NCO/NH$_2$ Ratio in Ureaurethane Elastomers and Microphase Separation

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Synopsis

Several polyureaurethanes were prepared from Adiprene prepolymers and 3,3'-dichloro-4,4'-diaminodiphenylmethane. The NCO/NH$_2$ ratio was allowed to vary from 0.97 to 1.29. The polymers were investigated with pulsed NMR technique and characterized thermomechanically. The results show that, contrary to diol extended polyurethanes, the crosslinking resulting from excess isocyanate does not affect the microphase separation developing in these systems. It does affect, however, mechanical properties of these polymers.

INTRODUCTION

The polymers in question are known to possess excellent mechanical properties that are now generally ascribed to the microphase separation of the hard segments from the soft segment matrix. Their properties can be varied in a broad range mainly by changes in the nature of the components and in the ratio of the reacting groups. As far as this ratio is concerned, it is well known[1] that in the cast polyurethane technology usually a slight overall excess of the isocyanate groups is necessary to obtain the best mechanical properties. In previous works from this laboratory,[2,3] it was demonstrated that the properties of polyurethanes based on a polyester, methylene diisocyanate (MDI), and extended with a diol are very sensitive to this overall ratio and was shown that both the amount of the hard segments aggregated into hard domains as well as the amount of the material involved in the interphase formation are remarkably affected by changes in this ratio. It is obvious that the overall NCO/OH ratio determines the extent of allophanate branching and/or crosslinking. From the above quoted works it thus follows that the "allophanization" of urethane groups exerts a very strong effect on microphase separation in the diol extended polyurethanes. On the other hand, the urethane prepolymers are often extended with diamines to produce polyureaurethanes. The introduction of urea linkages which enter in strong hydrogen bonding interactions results in a higher level of mechanical properties and in a more stable structure.[1] The aim of this work is to check to what extent the changes in NCO/NH$_2$ ratio, i.e., the changes in the amount of biuret crosslinking and/or branching, affect the microphase separation and some properties of ureaurethane elastomers. As such, this paper supplements the one already published.[3]

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Polymer symbol	NCO/NH$_2$
AD-0	0.97
AD-1	1.03
AD-2	1.07
AD-3	1.11
AD-4	1.16
AD-5	1.19
AD-6	1.29

EXPERIMENTAL

Materials

The polyureaurethanes investigated in this work were prepared by a pre-polymer method from Adiprene L 167 and 3,3'-dichloro-4,4'-diamino-diphenyl-methane (MOCA). Adiprene L 167 is a TDI prepolymer based on a polyether diol and manufactured by DuPont. The isocyanate content in the prepolymer was $5.9 \pm 0.1\%$. Prior to the reaction with MOCA the prepolymer was de-gassed under reduced pressure (385 K, 3 mm Hg, 10 min). The chain extension was achieved in a centrifuge at about 350 K for 5 min and completed in an oven for 24 h at 350 K. The ratio of NCO/NH$_2$ groups for the obtained polymers was in the range of 0.97–1.29, as is shown in Table I. MOCA was melted before mixing with Adiprene and the mixing was carried out in a small vessel by means of a high speed homogenizer prior to pouring the mixture into the centrifuge.

MEASUREMENTS

Thermomechanical measurements were 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 instrument. Then they were cooled down to 180 K and loaded with a force of 1 N. The samples were heated at a ratio of 2 K/min up to 470 K, and their deformation was recorded. The accuracy for temperature readings was of 0.5 K and that for relative elongations was of 0.25%. A typical thermomechanical curve is presented in Figure 1. The glass temperature of soft phase, T_g, and hard phase, T_g', were determined as shown in this figure.

The NMR measurements were performed by means of a Bruker SXP 4-100 spectrometer operating at 25.5 MHz in the phase-sensitive detection mode, at the Institute of Nuclear Physics, Cracow, Poland. The transverse magnetiza-tion was produced with $\pi/2$ pulse of 2 μs length. The pulses were spaced 1 s apart. For every measurement, 200 decays were collected and averaged by computer (Mera 400). All the measurements were performed at room temper-ature.

The tensile moduli for 100 and 300% elongation, and the tensile strength of the specimens were measured on a tensile tester on the samples of dumbbell shapes and of 1 mm in thickness.
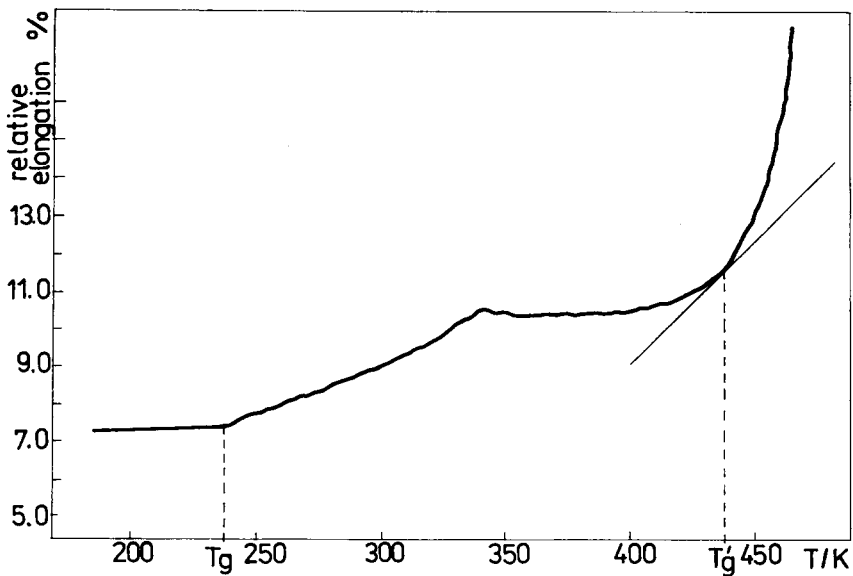
Fig. 1.   Thermomechanical curve of AD-2 polymer.

RESULTS AND DISCUSSION

The glass transition temperatures (the investigated polyurethanes exhibit no crystalline effects as judged by DTA traces) found as given above are shown in Figure 2. Both transitions are almost independent of the NCO/NH$_2$ ratio. As far as the low temperature transition is concerned (soft phase glass transition), its insensitivity to this ratio is basically in line with the findings for diol extended polyurethanes[3] and suggests that the changes in the ratio of NCO/NH$_2$ have no effect on the purity of the soft phase. However, the upper transition (hard phase glass transition) in the diol extended polyurethanes is
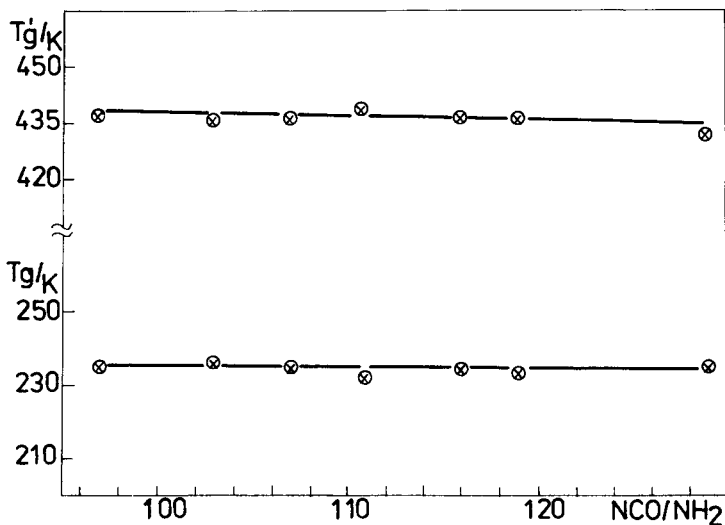

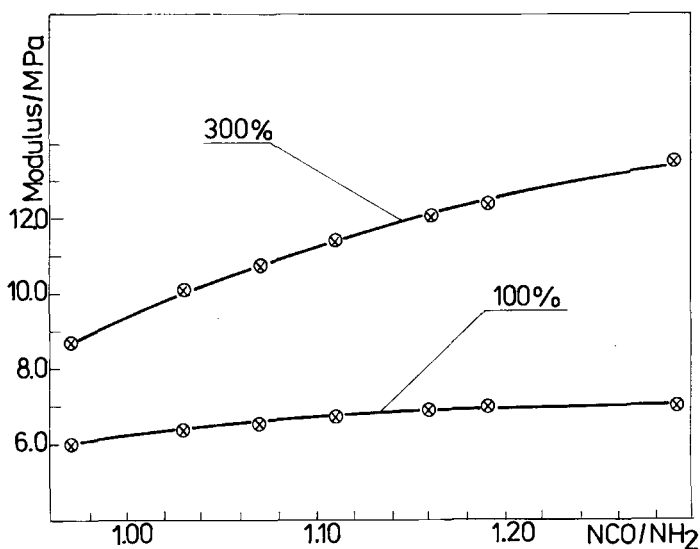Fig. 2. T_g and T_g' vs. NCO/NH$_2$.

Fig. 3.   Effect of NCO/NH$_2$ ratio on modulus in extension.

very sensitive to changes in the NCO/OH ratio and the variation in T_g' is accompanied by distinct changes in mechanical properties.[2] The lack of any essential changes of T_g' in the investigated range for the polyureaurethanes is rather unexpected, the more so as the mechanical properties of these systems do change with changes in the ratio of NCO/NH$_2$, as is exemplified by the tensile moduli presented in Figure 3 and by the tensile strength shown in Figure 4. Thus, it may be suspected that the glass transition temperature does not reflect properly the changes in perfection of the microphase separation. After all, the observed variations in mechanical properties suggest some changes in the microphase separation. In fact, it has been already shown in a previous work[4] that the glass transition found from the thermomechanical
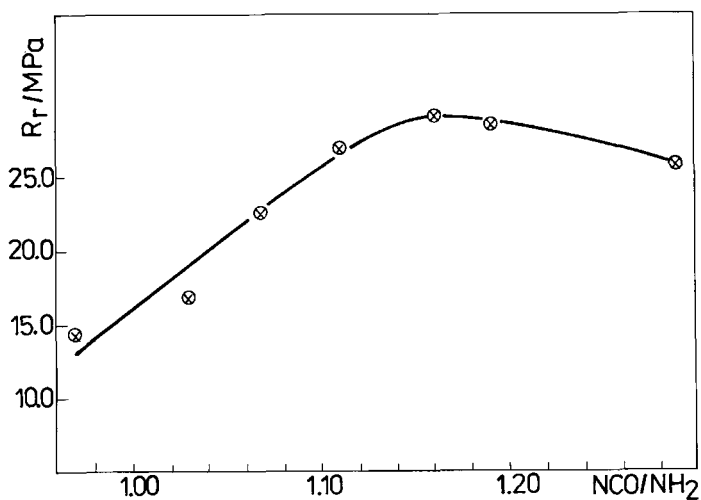

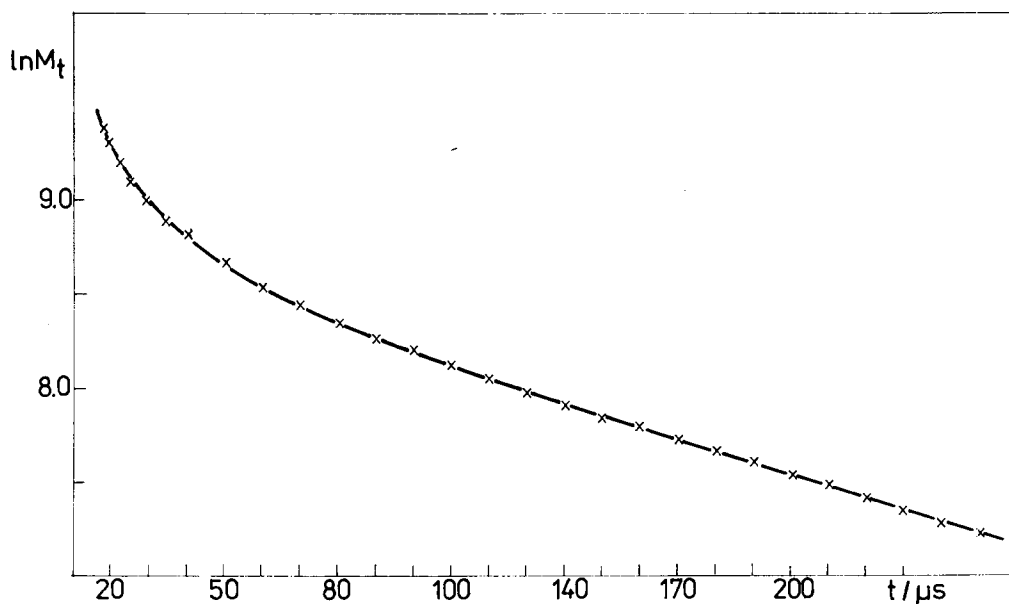Fig. 4.   Effect of NCO/NH$_2$ ratio on tensile strength.

Fig. 5.   The magnetization decay of AD-2 polymer, M_t is given in arbitrary units.

measurements reflects properly the changes in the separation only if the interphase effects are negligible. It is thus necessary to carry out measurements that distinguish between the imperfection of separation consisting in solubilization of hard segments in the soft matrix and the imperfection resulting from the existence of the interphase between the two phases. As was shown,[4,5] this can be achieved with the pulsed NMR technique. Figure 5 presents a typical magnetization decay for an investigated sample obtained from the NMR measurements. This decay can be easily resolved[4] into three components corresponding to the magnetization decays in the hard phase, the soft phase, and the interphase between the phases. Since the magnetization at the beginning of the component decays is proportional to the amount of protons in the respective phases, the fractions of the "hard" protons, "soft" protons, and "interphase" protons can be relatively easily calculated. The results of the calculations are presented in Table II.

The values from this table should be related to the chemical composition of the polymers to calculate the fraction of the segments that are aggregated into respective domains, e.g., the ratio of the hard phase protons to the hard segment protons. Such a fraction would be the most direct measure of the perfection of separation. Unfortunately, the composition of the Adiprene prepolymer is not known exactly to carry out such calculations. The weight percent of the hard segments is, however, approximately constant within the investigated series and consequently the values from Table II reflect indirectly the perfection of the separation as well. As can be noticed, there are no essential differences among the data in the columns of Table II, i.e., the perfection of the separation is not altered by the changes in the NCO/NH$_2$ ratio in the investigated range. Thus, the results of this work seem to indicate that the changes in the mechanical properties of the investigated ureaurethane

TABLE II
Fractions of Protons Involved in Formation of Phases and Interphase (%)[a]

Polymer	Soft phase protons	Hard phase protons	Interphase protons
AD-0	53.0	32.0	15.0
AD-1	49.2	33.3	17.5
AD-2	50.8	31.3	17.9
AD-3	49.3	35.2	15.5
AD-4	49.2	35.1	15.7
AD-5	48.7	32.3	19.0
AD-6	51.9	31.2	16.9

[a] Details of the calculations can be found in Ref. 4.

elastomers are not accompanied by changes in the perfection of the separation. In other words, the quantitative information on the perfection of separation is not sufficient for predicting the mechanical properties of these microphase separated systems. A few words of comment should be, however, given on the origin of the variation in mechanical properties of these polymers (Figs. 3 and 4). As was suggested by Bonart,[6] upon a limited elongation, sliding of some of the hard segments from the domain may take place to distribute the internal stresses produced by the extension forces. This leads to restructuring of hard segments in new arrangements. These slidings may be, however, hindered by crosslinking, which in the case of the investigated systems stems from the biuret groups. The limitation of the sliding processes is equivalent to increased stiffness of the polymers, which is reflected in the increase of the extension moduli (Fig. 3). The above-mentioned effects are more clearly seen for moduli at 300% extension than for the ones at 100%. It is understandable, since larger extensions exert stronger influence on the hard domains than the moderate ones. On the other hand, these sliding processes making possible more uniform distribution of the internal stresses should contribute to the good tensile strength of these materials. Thus, excessive biuret crosslinking should exert deteriorating effect on the strength due to hindering rearrangements of the hard segments within the hard domains. The picture emerging from Figure 4 is, however, more complicated. As is seen, up to NCO/NH_2 about 1.15 the strength is actually improved, while the amount of biuret groups can be firmly expected to be increased on going from AD-0 to AD-4. In the case of diol extended elastomers the dependence of R_r on NCO/OH is similar[2] to the one shown in Figure 4. It is, however, accompanied by remarkable changes in microphase separation,[3] and, considering the hard domains to be multifunctional volume elements, it was quite natural to ascribe the changes in tensile strength R_r to changes in the degree of separation. This reasoning can not be applied to the investigated ureurethane elastomers, as follows from the presented data. One might, however, speculate that the biuret crosslinking is more efficient for higher NCO/NH_2 ratios, while below $NCO/NH_2 = 1.15$ the biuret branching prevails over crosslinking. The biuret branches certainly contribute to the molecular interactions and might act as a stiffening factor at small extensions while at the extensions close to the break they might not prevent the rearrangements within the hard

domains. These speculations would reconcile all the data presented in this work. They are unfortunately rather difficult to test, even if it were easy to distinguish analytically between biuret branchings and biuret crosslinking. Putting aside the speculations about the relation on the strength and biuret branching and/or crosslinking, the author wants to stress the main conclusion of the work. As was already pointed out, in the case of diol extended polyurethanes the effect of excess isocyanate branching and/or crosslinking is seen not only in the mechanical properties of the systems but also in the microphase separation. In other words, the crosslinking and branching is closely related to the separation while in the case of polyureaurethanes the biuret branching and/or crosslinking seem to be an independent parameter controlling the properties of these polymers independently of the microphase separation.

References

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