, *Rubber Chem. Technol.*, **33**, 1259 (1960).

Received June 21, 1979

Revised September 28, 1979