Formation kinetics and viscoelastic properties of semi-interpenetrating networks based on crosslinked polyurethane and poly(butyl methacrylate)

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The interconnection between the kinetics of semi-interpenetrating network (semi-IPN) formation, phase separation during the process and viscoelastic properties has been investigated. The semi-IPN based on crosslinked polyurethane (PU) and poly(butyl methacrylate) (PBMA) was synthesized in two ways: (1) by introducing PBMA into the reaction mixture for PU formation and (2) by simultaneously carrying out both the polyaddition reaction of PU formation and the polymerization of butyl methacrylate, the latter being produced using initiators and ultra-violet light. The kinetic constants, degrees of conversion at the onset of phase separation and viscoelastic properties have been estimated. It was shown that viscoelastic properties are changed essentially depending on the semi-IPN formation conditions, the degree of segregation (degree of phase sepration) being dependent on the kinetic conditions. The dependence of viscoelasticity on the kinetics is explained by various degrees of segregation fixed by crosslinking and by the formation of two phases of different composition.

(Keywords: kinetics; viscoelastic properties: interpenetrating networks; phase separation; crosslinking; polyurethane; poly(butyl methacrylate))

INTRODUCTION

The need for a substantial improvement of physico-mechanical and other properties of polymeric systems has resulted in the active development of a new class of binders, so-called hybrid matrices.

By definition[1], a common attribute of hybrid binders is the emergence of thermodynamic incompatibility of the components in the course of their curing or during their crosslinking reaction, the consequence of which is incomplete microphase separation of the system.

The properties of hybrid matrices for polymeric composite materials based on interpenetrating networks (IPN) are known to depend on the thermodynamic compatibility of the components of the networks and on the kinetics of the chemical reactions, which fix the microphase separation at a certain level. Only for a few systems, however, are data on the kinetics of their formation available[2–10]. Thus, the kinetics of formation of individual networks under conditions close to the conditions of synthesis of IPN based on crosslinked polyurethanes (PU) and poly(methyl methacrylates) was studied in refs. 2 and 3. The study of the kinetics of polyurethane formation in IPN based on PU and polyurethane acrylate (PUA), aimed at determining the effect of the concurrently forming second network (PUA) on the rate of formation of the first one, was done in ref. 4. In some works[5–9] the mutual influence of the components of the forming IPN on the kinetics of synthesis of each constituent network has been established. This influence was explained in particular by changing the viscosity of the reaction medium[5,6,9] and by early onset of a gel effect.

Among other investigations it is worth noting the study of the kinetics of IPN formation in the adiabatic regimens corresponding to the reaction injection moulding (RIM) process[10]. However, in the major part of the work cited[2,3,6–9] no account was taken of the most important factors influencing IPN formation – microphase separation in the course of the chemical reaction. A thorough analysis of this process was given in refs. 11 and 12. IPN structure results from the superposition of the processes of microphase separation, caused by the appearance of thermodynamic incompatibility of fragments of dissimilar networks at a certain degree of conversion on chemical reactions.

However, the features of IPN formation kinetics under conditions where the system undergoes microphase separation at a certain stage have not so far been determined.

The present study involved an attempt to relate the features of the kinetics of the concurrent formation of two polymers, proceeding through different mechanisms, to the physical process of microphase separation of the reaction system, superimposed on the chemical processes, and to ascertain the effect of the parameters of the processes on the viscoelastic and mechanical properties of such systems.

The kinetics of the reactions of radical polymerization of butyl methacrylate and polyaddition resulting in formation of crosslinked polyurethane was studied for this purpose.

EXPERIMENTAL

Semi-IPN were prepared in two ways. The first method consisted of the formation of crosslinked polyurethane

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in the presence of poly(butyl methacrylate), $MW = 3 \times 10^5$, dissolved beforehand in butyl acetate (75% solution). The polyurethane component was prepared from poly(oxypropylene glycol) (POPG), $MW = 2 \times 10^3$, tolylene diisocyanate (TDI) and trimethylolpropane (TMP) in the molar ratio 1:2:0.66 respectively. The catalyst was dibutyltin laureate, whose mass fraction was varied from 0.005% (50 ppm) to 0.5%. POPG and TMP were pre-dried in vacuum at 363 K and 313 K respectively. TDI (mixture of 2,4- and 2,6- isomers at a ratio 65:35) was purified by vacuum distillation, and poly(butyl methacrylate) (PBMA) was purified by precipitation from acetone. After IPN synthesis, the IPN obtained was carefully dried in vacuum at 80°C for 24 h to remove butyl acetate.

The kinetics of PU network curing in the presence of PBMA was studied on a DAK-1-1A automatic differential calorimeter using a method described in ref. 13. The ratio between NCO and OH functional groups in all experiments was equimolar.

The kinetic parameters of the reaction for pure PU and PU in the presence of PBMA have been calculated from the kinetic equation for a second-order reaction:

$$K = \left[\left(\frac{\alpha}{1-\alpha} \right) / A_0 \right] t$$

where α is the degree of conversion, A_0 is the initial concentration of reacting groups and t is the reaction time. The reaction rate constant was calculated by the generally accepted method from the linear dependence of $\alpha/(1-\alpha)$ on t. The reaction rate constant for urethane formation was estimated only for the initial linear part of this dependence where the reaction proceeds according to second order. The initial composition (PU components and PBMA) was charged into a glass ampoule, which was sealed and then placed in the calorimeter cell.

When studying semi-IPN with PBMA introduced into the reaction mixture, samples for dynamic mechanical investigation were prepared separately under the same conditions (the completeness of NCO group conversion was controlled by i.r. spectroscopy).

The second method of semi-IPN formation consisted of simultaneously carrying out two reactions: polyaddition leading to crosslinked PU formation and butyl methacrylate (BMA) radical polymerization. The semi-IPN for calorimetric study on the DAK-1-1A differential calorimeter was prepared by forming crosslinked polyurethane based on TDI, POPG 2000 and TMP in the presence of BMA where a radical polymerization initiator, azobisisobutyronitrile (AIBN), had been dissolved beforehand. The molar concentration of the initiator was varied from 1.08×10^{-1} to $.074 \times 10^{-2}$ mol dm^{-3}, while the molar concentration of the catalyst in all experiments was constant, 1.4×10^{-4} mol dm^{-3}. Kinetic studies for simultaneous semi-IPN formation reactions were conducted at a temperature of 333 ± 1 K, both with different component ratios PU/BMA of 85/15, 75/25, 65/35 at a constant molar concentration of the initiator of 5.4×10^{-2} mol dm^{-3}, and with a constant ratio of 75/25 at different initiator concentrations. For stepwise reactions, the first stage was formation of the polyurethane network at 313 K, $[\mathrm{cat}] = 7.0 \times 10^{-4}$ mol dm^{-3}, to a degree of conversion of 0.85–0.9; and the second stage was PBMA formation at 333 K, at a molar concentration of initiator of 5.4×10^{-2} mol dm^{-3}. The composition and properties of semi-IPN obtained are presented later in *Table 3*. For viscoelastic properties of semi-IPN obtained in this way, samples were cut from the polymer material cured in the calorimeter cells.

The dynamic mechanical properties have been studied using a Rheovibron DV-11 at a forced sinusoidal vibration frequency of 110 Hz. The temperature range of measurements was from 203 to 393 K. Concurrently, for the same systems and under the same kinetic conditions, the beginning of microphase separation in the course of reaction was determined by the cloud-point method on an FPS-3 photocolourimeter. The compositions of semi-IPN studied and the microphase separation onset time are presented in *Tables 1–4*.

For all samples their main structural characteristic was estimated – the degree of segregation, which according to Bonart is a measure of incomplete phase separation in systems with restricted thermodynamic compatibility[14]. The degree of segregation (*DS*) was estimated from viscoelastic data according to the method described in refs. 11 and 15.

RESULTS AND DISCUSSION

Semi-IPN formed by curing of PU network in the presence of PBMA

To establish the interconnection between kinetics and phase separation processes, we have to study first some viscoelastic characeristics of semi-IPN with various compositions.

From *Figure 1*, where the temperature dependences of the elastic modulus and of the mechanical loss are presented, it follows that, except for samples 1 and 8 (pure components) and sample 7, the semi-IPN studied

Table 1 Composition and properties of semi-IPN (PU/PBMA)

Sample nos.	Composition of PU/PBMA (mass %)	Tensile strength, σ (MPa)	Relative elongation, ε (%)	PU glass transition temperature, T_{g1} (K)	PBMA glass transition temperature, T_{g2} (K)
1	100/0	0.56 ± 0.02	240 ± 5	248 ± 1	–
2	91/9	0.38	124	253	–
3	87/13	0.45	68	248	308 ± 1
4	83/17	0.31	100	238	318
5	77/23	0.47	128	238	318
6	67/33	8.40	176	238	323
7	56/33	9.50	198	–	323
8	0/100	7.00	80	–	343

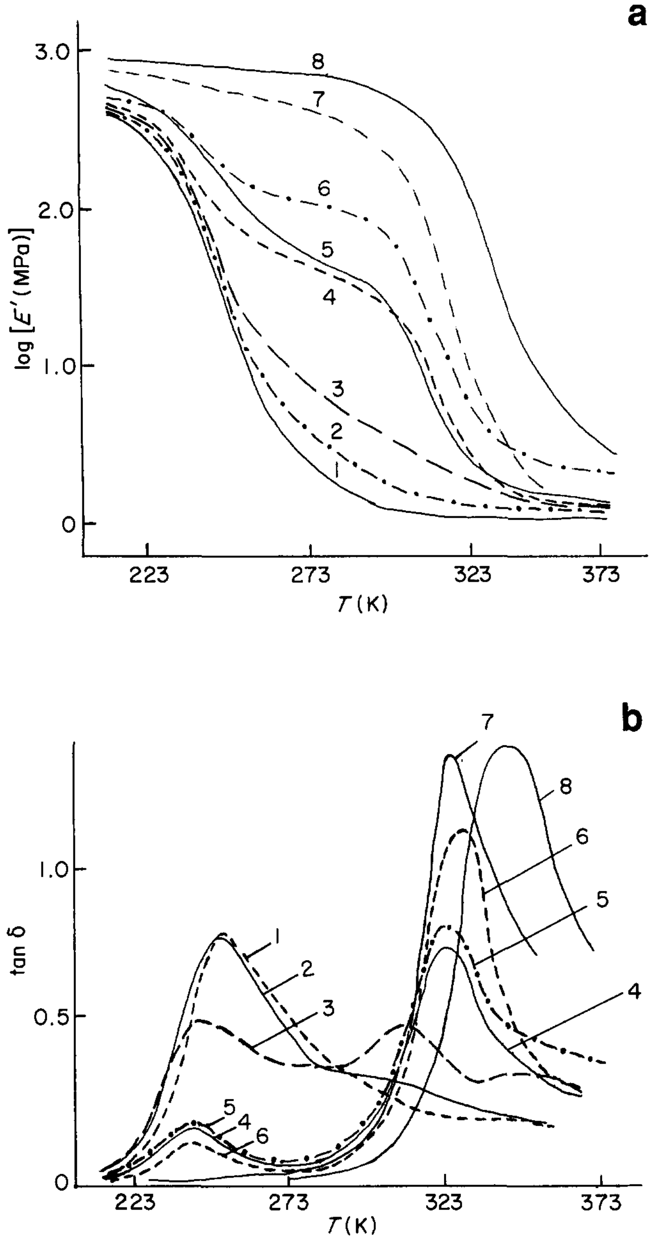

Figure 1 Temperature dependences of (a) elastic modulus and (b) mechanical loss of semi-IPN (PU/PBMA). For designations, refer to *Table 1*

is a typical two-phase polymeric system; this is evidenced both by the existence of two glass transition temperatures T_g (from maximum of $\tan\delta$) at all the other concentrations of components and by the form of the temperature dependences of the elastic modulus, characteristic of two-phase systems. At the same time, a substantial shift of T_g of the linear polymer (PBMA) from 343 to 308 K (samples 8–3) and a less marked shift of T_g of the polyurethane network indicate formation in the system of two phases of dissimilar compositions, differing in properties from the pure components. The concurrent processes of PU network formation and microphase separation caused by thermodynamic incompatibility of the components results in the formation of phases enriched in one of the components.

Some features of the phase structure of the studied system, which follow from its viscoelastic properties, can be pointed out. The continuous medium for samples 2–6 is evidently the phase enriched in the polyurethane network, which is evidenced by a plateau of high elasticity at temperatures above 343 K. A drastic decrease of the elastic modulus above this temperature for sample 7 (PBMA mass fraction 44%) unambiguously indicates a high enrichment of the continuous phase in PBMA. As for many IPN and semi-IPN described earlier, inversion of phases enriched in one of the components occurs in the region of medium compositions[16].

Since the microphase separation process proceeds under non-equilibrium conditions, it results in the formation of two continuous phases whose compositions is fixed by crosslinking. Each of the phases consists of both IPN components and can be treated as an independent IPN where mixing of components at the molecular level through topologic entanglements takes place (the ‘forced’ compatibility effect[11,12]).

Let us discuss the effect of the polyurethane network curing kinetics on the microphase separation process and semi-IPN properties.

Table 2 presents the values of the degree of PU conversion in a forming semi-IPN at the moment of microphase separation and the reaction rate constants at different mass fractions of the catalyst and different curing temperatures at a constant PBMA content. Analysis of these results shows microphase separation beginning to be directly dependent on the urethane

Table 2 Physico-chemical parameters of PU networks (samples 9–11) and semi-IPN (mass fractions: PU, 85%, PBMA, 15%)

	Sample nos.							
Parameters	9	10	11	12	13	14	15	16
Curing temperature (K)	333 ± 1	333	313	333	333	333	353	313
Catalyst mass fraction	0.005 ± 0.001	0.010	0.010	0.010	0.005	0.050	0.010	0.010
Reaction rate constant (kg mol^{-1} s^{-1}) $\times 10^{-4}$	3.46	7.63	1.90	2.62	1.3	8.1	7.05	0.73
Phase separation onset time (min)	–	–	–	43 ± 1	100	28	30	29
Degree of conversion at onset of phase separation, α	–	–	–	0.23 + 0.01	0.13	0.39	0.56	0.48
Degree of conversion at anamorphose inflection point, α	–	–	–	0.68 ± 0.01	0.58	0.74	0.82	0.47
Glass transition temperature of PU-enriched phase (K)	253 ± 1	251	255	253	261	248	265	249
Glass transition temperature of PBMA-enriched phase (K)	–	–	–	316 ± 1	333	323	315	318
Degree of segregation, *DS*	–	–	–	0.33	0.32	0.35	0.32	0.34

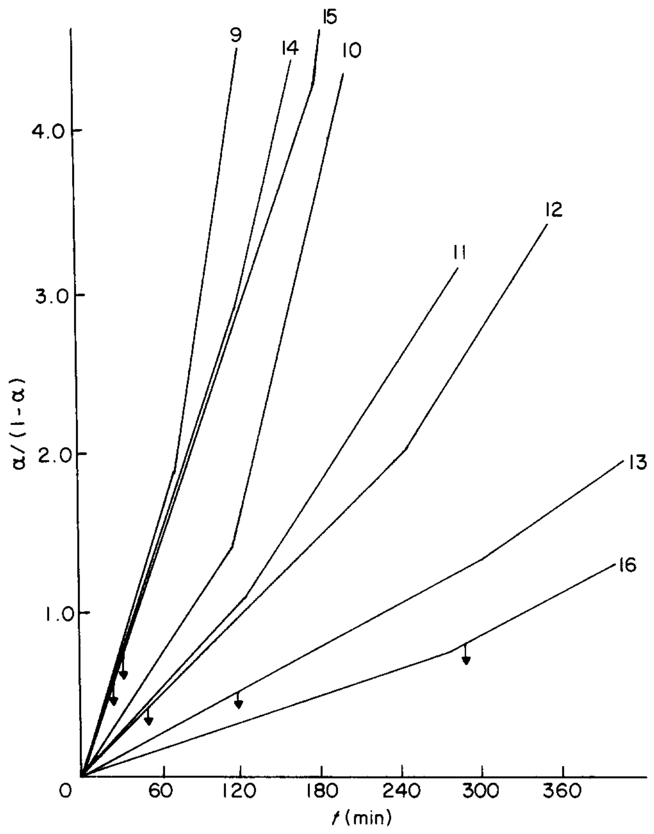

Figure 2 Anamorphosis of kinetic curves of the urethane formation process in the presence of PBMA (15 mass%). For designations, refer to *Table 2*. Arrows show beginning of phase separation

formation reaction rate consant. Changing the urethane formation reaction rate by varying the mass fraction of the catalyst changes the degree of conversion corresponding to the onset of phase separation from 23 to 39%. Varying the reaction rate by changing the temperature from 313 to 353 K results in a greater scattering, from 23 to 56%, in the degree of conversion.

Figure 2 presents anamophosis of kinetic curves of the formation reaction of crosslinked polyurethane in the absence (curves 9–11) and in the presence of PBMA (curves 12–16), investigated at various temperatures and catalyst mass fractions. Both for the pure crosslinked polyurethane and for semi-IPN (PU+PBMA), the obtained anamorphosis of kinetic curves exhibit two parts, which evidence a change of reaction rate in the system on reaching a certain degree of conversion. It can be noted that a comparison of experiments 9 and 12, 10 and 13, or 11 and 16 shows a threefold decrease of the urethane formation reaction rate in the presence of poly(butyl methacrylate), while the character of anamorphosis of kinetic curves remains qualitatively unchanged.

Analysing these results, it should be noted that only in one case (curve 16) does the degree of conversion at which microphase separation begins coincide with the conversion corresponding to the inflection of anamorphosis. Probably, as noted earlier[5], at low degrees of conversion, owing to the higher viscosity of the system, microphase separation is slowed down and gets experimentally fixed at higher degrees of conversion, which in fact corresponds to the appearance of thermodynamic incompatibility of the components. The absence of inflections of kinetic curves[12] at the microphase separation onset point is most likely due to the absence of volume changes brought about by microphase separation, while the latter itself does not affect the rate of reactions. The obtained data, as has already been noted, do not indicate a change in the reaction kinetics at the start of microphase separation or near the degree of conversion corresponding to it. The above-presented results demonstrate that in the studied system onset of microphase separation depends substantially on the urethane formation reaction kinetics.

Let us dwell on the results of studying the synthesized semi-IPN by dynamic mechanical spectroscopy. First it seems expedient to trace the effect of kinetic factors on viscoelastic properties of the POPG 2000 based polyurethane network. From *Figure 3*, where temperature dependences of the mechanical loss tangent, tan δ, are presented, it follows that changes in the curing temperature and catalyst mass fraction and, as a consequence, in reaction rate constants have little effect on the viscoelastic behaviour of the polyurethane network. These results subsequently make possible a more correct analysis of the viscoelastic behaviour of the two-phase system.

We will examine the viscoelastic behaviour of the semi-IPN with the use of temperature dependences of the mechanical loss (*Figure 3*). A visual analysis of the curves discloses differences in viscoelastic properties of semi-IPN samples synthesized under dissimilar kinetic conditions. The data of *Table 2* show that the growth of the polyurethane network formation reaction rate constant due to increase of the catalyst mass fraction at a constant temperature of 333 K results in formation of a less crosslinked PU network. The T_g shifts towards lower values (from 261 to 248 K). However, the increase

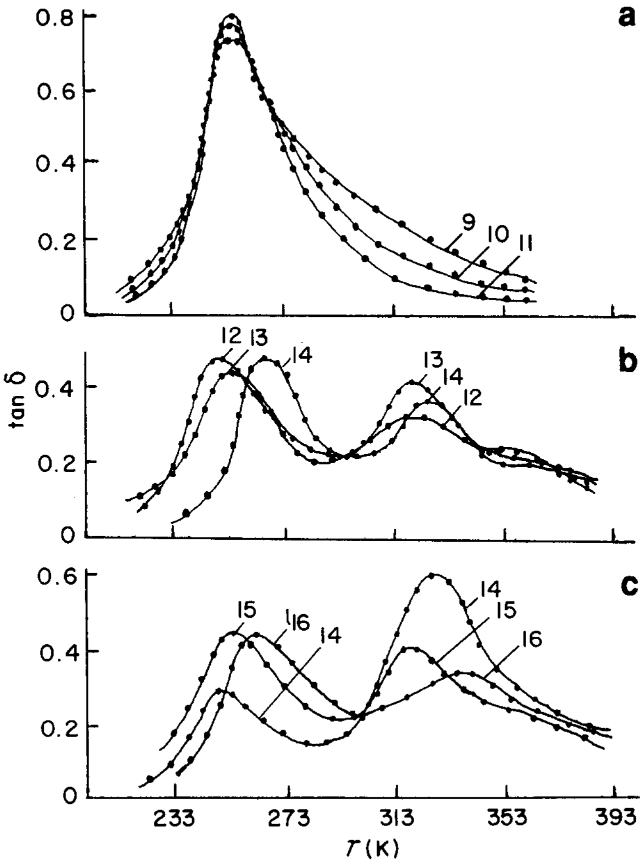

Figure 3 Temperature dependences of mechanical loss of polyurethane network and semi-IPN (PU/PBMA). For designations, refer to *Table 2*

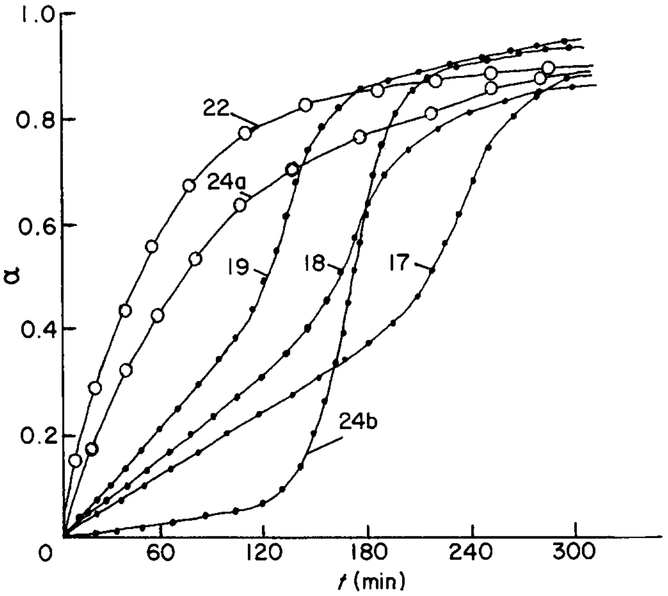

Figure 4 Kinetics of PU formation and BMA polymerization at various initiator concentrations: 19, PBMA, [I] = 2.96×10^{-2} mol dm^{-3}; 18, PBMA, [I] = 1.48×10^{-2} mol dm^{-3}; 17, PBMA, [I] = 0.74×10^{-2} mol dm^{-3}; 22, PU; 24a, PU in semi-IPN (see *Table 3*); 24b, PBMA in semi-IPN (see *Table 3*)

in reaction rate constant caused by a change in the curing temperature in the series 313, 333, 353 K led to the opposite results with respect to the preceding case. The T_g of the polyurethane network shifts from 249 to 265 K, while the T_g of PBMA remains practically unchanged. The observed changes in the relaxation behaviour of the semi-IPN seem quite logical when considered from the standpoint of concepts of formation of phases enriched in one of the components of a two-phase system, which was already mentioned above.

In the above-considered series the increases in T_g of the PU-enriched phase appears to be associated with the decrease in the reaction system viscosity, which results in the formation of a more regular structure of the polyurethane network. As would be expected, as the curing temperature is lowered to 313 K, the glass temperature of the PU-enriched phase shifts somewhat to lower values since a more defective structure of the PU network forms with increasing viscosity of the reaction system.

Thus, an ambiguous effect of the urethane formation rate constant on the structure of the network in the two-phase system has been ascertained. A substantial part is played by the method of changing the reaction rate constant: when this parameter is varied by changing the mass fraction of catalyst, the initial viscosity of the reaction system remains unchanged, whereas changing the curing temperature substantially alters both the reaction rate constant and the system viscosity, which leads to formation of a different structure and, as a consequence, to semi-IPN with differing properties.

Semi-IPN produced by simultaneous curing of PU network and polymerization of butyl methacrylate

For a further study of features of IPN formation based on polyurethane and poly(butyl methacrylate), we have conducted kinetic investigations of polyurethane network curing and BMA polymerization for reactions proceeding simultaneously and stepwise, and studied viscoelastic properties of the obtained compositions.

Kinetic curves for the initial polyurethane and poly(butyl methacrylate) with different mass fractions of the initiator are shown in *Figure 4*. As can be seen, the poly(butyl methacrylate) formation rate (curves 17, 18 and 19) increases with the initiator concentration. Based on the principle of additivity and determining the polyurethane degree of conversion by an independent method (titration of NCO groups), we determined the heat release area corresponding to PBMA formation and hence also the degree of PBMA conversion into a semi-IPN from the difference between the total heat release area and the area corresponding to polyurethane, calculated from the degree of conversion. Kinetic curves for polyurethane and poly(butyl methacrylate) in the semi-IPN at a PU/BMA ratio of 75/25 and a molar concentration of initiator of 1.48×10^{-2} mol dm^{-3} are shown as well in *Figure 4* (curves 24a, 24b). It was found that for simultaneously proceeding reactions the PBMA formation rate increases with the molar concentration of initiator (*Figure 5*, curves 23b, 24b, 25b, 26b) while the polyurethane network formation rate declines with respect to the initial one (*Figure 5*, curves 23a, 24a, 25a, 26a). As the PBMA formation rate increases, the degree of conversion rises at a certain time, which increases the viscosity of the medium and thereby impedes diffusion for macromolecules that form polyurethane chains (*Figure 5*).

The comparison of the reduced rate of PBMA formation in the semi-IPN and the initial rate (*Figure 6*) shows an increase in W_{red} of PBMA formation in the mixture with respect to the initial one (*Figure 6*, curves 19 and 25b, 18 and 24b, 17 and 23b). This, according to refs. 7 and 9, may be due to an increase of the initial viscosity of the semi-IPN system, which rises in the course of PU and PBMA formation, thereby sharply reducing the termination constant (K_t) as against the growth constant (K_{gr}) and accordingly increasing the K_{gr}/K_t ratio

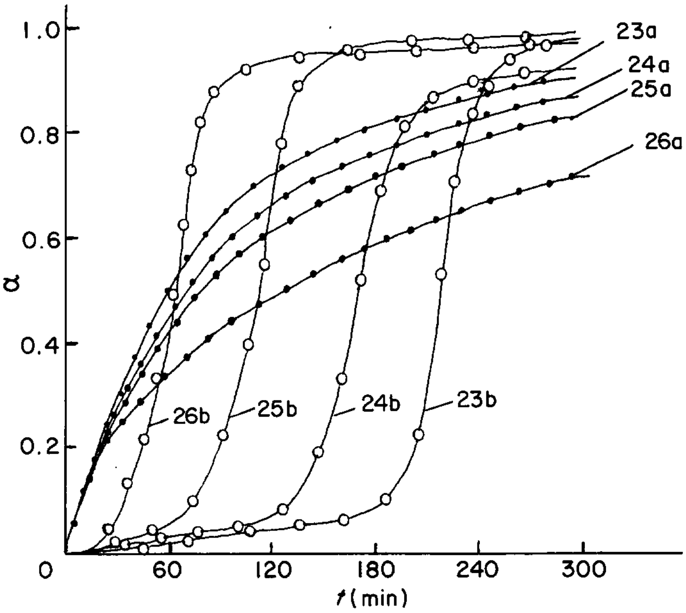

Figure 5 Kinetics of PU formation and BMA polymerization in semi-IPN at various initiator concentrations: 23a, PU in semi-IPN; 23b, PBMA in semi-IPN (*Table 3*); 24a, PU in semi-IPN, 24b, PBMA in semi-IPN (*Table 3*); 25a, PU in semi-IPN; 25b, PBMA in semi-IPN (*Table 3*); 26a, PU in semi-IPN; 26b, PBMA in semi-IPN (*Table 3*)

and the chain growth rate V_{gr} with increasing completeness of the reaction. This follows from the equation:

$$V_{gr}=\frac{K_{gr}[M]\sqrt{V_{in}}}{K_t}$$

where [M] is the monomer concentration and V_{in} the initiator decomposition rate.

Figure 7 presents kinetic curves for polyurethane and poly(butyl methacrylate) for various ratios in the mixture, 85/15, 75/25 and 65/35, at a constant molar concentration of the initiator and of the catalyst (*Table 3*). Calculated W_{red} values for PBMA in the mixture show the PBMA formation rate to increase from experiment 29 to experiment 27 over the initial one (curves 29a, 28a, 27a), which is due to the increase in the system viscosity; in experiment 27, it is higher than in experiment 29, and hence K_t decreases, while K_{gr} and K increase. The polyurethane formation rate in the mixture decreases compared to the initial one from experiment 27 to experiment 29 (curves 29a, 28a, 27a).

A change in the rate of formation of both PBMA and PU is thus observed in a polymeric system where two processes proceed concurrently. It should be pointed out here that the PU formation rate, regardless of the ratios of components and initiator, drops as compared with the initial rate, whereas the PBMA formation rate depends on any factor increasing the system viscosity. In this case it is associated with the gel effect[7,9,17]. It can also be noted that an inverse dependence of the polyurethane formation rate on the poly(butyl methacrylate) formation rate is observed in a series with different molar

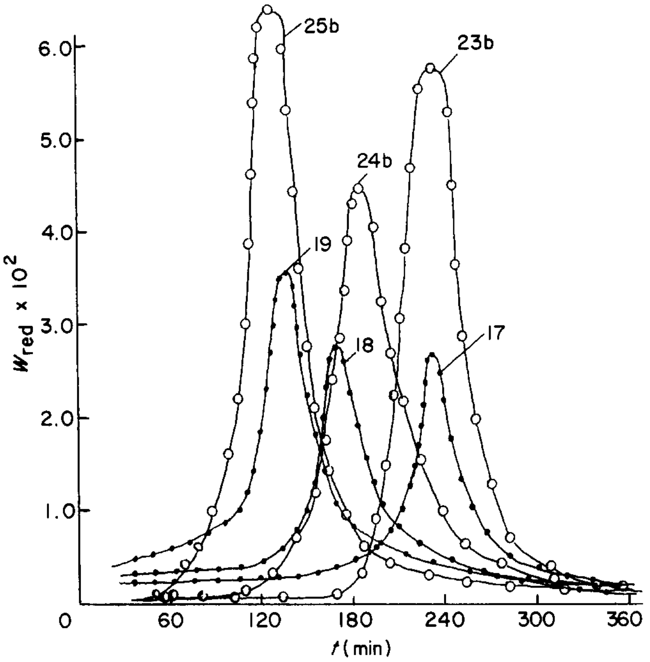

Figure 6 Variation of reduced rate W_{red} of BMA polymerization at various initiator concentrations: 19, pure PBMA, $[I]=2.96\times10^{-2}$ mol dm^{-3}; 18, pure PBMA, $[I]=1.48\times10^{-2}$ mol dm^{-3}; 17, pure PBMA, $[I]=0.74\times10^{-2}$ mol dm^{-3}; 25b, PBMA in semi-IPN, $[I]=2.96\times10^{-2}$ mol dm^{-3}; 24b, PBMA in semi-PIN, $[I]=1.48\times10^{-2}$ mol dm^{-3}; 23b, PBMA in semi-IPN, $[I]=0.74\times10^{-2}$ mol dm^{-3}

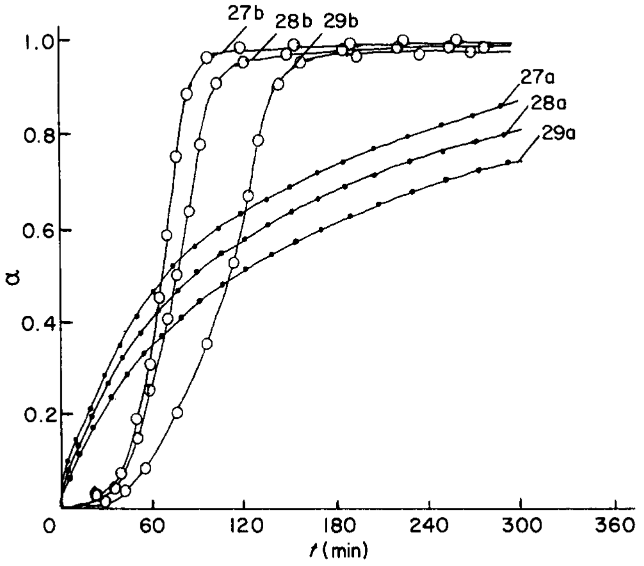

Figure 7 Kinetics of PU formation and BMA polymerization in semi-IPN at various component ratios: 29a, PU in semi-IPN; 29b, PBMA in semi-IPN (*Table 3*); 28a, PU in semi-IPN; 28b, PBMA in semi-IPN (*Table 3*); 27a, PU in semi-IPN; 27b, PBMA in semi-IPN (*Table 3*)

Table 3 Physico-chemical parameters of semi-IPN (PU/BMA)

Sample nos.	Component ratio of PU/BMA (mass %)	Catalyst concentration, [cat] (mol l^{-1}) $\pm0.07\times10^{-4}$	Initiator concentration, [I] (mol l^{-1}) $\pm0.03\times10^{-4}$	Glass transition temperature of PU-enriched phase (K)	Glass transition temperature of BMA-enriched phase (K)	Degree of segregation, *DS*
17	PBMA	–	0.74×10^{-2}	–	338 ± 1	–
18	PBMA	–	1.48×10^{-2}	–	338	–
19	PBMA	–	2.96×10^{-2}	–	338	–
20	PBMA	–	5.4×10^{-2}	–	343	–
21	PBMA	–	1.08×10^{-1}	–	338	–
22	PU	1.4×10^{-4}	–	248 ± 1	–	–
23	75/25	1.4×10^{-4}	0.74×10^{-2}	265	323	0.11
24	75/25	1.4×10^{-4}	1.48×10^{-2}	263	333	0.12
25	75/25	1.4×10^{-4}	2.96×10^{-2}	263	330	0.28
26	75/25	1.4×10^{-4}	1.08×10^{-1}	258	351	0.28
27	85/15	1.4×10^{-4}	5.4×10^{-2}	265	358	–
28	75/25	1.4×10^{-4}	5.4×10^{-2}	263	368	0.28
29	65/35	1.4×10^{-4}	5.4×10^{-2}	258	350	–

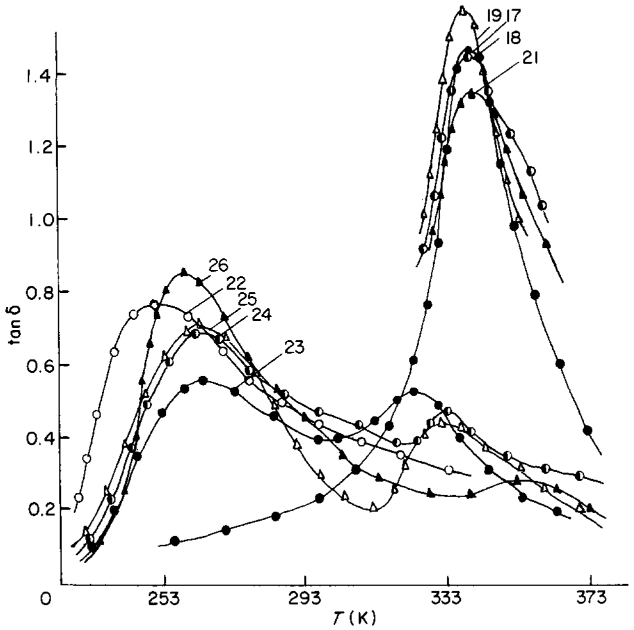

Figure 8 Temperature dependence of mechanical loss of initial components (PU, PBMA) and of semi-IPN, based on them, at various initiator concentrations: 22, PU; 23, semi-IPN PU/BMA; 17, PBMA, $[I]=0.74\times10^{-2}$ mol dm^{-3}; 24, semi-IPN PU/BMA; 18, PBMA, $[I]=1.48\times10^{-2}$ mol dm^{-3}; 25, semi-IPN PU/BMA; 19, PBMA, $[I]=2.96\times10^{-2}$ mol dm^{-3}; 26, semi-IPN PU/BMA; 21, PBMA, $[I]=1.08\times10^{-1}$ mol dm^{-3}

concentrations of initiator; this is a consequence of various conditions of PU and PBMA formation in the mixture as compared with the initial ones.

Let us now discuss the viscoelastic properties of semi-IPN synthesized under different kinetic conditions. Our analysis will be based on the temperature dependences of the mechanical loss of both the initial components, PU and PBMA, and the semi-IPN obtained at the same molar concentrations of the catalyst and initiator. *Figure 8* shows that with increasing initiator concentration in the series of experiments 23, 24, 25, 26 (*Table 3*), i.e. with increasing BMA polymerization rate, the glass transition temperature of samples changes only insignificantly, its shift on the temperature scale being within 2 K. At the same time, different BMA polymerization rates result in significant changes in viscoelastic properties of semi-IPN.

A rise in T_g of PBMA or, more exactly, of the PBMA-enriched phase of semi-IPN is observed with increasing V_{gr} of PBMA, deviations towards both higher and lower (curves 23, 26) temperatures taking place. In the studied semi-IPN, the T_g of the PU-enriched phase in all cases (curves 23–26) shifts towards higher temperatures from 248 K (of the initial PU network) to 265 K in the semi-IPN. The observed changes in the viscoelastic behaviour evidence an incompleteness of microphase separation processes in semi-IPN and a significant influence of kinetic parameters on this process. As for the case of semi-IPN formation from PU and PBMA solution in butyl acetate[18], it can be asserted as a result of forming two non-equilibrium phases whose composition gets fixed by the crosslinking of the PU network. Useful information on the semi-IPN structure can be extracted by analysing the elastic modulus values in the plateau region (*Table 3*). The observed increase of E_∞ for samples in experiments 23–26 with respect to the initial PU network appears to be associated not only with the contribution of topologic entanglements between components, but also with an increase in the intermolecular interaction between them and, possibly, with a growth of degree of crosslinking in the polyurethane component; this is convincingly evidenced by the increase in T_g of the PU-enriched phase (*Figure 8, Table 3*). This effect differs substantially from the result obtained for the preceding semi-IPN series, where an already macromolecular PBMA was introduced into the system. Evidently, the system viscosity decrease due to introduction of monomer gives rise to a more regular network structure and increases intermolecular interaction and hence accordingly raises T_g.

The shift of T_g of the PBMA-enriched phase towards low temperatures depends on the PBMA formation rate. It seems that the lower the PBMA formation rate, the more favourable the conditions for the intermolecular interaction between forming PBMA macromolecules and the PU network being formed and the lower T_g of PBMA in semi-IPN (*Table 3*).

The viscoelastic behaviour of the sample obtained at the highest PBMA and the lowest PU network formation rate is somewhat unusual. The least E_∞ values of the PU-enriched phase (*Table 4*) indicates a more defective structure of the network. This fact can be interpreted as follows: it is possible that in this case the earlier formed PBMA phase has the form of disperse inclusions, while the polyurethane network forms in the presence of such a polymeric filler and, as was ascertained elsewhere[19], a more defective network structure develops in such cases.

It seems interesting to compare viscoelastic properties of semi-IPN samples obtained with the use of the BMA monomer and PBMA. The temperature dependences of the mechanical loss for this sample series are shown in *Figure 9*, where it can be seen that the method of PBMA introduction into the composition (BMA monomer or PBMA) radically changes the semi-IPN structure and viscoelastic properties. Of course, the semi-IPN is in all cases a heterogeneous system with incompatible components, but significant changes in the glass transition temperature and tan δ maximum unambiguously indicate a change in the phase structure of the composition. As known from numerous literature data[20]

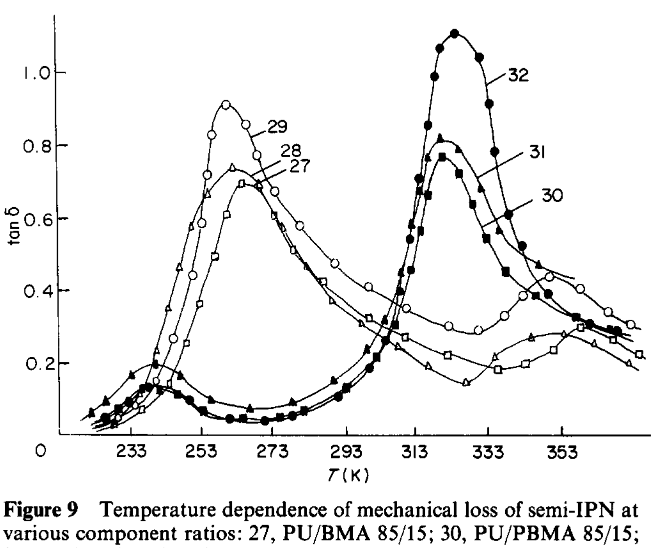

Figure 9 Temperature dependence of mechanical loss of semi-IPN at various component ratios: 27, PU/BMA 85/15; 30, PU/PBMA 85/15; 28, PU/BMA 75/25; 31, PU/PBMA 75/25; 29, PU/BMA 65/35; 32, PU/PBMA 65/35

Table 4 Physico-chemical characteristics of semi-IPN of composition PU/BMA 75/25

Experiment no.	Molar concentration of catalyst, [cat] (mol dm^{-3}) $\pm 0.07 \times 10^{-4}$	Molar concentration of initiator, [I] (mol dm^{-3}) $\pm 0.3 \times 10^{-2}$	Semi-IPN production method		Glass transition temperature, T_{g1} (K)	Glass transition temperature, T_{g2} (K)	Equilibrium modulus, E_∞ (MPa)	Degree of segregation, *DS*
33	1.4×10^{-4}	5.4×10^{-2}	1st stage 2nd stage	Simultaneous curing at 333 ± 1 K	263 ± 1	348 ± 1	1.51 ± 0.02	0.29
34	–	5.4×10^{-2}	1st stage 2nd stage	Photopolymerization at 298 ± 1 K Thermal curing at 333 ± 1 K	243	328	1.12	0.54
35	7.0×10^{-4}	5.4×10^{-2}	1st stage 2nd stage	Photopolymerization at 298 ± 1 K Thermal curing at 333 ± 1 K	258	348	1.26	0.26
36	1.4×10^{-4}	5.4×10^{-2}	1st stage 2nd stage	Thermal curing at 313 ± 1 K Thermal curing at 333 ± 1 K	268	–	1.41	–
37	0.7×10^{-4}	5.4×10^{-2}	1st stage 2nd stage	Thermal curing at 298 ± 1 K Photopolymerization at 298 ± 1 K	258	348	1.45	0.21

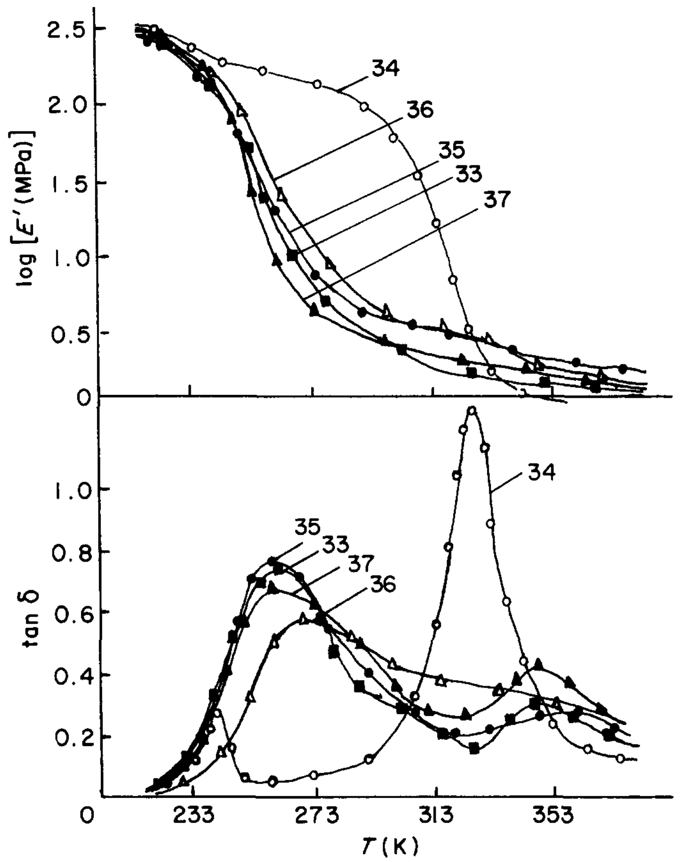

Figure 10 Viscoelastic properties of semi-IPN differing in polyurethane network formation rate. For designations, refer to *Table 4*

the height of the tan δ maximum of a phase that is a continuous medium always exceeds the tan δ maximum of a phase that is a disperse inclusion.

The following can be inferred unambiguously from the temperature dependences of the mechanical loss, presented in *Figure 9*: changing the semi-IPN production method results in changing the continuous medium of the composite. When PBMA in an amount of 15 mass% is introduced, the continuous medium (matrix) is the PBMA-enriched phase, while the PU-enriched phase is the continuous medium when BMA monomer is used (*Figure 9*, curves 27 and 30). Of course, an inversion of phases occurs in either of the two cases, but the concentration range, in which this is observed, depends on the method of PBMA introduction into the system.

Evidently, the phase inversion is in the former case observed in the region of small PBMA mass fractions (less than 13%), while in the latter case, at a PBMA mass fraction of 35%, the continuous phase is the PU-enriched one.

As has been noted above, kinetic parameters of semi-IPN formation substantially affect the structure and viscoelatic properties of samples under study. However, according to ref. 21, the most radical change of IPN and semi-IPN properties is attained by varying the component curing sequence and by the use of photopolymerizing components. As seen from *Table 4*, the semi-IPN production conditions were varied for simultaneous and two-stage processes using BMA photopolymerization. For the BMA photopolymerization, an initiator, trigonal (mixture of benzoyl ethers), and an ultra-violet irradiation source, LUF-80, were used.

The PU network formation rate was controlled by varying the concentration of catalyst (dibutyltin laureate) from 7×10^{-4} to 0.7×10^{-4} mol dm^{-3}; in sample 34 (*Table 4*) the catalyst was absent.

Figure 10 presents the temperature dependences of mechanical loss and elastic modulus for the above-described series.

When comparing the viscoelastic functions for samples 33, 34, 35 and 36, it was found that in the case of a stepwise heat treatment the loss maximum corresponding to PBMA is absent, but a plateau in the PBMA glass transition temperature region is observed. In contrast, two distinct maxima of the mechanical loss are observed for simultaneous semi-IPN formation. It appears that in sample 36 PBMA formation occurs in a fully formed PU network; in the network formation process, a spontaneous distribution of BMA with the initiator in the PU network matrix occurs at 313 K, and then at 333 K (second stage) the BMA polymerization proceeds in localized regions without formation of the intrinsic phase.

The most interesting is the viscoelastic behaviour of samples 34 and 35, substantially differing in the polyurethane network formation rate (*Figure 5*). As a high rate of polyurethane network formation in sample 35 is reached, BMA photopolymerization seems to occur simultaneously with network formation. In the absence of catalyst (sample 34) the BMA photopolymerization rate substantially exceeds the PU network formation rate. A high maximum for the sample evidences formation of a continuous PBMA phase, while the polyurethane network appears to represent disperse inclusions in the PBMA matrix. This radically changes the form of the temperature dependence of the elastic modulus (*Figure 10*), and the highest degree of segregation ($DS=0.54$) with respect to all the studied semi-IPN is observed. As would be expected, no high elasticity plateau is observed for this sample. An appreciable decrease of T_g of the polyurethane network, compared with that of other samples as well as that of the initial network, should be noted, which indicates formation of a defective structure of the network forming in the presence of already formed PBMA.

PBMA formation by photopolymerization at the second stage (sample 37) brings about no significant changes in the structure and viscoelastic properties with respect to those of samples 35 and 36.

Thus, the following has been ascertained by studying the kinetics of curing of the semi-IPN (PU/PBMA) and its viscoelastic properties: the viscoelastic properties (tan δ, E') as well as the component degree of segregation and phase structure of the semi-IPN can be controlled to a significant extent by varying the kinetic parameters (polyurethane network curing rate, BMA polymerization rate), the component curing sequence and the BMA polymerization method.

CONCLUSIONS

The analysis of results obtained here leads to the conclusion that the microphase separation process in semi-IPN formation proceeds under non-equilibrium conditions with formation of phases whose composition gets fixed as a result of the chemical crosslinking. Varying the kinetic parameters of the two-phase system formation is an effective technique for controlling the structure and properties of hybrid binders of such a type.

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