ELSEVIER

Polymer 40 (1999) 6485–6492

polymer

The interrelation between the kinetics of the IPN formation at the interface with solid and surface segregation

Y.S. Lipatov*, G.M. Semenovich

Institute of Macromolecular Chemistry, National Academy of Sciences, Kiev 253660, Ukraine

Received 2 March 1998; received in revised form 4 November 1998; accepted 24 November 1998

Abstract

Surface segregation of components in semi- and full interpenetrating networks based on cross-linked polyurethane, poly(esteracrylate), poly(butyl methacrylate) and poly(vinyl acetate) has been studied at the interfaces with solids of high and low free surface energy. The method of attenuated total reflectance in IR spectra was used to estimate the composition of the system near the interface. It was found that the composition of the surface layers changes as compared with that of initial interpenetrating polymer networks (IPN) depending on the nature of the surface. It was also established that the surface segregation depends on the kinetic conditions of the reaction and on the method of curing. The latter effects are connected with microphase separation proceeding simultaneously with curing.

Keywords: Surface segregation; Semi-interpenetrating networks; Full-interpenetrating networks

1. Introduction

Earlier we have shown that one of the most important factors in polymer blend reinforcement is the surface segregation (or selective adsorption) of one of the blend components at the interface with solid [1–6]. As a rule, the concentration of components with higher surface tension increased in the vicinity of the interface of high surface energy and, vice versa, at the polymer–air interface the components with lower surface tension are concentrated. In such a way the composition of the surface layers at the interface with solid is different from that in the bulk. During the recent years the processes of surface segregation became the subject of many experimental and theoretical investigations [7–16] owing to the importance of polymer composite materials, adhesion and other applications of multicomponent polymeric systems. The investigation of interpenetrating polymer networks (IPNs) and semi-IPNs have shown that the structure and composition of the surface layers formed near the interface with solid are dependent on the surface energy of solid [17,18].

From this point of view it is significant to establish the behavior of IPNs at the interface with solids. The processes of the surface segregation in IPNs up to now have not been studied. For IPNs the surface segregation is possible only before reaching the gel point, i.e. at conditions where cross-linking reactions of IPN formation proceed simultaneously with microphase separation and segregation [19,20].

The aim of this article is to establish the main feature of the effect of reaction kinetics on the surface segregation and composition of the surface layers of IPNs.

2. Experimental

In this work the semi-IPNs, full-IPNs and ternary alloy based on cross-linked polyurerthane (PU) were investigated. PU was synthesized from the adduct of 2,4- and 2,6-toluylene diisocyanate (65:35) and trimethylolpropane and various glycols. As glycols in the semi-IPNs and ternary semi-IPN, poly(oxypropylene glycol) with a molecular mass 2000 was used, whereas in IPNs poly(tetramethylene glycol) with a molecular mass 1000 was used. With the formation of the semi-IPN linear PBMA was obtained by polymerization of a monomer. The full-IPNs were obtained on the basis of cross-linked PU mentioned simultaneously with radical polymerization of oligoesteracrylate(OEA)-trioxyethylene-α,ω-dimethacrylate. The ternary semi-IPN consisted of two linear polymers: poly(vinylacetate) (PVA) and PBMA.The initially obtained PBMA was introduced into the reaction mixture in solution in vinylacetate which was polymerized by radical mechanism simultaneously through curing PU network. The ratio of

* Corresponding author. Fax: + 380-44-552-4064.
E-mail address: lipatov@imchem.kiev.ua (Y.S. Lipatov)

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00848-9

Table 1
Conditions of curing of IPN based on PU and PBMA (75/25 mass %)

Network no.	Concentration of initiator (mol l^{-1})	Concentration of catalyst (mol l^{-1})	Semi-IPN formation conditions
1	0.74×10^{-2}	1.4×10^{-4}	Simultaneous curing at $T = 60$°C
2	1.08×10^{-1}	1.4×10^{-4}	The same
3	5.40×10^{-2}	1.4×10^{-4}	1st stage photopolymerization at $T = 25$°C (5 h); 2nd stage thermocuring at $T = 60$°C
4	5.40×10^{-2}	1.4×10^{-4}	1st stage thermocuring at $T = 40$°C (8 h); 2nd stage thermocuring at $T = 60$°C

PBMA:VA was 2:1 for all systems. As initiator of radical polymerization, azo-*bis*-iso-butirodinitrile (ABIN) was used. Varying the content of ABIN allowed to have change in the ratio of the rates of the formation of different networks in the IPN or in linear polymer in semi-IPNs. For the same purpose in some cases the catalyst of the urethane formation reaction was used (dibutyltinlaurate).

To estimate the validity of the comparison of the quantitative relations between various components obtained from attenuated total reflectance (ATR) data of the systems at the surface and in bulk (thick specimens), theoretical analysis of the change in contrast to the ATR spectra in the conditions of the experiment using the KRS-5 prism was carried out. According to the ATR spectroscopy theory, the value of the electric field in polymeric material which is in optical contact with the ATR prism, exponentially diminishes. This change depends on the indices of a polymer n_2, incidence angle Θ of a beam in ATR prism and the wavelength of the penetrating light. Of interest is the behavior of the penetration depth d_p (when the electric field diminishes e times) in the limits of the refraction index change $n_2 =$ 1.45–1.50, incidence angle $\Theta = 45$–$55°$ and wave number

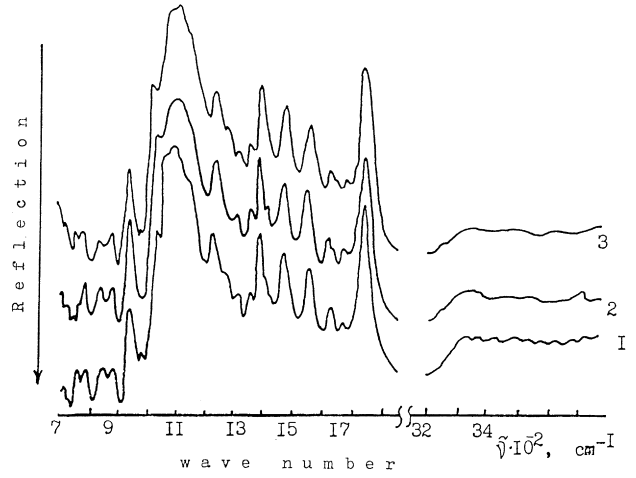

Fig. 1. ATR spectra of the cut section (1) and surfaces of networks 1 (2) and 2 (3).

in the ATR spectrum from 600 to 3450 cm^{-1} was known. The analysis showed that by transition from $n_2 = 1.45$ to $n_2 = 1.50$, the d_p only slightly increased to 1.04 times at $\Theta =$ 55° and 1.1 times at 45°. Upon transition from 45 to 55° d_p value diminishes 1.6 times in the whole spectrum diapason. The most essential value d_p changes for various wave lengths, i.e. for wave number of the band under analysis. For example, at $\Theta = 45°$ by transition from 760 to 1600 and from 760 to 3420 cm^{-1}, d_p value diminishes by 2.1 and 4.3 times correspondingly, which is equal to 2. 63, 1.25 and 0.6 mcm. This analysis was taken into account when discussing experimental data.

The semi-IPNs were obtained by both simultaneous and sequential curing (Table 1), whereas full-IPNs and ternary IPNs were synthesized only simultaneously. In our investigation the process of the surface segregation in semi-IPNs and full-IPNs was studied at the interface with solids of high and low surface energy. The specimens for the determination of the surface segregation were prepared by casting the reaction mixture on the glass surface or directly on the crystal used for the taking IR spectra of ATR (glass KRS-5). The second method of specimen preparation consisted of pouring the composition into dismantled form between the sheets of poly(ethylene terephtalate) (PETF) and for ternary IPNs on the surfaces of glass and poly(tetrafluoroethylene) (PTFE). The surfaces were carefully purified and dried. The thickness of polymers between two surfaces was about 2 mm. The composition of the surface layers were studied using IR spectra of ATR (UR-20 Spectrometer).

The kinetics of the PU and PBMA formation in semi-IPNs were investigated by the calorimetric method using a differential microcalorimeter DAK-1-1A. The kinetics of the formation of IPNs and ternary composition were scanned using transmission IR spectra. The reaction mixture was placed in a thermostatted cell in the caved section of spectrophotometer. The reaction rates of urethane formation and radical polymerization were followed by the bands of valent vibration of NCO-groups and C=C bonds at 2270 and 1640 cm^{-1}. As an inner standard, the band of valent vibrations of CH_2-groups was used.

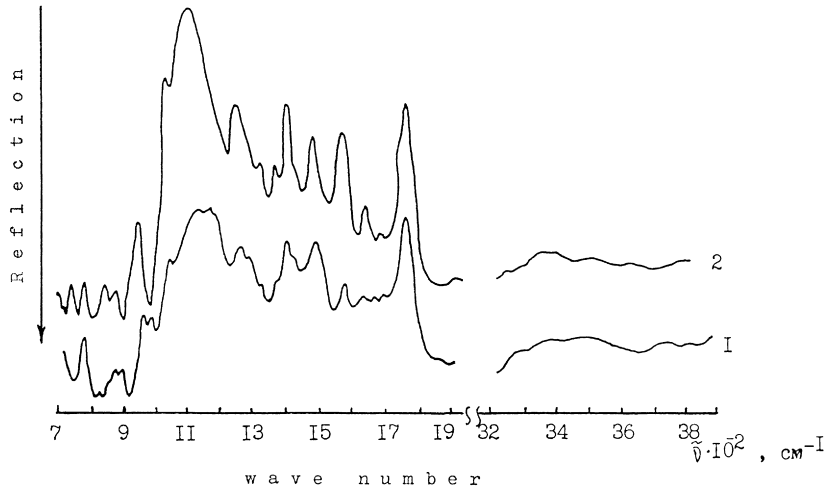

Fig. 2. ATR spectra of the surfaces of networks 3 (1) and 4 (2).

3. Results and discussion

3.1. Semi-IPN based on cross-linked polyurethane and linear poly(butyl methacrylate)

Fig. 1 shows the IR ATR spectra of the surfaces of the semi-IPNs based on PU and PBMA at the interface with PETP and spectra of cut section taken from the center of sample. The specimens were obtained by simultaneous curing and contained various amounts of ABIN (Table 1). The comparison of the spectra of the surface layers and cut section shows that the layer formed near PETP surface in network 2 has no distinctions from the spectra of the specimen in bulk. In the spectra the distribution of the intensities is practically the same. For example, the ratio of relative intensities of bands at 750 and 768 cm^{-1} belonging to PBMA and PU respectively was not changed by transition from the surface to the center. The positions and the band shapes of valent vibrations of C=O and NH–groups in both spectra are the same as well. At the same time, in the spectrum of network 1 the intensity of the band at 750 cm^{-1} strongly decreased and the relative intensity of the band at 1600 cm^{-1} of PU became much higher. These data show the surface layer of network 1 is enriched in PU.

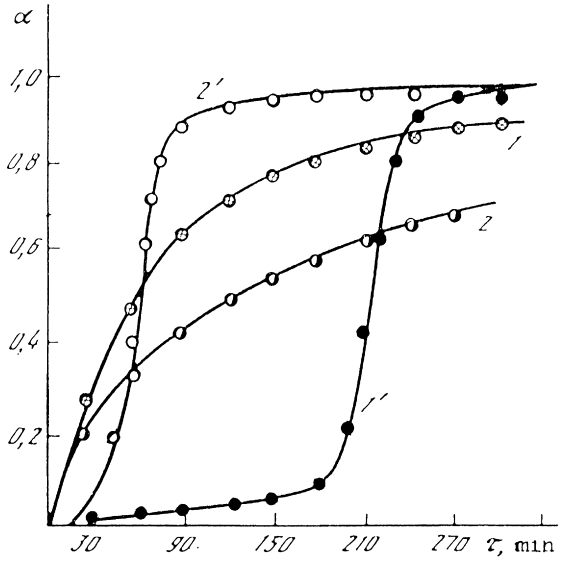

Fig. 3. Kinetic curves of the formation of PU (1,2) and PBMA (1′, 2′) in IPN 1 (1,1′) and 2 (2,2′).

The IR ATR spectra of networks 3 and 4, obtained by sequential curing are presented in Fig. 2. In the spectrum of the surface of network 3, the bands belonging to PBMA are prevailing; the band of PU at 780 cm^{-1} is revealed as a weak shoulder on the background of the band 750 cm^{-1} of PBMA. The spectrum of the surface of network 4 fully agrees with the spectrum of PU.

The analysis of the kinetic data shows that division of the networks in the systems with simultaneous and sequential curing is rather relative (Fig. 3). For example, in the network 1, the radical polymerization rate at the initial stages of curing is lower as compared with the rate of urethane formation. After curing for 3 h the conversion degree of the double bonds hardly reaches 10%, whereas the conversion of NCO-groups reaches 80%. This means that the main part of butyl methacrylate is polymerized practically in already formed PU network. As a result, the network 1 is almost the same as network 4 which is cured sequentially, and the surface layers of networks 1 and 4 are being enriched in PU. In network 2 both reactions of polymerization and urethane formation proceed with similar rates. Correspondingly in the surface layers of network 2 the ratio PBMA:PU is almost the same as in bulk. In network 3, PBMA is formed at the first stage only and in the network near the interface of PETP the surface layer has excess concentration of PBMA.

The data obtained show that in semi-IPNs the surface layers near the interface of PETP are formed with excess amount of the component having higher curing rate. At the comparable reaction rates of polymerization and urethane

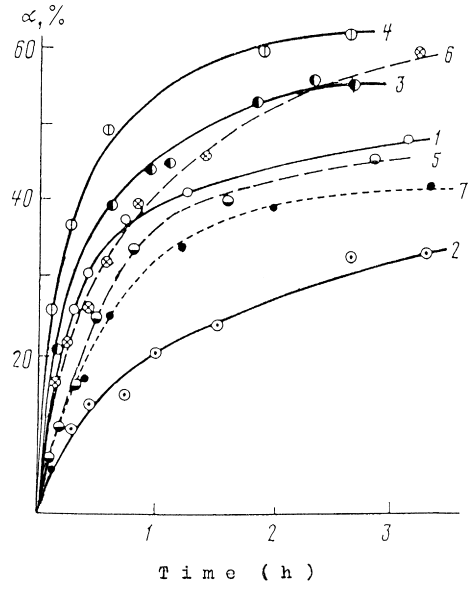

Fig. 4. Kinetic curves of curing of pure PU (1) and PU in IPN with 0.3 (5), 0.5 (2), 2.0 (3,6,7) and 20,0 (4) mass% PEA. 1–4-series 1; 5,6-series 2; 2,7-series 3.

formation the composition of the surface layers in semi-IPNs do not differ from those of the semi-IPN bulk.

Let us consider the reasons which lead to the surface segregation and formation of the surface layers differing in composition as compared with the initial reaction mixture. When applying the composition at the surface, an excess interfacial energy arises between solid and polymer mixture as a result of the difference in the surface tension of substrate and composition. As a result those components are concentrated at the interface, which compensate this difference. The PETP used as substrate has a surface tension 40–41 mN/m, whereas the surface tension of PBMA and PU varied in the limits 30–35 and 40–45 mN/m, correspondingly (all the values are given at room temperature). The closeness of the values of the surface tension of the substrate and mixture components allow avoidance of sharp redistribution of the components near the interface.

In the course of curing, the surface layer will be enriched in the component whose surface tension reaches faster its limiting value i.e. has higher reaction rate (we remember that the surface tension of polymers increases with molecular weight [1]. Microphase separation arising at a definite stage of the curing has also its effect on the composition of the surface layer. At the onset of the microphase separation in the network 1 the NCO conversion degree reaches 57%, whereas conversion of double bonds reaches only 3.5%. In the network 2 these values are correspondingly 21 and 9%. It is evident that the probability of a rise of molecular entanglements is higher in the latter case. This effect may decrease the composition gradient near the PETP surface.

Thus it is evident that the composition of the surface layers in semi-IPNs is dependent on the kinetic factors. The main role belongs to the sequence of curing of components. At the simultaneous curing the ratio of the reaction rates plays a predominant role. The ratio of associated and weakly bonded hydrogen bond groups changes in the surface layer as compared with bulk because of the difference in their compositions (Figs. 1 and 2).

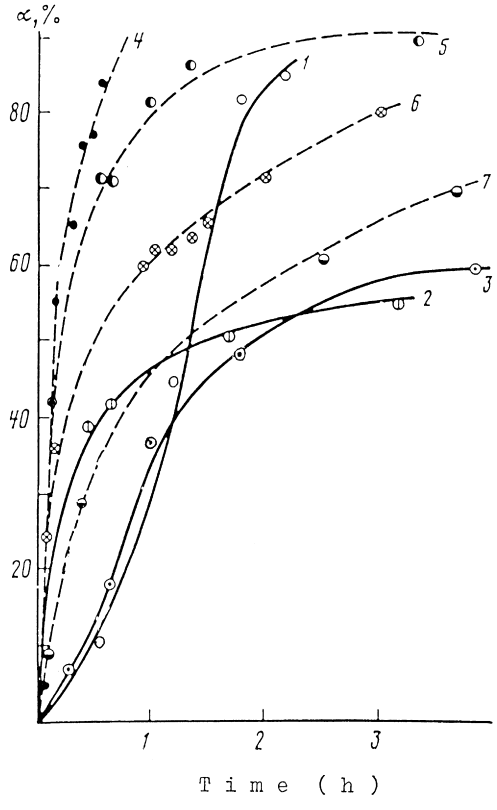

Fig. 5. Kinetic curves of pure PEA (1,4) and PEA in IPN with 10 (5), 30 (2,6) and 50 (3,7) mass% PU. 1–3-series 1; 4–7-series 2.

3.2. IPNs based on cross-linked polyurethane and oligoesteracrylate

For full-IPNs, glass and crystal KRS-5 were used as supports. The curing rate of PU was regulated by the adduct/poly(oxytetramethylene glycol) ratio whereas rate of polymerization of PEA varied by the amount of the initiator (0.01 mass in 1, 0.5 in 2 and 3.0 in 3 series). IPNs with various ratios of constituent networks were studied. In this case the ATR spectra for the 50:50 PU/PEA-IPN were taken from the interface with glass and air. The comparison of spectra shows that near the interface with glass and air the surface layers are formed strongly differing in composition. The layer near the glass surface is enriched in PEA, whereas at the interface with air, IPN has an excess concentration of PU. The comparison of spectra taken at $\Theta = 45°$ and 55° shows that by approaching the interface the concentration of excess components increases. The picture of redistribution of IPN components near the interface is preserved in a broad interval of IPN composition up to 70% of PEA. More

pronounced effects are observed in IPNs with PEA which amounts to 10–50% by mass. ATR spectra for IPN with PEA which amount to 70% more by mass taken from both interfaces are practically the same. The bands associated with PEA are observed preferentially; PU bands being much weaker.

As the effect of the surface manifests itself more markedly in the intermediate range of compositions, the investigation of the influence of reaction kinetics on the composition of the surface layer were carried out for IPN with PU:PEA ratio of 50:50 (by mass). The reaction mixture was applied directly to the ATR element at 353 K. The element is half-cylinder made of glass KRS-5 and represents the surface with a high surface energy. And in that surface the layer of IPN was formed. The d_p of radiation into the layer was in the limit 2–0.7 mkm.

The comparison of the ATR spectra with reaction kinetics (Figs. 4 and 5) shows that there exists some interdependence between the rate of curing of constituent networks and the composition of the surface layer. In specimens of series 1, PEA is cured much slower at the initial stages as compared with PU. In series 2 the rates of the formation of the two networks are very close. For series 3 the rate of radical polymerization is much higher than the rate of the polyaddition reaction. ATR spectra for this series almost nearly coincides with the spectrum of individual PEA network. In the spectra of series 1 and 2 the intensities of the spectra of both the networks are comparable. However, increasing the intensity of bands of PU at 1220 and 1600 cm^{-1} for series 2 as compared with the band 1100 cm^{-1}, belonging to both PU and PEA, testifies to higher concentration of PU in the surface layer of the specimens of this series.

In a similar manner the content of PU and PEA networks in the surface layer at the interface with solid of high surface energy depends on the ratio of the reaction rates of curing of both networks. However, it is necessary to have in mind that the rates of both radical polymerization and polyaddition by the IPN formation are not of independent values [20]. This effect is determined by the interdependence of curing and microphase separation. The latter is because of the rise in thermodynamic immiscibility of two forming networks. The investigations carried out for IPNs based on PU and PEA and for other IPNs shows that the onset of microphase separation depends on the IPN composition and on the ratio of the reaction rates of curing of constituent networks [21]. In IPNs with comparable amounts of both networks, the microphase separation begins usually before the gelation of individual networks, which proceeds rather fast and is characterized by the high degree of segregation. Sharp distinction in the reaction rates also leads to the marked decrease in the time for the onset of microphase separation. In IPNs with a small amount of one of the network, the onset of phase separation begins much later. Cured IPNs have low segregation degree of components and diffuse phase borders.

Taking into account of these concepts, let us consider the formation of the surface layers in IPNs under investigation. The bands of self-associated urethane groups, testifying to the evolution of PU enriched (in IPNs with small amount of PEA) appear after 20–30 min of reaction for series 1, whereas for series 2 they do not appear even after 5 h of curing. Increasing amount of PEA up to 2% leads to the appearance of these bands in specimens of series 1 practically instantly. For series 2 at the same composition the bands do not appear again. These data may be interpreted as an evidence that in series 2, where the reaction rates of polymerization and polyaddition are very close, the microphase separation is hindered as a result of the formation of molecular entanglements between chains of various networks. In series 1, the rate of curing of PEA is much lower as compared with PU and in series 3, it is much higher than for PU microphase separation which proceeds more completely. In this case, the phase enriched in PEA appears near the surface of high surface energy, whereas at the interface with air the phase enriched in PU will be present. Rigid cross-linked PEA having short chains of thrioxyethylene-α,ω-dimethacrylate should have higher free surface energy as compared with flexible poly(oxytetramethylene glycol) block The investigations made for pure PU, cured at the interface with glass confirm its diphility. In the spectra of the free surface the magnitude of half-width of the band ν(C=O) groups are 10–12 cm^{-1} lower as from the side of the interface with glass, the shoulder at 3420 cm^{-1} (absorption by weakly-bonded NH-groups) is more pronounced. The changes in the spectra show that by curing pure PU, the flexible fragment is segregated near the interface with air, the concentration of self-associated groups being lower. The ATR spectra of cured pure PEA are the same both from the side of solid and the air.

Thus the composition of the surface layers, formed in IPN at the interface with solid, depends on the free surface energy of solid, initial composition of IPN and on the ratio of the reaction rates of curing for different networks. Effect of the reaction kinetics on the segregation is determined by the onset of microphase separation as a result of growing immiscibility of two the networks.

Superposition during the IPN formation of the adsorption and wetting processes and of the processes of microphase separation determines very complicated dependence of the composition of the surface layer on the kinetic condition of curing. It may be supposed that the main parameters are the adsorption rate and the time for the onset of microphase separation before gel-point. The correlation between these parameters should determine the conditions of the formation of the surface layer; is it formed from the one-phase or the two-phase system. It is evident that the transition from one-phase to two-phase systems changes the mechanism of the formation of the surface layer. In the first case the selective adsorption of one of the components takes place during the surface layer formation. However, if the time for the onset the phase separation is low, the formation of layer proceeds simultaneously with microphase separation. The phases that

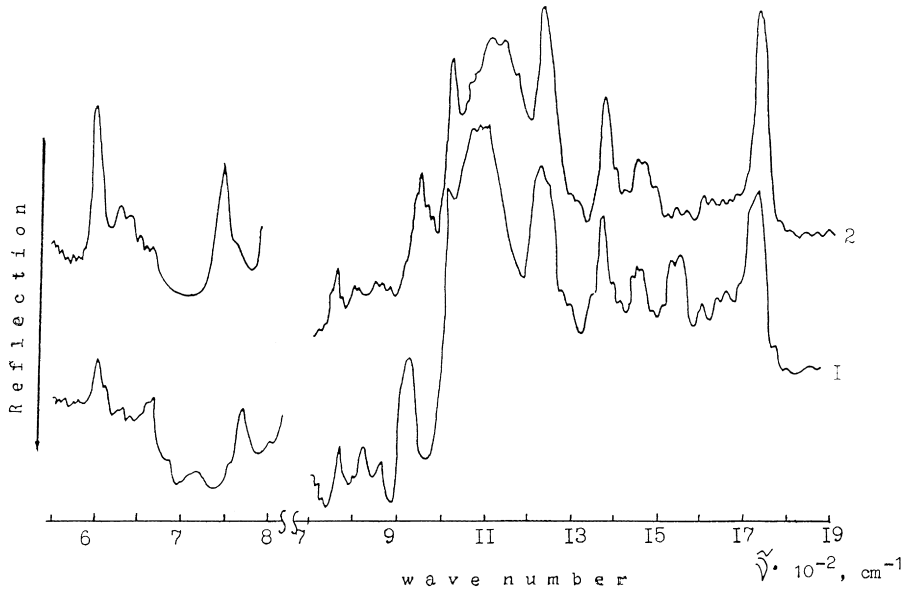

Fig. 6. ATR spectra of the ternary mixture without catalyst (30 mass % of PU). 1-interface with glass, 2-interface with PTFE.

are formed in this process should be considered as the liquids wetting the surface, in accordance with the concept, developed in the work [7–9]. Hence, for polymer blends the wetting surface layer is enriched in the phase with higher concentration of the polymeric substance having higher surface tension. It is evident that the thickness of the layer and its composition will differ much more from the initial composition as compared with the first case.

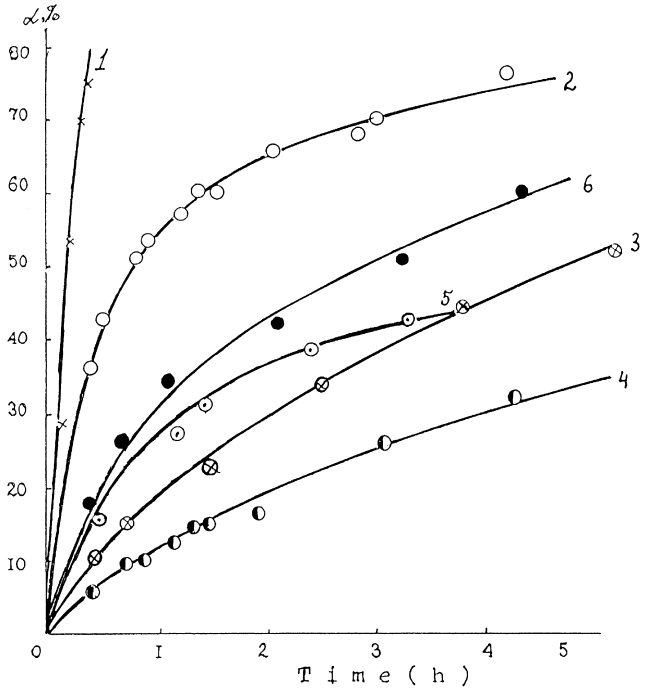

Fig. 7. Kinetic curves of curing pure PU and PU in the ternary mixture: 1, pure PU in presence of catalyst; 2, the same without catalyst; 3,4,5-PU/PBMA–PVA without catalyst with mass % of PU 30, 40 and 70, 6-ternary mixture with catalyst (30% PU).

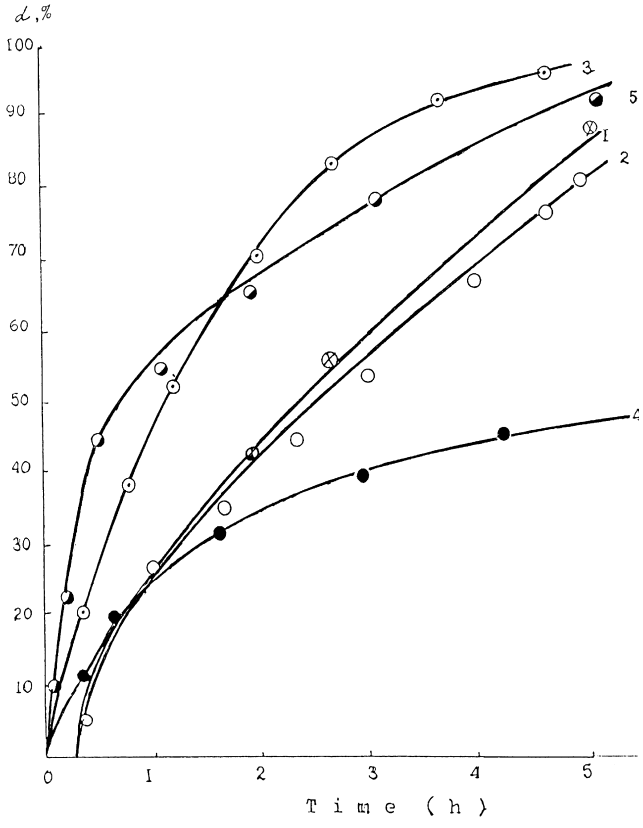

Fig. 8. Kinetic curves of polymerization of VA in binary mixture PVA–PBMA and in the ternary IPN: 1, the binary mixture; 2-4, ternary mixture without catalyst with 30, 40 and 70 mass % of PU; 5, ternary mixture with catalyst at 30% PU.

3.3. Ternary system cross-linked PU-linear PBMA and PVA

Investigations of more complex system, semi-IPN based on cross-linked PU and two linear polymers, PBMA and PVA were continued. The specimens were prepared by curing the reaction mixture between the two surfaces of glass and poly(tetrafluoroethylene), which have a high and low surface energy.

To estimate the composition of the surface layers the following analytic bands were chosen: 607, 750 and 772 cm^{-1}, for PVA, PBMA and PU, respectively. The study of the spectra of ATR for composition with various ratios VA:PBMA:PU shows that the effect of the surface on the segregation is observed only in the rather narrow range of compositions. The most distinct differences between the spectra of both the surfaces were found for the IPN containing 30 mass% of PU, formed without a catalyst (Fig. 6).

Near the interface with PTFE the layer is formed with a composition close to the binary mixture of PVA–PBMA. The surface layer from the glass side consists of PU with a small amount of PVA.

The analysis of the kinetic curves of reaction of polymerization and polyaddition (Figs. 7 and 8) shows that the rates of these two reaction are interconnected. For reaction without a catalyst, the rate constant diminishes four times by decreasing the PU amount up to 40% (from 8.28×10^{-4} to 4.24×10^{-4} kg mol^{-1} min^{-1}). A subsequent decrease in PU concentration up to 30% increases the reaction rate, i.e. diminishes the effect of the binary mixture VA:PBMA in the curing process of PU. A sharp increase of the reaction rate for this composition allows us to suppose that the initial mixture, containing 30% of PU, is thermodynamically less stable as compared with other compositions. It is possible that by applying such thermodynamically unstable composition to the surface, the latter initiates the microphase separation and the surface layer from the beginning is formed in the heterophase conditions. At the interface with the surface of high surface energy the phase enriched with a small amount of PVA in PU is formed, whereas at the interface, a surface of low energy the layer is formed, enriched with the binary mixture PVA–PBMA.

In the ternary compositions, as well as in the case of semi- and full-IPNs, the surface segregation depends on the ratio of the rates of two reactions. When the catalyst was used for the urethane formation reaction, the difference in the layer compositions near glass and PTFE is not as impressive as in the case when the catalyst was not applied. ATR spectra of both the surfaces are almost the same, although near the interface with glass the PU concentration is a little higher as compared with the surface near PTFE.

4. Conclusions

In simultaneous and sequential IPNs, the composition of the layers formed near the interfaces depend on the surface energy of the surface. As the surface layers are formed under conditions of simultaneous change in the composition and the surface energy of the reaction media, the role of kinetic factors in surface segregation becomes very significant. The determining role belongs to the sequence of the component curing. At the simultaneous curing the main role belongs to the ratio of the reaction rates. This ratio, together with the mixture composition, determines the degree and the rate of microphase separation. The dependence between the free surface energy of solid and surface segregation manifests itself more clear in the intermediate range of the composition, which are characterized by the highest degree of microphase separation. For these systems a small time for the onset of microphase separation are typical. Surface layers are formed simultaneously with phase separation. The evolved phases interact with solid surface. The competition between two phases in the course of wetting determines the segregation on the scale on microphases, and not in individual components. The surface layer is enriched in phase that contains higher concentration of the polymer with higher surface tension. However, it is also possible that the selective adsorption from each phase proceeds contributing to the segregation process. It is evident that in such cases both layer thickness and distinctions in composition of the segregated phases and the bulk will be more significant as compared with the case when the segregation of individual components of the blend proceeds from one-phase system. However, it may be supposed that the completeness of the microphase separation as a result of the formation of entanglements in the course of chemical reactions may diminish to some extent the effect of the surface on the surface segregation.

Acknowledgements

Authors express their gratitude to Dr.Vasilii Khranovsky for his help in interpretation of the spectral data and fruitful discussion.

References

[1] Lipatov YS. Colloid chemistry of polymers. Amsterdam: Elsevier, 1988.
[2] Lipatov YS. Polymer reinforcement. Toronto: ChemTec Publishing, 1995.
[3] Lipatov YS. In: Ishida H, editor. Controlled interfaces in composite materials, Amsterdam: Elsevier, 1990. p. 599.
[4] Lipatov YS, Todosijchuk TT, Chornaja VN. Composite Interfaces 1994;2:53.
[5] Lipatov YS, Todosijchuk TT, Chornaja VN. J Coll Interface Sci 1988;123:143.
[6] Mikhal'chuk VM, Lipatov YS, Stroganoff VF, Yagund EM. Polym Networks and Blends 1997;7(4):133.
[7] Steiner U, Eiser E, Budkowski A, Fetters L, Klein J. Berichte der Bunsenges fur Phys Chem 1994;98:366.
[8] Steiner U, Eiser E, Budkowski A, Fetter L, Klein J. Ordering in macromolecular systems. Berlin: Springer, 1994 p. 313.

[9] Steiner U, Kleine J, Fetter L. Phys Rev Lett 1994;72:1498.
[10] Lipatov YS, Khramova TS, Todosijchuk TT, Gudova EG. Polym Sci USSR A 1988;30:443.
[11] Composto RJ, Stein RS, et al. Phys B 1989;156–157:434.
[12] Jones RA, et al. Europhys Lett 1990;12:41.
[13] Dee GT, Sauer BB. Macromolecules 1993;26:2771.
[14] Dee TG, Sauer BB. Macromolecules 1993;26:2771.
[15] Cifra P, Bruder F, Brenn K. J Chem Phys 1993;99:4121.
[16] Genzer J, Faldi A, Composto RJ. Phys Rev E 1994;50:2373.
[17] Lipatov YS, Semenovich GM, Sergeeva LM. Polym Sci USSR B 1987;29:530.
[18] Lipatov YS. Rev Macromol Chem Phys C 1990;30:209.
[19] Lipatov YS. In: Klempper D, Frisch K, editors. Advances in interpenetrating polymer networks, 1. Lancaster, PA: Technomic, 1989. p. 261.
[20] Lipatov YS, Alekeseeva TT. In: Kim L, Sperling L, editors. IPNs around the world, New York: Wiley, 1997. p. 75.
[21] Lipatov YS, Alekseeva TT, Rosovitsky VF, Babkina NV. Polym Networks and Blends 1994;4:9.