

# Overall NCO/OH Ratio and Microphase Separation in Urethane Elastomers

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## Synopsis

Several polyurethanes were prepared from poly(ethylene adipate) glycol, 4,4'-diphenylmethane diisocyanate (MDI), and 1,4-butanediol. The overall NCO/OH ratio was allowed to vary from 0.94 to 1.21. Thus, the obtained elastomers differed in the amount of allophanate groups and perfection of microphase separation. These effects were studied by dielectric and pulsed NMR techniques. The results show that quite subtle effects concerning molecular mobility and its restriction due to interfacial region, perfection of the separation, and inadequacy of thermomechanical measurements can be investigated in the presented way.

## INTRODUCTION

In spite of the great attention that has been already paid to the microphase separation of soft and hard segments of polyurethane chains, there are still many unanswered questions concerning the behavior of these systems, even in relation to their chemical composition. One of these questions concerns the effect of allophanate groups on the properties. The formation of these groups proceeds simultaneously with the basic reaction of NCO and OH. However, the rate of allophanate formation is much slower than that of the basic urethane reaction (e.g., Ref. 1). Therefore, the allophanate groups are formed mainly when the chain extension is being completed during annealing, if the overall ratio of NCO/OH is higher than 1. Up to about 40% of the groups that are formed can serve as crosslinking points, while the other groups form only branchings.<sup>2</sup>

As early as in 1968 Cooper et al.<sup>3</sup> investigated the stress softening in MDI crosslinked urethane systems and found that increasing amounts of the diisocyanate led to modulus enhancement due to increased aromaticity but did not prevent rearrangement of the hard domains upon straining, so that the stress softening characteristics of the crosslinked systems did not differ remarkably from their uncrosslinked analogs. Dzierża<sup>4</sup> found that changes in the concentration of allophanate groups exerted no essential effect on the stress-strain properties, as expressed by the ratio of Mooney-Rivlin constants  $C_2/C_1$ . On the other hand, the relative relaxation rate within time interval of 100 s was found to depend strongly on the excess of the crosslinking diisocyanate and was smaller (closer to the ideal rubber case) for higher ratios of the overall NCO/OH. The same author in another work<sup>5</sup> comes to the conclusion that the thermoelastic behavior of segmented urethane elastomers is determined rather by domain structure development in these systems than by allophanate crosslinks, a conclusion that is in line

with data from this laboratory.<sup>6</sup> Other data of ours indicate that a certain level of allophanate crosslinking or branching is beneficial for the tensile strength of these materials.<sup>7</sup>

As is seen from the above given examples, it is not so far possible to generalize the effect of allophanate groups on the properties of urethane elastomers. The chief factor controlling the properties of these systems seems to be the microphase separation. Thus, the effect of "allophanization" of urethane groups should be considered jointly with this separation, and the aim of the present study is to contribute more information on this question and to supplement the work already published in this field.<sup>7</sup>

## EXPERIMENTAL

### Materials

The polyurethanes investigated in this work are based on poly(ethylene adipate) glycol of MW 2000 (PEA), 4,4'-diisocyanate diphenylmethane (MDI), and 1,4-butanediol (BDO). They were prepared in a two-step process by a centrifuge casting technique. Details of the preparation are described in our previous work.<sup>7</sup> The molar composition of the investigated samples are given in Table I.

### Measurements

Dielectric spectra were taken at frequency  $f = 1592$  Hz in the temperature range of 230–450 K. Silver electrodes were deposited onto cleaned, fat-free surfaces of disc-shaped samples by a vacuum evaporation technique. The conductance  $G$  and capacity  $C$  were measured by means of a Tesla BM 484 Bridge and the real part of the dielectric constant  $\epsilon'$  together with the dielectric loss  $\tan \delta$  were calculated<sup>8</sup> as

$$\epsilon' = C/C_0 \text{ and } \tan \delta = G/2\pi fC$$

where  $C_0$  is the capacity in vacuum. During the tests the samples were kept in a chamber filled with neutral gas ( $N_2$ ) under normal pressure. The mea-

TABLE I  
Molar Compositions of the Investigated Polymers

Polymer <sup>a</sup>	PEA	MDI	BDO	NCO/OH
UB-45.0	1	5	4.32	0.94
UB-44.4	1	5	4.01	0.99
UB-44.3	1	5	3.79	1.04
UB-44.1	1	5	3.69	1.07
UB-44.0	1	5	3.59	1.09
UB-43.8	1	5	3.46	1.12
UB-43.7	1	5	3.38	1.14
UB-43.3	1	5	3.12	1.21

<sup>a</sup> The figure following the polymer symbols indicates the weight fraction of hard segments in percent.

measurements were taken at 2–4 K intervals; the equilibrium time was about 30 min. DC current was determined electrometrically under a constant voltage (100 V) by means of a Unipan 219 Electrometer. The steady state current was reached after 14 h, and it was found the DC effects do not affect essentially  $\tan \delta$  characteristics in the investigated temperature range.

Pulsed NMR measurements were performed by means of a Bruker SXP4-100 Spectrometer operating at 25.5 MHz in the phase sensitive detection mode. The details of the measurements and the way the data were processed are given in another work.<sup>9</sup>

## RESULTS AND DISCUSSION

The dielectric constant of polymers can be estimated from the group contributions to the molar polarization, as shown by van Krevelen,<sup>10</sup> and the agreement with the experimental values is more than satisfactory. Applying this method to the investigated polyurethanes, it was found that at room temperature the dielectric constant should be about 3. This value is, however, far from the values obtained experimentally. Typical results of the dielectric measurements are shown in Figure 1, and it is clearly seen that  $\epsilon'$  is much higher than 3 (in fact, within the investigated series, it is in the range 6.5–8.5). The discrepancy between the calculations and experimental data is most probably due to the so-called interfacial polarization,<sup>8</sup> which in the case of this class of polymers should result from their domain structure and consist in trapping mobile charge carriers at the domain boundaries. The charge carriers can come from impurities, although a proton transfer<sup>11</sup> along the chains cannot be excluded. The significance of interfacial polarization in urethane elastomers has been already demonstrated by North and Reid.<sup>12,13</sup> Most probably, a detailed work on the in-

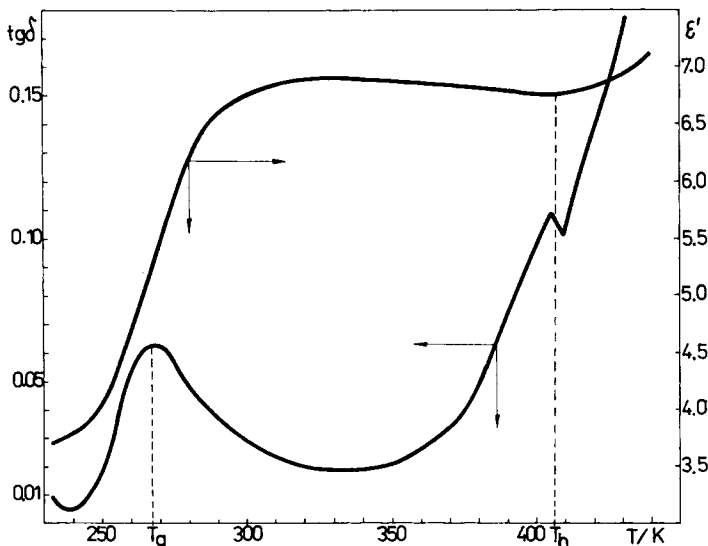


Fig. 1. Dielectric properties of UB-44.4.

terfacial polarization would deliver the most precise dielectric characterization of the heterophase structure. For such a detailed study the domain geometry should be, however, known, while in the case of the investigated elastomers this geometry is difficult to specify. Therefore, in this work, it is only referred to this polarization to stress that the mere value of  $\epsilon'$  found in the polyurethanes in question indicates the existence of domain morphology.

This morphology is also clearly reflected in the temperature dependence of  $\epsilon'$ . As is known, for amorphous polymers (the investigated polyurethanes do not show any crystalline effects, as judged by DTA) such a dependence usually exhibits one maximum only. In a low temperature region (below the glass transition) the dipoles are basically frozen and are not able to line with the electric field. Consequently, the polarization of the sample and its dielectric constant are small. As temperature increases and the glass transition is approached, the influence of the electric field on the dipoles becomes greater, which is reflected in a rise of the dielectric constant (or its real component, if the constant is a complex number). The dielectric constant should increase with temperature only up to a certain point, however. At an appropriately high temperature thermal agitation kicks the dipoles around so violently that the electric field again can exert a relatively small effect on them, only. From this temperature on the dielectric constant should decrease. In the light of what has been said above, the upturn in the temperature dependence observed for investigated elastomers (at temperature  $T_h$ , Fig. 1) is rather unusual. It is, however, easy to explain in terms of the domain morphology originating from the urethane groups aggregated into glassy domains. Apparently, the dipoles attached to the groups are not able to rearrange themselves with respect to the applied field at temperatures below  $T_h$ . Above this critical temperature the glassy domains become devitrified, and the urethane dipoles gain some freedom of motion. Thus, above  $T_h$  two opposite effects are in operation. On the one hand, thermal agitation of the ester dipoles (the dipoles are connected to the soft, flexible segment) is so effective that they are unable to follow changes in the electric field, and this effect tends to decrease the dielectric constant. On the other hand, the urethane dipoles that were frozen in the glassy urethane domains gain the possibility of being aligned more or less parallel in the direction of the field. The latter effect leads to a rise of the dielectric constant. The net effect depends on the relative polarities of the groups in question and on the perfection of separation. Since the urethane groups are certainly more polar than the ester ones, one could really expect the dielectric constant to be increased above  $T_h$ , if the perfection of the separation is sufficiently high. Consequently,  $T_h$  can be taken as a measure of domain stability. The stability in terms of  $T_h$  vs. NCO/OH is presented in Figure 2. To be sure, in Figure 1 is seen that close to the minimum on  $\epsilon'$  vs.  $T$  curve a peak on  $\tan \delta$  vs.  $T$  curve exists. This peak, however, is not so distinctly shaped in the case of other elastomers so that  $T_h$  is determined more accurately from  $\epsilon'$  vs.  $T$  plots.

In the work<sup>7</sup> already quoted the glass transition of the hard domains,  $T'_g$ , obtained from thermomechanical measurements on the same systems, can be found. The glass transition  $T'_g$  also reflects the stability of the domain

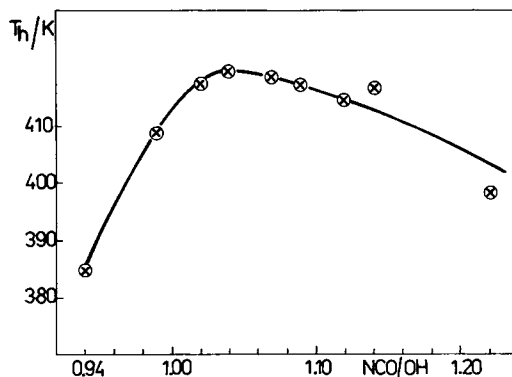


Fig. 2. Domain stability and the overall NCO/OH ratio.

morphology. There is, however, a remarkable difference between  $T_h$  vs. NCO/OH (Fig. 2 in this work) and  $T'_g$  vs. NCO/OH (Fig. 3 in Ref. 7). It should be obvious that the separation is more stable for longer hard segments. Thus, the most stable domains should be obtained when NCO/OH is 1. It is not, however, the case. Both  $T_h$  and  $T'_g$  reach their maximum values if NCO/OH is about 1.1. The shift in maximum for  $T'_g$  was explained<sup>7</sup> as a result of a joint action of allophanate branching or crosslinking and length of the hard segments. The same reasoning presented in the quoted work can be also applied to the shift in  $T_h$ , and in this sense the data published now support the previous conclusions. What makes the difference between the present data and the ones already published<sup>7</sup> is that the drop in  $T'_g$  is basically the same below and above NCO/OH equal 1.1, while  $T_h$  is more stable above this ratio than below it. The average length of the hard segments certainly becomes smaller below and above NCO/OH = 1, but the effects of this drop in length should be, at least partly, compensated by allophanate groups, unless the groups are formed only on urethane segments solubilized in the soft matrix. This suggestion, however, cannot be accepted. In such a case, the above-mentioned shift in  $T'_g$  and  $T_h$  maximum would be difficult to explain. Further, the concentration of urethane groups is obviously higher within the hard domains than in the soft phase, and it is more probable that the excess isocyanate molecules react with urethane segments from the hard domains than with the ones from the soft matrix. Any parameter sensitive to molecular mobility should reflect the presence of allophanate groups within the hard domains. Thus, comparing  $T'_g$  and  $T_h$  dependence on NCO/OH, one must conclude that the effect of allophanate groups is not seen so distinctly in the data obtained from the thermomechanical measurements as in the dielectric ones. It is one more confirmation of the fact<sup>9</sup> that thermomechanical measurements do not reflect changes in the separation in a sufficiently detailed way.

The present findings are additionally supported by pulsed NMR results. This technique makes possible the determination of the quantity of material aggregated into the domains.<sup>9,14</sup> In Figure 3 this quantity is presented vs. the overall NCO/OH ratio. As is seen, the drop in the amount of hard domains is much smaller above NCO/OH = 1.1 than below this value,

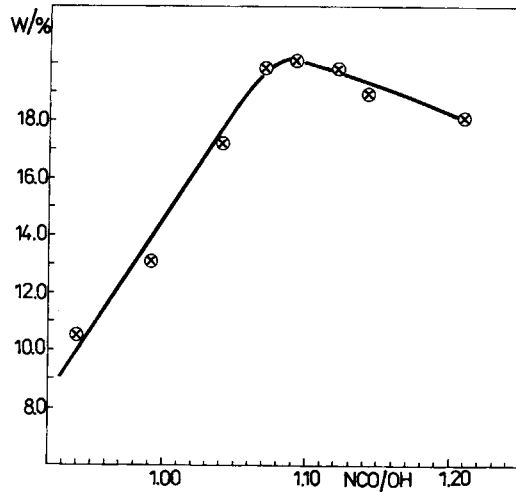


Fig. 3. The weight fraction of the material aggregated into hard domains versus NCO/OH.

which certainly reflects the effect of allophanate groups on domain stability and on rigidity of the system.

From comparison with the chemical composition of the investigated samples (Table I) it also follows from Figure 3 that 30–50% of all hard segments are present within separated domains. Thus, the glass transition of the soft phase should be affected and reflect the changes in the varying perfection of the separation. The glass transition temperature can be taken as the maximum of the dielectric loss ( $T_g$ , Fig. 1), and  $T_g$  vs. NCO/OH is shown in Figure 4. From what has been said above, one could expect the lowest glass transition temperature to be for NCO/OH equal about 1.0, i.e., when the perfection of the separation is the best. Since below and above this ratio the perfection is poorer, the glass transition should be in this NCO/OH region higher. Contrary to the expectations, the dependence shown in Figure 4 is not in line with the above reasoning, even a slightly reverse trend can be noticed. To explain such an unexpected behavior, one must take into account that the mobility of soft phase is controlled not only by the dissolved hard segments but also by the chemical attachment of the soft segment ends to the hard domains, the more so as the border between the soft and hard phases is—at least as a consequence of polydispersity of hard segments—diffuse. Thus, Figure 4 suggests that the anchoring of end parts of

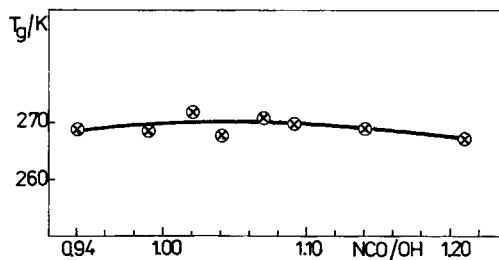


Fig. 4. The glass transition of the soft phase versus NCO/OH.

the soft segments is more restrictive to the mobility of the soft phase than the presence of the solubilized hard segments in this phase, especially if one takes into account that some allophanate groups are dispersed in the soft phase, too. It is obvious that the hard segments with allophanate groups should increase the rigidity of soft phase to a greater extent than the unbranched urethane segments. In agreement with this conclusion are the data shown in Figure 5, where the quantity of the material that is involved in formation of the interfacial layer is presented (this quantity can be also calculated from NMR measurements<sup>9</sup>). It should be noted that the interfacial layer is smaller the poorer is the microphase separation. Consequently, the above-mentioned anchoring effects are much greater for NCO/OH about 1.1 than for the higher and lower ratios. The importance of such anchoring effects for urethane elastomer behavior has been already pointed out in a previous work of the author.<sup>9</sup> Also an earlier work of Seefried et al.<sup>15</sup> can be here quoted. In their work they found that the glass transition of the soft segment was decreased from about 330 to 210 K if the molecular weight of the segments was increased from 340 to 3140. Generally, the glass transition moves up with increase of molecular weight. As the authors explain, the completely reverse trend in the transition is due to a substantial decrease in the restrictive influences on the soft segments, as the length of the segments increases. In the polymers investigated in this work the length of soft segment is constant, so that any restrictive influences on the soft segments can be seen if the hard domains and the interface are affected. Changes in the overall NCO/OH ratio make it possible.

The restriction of mobility of soft segments might be also treated in terms of the so-called interlocking phase model<sup>16</sup> formulated by Seymour and Cooper. According to this model, above a certain hard segment content it is not possible to have independent hard domains and an interlocking structure is formed. The investigated polyurethanes fall in the composition range where the interlocking morphology can be developed and such a morphology might be also taken as a factor limiting the mobility of soft segments. With decreasing hard segment lengths ( $\text{NCO/OH} < 1$  and  $\text{NCO/OH} > 1$ ) these interlocking restrictions are vanishing, which could lead to greater mobility and to lower glass transition. The data presented in Figure 5 favor, however, explanation in terms of the interfacial anchoring.

The results presented here should be accompanied by analytical meas-

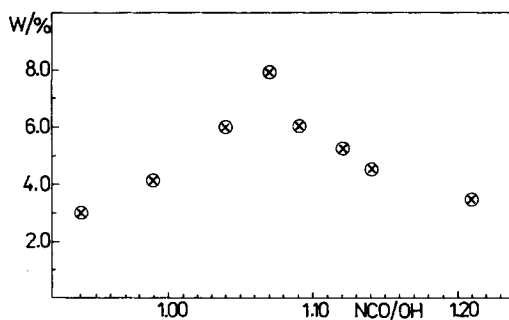


Fig. 5. The weight fraction of the material involved in the interface versus NCO/OH.

urements of the concentration of allophanate groups. Unfortunately, the amine degradation method,<sup>2</sup> which could be employed in this case, does not yield results which are accurate enough. The investigated systems show, however, all features of chemically crosslinked systems,<sup>7</sup> and—keeping in mind the preparation scheme—allophanate groups can be the only crosslinks acting in these polymers. From the results given above and the discussion it follows that it would not be proper to ignore the effects of these crosslinks on properties. Nevertheless, the effects are dominated by the effects originating from the microphase separation.

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### References

1. L. Thiele, *Acta Polym.* **30**, 323 (1979).
2. T. Yokoyama and M. Furukawa, *International Progress in Urethanes*, Technomic, Westport, Conn., Vol. 2, p. 125, 1976.
3. S. L. Cooper, D. S. Huh, and W. J. Morris, *Ind. Eng. Chem. Prod. Res. Dev.*, **7**, 248 (1968).
4. W. Dzierża, *J. Appl. Polym. Sci.*, **22**, 1331 (1978).
5. W. Dzierża, *Makromol. Chem.* **184**, 1519 (1983).
6. W. Nierzwicki and E. Szpilewicz, *J. Appl. Polym. Sci.*, **23**, 2147 (1979).
7. W. Nierzwicki and E. Wysocka, *J. Appl. Polym. Sci.*, **25**, 739 (1980).
8. A. R. Blythe, *Electrical Properties of Polymers*, Cambridge University Press, Cambridge, 1979.
9. W. Nierzwicki, *J. Appl. Polym. Sci.*, **29**, 1203 (1984).
10. D. W. van Krevelan, *Properties of Polymers, Correlations with Chemical Structure*, Elsevier, Amsterdam, 1972.
11. P. Hedvig, *Dielectric Spectroscopy of Polymers*, Akademiai Kiado, Budapest, 1977.
12. A. M. North and J. C. Reid, *Eur. Polym. J.*, **5**, 565 (1969).
13. A. M. North and J. C. Reid, *Eur. Polym. J.*, **8**, 1129 (1972).
14. R. A. Assink, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 59 (1977).
15. C. G. Seefried, J. V. Koleske, and F. E. Critchfield, *J. Appl. Polym. Sci.*, **19**, 2493 (1975).
16. R. W. Seymour and S. L. Cooper, *Rubber Chem. Technol.*, **47**, 19 (1974).

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