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Reactive Compatibilization in Phase Separated Interpenetrating Polymer Networks

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Summary: The effects of compatibilizing additives (monomethacrylic ester of ethylene glycol (MEG) and oligo-urethane-dimethacrylate (OUDM)) on the kinetics of interpenetrating polymer network (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 various amounts (3-10 mass%) of the additive MEG and 20 mass% OUDM introduced into the initial reaction system prevent microphase separation in the IPN. In the course of the reaction the system undergoes no phase separation up to the end of reaction, as follows from the light scattering data. The viscoelastic properties of modified IPN are changed in such a way that instead of two relaxation maxima characteristic of phase-separated system, only one relaxation maximum is observed, what is result of the formation of compatible IPN system. The position of this relaxation transition depends on the system composition and on the reaction conditions.

Keywords: compatibilization; interpenetrating polymer network (IPN); microphase separation; relaxation transitions

Introduction

The problem of improvement of compatibility of polymers by introduction of various compatibilizers attracts a great attention. [1-5] The analysis of the data available allows to distinguish two kinds of compatibilization. The essence of the first consists in the reinforcement of the interface in incompatible blends of linear polymers. The interaction between the two constituent phases may be improved by introduction of some bifunctional additives. The most popular type of such additives are block-copolymers, which are localized at the interface and can physically interact with both phases through the two constituent blocks. Usually, the compatibilizer lowers the interfacial tension between phases which leads to the decrease of the average dimensions of a dispersed phase. Such compatibilizers do not affect the thermodynamic stability of the system, but it changes the morphology leading to a finer dispersion degree of components in the course of blending.

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The second definition, based on thermodynamic principles, assumes that a compatibilizer is distributed throughout the whole volume of the system. In this context, the compatibility means the formation of a single-phase stable system characterized by the decrease of the mixing free energy. Two incompatible (immiscible) polymers become compatible (miscible) in the presence of a third component. Thermodynamic compatibility is achieved when the free energy of mixing becomes negative.

Interpenetrating polymer networks are one of the most distributed types of polymer blends. Mainly, these systems are formed in the course of chemical reactions of formation of two non-interacting components (simultaneous IPNs). The thermodynamic incompatibility arises in these systems during reaction, accompanied by the incomplete microphase separation. Such systems are characterized by the existence of two glass transition temperatures T_g corresponding to the evolved phases.

Improving compatibility of IPNs may be achieved by the parallel reaction of grafting [1], by introduction of compatibilizers, [2] or by changing the reaction kinetics (the ratio of the rate of formation of constituent networks).[3] Better compatibility may be also the result of the sequential curing, changing the sequence of the networks formation, [4] and due to specific interaction between opposite charged groups or due to formation of hydrogen bonds. [5] The grafting of one network onto another is realized by the introduction of some heterofunctional monomers or oligomers into the initial reaction mixture, which are capable to interact with both networks in the course of their formation.

It is known that the formation of IPN is characterized by superposition of chemical kinetics of network formation and physical kinetics of phase separation, both processes proceeding under nonequilibrium conditions. The reaction kinetics is one of the most important factors determining the onset of the phase separation in the system. It can expect that the presence of compatibilizer in the reaction system will affect both the kinetics of reactions and conditions of phase separation in the reaction system.

In the present work the effects of compatibilizing additives (monomethacrylic ester of ethylene glycol (MEG) and oligourethanedimethacrylate (OUDM)) on the kinetics of the formation of IPN based on cross-linked polyurethane and linear polystyrene and their influence on the microphase separation, viscoelastic and thermophysical properties of the IPN have been investigated.

Experimental

Semi-IPNs were obtained by simultaneous curing of crosslinked polyurethane (PU) in the presence of styrene at 333 K. PU was based on the macrodiisocyanate (MDI) consisting of 2,4-2,6 toluene diisocyanate (TDI), poly(oxypropylene glycol) (PPO, MM 1000) and trimethylolpropane as crosslinking agent. The PU/PS ratio was taken 70/30, 50/50 and 30/70 by mass. The concentration of the initiator [I] for the radical polymerization of styrene (2,2'-azo-bis-isobutyronitrile) was $1 \cdot 10^{-2}$ mol/l. The concentration of the catalyst [kt] for PU formation (dibutyl tin laurate) was $0.3 \cdot 10^{-5}$ mol/l.

As a compatibilizing agents monomethacrylic ester of ethylene glycol (MEG) and oligourethanedimethacrylate (OUDM) were used. OUDM was synthesized from macrodiisocyanate (TDI, PPO, MM 1000) with MEG at a ratio of 1:2 at 313 K with the catalyst-dibutyl tin dilaurate (0.01 mass%) according to

$$\underset{\text{MDI}}{\text{OCN–R–NCO}} + 2\ \underset{\text{MEG}}{\text{HO–CH}_2\text{–CH}_2\text{–O–C(O)–C(CH}_3\text{)=CH}_2} \rightarrow$$

$$\underset{\text{oligourethanedimethacrylate (OUDM)}}{\text{CH}_2\text{=C(CH}_3\text{)–C(O)–O–CH}_2\text{–CH}_2\text{–O–C(O)–NH–R–NH–C(O)–O–CH}_2\text{–CH}_2\text{–O–C(O)–C(CH}_3\text{)=CH}_2}$$

where R is $\text{–C}_6\text{H}_3\text{(CH}_3\text{)–NH–C(O)O–[–CH}_2\text{–CH(CH}_3\text{)–O–]}_{17}\text{O(O)C–NH–C}_6\text{H}_3\text{(CH}_3\text{)–}$.

The reaction kinetics of PU and polystyrene (PS) formation without and in the presence of compatibilizer was investigated at 333 K using a differential calorimeter DAK-1-1A by methods described elsewhere. [6] The kinetic parameters of the reaction of PU formation have been calculated from the kinetic equation for a second-order reaction: $K = \alpha/(1-\alpha)\, C_0\tau$ [6, 7].

The onset of microphase separation (MPS) during curing (τ_{MPS}) was established by the light scattering from the cloud points, using the photocalorimeter FPS-3. From the time dependence of the intensity of light scattering we have calculated the coefficient of the rate of growth of fluctuations in the system R_q as the ratio of $\ln I/\tau$, which characterizes the rate of MPS. [8] The compositions of the systems under consideration, the kinetic parameters of reactions, and parameters of MPS are given in Table 1.

The viscoelastic properties were studied by dynamic mechanical analysis (DMA) using a frequency relaxometer. The measurements were done on the frequency of forced sinusoidal vibration of 100 Hz in the temperature interval 220-450 K. The IPNs were studied also by differential scanning calorimetry using the calorimeter DSK-D of Perkin-Elmer type in the temperature interval 150-400 K. The parameters of relaxation transitions (increments of heat capacities ΔC_p at T_g) and data of DMA are presented in Table 2.

Results and Discussion

Kinetic investigations

Introduction of MEG containing two functional groups into the semi-IPN PU/PS for simultaneously proceeding reaction lead to the decrease of the rate of PU formation and increase of the beginning rate of PS formation respecting the initial one free of additive (Table 1, Figure 1). It is connected with chemical interaction between functional groups of MEG and component of PU-phase, as well as component of PS-phase, forming grafted IPNs. Figure 1 displays the kinetic curves of the PU and PS formation for semi-IPNs with 5 mass % of MEG at various ratio PU/PS and for the system without MEG. Increasing amount of PU components in the reaction system in both cases increases the rate of urethane and of PS formation (Table 1). This effect for PS formation is probably connected to the increasing the viscosity of the reaction system due to higher amount of PU. It lead to sharp reducing the termination constant (K_t) as against the growth constant (K_{gr}) and accordingly increasing the K_{gr} / K_t ratio and the chain growth rate V_{gr} according to eguation: $V_{gr} = K_{gr} [M] V_{in}^{1/2} / K_t^{1/2}$ [7]. The maximum values of reduced rate ($W_{red} = V/[M]$, where $V = dM/dt$ is reaction rate and M is the amount of unreacted monomer) of PS formation in initial IPNs change in the following series: 30/70 < 50/50 < 70/30 as a result of the growth in viscosity. Introduction of MEG in IPNs decreases the maximum values W_{red} of PS formation in the series 50/50 > 70/30 > 30/70 (Figure 2).

Table 1. Parameters of microphase separation (MPS) and reaction rate of formation initial semi-IPN and with different contents of MEG and OUDM.

PU/PS mass %	MEG, mass %	OUDM mass %	$K^{1)} \cdot 10^5$, $kg \cdot mol^{-1} \cdot s^{-1}$	$maxW_{red} \cdot 10^2$, min^{-1}	τ_{MPS}, min	$R(q) \cdot 10^2$, min^{-1}	$\alpha^{2)}$ PU	$\alpha^{2)}$ PS
70/30	–	–	10.2	1.08	18.0	1.84	0.10	0.003
70/30	3.5	–	8.7	1.01	–	–	–	–
70/30	5.0	–	7.1	0.88	–	–	–	–
70/30	10.0	–	5.9	0.88	–	–	–	–
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	0.12	0.005
70/30	–	10.0	13.3	0.75	–	–	–	–
70/30	–	20.0	14.3	0.57	–	–	–	–
50/50	–	–	8.7	0.83	35.0	1.62	0.13	0.004
50/50	5.0	–	5.7	0.97	–	–	–	–
50/50	–	20.0	12.2	0.91	–	–	–	–
30/70	–	–	7.2	0.37	50.0	1.43	0.08	0.004
30/70	5.0	–	3.9	0.58	–	–	–	–
30/70	–	20.0	15.2	0.73	–	–	–	–

1) –constant of the reaction rate of urethane formation;

2) – conversion degree at the onset of MPS

Introduction of various amounts of MEG into the reaction system changes the kinetics parameters of IPN formation respecting initial one (Table 1). MPS does not proceed during all the time of reaction (light scattering data). The film obtained remain transparent.

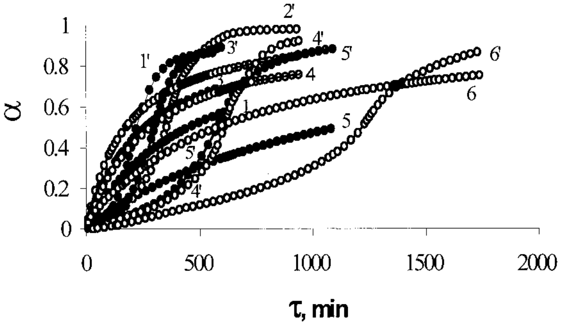

Figure 1. Kinetic curves for PU (1-6) and PS (1'-6') formation in initial semi-IPN (2,2', 4,4', 6,6') and with 5 mass % of MEG (1,1', 3,3', 5,5') at different PU/PS ratio, mass %: 1,1', 2,2' – 70/30; 3,3', 4,4' – 50/50; 5,5', 6,6' – 30/70.

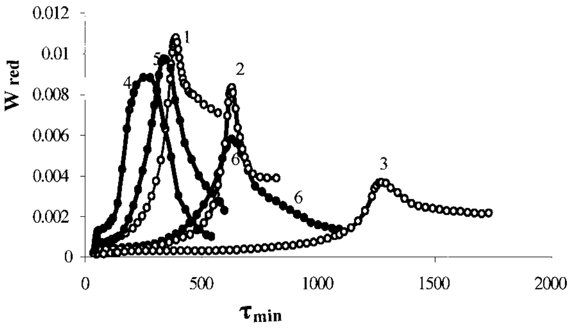

Figure 2. Dependence of reduced rate (W_{red}) of PS formation in IPNs (initial IPN – open symbol; IPN with 5 mass % MEG – close symbol) on time at different PU/PS ratio, mass % : 1, 4 – 70/30; 2, 5 – 50/50; 3, 6 – 30/70.

Introduction of OUDM (2-20 mass %) into semi-IPN PU/PS increases the PU formation rate and reduces the rate of PS formation at different PU/PS ratio respecting initial one (Table 1). Increasing amount of PU components in the reaction system with 20 mass % of OUDM decreases the rate of PU formation in series: 30/70 >70/30 > 50/50 and maximum values of reduced rate of PS formation change in the following series: 50/50 > 30/70 > 70/30 (Figure 3, Table 1). Introduction of 2-5 mass % of OUDM into the reaction system delays the microphase separation, but introduction of 10 and 20 mass % of OUDM prevents microphase separation during IPN formation (Table 1).

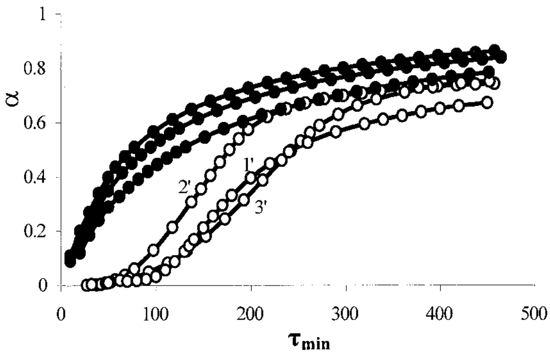

Figure 3. Kinetic curves for PU (1-3) and PS (1'-3') formation in semi-IPN with 20 mass % of OUDM at different PU/PS ratio, mass %: 1,1' – 70/30; 2,2' - 50/50; 3,3' – 30/70.

Dynamic Mechanical Analysis (DMA)

From DMA data of Table 2 and Figure 4a follows that initial IPNs are typical two-phase systems at all component ratios. Introduction of 20 mass % of OUDM in semi-IPN of various compositions essential changes the relaxation properties of the system. Experimental data of Table 2 and Figure 4b shows that for semi-IPNs only one relaxation maximum is observed. Introduction of 5 mass % of MEG in semi-IPNs of various compositions shows only one relaxation transition too (Figure 4c). Its position and height depend on the ratio of the components in the IPN. Thus the increasing amount of the rigid PS component in the IPN containing the compatibilizer show the increase of the single T_g by almost 50 K for the 70/30 compared for the 30/70 IPN. That means that the glass transition in compatibilized IPN depends strongly on the component ratio, being an additional proof for the formation of compatible systems. The reduction in the broadness of the relaxation peak and corresponding increasing the height of maximum also confirm the increasing compatibility and diminishing sizes of phase domains.

By increasing the amount of MEG the glass transition temperature practically does not change (T_g = 323-328 K), although height of relaxation peak (tg δ_{max}) increases (Table 2). One may suppose that increasing amount of the compatibilizer provides the formation of more homogeneous system. In all cases during the reaction no turbidity was observed. For IPNs containing 5 and 10 mass % of OUDM two glass transition temperatures were observed.

Table 2. Parameters of relaxation transition on DSC and DMA data for semi-IPN and grafted IPN based on PU and PS

PU/PS, mass%	OUDM mass%	MEG, mass%	DSC				DMA			
			T_g, K		ΔC_p, J/g·K		T_g, K		tg δ_{max}	
			PU	PS	PU	PS	PU	PS	PU	PS
100/0	–	–	251	–	0.68	–	283	–	0.88	–
0/100	–	–	–	368	–	0.42	–	388	–	3.26
70/30	–	–	255	373	0.55	0.35	288	408	0.68	0.46
70/30	–	3.5	268*		0.65*		323*		0.66*	
70/30	–	5.0	278*		0.68*		328*		0.70*	
70/30	–	10.0	283*		0.85*		323*		0.96*	
70/30	2.0	–	255	368	0.50	0,25	–	–	–	–
70/30	5.0	–	255	368	0.50	0,20	293	398	0.44	0.18
70/30	10.0	–	255*		0.60*		300	375	0.39	0.39
70/30	20.0	–	255*		0.60*		358*		0.52*	
50/50	–	–	258	370	0.40	0.36	293	418	0.59	0.65
50/50	–	5.0	295*		0.48*		368*		0.84*	
50/50	20.0	–	275*		0.50*		358*		0.89*	
30/70	–	–	258	368	0.35	0.35	303	413	0.43	0.88
30/70	–	5.0	330*		0.40*		375*		1.35*	
30/70	20.0	–	315*		0.30*		373*		1.00*	

* – one relaxation transition is observed

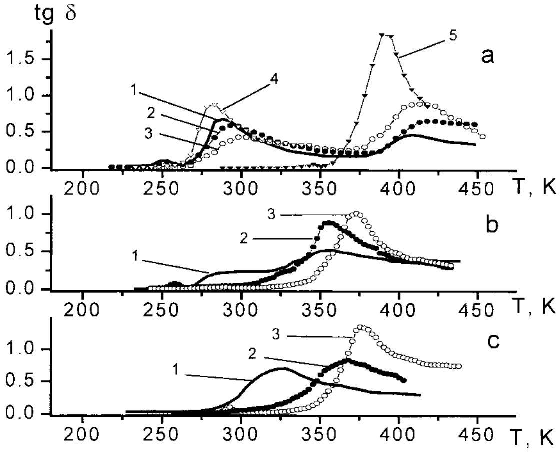

Figure 4. Temperature dependence of mechanical losses for a – initial semi-IPN (1-3), PU (4), PS (5); b – semi-IPN with 20.0 mass % of OUDM (1-3); c – semi-IPN with 5.0 mass % of MEG (1-3) at various ratio PU/PS , mass %: 1 - 70/30, 2 – 50/50, 3 – 30/70.

With increasing the amount of OUDM the glass transition temperature of PU-phase increases from 288 K (without OUDM) to 300 K (with 10 mass % of OUDM) and the T_g of PS-phase decreases from 408 K to 375 K. Introduction of 20 mass % of OUDM into IPNs results in only one glass transition temperature at various ratio PU/PS. With increasing the content of the rigid PS component into the system T_g and height of relaxation peak increase (Table 2).

Differential Scanning Calorimetry (DSC)

In Table 2 the DSC data for the initial specimens of pure components, PU and PS and for the same components in the presence of OUDM and MEG are given. The temperature dependences of heat capacity for IPNs show two jumps: a low- temperature jump, which is related to the glass transition of the oligoether component of PU network at 255-258 K, and a high-temperature jump at 368-370 K, the PS glass transition. The introduction of 2-5 mass % of OUDM into IPNs does not change the glass transition temperature of the PU and PS phase but causes a decrease in the heat capacity jump at T_g respecting initial one. IPNs of various composition obtained in presence of the 10-20 mass % of OUDM show only one jump the heat capacity in the glass temperature region with different values of T_g and ΔC_p. With increasing the content of the rigid PS component in the system ΔC_p decreases and T_g increases. An decrease in ΔC_p is related to the increase of the degree of polymer ordering at temperatures above T_g. It may be supposed that OUDM chemically interact with the PS component and physically interact with PU-component, therefore increasing the content of the rigid PS in the system leads to an increase of their T_g.

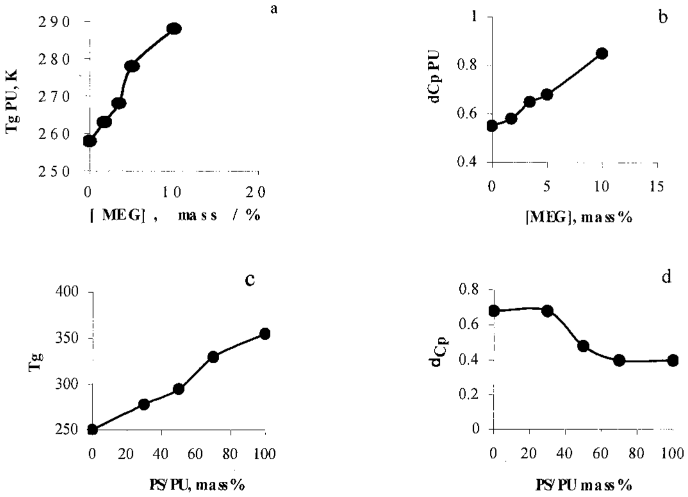

Figure 5. Dependence of glass transition temperature T_g (a, c) and the value of heat capacity jump ΔC_p (b, d) on contents of MEG (a, b) in semi-IPN (PU/PS = 70/30 mass %) and on ratio components PU/PS in semi-IPN with 5 mass % of MEG (c, d) (DSC-data).

The effect of various amounts of MEG was studied for IPN of the 70/30 composition. It was observed only one heat capacity jump in the temperature interval 263-283 K, depending on MEG amount. Values of T_g and ΔC_p increases with increasing MEG concentration (Table 2, Figure 5a, b). One can suppose that due to chemical grafting of PU onto PS via MEG the flexibility of PU component lowers as it can be judged from the increasing glass transition temperature of the system in relation to the T_g of the PU-component. The growth of ΔC_p by introducing MEG may be connected with the formation of an irregular and more defective network structure. With increasing the content of the PS component in the system ΔC_p decrease and T_g increases respecting initial one (Figure 5c, d).

Conclusions

The possibility of compatibilization of IPN's by addition of monomethacrylic ester of ethylene glycol (MEG) and oligo-urethane-dimethacrylate (OUDM) is established. Due to their chemical nature these compatibilizers are able to chemical interaction with components of IPNs (OH-groups and double bounds). As result the formation kinetics of IPNs, the onset of microphase separation, the viscoelastic and the thermophysical properties are essentially changed.

It was established, that various amount (3.5-10.0 mass %) of additives MEG and 20.0 mass % OUDM introduced into the initial reaction system prevent microphase separation of the system. In the course of the reaction the system undergoes no phase separation up to the end of reaction, as follows from the light scattering data. The viscoelastic properties of modified IPNs are changed in such a way that instead of two relaxation maxima characteristic for phase-separated system, only one relaxation maximum is observed. The position of this relaxation transition depends on the system composition and on the reaction conditions.

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