

Dependence of Viscoelastic Properties on Segregation Degree of Components in Interpenetrating Polymer Networks

YU. S. LIPATOV, V. F. ROSOVIZKY, P. V. DATSKO, and YU. V. MASLAK, *Institute of Macromolecular Chemistry, The Ukrainian SSR Academy of Sciences, 252160, Kiev, USSR*

Synopsis

The temperature dependences of elastic moduli, loss moduli, and mechanical loss angle tangent were investigated for the interpenetrating polymer networks: polyurethane-polyurethane acrylate by the method of dynamic mechanical spectroscopy (DMS). The segregation degree of components due to phase separation have been calculated from the parameters of relaxation maxima. An essential change was found in the segregation degree of components with the curing sequence of individual networks being changed. It was shown that, with the conditions and sequence of IPN formation changed, the phase separation degree can be fixed at a particular stage, i.e., the structures with a different segregation degree of components are obtainable. For the IPNs under investigation the variation of elastic moduli of the composites proved possible by fixing the separation degree of components.

INTRODUCTION

As was established before,^{1,2} the interpenetrating polymer networks (IPNs) are characterized by a structural microheterogeneity caused by the thermodynamic incompatibility of the components, arising in the course of curing. However, in most cases the microphase separation occurring together with the IPN forming reactions is not fully accomplished due to diffusion obstacles (high viscosity). The process of segregation of the components does not terminate by a complete phase separation and the structure of IPN can be characterized by the segregation degree of components determined by one of the structure-sensitive methods.

This paper presents for the first time the dependence of viscoelastic properties of the polyurethane (PU)-polyurethane acrylate (PUA) IPN on the segregation degree of the components. As the processes of microphase separation are closely associated with IPN formation kinetics,³ we have used several methods of changing these parameters that allowed their interrelation to be estimated.

EXPERIMENTAL

Individual polymer networks PU and PUA cure following different mechanisms and that allows IPN to be obtained in both the sequential and simultaneous curing. Oligourethane acrylates are known⁴ to be cured with a photoinitiator at a room temperature at high rates that essentially exceed the reaction rate between polyoxypropylene glycols (POPG) and triisocyanate, the

latter being the product of interaction of trimethyl propane (TMP) with 2,4-tolulene diisocyanate (TDI).

The composition under investigation contained the above adduct TMP-TDI, polyoxypropylene glycol of molecular mass 600 (POPG-600) at a ratio NCO/OH = 1.1 and oligourethane acrylate (OUA-2000) synthesized from POPG-2000 (1 mol); 2,4-tolulene diisocyanate (2 mol) and ethylene glycol monomethacrylic ester (2 mol). The content of OUA-2000 in reaction mixture was 40 mass %. Used as an initiator of photopolymerization it was "trigonal," as an inhibitor of thermally initiated polymerization it was hydroquinone in amounts of 0.5 and 0.2% of the mass of OUA, respectively.

The PU component was cured at 20°C for 7 days or at 100°C for 2 h. Kinetics of the PU network formation was studied by measuring the quantity of unreacted isocyanate groups. The content of the latter was determined by titration using the swelling capacity of crosslinked polymer in a solvent containing a known amount of dibutyl amine.^{5,6} The OUA component was cured by UV radiation for 2 h using an LUF-80 lamp. The segregation degree of components in IPN was varied applying the following procedures:

1. Varying the curing sequence of the networks:

a. Stage 1—curing of PU (7 days); stage 2—curing of OUA (2 h);

b. Stage 1—curing of OUA (2 h); stage 2—curing of PU (7 days).

Operations of a and b were conducted at $T = 20^\circ\text{C}$.

2. Ditto as in item 1 at 100°C for 2 h.

3. Simultaneous curing of the initial networks at $T = 20^\circ\text{C}$.

4. Curing of OUA network at various stages of the crosslinking reaction of PU component at 20°C (after 4, 20, 64, and 100 h).

The dynamic mechanical measurements were made applying the instrument described in Ref. 7. The temperature measurement range was -160 – $+120^\circ\text{C}$. The segregation degree of components was determined according to the data of dynamic mechanical measurements following the procedure⁸

$$\alpha = (h_1 + h_2 - \lambda_t - \lambda_m) / (h_1^0 + h_2^0)$$

where h_1^0 and h_2^0 are the values of relaxation maxima for pure components (case of complete phase separation), while h_1 and h_2 are those for each component at a different degree of segregation; t is the empirical parameter, considering the shift of relaxation maximum across the temperature scale for phases 1 and 2:

$$\lambda_t = 1/L(l_1 h_1 + l_2 h_2)$$

where l_1 and l_2 are the shifts of the maximum across the temperature scale and L is the interval between the glass temperatures of the pure components. The appearance of a relaxation maximum in the interphase region is considered using another parameter:

$$\lambda_m = (l_m h_m) / L$$

where l_m is the maximum shift of interphase layer across the temperature scale as related to phase 1.

RESULTS AND DISCUSSION

As follows from Figure 1 presenting the temperature dependences of loss modulus $E'' = f(T)$ for the initial networks and IPNs based on them, all the investigated IPNs are heterogeneous systems with two glass transition temperatures. It is quite evident, however, that the forming sequence of networks as well as the curing rate of the PU network is responsible for essential changes in the process of microphase separation and, consequently, in a relaxation behavior of IPNs.

The quantitative analysis of relaxation maxima E'' allowed the segregation degree of components to be calculated. The experimental data presented in Table I proved the expected agreement of increase of the segregation degree with increase of the difference of component glass transition temperatures. At the same time, these calculations indicate that the phase separation process is most affected by the curing sequence. It follows from the segregation degree comparison of samples 1 and 2 that if PU is the first to cure (case 1), an IPN is obtained whose segregation degree of components is far greater ($\alpha = 0.29$) than that ($\alpha = 0.11$) in the case of OUA being the first to cure. It is evident that the structure of the PU network is formed differently with OUA oligomer present as compared with the pure PU network.⁹ However, still greater changes occur if the PU network is formed in the OUA network (sample 2). In this case T_g of PU changes greatly (from 55°C down to -10°C) and hence the

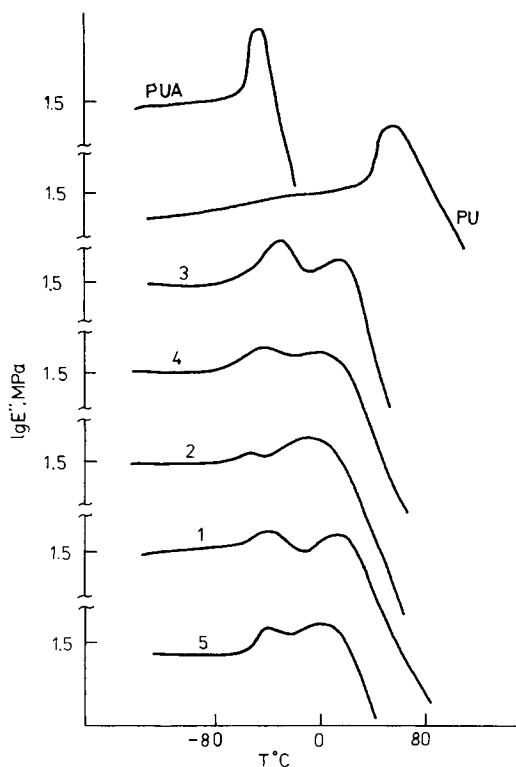


Fig. 1. Temperature dependences of loss modulus (E'') of initial polymer networks and IPN based on them. Numbers of the curves correspond to numbers of the samples in Table I.

TABLE I
Some Physicochemical Properties of Initial Polymer Networks and IPN Based on Them

Properties	Nos. of IPN samples and curing conditions (PU 60% in mass, PUA 40% in mass)										
	1		2		3		4		5		
	Network of PU (sl) ^a	Network of PUA (uv r) ^a	st.1 PUA (uv r) ^a	st.2 PUA (uv r) ^a	st.1 PU (r) ^a	st.2 PU (sl) ^a	st.1 PUA (uv r) ^a	st.2 PUA (uv r) ^a	st.1 PUA (uv r) ^a	st.2 PU (r) ^a	Simultaneous curing of PU and PUA
T_g of PUA (°C)	—	-45	-50	-50	-35	-50	-50	-50	-50	-50	-40
T_g of PU (°C)	55	—	-10	-10	20	-5	-5	-5	-5	-5	-5
Segregation degree α	—	—	0.29	0.11	0.32	0.21	0.21	0.21	0.21	0.21	0.24
E' (MPa) at 20°C	200	9.3	178	76.6	129	87	87	87	87	87	93
Breaking strength α (kg/cm ²)	28	23	16.9	13.9	—	21.5	21.5	21.5	21.5	21.5	24.4

^aNote: sl = slow curing at 20°C for 7 days; r = rapid curing at 100°C for 2 h; uv r = curing, when acted upon by UV radiation.

segregation degree of components varies from 0.29 to 0.11. It is worth noting that in the case where the PUA network is the first to be formed, T_g of PUA shifts toward negative temperatures (from -40°C down to -50°C , samples 2 and 4), indicating that the PUA network structure formed is lower cross-linked. To reveal the effect of the PU network curing rate on the IPN properties, compare samples 1, 3 and 2, 4. In the first case, with the PU network formed at the first stage, a change in the curing time did not practically affect the position of glass transition temperatures of components. In this case the segregation degree also varied insignificantly (0.29–0.32). However, in the case where PUA is formed first, the PU network curing rate leads to substantial changes in the microphase separating process. A rise of the PU network forming rate (at 100°C twice) sharply increases the segregation rate (from 0.11 to 0.21). However, the relative value of segregation degree is markedly lower than that in case of PU network formed at stage 1.

To have more insight into the relation between the IPN formation and microphase separating processes, one more series of IPN samples was investigated. The PU component was cured at 20°C whereas the curing of the PUA component was effected by UV radiation at various stages of PU crosslinking (after 4, 20, 64, and 100 h).

Figure 2 shows the dependence of PU network conversion degree on the time logarithm. It is of a form typical for the kinetic curves of such a kind. As in the preceding case, a viscoelastic behavior of IPN was investigated, and the segregation degree of components was determined. Figure 3 presents the dependence of segregation degree on the conversion degree of NCO groups in the PU network. The curve is of a strongly pronounced extreme character. The maximum value of segregation degree is achieved in the conversion of 80% of NCO groups. This behavior of the system can be explained from the point of view of structural gelation theory.¹⁰ In the formation of the PU network the first formed are microgel particles which are the nuclei of the space network and are responsible for a microseparation of the system into two phases. Thus, the PUA network is formed as a matter of fact in the microhet-

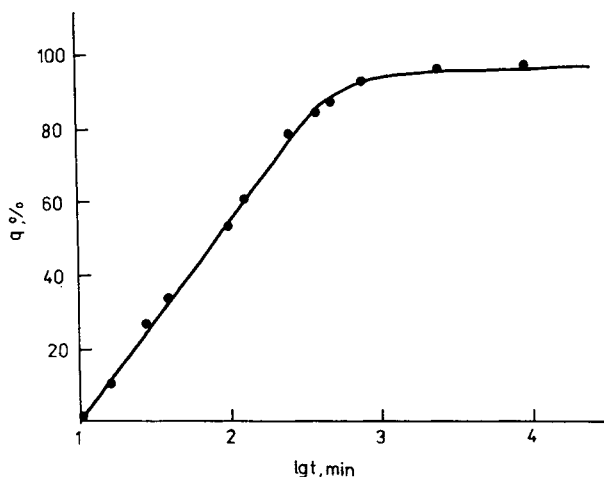


Fig. 2. Kinetic dependence of conversion of isocyanate groups in PU network.

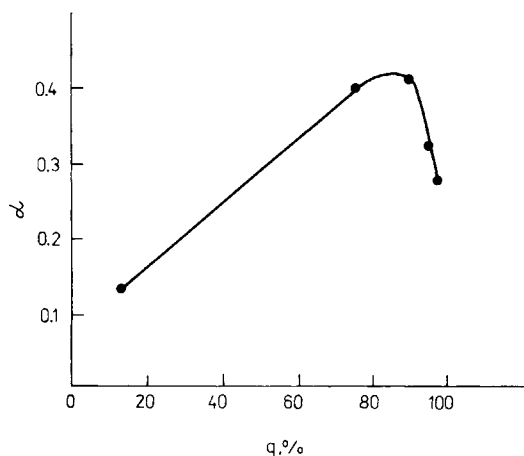


Fig. 3. Dependence of segregation degree of IPN components on conversion degree of isocyanate groups in PU network.

erogeneous network matrix from polyurethane.¹¹ Evidently, the microphase separation degree will depend, in this case, both on the size of microgel particles and the degree to which the microgels are intercoupled by interpenetrating chains.

A conclusion may be drawn, when comparing Figures 1 and 3, that the linear dependence between the conversion degree of NCO groups and the segregation degree of components correspond to the linear part of the kinetic curve. Consequently, with a growth of the sizes of microgels, the segregation degree of the IPN components increases up to the formation of PU macrogel. The maximum segregation degree is observed in the system when the PUA-network-forming reaction is initiated at the moment of macrogel formation or somewhat earlier. If the PUA network forming reaction is engaged at very deep conversions of NCO groups, the segregation degree of components sharply drops. This is accounted for by the fact that the PU network has already been formed and there exist strong steric hindrances for the separation of the two networks.

Further, consider the dependence of the IPN final properties on the segregation degree of components. As follows from Figure 4 presenting the IPN elastic modulus, its dependence on the segregation degree of components is of an extreme character. The origin of this maximum is not clear. Probably, its appearance is connected with variations both in size and distribution of microregions of phase separation.

A drop of the elastic modulus values at higher segregation degrees ($\alpha = 0.3$) for this IPN is evidently associated with a growth of the presence of defects in individual networks. The measurement of strength indices did not reveal any correlations with the degree of microphase separation of the components and further investigations are required.

In a recent paper,¹² one of the authors analyzed the data available in the literature in all aspects of obtaining and investigating the IPN, and now we can make up a structure diagram of the problem (Fig. 5). The preceding

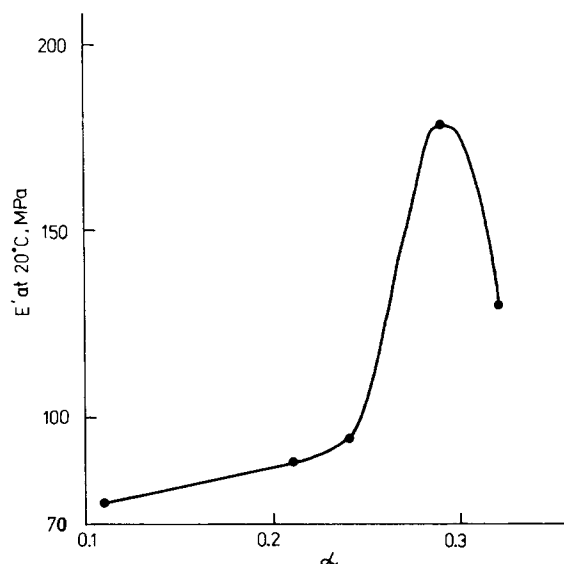


Fig. 4. Dependence of elastic modulus (E') values at 20°C on segregation degree.

papers concerning IPN dealt, as a rule, with synthesis or connection between the composition and properties of IPN only. Later on, a great amount of data on the phase structure and its connection with properties was obtained. In the course of time it became evident that the key link in the diagram represents microphase separation processes. However, at present only the qualitative dependences between the factors interacting in obtaining IPN have been established. Special attention should be given to the investigation of a feedback (apparently a negative one) between the kinetics of component crosslinking reaction and the microphase separation. Nevertheless, the most urgent task now is to investigate all the structure elements for a particular IPN, as a whole.

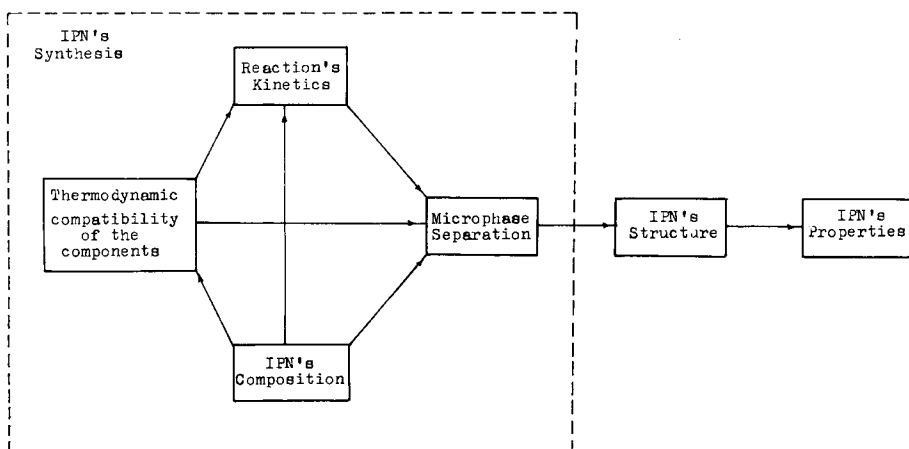


Fig. 5. Functional diagram of IPN investigation.

CONCLUSION

Thus, from all the above data it follows that the final properties of IPNs substantially depend on the segregation degree of components, which, in turn, depends on the kinetic and thermodynamic factors of IPN formation. There is no doubt that the optimum segregation degree is obtainable to realize high final properties of a particular material.

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