Viscoelastic Behavior of Segregated Networks

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Synopsis

Temperature dependences of real E' and imaginary E'' parts of the complex dynamic modulus for new types of so-called segregated networks were investigated. These networks are formed by three different elastic active network chains which chemically interact one with another, distinct from interpenetrating networks. Networks based on oligourethane acrylate, methyl methacrylate, methacrylic acid, and epoxy resin taken at various ratios were investigated. The viscoelastic characteristics were determined on different stages of the network structure formation. For such networks, a very wide peak E'' is typical, which is connected with a high degree of microphase segregation. The mutual influence of the constituent networks on their relaxation maxima was observed.

INTRODUCTION

Polymeric networks such as interpenetrating polymeric networks (IPNs), semi-IPN, and others attract attention because of their valuable physical and mechanical properties.[1,2] Now it is established that these networks have a complicated microphase structure.[3] Of special interest may be crosslinked systems formed by two interpenetrating and chemically bonded networks. Using X-ray diffraction, it was of IPN, such networks may be formed in two stages, one according to the mechanism of radical polymerization and another according to polyaddition mechanism. This investigation is concerned for the first time with the viscoelastic properties of segregated networks.

EXPERIMENTAL

Compositions for preparing segregated networks included two main constituent parts. The first network was oligourethane–ester acrylate (OUEA) of molecular weight 2000, methacrylic acid (MAC), methyl methacrylate (MMA), and a polymerization initiator (benzoin methyl ether). The second network consisted of commercial epoxy resin ED-20 and trimethyleneamine as a catalyst. At the first stage of curing, the liquid composition was poured between two glasses and polymerized under the action of UV radiation. The crosslinked polymer was formed due to radical copolymerization of three unsaturated comonomers. The network formed has some side carboxylic groups (residue of MAC) between crosslinks. At the second stage, these groups interacted with curing epoxy resin, with additional crosslinks being formed between the two networks. Epoxy resin component was cured at 130° for 30 min. Thus, the network under consideration includes three types of elastically active network chains (EANCs): (1) EANC formed by polymerization of vinyl groups of OUEA; (2) fragments of the main chain of OUEA; and (3) EANC of epoxy resin. The compositions of the networks studied are given in Table I.

TABLE I
The Compositions of the Networks Investigated (weight parts)

No.	OUEA 2000T	ED-20	MAC	MMA
1	0.6	0.3	0.1	—
2	0.5	0.3	0.1	0.1
3	0.4	0.3	0.1	0.2
4	0.2	0.3	0.1	0.4
5	0.5	—	0.1	0.1

For the network films (40 × 5 × 0.3 mm) dynamic tests were performed with a frequency relaxometer[5] at 100 Hz in a regime of sine-shaped forced vibration. The experiment was carried out between −100 and +150° at temperature increasing at a rate of 1°/min. As a result, the temperature dependences of the loss (E'') and storage (E') parts of the complex Young's modulus E^* were obtained.

RESULTS AND DISCUSSION

Figure 1 shows the results of dynamic mechanical measurements for the composition after the first stage of curing (only one network is formed). As was expected, sample 1 obtained in the absence of MMA shows a very narrow temperature peak E' at −20° (curve 1), which corresponds to the OUEA glass transition point T_g.[6] Some shift of T_g as compared with dilatometric data is connected with the frequency of the mechanical measurements. Increase in the fraction of MMA (curve 2) leads to a broadening in the E'' peak and to its shift to a higher temperatures. At the same time, the maximum E'' appears (curve 2), which may be attributed to T_g of PMMA. The essential shift of this maximum to a lower temperature as compared with pure PMMA ($T_g = 100°$) may be explained by the plastizing action of the epoxy resin present in the system. The E' curves are correspondingly shifted to higher temperatures.

It is worth noting that on curve 1 one can distinguish a peak E'' at +45°, which we are prone to relate to dissociation of hydrogen bonds between carboxilic
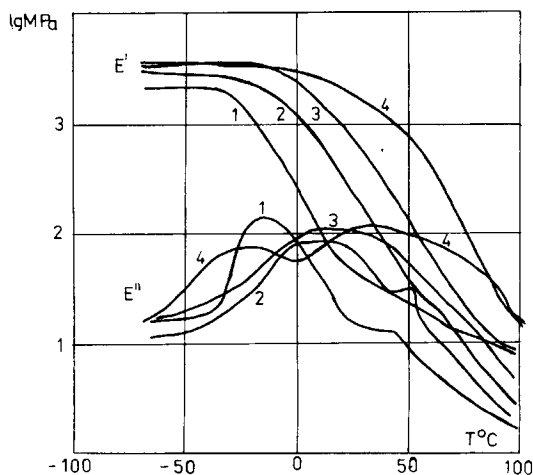

Fig. 1. Temperature dependence of viscoelastic functions E' and E'' after the first curing stage.

groups of MAC and urethane groups of OUEA.[8] At a high concentration of MMA in the system, the molecular mobility of other components with lower T_g is strongly restricted, and as a result, one diffuse peak E'' is observed for these components. We believe the process of phase separation to proceed in this composition range, which leads to the formation of a strongly pronounced two-phase structure. However, the eroding of the E'' peaks and their superposition (curves 2–4) allows one to predict strong interphase interaction in the system between various components.

Thus, after the first stage of curing, the systems show the existence of two relaxation mechanisms corresponding to molecular motions in OUEA and PMMA, their mutual influence, and the influence of epoxy resin on the positions of maxima being appreciable.

The results of viscoelastic properties measurements after the second stage of curing are given in Figure 2. The introduction of the third type of EANC (short rigid chains of epoxy resin) has lead to the essential broadening of the E'' peak and to an unusually smooth change in E' (curves 2–4). Let us discuss these data in more detail.

The high and sharp E'' peak (curve 1) and some of its displacement to lower temperatures testify to segregation of the OUEA component into separate domains, leading to pronounced relaxation transition. The EANCs formed by epoxy resin are situated probably between segregated OUEA domains. It is evident that the processes of phase separation take place during the second stage of curing as well. As a result, we have a very sharp and high E'' peak (curve 4), this peak corresponding to PMMA segment motions. As before, in this case we can also suppose the microsegregation of formation of microdomains enriched by PMMA. It is worth noting that in both cases (curves 1 and 4) the concentration of components able to segregate is high enough (60% OUEA, 40% PMMA). The horizontal parts of function $E'' = f(T)$ are seen in Figure 3, these being probably eroded E'' peaks of OUEA and epoxy-AENC.

From all these data, it follows that the heterogeneity of the network under consideration was formed at the first stage of curing. The character and position of curves 2 and 3 (Fig. 3) are very similar. One unusually wide peak (if it may
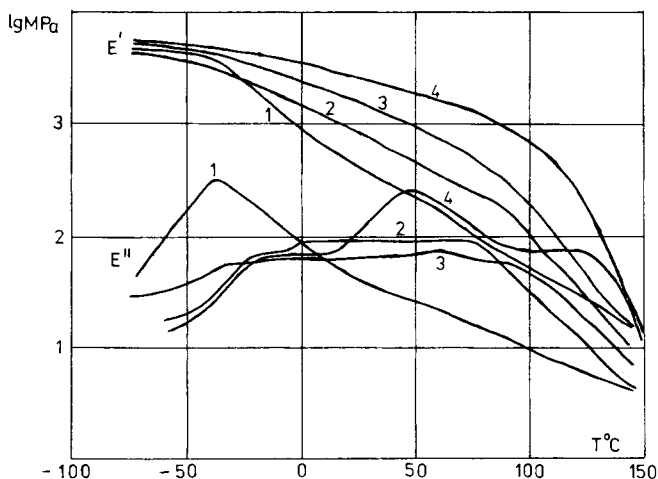

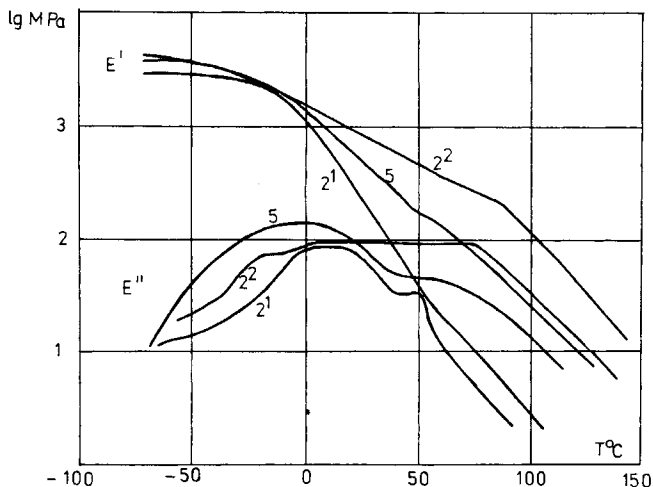Fig. 2. Temperature dependence of E' and E'' after the second curing stage.

Fig. 3. Comparison of E' and E'' for sample 5 and 2 (2^1 and 2^2 curves denote samples after first and second curing stages).

be considered a peak, not a plateau) is considered by many authors the result of component thermodynamic compatibility. However, we are far from certain that we are dealing with one-phase homogeneous system. Moreover, we believe that these systems are heterogeneous with a high degree of segregation. The reason for this supposition lies in the results of X-ray experiments for a very similar system,[4] namely, the network formed in two stages on the basis of oligoisoprene dihydrazide and epoxy resin. Small-angle X-ray data have shown that the distinctive feature of such a network with EANC of very different chemical nature is the high degree of microphase decomposition with the formation of microheterogeneity regions of size 6–7 nm. It is very possible that curves 2 and 3 are typical for such systems called segregated networks as distinct from IPNs, where the microphase separation is not so high. In connection with this, the question arises: What is the heterogeneity level (the size of microdomain) at which the resolution of relaxation maxima becomes possible for each component?

The diffuse E'' peak may be regarded as a sign of formation of diffuse microregions of phase decomposition, these regions being enriched by one of the components. It may be possible only when phase separation proceeds inside spinodal, i.e., according to the mechanism of spinodal decomposition.[7] The detailed X-ray data for the system under consideration will be presented in the next communication.

To have more insight into changes of viscoelastic properties of segregated networks with epoxy fragment, between crosslinks, we have studied a sample similar to No. 2 but obtained without epoxy resin (No. 5, Table I). The results for this sample show, as can be expected, that epoxy oligomer really plasticizes other components of the composition (lower E' value at equal temperature, curves 2^1 and 5). The relaxation maxima in the presence of a plasticizer are sharper and closer to one another. The formation of epoxy-EANC has led to our essential increase in rigidity of the network (at 20°, E' increases fivefold; at 50°, tenfold (curves 2^1 and 2^2).

In such a way, the study of viscoelastic properties of polymeric segregated

networks consisting of three types of EANC shows the marked difference in their behavior as compared with IPN. In these networks, each EANC contributes to the total relaxation behavior, which is very complicated due to its appearance in the system of microregions of microphase segregation.

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