

HETEROGENEITY AND PHASE SEPARATION OF METAL CONTAINING SIMULTANEOUS SEMI-INTERPENETRATING POLYMER NETWORKS. REACTION KINETICS VS. COMPLEX FORMATION

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Abstract. Heterogeneity and phase separation that occurs during formation of simultaneous semi-interpenetrating polymer networks based on incompatible poly (urethane) network and linear poly(methyl methacrylate) with introduced in situ iron, copper, and chromium chelates has been investigated. It has been shown that, introduction of iron and copper chelate compounds into the semi-interpenetrating polymer networks with poly(urethane) to poly (methyl methacrylate) ratio 50/50 causes inhibition of phase separation due to high rates of poly(urethane) and poly(methyl methacrylate) formation and the interaction of the chelates with both blend components. A high degree of phase separation in metal-containing semi-interpenetrating polymer networks with PU to PMMA ratio 70/30 is a result of opposite action of chemical kinetics and complexation processes which prevail in the system

Keywords: *polymer blend, heterogeneity, phase separation, kinetics, coordination metal complex, paramagnetic probe.*

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1. Introduction

Segregation of incompatible components of polymer blends and alloys is an important problem in the field of creating of new hybrid polymer materials. Topological entanglements inhibit phase separation process to form polymer systems that are characterized with incomplete micro phase separation (Lipatov, 2001).

For interpenetrating polymer networks (IPN) and semi-IPN the degree of incompleteness of this process essentially depends on the kinetic characteristics of polymerization processes. The higher are the reaction rates of the forming components the lower is the degree of the phase separation.

The phase separation in polymer blends may be inhibited also by the specific additives (compatibilizers) - compounds that contain fragments compatible with each of the components of the mixture or that can interact or form complex with each of the components. (Lipatov, 1999; Alekseeva, 2005). As is known (Nizelskii,1983) chelates of 3d- and 4f-metals are capable of strong specific donor-acceptor interaction with molecules containing polar groups. Modification of polymer blend by metal chelate compounds leads to enrichment of polymer matrix with hetero-ligand macro complexes that act like coordination linkages between macro chains and can essentially improve miscibility of the blend components.

It should be noted, that applying of both approaches not always improve polymer system compatibility because the influence of reaction kinetics and

hours with subsequent keeping at 293K for 24 hours. To introduce complex SP into SIPN samples they were held in 0.02 M solution of the probe in dichloromethane at 293K for 60 min with subsequent drying under vacuum at the same temperature to ensure constant weight of each sample. Correlation time (τ) of SP rotational diffusion in the range of its fast motion ($10^{-11}\text{s} < \tau < 10^{-9}\text{s}$) was calculated according to (Vasserman, 1986). Ultra-slow SP motion was analyzed by Saturation Transfer EPR (Livshits, 1982). The electron-spin parameters (g and A) for $\text{Cu}(\text{eacac})_2$ used as complex spin probe were calculated according to standard procedure (Lipatova, 1972).

Phase separation that occurs during formation of SIPNs of various compositions has been studied by the methods of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The DSC in temperature range of 133–473K and heating rate of 2K/min was performed on a differential scanning calorimeter equipped with a diathermic shell. The degree of system segregation was estimated from the share of the interfacial region using Fried approximation (Fried, 1976).

3. Discussion

Reaction kinetics

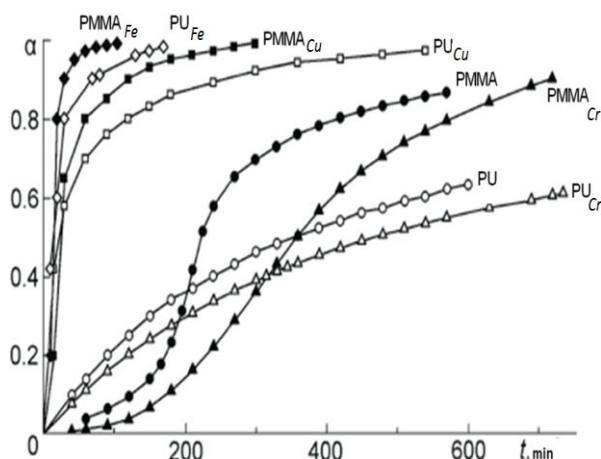


Figure 1. PU and MMA conversion ratio in SIPN (50/50) in the presence and without metal chelates

According to data obtained in the SIPN with PU/PMMA ratio of 50/50 the growth of urethane formation rate under the catalytic influence of copper and iron chelates essentially accelerates formation of PMMA. The accelerated polymerization of MMA is induced by the increase of the system viscosity resulting in the decrease of the PMMA macro radicals' termination constant. Increasing the urethane fraction in SIPN from 50 to 70 is accompanied by an increase of both PU and PMMA formation rates. In addition, from the kinetic data it is clear that influence of various metal chelates on the rates of formation of PU and PMMA in the SIPN does not depend on the ratio of components. In all cases, the presence of $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{eacac})_2$ in the reaction mixture accelerates the process, while the presence of $\text{Cr}(\text{acac})_3$ always slows down the formation of the SIPN in comparison with the initial metal free system. The detailed analysis of kinetic characteristics of the formation of various SIPN is given in (Kosyanchuk, 2006; Kosyanchuk and Kozak, 2008).

System heterogeneity

Simultaneous SIPNs based on incompatible components are characterized by a micro heterogenic structure due to the incomplete micro phase separation process.

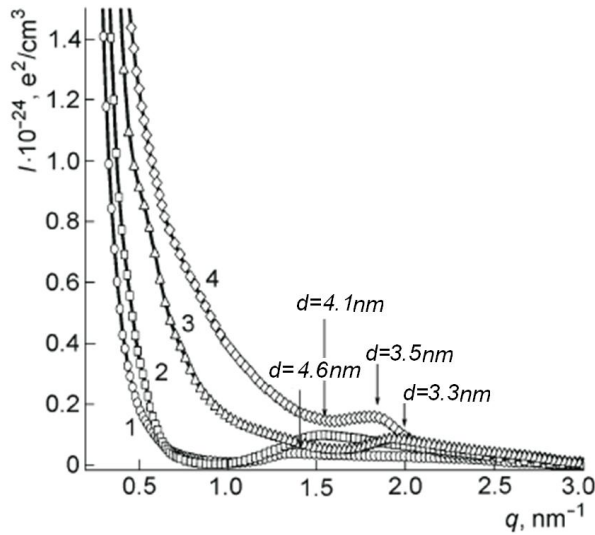


Figure 2. SAXS scattering intensity profiles of SIPN (50/50): SIPN-Cr (1); SIPN metal free (2); SIPN-Cu (3); SIPN-Fe (4).

X-ray investigation of the structural heterogeneity of the SIPNs (Kozak, 2005) indicates that SIPN studied are heterogeneous systems with the period of heterogeneity d being of nano-scale. It was determined by Bragg’s law from the maximum position of the SAXS scattering intensity profiles. Introduction of the chromium chelate into SIPN caused Bragg’s period increasing, whereas the influence of the copper and Fe chelates is the opposite and leads to a decrease in the heterogeneity period of the system.

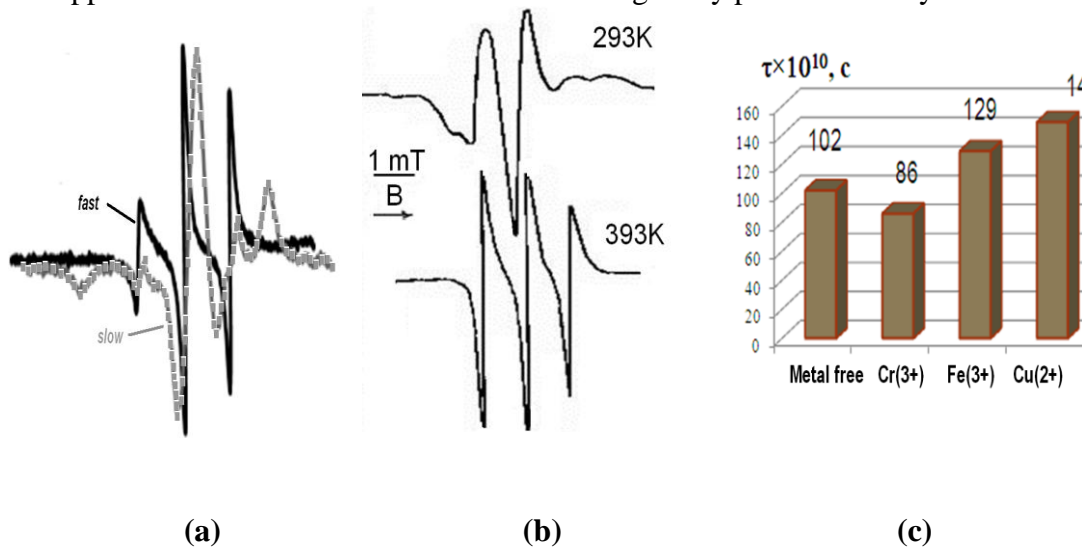


Figure 3. Nitroxide probe mobility: “slow” and “fast” signal superposition (a); SIPN spectrum shape changes under heating (b); metal nature influence on correlation time (c).

The consequence of structural heterogeneity of SIPNs analyzed is their dynamic heterogeneity. EPR spectra of nitroxide probe TEMPO in SIPN at room temperature confirm the heterogeneity of the system under consideration. The spectra have an asymmetric broadened shape with a significant increased intensity of the central component.

Depending on the time range of the rotation of the probe, the shape of its spectrum varies from the narrow isotropic for the fast movement to a wide non-symmetric for the slow movement of the probe. Thus EPR spectra of TEMPO in SIPN can be a superposition of signals of "fast" and "slow" probes located in areas of the SIPN with different mobility. The temperature experiments support this supposition. Under polymer system heating the mobility of probes in various regions of the sample becomes close, the signal from "slow probes" disappears and spectrum becomes an isotropic form. The calculated correlation times of the probe for the investigated SIPNs can be arranged as follows: $\tau(\text{Cu}) > \tau(\text{Fe}) > \tau(\text{metal free}) > \tau(\text{Cr})$ that agrees with kinetics and SAXS data.

Changes in the micro heterogenic structure of the SIPN containing metal chelates can be explained by the structuring of the polymer matrix formed in their presence due to ability of the metal compounds to form numerous coordination bonds with the components of the SIPN. That results in the concentration of certain functional groups of the polymer near the metal chelate modifier.

Complex formation

To investigate the effect of complex formation on the SIPN copper ethyl acetoacetate was applied as ion paramagnetic probe. As proposed in (Kozak, 2000) this method uses the sensitivity of copper chelates electron-spin parameters to symmetry and chemical nature of $\text{Cu}(2+)$ neighborhood and allows evaluation the polymer functional groups that did not participate in complex formation with metal chelate modifier. Formation of adducts between the copper chelate and the electron-donating centers is accompanied by a regular increase of g_{II} and a decrease of the HFS constant (A_{II}). The higher is the donating ability of the electron donor the greater changes occur in the copper chelate electron-spin parameters. According to such ability the SIPN donor groups can be arranged as -O-, C=O, -N(H)-.

The EPR spectrum of the ion SP introduced to the metal free SIPN is superposition of the SP signals located in different environments. In this case, the parameters of complex I are characteristic for the complexes SP with nitrogen or oxygen containing donor groups such as urethane or ester-group, and the parameters of the complex II are characteristic for the SP complexes with oxygen-containing donor species such as ether-group. This indicates the presence in SIPN of spatially separated regions enriched with -N(H)C(O)- or -C(O)O- groups, as well as regions enriched with -C-O-C- groups.

From the data in the table, it is clear that in the SIPN-Cu and SIPN-Fe remained free to interact with the SP mostly ether groups, while in the SIPN-Cr remained groups of greater electron-donor power (urethane groups of PU and/or PMMA ester groups). That is, the copper and iron chelates in the corresponding SIPN interact with both PU and PMMA. In contrast, $\text{Cr}(3+)$ chelate forms complexes mainly with the glycol component of PU and promotes segregation of the latter.

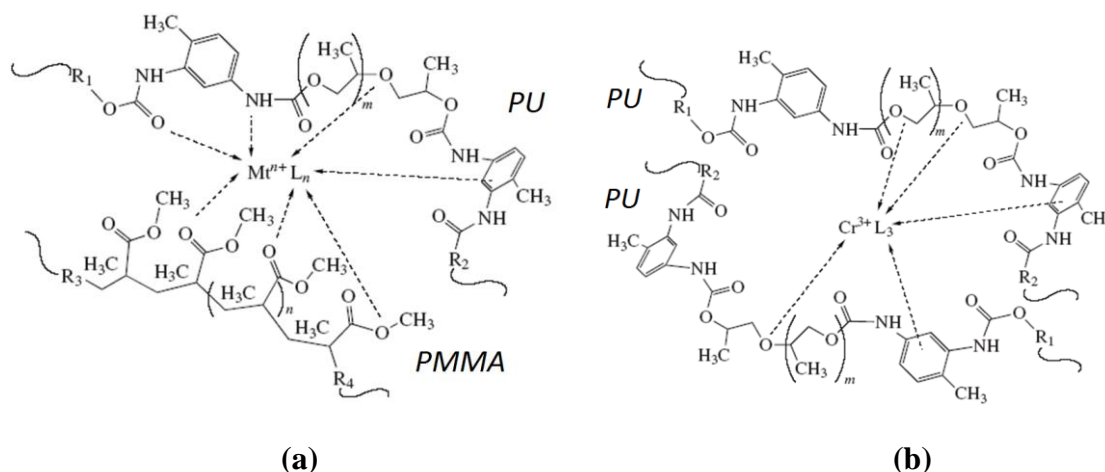


Figure 4. Coordination junction points in the modified SIPN (50/50): SIPN-Fe and SIPN-Cu (a); SIPN-Cr (b).

Table 1. Principal electron-spin parameters of copper SP in SIPN

System	Metal free SIPN	SIPN-Fe	SIPN-Cu	SIPN-Cr	Cu(eaac) ₂
$g_{ }$	2.273 and 2.256	2.267	2.273	2.284	2.276
$A_{ }$	164 and 178	171	164	164	187

According to EPR data in SIPNs (70/30) where part of PU component predominates the SP spectra parameters of chromium modified SIPN remain practically unchanged. On the contrary in the iron- and copper chelate modified SIPNs the SP parameters become similar to SIPN-Cr indicating iron- and copper chelate modifier complexation mainly with ether groups of PU.

Structural and dynamic inhomogeneity of SIPN systems leads to the existence of a wide range of the nitroxide SP correlation times. Evaluation of minimum width of the correlation times distribution can serve as quantitative measure of SIPN heterogeneity. According to (Livshits, 1982) the lower limit of the correlation times distribution can be estimated in terms of the $\Delta\tau_{\min}$, which is the difference of the values obtained from the traditional EPR spectra and the EPR spectra with saturation transfer. Traditional EPR spectrum takes into account high frequency distribution part ($10^{-11}\text{s} < \tau < 10^{-9}\text{s}$) and EPR spectrum with saturation transfer as the mean distribution also takes into account ultra-slow probes ($10^{-6}\text{s} < \tau < 10^{-5}\text{s}$).

As it can be seen from the table 2 for metal free SIPN, value of $\Delta\tau_{\min}$ corresponds to a significantly higher level of heterogeneity of the metal free system based on incompatible pair than a metal free PU. For SIPN-Fe, a significant narrowing of the distribution width indicates a noticeable improvement in the uniformity of the system. Such a decrease in the degree of heterogeneity of the metal-containing SIPN can be interpreted as evidence of improved compatibility (miscibility) of their components due to presence of iron chelate, which forms complexes with both PU and PMMA.

The SEM micro images of cryogenic cross-fractured surface of SIPNs (50/50) support the above results (Figure 5).

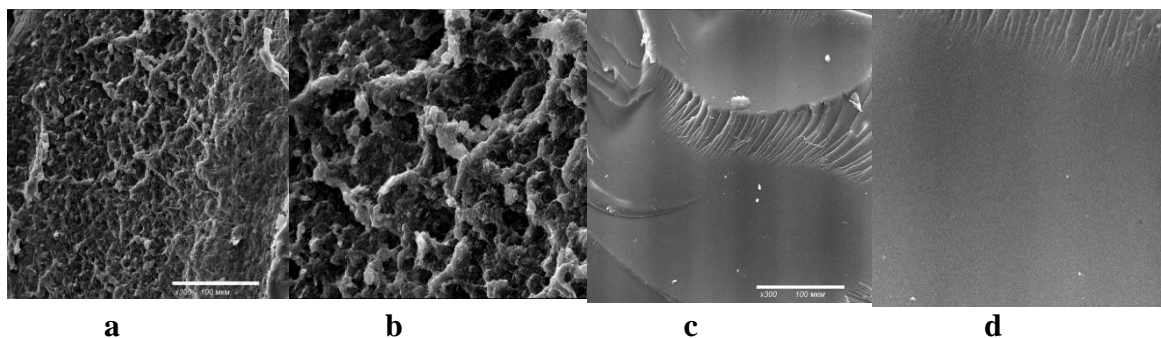


Figure 5. SEM micro images of metal free SIPN (a,b) and SIPN-Fe (c,d): fragments of the image with a side of 100 μm (b,d)

Phase separation

Due to retardation of micro phase separation in the course of reaction of SIPN formation the system is composed of two partially segregated phases and the interfacial region between them. The higher are the reaction rates of the forming components the lower is the degree of the phase separation which manifests itself as widening of the interfacial region. On the other hand, in the SIPNs containing iron and copper β -diketonates, formation of complexes between chelates of these metals and donor groups of PU and PMMA promotes mutual penetration of PU and PMMA phases. As a consequence, the degree of their separation decreases and the interphase region should widen. Influence of the SIPN composition of both of these factors was analyzed using DSC. As it was shown in (Kosyanchuk, 2008) all DSC temperature dependences of specific thermal capacity and heat flow for SIPN demonstrate two heat capacity jumps, thus suggesting the two-phase state of all SIPNs studied.

The degree of SIPNs segregation was estimated from the evaluation of the interphase region share according to Fried approximation (Fried, 1976) as

$$1 - F = 1 - (W_1 \Delta C_p1 + W_2 \Delta C_p2) / (W_1 \Delta C_p1^{ind} + W_2 \Delta C_p2^{ind})$$

where W_1 and W_2 are total weight fractions of components; ΔC_p1 and ΔC_p2 are heat capacity jumps of segregated phases; and ΔC_p1^{ind} and ΔC_p2^{ind} are heat capacity jumps of individual components. The data obtained are listed in Table 2.

Table 2. SIPN interfacial region share

PU/PMMA ratio,%	100/0	0/100	50/50	50/50	50/50	50/50	70/30	70/30	70/30	70/30
Metal ion	-	-	-	Fe(3+)	Cu(2+)	Cr(3+)	-	Fe(3+)	Cu(2+)	Cr(3+)
<i>I-F</i>	-	-	0.32	0.53	0.48	0.34	0.37	0.16	0.31	0.31

As it can be seen the influence of metal chelates on the phase separation of SIPNs differs for different system compositions. The growth of interfacial region in SIPNs (50/50) in the presence of $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{eacac})_2$ agrees with SAXS, SEM and EPR results as well as narrowing of the interface region in the presence of $\text{Cr}(\text{acac})_3$. The presence of the same amount of β -diketonates in the SIPNs (70/30) leads to pronounced phase separation. The share of the interfacial region narrows from 0.37 for the metal free SIPN to 0.16 for the iron-containing SIPN, the presence of $\text{Cu}(\text{eacac})_2$ has

practically no effect on phase separation. The behavior of chromium-containing SIPNs of both compositions is nearly the same. By their effect on phase separation in SIPNs of various compositions, chelate compounds may be arranged as follows: $\text{Cr}(\text{acac})_3 < \text{Cu}(\text{eacac})_2 < \text{Fe}(\text{acac})_3$. This sequence is consistent with the results of EPR studies with the use of the paramagnetic probe, where a change in electron-spin parameters of the complex paramagnetic probe follows the same tendency.

Similar conclusions allowed to make the results obtained in the study of viscoelastic characteristics of the IPN in (Kosyanchuk, 2008) using the DMA method and procedure for allocation of Gaussian components in experimental relaxation curves for detailed analysis of several relaxation transitions in SIPN. The DMA data have demonstrated that the retardation of phase separation exists in iron- and copper-containing SIPNs (50/50) and that the share of the interfacial region for chromium-containing SIPNs (50/50) remains invariable. This phenomenon may be attributed to the synergistic effects of the kinetics of formation of such SIPNs and the complexation of iron, copper and chromium chelates with blend components. In iron- and copper-containing SIPNs (70/30), a more pronounced phase separation takes place owing to opposite effects of chemical kinetics and complexation processes.

4. Conclusion

Analysis of the kinetics and complex formation as well as heterogeneity and phase separation in metal containing semi-interpenetrating polymer networks (SIPN) based on incompatible cross-linked polyurethane and linear poly(methyl methacrylate) allows to conclude that influence of reaction kinetics and complexation on the miscibility of the components is synergistic for SIPN (50/50) and opposite for SIPN (70/30). The improvement of SIPN components miscibility occurs under catalytic and complexing action of Fe- and Cu- chelates in SIPN (50/50) where as Cr-chelate favors polyurethane component segregation. In spite of the significant increase in the reaction rates in the SIPNs (70/30), the effect of kinetics is offset by a change in the conditions of metal compounds complexation, which has a prevailed influence on phase separation and heterogeneity of the polymer in that system.

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