Polymer Bulletin 58, 105–118 (2007)
DOI 10.1007/s00289-006-0632-1

Polymer Bulletin

Interfacial regions in the phase-separated interpenetrating networks

Yuri S. Lipatov

Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kiev 02160, Ukraine
E-mail: lipatov@i.kiev.ua

Received: 15 July 2005 / Revised version: 18 October 2005 / Accepted: 20 December 2005

Summary

Formation of interpenetrating networks (IPN) is accompanied by microphase separation due to the appearance of thermodynamic incompatibility of growing polymer chains of different nature. The phase separation remains incomplete as a result of high viscosity of the reaction medium and diffusion limitations. As a result the phase regions in phase-separated networks are separated by an interfacial region. The chemical and physical factors are discussed that determine the conditions of incomplete phase separation, degree of component separation and fraction of an intermediate region. This region preserves the structure of the reaction system before the onset of phase separation and remains in the state of forced compatibility. The final structure of phase-separated IPNs is characterized by the presence of three conventional phase regions which differ in composition, each region being an IPN with molecular level of mixing. All three regions are thermodynamically nonequilibrium, but the degree of deviation from equilibrium is different for each part of the system.

Introduction

The formation of interpenetrating networks (IPN) adheres to the general rules of polymer network formation. As early as the 60′s Dusek [1,2] in his classical works has shown that the network formation is accompanied by the phase separation of the reaction mixture (especially near the gel point) even if the starting reaction system is homogeneous. Dusek has formulated the conditions at which phase separation is possible in the course of reaction and derived equations describing phase equilibrium in such systems.

Most interpenetrating polymer networks are two-phase systems as a result of the phase separation proceeding during their formation. The characteristic features of the process of IPN formation have been studied experimentally for various IPNs and semi-IPNs. [3,4] It was established that the main role in the process is played by the superposition of the chemical kinetics of the synthesis of two networks and of the physical kinetics of the phase separation, its driving force being the appearance of the

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Presented at 44th P.M.M. Microsymposium “Polymer Gels and Networks”,
Prague, 10–14 July 2005

thermodynamic incompatibility of two components at a definite conversion degree. Both processes proceed under nonequilibrium conditions.

The result is the incomplete phase separation and the lack of interpenetration on the molecular level over the entire volume of the system. Phase separation in reacting systems obeys the mechanism of spinodal decomposition [5]. The formed phases may be considered as quasi-equilibrium with molecular level of mixing. The degree of phase separation (segregation degree) depends on the system composition and kinetic conditions of the reaction. The segregation degree may serve as a measure of thermodynamic nonequilibrium. The structures developing at the initial stages of reaction are fixed by reaching the gel-point. Completion of both reactions proceeds in two formed phases [6].

As a result of incomplete phase separation an interfacial region appears (interphase) coexisting with the two formed phases. Its volume fraction depends on the reaction kinetics. This interphase may also be considered as an independent quasi-equilibrium IPN with variable composition. By its physical meaning, interphase is the region of the system where phase separation has not proceeded. The volume of interphase may be regulated by changing composition of the system, reaction conditions and by using compatibilizing agents and fillers. Physical and viscoelastic properties of IPNs are determined by the compositions of two formed phases and by the volume fraction of the interfacial region.

Thus with IPN formation, a definite hierarchy of structures appears which, due to thermodynamic and kinetic reasons, are in the state of thermodynamic nonequilibrium. The real structure of IPNs is multiphase, determined by the coexistence of at least three “quasi-phases”. Full description of the structure and properties of IPNs may be done only by accountingfor the presence of an interfacial region.

The aim of this presentation is to establish the main factors that determine the formation and fraction of interfacial region in phase-separated IPNs. The experimental data show that the interfacial region presents an essential part of any IPN, being the region where phase separation has not proceeded.

Interfacial region in IPN

Incomplete phase separation leads to the formation of transition regions between two phases. This is that part of the system remining for kinetic reasons in the unseparated state and preserving the structure of the reaction mixture before the onset of phase separation. The problems associated with the origin of interfacial regions were discussed in detail in [3, 4]. The temperature dependence of the second moment of signal intensity distribution in NMR spectra of IPN based on crosslinked polyurethane and styrene-divinylbenzene copolymer shows three glass transition temperatures. The transitions near –70 °C and +60 °C are related to network phases as independent components of the system. The appearance of a third intermediate transition between +25 °C and 60 °C indicate the presence of an interphase region. From NMR data the activation energies of transitions in IPNs were calculated. It was established that introduction of a second network in a polyurethane (PU) leads to an essential decrease in activation energy (from 12.5 kcal/mol to 4 kcal/mol for the first and from 37 kcal/mol to 23 kcal/mol for the second network). Activation energies for the interfacial region have intermediate values and depend on the component ratio in IPN. These data show the differences in molecular mobility in various parts of IPN.

The intermediate region was found also by inverse gas chromatography. Again, three temperature transitions were observed. Inverse gas chromatography allows to calculate the enthalpy of mixing ΔH_{12} of two networks and the fraction q of an interfacial region, (Fig.1). As is seen, increasing the amount of the second network in IPN increases these values showing the nonequilibrium state of the IPN.

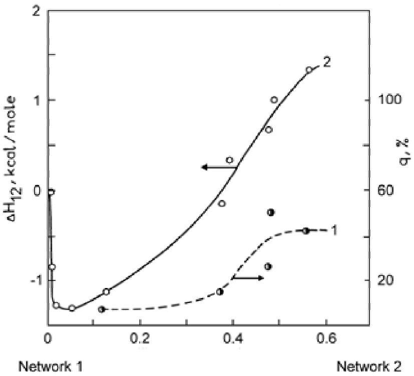

Figure 1. Polyurethane-polystyrene sequential IPN. Dependence of (1) fraction of interfacial region, q, and (2) the mixing enthalpy of the two networks on the concentration of the second network.

The increase in ΔH_{12} is accompanied by an increase in q, i.e. by an increase in the region where thermodynamic incompatibility is observed**.** Thus, the heat of mixing, a strictly thermodynamic quantity, indicates the emergence of phase boundary material-interfacial region [3, 4].

On the segregation degree in IPNs

The concept of the segregation degree was introduced by Bonart [6] to describe the microphase separation in block copolymers. The segregation degree is the effective measure of the part of the system which is phase-separated. The Bonart method is based on the determination of electron density of the system and neat components.

In the majority of our work describing the segregation degree we have used the data of dynamic mechanical properties. [7]. The method is based on the estimation of the tangent of mechanical losses. As known its maximum is in the area of relaxation transition. The polymer-polymer miscibility can be established from the appearance of one or two maxima of mechanical losses.

Figure 2 shows schematically the temperature dependence of mechanical losses of the system consisting of two noninteracting (immiscible) components. Two relaxation maxima are present. By improving the compatibility the maxima shift and become closer. A compatible system reveals only one broad maximum. The segregation degree is calculated from the parameters of the maxima and can be calculated as follows:

$$\alpha = \frac{h_1 + h_2 - \left(h_1 l_1 + h_2 l_2\right)/L}{h_1^0 + h_2^0} \qquad (\mathbf{1})$$

The case $\alpha = 1$ corresponds to complete phase separation; $\alpha = 0$ meets the condition of full miscibility. Low values of the segregation degree show that a great amount of the system is preserved in the unseparated state whose structure is the “frozen” state of the system before separation. The method gives only an effective measure of the part of the system which is phase separated. At the same time in all cases α is a very good and convenient characteristic.

Another method of the estimation of the segregation degree - the fraction of an interfacial region between two evolved phases - is based on the fundamental thermodynamic properties [8].

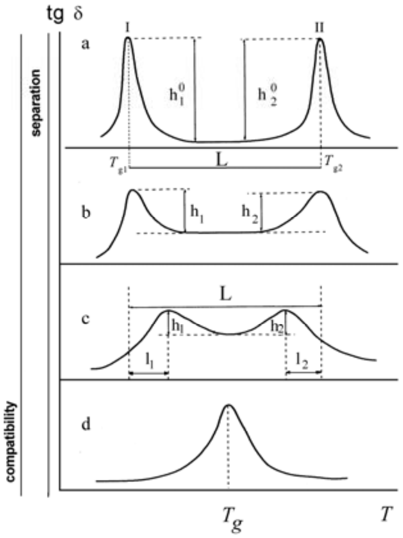

Figure 2. Schematic representation of the temperature dependence of mechanical losses for the systems having different degree of component segregation and miscibility.

The higher is this fraction, the lower is the segregation degree. Thermograms of a two-phase polymer system are characterized by the presence of two transition regions corresponding to glass temperatures of the formed phases. The region between two main maxima is considered to be the interfacial regions. We believe that in the systems, where during the reaction incomplete phase separation proceeds, the two phase region has the composition of the system before the onset of phase separation ("frozen compatibility").

Experimental data on ΔC_P allow to calculate the fraction of the interfacial regions in the systems under consideration using the Fried equation [8] which was applied by many authors [9, 10, 11]:

$$F = \frac{\left(W_1 \Delta C_{P1} + W_2 \Delta C_{P2}\right)}{\left(W_1 \Delta C_{P1}^0 + W_2 \Delta C_{P2}^0\right)} \qquad \mathbf{(2)}$$

where W_1 ,W_2 are mass fraction of components, ΔC_{P1} and ΔC_{P2} are heat capacity jumps for the formed phases, $\Delta C^0{}_{P1}$ and $\Delta C^0{}_{P2}$ are the same for neat components. The value (1-F) is a qualitative measure of the interphase amount in polymer blend. When (1-F) is equal to 0, no interphase exists. When (1–F) = 1, all the polymers are assumed to be in the interphase. The validity of the Fried equation has been discussed in [9]. The authors have shown that the Fried ratio provides a qualitative measure of the extent of the actual diffuse interphase in polymer blends. This is only an approximation since the contribution of the interphase is overestimated using the total weight fractions. However, the authors conclude that such a treatment may have importance in analysis of the binary systems where the interphase plays an important role and the only data available are DSCD thermograms. Analysis of IPNs with application of the Fried equation has been done by Hourston [10].

It is evident that the phase-separated systems with largest fractions of interphase are the most nonequilibrium. This part of the system preserves the “frozen” one-phase structure typical of the system before phase separation. It is alluring to consider the interfacial region as a part of the system where compatibility occurs. Preserving one-phase structure, this region may be considered as a nonequilibrium compatible fraction of IPN.

Both the segregation degree and fraction of interphase should be considered as a measure of deviation of the system from the state of thermodynamic equilibrium. These values may be regulated by the kinetics of the reactions of IPN formation and by the rate of the transfer of the system through the binodal in the course of reaction. Thus various nonequilibrium states of IPN appear, which depend on the path of the process.

Interrelation between chemical kinetics and microphase separation

The reaction kinetics in IPN formation plays a very important role in the formation of the final structure. It determines both the segregation degree and fractions of interfacial regions. In some of our works on semi-IPNs and IPNs the effect of kinetic parameters on the microphase structure has been investigated in detail. For IPNs based on crosslinked polyurethane and styrene, butyl methacrylate or methyl methacrylate, the effect of the following factors on the process has been investigated: the ratio of components in the starting reaction mixture, concentrations of catalyst and radical initiator, the time of the onset of microphase separation (by light scattering), the conversion degrees of both components at the onset of phase separation, segregation degrees α and the interfacial layer fraction $(1-F)$ in reaction products. Some data are given in Table 1. It is seen that the segregation degree and fraction of the interfacial region depend concurrently on many factors, the conversion at the point of the onset of phase separation being the most important. The segregation degree α is determined by:

(1) the rate of the onset of phase separation, i.e. the rate of reaching the critical molecular weight at which incompatibility arises

(2) conversion degree at which phase separation begins

(3) reaction rates of the formation of both components

(4) molecular weights of both components at the onset of phase separation.

The problem is that the reaction rates of formation of both components in the reaction mixture depend on the presence of a second component and are not equal to the reaction rates for neat components. In this case one network is formed earlier and the formation of the second one proceeds in the matrix of the first. At a higher rate of formation of one of the networks, the critical molecular weight for the onset of phase separation is reached faster. It is worth noting that the concentration of the crosslinking agent plays almost no role in segregation because the latter proceeds before reaching the gel point. In a series of special investigations we have studied the in situ formation of blends of two linear polymers which are formed according to various mechanisms (principle of the IPN formation). The observed regularities of this process are similar to those for IPNs, thus suggesting a similar mechanism of the phase separation in the absence and in the presence of crosslinking agent [12, 13].

Molecular weights at the onset of phase separation are the determining factors in the appearance of thermodynamic incompatibility of network fragments. At the same time, up to now there have been no experimental data on the molecular weights of both components at various reaction stages and at the onset of phase separation.

For the blends of linear PU and PMMA synthesized in situ, we have determined molecular weights of both components after completion of the reaction. These values were estimated also for neat components obtained at the same conditions. It was found that kinetic conditions of the reaction determine the molecular weights and molecular weight distribution by simultaneous curing, which are different from the results of polymerization of neat components.

Table 1. Semi-IPN PU/PS. Relations between IPN formation conditions, segregation degrees and fractions of interfacial regions (1-*F*).

Catalyst conc. [cat] $\times 10^5$ mol/l	Rate constant $k \times 10^{-3}$ [kg/mol·s]	Onset of phase separation [min]	Segregation degree α	Fraction of interphase (1-*F*)
		PU/PS (70/30), [I]=1.0×10^{-2} mol/l		
0	5.0	45	0.20	0.20
0.3	10.2	18	0.31	0.18
		PU/PS (70/30), [cat]=0.3×10^{-5} mol/l		
Initiator conc. [I] $\times 10^2$ mol/l				
1	10.2	18	0.31	0.18
5	8.0	25	0.21	0.26
		[cat]= 0.3×10^{-5} mol/l, [I]=1.0×10^{-2} mol/l		
PU/PS ratio				
70/30	10.2	18	0.31	0.18
50/50	8.7	35	0.33	0.26
30/70	7.2	50	0.35	0.30
		Semi-IPN PU/PMMA		
PU/PMMA ratio				
70/30	19.3	51	0.87	0.30
60/40	18.3	34	0.61	0.37
50/50	15.1	58	-	0.40

Tables 2 and 3 show the effect of the component ratio on molecular characteristics and the effect of initiator concentration. These data confirm the marked effect of the reaction conditions on the molecular weights and contribute to the understanding of the effect of reaction conditions on the phase segregation and fraction of the interfacial region.

(5) Microphase separation depends also on the ratio of components in the starting reaction mixture. This ratio determines the reaction kinetics and time of the onset of phase separation.

Due to a great number of factors it is not possible to establish direct relation between them and the segregation degree. However, the general rule is valid: the higher is the segregation degree α the lower is the fraction of intermediate region ($1-F$) as the latter is the measure of the unseparated part of the system.

Table 2. Molecular weights of in-situ blends PU/PMMA (75/25) at various initiator concentrations.

[I] mol/l	M_w PMMA	M_w/M_n PMMA	M_w PU	M_w/M_n PU
0.02	847 000	1.75	24600	2.11
0.01	911 000	1.68	27000	2.21
0.005	1100 000	1.70	27700	2.13
0.00225	1140 000	1.49	28000	2.34
0.00112	1126 000	1.64	35500	2.47

Table 3. Molecular weights of PU and PMMA in blends obtained in situ at various component ratios.

Ratio of components	PMMA		PU	
	M_w	M_w/M_n	M_w	M_w/M_n
0:100	633,000	1.63	-	-
25:75	867,000	2.20	7,100	1.50
50:50	692,000	1.99	14,700	1.75
66:34	911,000	1.84	23,700	2.58
75:25	1100,000	1.74	27,700	2.13
100:0	-	-	37,000	2.14

By considering the effect of the reaction kinetics on the microphase separation in reaction systems of IPNs, three cases may be selected [14].

1. If one network is formed much faster than the other, its formation proceeds in the liquid medium of components of the second network. In such a case the phase separation may reach a high degree of completeness without any steric hindrance. The swollen phase of this network can form in the liquid phase formed by the second network components. The latter forms the network at the latest stages. As a result the microphase structure with a high degree of segregation is formed. It is evident that the higher segregation degree the lower is the fraction of interfacial region.
2. In the case of high rates of both reactions the microphase separation has no time to proceed and the structure is frozen as is typical of one-phase state. Such a system is thermodynamically nonequilibrium with the quenched structure of initial reaction mixture. Freezing of the one-phase structure implies the absence of any interfacial regions.
3. The most typical case is when the reaction rates are comparable. Microphase separation begins at earlier reaction stages and then slows down with increasing the system viscosity and crosslinking up to the gel point. The composition of two phases formed depends both on the reaction rates and on the rate of phase separation (superposition of the two processes determines the fraction of the interfacial region).

Effect of compatibilizers

In some of our works the effect of potential compatibilizers on the viscoelastic properties and kinetics of IPN formation have been investigated [15, 16]. It was established that compatibilizers can affect the reaction kinetics. Depending on the nature of compatibilizer the phase separation in forming system may be accelerated or eliminated. In the latter case an additive prevents phase separation and leads to the appearance of a thermodynamically single phase ternary system with one loss maximum.

Table 4. Effect of compatibilizers on the formation of semi-IPNs PU/PS at [cat] = 0.3×10^{-5} mol/l and [I] =1.0×10^{-2} mol/l.

System	Compatibilizer (%-wt)	$k\times10^5$ [kgmol/s]	Onset of phase separation [min]	α	Fraction of interphase (1–F)
70/30	0	10.2	18	0.31	0.18
	5 OUDM	12.2	30	0.18	0.32
	20 OUDM	14.3			
	3.5 MEG	8.7	single phase		
	5 MEG	7.1			
	10 MEG	5.9			
50/50	0	8.7	35	0.33	0.26
	20 OUDM	12.2	single phase		
	5 MEG	5.7			
	2 OBDR	-	-	0.35	0.27
	2 OA	-	-	0.35	0.41
30/70	0	7.2	50	0.35	0.30
	20 OUDM	15.2	single phase		
	5 MEG	3.9	single phase		
	2 OBDR	-	-	0.26	0.23
	2 OA	-	-	0.40	0.44

OUDM-oligourethane dimethacrylate, MEG- ethylene glycol monomethacrylate, OBDR-oligobutadienediol rubber, OA-oleic acid

Some characteristics of compatibilizer effects are given in Table 4 for PU/ PS IPNs. The addition of oligourethane dimethacrylate (OUDM) in small quantities hinders the phase separation and 1–F is higher compared with the original system. This fraction increases with increasing amount of the compatibilizer. All the INPs containing 20 %-wt. of OUDM do not show any sign of phase separation as follows both from the light scattering data during the reaction and from single relaxation maximum. Such systems, which may be considered as fully compatible, have no interfacial region and no component segregation.

Generally, compatibilizers affect the reaction kinetics and in an indirect way determine the process of phase separation. The effect depends on the compatibilizer amount. When a small amount of compatibilizer is added both relaxation maxima are preserved. However, the value of 1–F increases due to the slow-down of the phase separation. At higher amounts of compatibilizer, two phases disappear, i.e. real compatibilization arises. In some other cases the additives only increase the fraction of interfacial region, i.e. the region that preserved the nonequilibrium structure of the system before phase separation. Formally the diminishing amount of the formed phases may be considered as the increasing nonequilibrium compatibility. In any case it is evident that various additives exert rather compex effects on phase separation and the fraction of interfacial region.

Effect of interface with solid on the phase separation and segregation

In some works [17-20] an effect was found of filler introduction into the blends of linear polymers on their compatibility. It was shown that the filler may increase the thermodynamic stability of the blend, which manifests itself in diminishing the thermodynamic interaction parameter χ_A between two species. This effect was explained by the changes in conditions of intermolecular interaction in thin layers near the solid surface due to the conformational changes leading to variation of the coordination number of the lattice, which determines the value of χ_{AB}. Correspondingly, the filler introduction changes the position and shape of the phase diagram of filled blends. It was also established that filler introduction impedes the phase separation due to diminished molecular mobility of polymer chains at the interface, which is the result of strong adsorption [21]. This effect lowers the possible segregation degree and correspondingly increases the fraction of interfacial region in the phase-separated blend.

Introduction of a filler into the starting reaction mixture for IPN synthesis leads to changes in the thermodynamic stability of the filled system. The measurements of the Gibbs energy of mixing of two polymeric components in IPNs in the presence of a filler have shown that this value strongly depends on the filler nature and amount, being determined by the affinity of the components to the filler surface. Figure 3 shows the dependence of the Gibbs energy of mixing on the IPN nature and filler amount (carbon fibers). It is seen that filler introduction provokes the improvement of the system. A similar picture was observed when, e.g., high-modulus fibers were used as filler. The filler affects also viscoelastic properties of IPNs. Figure 4 shows the temperature dependence of tanδ for unfilled and filled IPNs. The starting IPN characterized by the two relaxation maxima leads to the disappearance of two maxima and to the appearance of a single very broad maximum. This effect points to the essential structural changes in IPN leading to broadening of the glass transition region and apparently improved compatibility of two networks.

The latter follows also from the determination of the segregation degrees which are much lower than those in unfilled IPNs. In many experiments it was found that the

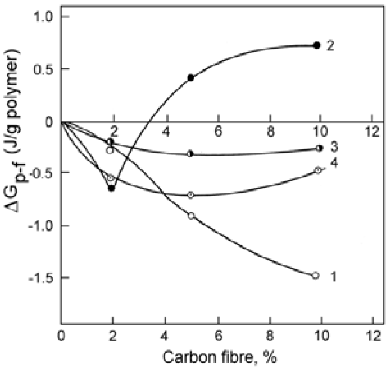

Figure 3. Gibbs energies of mixing of individual networks and IPNs on the amount of introduced carbon fiber (% wt): *1* PU, *2* crosslinked PU ionomer, *3* IPN with 3 % of ionomer, *4* IPN with 10 % of ionomer.

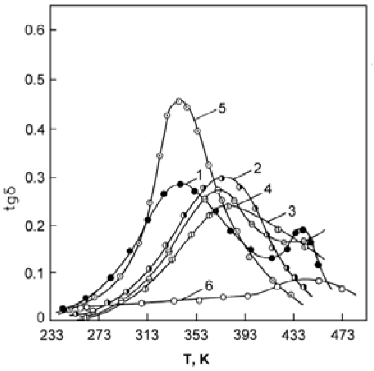

Figure 4. Temperature dependence of the loss tangent of PU/PEA IPNs without filler (2), with 5 % of Al_2O_3 (3), with fumed silica (4) polyester acrylate (5) neet PU (1) and PEA (6).

segregation degree in the filler presence depends both on the filler amount and reaction rate. The rates of both reactions, conversion degrees at the onset of phase separation and its time - all these important parameters depend on the presence of filler.

Generally, increasing the amount of filler hinders phase separation and diminishes the segregation degree. Correspondingly, the fraction of interfacial region increases. The effect depends on the filler nature. Typical data are presented in Table 5.

Table 5. Effect of the filler (1%-wt.) on the segregation degree in semi-IPN PU/PBMA (75/25).

Filler	Segregation degree α
Fumed silica A-175	0.54
A-175 modified with diethylene glycol	0.76
A-175 modified with propyl methacrylate	0.50

Generally, the effect of a filler on the segregation degree may be determined: (1) by improvement of thermodynamic compatibility, (2) by the filler effect on the reaction kinetics, which, in turn, affects the segregation degree and (3) by hindering phase separation.

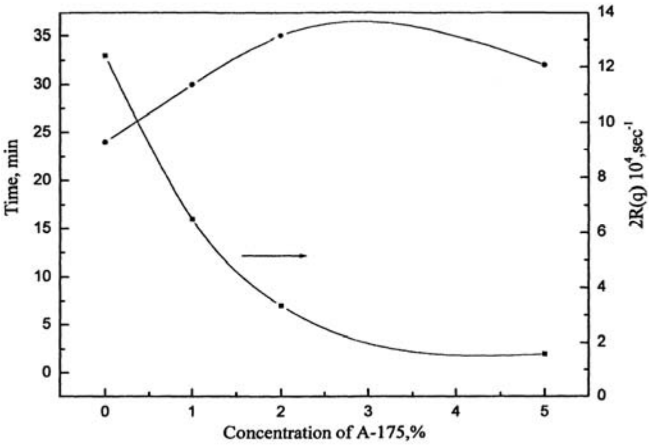

Figure 5. Dependence of the time of the onset of phase separation (•) and parameter 2*R*(*q*) (■) on the filler concentration in PU/PMMA in situ blend.

For example, Figure 5 [22] presents the dependence of the time of the onset of phase separation on the filler concentration and corresponding dependence of the amplification factor *R*(*q*), calculated from the light scattering data. The value of *R*(*q*) characterizes the rate of growth of concentration fluctuations. It is seen that with increasing filler amount the time of the onset of phase separation increases whereas *R*(*q*) diminishes. In Ref. [23] the effect of a filler (fumed silica) on thermophysical properties of polyurethane/poly(butyl methacrylate) has been estimated (Table 6). For filled blends obtained in situ, the increments ΔC_p and corresponding transition temperatures (T_g) were obtained from the experimental data. Using the data on ΔC_p and T_g and the Fox and Couchman equations [24, 25], the compositions of the two phases formed in the course of the reaction blending were estimated. It was found that the composition of the two phases also depends on the presence of filler, i.e. the conditions of phase separation in the presence of filler are not the same as in unfilled system.

Table 6. Thermophysical properties of the unfilled and filled blends of IPN composed of PU/PMMA. T_g in K ΔC_P in J/g K.

PU/PMMA (w/w)	Filler %-wt	T_g PU-eph*	T_g bound layer	T_g PMMA-eph*	ΔC_P PU-eph*	ΔC_P bound layer	ΔC_P PMMA-eph*
100/0	0	253	-	-	0.9	-	-
70/30	0	258		350	0.53	-	0.41
	1	261	313	358	0.44	0.23	0.30
	2	264	320	358	0.48	0.17	0.36
	5	278	325	360	0.48	0.25	0.38
50/50	0	255	-	353	0.50	-	0.35
	1	265	324	353	0.45	0.23	0.20
	2	268	317	353	0.39	0.20	0.24
	5	273	323	354	0.36	0.23	0.25
30/70	0	260	-	347	0.32	-	0.33
	1	267	323	367	0.29	0.22	0.26
	2	273	315	368	0.30	0.17	0.25
	5	273	320	368	0.26	0.20	0.27
0/100	0	-	-	383	-	-	0.30

*eph: enriched phase

continued

PU/PMMA (w/w)	Filler %-wt	1-*F*	PU fraction in PMMA-eph*	PMMA fraction in PU-eph*
100/0	0			
70/30	0	0.30	0.08	0.13
	1	0.45	0.06	0.20
	2	0.40	0.06	0.20
	5	0.40	0.05	0.47
50/50	0	0.29	0.07	0.06
	1	0.46	0.07	0.28
	2	0.47	0.07	0.33
	5	0.49	0.07	0.40
30/70	0	0.33	0.10	0.18
	1	0.45	0.04	0.31
	2	0.44	0.04	0.40
	5	0.45	0.04	0.40
0/100	0			

On the thermograms an additional temperature transition appeared which we relate to the surface layer of the interface with solid (Fig. 6). Earlier it was established [26] that the compositions of the surface layer in filled polymer blends differ from that in the matrix. These layers are formed due to the preferential adsorption of one of the blend components at the interface with solid. Details of the mechanism of the formation of

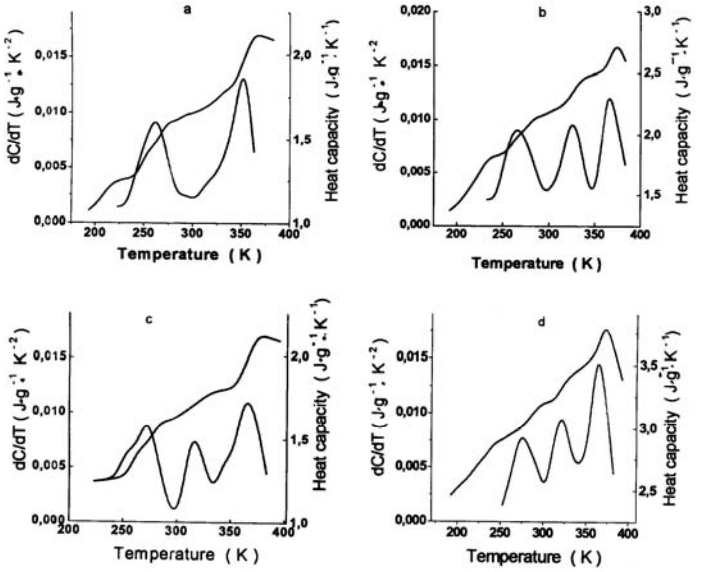

Figure 6. Integral and differential DSC curves for the PU/PMMA in situ blends (30/70) at various %-wt. of filler: a) 0; b) 1; c) 2; d) 5.

surface layers in polymer blends are described elsewhere [26]. The corresponding data are presented in Table 6.

For unfilled systems the fraction of interfacial region increases with growing MMA content in the starting reaction system. A similar picture was observed for the reaction of PMMA with another PU. From Table 6 follows that introducing a filler broadens the transition region between two phases, i.e. increases the fraction of an intermediate region. This effect may be associated with the suppressing action of a filler on the phase separation [21].

The T_g of the surface layer for filled blends of all compositions are in a rather narrow temperature interval (315-325 K). This fact implies that the ratio of the starting components of reaction (DEG and MMA), adsorbing at the interface at the initial reaction stages, is almost the same for all compositions of the reaction mixture. This ratio seems to be preserved when the starting components transform into the polymer state.

Thus we may speak about the effect of filler on the compatibility of blends of linear polymers and IPNs. It manifests itself in the disappearance of two maxima of mechanical losses on filler introduction and the appearance of one very broad maximum. Increasing compatibility follows also from the values of the segregation degree, which are much lower compared with unfilled IPNs. The effect may be associated with the true equilibrium compatibilization, i.e. with increasing thermodynamic stability, and with the so-called nonequilibrium compatibilization [27]. Its essence consists in suppressing the processes of phase separation due to purely kinetic reasons resulting form a sharp decrease in chain mobility at the interface with a solid. In this case the system preserves the structure corresponding to that closer to equilibrium with a lower segregation degree and higher fraction of the interfacial region. In this respect one may state that increasing this fraction means a higher degree of nonequilibrium compatibilization (the degree of phase separation is much lower in the filler presence).

We assume that in filled systems the value of 1–*F* consists of two parts: the contribution of the interfacial region formed as a result of incomplete phase separation in the reaction mixture and that of the surface layer at the interface with solid filler. The appearance of this layer is associated with adsorption effects at the interface which form an additional region of nonuniform distribution of the system components. This region contributes to the total amount of components which do not enter the main two phases. The value of 1–*F* for all compositions increases 1.5 times when 1 % of filler is introduced. Generally, an increase in the total fraction of interfacial region may serve as a sign of low segregation degree in the system. The filler prevents phase separation and increases the fraction of interfacial region. At the same time, an increase in the amount of the introduced filler does not lead to essential changes in 1–*F*. The total fractions of the interfacial region between the two formed phases and of the surface layers remain practically unchanged. The fractions do not depend on the component ratio or on the filler loading.

All the data on the filler effect on phase separation are in accord with the kinetic results of phase separation and thermodynamic analysis of the phase diagrams of filled blends [17]. The filler effect manifests itself in impeding phase separation and in an increase in the intermediate region fraction which may be erroneously considered as an improvement of compatibility.

Conclusing remarks

The presented experimental data on the structure of IPNs allow the following conclusions.The incomplete phase separation in the IPN formation and formation of the thermodynamically nonequilibrium system results in the formation of two phases of variable composition. Each phase may be considered as quasi-equilibrium phase with molecular level of mixing. The IPN as a whole is the system with no interpenetration on the molecular level over the entire volume of the system. One may speak only about interpenetration of various phase regions. The most distinguishing feature of IPNs consists in the existence of the interfacial region which may be conventionally considered as a nonequilibrium third quasi-phase. Its appearance is the result of the spinodal mechanism in which there is no sharp interface between coexisting regions of phase separation. The interfacial regions preserve the level of molecular mixing of the system before the onset of phase separation (frozen compatibility).

The existence of an interfacial region strongly affects viscoelastic properties of IPNs. This was proved by model calculations for a three-parameter model of a two-component system with an interphase [28]. The calculations have shown that the effect of interphase depends on its complex module. In [29] for PU/PMMA IPNs it was shown both experimentally and theoretically that mechanical properties depend on the interphase fraction.

Thus in the course of IPN formation a hierarchy of structures appears which remains in the thermodynamically nonequilibrium state due to kinetic and thermodynamic reasons. The kinetic stability of all these system is very high.

An important finding is that the correlations between compositions of the formed phases (after full conversion) and initial conditions of phase separation show that the final structure of the material is formed at early stages of the reaction. Phase separation proceeds in a four-component system (two initial components and two various network fragments) according to the spinodal mechanism. Full conversion of functional groups at the latest stages of reaction after reaching the gel-point takes place after phase separation, having no essential influence on the initially formed structure. This also explains the fact that the regularities of the reactions and of phase separation are practically the same for the formation of IPNs (in the presence of a crosslinking agent) and for blends of linear polymers formed in situ by various mechanisms.

The final structure of phase-separated IPNs is characterized by the presence of three conventional phase regions which differ in composition, each region being an IPN with molecular level of mixing. All three regions are thermodynamically nonequilibrium, but the degree of deviation from equilibrium is different for each part of the system. In this report the factors determining the conditions of incomplete phase separation and the fraction of the interfacial regions were shown.

Acknowledgements. The participation in these investigations of Dr. T. Alekseeva, Dr. L. F. Kosyanchuk, Dr. N. V. Babkina, and Mrs. N. Yarovaya is highly appreciated.

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