

INVESTIGATION OF PHASE SEPARATION AND MORPHOLOGY OF ORGANIC-INORGANIC INTERPENETRATING POLYMER NETWORKS

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The paper investigates the process of phase separation and morphology of organic-inorganic interpenetrating polymer networks (OI IPNs) based on the cross-linked polyurethane (PU), poly(hydroxyethyl methacrylate) (PHEMA) and poly(titanium oxide) ($-\text{TiO}_2-$)_n obtained by sol-gel method in the presence of poly(oxypropylene glycol) (POPG) at various molar ratio of titanium (IV) isopropoxide ($\text{Ti}(\text{OPr}^i)_4$) and water. It has been established that the phase separation in OI IPNs depends on the kinetics of PHEMA-component formation and it occurs through the mechanism of the spinodal decomposition. It has been shown that by varying the ratio of IPNs components, content of inorganic component and $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ molar ratio it is possible to control the phase separation process and obtain OI IPNs with a different phase structure.

Keywords: *Interpenetrating polymer networks, light scattering, phase separation, poly(titanium oxide), radical polymerization.*

1. INTRODUCTION

One of the ways to solve the problem of creating new materials with the required complex of physical and mechanical properties is to obtain polymer blends, which allows combining the valuable properties of each component. A promising method for obtaining such blends is reaction mixing, in particular, the synthesis of interpenetrating polymer networks (IPNs) [1], [2].

A specific feature of IPNs is that at a

certain stage of cross-linking reactions, phase separation occurs as a result of thermodynamic incompatibility of high-molecular components and, as a consequence, the structure of such a system becomes heterogeneous [3], [4]. Since the phase separation process and chemical reactions occur simultaneously, the composition and ratio of components change with time. Thus, the IPNs formation proceeds under thermody-

namically non-equilibrium conditions. In addition, this process is usually incomplete due to the high viscosity and the entanglement of the chains causing the “forced” kinetic stability of the networks without macrophase formation of the components. The final structure of such polymer systems is conventionally characterised by the presence of three regions of different composition: two phases and the interfacial region (IFR), which is a measure of the unseparated part of the system [2]. The larger the IFR fraction, the smaller the degree of separation and the higher the nonequilibrium of the system as a whole.

The whole complex of properties of IPNs is determined by their final structure, which depends on the phase separation rate. In turn, the phase separation rate is determined by the kinetics of chemical reactions of IPN components formation. Therefore, it is possible to control the phase separation process by changing the factors affecting the reaction rate. These are temperature, ratio of components, concentration of polymerisation initiator, presence of catalyst, crosslinking agent, filler and compatibiliser, curing sequence [3], [4]. Depending on the conditions of IPN formation, phase separation can occur either by the nucleation and growth or by the spinodal decomposition mechanism [3], [4].

While the phase separation process for IPNs has been studied quite fully [2]–[4], there are practically no data on the study of phase separation in organic-inorganic interpenetrating polymer networks.

2. EXPERIMENTAL

Poly(titanium oxide) used as an inorganic component in OI IPNs was synthesized by hydrolysis-condensation reaction of titanium (IV) isopropoxide in POPG

One of the most promising inorganic components of OI IPNs is titanium dioxide TiO_2 in amorphous or crystalline state. This is due to its wide range of applications for the implementation of photochemical processes, for the creation of membranes, catalytic sensors, photosensitive materials, for stimulation of various biochemical and biophysical processes [5]–[15].

The promising sol-gel method is used to obtain the inorganic component of the OI IPNs due to its simplicity, environmental safety and the possibility of its uniform distribution in the polymer matrix even at the molecular level [16].

Works on the incorporation of poly (titanium oxide) gel into an organic matrix began to appear about fifteenth years ago. The organic component in such organo-inorganic materials has traditionally been represented by the acrylate [17], [18]. In these works, for such purposes, a unique mixture of thermodynamically incompatible polymers was chosen, but it was linked to each other due to the mechanical interweaving of polymer chains at the molecular level. At this moment, there is little information about the preparation and study of such polymer systems.

The aim of the study is to investigate the phase separation process and morphology of OI IPNs based on cross-linked polyurethane, poly(hydroxyethyl methacrylate) and poly(titanium oxide) prepared by sol-gel method in poly(oxypropylene glycol) medium depending on the kinetics of PHEMA component formation.

medium (MM 1000).

The $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ ratio was 1/1 and 1/2 mol/mol, and the $\text{Ti}(\text{OPr}^i)_4$ content in POPG was 0.5; 5.0; 10.0 wt%, which in terms

of TiO_2 was 0.14; 1.40; 2.80 wt%, respectively. The prepared $(-\text{TiO}_2-)_n$ gels were evacuated at 85 °C with residual pressure of 2 mm Hg to remove water and isopropyl alcohol, which were formed by hydrolysis-condensation reactions.

Macrodiisocyanate was synthesized on the base of $(-\text{TiO}_2-)_n$ gel and toluylene diisocyanate (TDI) (a mixture of 2,4- and 2,6-TDI isomers in 80/20 wt.% ratio). Further, a crosslinking agent was added to the macrodiisocyanate, and titanium-containing urethane composition was obtained. To form OI IPNs, 2-hydroxyethyl methacrylate (HEMA) was added to this composition with the radical polymerisation initiator 2,2-azobis-isobutyronitrile (AIBN) at a concentration of 0.025 mol/L. After stirring, the reaction mixture was poured into an antiadhesive treated hermetic form followed by polymerisation at 60 °C (20 h) and 100 °C (2.5 h). The initial IPNs were prepared on the basis of PU and PHEMA without $(-\text{TiO}_2-)_n$. The ratio of PU/PHEMA components in the initial and OI IPNs was 70/30, 50/50, 30/70 wt%.

The kinetics of polymerization of initial PU, titanium-containing PU, initial IPNs and OI IPNs were studied at 60 °C on a DAK-1-1A differential calorimeter.

The study of the formation kinetics of initial PU and titanium-containing PU showed that $(-\text{TiO}_2-)_n$ acted as a catalyst for the urethane formation reaction. For pure PU, the reaction rate constant (K_r) was $6.4 \cdot 10^{-5}$ kg/mol·s, while for titanium-containing PU, $K_r = 1.5 \cdot 10^{-4}$ kg/mol·s (0.5% $\text{Ti}(\text{OPr})_4$ in POPG). Therefore, the HEMA polymerisation process takes place *in situ* in the already formed cross-linked PU. It seemed only possible to investigate the polymerization kinetics of HEMA for IPNs and OI IPNs.

To study the kinetics of PHEMA formation in IPNs and OI IPNs, its parameters such as the time to reach the maximum of reduced rate of PHEMA formation (τ_{max}) and the max-

imum value of its reduced rate (W_{max}) were determined (Tables 1 and 2). The reduced reaction rate of PHEMA formation calculated from $W_{\text{red}} = V/M$, where $V = dM/d\tau$, M is the amount of unreacted monomer and τ is reaction time.

Since the chemical reactions of OI IPN formation are accompanied by phase separation, this process was simultaneously investigated by light scattering. For this purpose, homogeneous reaction mixtures (Ti-containing urethane composition and HEMA with AIBN) were placed between two glasses in the chamber of a light scattering device heated to 60 °C and the change of light scattering intensity (I) was observed over time (τ). It is known that, regardless of the mechanism of phase separation, the process of transition of the system from a single-phase to a two-phase state is accompanied by a kink in the dependence $I = f(\tau)$. The kink point on this dependence determined the time of phase separation onset. The time dependences of the logarithm of the light scattering intensity at the initial stages of phase separation were linear in all cases. According to [19], this is one of the criteria of the spinodal mechanism of phase separation, and the light scattering data were processed and interpreted in the framework of the Cahn–Hilliard theory [20] to calculate the so-called enhancement factor $2R(q)$. The enhancement factor characterises the rate of increase of concentration fluctuations during isothermal phase separation according to the equation $\ln(I/I_0) = 2R(q)\tau$, where q is the wave number. Generally, phase separation by the spinodal mechanism begins with the formation of a continuously interconnected periodic structure, which gradually shifts to droplet as a result of the decomposition of spinodal structures at the last stages of phase separation due to an increase in the interfacial tension.

The morphology of the obtained initial IPNs and OI IPNs was investigated by optical microscopy.

Table 1. Kinetic Characteristics of HEMA Polymerisation in IPNs and OI IPNs with a Molar Ratio of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O} = 1/1$ and Parameters of Their Phase Separation

| Sample | $(-\text{TiO}_2-)_n$ in POPOG, wt% | PU/ PHEMA / $(-\text{TiO}_2-)_n$, wt% | $W_{\text{max}} \times 10^2$, min^{-1} | τ_{max}' , min | τ_{ps} , min | α_{ps} | $2R(q) \cdot 10^3$, s |
|------------|------------------------------------|--|--|----------------------------|--------------------------|----------------------|------------------------|
| IPNs -1 | - | 50/50/0 | 20.00 | 38 | 15.0 | 0.003 | 4.07 |
| IPNs -2 | - | 30/70/0 | 26.00 | 30 | 13.5 | 0.005 | 5.50 |
| OI IPNs -1 | 0.14 | 69.96/29.98/0.06 | 9.20 | 51 | 20.0 | 0.009 | 3.17 |
| OI IPNs -2 | 0.14 | 49.98/49.98/0.04 | - | - | 18.0 | - | 3.40 |
| OI IPNs -3 | 0.14 | 29.99/69.98/0.03 | - | - | 17.5 | - | 3.67 |
| OI IPNs -4 | 1.40 | 69.55/29.78/0.67 | 3.33 | 66 | PS not observed * | | |
| OI IPNs -5 | 1.40 | 49.80/49.80/0.40 | 15.00 | 46 | PS not observed * | | |
| OI IPNs -6 | 1.40 | 29.92/69.80/0.28 | 20.65 | 32 | 25.0 | 0.015 | 2.42 |
| OI IPNs -7 | 2.80 | 69.08/29.58/1.34 | 1.05 | 70 | PS not observed * | | |

* the duration of the experiment for 2 hours

Table 2. Kinetic Characteristics of HEMA Polymerisation in IPNs and OI IPNs with a Molar Ratio of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O} = 1/2$ and Parameters of Their Phase Separation

| Sample | $(-\text{TiO}_2-)_n$ in POPOG, wt% | PU/ PHEMA / $(-\text{TiO}_2-)_n$, wt% | $W_{\text{max}} \times 10^2$, min^{-1} | τ_{max}' , min | τ_{ps} , min | α_{ps} | $2R(q) \cdot 10^3$, s |
|-------------|------------------------------------|--|--|----------------------------|--------------------------|----------------------|------------------------|
| OI IPNs -8 | 0.14 | 69.96/29.98/0.06 | 10.30 | 53 | 17.0 | 0.004 | 3.33 |
| OI IPNs -9 | 0.14 | 29.99/69.98/0.03 | - | - | 16.1 | - | 4.17 |
| OI IPNs -10 | 1.40 | 69.55/29.78/0.67 | 6.10 | 64 | PS not observed * | | |
| OI IPNs -11 | 1.40 | 49.80/49.80/0.40 | 15.30 | 44 | 26.0 | 0.006 | 1.22 |
| OI IPNs -12 | 1.40 | 29.92/69.80/0.28 | 22.20 | 30 | 20.1 | 0.009 | 3.17 |
| OI IPNs -13 | 2.80 | 69.08/29.58/1.34 | 1.10 | 74 | PS not observed * | | |

* the duration of the experiment for 2 hours

3. RESULTS AND DISCUSSION

Figure 1 shows the dependence of $\ln(I/I_0) = f(\tau)$ for IPNs with 30/70 wt% PU/PHEMA ratio (curve 1) and OI IPNs at the same PU/PHEMA ratio and different $(-\text{TiO}_2-)_n$ content in POPG and $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ molar ratio (curves 2–5). Similar linear dependencies were obtained for all investigated IPNs for which phase separation was observed. Such linearity, as mentioned ear-

lier, is one of the criteria for the spinodal mechanism of phase separation. From the slope of the plots of the relationship $\ln(I/I_0) = f(\tau)$, the values of $2R(q)$ were calculated. These values, as well as the time of phase separation onset (τ_{ps}) and the degree of HEMA conversion at the time of phase separation onset (α_{ps}) are shown in Tables 1 and 2.

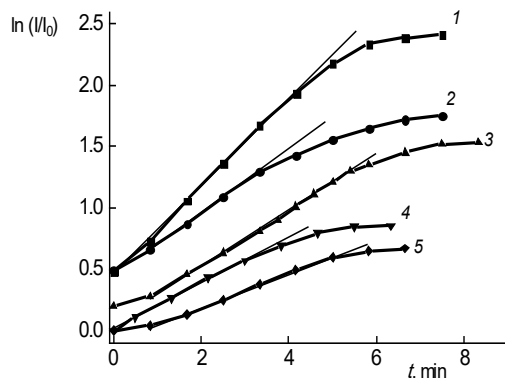


Fig. 1. Time dependence of $\ln(W/W_0)$ for the initial IPNs (1) and OI IPNs (2-5) of PU/PHEMA of 30/70 wt% composition with $(-\text{TiO}_2)_n$ content in POPG of 0.14 (2, 3) and 1.40 wt% (4, 5) and $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ ratio = 1/2 (2, 4) and 1/1 mol/mol (3, 5).

The data of Tables 1 and 2 show that an increase in PU amount both in the initial IPNs (IPNs -1 and IPNs -2) and in OI IPNs with the same content of $(-\text{TiO}_2)_n$ in POPG and molar ratio $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ (OI IPNs - 1, OI IPNs - 2 and OI IPNs - 3; OI IPNs - 8 and OI IPNs - 9; OI IPNs - 11 and OI IPNs - 12) leads to an increase in the initiation time of phase separation and a decrease in its rate. This is due to the fact that the phase separation rate is determined by the rate of chemical reactions. As it follows from Tables 1 and 2, with increasing PU content, the reaction of radical polymerisation of HEMA slows down (the value of W_{max} decreases and the time to reach this maximum increases t_{max}). This is probably due to the fact that increasing the PU content increases the viscosity and crosslinking density of the system as a whole, making it more difficult for AIBN radicals to escape from the “cage”. The so-called “cage” effects [21] increase the probability of recombination of initial radicals and reduce the efficiency of initiation, which causes a decrease in the reaction rate of HEMA radical polymerization. Therefore, those values of HEMA monomer conversion (a_{ps}), which are sufficient for loss of compatibility in the

reaction system, are reached much later.

The essential factors affecting the phase separation process in OI IPNs are the content and structure of the inorganic component $(-\text{TiO}_2)_n$. From the results shown in Tables 1 and 2, it is evident that for OI IPNs of the same PU/PHEMA composition and $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ molar ratio (OI IPNs -3 and OI IPNs -6; OI IPNs -9 and OI IPNs-12), phase separation slows down with increasing $(-\text{TiO}_2)_n$ content. As mentioned above, poly(titanium oxide) catalyses the urethane formation reaction, as a consequence of which the polymerisation of HEMA in OI IPNs takes place in an almost formed cross-linked PU; in this case, donor-acceptor interaction between the C=O group of HEMA and titanium atoms is possible [22]. All this leads to an increase in the viscosity of the system and an enhanced influence of the “cage” effect, which is reflected in a decrease of the initiation efficiency and, as a consequence, a reduced rate of PHEMA formation of OI IPNs component. This, in turn, leads to an increase in the time of the onset of phase separation and a decrease in its rate (Tables 1 and 2). It is worth mentioning that for the OI IPNs with a PU/PHEMA ratio of 70/30 wt. %, $(-\text{TiO}_2)_n$ content of 0.67

and 1.34 wt. % and $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ molar ratio 1/1 and 1/2 (OI IPNs -4, OI IPNs -7, OI IPNs -10, OI IPNs -13, Tables 1, 2), as well as for OI IPNs with a PU/PHEMA ratio of 50/50 wt. %, $(-\text{TiO}_2-)_n$ content of 0.40 wt. % and a molar ratio of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ 1/1 (OI IPNs -5, Table 1), no change of the light scattering intensity was observed during the experiment (about 2 hours). This indicates the absence of phase separation in such systems, or that the phase separation in OI IPNs starts at higher degrees of component conversion. The significant increase in the compatibility in OI IPNs with such $(-\text{TiO}_2-)_n$ content is possible also due to the higher grafting of $(-\text{TiO}_2-)_n$ to both components of the IPNs (PU and PGEMA). On the one hand, poly(titanium oxide) can be grafted to POPG during the sol-gel synthesis, and, on the other hand, probably to PHEMA as a result of exchange reaction between residues of non-hydrolysed isopropoxide groups (OPrⁱ) in $\text{Ti}(\text{OPr}^i)_4$ with hydroxyl groups of HEMA during the formation of OI IPNs.

It is known [23] that during sol-gel synthesis, depending on the $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ ratio, different structures of poly(titanium oxide) can be formed. Thus, when the ratio of $\text{H}_2\text{O}/\text{Ti}(\text{OPr}^i)_4 \leq 1$, as a rule, linear poly(titanium oxide) is formed, and when the ratio of $\text{H}_2\text{O}/\text{Ti}(\text{OPr}^i)_4 \geq 1$, branched poly(titanium oxide) is obtained. It can be assumed that the structure of the resulting poly(titanium oxide) will also affect the phase separation parameters. Comparing the time of the onset of phase separation and its rate in the OI IPNs with the same PU/PHEMA ratio and the same $(-\text{TiO}_2-)_n$ content, but obtained at different molar ratios of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ (OI IPNs -1 and OI IPNs -8; OI IPNs -3 and OI IPNs -9; OI IPNs -6 and OI IPNs -12), it is evident (Tables 1 and 2), that for the OI IPNs where

the poly(titanium oxide) is formed at a molar ratio of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O} = 1/1$, the time of the onset of phase separation increases and its rate decreases compared to the OI IPNs where $(-\text{TiO}_2-)_n$ formed at $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O} = 1/2$. The most likely reason for this effect could be that $(-\text{TiO}_2-)_n$ with a linear structure is more bound to POPG and probably has more residues of non-hydrolysed isopropoxy groups (OPrⁱ) for possible grafting to PHEMA during OI IPNs formation than $(-\text{TiO}_2-)_n$ with a branched structure, which in turn may limit the number of such interactions due to the appearance of steric complications.

The results of the study of the phase separation process in the IPNs and OI IPNs are confirmed by optical microscopy data. As an example, microphotographs of IPNs and OI IPNs films with 50/50 wt% PU/PHEMA ratio, different $(-\text{TiO}_2-)_n$ content and $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ molar ratio are shown in Fig. 2. It follows from Fig. 2 that phase separation in the investigated mixtures occurs by the spinodal mechanism. The initial IPN is characterised by clear interconnected structures (Fig. 2a), which become finer and less distinct for OI IPNs (Figs. 2b, 2c) as a result of a slower phase separation process. The sizes of structural formations in Fig. 2c (1.4 wt% $(-\text{TiO}_2-)_n$ in POPG) are slightly smaller than those in Fig. 2b (0.14 wt% $(-\text{TiO}_2-)_n$ in POPG). Obviously, the phase separation rate decreases with increasing $(-\text{TiO}_2-)_n$ content in POPG, and no phase separation is observed at all when the ratio of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ is changed from 1/2 (Fig. 2c) to 1/1 (Fig. 2d). It should be noted that morphological structures very similar to each other are observed for all phase-separated OI IPNs with different contents of $(-\text{TiO}_2-)_n$ and different molar ratios of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$.

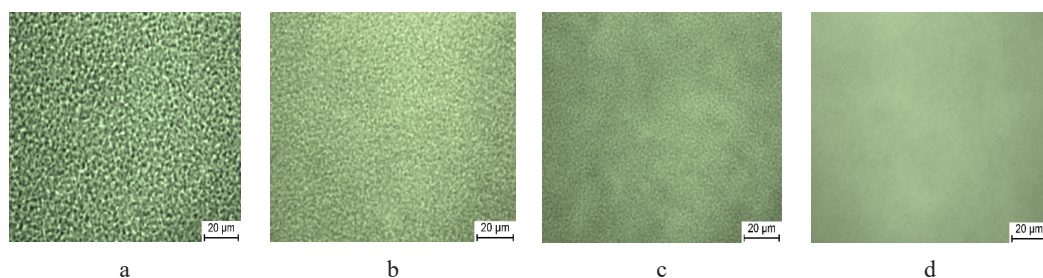


Fig. 2. Microphotographs of the initial IPNs (a) and OI IPNs (b-d) with 50/50 wt% PU/PHEMA and $(-\text{TiO}_2-)_n$ content in POPG: 0.14 (b); 1.40 wt% (c, d) and $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ ratio: 1/2 (b, c), 1/1 mol/mol (d).

4. CONCLUSIONS

The studies have shown that during the formation of both IPNs and OI IPNs, phase separation occurs by the spinodal decomposition mechanism. At the same time, the phase separation rate in OI IPNs depends on the PU/PHEMA ratio, $(-\text{TiO}_2-)_n$ content, and its structure. It has been found that the phase separation rate is lower in the formation of OI IPNs than in the initial IPNs with the same component ratio. This process slows down when the amount of $(-\text{TiO}_2-)_n$ increases

and the molar ratio $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O} = 1/1$. At a certain content of $(-\text{TiO}_2-)_n$ in OI IPNs, phase separation is not observed at all during the experiment, which indicates a high level of compatibility in such systems. Thus, it is shown that by varying the ratio of IPNs components, the content of the inorganic component and the molar ratio of $\text{Ti}(\text{OPr}^i)_4/\text{H}_2\text{O}$ it is possible to control the phase separation process and to obtain OI IPNs with different phase structure.

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