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Reaction compatibilization in interpenetrating polymer networks II. Polyurethane–polystyrene–oligourethane dimethacrylate system

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Abstract

The effects of compatibilizing additive (oligo-urethane dimethacrylate) on the kinetics of IPN formation based on cross-linked polyurethane and linear polystyrene and its influence on the microphase separation, viscoelastic and thermophysical properties have been investigated. It was established, that 10, 20 mass% of OUDM introduced into the initial reaction system, prevent microphase separation of the system and lead to the formation of compatible IPNs, as follows from the data on light scattering. The viscoelastic and thermophysical properties of modified IPN (20 mass% OUDM) are changed in such a way that instead of two relaxation transitions characteristic for phase-separated system, only one relaxation transition is present. It is results of change the morphology of system. The position of this relaxation transition depends on the system composition and on the reaction conditions.

Keywords: Interpenetrating polymer networks; Compatibilization; Relaxation transitions

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1. Introduction

It is very well known that in the course of the formation of interpenetrating polymer networks (IPNs) there proceed the processes of microphase separation, which lead to the appearance of the heterogeneous two-phase systems [1]. Because of it, the problem of compatibilization of IPNs is of great importance. In some works [2–5], it was established the possibility of compatibilization of IPNs by using compatibilizing additives. The effect is based on the interaction between additives and IPNs components, which increases interaction at the interface between two phases.

The formation of semi-interpenetrating polymer networks (semi-IPNs) based on cross-linked polyurethane (PU) and linear polystyrene (PS) has been studied under various kinetic conditions [6]. It was found that in all cases the two-phase systems were formed. Addition to the initial reaction system of various amounts of compatibilizer (mono-methacrylic ester of ethylene glycol) results in the formation of IPNs which is characterized by a single relaxation maximum whose position depends on the system composition. Studies of reaction kinetics complemented by light scattering data have shown that the reaction proceeds up to a full conversion without phase separation. The position of a single relaxation maximum depends on the kinetic conditions of the reaction and on the system composition. The data derived from differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) experiments allowed to establish the regularities of changes in a position of a single relaxation maximum and its parameters. It was concluded that in the cases under consideration one dealt with a compatibilization phenomenon characterized by formation of a stable, single-phase system due to either the formation of thermodynamically miscible ternary system, or the grafting of PU chains onto PS macromolecules via the third component.

For IPNs based on cross-linked polyurethane (PU) and linear poly (butyl methacrylate) (PBMA) it was found [4,5] that introduction of the compatibilizer (oligourethane dimethacrylate) into the initial reaction mixture for IPN formation affects the reaction kinetics and viscoelastic properties of IPNs. The addition of 10 mass% of OUDM suppresses the phase separation during reaction, which is regarded as evidence for the formation of a single-phase

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system, as follows from the data on the time dependence of light scattering by a reacting system. Instead of two relaxation maxima of the compatibilized system is characterized by only one maximum of mechanical losses.

Meanwhile, many questions related to compatibilization of IPNs up to now are open. Of the interest are the effects of the amount of compatibilizer on the development of the one-phase system. The successive increasing concentration of additive should lead to the step-wise disappearing of two relaxation maxima. This process should be accompanied by the continuous changes in the degree of segregation of IPNs component. It is known [7] that almost in no case the phase separation under IPN formation is equilibrium due to steric hindrances, chain entaglements and high viscosity. The arising of nonequilibrium states determines the appearance of an intermediate or interfacial regions between two nonequilibrium phases. Many years ago, these problems were investigated in our works [8,9]. Recently, Hourston et al. applied the DSC method to estimate the fraction of intermediate regions in some IPNs. However, the effect of compatibilizer on the appearance and the fraction of these regions has never been investigated.

In the present paper, we try to establish the effect of the chemical nature of additive on the conditions of compatibilization and on the phase separation in simultaneous semi-IPNs based on cross-linked polyurethane and polystyrene. Our goal was to estimate the fraction of intermediate regions and segregation degree at various kinetic conditions of IPN formation in the presence of compatibilizing additive.

2. Experimental

Semi-IPNs were obtained as in the preceding paper [6] by the simultaneous curing of cross-linked PU in the presence of styrene at 330 K. PU was based on the macrodiisocyanate (MDI) and trimethylolpropane. MDI was synthesizes from 2,4-2,6 toluлene diisocyanate and poly (oxypropylene glycol) MM 1000. Concentration of catalyst $[kt]$ for PU formation (dibutyl tin dilaurate) was 0.3×10^{-5} mol/l. Concentration of initiator $[I]$ of radical polymerization of styrene (2,2′ -azo-bis-isobutyronitrile) was 1.0×10^{-2} mol/l. As a compatibilizing agent oligourethane dimethacrylate (OUDM) has been chosen that was synthesized from macrodiisocyanate (2,4-2,6 toluene diisocyanate, poly(oxypropylene glycol) MM 1000) and monomethacrylic ester of ethylene glycol. This compound contains functional groups (double bond) and may serve as cross-linking agent for styrene. The PU/PS ratio was taken 70/30, 50/50 and 30/70 by mass.

The reaction kinetics of PU and PS formation without and in the presence of compatibilizer was investigated at 333 K using differential calorimeter DAK-1-1A, according to the methods described elsewhere [10]. The kinetics parameters of the reaction for pure PU and PU in the IPNs have been calculated from kinetic equation for a second-order reaction:

$$K = (\alpha/1 - \alpha)/A_0 t,$$

where α is the degree of conversion, A_0 is the initial concentration of reacting groups and t, the reaction time. The reaction rate constant was calculated by generally accepted method from linear dependence of $\alpha/1 - \alpha$ on t. The reaction rate constant for urethane formation was estimated only for the linear part of this dependence where the reaction proceeds according to second order.

The reduced reaction rate of PS formation calculated from

$$W_{\mathrm{red}} = V/M,$$

where $V = \mathrm{d}M/\mathrm{d}t$, M is the amount of monomer unreacted and t, the reaction time.

These investigation were based on the assumption, that the total heat evolution during the reaction is the additive sum of the heats of formation of each IPN component and using titration by the Stagg method [11] as independent determination of conversion of the reaction of the urethane formation.

The time of the onset of microphase separation (MPS) during curing (τ_{MPS}) was monitored by the light scattering from the cloud points, using photocalorimeter FPS-3. From the linear parts of the relationship $\ln I = f(\tau)$, the amplification factors $R(q)$ (q is the wave number), that characterizes the rate of the growth of concentration fluctuations were calculated according to Ref. [12]:

$$\ln(I/I_0) = 2R(q)\tau$$

The compositions of the systems under consideration, the kinetic parameters of reactions and parameters of MPS are given in Table 1.

Dynamic mechanical analysis (DMA) was used for the characterization of viscoelastic properties. The measurements were done at the frequency of the forced sinusoidal vibration 100 Hz in the temperature interval 220–470 K. From the temperature dependencies of the tangent of mechanical losses the glass transition temperatures were found. The segregation degree (α_{segr}) of components was determined from the parameters of the maxima of mechanical losses using following procedure [13]

$$\alpha_{\mathrm{segr}} = (h_1 + h_2 - \lambda_t)/(h_1^0 + h_2^0)$$

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

$$\lambda_{\mathrm{t}} = (h_1 l_1 + h_2 l_2)/L$$

where l_1 and l_2 are the shifts of the maxima across the

Table 1
Compositions, microphase separation (MPS) parameters and reaction rate of formation of initial semi-IPN with different contents of OUDM

PU/PS, mass (%)	OUDM, mass (%)	$K \times 10^5$ (kg mol^{-1} s^{-1})[a]	$W_{max} \times 10^2$ (min^{-1})	τ_{MPS} (min)	$R(q) \times 10^2$ (min^{-1})	α[b]	
						PU	PS
PU	0	12.5	–	–	–	–	–
PU	5.0	13.6	–	–	–	–	–
PU	20.0	16.0	–	–	–	–	–
PS	0	–	2.96	–	–	–	–
PS	20.0	–	2.02	–	–	–	–
70/30	0.	10.2	1.08	18.0	1.84	0.10	0.003
70/30	2.0	10.9	1.06	23.0	1.70	0.13	0.001
70/30	5.0	12.2	0.86	30.0	1.38	0.17	0.005
70/30	10.0	13.3	0.75	–	–	–	–
70/30	20.0	14.3	0.57	–	–	–	–
50/50	0	8.7	0.83	35.0	1.62	0.13	0.004
50/50	20.0	12.2	0.91	–	–	–	–
30/70	0	7.1	0.37	50.0	1.43	0.08	0.004
30/70	20.0	15.2	0.73	–	–	–	–

[a] Constant of the reaction rate of urethane formation.
[b] Conversion degree at the onset of MPS.

temperature scale and L is the interval of temperature between the glass transition temperatures of the pure components.

Thermophysical properties of IPNs were studied by the differential scanning calorimetry in the temperature interval 150–400 K. The calorimeter DSK-D of Perkin–Elmer type has been used. From the temperature dependence of the heat capacity $C_p = f(t)$ the glass transition temperatures were found according to traditional procedure and the increments of heat capacities ΔC_p were calculated. The kinetic parameters of reactions, parameters of relaxation transitions (increments of heat capacities ΔC_p at the glass transition temperature T_g) and data of DMA are presented in Table 2.

3. Results and discussion

3.1. Kinetic studies

Earlier it has been shown [4,5] that introduction of 10 mass% of OUDM into the semi-IPN based on PU and PBMA changes the kinetics of the formation of both constituents of the IPN. The rate of urethane formation decreases whereas the polymerization rate of BMA increases as compared to the initial IPN. The kinetic of IPN formation in the presence of OUDM seems to be the result of the presence in OUDM of the urethane block (MM 1400) and of two methacrylate end groups. The latter may chemically interact with forming PBMA phase whereas the

Table 2
Parameters of relaxation transitions on DSC and DMA for initial and modified semi-IPNs

PU/PS, mass %	OUDM, mass %	DSC								DMA				
		T_g (K)		ΔC_p (J g^{-1} K^{-1})		1-F (%)	$\sum\delta$ (%)	δ (%)		T_g (K)		T_g δ		α_{segr}
		PU	PS	PU	PS			PU	PS	PU	PS	PU	PS	
100/0	–	251	–	0.68	–	–	–	–	–	283	–	0.88	–	–
100/0	5	265	–	0.65	–	–	–	–	–	288	–	0.94	–	–
100/0	20	255	–	0.70	–	–	–	–	–	286	–	1.06	–	–
0/100	–	–	368		0.42	–	–	–	–	–	388		3.26	–
0/100	20	–	355		0.35	–	–	–	–	–	380		1.77	–
70/30	–	258	373	0.55	0.37	17.6	17.0	13.4	3.6	288	408	0.68	0.46	0.31
70/30	2	255	368	0.50	0.25	29.3	30.7	18.7	12.0	–	–			–
70/30	5	255	368	0.50	0.20	31.6	34.0	19.0	15.0	293	398	0.44	0.44	0.18
70/30	10	255[a]		0.60[a]		–	–	–	–	301	375	0.39	0.39	0.10
70/30	20	255[a]		0.60[a]		–	–	–	–	358[a]		0.52[a]		–
50/50	–	258	370	0.40	0.36	30.9	27.7	20.6	7.1	293	418	0.59	0.65	0.33
50/50	20	275[a]		0.50[a]		–	–	–	–	358[a]		0.89[a]		–
30/70	–	258	368	0.35	0.35	29.7	26.3	14.6	11.7	303	413	0.43	0.88	0.35
30/70	20	315[a]		0.30[a]		–		–	–	373[a]		1.00[a]		–

[a] One relaxation transition is observed.

urethane block physically interact with PU-phase. In such a way the better interaction at the interface between two incompatible polymers may be achieved.

Preliminarily the effect of OUDM on the kinetics of the formation of pure components (linear PS and cross-linked PU) was studied. It was observed that both the rate of the urethane formation and of styrene polymerization in the presence of 20 mass% of OUDM formation increase as compared with pure components up to the onset of autoacceleration. The introduction of OUDM into the reaction mixture for IPN formation (PU/PS 70/30 mass%) increases the rates of both reactions. The onset of autoacceleration for PS (τ_a), the conversion degree of styrene (α) and maximum of reduced rate (W_{max}) PS formation diminish in comparison to initial IPN (Fig. 1, Table 1).

By increasing the OUDM concentration from 2 to 20 mass% the increasing the rate of PU-constituent and diminishing W_{max} PS formation is observed (Table 1). Both values of τ_a and α diminish (Fig. 1, curves $2'$–$6'$). At higher concentrations of OUDM the autoacceleration is completed at lower conversion degrees of styrene. Simultaneously the maximum of the reduced rate of styrene polymerization (W_{max}) shifts to lower times (Fig. 2(a)).

The possible scheme of the IPN formation in the presence of OUDM may be presented in the following way:

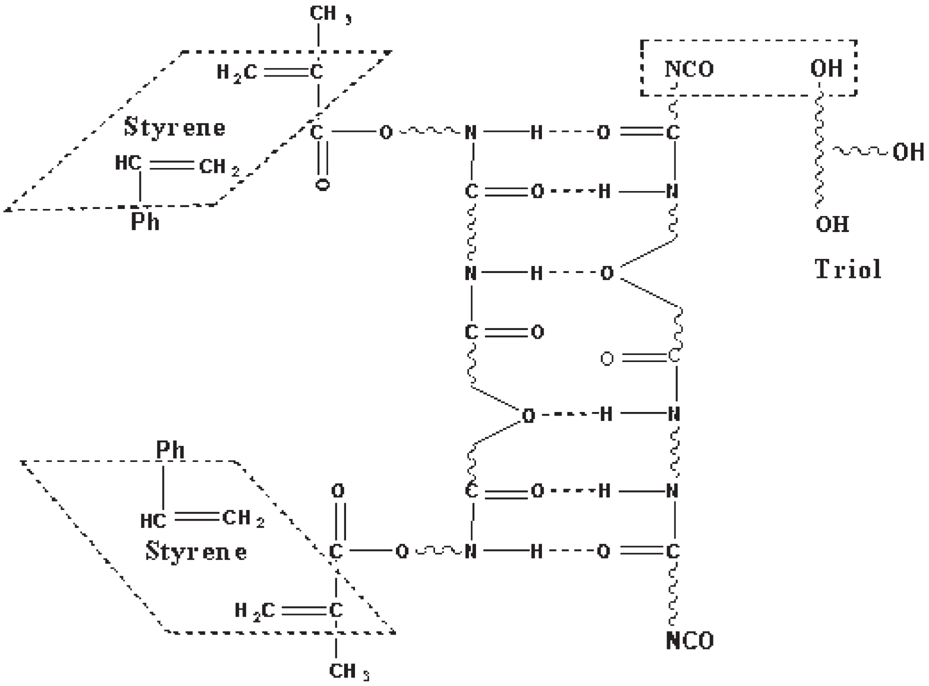

Fig. 3 shows the kinetic curves of formation of PU and PS constituents in the mixture at 20 mass% of OUDM for various ratios PU/PS. For such a case the rate of urethane formation decreases in the following series: 30/70 > 70/30 > 50/50. Calculated value of the maximum W_{red} for PS formation decreases in the following series: 50/50 > 30/70 > 70/30 (Fig. 2(b), Table 1) as distinct from initial IPNs (Table 1).

Therefore the introduction of OUDM into the semi-IPN changes the kinetics of the formation of the systems. These changes affect the time of the onset of phase separation. It is seen from the Table 1 that introduction of small amount of OUDM (2.0 and 5.0 mass%) into the reaction system delay the microphase separation. The time of the onset of phase separation increases, whereas value R_q diminish. Both the conversion degree of styrene and the degree of the reaction completeness of urethane formation at the onset of phase separation growth compared to the initial system. Increasing the OUDM amount (10.0 and 20.0 mass%) has as a consequence the lack of phase separation. It seems to be possible that the increasing additive amount increases the total number of hydrogen bonds between OUDM and PU, whereas at the same time methacrylate groups partially cross-links PS and partially leads to the formation of branched PS. These factors may improve the compatibility.

3.2. DMA investigation

To estimate the effect of application of OUDM as a compatibilizer on the viscoelastic properties IPNs preliminarily there was studied its effect on the viscoelastic properties of initial components: cross-linked PU and linear PS. Fig. 4 presents the temperature dependencies the tangent of mechanical losses (tan δ) of cross-linked PU (curve 1), PS (curve 4), PU network formed in the presence of 5 mass% of OUDM (curve 2) and 20 mass% (curve 3) and PS

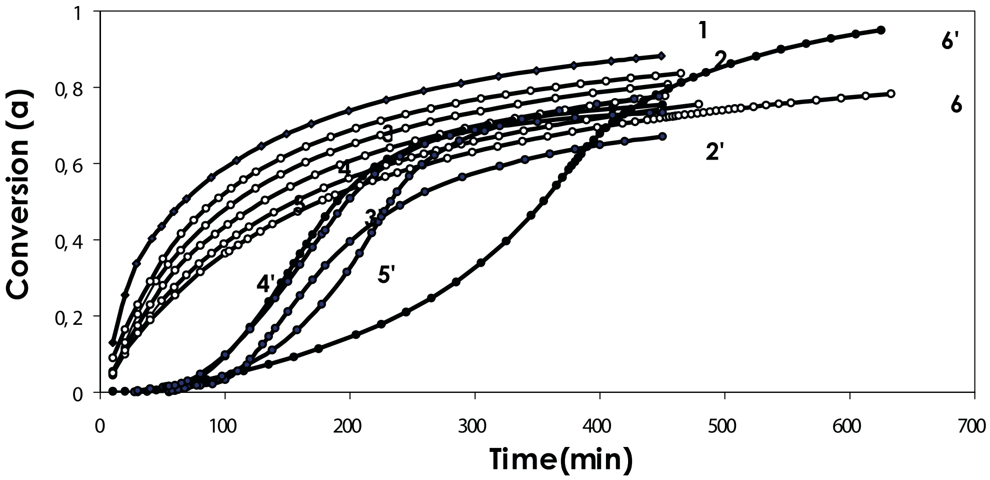

Fig. 1. Kinetic curves for PU formation with 20 mass % OUDM (1) and PU (2–6) and PS (2′–6′) formation in semi-IPN of the composition 70/30 mass % at different contents of OUDM. Concentrations of OUDM, mass %: 2,2′—20.0; 3,3′—10.0; 4,4′—5.0; 5,5′—2.0; 6,6′—0. Initiator concentrations $[I] = 1 \times 10^{-2}$ mol/l, catalyst concentrations $[kt] = 0.3 \times 10^{-5}$ mol/l.

formed in the presence of 20 mass% of OUDM (curve 5). Table 2 summarizes the glass transition temperatures T_g and height of relaxation maxima of initial and modified IPNs.

As is seen from Fig. 4 and Table 2, the introduction of OUDM in forming PU network slightly increases T_g and the level of mechanical losses, the broadening of the relaxation maximum also occurs (curve 1–3).

It is possible that under formation of PU in the presence of OUDM, its urethane block and end double bonds the more inhomogeneous and nonregular network arises. Some structural changes may increase the segmental mobility at the glass transition and higher temperatures. The kinetic data the PU formation in OUDM presence meet these assumption (increasing the rate of urethane formation by adding OUDM as compared with pure PU (Table 1)).

Under the styrene polymerization the introduction of OUDM decreases T_g from 388 K for linear PS to 380 K for PS with 20 mass% of OUDM. Besides, the height of maximum tan δ decreases essentially (Fig. 4, curves 4, 5; Table 2). The changes in viscoelastic properties of PS may be prescribed to the formation of chemical cross-links (OUDM contains two unsaturated end groups), which diminish the molecular mobility of the chains. At the same time the oligoether block (MM 1000) may exert a plasticizing action (T_g of PS with OUDM diminishes as compared with pure PS).

To estimate the compatibilizing action of OUDM on the viscoelastic properties of IPNs, we have selected the semi-IPN based on cross-linked PU and PS at the ratio of components 70/30 by mass. Fig. 5 shows the temperature dependencies of tan δ for initial semi-IPN PU/PS (a) and for semi-IPNs, containing 5 (b), 10 (c) and 20 mass% of OUDM (d). Values of T_g are given in Table 2. It is seen from Fig. 5(a), that initial semi-IPN with component ratio 70/30 mass% is characterized by two sharp maxima corresponding to two phases enriched in one of the components. For IPNs with 5 and 10 mass% of OUDM these two maxima are preserved, although the shape of the relaxation curves changes. The closening, broadening and diminishing the height of relaxation maxima proceed simultaneously. With increasing amount of OUDM, the glass transition of PU-phase growths from 288 K for IPNs without compatibilizer up to 300 K for IPN with 10 mass% of OUDM. T_g of PS-enriched phase at the same conditions diminishes from 408 K up to 375 K (Fig. 5(a)–(c); Table 2).

Diminishing of the heights of relaxation maxima of PU and PS constituents, their closening and broadening as well the increasing level of losses between maxima may testify to diminishing amount of two phases due to transition of some part of PU and PS into the interfacial region as the result of interaction with OUDM.

An important characteristic of the two-phase systems is the degree of segregation α_{segr} [13]. Calculation of α_{segr} has shown that increasing amount of OUDM essentially diminish this value from 0.31 for IPN without compatibilizer up to 0.10 for IPN containing 10 mass%. That means that the introduction of the compatibilizing additive OUDM in the course of chemical reactions of the IPN formation, prevents microphase separation in the system, i.e. increases the compatibility.

The most remarkable change in the relaxation properties occurs under introduction into the reaction system of 20 mass% of OUDM (Fig. 5(d); Table 2). In this case instead of two maxima one observes only one broad maximum at 358 K, whereas maximum corresponding to PU-phase degenerates and reveals only as a shoulder (Fig. 5(d)).

Such changes in the viscoelastic behavior may also be the result of the morphological transformation [14]. Under the formation of semi-IPN in the presence of 20 mass% of OUDM the compatibility in the system increases.

It is evident that the compatibilizing effect should depend on the ratio of the components in IPN. Fig. 6 presents the

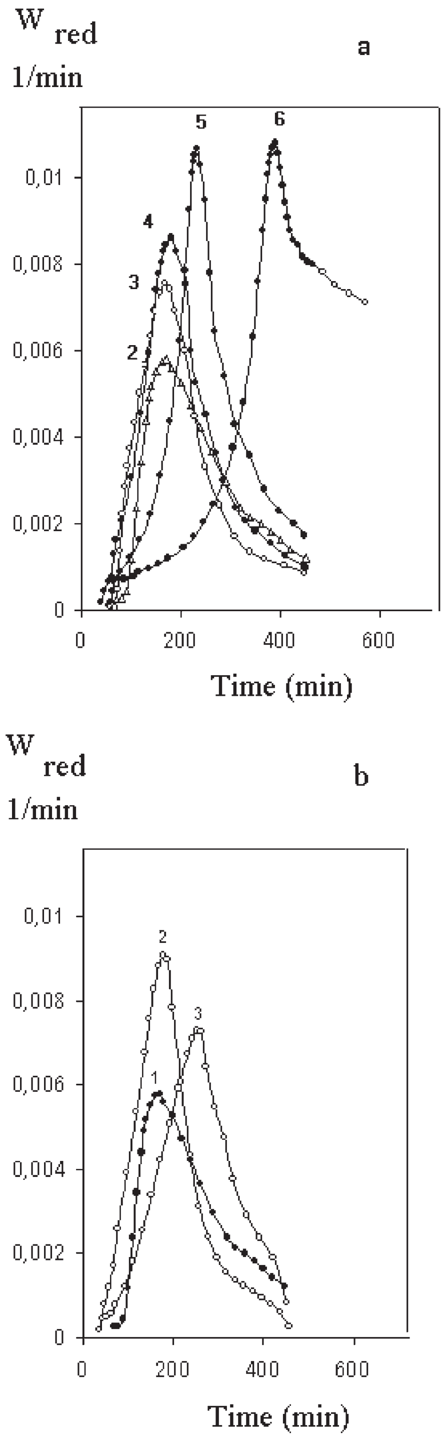

Fig. 2. Dependence of reduced rate (W_{red}) of PS formation on time in IPNs: (a) PU/PS 70/30 mass % at different contents of OUDM, mass %: 2—20.0; 3—10.0; 4—5.0; 5—2.0; 6—0; (b) IPN with 20 mass % of OUDM at different ratio PU/PS, mass %: 1—70/30; 2—50/50; 3—3 0/70.

temperature dependencies of the mechanical losses for PU/PS semi-IPNs of various compositions: 70/30 (curve 1), 50/50 (curve 2) and 30/70 (curve 3) and for the same compositions, but formed in the presence of 20 mass% of OUDM (curves $1'$, $2'$ and $3'$), correspondingly. It follows that initial IPNs are two-phase systems (curves 1–3). Calculations of the degree of segregation have shown slight increasing of the value α_{segr} with diminishing of the amount of PU (Table 2).

Introduction of 20 mass% of OUDM in all the cases changes relaxation properties (curve $1'$–$3'$), especially for PU/PS compositions 50/50 (curve $2'$) and 30/70 (curve $3'$). Instead of two maxima, these systems reveal only one maximum situated on the temperature scale between temperatures of relaxation transitions separated phases in the initial IPNs. For these modified IPNs MPS was not observed (Table 1). As is clearly seen from Fig. 6, the height of the maximum and its temperature position depend on the component ratio.

It is clear that all the changes described here testify to the formation of one phase compatible systems under introduction of large amount of compatibilizer, although the final conclusion can be done only after thermodynamic measurements of the free energy of mixing [14].

It is worth noting that increasing the amount of OUDM changes the properties of IPNs step-wise. However, if the small amounts of additive may be considered as compatibilizer, the greater amounts (10, 20 mass%) hardly may be described in the same way. In reality the IPNs with such amounts of additive are tree-component IPNs and the changes in their properties are determined by their chemically different structure in relation to the initial two-component IPNs.

3.3. DSC-measurements

It is known that the temperature dependence of heat capacities of two-phase polymer systems reveals two transition regions corresponding to the coexisting phases. The glass transition regions are divided by the region of nonlinear change of heat capacity, the latter being prescribed to the smoothly changing composition profile of the interfacial regions (IFR) (interphase) [15]. The compatibilization of heterogeneous blend usually resulted in the formation of IFR with specific characteristics. The thickness of the interphase was estimated as few nanometers. These questions were thoroughly studied by H. Eklind [16].

Introduction of compatibilizers into the two-phase system also increases the specific area between the phases and may result in complete change in blend morphology [17]. Diminishing the dimensions of phase region is accompanied by the increasing fraction of IFR. In such a way, the increasing compatibility in polymer blends by compatibilization may be connected to the formation of an interfacial region between two coexisting phases. The higher is the fraction of this region, the higher should be the compatibility.

Studying the thermophysical properties allows to calculate this fraction from the data on the heat capacity increments at temperature transition. First attempt in this direction were done in [18]. Hourston et al. [19] have used

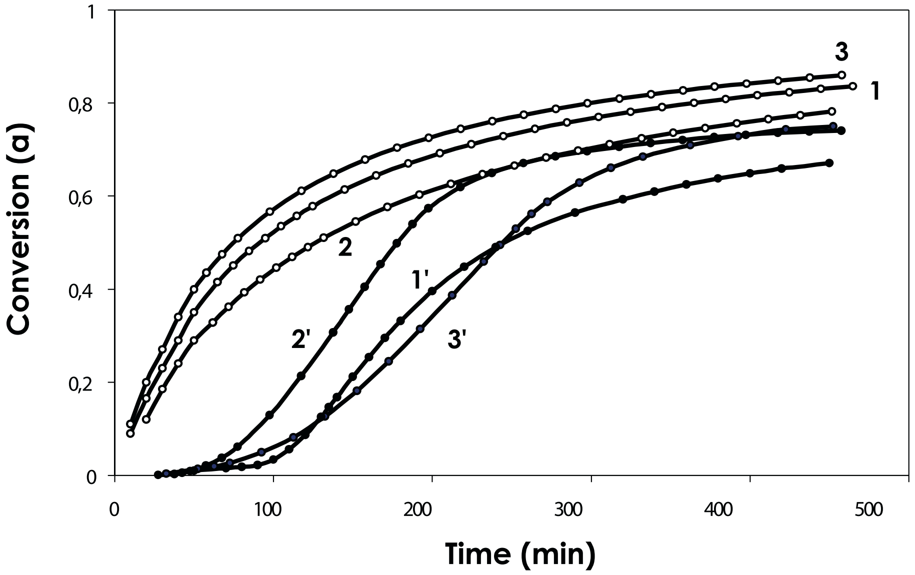

Fig. 3. Kinetic curves for PU (1–3) and PS (1′–3′) formation in semi-IPN with 20 mass % of OUDM at different ratio components PU/PS, mass %: 1,1′—70/30; 2,2′—50/50; 3,3′—30/70. Initiator concentrations $[I] = 1 \times 10^{-2}$ mol/l, catalyst concentrations $[kt] = 0.3 \times 10^{-5}$ mol/l.

for this purpose the equation:

$$F = (\omega_{10}\Delta C_{P1} + \omega_{20}\Delta C_{P2})/(\omega_{10}\Delta C_{P10} + \omega_{20}\Delta C_{P20}) \qquad (1)$$

where ω_{10} and ω_{20} are the mass fractions of a polymers 1 and 2, ΔC_{P1} and ΔC_{P2} are heat capacity increment at T_g for polymers 1 and 2 and ΔC_{P10} and ΔC_{P20} are heat capacity increments in the blend. This equation was applied to estimate the fraction of interfacial regions as $(1 - F)$. We have also used Eq. (1) to estimate $(1 - F)$ for our systems. The mass fractions of both polymers δ_1 and δ_2 entering the interfacial regions were calculated for multicomponent

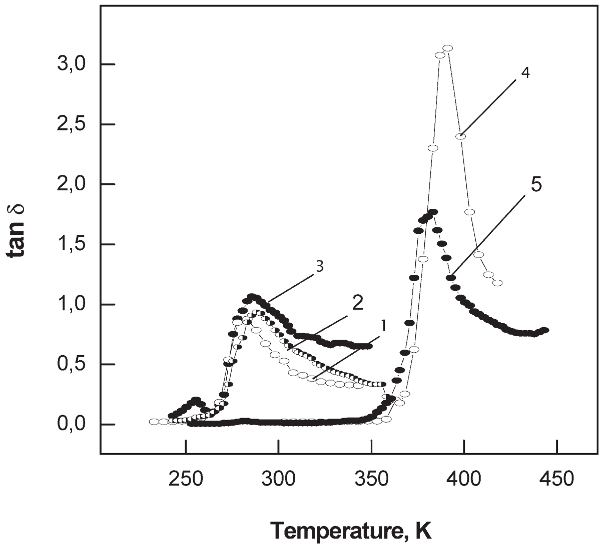

Fig. 4. Temperature dependence of mechanical losses for PU-network (1) and PU-network with 5.0 mass % of OUDM (2), 20.0 mass % of OUDM (3) ($[kt] = 0.3 \times 10^{-5}$ mol/l); PS (4) and PS with 20.0 mass % of OUDM (5) ($[I] = 5 \times 10^{-2}$ mol/l).

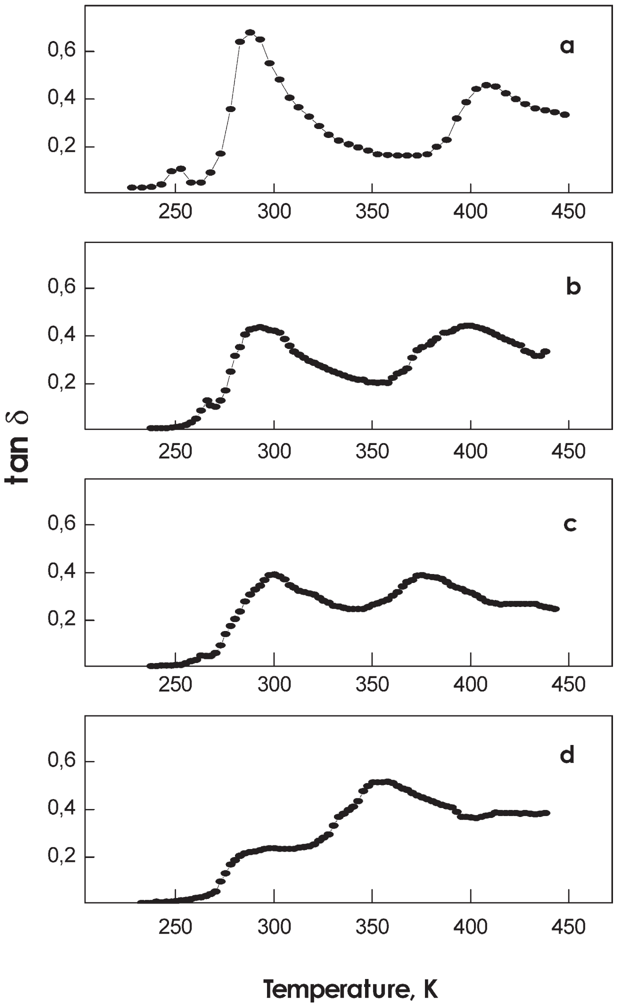

Fig. 5. Temperature dependence of mechanical losses for semi-IPNs PU/PS 70/30 mass % ($[kt] = 0.3 \times 10^{-5}$ mol/l, $[I] = 1 \times 10^{-2}$ mol/l) with OUDM, mass %: a—0, b—5, c—10, d—20.

polymers system on DSC data using Eq. (2) [19]:

$$\delta_1 = \omega_{10} - (\Delta C_{p1}/C_{p10})\omega_{10}$$
$$\delta_2 = \omega_{20} - (\Delta C_{p2}/C_{p20})\omega_{20} \tag{2}$$

To find the values of δ_1 and δ_2 have applied the following equations similar to proposed in [18]. The increments of heat capacities, glass transition temperatures and characteristics of the interfacial regions $(1 - F)$ and $\sum\delta$ for modified IPNs are summarized in Table 2.

The data collected in Table 2 show that values of increments of heat capacity for each phase and temperature position of the transition depends on the ratio of components in IPNs. DSC data show that values of increments of heat capacities for initial PS and PU are higher than for the same constituents in IPN (Table 2) in agreement with the data for polymer blends [18]. Increasing amount of PS in IPN leads to the growth of the fraction of PS in the interfacial region, whereas the change of the PU fraction has nonlinear dependence on composition, showing the complicated character of the distribution of IPN components in the interphase. However, for all the systems growth of the content of PS increases the value of $(1 - F)$ (Table 2) which indicate the improving of the compatibility [18]. It is worth noting that values $(1 - F)$ agree with more correct estimation of the interfacial regions obtained by summarizing of values δ_{PS} and δ_{PU}.

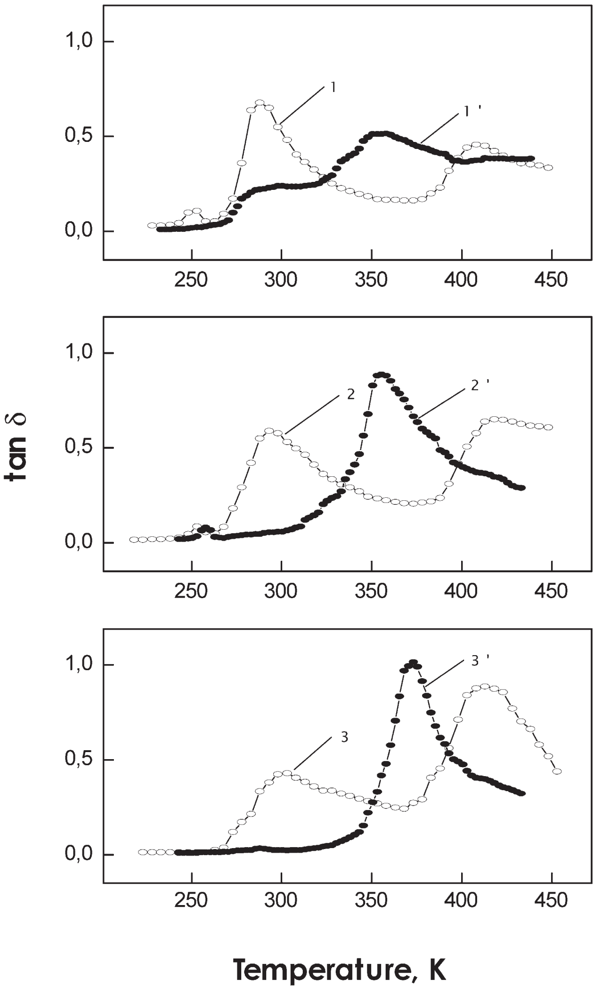

Fig. 6. Temperature dependence of mechanical losses for initial semi-IPNs (1–3) and semi-IPNs with 20.0 mass % of OUDM (1′–3′) at various component ratio PU/PS, mass %: 1,1′—70/30, 2,2′—50/50, 3,3′—30/70 ($[kt] = 0.3 \times 10^{-5}$ mol/l, $[I] = 1 \times 10^{-2}$ mol/l).

As follows from the experimental data (Table 2), introduction of small amounts of OUDM (2 and 5 mass%) into IPN 70/30 mass% results in the increasing the value of $\sum\delta$ and $(1 - F)$, i.e. the fraction of the IFR increases testifying to the increasing the system compatibility. Simultaneously the fractions of PU and PS in the IFR increase 1.3 and 4 times as compared with initial IPN.

However, by introduction of higher amount of OUDM (10, 20 mass%) only one jump in the heat capacity occurs (Fig. 7). Its position is close to position of this peak for PU-phase in PU/PS IPNs (70/30 mass%). It may be supposed that with increasing OUDM amount, more fraction of PS transits into the interfacial region and PS content in PU enriched phase becomes less. With increasing the PS content in IPN T_g shifts to higher temperatures and heat capacity increments diminishes (Fig. 8(a) and (b)).

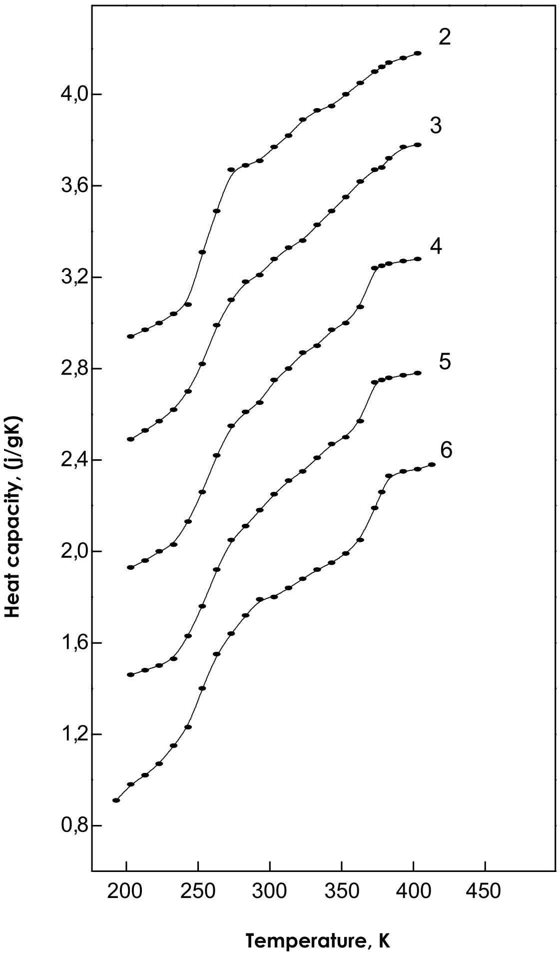

Fig. 7. DSC curves of initial IPN PU/PS 70/30 mass % (6) and IPNs with OUDM, mass %: 2.0 (5); 5.0 (4); 10.0 (3); 20.0 (2).

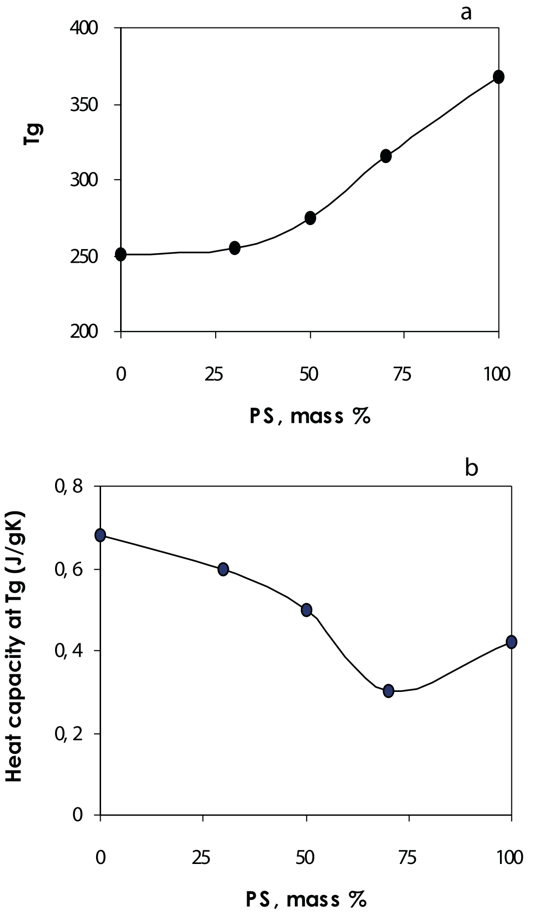

Fig. 8. Dependence of glass transition temperature T_g (a) and the value of heat capacity jump ΔC_p (b) on ratio components PU/PS in semi-IPN with 20 mass % of OUDM on DSC-data. Initiator concentrations $[I] = 1 \times 10^{-2}$ mol/l, catalyst concentrations $[kt] = 0.3 \times 10^{-5}$ mol/l.

Thermophysical characteristic of the blends containing 20 mass% of OUDM are markedly change with component ratio (50/50 and 30/70 mass%, Fig. 8(a) and (b)). Correspondingly, calculations $(1 - F)$ become impossible, as the system consists of only one phase. Such a system is characterized by only one maximum of mechanical losses. The appearance only one relaxation maximum with the increasing amount of compatibilizer may be interpreted as the transition of all the polymers into the state ‘interphase’, i.e. the border between two phases fully disappears.

4. Conclusions

The experimental data on the introduction into the phase-separating IPNs of compatibilizing agent allow the following conclusions to be drawn. Compatibilizer exerts marked effects on the kinetics of the formation of both constituents of IPN, and in such a way changes the conditions of the phase separation during the chemical process. Both the time of the onset of the microphase separation and its rate depend on the amount of compatibilizer and on the ratio of the IPN components. The degree of segregation of the IPN components depends on the reaction kinetics, and its change under compatibilization inevitable affects this value. Successive increasing the amount of compatibilizer leads to the reapproachment of the position of two relaxation maxima appearing in the phase-separated system. Besides, introduction of the compatibilizer, increasing the interaction between two IPN components, decreases the segregation degree the more, the higher the amount of compatibilizer. This effect depends also on the ratio of the IPN components.

The compatibilizing effect reveals itself also in the increasing the fraction of the interfacial region existing between two phases in the systems where the phase separation is not completed. The fraction of the interfacial region increases with increasing amount of the compatibilizer.

All the IPNs containing 20 mass% of OUDM do not show any sign phase separation, as follows both from the measurement of the light scattering during reaction and from single relaxation maximum. Correspondingly, such a systems, which may be considered as fully compatible, have no interfacial region and no component segregation. We suppose that effect of the full compatibilization by the introduction of the great amount of compatibilizer is connected not only with strong improving the interactions at the interface between two phases, but with the change of the thermodynamic interactions in the ternary system component I–component II–compatibilizer, which may lead to the diminishing the free energy of mixing in the ternary system.

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