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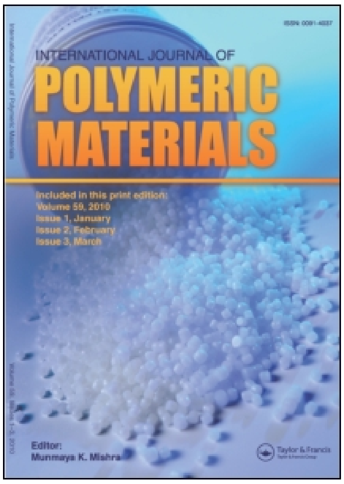

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Kinetics and Mechanism of the Late Stage of Cure Reaction-induced Microphase Separation

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Reaction-induced phase separation in oligomer modified epoxy resin cured by tertiary amine as a catalyst was studied. Evolution of the reaction system morphology was observed *in situ* by optical microscopy technique. Intensity of the coalescence that proceeds at the late stage of phase separation depends on conditions of the cure, *i.e.*, formulation and temperature. The final morphology of the reaction system was shown to depend on a chemical mechanism of the cure process, first of all, polycondensation or polymerization reaction paths.

Keywords: Phase separation; Polymer morphology; Cure reactions; Epoxy polymers

1. INTRODUCTION

The process of phase separation induced by curing reaction (CRIPS) in a oligomer – oligomer mixture is a subject of extensive study because it is one of the better ways of formation of materials with enhanced toughness and impact properties. There are many investigations concerning the thermodynamic and kinetic aspects of phase decomposition. Most of them are reviewed in [1–4]. Later, approaches to non-equilibrium quantitative description of the phase separation was

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*Corresponding author. e-mail: kuzub@icp.ac.ru formulated [5–7]. Both the additive concentration in onset reaction mixture formulation and the relationship of rates of chemical reaction and phase separation define the way the phase decomposition proceeds: *via* nucleation growth or spinodal demixing [1,4]. A mechanism of phase separation is well known to control the morphology of the generated phase (*i.e.*, volume fraction of modifying particles, their size distribution function), that, in turn, influences the properties of the modified thermosets. The formation of the final morphology of heterophase polymers is completed at the latest stage of a phase separation process *via* coarsening of particles realized by Lifshitz and Slyozov mechanism [8] (it is known also as Ostwald ripening) and coalescence. Regularities of this latter process, obviously, depend on the cure reaction mechanism, and is still rather obscure. The objective of this work is to observe the evolution of morphological structure of epoxy blends in the course of anionic polymerization initiated by tertiary amine.

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2. EXPERIMENTAL

Diglycidyl ether of bisphenol A (DGEBA), $M_n = 360$, was used as the compound forming the polymer matrix. It was cured with dimethylbenzene amine (DMBA) as a catalyst; its concentration was 0.21 mol/l. Poly(propyleneglycol)-*bis*-(tolylenediurethanethyleneacrylate), $M_n = 2500$, was used as a phase forming additive. Its concentration was varied from 5 to 22% wt. The additive was first dissolved at 50°C in DGEBA, the mixture was evacuated, and DMBA was then added.

The reaction mixture was placed between two glass plates inside the electrical heater; thickness of the reaction layer was $30 \div 50\,\mu m$. This assembly was placed under the optical microscope objective. The cure was performed at temperature range $50 \div 90°C$.

Optical microscope technique with computer analysis of the images was used to observe the generated morphology during the cure process. The reliably achieved resolution was 1 μm, the observation area was $\sim 1\,mm^2$ and the duration of the image scanning was not more than 1 min. The micrographs were analyzed using image processing software created in our laboratory. It allowed us to obtain the number of particle, their radii and coordinates of particle centers.

3. RESULTS AND DISCUSSION

3.1. Features of Segregation Process

It is well known that the onset of CRIPS displays as a moment when the initially transparent reaction system becomes cloudy. Light scattering technique is used, as a rule [1,4], to define the cloud point conversion (CPC) connected with the appearance of particles of the segregating phase of submicron sizes. Optical microscopy technique can be suitable for that too, though it allows to characterize generated morphological structure when its particle sizes are more than 1 µm. That is why the latter technique is most appropriate to observe *in situ* the time evolution of morphological structure in the latest stage of phase separation when coarsening of the particles of dispersed phase takes place.

In Figure 1 dependencies of cloud point and gel point conversion on formulation and temperature are shown. Estimation of the reaction conversion was done using kinetic data [9]. As one can see the reaction system becomes instable when the cure conversion is well before the gel point. The higher the additive concentration the lower the CPC and lower the viscosity of the reaction system. It makes easier the process of coarsening of particles of the dispersed phase.

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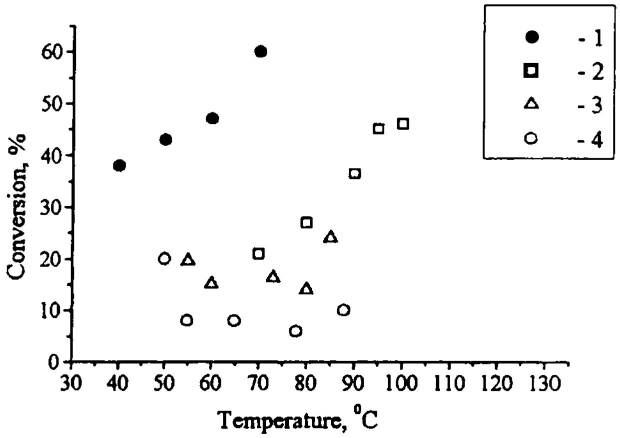

FIGURE 1 Dependencies of conversion at gel point (1) and cloud point (2–4) on temperature and concentration of the additive. The additive concentration, % wt.: 5(2), 10(3), 22(4).

The generated morphology right after the cloud point is presented in Figure 2. High concentration of the dispersed phase settled out when CPC is reached. The weak contrast of the image that is a result of a small difference between refractive indexes of matrix and dispersed phase is an evidence of rather low concentration of the additive in the segregating phase. This fact allows us to suppose that spinodal demixing takes place in this case. Note, at weak contrast of the images temperature elevation leads to the development of structural elements the sizes of which are larger the higher temperature.

The reason of that is expected to be as follows. On the one hand, this fact can be stipulated by temperature dependence of the wavelength of fluctuations growing in the course of spinodal demixing [7]. On the other hand, temperature influences the medium viscosity and the degree of segregation that occurs during the scanning time. Therefore, the higher temperature the higher degree of segregation we register.

The morphological structure in the course of the cure process as function of temperature and concentration of the additive is shown in Figures 3–6. All micrographs were obtained from the same area of the reaction system. In all cases, an increase of the image contrast takes place. In the course of the segregation process final particle sizes

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FIGURE 2 Temperature dependence of the reaction system morphology immediately after cloud point. T°C: 50(1), 55(2), 70(3), 90(4). The additive concentration is 22% wt.

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a b

FIGURE 3 The change of the reaction system morphology in the course of the cure process. *Concentration of the additive is* 22% *wt.* (a) $T=50°C$. *Time after cloud point*, min: 1(1), 10(2), 15(3), 70(4); (b) $T=70°C$. Time after cloud point, min: 1(1), 2(2), 5(3), 11(4).

are close to those of the initial structural elements. Their concentration does not change noticeably too.

Essential increase of sizes and decrease of concentration of particles can be seen (Fig. 6) only at the highest temperature (90°C) and additive concentration (22% wt.). These conditions are when coalescence displays itself clearly. Actually, in this case the viscosity

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FIGURE 4 The change of the reaction system morphology in the course of the cure process. $T = 90°C$. The additive concentration is 22% wt. Time after cloud point, min: 1(1), 2(2), 3(3), 4(4), 5(5), 6(6), 8(7), 16(8). Merging particles are designated by shading.

of the reaction medium is the lowest, *i.e.*, conditions are created for motion, collision and merging of particles. It is possible too that coalescence occurs in all investigated cases but its intensity is rather low because of the higher viscosity of the systems (see Fig. 1).

3.2. Kinetics of Coalescence

Regularities of coalescence have been investigated in detail for the case shown in Figure 6. Particle population has been counted on

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FIGURE 5 The change of the reaction system morphology in the course of the cure process. Concentration of the additive is 5% wt. $T = 90°C$. Time after cloud point, min: 2(1), 4(2), 10(3), 20(4), 40(5), 60(6).

area of $100 \times 100\,\mu m$. Figure 7 shows the transformation of particle size distribution (PSD) in the course of coarsening of particles of the dispersed phase. At the beginning of the process PSD is close to uniform. Then this distribution is expanded because of the appearance of larger particles fraction. At the same time the low size mode remains practically constant. One can suggest that the modality of PSD is changing. Note, the noticeable increase of particle sizes involves only a small fraction of the dispersed phase. Dependence of particle quantity (sizes of which are more than $1\,\mu m$) on time obeys a kinetic law of 2nd order (Fig. 8). It means that coarsening of particles occurs *via* their direct merging.

In Figure 9 an example is shown of displacement of merging particles with time (in 2D space). Three particles of practically the same radii were chosen arbitrary and their path was followed. The displacement of particles 2 and 3 led to their merging. The rate of

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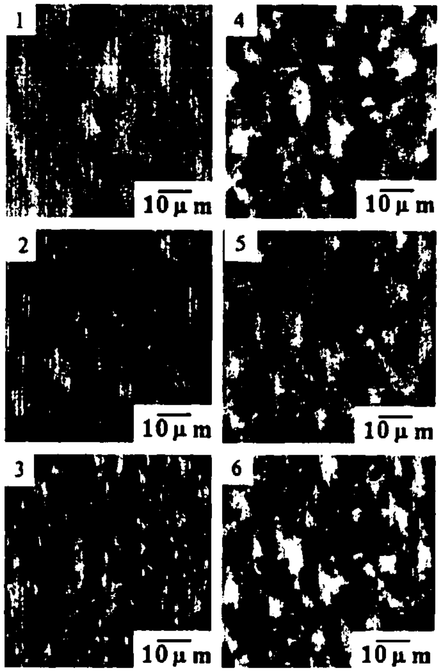

FIGURE 6 The change of the reaction system morphology in the course of the cure process. Concentration of the additive is 10% wt. $T = 90°C$. Time after cloud point, min: 1(1), 2(2), 5(3), 6(4), 8(5), 10(6).

this move corresponds to the value of the diffusion coefficient $D = \delta^2/t \sim 10^{-14}\,m^2/s$ (δ is particle displacement). Such value of the diffusion coefficient corresponds to viscosity of the reaction medium $\sim 10^{-2}$ Pa · s. It is unlikely that this low viscosity can be characteristic of the total volume of the reaction system. It is more probable to suggest that there are some limited regions with low viscosity where the displacement of particles proceeds with a noticeable rate. It explains why only ca. 10% particles take part in the coalescence process. We suggest that peculiarities of the late stage of phase separation depend on the path of the curing reaction. If the cure process proceeds as polymerization, the reaction medium is well known to be inhomogeneous due to localization of chemical reaction [10], particularly, at the onset stages. The localization of particle diffusion is supposed to be a consequence of this feature of the cure process. A different situation can take place when the curing proceeds as polycondensation and the reaction medium is homogeneous.

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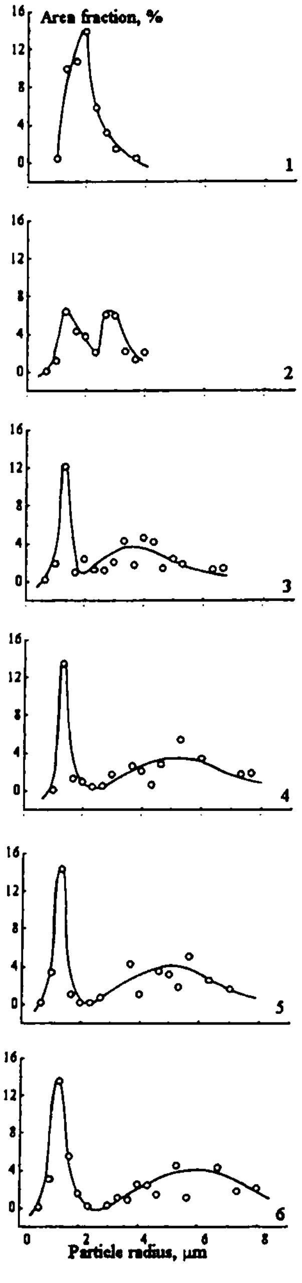

FIGURE 7 The change of the particle size distribution during coalescence process. $T=90°C$. N_0 and N_t are initial and current particle quantity. Concentration of the additive is 22% wt. Time, min: 1(1), 2(2), 3(3), 4(4), 6(5), 23(6).

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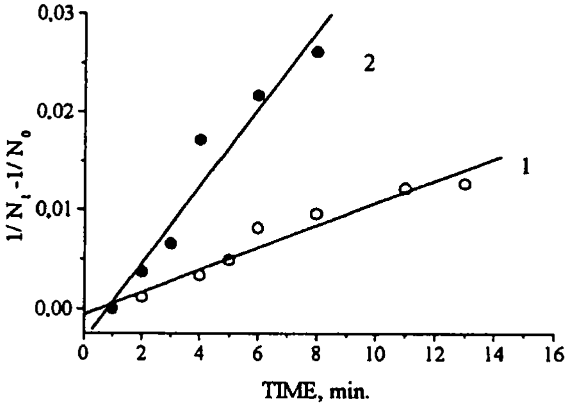

FIGURE 8 The change of the particle number in time. $T = 90°C$. Concentration of the additive is 22% wt. Temperature, °C: 70(1), 90(2).

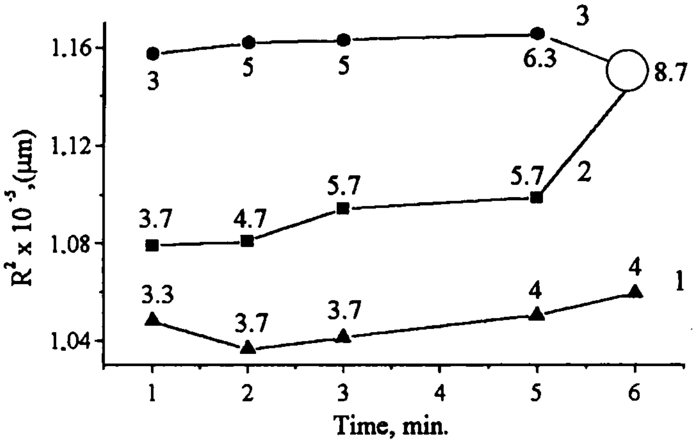

FIGURE 9 Displacement of merging particles in time. R^2 is displacement square of the particle. Numbers on the curves show particle radius, μm.

4. CONCLUSIONS

This work showed that the kinetics of the chemical reaction of cure affects the process of phase separation. According to wide spread point of view [1] this influence consists of a possibility to reach the equilibrium state: high rate of curing reaction does not allow to complete the phase separation due to dramatically increasing viscosity. Here another effect was demonstrated: the intensity of the coalescence process depends on the kinetics and mechanism of polymer formation. As far as terminal PSD is defined by the development of the coarsening process, this circumstance should be taken into account when polymer materials are manufactured by CRIPS technology.

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