

TMA CHARACTERIZATION OF URETHANE ELASTOMERS, WITH THE STRUCTURE VARYING FROM CHAIN TO NETWORK

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TMA has been used to investigate the thermomechanical behaviour of six series of elastomers in connection with their chemical constitution and physical structure. The elastomers were synthesized from an NCO-terminal pre-polymer, based on oligo(ethylene adipate), 1,4-butanediol and 2,4-toluylene diisocyanate, by curing with systems of two agents: a bifunctional one (1,4-butanediol, bistethylene glycol)terephthalate, or mono-ethanolamine), and a trifunctional one (1,1,1-trimethylolpropane or diethanolamine). The TMA results are presented as due to the superposition of the chemical cross-linking and the physical network, formed through microphase segregation. The TMA suggests that diethanolamine unexpectedly acts as a chain extender, rather than a cross-linking agent.

TMA is known to be a most efficient technique for investigating the polyurethanes of different types with respect to their phase structure [1]. Such urethane elastomers (UE) [2] as cured cast soft-chain urethanes may have both linear and network structures, depending on the nature of the curing agent. By reacting bifunctional pre-polymers with various amounts of poly- and bifunctional curing agents, it is possible to pass over continuously from one type of UE to another. The former agents lead to branching and cross-linking (formation of a chemical network), and the latter to chain elongation, whereas the "hard" segments which occur in a multitude of the molecules may undergo self-association and segregate into a microphase, forming hard domains – knots of a specific "physical" network.

Some UE of such a transient type have already been investigated by several techniques other than TMA [3, 4], but in discussions of their intermolecular interactions no special attention was paid to phase segregation. However, it is the segregation and co-existence of both chemical and physical networks that determine many of the specific properties of the UE [5, 6].

In the present work, six series of UE have been investigated. The soft block of the polymers is comprised of an equimolar mixture ($\bar{M}_n \approx 1000$) of oligo(ethylene adipate) $\bar{M}_n \approx 1800$ (OEA) and 1,4-butanediol (BD). On reacting with an equivalent amount of 2,4-toluylene diisocyanate (TDI), the mixture was converted into a pre-

polymer with terminal isocyanate groups. Modification of the starting oligomer (OEA) with BD makes it possible for the latter to participate together with the curing agents in forming the "hard segments", thereby increasing the possibility of microphase segregation.

Mixtures of BD or bis(ethylene glycol) terephthalate (BEP) or monoethanolamine (MEA) with 1,1,1-trimethylolpropane (TMP) or diethanolamine (DEA) were used as curing agents. The proportions of the bi- and trifunctional components were varied. All the UE were prepared with the amounts of the pre-polymer and the curing system strictly equivalent. This is usually considered to prevent the formation of allophane or of biuret bonds, which occurs with excess of NCO groups. As has been shown by X-ray analysis, the elastomers have no signs of crystallinity. The compositions of the polymers studied, as well as the TMA values of the glass-transition and fusion temperatures (T_g and T_f), are given in the table. TMA was performed using an automatic device [7], the loading being constant (0.64 MPa) and the heating rate 3 deg/min.

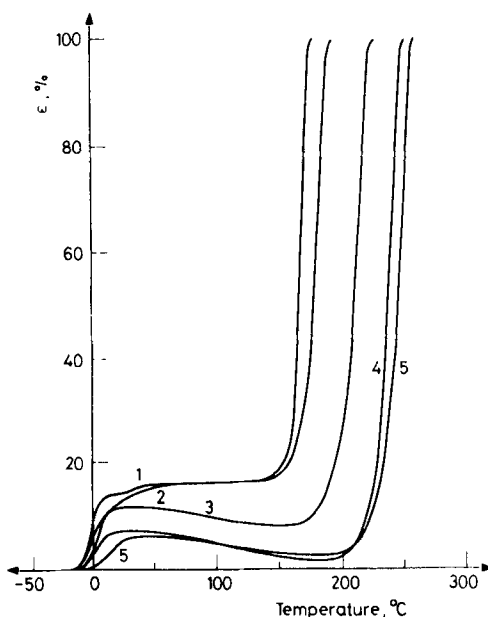


Fig. 1 TMA curves of the urethanes obtained by curing with the system BD-TMP. The content of TMP in the curing system (equivalent %) is: 1-0, 2-10, 3-30, 4-60, 5-100

Figure 1 shows the TMA curves obtained for series I. The thermomechanical characteristics altered regularly, depending upon the relationship BD:TMP. Thus, the T_f 's steadily rise (the alterations in T_g 's are less definite), and the level of the high elasticity plateau becomes lower, as is characteristic of space-structured polymers synthesized from oligomers, when the density of cross-linking rises. At the same time, the plateau itself becomes more and more tilted in the direction of elevated tempera-

Table 1 Curing systems and the TMA values of T_g and T_f for the UE

| Series number | Component contents, eq | | | | | T_g , °C | T_f , °C |
|---------------|------------------------|-----|-----|------|-------|------------|------------|
| | BD | BEP | MEA | TMP | DEA | | |
| I | 1.0 | — | — | — | — | -8 | 163 |
| | 0.9 | — | — | 0.1 | — | -11 | 171 |
| | 0.7 | — | — | 0.3 | — | -6 | 200 |
| | 0.4 | — | — | 0.6 | — | -7 | 232 |
| | — | — | — | 1.0* | — | -1 | 245 |
| II | — | 1.0 | — | — | — | 2 | 51 |
| | — | 0.9 | — | 0.1 | — | 2 | 146 |
| | — | 0.7 | — | 0.3 | — | 3 | 206 |
| | — | 0.4 | — | 0.6 | — | -1 | 232 |
| III | — | — | 1.0 | — | — | -13 | 180 |
| | — | — | 0.9 | 0.1 | — | -11 | 180 |
| | — | — | 0.7 | 0.3 | — | -8 | 195 |
| | — | — | 0.4 | 0.6 | — | -8 | 219 |
| IV | 1.0 | — | — | — | — | -8 | 163 |
| | 0.9 | — | — | — | 0.1 | -6 | 164 |
| | 0.7 | — | — | — | 0.3 | -6 | 176 |
| | 0.4 | — | — | — | 0.6 | -11 | 170 |
| | — | — | — | — | 1.0** | -5 | 179 |
| V | — | 1.0 | — | — | — | 2 | 51 |
| | — | 0.9 | — | — | 0.1 | -1 | 156 |
| | — | 0.7 | — | — | 0.3 | -2 | 172 |
| | — | 0.4 | — | — | 0.6 | -1 | 176 |
| VI | — | — | 1.0 | — | — | -13 | 180 |
| | — | — | 0.9 | — | 0.1 | -6 | 166 |
| | — | — | 0.7 | — | 0.3 | -8 | 176 |
| | — | — | 0.4 | — | 0.6 | -4 | 177 |

* This specimen is to be regarded as the last term of the series II and III as well.

** This specimen is to be regarded as the last term of the series V and VI as well.

tures (cf. curves 3, 4 and 5). Such a "reverse course" of the deformation record is connected with the entropy nature of the high elastic deformation: the elasticity modulus of flexible-chain polymers rises with temperature. In systems in which elasticity is caused by formation of a microheterogeneous structure, such tilting of the plateau is not to be observed. Such are the polymers synthesized without TMP or with only the least amount of it (curves 1 and 2, which do not differ much).

These results are to be compared with those obtained for series II and III (Figs 2 and 3). When the content of the space-structuring agent (TMP) is high enough, the behaviour of the systems with different bifunctional agents becomes rather identical. However, when the content of TMP is low, and especially when it is totally absent,

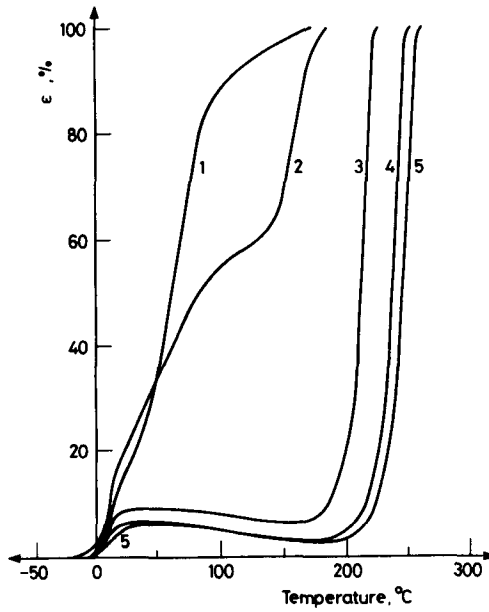


Fig. 2 TMA curves of the urethanes obtained by curing with the system BEP-TMP. Notations as in Fig. 1

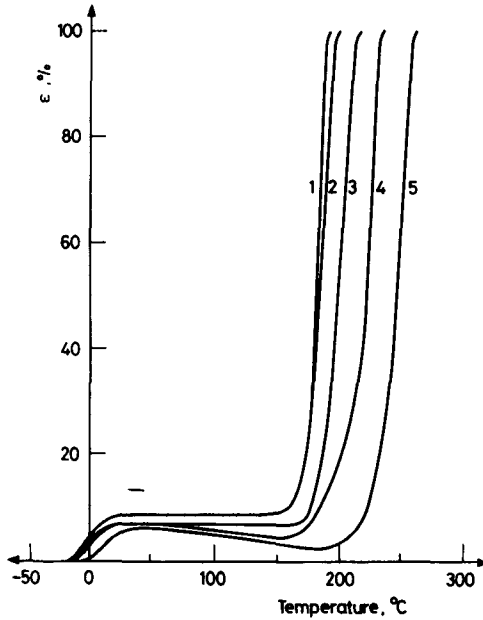


Fig. 3 TMA curves of the urethanes obtained by curing with the system MEA-TMP. Notations as in Fig. 1

the differences in the chain extenders as concerns their effect on forming the properties of an elastomer are well defined.

Thus, in the case of BEP the urethane (as shown by curve 1, Fig. 2) exhibits no properties of an elastomer (there is no distinct plateau in the TMA curve), which may suggest that insufficient segregation is reached. The poor segregation in this case (compared to BD, see curve 1, Fig. 1) may be due to the increased size of the diol-urethane segment, which diminishes the concentration of the urethane groups inside it, the interaction of the latter being the main factor of the self-association of these segments, bringing about the domain structure.

In contrast, in the case of MEA (curve 1, Fig. 3) the domain structure which appears seems to be even more perfect than the one in the case of BD: the polymer exhibits a lesser level of the deformations through the plateau and a higher value of T_f . The latter is probably also affected by the formation of somewhat more thermostable urea bonds instead of some of the urethane bonds.*

TMA of the UE studied leads one to conclude that the "fusion" is connected with the beginning of thermal degradation of the polymer, so that the flow represents the "chemical flow", meaning scission of the chains. This is the only possibility for flow for polymers with a chemical network, but it may also occur in some linear polymers. As for the segmented polymers, it is mainly considered that raising the temperature improves the miscibility of the microphases and leads to the homogenization of the system (and as a consequence to its transition into the flow state) above some critical point.

New tempering of such a homogenized polymer at a suitable lower temperature would involve restoration of the domain structure, as is characteristic of thermoplastic elastomers. However, in particular cases thermal degradation may start at temperatures lower than the critical point of homogenization. The reversibility of fusion and, hence, the recovery of the domain structure may be achieved only when no marked degradation of the polymer occurs.

Valuable information on the states of the polymer may be obtained when analysing specimens thermally pre-treated. For this purpose, a given specimen was heated up to a certain point at the usual heating rate, then quenched in liquid nitrogen, and a TMA curve was recorded - immediately or after tempering at a chosen temperature. (A new quenching then followed.) These experiments show differences in the behaviour of the UE with the chemical net and those without it. The curves obtained for polymers synthesized with only the chain extender (BD) and with only TMP are given in Figs 4 and 5, respectively.

In the first case (Fig. 4) the pre-heating to 200°, as well as to 180 and even to 160°, leads to the loss of the high elasticity properties, which provides evidence on the decomposition of the domain structure. Heating of the same UE to only 80° does not involve such changes; the somewhat higher level of the elasticity plateau, which

*Effects of the nature of the chain extenders on the domain structure of various UE have been studied in [8--10].

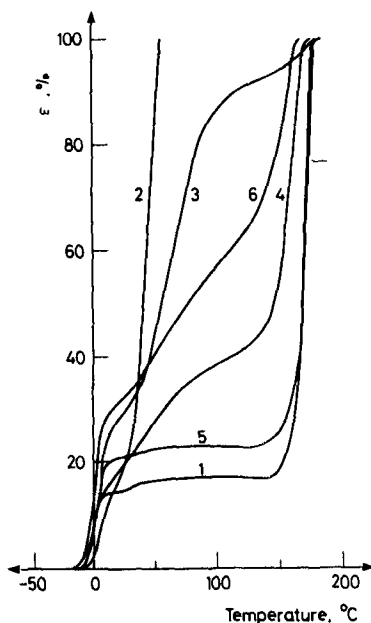


Fig. 4 TMA curves of the UE obtained by curing with the BD, as received (1) and pre-heated to 200°C (2), 180°C (3), 160°C (4), 80°C (5), then quenched. Curve 6 is for a specimen treated as (3), then tempered at 120°C during 10 h

remains undisturbed (curve 5), is solely due to the destruction of the least stable linkages.

The alterations in the polymer heated up to 160–200° seem to be irreversible. Rather long tempering at 80–130° (which is meant to be optimum for the domain formation in UE) does not involve recovery of the original properties of the polymer. The TMA curves of such tempered specimens exhibit only slight shifts (as is shown, e.g. by curve 6, Fig. 4), but still remain very far from the course for the original UE. This suggests that the pre-heating destroys not only the domain structure, but also to some extent even the polymer chains themselves.

The effect of such heating on polymer with a chemical network is quite a different one (Fig. 5). The existence of the network markedly raises the thermal stability of the polymer, though the nature of the linkages is the same as in the main chains (urethane bonds). Heating to 200° proves to be insufficient to destroy the network: the specimen retains both its ability to reversible deformations, and the value of T_f . It is true that after heating the level of the high elasticity plateau becomes much higher (cf. curves 1 and 2), which is a consequence of the dissociation of the less stable linkages, mostly physical. These linkages are easy to restore: one hour of tempering at 80–120° makes their state approach the original one (see curves 3–5). Thus, the maintenance of the chemical network permits recovery of the physical interactions network as well.

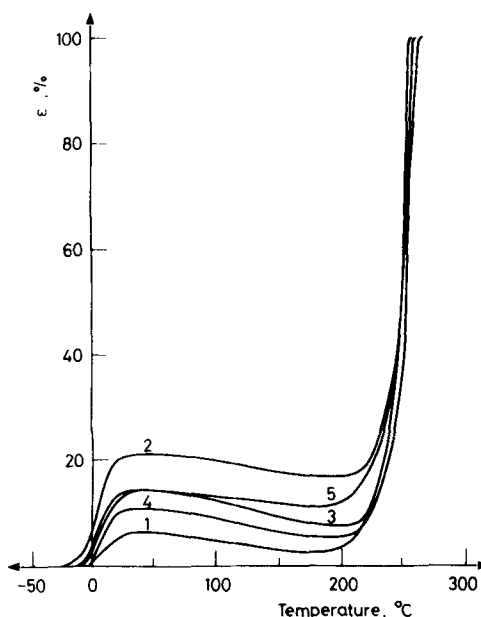


Fig. 5 TMA curves of the UE obtained by curing with pure TMP, as received (1) and pre-heated to 200°C, and quenched, then analyzed immediately (2) and after tempering during 1 h at 80°C (3), 100°C (4), and 120°C (5)

Among the polymers synthesized with mixed curing agents, of greatest interest are the ones which contain the least amount of the triol sufficient for the formation of the chemical network. Evidently, this is achieved with the TMP content being 0.3 M for the series I–III. The results obtained for such a polymer of series I, pre-heated up to 200°, are presented in Fig. 6. Its TMA behaviour is nearly the same as that of the polymer in Fig. 5, showing the presence of the rather thermostable chemical network in this case too. It may be noted that in both cases the best temperature for recovering the physical linkages has been shown to be 100°.

In the series IV–VI, DEA was taken as branching and net-forming agent. The TMA curves for the polymers of series IV are presented in Fig. 7. Consideration of the results obtained makes us conclude that DEA unexpectedly works as a bifunctional agent, rather than a trifunctional one. If DEA were to act as a cross-linking agent, the network might be even more thermostable than in the case of TMP, because of the virtual presence of urea bonds, but in fact this is not the case.

No thermally stable network is formed in the case of the BD–DEA curing system. Indeed, TMA curves are obtained in which the flow branches for all the polymers roughly coincide, independently of the DEA content. Nearly the same is characteristic of the systems BEP–DEA and MEA–DEA too. This is in contrast with the results for systems containing TMP. The plateau of high elasticity is shorter and there is no

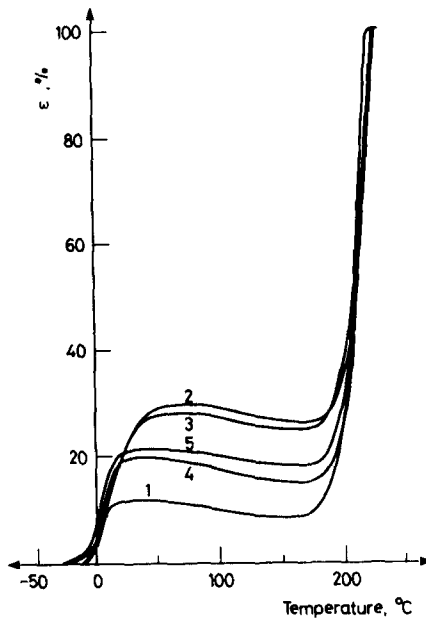


Fig. 6 TMA curves of the UE obtained by curing with a mixture of 70% BD + 30% TMP (equivalent %). Notations as in Fig. 5

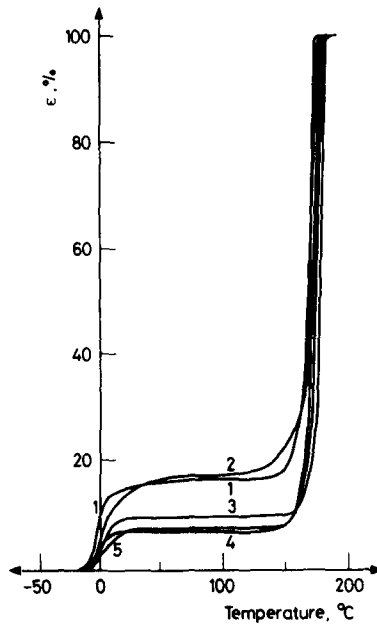


Fig. 7 TMA curves of the urethanes obtained by curing with the system BD-DEA. The content of DEA in the curing system (equivalent %) is: 1-0, 2-10, 3-30, 4-60, 5-100

"reverse course" of the curves, inherent to sufficiently well chemically netted elastomers. Specimens pre-heated and then tempered as the ones above, even with pure "trifunctional" DEA as curing agent, showed TMA curves very similar to those obtained in the case of pure BD (see Fig. 4), i.e. for UE without any thermally stable chemical network.

As DEA works only as a bifunctional agent, 1/3 of the amount of the diisocyanate taken may remain free to react with the urethane groups, forming a network by means of allophanate bonds. The latter are rather thermolabile, but at lower temperatures undoubtedly add to the mechanical properties of the UE, making them good enough. Thus, the reactivity of the secondary amino group in DEA with respect to the NCO-terminal pre-polymer proves to be less than that of the NH group in the urethane linkages.

It is worth noting that Sinyavsky and co-workers [11] used a mixture of DEA and triethanolamine (TEA) as curing agent and stated that the mixture produces UE with better properties than do equivalent amounts of the components taken separately. This may be due to the fact that the components carry different functions supplementing each other: DEA works, as in the presented case, as a chain extender, whereas TEA (as well as the excess of diisocyanate) gives rise to the space network.

Finally, it may be concluded that the TMA of a number of series of UE allowed us not only to estimate the thermomechanical properties of the polymers, which is valuable from the point of view of their practical use, but also to draw rather well-grounded conclusions on their chemical constitution and physical structure. It might be emphasized that the rather unexpected conclusions on chemical reactivity have been made on the basis of the thermal method alone and could hardly be obtained otherwise.

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Zusammenfassung — TMA wurde zur Untersuchung des thermomechanischen Verhaltens von 6 Serien von Elastomeren in Hinblick auf deren chemischer Konstitution und physikalischer Struktur herangezogen. Die Elastomeren wurden aus einem auf Oligo(äthylenadiapat), 1,4-Butandiol und 2,4-Toluylendiisocyanat basierenden, NCO-terminalen Praepolymer durch Vernetzung mit Systemen zweier Agentien, eines bifunktionellen (1,4-Butandiol, Bis(äthylenglykol) terephthalat oder Monoäthanolamin) und eines trifunktionellen (1,1,1-Trimethylolpropan oder Diäthanolamin), hergestellt. Die TMA-Ergebnisse werden als eine Überlagerung der chemischen Vernetzung und der durch Mikrophasensegregation gebildeten physikalischen Vernetzung dargestellt. Die TMA-Ergebnisse deuten darauf hin daß Diäthanolamin unerwarteterweise eher als Kettenverlängerer denn als Vernetzungsmittel wirkt.

Резюме — TMA использован для исследования термомеханических свойств шести серий эластомеров в связи с их химическим строением и физической структурой. Эластомеры синтезированы из преполимера с концевыми NCO-группами на основе олигоэтиленадипината, 1,4-бутандиола и 2,4-толуилендиизоцианата действием системы двух отвердителей: бифункционального (бутандиол, бис(этиленгликоль) терефталат или моноэтаноламин) и трифункционального (1,1,1-триметилпропан или диэтаноламин). Результаты TMA объясняются взаимным влиянием химической сетки и физической сетки, образуемой благодаря сегрегации микрофаз. Показано, что диэтаноламин, вопреки ожиданиям, действует не как разветвляющий агент, а как удлинитель цепи.