

TMA AS A METHOD OF INVESTIGATION OF THE PHASE STRUCTURE OF SEGMENTED POLYURETHANES

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A complex of methodical approaches for investigating structural changes under the influence of temperature are presented on the basis of modern concepts of the domain structure of block copolymers. Effects of formation of structure due to phase segregation, crystallization processes and those of thermal homogenization have been considered in connection with the deformational properties of polymers. One and the same polymer appears to have quite different phase structures and properties when obtained by altering its thermal conditions. Thermomechanical analysis is shown to be a most efficient technique for investigating the changes in the phase structure of a wide series of polyether(ester)urethanes and -urethaneureas.

A specific feature of segmented polyurethanes is their aptitude to phase segregation, i.e. to forming a characteristic domain structure, imparting to them the properties of elastomers [1-3]. For investigation of these compounds we employed thermomechanical analysis (TMA) as one of the well accepted thermoanalytical techniques [4].

In the present work series of polymers with fairly linear structures, based on oligoethers or oligoesters of different molecular masses, have been studied. The "hard segment" consists of diisocyanates and diols (sometimes diamines) of different natures. The synthesis of these polymers was undertaken at the S. V. Lebedev All-Union Institute of Synthetic Rubber, and conducted by Prof. N. P. Apukhtina.

TMA is known to be a very useful technique for investigating polymers [5]. The deformation of a specimen under an appropriate load is continuously recorded at rising temperature. Thus, the curve obtained reflects all the transitions of the polymer.

We used a self-made set, which allowed performance of the TMA at a constant heating rate ($2-3 \text{ degree} \cdot \text{min}^{-1}$) by penetrating under a constant load. In some cases a periodical impulse loading (in addition to a small constant load) was applied, which enabled us to record the compliances at a series of points. The duration of the impulses varied from 10 to 120 sec, and the periods were 2 or 4 min [6].

Results

A well-known TMA curve characteristic of rubber is shown in Fig. 1a [7]. The corresponding curve recorded using impulse loading is shown in Fig. 1b. The shapes of the TMA curves of urethane thermoplastic elastomer are the same in principle too, which is a result — as well as evidence — of phase segrega-

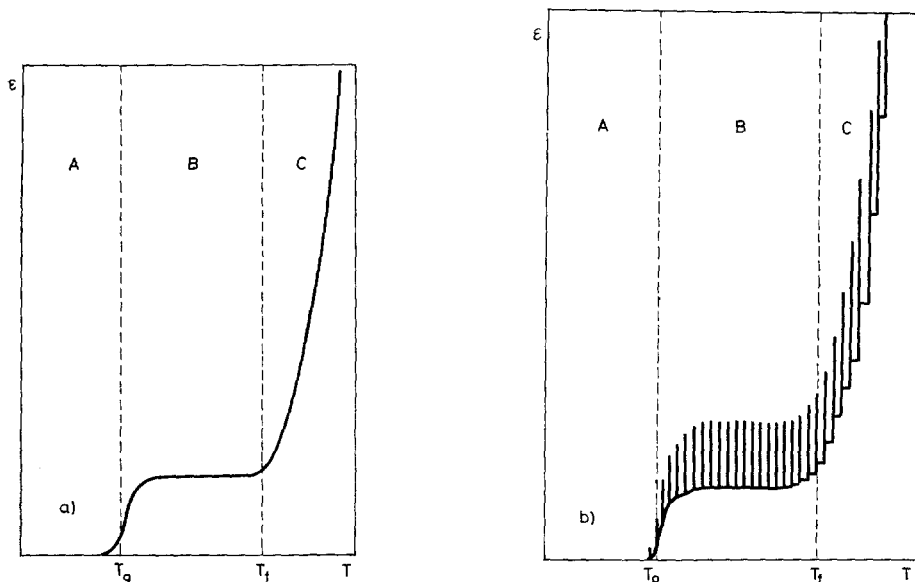


Fig. 1. Schematic TMA curves of a polymer. A, B and C are the areas of glassy, high elastic and viscous-flow states, respectively; T_g = glass-transition and T_f = fusion temperatures. a — constant load, b — impulse load (superimposed with a tiny constant additive)

tion. In this case the glass-transition (at T_g) is due to softening of the phase consisting of oligomer blocks, the fusion (at T_f) being due to fusion — or melting — of the other phase, i.e. the domains formed by association of the hard segments.

However, the curves obtained are often rather complicated. When the “soft” block is more or less crystallized, elastic deformations are reduced, so that the TMA curve shows a jump at the melting point of the crystals (Fig. 2). For a specimen pre-heated above the melting point and then quenched, no such jump is observed.

Crystallization sometimes proceeds in the course of the TMA. It is most clearly detectable by the impulse method (Fig. 3). The decrease of the deformation amplitude is due to crystallization; the following increase of the amplitude is indicative of the melting of the soft block phase. If the specimen has been crystallized prior to the TMA experiment, the corresponding curve looks like that in Fig. 4. Having been crystallized, the “soft” block behaves as a hard component.

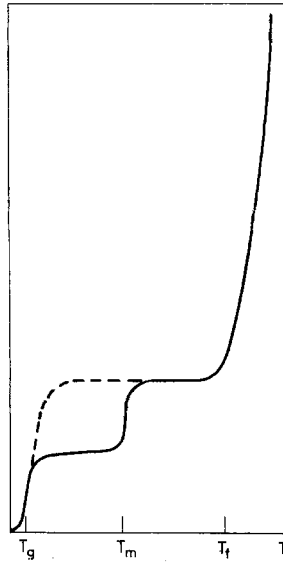


Fig. 2. Schematic constant-load TMA curve of a partly crystalline polymer (solid line) and the same after being heated above the melting point, T_m (dashed line)

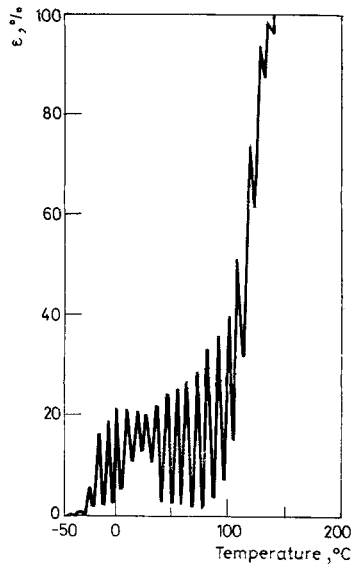


Fig. 3. Impulse TMA curve of a polyesterurethane undergoing crystallization of the oligoester block during the TMA experiment. (Loads of 3.20 and 0.063 MPa alternating each 2 min.)

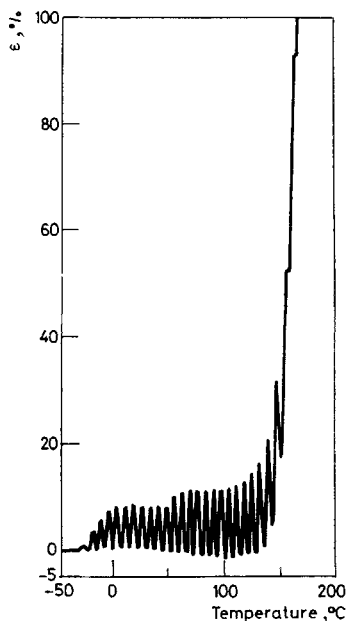


Fig. 4. Impulse TMA curve of a polyesterurethane, the oligoester block being crystallized prior to the TMA experiment. (Loads of 1.63 and 0.063 MPa alternating each 2 min.)

As regards the crystallization of the "real" hard diolurethane (or diamine-urea) segments, the melting points may usually be said to be higher than the fusion temperatures of the same uncrystallized polymers.

Viscoelastic properties, values of transition temperatures as well as crystallizability depend on the nature and lengths of the blocks. Thus, the longer the block, the more it is apt to crystallize. This is true for both the hard and the soft segments. Crystallization of one of the blocks markedly hinders the same process for the other one. Polyetherurethanes usually exhibit T_g 's lower than those of polyesterurethanes. Polymers containing urea groups exhibit T_f 's higher than those of pure urethane polymers.

For any polymer investigated, the specimens may differ in degree and even in character of phase segregation, which greatly depends on the thermal history of the material. Different states (the limiting ones being homogeneous and completely segregated) may be attained by thermal treatment, quenching and annealing. Increase of the temperature usually leads to homogenization. Lowering of the temperature, on the other hand, drives the system to phase segregation. Whether or not the formation of a homogeneous system occurs in a particular case depends on the interrelations of the segments, the latter being considered to be components of some kind of a liquid-liquid system.

Materials in which homogenization does occur lose their original properties of elastomers; the TMA curves exhibit elevated T_g 's and degeneration of the elasticity

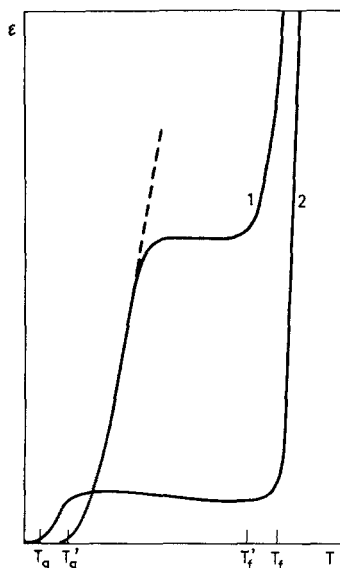


Fig. 5. Schematic constant-load TMA curve of a homogenized urethane thermoplastic elastomer undergoing structure formation during the TMA experiment (1). The dashed branch shows the imaginary case when no structure formation would take place. 2 is the curve for the starting material. Note the shifts of the T_g and T_f points due to homogenization

plateau. Yet during a certain period, when the temperature conditions allow, processes of structure formation due to phase segregation proceed once again and the properties are restored.

These processes may even be observed immediately in the course of the TMA of homogenized specimens (Fig. 5). Increase of deformation, which starts from the T_g on, when reaching a certain temperature grows slower and a distinct horizontal plateau appears, which serves as evidence of structure formation, making plastic deformations for the material impossible. The level of elastic deformations diminishes too, as is shown by means of the impulse load for a certain homogenized polyurethane (Fig. 6).

Homogenized polymers may undergo different routes of structure formation, so that different, as it were "structural modifications" of the same substance may be obtained, all of them exhibiting different thermomechanical properties. Figure 7 shows some noteworthy results obtained for one of the polyetherurethaneureas studied. Curve 1 is characteristic of a thermoplastic elastomer. Heating up to 220° followed by quenching makes it rather homogeneous (curve 2).

Such an amorphized polymer at room temperature undergoes crystallization of the oligoester block. When the melting point of this block is reached, the specimen passes into the flow state (curve 3). Thus, curves 1 and 3 reflect two quite different phase structures: the dispersed phase consisting of domains, formed by the associ-

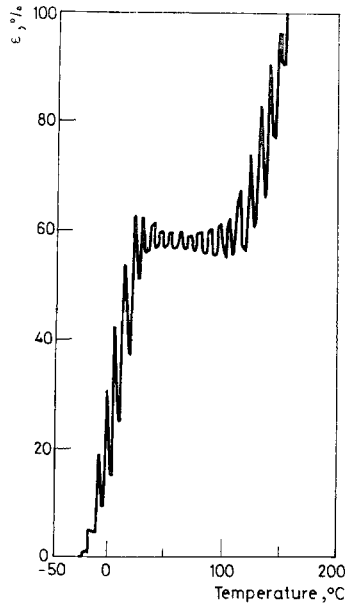


Fig. 6. Impulse TMA curve of a certain homogenized thermoplastic elastomer showing structure formation. (Loads of 0.69 and 0.063 MPa alternating each 2 min.)

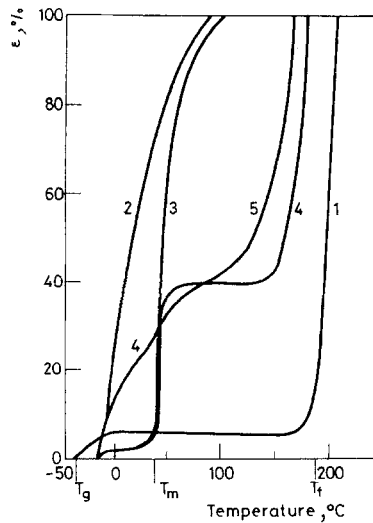


Fig. 7. TMA curves of a polyesterurethaneurea exhibiting different phase structures: 1 — as received; 2 — heated to 220° and quenched (homogenized); 3 — the same as 2, then exposed for 2 weeks to 20°; 4 — the same as 2, then exposed for 10 hours to 120° and 2 weeks to 20°; 5 — the same as 4, except for quenching after heating to 220°. Constant load 1.57 MPa

ates of the hard segments in the first one, and of the crystallized oligoester sequences in the other.

By altering the thermal conditions, for instance by exposing the amorphized specimen successively to 120 and to 20°, one may obtain materials with both dispersed phases. The ratio of the latter may be estimated when comparing such elements of curves 4 and 5 as the rise near the melting point of the oligoester and the plateau due to domains of hard segments. The same heating (120°, 10 hours) appears much more effective in the formation of the hard-segment domains from a homogeneous material when first quenched (curve 4). This may be attributed to more effective nucleation, which controls the formation of a new phase.

There is sufficient evidence to consider that some polyesterurethanes do not homogenize even when the dispersed domains fuse or melt. Such polymers are to be regarded as a system in which the liquid diol-urethane domains are dispersed in a liquid polyester-block medium. The maintenance of the segregated structure in the melt provides conditions for prompt crystallization. In some cases, even quenching the samples in liquid nitrogen is not efficient enough for obtaining an amorphous material [8].

The most complete segregation is in need of polymer molecules consisting of blocks of strictly uniform lengths. Such molecules form perfectly ordered structures, known as supercrystals, the latter having thermal stability highly exceeding the T_f of even the less fusible block. For the polymers investigated the uniformity of the block lengths was not controlled; still, the structure obtained seems to be ordered enough to increase the T_f .

Often the polyurethanes are synthesized with an excess of diisocyanate, which results in the formation of intermolecular linkages due to allophanate bonds (or biuret, when urea groups are present). Formation of such a chemical net after the microphase segregation is accomplished is an additional factor contributing to stabilization of the domain structure and reinforcement of the polymer. The bonds are concentrated mainly within the diol-urethane (diamine-urea) domains. In contrast, existence of the net prior to the commencement of phase segregation will inhibit the process and hinder the formation of the dispersed structure. Meanwhile, it may be noted that few cross-linkings, forming a net with a rather low density, do not stop the segmental motion, and hence the phase segregation may progress. Sometimes the changes in the phase structure proceed very slowly and the thermomechanical properties of a polymer analyzed after months and years have elapsed seem not to be stable.

It may also be noted that the allophanate and biuret bonds are thermally labile and dissociate above 110–130° [9]. Thus, the highest values of T_f are to be attributed simply to the fact of phase segregation, especially when it leads to crystallization of the hard segments and even to formation of supercrystals.

All the above clearly shows that TMA proves to be a most efficient technique for investigating the phase structure for the class of the substances studied. It may

be concluded that the main features of the formation and changing of the segregated phase structure observed may be generalized for any blockcopolymer, as well as for some other system with an aptitude to microphase segregation.

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RÉSUMÉ — On présente un ensemble de méthodes d'approximation pour l'étude des variations structurales sous l'influence de la température, reposant sur des concepts modernes sur la structure en domaine des copolymères en bloc.

Les effets de la ségrégation des phases, de la cristallisation et de l'homogénéisation thermique ont été examinés en connexion avec les propriétés de déformation des polymères. La même polymère semble avoir des structures de phases et des propriétés tout à fait différentes, quand il est obtenu sous différentes conditions thermiques. On montre sur une large série de polyéther (ester)uréthanes et -uréthane urées que l'analyse thermomécanique est une technique très efficace pour étudier les variations de la structure des phases.

ZUSAMMENFASSUNG — Ein Komplex methodischer Näherungen zur Untersuchung von Strukturänderungen unter dem Einfluss von Wärme werden vorgeführt, welche auf den modernen Konzepten der Gebietstruktur von Block-Kopolymeren beruhen. Die Effekte der Strukturbildung durch Phasensegregation, Kristallisationsvorgänge und thermische Homogenisierung wurden im Zusammenhang mit den Deformationseigenschaften der Polymeren in Betracht gezogen. Das gleiche Polymer scheint ganz verschiedene Phasenstrukturen und Eigenschaften zu haben, wenn es unter veränderten thermischen Bedingungen erhalten wird. Es wird gezeigt, dass die thermomechanische Analyse eine sehr wirksame Technik zur Untersuchung der Phasenstrukturänderungen einer ganzen Reihe von Polyäther(ester)urethanen und -urethan-karbamiden ist.

Резюме — На основе современных представлений о доменной структуре блок-кополимеров излагается совокупность методических приемов для исследования изменений структуры под влиянием температуры. Рассмотрены явления структурообразования в результате микрофазового разделения, кристаллизационные эффекты и процессы термической гомогенизации в их связи с деформационными свойствами полимеров. Вариацией термических условий один и тот же полимер может быть получен с различными фазовыми структурами и, соответственно, свойствами. Показана эффективность термомеханического анализа для исследования закономерностей изменения фазовой структуры обширных рядов полиэфируретанов и -уретаномочевин.