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EFFECT OF COMPATIBILIZERS ON KINETIC OF INTERPENETRATING POLYMER NETWORKS FORMATION AND THEIR MICROPHASE STRUCTURE

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SUMMARY: The effects of various potential compatibilizers on the viscoelastic properties and kinetics of formation of semi-interpenetrating polymer networks (semi-IPN) based on cross-linked polyurethane and linear poly (butyl methacrylate) has been investigated. All the additives investigated affect the reaction rate of formation of components of IPNs. It was established depending on the nature of compatibilizers the phase separation in forming system may be accelerated or eliminated. The investigation of the effects of some compatibilizers, which differ on chemical constitution, allows to establish two different types of their compatibilizing action.

INTRODUCTION

During last years many works have been published dedicated to the improving compatibility between two immiscible polymers in blends[1,2]. Therefore reinforcement of such an interface becomes an important subject in designing polymer materials such as phase separated blends. In most cases this purpose is reached by introduction into the blend of some components (compatibilizers) capable to interact (physically or chemically) at the interface with both polymers comprising the blend. Compatibilizers are known to improve interphase mixing and interfacial adhesion in incompatible polymer blends.

One of the most distributed type of polymer blends are interpenetrating polymer networks (IPNs). As a rule, these systems in the course of curing undergo nonequilibrium microphase separation due to thermodynamic incompatibility of constituent networks. IPNs present two-phase systems with phases of varying composition. All such systems are characterized by the existence of two relaxation maxima corresponding to the constituent phases[3-5]. Because of it, the problems of compatibilization in IPNs are of as great importance.

The aim of this investigation is to establish the effect of various compounds, that could be potentially considered as compatibilizers, on the reaction kinetics and viscoelastic properties, supposing that improving interfacial interaction will lead to the diminishing the segregation degree in IPNs.

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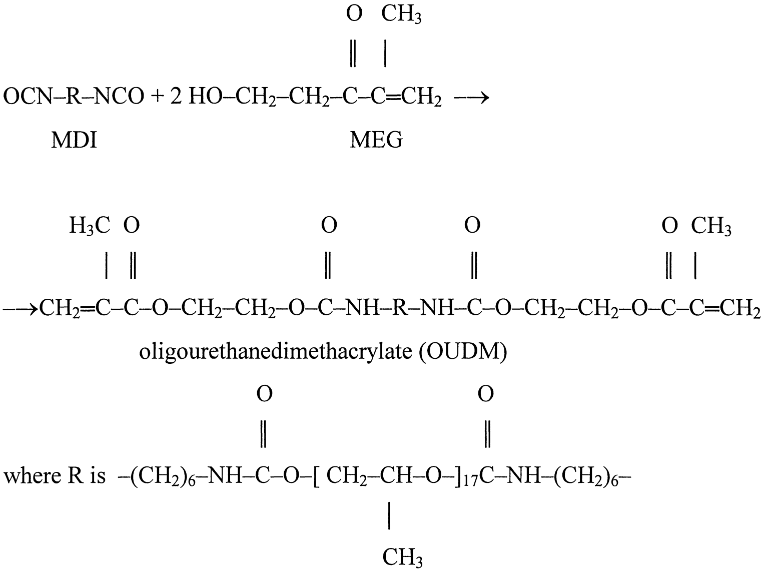
EXPERIMENTAL

Interpenetrating polymer networks based on crosslinked polyurethane (PU) based on adduct (2,4-2,6-tolylene diisocyanate and trimethylolpropane in ratio 3:1) and poly(oxypropylene glycol) MM 2000 with catalyst-dibutyl tin dilaurate, concentration - $1.4\cdot 10^{-4}$ mol/l and butyl methacrylate - (monomer) with initiator of radical polymerization 2,2-azo-bis-isobutyronitrile, concentration - $2.96\cdot 10^{-2}$ mol/l have been investigated. Ratio PU/PBMA - 75/25, 50/50 mass%. Temperature reaction - 60°C. As a possible compatibilizers the following compounds have been tested:

1.Commercial product monomethacrylester of ethylene glycol (MEG) containing two functional groups - double bond and OH-group;

2.Oligourethane dimethacrylate (OUDM) with two end double bonds;

OUDM was synthesized from macrodiisocyanate based on oligopropylene glycol with MM 1000, hexamethylene diisocyanate (HMDI) and MEG at ratio 1:2 at 40°C with the catalyst-dibutyl tin dilaurate (0.01 mass%) according to the scheme:



$$\underset{\text{MDI}}{OCN{-}R{-}NCO} + 2\,\underset{\text{MEG}}{HO{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2} \longrightarrow$$

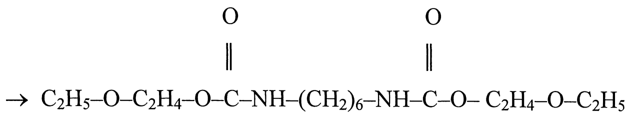
$$\longrightarrow CH_2{=}\overset{\overset{H_3C}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

oligourethanedimethacrylate (OUDM)

where R is $-(CH_2)_6{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}[\,CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}O{-}]_{17}\overset{\overset{O}{\|}}{C}{-}NH{-}(CH_2)_6{-}$

3.Triblockurethane containing urethane block and two CH_3CH_2-O-CH_2CH_3 groups was synthesized from HMDI and monomethyl ether of ethylene glycol (MEE) according to the scheme:

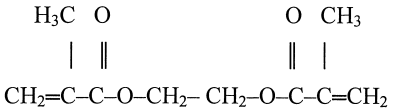
$$\underset{\text{HMDI}}{OCN{-}(CH_2)_6{-}NCO} + 2\,\underset{\text{MEE}}{HO{-}CH_2{-}CH_2{-}O{-}C_2H_5} \rightarrow$$



$$\rightarrow C_2H_5{-}O{-}C_2H_4{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}(CH_2)_6{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}C_2H_4{-}O{-}C_2H_5$$

triblockurethane

4.Dimethacrylate ethylene glycol (DMEG) - cross-linking agent



$$CH_2{=}\overset{\overset{H_3C}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

DMEG

For a study of features of IPN formation based on polyurethane (PU) and poly(butyl methacrylate) (PBMA) using various compatibilizers have been conducted kinetic investigations of polyurethane network curing and butyl methacrylate (BMA) radical polymerization for reaction proceeding simultaneously using differential calorimetry method[6]. At the same reaction conditions for the same systems the effect of compatibilizers on the time of onset of phase separation was studied using laser light scattering method (cloud-point curve). Polymer films of the obtained compositions were studied by method of dynamic mechanical analysis (DMA) using the frequency relaxometer at frequency of forced sinusoidal vibrations 100 Hz[7].

RESULTS AND DISCUSSION

1. IPNs with component ratio 75/25

a) Introduction of Internetwork Grafting

Kinetic curves of PU formation and BMA polymerization in semi-IPN with various compatibilizing agents are shown in Fig. 1,4,6. As can be seen, introduction into the system of 5 mass% of MEG (Fig. 1, curve 2,2') containing two functional groups (OH and double bond) for simultaneously proceeding reaction lead to the increase as the PBMA formation rate (curve 2'), as the PU formation rate (curve 2) with respect to the initial one (curve 1,1').

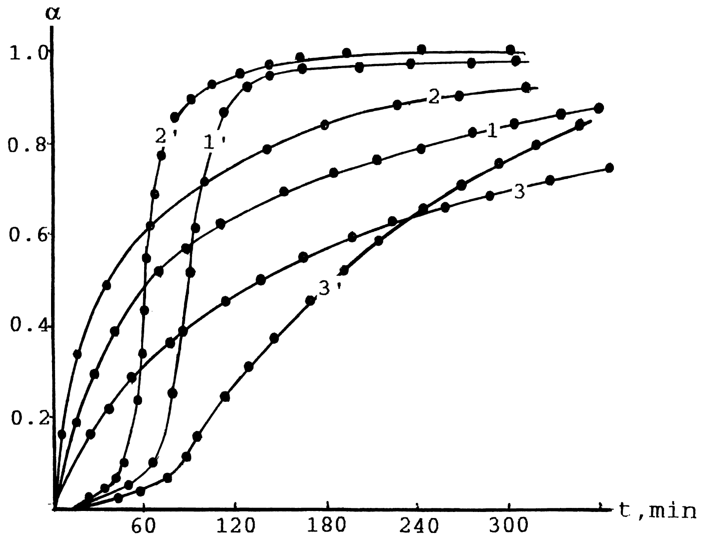


Fig. 1: Kinetic curves for PU (1,2,3) and PBMA (1',2',3') formation in semi-IPN of the composition 75/25 mass%: initial (1,1'), 5 mass% of MEG (2,2'), 5 mass% of triblockurethane (3,3')

This effect is supposed to be connected with chemical interaction between functional groups MEG and corresponding groups of IPN, forming grafted IPNs. At the same time, the possible grafting does not prevent microphase separation. The time of onset of microphase separation in this case is smaller and separation begins at lower degrees of conversion of both components as compared with IPNs formed without additive. As is seen (Table) introduction of 5 mass% MEG leads at 60°C to the fast appearance of the system turbidity (8 min) at conversion degree for PU $\alpha_{PU} = 0.\ 25$ and for PBMA $\alpha_{PBMA} = 0.01$. The experimental curve of the time dependence of light scattering intensity is characterized by sharp growth of intensity testifying to the high rate of phase separation. As is seen introduction of grafting agent into the forming IPN initiates the change in the reaction kinetics of IPN components, which in turn reflects on the onset of microphase separation and viscoelastic properties.

Table. Some features of the compatibilizer action on the formation and properties of IPNs

System	Compatibilizer	Time of the onset of separation, min	Conversion degree at the onset of separation, α		Tg PU, °C	Tg PBMA, °C
			PU	PBMA		
PU	-	-	-	-	-20	-
PBMA	-	-	-	-	-	75
75/25 IPN	-	56	0.40	0.05	-5	60
75/25 IPN	5% MEG	8	0.25	0.01	one $T_g = 25$	
75/25 IPN	10% OUDM	no separation	-	-	one T= 25	
75/25 IPN	5% TBU	60	0.3	0.04	one Tg = 5	
75/25 IPN	10% DMEG	55	0.35	0.07	-7	85
50/50 IPN	-	93	0.38	0.15	0	75
50/50 IPN	5% DMEG	70	0.25	0.08	-	85
50/50 IPN	5% OUDM	no separation	-	-	0	30

Really, the temperature dependence of the loss maximum tg δ for IPNs components and semi-IPN (75/25) show the existence of two expressed maxima (Fig. 2) with glass transition temperatures - 5°C for PU phase and 60°C for PBMA phase. That means that IPN is typically two-phase system.

For IPN containing 5 mass% of MEG Fig. 3a shows only one broad maximum. The existence of only one maximum may be the result of either compatibilization leading to the formation of one-phase system or to the formation of heterogeneous system with broad interphase regions between two phases and with small dimensions of domains of one of the phases. As microphase separation for the systems with introduced MEG begins much faster than for the IPN without additive, it is evident that this system is not one-phase one. On this ground the conclusion can be drawn that possible chemical grafting, following from kinetic data (Fig. 1, curves 2,2'), facilitates the formation of the system consisting of small domains and broad interfacial region.

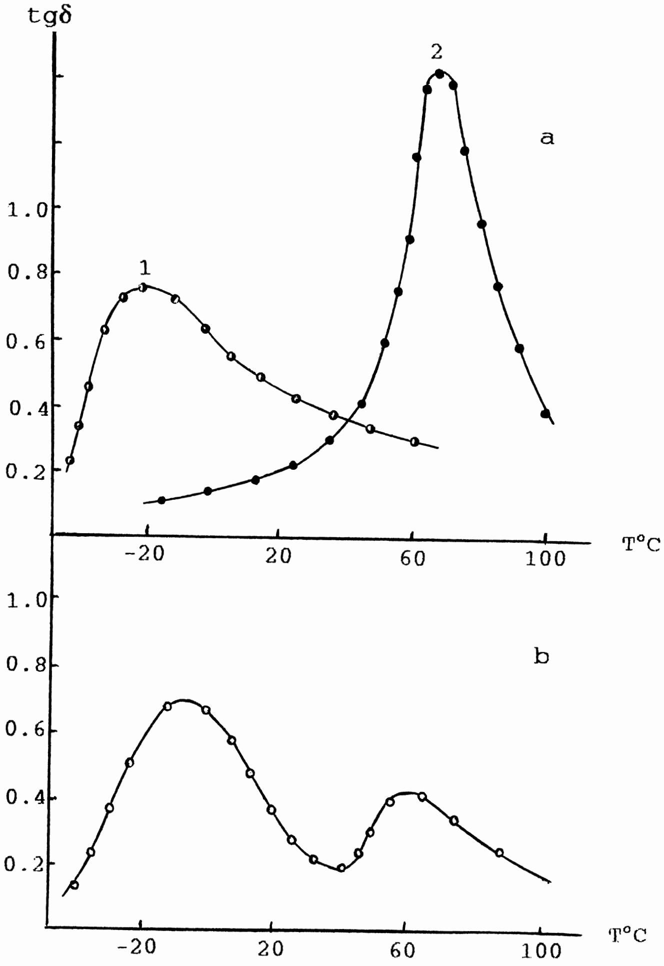


Fig. 2: Temperature dependence of mechanical losses for PU network (1 a), PBMA (2 a) and semi-IPN PU/PBMA (75/25) (b)

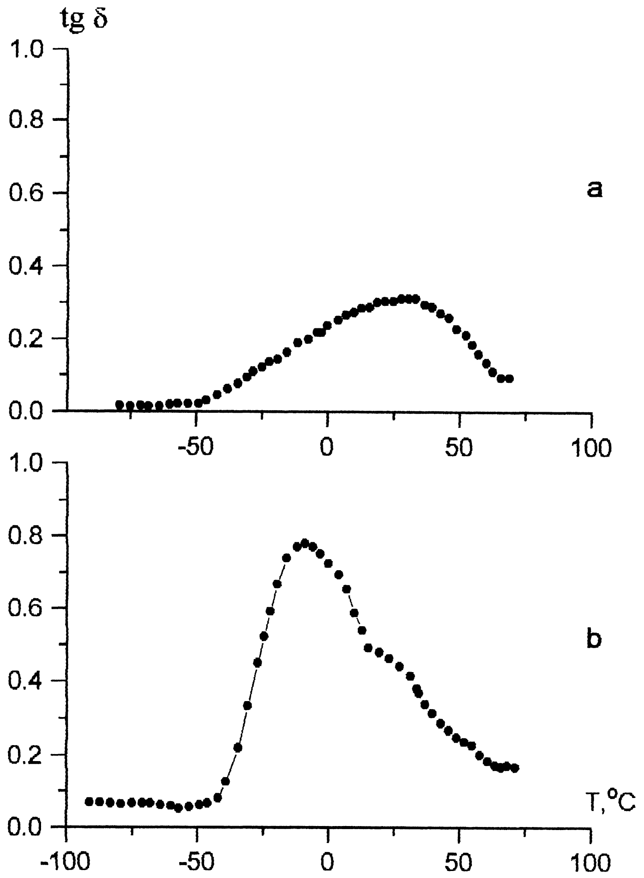


Fig. 3: Temperature dependence of tg δ for semi-IPN (75/25) with 5 mass% of MEG (a) and 5 mass% of triblockurethane (b)

b) Introduction of cross-linking agent

Using dimethacrylate ethylene glycol (DMEG) in amount of 10 mass% as a cross-linking agent for butyl methacrylate increases the rate of BMA polymerization and decreases the rate of PU formation (Fig. 4, curves 2,2'). In this case the time of onset of microphase separation is the same as for pure IPN, although proceeds at somewhat lower conversion degree $\alpha_{PU} = 0.35$ for PU and $\alpha_{PBMA} = 0.07$ for PBMA because of change in the reaction rates (Table).

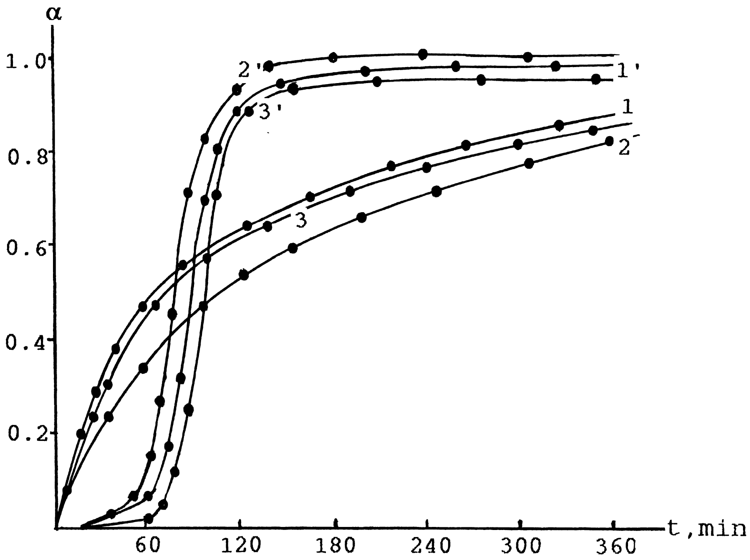


Fig.4: Kinetic curves for PU (1,2,3) and PBMA (1'.2',3') formation in semi-IPN (75/25): initial (1,1'), 10 mass% of DMEG (2,2'), 10 mass% of OUDM (3,3')

Using DMEG as a compatibilizer leads to the appearance of the system turbidity in 55 min after the reaction beginning and the light scattering intensity-time curve has, as in precedent case, sharp inflection point being the sign of the high rate of microphase separation. On the temperature dependence of tg δ (Fig. 5 a, Table) there are seen two expressed maxima in the regions of -10 and 85°C. Glass transition temperature of the PBMA-enriched phase is shifted to higher temperatures as compared with initial semi-IPN. Using DMEG increases the rate of PBMA formation and decreases the rate of formation of PU. It may be suppose that such ratio of the reaction rate leads to the phase inversion where cross-linked PBMA plays the role of dispersion media where in PU domains are distributed. It is evident that in this case no compatibilization takes place.

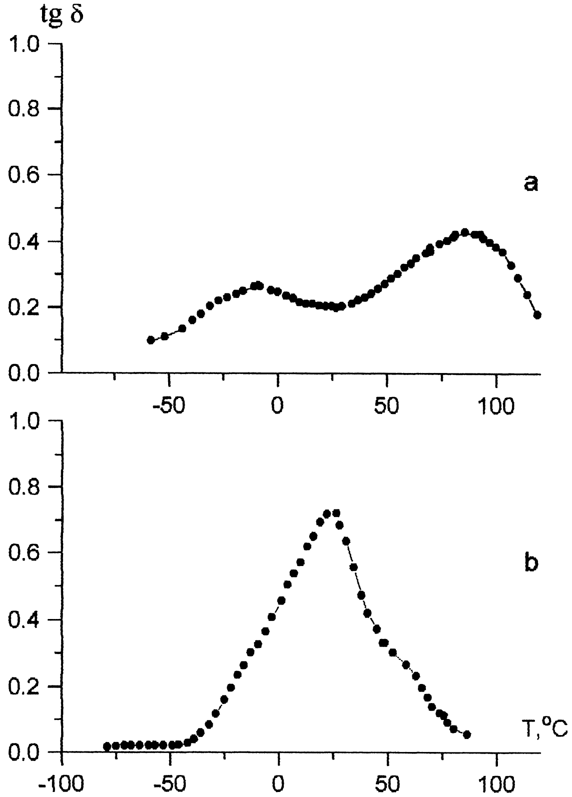


Fig. 5: Temperature dependence of tg δ for semi-IPN (75/25) with 10 mass% of DMEG(a) and 10 mass% of OUDM (b)

c) Introduction of compatibilizers

It is generally supposed that compatibilizers improve the degree of component mixing and increase the interfacial adhesion between two phases. We have used two compatibilizers: triblockurethane (TBU) which has urethane block with long aliphatic chain (C_6) and two CH_3CH_2-O-CH_2CH_2 - groups and oligourethane dimethacrylate (OUDM).

Introduction of 5 mass% of TBU that does not interact chemically with network components, diminishes both the rate of BMA polymerization and PU formation as compared with initial semi-IPN (Fig. 1, curves 3,3'). TBU does not change the time of the microphase separation onset, which, however, begins at lower conversion degrees due to reaction rates retardation. The appearance of turbidity begins after 60 min of reaction. The intensity scattering curve has more stepwise character pointing to slower rate of microphase separation. The turbidity in this system appears at α_{PU} = 0.3 and α_{PBMA}= 0.04

(Table). Introduction of TBU results in the appearance only one high maximum at -10°C and small shoulder in the temperature region 25-40°C (Fig. 3 b). Combination of kinetic and mechanical data shows that this IPN is phase-separated two-phase system where TBU is possibly localized at the phase interfaces, leading to sharp diminishing the domains sizes. This follows from the chemical constitution of TBU containing blocks identical to IPN components. It is evident that TBU diminishes the degree of phase separation in the system and as a result only one maximum of tg δ appears corresponding to continuous PU-phase, which contains discrete inclusions of the second component.

The most interesting results have been obtained when oligourethane dimethacrylate was used as a compatibilizer. This compound containing two end double bonds may serve as cross-linking agent for butyl methacrylate. However, as distinct from DMEG, OUDM includes also urethane block with molecular mass about 1,500, which is identical to PU component of IPN. The kinetic curves of polymerization of butyl methacrylate and of PU formation in presence of 10 mass% of OUDM are presented in Fig. 4 (curves 3,3'). As is seen from these data, introduction of OUDM slightly decreases the reaction rates for both components, which may be prescribed to some increase of viscosity of the reaction mixture (OUDM is viscous liquid soluble in monomer). It is important that in the course of the reaction the system undergoes no phase separation up to the end of reaction. Temperature dependence of the tg δ shows only one high maximum with feebly marked inflection point in the temperature region 45-55°C (Fig. 5 b). From these data the conclusion can be drawn that introducing OUDM into the reaction mixture really improves miscibility in such a ternary system, i.e. determines the equilibrium compatibilization. As a result, ternary compatible IPN is formed. It may be supposed that OUDM physically interact with both IPN components, like TBU; however, in this case some cross-linking of BMA is also possible. The system is characterized by one relaxation maximum located between glass transition temperatures of initially two incompatible phases.

2. IPNs with component ratio 50/50

It is known that the degree of compatibility of two incompatible polymers depends on the ratio of components. To establish the effect of the component ratio on the compatibilization, the experiments have been done also with 50/50 IPNs. Fig. 6 presents the kinetic curves of the formation of both PBMA and PU in IPN in presence of 5 mass% of DMEG (curves 2,2') and OUDM (curves 3,3'). Introduction of both DMEG and OUDM increases the rate of PBMA polymerization and diminishes the rate of the PU formation.

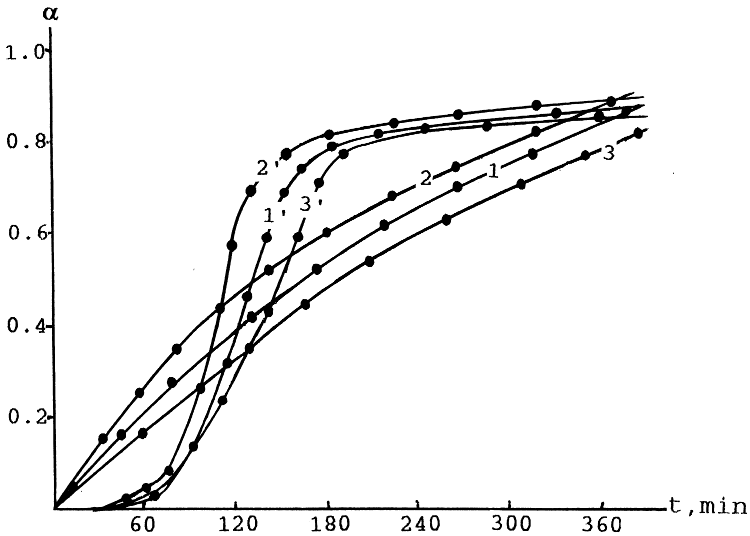


Fig. 6: Kinetic curves for PU (1,2,3) and PBMA (1',2',3') in semi-IPN (50/50): initial (1,1'), 5 mass% of DMEG (2,2'), 5 mass% of OUDM (3,3')

The data on the time of onset of phase separation are given in the Table. For 50/50 IPN the phase separation begins in 93 min at conversions α_{PU} = 0.38 and α_{PBMA} = 0.15. Introducing DMEG diminishes the time of phase separation up to 70 min at conversions α_{PU} = 0.25 and α_{PBMA} = 0.08. The curve on the time dependence of the light scattering intensity is characterized by sharp increase in presence of DMEG, as distinct from this curve for initial IPN. For IPNs containing 5 mass% of OUDM no phase separation was observed and the system stayed transparent up to the end of reaction.

Initial 50/50 IPN is a typical two-phase structure with two distinct relaxation maxima corresponding to constituent phases (Fig. 7 a). Glass transition temperatures of both phases are shifted by 5°C to higher temperatures as compared with 75/25 IPNs. When 5 mass% of DMEG is introduced into the system (Fig. 7 b), one pronounced glass transition of the PBMA-enriched phase is observed which position is shifted by 10-15°C as compared with initial IPN.

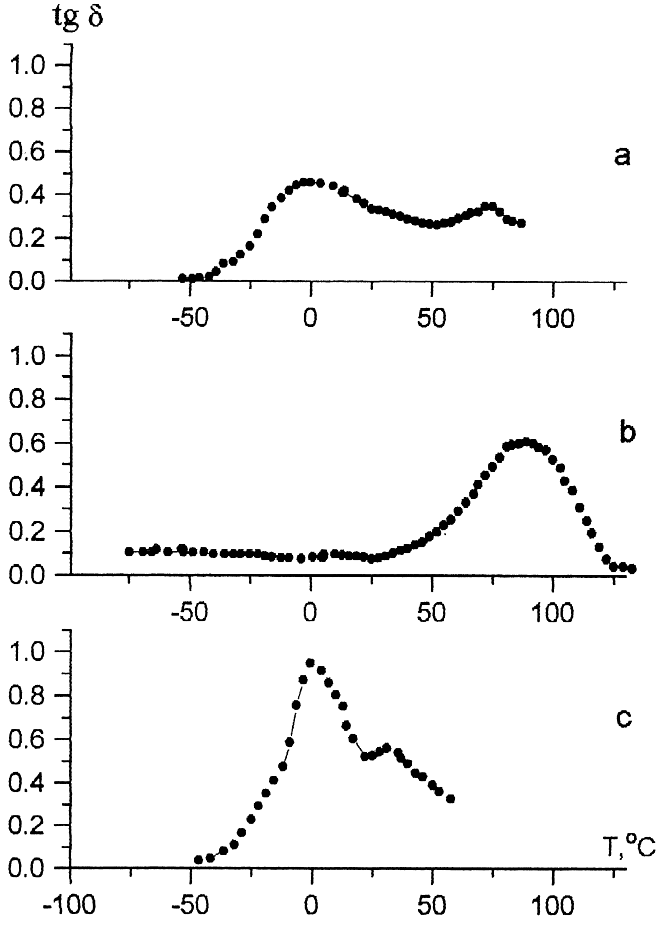


Fig. 7: Temperature dependence of tg δ for semi-IPN (50/50) (a), with 5 mass% of DMEG (b) and 5 mass% of OUDM (c)

This shift may be attributed to the cross-linking BMA by DMEG. Only small maximum of tg δ is seen in the region of PU glass transition, as compared with 75/25 IPN. As is seen from kinetic data (Fig. 6, curves 2,2') introduction of DMEG increases the rate of BMA polymerization and diminishes the rate of PU formation, which finds its reflection in viscoelastic behaviour. At α_{PU}= 0.25 the rate of formation of cross-linked PBMA sharply increases. This fact allows to suppose that in IPN forming under such conditions, PBMA forms continuous matrix with small imbedded particles of PU. These particles seem to be of small sizes and because of it; their relaxation transition is almost not detected on the curves of temperature dependence of tg δ.

Introduction of OUDM into 50/50 IPN shows only one broad relaxation maximum with high level of losses (Fig. 7 c). However, as distinct from 75/25 IPN, this maximum is located not between glass transition temperatures of components, but in the region of PU component (0°C). Feebly marked relaxation transition is seen in the region 30-35°C. In this system during curing there was observed no appearance of turbidity and the system seemed to be one-phase (Table). In this case, in the same way as for 75/25 IPN, one can suppose the formation of ternary compatible IPNs, which is, however, rather inhomogeneous, this being the reason the appearance of some additional transition region.

CONCLUSION

Thus, the investigation of the effects of some additives, which according to their chemical constitution could be considered as potential compatibilizers for IPNs, allows to establish two different types of their compatibilizing action.

In one case, the additive introduced into initial reaction system prevents microphase separation of the system. In this case the viscoelastic properties are changed in such a way that instead of two loss maxima characteristic for phase-separated system, only one maximum is present, what is possible result of the formation of one-phase ternary system.

In another case, compatibilizers effect on the reaction kinetics and because of it accelerate microphase separation in the system, which proceeds at lower conversion degrees as compared with pure IPNs. Under such conditions, thermodynamic compatibility of IPN components in the presence of additives decreases. The acceleration of the reaction in the presence of additives only shortens the time for the onset of phase separation. However, in this case there proceeds also the transition from the systems with two relaxation maxima (two-phase system) to the system with one, broad or narrow, maximum. This may be the result of concentration of the additive in the interfacial region between two phases. It is evident that the morphology of such a system also undergoes changes and that instead of discrete phases, the diffuse structure or structure of the matrix-inclusion type is formed. In such structures the sizes of phase domains (inclusions) of component present in smaller amount are rather small to be detected by the methods of dynamic mechanic analysis. In fact, detection of a single Tg only signifies that the size of the blend domains is very low[1,2].

The effect of additives on the kinetics of formation of the IPN components and on the time of onset of phase separation may serve as a test on the compatibilization mechanism. The additive is introduced into the homogeneous reaction mixture and so is distributed uniformly throughout the whole volume of it. If the additive acts as a third component improving miscibility, the onset of the phase separation should be shifted on the time scale to higher times or should be fully absent. On the contrary, if the additive has no effect on miscibility or has negative effect (increasing the thermodynamic interaction parameter of the ternary system) one should suppose that this additive is concentrated at the interface between two phases, changing the morphology of the system that is formed in the course of IPN curing.

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