Relaxation behaviour of interpenetrating polymer networks based on crosslinked polyurethane and weakly crosslinked poly(butyl methacrylate) in a wide frequency range

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The frequency dependence of the dynamic shear modulus and mechanical losses have been measured for interpenetrating polymer networks (IPNs) based on crosslinked polyurethane and weakly crosslinked poly(butyl methacrylate) with component ratios (by weight) of 65/35 and 50/50. The frequency range used was 0.1–100 Rad s^{-1} over the temperature range from 133 to 413 K. According to the experimental data the IPNs have a two-phase structure with a segregation degree of 0.35–0.40. For each phase the apparent activation energy has been determined and relaxation spectra have been constructed using the method of reduced variables. The conclusion is that the relaxation behaviour of IPNs is dependent on the phase composition and morphological features.

(Keywords: interpenetrating polymer networks; dynamic mechanical properties; relaxation spectrum; activation energy; phase separation; segregation degree)

INTRODUCTION

The study of interpenetrating polymer networks (IPNs) has great practical importance. As a rule, they are two-phase systems and their viscoelastic properties are determined by the conditions of the chemical reaction and phase separation. The characteristic feature of IPN formation is the superposition of the chemical reaction of crosslinking and the physical process of microphase separation[1]. The viscoelastic properties of IPNs have been studied by many authors[2–5]. The peculiarities of IPN formation have been connected with the interdependence between the chemical kinetics of reaction and the physical kinetics of phase separation[6,7]. It has been established that changing the kinetic conditions of the reaction greatly affects the viscoelasticity. The kinetic conditions determine the degree of microphase separation during the course of the reaction (segregation degree)[8], whereas the segregation degree is one of the most important factors determining the viscoelastic properties[9]. It has also been found that changing the method of IPN formation leads to various viscoelastic properties, this effect also being connected with the segregation degree[8]. In the works cited the investigations of the viscoelastic properties of IPNs were performed over a wide temperature range at a constant frequency. It is evident that using only one frequency does not allow one to gain detailed information about the relaxation properties of IPNs. In the present work the first attempt, to our knowledge, has been made to estimate the relaxation properties of IPNs over a wide range of frequencies and to calculate the relaxation spectra and generalized viscoelastic functions. The evaluation of the activation energies for the relaxation processes in IPNs enables us to understand better the structural changes proceeding in the systems depending on the conditions of their formation. A very important characteristic of the phase separation in IPNs is the degree of segregation. This value gives the fraction of material α which undergoes phase separation. If $\alpha = 1$, the system is fully phase separated; $\alpha = 0$ corresponds to full miscibility. The value of α may be estimated from the characteristic maxima of the mechanical loss curves in accordance with the method of calculation proposed by us and described in detail elsewhere[9].

EXPERIMENTAL

IPNs based on a polyurethane (PU) network and weakly crosslinked poly(butyl methacrylate) (PBMA) were prepared for investigation. PU was synthesized from toluylene diisocyanate, poly(oxypropylene glycol) (molecular weight 2000) and trimethylolpropane in the molar ratio 2/1/0.66. As a catalyst dibutyltin dilaurate was used (concentration 1.4×10^{-4} mol l^{-1}). Into the reaction mixture was introduced monomeric butyl methacrylate and crosslinking agent dimethacrylate triethylene glycol with dissolved initiator (azobisisobutyronitrile (AIBN), concentration 2.96×10^{-2} mol l^{-1}). Two IPNs were prepared with weight ratios of the two networks (PU/PBMA) of 65/35 and 50/50. For the

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first IPN the concentration of crosslinking agent was 0.15 mol l^{-1} and for the second 0.03 mol l^{-1}. The difference in the concentration of crosslinking agent for PBMA, as established earlier, has no influence on the viscoelastic properties. The latter were measured using a Rheometric Recap II in the temperature range 133–413 K and at frequencies of 0.1, 0.31, 1.0, 3.1, 10.0, 31.1 and 100.0 Rad s^{-1}.

RESULTS AND DISCUSSION

Dynamic mechanical properties

Figures 1 and *2* represent the temperature dependence of the dynamic shear modulus G' and the mechanical loss $\tan\delta$ for the PU network, the weakly crosslinked PBMA and the IPNs with component ratios 65/35 and 50/50. Increasing frequency leads to a shift of the temperature dependence of the shear modulus to higher temperature. The plots of $\tan\delta$ show that the glass transition temperature (estimated as the temperature corresponding to the $\tan\delta$ maximum) increases with frequency for PU from 225 to 251 K and for PBMA from 313 to 338 K (*Figures 1a* and *1b*). More complicated plots of $\log G'(T)$ and $\tan\delta(T)$ are observed for the IPNs (*Figures 1c* and *1d*, *Figures 2c* and *2d*). The presence of two glass transition temperatures and the temperature dependence of G' testify that the IPNs under consideration really are two-phase systems. Two definitely marked maxima on the $\tan\delta$ against temperature curves show that the IPNs are thermodynamically incompatible systems with two phases enriched in PU and PBMA correspondingly, as follows from the shift in position of the two maxima when compared with the pure networks. For the 50/50 IPN with increase in frequency, the glass transition temperature of the PU-enriched phase is shifted from 223 to 233 K, whereas the corresponding shift for the PBMA-enriched phase is from 303 to 325 K. For the 65/35 IPN the glass transition temperature of the PU-enriched phase is shifted from 233 to 248 K and for the PBMA-enriched phase the shift is from 315 to 343 K.

For the 65/35 IPN (as distinct from the 50/50 IPN) there is also observed a third, intermediate maximum or shoulder near the maximum corresponding to the phase enriched in PU (*Figure 2c*). This maximum may be attributed to the interphase region between the two evolved phases[9]. It was impossible to trace the shift of this intermediate maximum with frequency because at higher frequencies this maximum degenerates into a shoulder (*Figure 2c*, curves F and G).

In accordance with the method proposed elsewhere[10], from the parameters of the relaxation maxima the segregation degrees have been calculated for the two IPNs (*Table 1*). As can be seen from *Table 1*, the frequency changes do not influence the values of the segregation

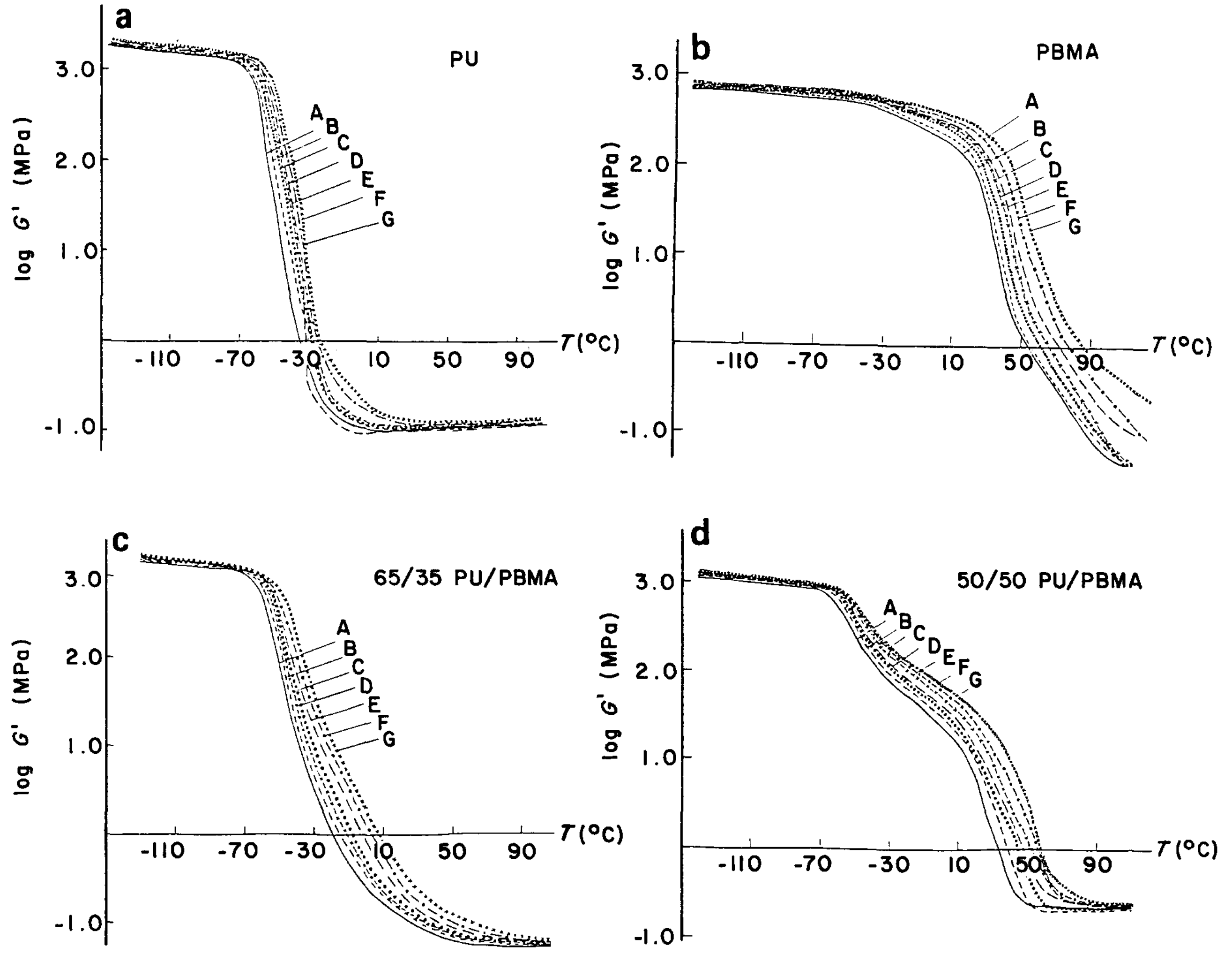

Figure 1 Temperature dependence of dynamic shear modulus for (a, b) initial networks and for IPNs with component ratios (c) 65/35 and (d) 50/50 at various frequencies (Rad s^{-1}): 0.1 (A); 0.31 (B); 1.0 (C); 3.1 (D); 10.0 (E); 31.1 (F); 100.0 (G)

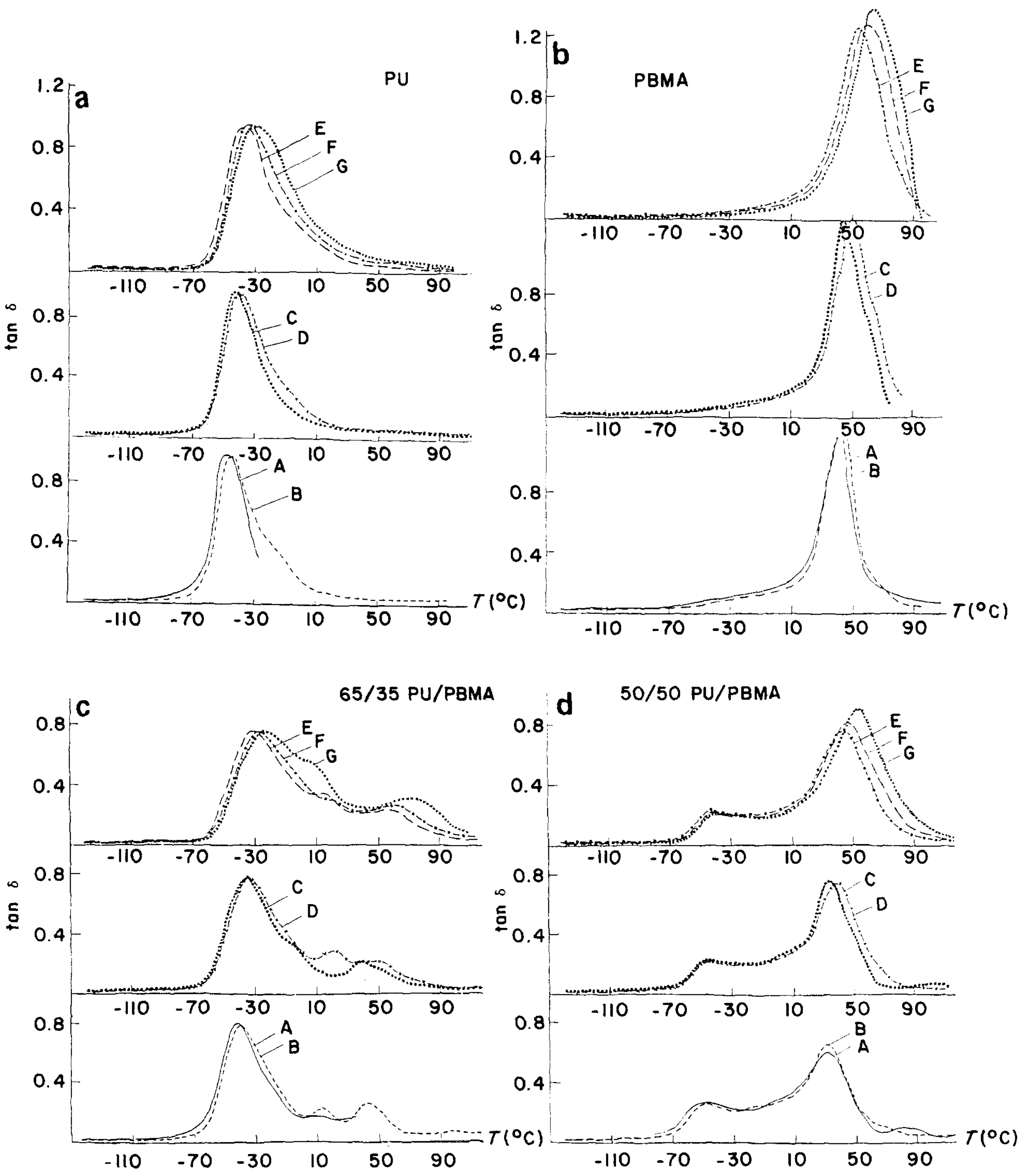

Figure 2 Temperature dependence of mechanical loss for (a, b) initial networks and for IPNs with component ratios (c) 65/35 and (d) 50/50 at various frequencies (as for *Figure 1*)

Table 1 Frequency dependence of the segregation degree

Frequency (Rad s^{-1})	Segregation degree α	
	65/35 IPN	50/50 IPN
0.1	No data	0.36
0.31	0.38	0.37
1.0	0.39	0.40
3.1	0.31	0.38
10.0	0.34	0.44
31.1	0.36	0.41
100.0	0.36	0.43

degree estimated from the relaxation maxima. The comparatively low values of the segregation degree show that a great amount of the system mass is preserved in the unseparated state; this means that the evolved phases are not pure components but mixtures of both networks. This is in accordance with the observed glass transition temperatures for each phase, which do not correspond to the values for the pure networks.

From the temperature dependence of tan δ it follows that for the 65/35 IPN the continuous phase is the PU-enriched phase, whereas for the 35/65 IPN the continuous phase is the PBMA-enriched phase. This conclusion follows from the corresponding maxima of tan δ^{11}. In such a way, changing the composition of the IPN leads to phase inversion.

Activation energies of relaxation processes in IPNs

From the temperature dependence of tan δ at various frequencies the activation energies of the relaxation processes in the IPNs have been calculated using an Arrhenius equation

$$\tau = A\exp(-E_a/RT)$$

where τ is the mean relaxation time, found from the condition $\omega\tau = 1$ for maximum tan δ (ω is the frequency).

The IPNs under consideration have two glass transition temperatures. Therefore it is possible to calculate an activation energy for each phase separately. The corresponding data are presented in *Table 2*. It can be seen that for each IPN the values of E_a are practically the same for both phases (enriched in PU or PBMA). For the 65/35 IPN E_a for both phases is very close to E_a for pure PU, whereas for the 50/50 IPN E_a is different for the two phases and only for the PBMA-enriched phase is E_a the same as for pure PBMA. This result seems to be rather strange and we not know how it can be explained. Of course, it is tempting to connect such a behaviour with phase continuity and phase inversion; however, we have no data on morphology.

Analysis of the relaxation spectra allows the conclusion to be drawn that the IPN with the longer relaxation time (50/50) has a higher activation energy in each evolved phase. The continuous changes in the relaxation spectrum do not allow distinction between those parts of the spectrum belonging to the different phases. However, the very existence of phase continuity cannot explain the coincidence of the activation energies. The data on activation energies probably show that the structures of the two evolved phases are very different for IPNs with different compositions. Presently we are not able to give any reasonable explanation for these data. However, we believe that the difference in the relaxation behaviour of the two phases is determined by a variable correlation between quasi-independent and cooperative segmental motions in each phase in accordance with the concept developed by Berstein[12]. Such behaviour is typical of multicomponent systems formed by various macromolecules. We should like to note that two evolved phases are not in a state of true thermodynamic equilibrium[13] and may be considered as dissipative structures[14,15]. The characteristics of dissipative structures in IPNs are strongly dependent on the conditions of phase separation in the system. In accordance with Berstein, in systems having a dissipative structure there is the possibility of the parallel occurrence of both α-relaxation and β-relaxation processes. The transition from α-relaxation to β-relaxation is accompanied by increases in both the cooperativity degree and the activation energy of transition. To explain the data obtained we need to conduct additional investigations on the phase structure, phase composition, free volume, intermolecular interaction, etc.

Table 2 Activation energies for the glass transitions in the pure networks and the IPNs

Network	Activation energy E_a (kJ mol^{-1})	
PU	180±15	
PBMA	280±25	
	PU-enriched phase	PBMA-enriched phase
65/35 IPN	170±15	180±15
50/50 IPN	350±30	290±25

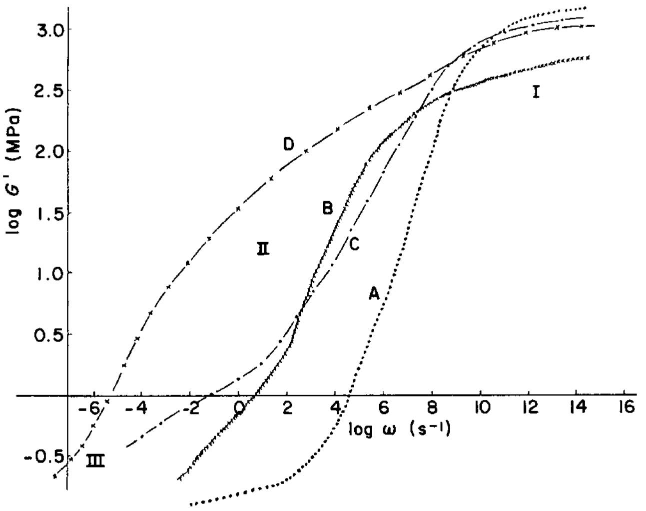

Figure 3 Generalized dependence of dynamic modulus reduced to 273 K: PU (A); PBMA (B); 65/35 IPN (C); 50/50 IPN (D)

Generalized viscoelastic functions

The temperature dependence of the dynamic shear modulus in the frequency range 0.1–100.0 Rad s^{-1} allows us to calculate the generalized curves of the viscoelastic functions. For this purpose we have used the method of reduced variables, which essentially allows the frequency ranges to be extended[16]. From the temperature dependence of G'' the frequency dependence of G' (with log ω) has been calculated in the temperature interval 153–393 K. The reduction temperature T_0 was chosen as 273 K and the curves for log $G''=f(\log\omega)$ were shifted along the logarithmic axis.

It is known that the reduction temperature may be chosen arbitrarily. As a rule it is chosen in such a way that $T_0 = T_g + 50$. As discussed above, the IPNs under investigation are two-phase systems and have two glass transition temperatures. The method for choosing the reduction temperature for thermorheologically complicated materials is discussed elsewhere[17]. We have chosen $T_0 = 273$ K because it lies between the values of T_g for the constituent networks. Four generalized curves have been constructed both for the initial components (crosslinked PU and weakly crosslinked PBMA) and for the two IPNs. The results are presented in *Figure 3*. The method of reduced variables has allowed the function of dynamic shear modulus to be spread over 16 decades along the frequency axis. The generalized curves may be considered as consisting of three regions. The first is the region of the glassy state (I), where the chain mobility is frozen. The second region is the transition zone from the glassy state to the rubber-like state (II). The viscoelastic properties in this zone are determined by the cooperative processes of segmental mobility. The third region (III) is a plateau of high elasticity where dynamic properties are connected with the existence of a network of molecular entanglements or chemical crosslinks. Analysis of the generalized curves shows that the PU network has the greatest value of G' in the glassy state (three to four frequency decades). For crosslinked PBMA the glassy region is spread over seven to eight decades along the frequency axis. IPNs are characterized by intermediate values of G' in the glassy state spread over five to six decades. The most marked distinctions in the generalized curves for the IPNs are observed in the transition region from the glassy to the rubber-like state (zone II). Analysis of the positions of the transition zones on the frequency axis shows that both PU and PBMA have rather narrow transition regions and the curves for these polymers are almost parallel. The transition zone for PU is shifted four decades to higher frequency compared with PBMA. Therefore the relaxation processes in PU in the region of the glass transition have shorter relaxation times than those processes in PBMA. The distinctive feature of IPNs is that they have very wide transition regions and therefore have broad sets of relaxation times. For the 50/50 IPN the transition zone is much broader than that of the 65/35 IPN and is spread to lower frequency over six to eight decades. We can conclude that the 50/50 IPN is characterized by relaxation processes with larger relaxation times. In such a way, changing the ratio of the components in the IPN leads to a change in the relaxation behaviour. *Figure 3* shows that in the elasticity zone for all four materials the low values of $\log G'$ ($\log \omega$) are typical. The plateau region is typical only for the PU network. The high elasticity zones for the IPNs are situated at lower frequencies compared with pure PU and PBMA.

It is known that the most fundamental characteristic of relaxation behaviour is the relaxation spectrum, which may be calculated from the equation[16]

$$G(t) = G_1 + \int_{-\infty}^{+\infty} H\,e^{-t/\tau}\,d\ln\tau$$

where $G(t)$ is the shear modulus at moment t, G_1 is the limit value of the shear modulus independent of frequency, H is the distribution function of the relaxation times and τ is the mean relaxation time. Using the generalized frequency dependence of the real part of the complex shear modulus, the relaxation spectra have been calculated using the method proposed by Ninomia and Ferry[16]. This method does not need the graphical differentiation of generalized curves and, being a variant of numerical differentiation, may be realized on a personal computer. The results are given in *Figure 4*. It can be seen that both the initial networks and the IPNs give a broad maximum on the relaxation spectrum which corresponds to the most common relaxation time in each case. The region of the sharp decrease in $\log H$ ($\log\tau$) is typical of the transition region from the glassy to the rubber-like state. The end zone for crosslinked PBMA is characterized by a drop in the relaxation spectrum, whereas in the pseudo-equilibrium region a plateau is observed (curve B). For crosslinked PU (curve A) the relaxation times are rather short and the maximum $\log H$ ($\log\tau$) occurs over the range $10^{-12} < \tau < 10^{-8}$ s. This means that in the PU network rapid conformational rearrangements are taking place. In the pseudo-equilibrium zone there is some sign of a plateau connected with the existence of a chemical network. For weakly crosslinked PBMA (curve B) the region of the glassy state is situated at shorter relaxation times. The maximum of the main relaxation transition is observed over the range $10^{-7} < \tau < 10^{-5}$ s. Comparison of the PU and PBMA spectra shows the slowness of the relaxation processes in PBMA compared with PU. At the same time, from the dependence of $\log H$ on $\log\tau$ it can be seen that the slopes of the plots for PU and PBMA are practically the same. According to theory[16], this slope for homopolymers is equal to $-1/2$, which corresponds to our data for PU and PBMA. For the IPNs there is a sharp deviation of the slope from $-1/2$, owing to the microheterogeneity of the system and the greater set of relaxation times than in the homopolymers. For the 65/35 IPN the maximum $\log H$ ($\log\tau$) is observed in the region $10^{-12} < \tau < 10^{-7}$ s and the transition from the glassy state is characterized by relaxation times in the range $10^{-12} < \tau < 1.0$ s (curve C). For the 50/50 IPN the broad maximum occurs over the same interval ($10^{-12} < \tau < 10^{-7}$ s) and the transition region is over the range $10^{-12} < \tau < 10^{5}$ s (curve D). Thus, the 50/50 IPN has a much greater set of relaxation times than the 65/35 IPN.

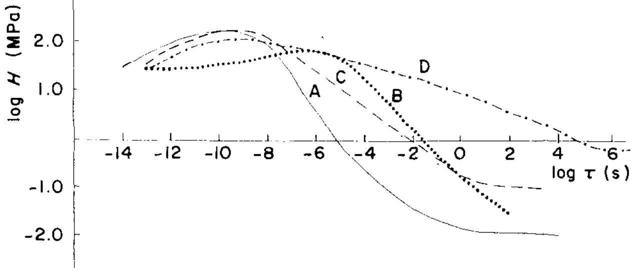

Figure 4 Relaxation spectra: PU (A); PBMA (B); 65/35 IPN (C); 50/50 IPN (D)

CONCLUSION

The results obtained show that IPNs have much greater sets of relaxation times than the pure constituent networks. The relaxation spectra of IPNs cannot be obtained by simple superposition of the spectra of the constituent components. The broader spectra of the IPNs may be explained by the existence of a two-phase structure where each phase is enriched in one of the components. At the same time, the existence of two phases is reflected in the relaxation spectra by their broadening and shift along the time axis. It is evident that in spite of the incompatibility of the two networks there exists a strong interaction between the macromolecular chains of dissimilar chemical nature. As chemical reactions between the two networks are absent, we have to suppose that these interactions are of a physical nature and may be described in terms of entanglement and strong polar interactions between the chains. The latter may be the reason why the 50/50 IPN has its relaxation spectrum shifted to higher relaxation times than the pure networks and the 65/35 IPN. We have also to take into account the morphological features of IPNs. It is evident that the morphological features influence the dynamic mechanical properties of the two-phase system (*Figure 3*). Therefore we cannot eliminate the influence of morphology on the relaxation characteristics and activation energies. As any relaxation process is connected with molecular mobility and interchain physical interactions, we have to admit that morphology has an effect on the molecular mobility.

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REFERENCES

1 Lipatov, Y. S. *J. Macromol. Sci., Rev.* 1990, **C30**, 209
2 Chang, M. C., Thomas, D. A. and Sperling, L. H. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1627
3 Hermant, I., Damyanidu, G. and Meyer, C. *Polymer* 1983, **24**, 1419
4 Sperling, L. H. in 'Sound and Damping with Polymers' (Eds R. Corsaro and L. H. Sperling), American Chemical Society, Washington, DC, 1990, p. 5
5 Fay, J. J., Thomas, D. A. and Sperling, L. H. *J. Appl. Polym. Sci.* 1991, **43**, 1617
6 Lipatov, Y. S., Rosovitsky, V. F., Alekseeva, T. T. and Babkina, N. V. *Dokl. Akad. Nauk Ukr. SSR Ser. B* 1988, **5**, 52
7 Lipatov, Y. S., Rosovitsky, V. F., Alekseeva, T. T. and Babkina, N. V. *Vysokomol. Soedin., Ser. A* 1989, **31**, 1493
8 Lipatov, Y. S. and Alekseeva, T. T. *Polym. Commun.* 1991, **32**, 254
9 Lipatov, Y. S. in 'Advances in Interpenetrating Polymer Networks' (Eds D. Klempner and K. Frisch), Technomic, Lancaster, Basel, 1989, p. 261
10 Lipatov, Y. S. and Rosovitsky, V. F. *Dokl. Akad. Nauk SSSR* 1985, **283**, 910
11 Miyamoto, T., Kodama, K. and Shibayama, J. *J. Polym. Sci. A* 1970, **2**, 2095
12 Berstein, V. A. and Egorov, V. M. 'Differential Scanning Calorimetry in the Physical Chemistry of Polymers' (in Russian), Chimiya, Leningrad, 1990
13 Lipatov, Y. S. *Polym. Mater. Sci. Eng.* 1990, **65**, 192
14 Lindenmeyer, P. H. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 1965
15 Lipatov, Y. S. 'Colloid Chemistry of Polymers', Elsevier, Amsterdam, 1988
16 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn, John Wiley, New York, 1980
17 Fesko, D. G. and Tschoegl, N. W. in 'Viscoelastic Relaxation in Polymers' (Ed. M. Shen), Interscience, New York, 1971