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ORIGINAL CONTRIBUTION

Kinetics of phase separation at the early stage of spinodal decomposition in epoxy resin modified with PEI blends

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Abstract The behavior at the early stage of spinodal decomposition (SD) for polyetherimide (PEI)/epoxy blends was investigated. It was found that the phase separation of PEI/epoxy blends took place by SD mechanism. The development of molar mass in the epoxy resin was gradual and then the three blends could still be considered as concentrated solutions of thermoplastic. The kinetics at the early stage of phase separation for these blends could be described by the Cahn–Hilliard–Cook linearized theory.

Keywords PEI/epoxy · Phase separation · Cahn–Hilliard–Cook linearized theory

Introduction

The kinetics at the early stage of phase separation has attracted increasing attention. However, most of the attention has been focused on thermal-induced phase separation (TIPS) of the binary or ternary blends of thermoplastic–solvent or thermoplastic–thermoplastic where there is only phase separation occurring after a quench into the unstable region. The dynamics of phase separation induced by thermal quenching has been studied numerically and experimentally [1–8]. For TIPS blends, it is usual that the process of spinodal decomposition (SD) at the early stage of phase separation can be well-fitted with the linearized Cahn theory.

On the other hand, the polymerization-induced phase separation (PIPS) is a practical way of forming composite materials. In the case of PIPS, phase separation and polymerization occur simultaneously [9–13]. It should be more complex. There are a few reports involved in a binary trifunctional monomer–small molecule solvent solution, and the Cahn–Hilliard linearized theory is used to describe the SD mechanism at the early stage [14]. However, there are fewer papers in the literature devoted to the discussion of kinetics on the phase separation of thermoplastic–thermoset blends, particularly, the kinetics at the early stage of phase separation. The effect of an organoclay on the reaction-induced phase separation kinetics and morphology of a polyetherimide (PEI)/epoxy mixture was investigated by Peng. The phase separation kinetics were analyzed by means of the temporal evolution of scattering vector q_m and scattering intensity I_m at the scattering peak [15]. Ryan studied the reaction-induced phase separation in the processing of poly(2,6-dimethyl-1,4-phenylene ether) with epoxy resin. A regime where ln $I(q,t)$ was linear with time was used to calculate the amplification factor $R(q)$, and the data plotted as $R(q)/q^2$ versus q^2 fitted a straight line, suggesting the validity of the linear theory [16]. Vayer studied phase separation induced by cross-linking in thermoset blend based on unsaturated polyester, styrene, and low molar weight saturated polyester. It was found experimentally that phase separation proceeded via SD and

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Table 1 Accelerator concentration of blends P720, HP720, and NP720

Blend	P720	HP720	NP720
BDMA (pbw)	0.2	0.1	0

apparent diffusion coefficients D_{app} were estimated using the Cahn–Hilliard–Cook theory [17]. Liao et al. presented synchrotron-based time-resolved small-angle X-ray scattering (SAXS) measurements of SD in a covalently cross-linked *N*-isopropylacrylamide gel. They found that, for early times, the Cahn–Hilliard–Cook linearized theory can be used to describe the time evolution of the scattered intensity [18].

In our previous work [19–22], it was found that the phase separation of PEI/epoxy blends took place by SD mechanism. The morphology evolution began with a cocontinuous structure, then shifted to a phase inversion structure, and finally, irregular PEI-rich macrophase domains were formed, which were dispersed in an epoxy-rich continuous phase. It was very close to the cocontinuous-type phase structure. The evolution of scattering vector q_{m} corresponding to the morphology evolution at the middle and later stage of phase separation followed the Maxwell-type relaxation equation. The relaxation time might be suggested as the time for the diffusion of the epoxy–anhydride *n*-mers from the PEI-rich phase by their relaxation movement, and thus the apparent activation energy of the relaxation movement at the middle and later stage of phase separation was obtained.

The aim of the present paper is to study the behavior at the early stage of phase separation by time-resolved light scattering (TRLS) and to describe the kinetics of the morphology evolution processes at the early stage of phase separation. Moreover, the effect of the accelerator on the cure rate and curing reaction rate will be discussed because the influence of accelerator can be important for industrial application. It is hoped that the results would aid in designing materials by the control of structure development in multicomponent thermosetting resins.

Experimental part

Materials

A commercial epoxy precursor DGEBA (DER 332 with an epoxide equivalent weight of 184–194 g/Eq) from Dow Chemical, a curing agent methyltetrahydrophthalic anhydride (MTHPA), and an accelerator benzyldimethylamine (BDMA) from Shanghai Third Reagent Factory were used without further purification. PEI was synthesized from bisphenol A dianhydride and 4,4′-[1,4-phenylenebis(1-methylethylidene)] bisaniline at a stoichiometric ratio of 1:0.985 as described previously [19]. The number- and weight-average molecular weight for PEI measured by gel permeation chromatography (GPC) were $\overline{M}_{\mathrm{w}} = 75,000$ and $\overline{M}_{\mathrm{n}} = 46,000$, respectively, and the glass transition temperature (T_{g}) determined by differential scanning calorimeter (DSC) was 220 °C.

Preparation of PEI/epoxy blends

Epoxy blends containing 20 parts by weight (pbw) PEI were prepared by dissolving PEI in DGEBA at 150 °C under gentle stirring in a flask. The mixture was cooled to 90 °C after a clear homogeneous solution was obtained, and 80 pbw MTHPA was added (with or without accelerator BDMA; Table 1), then the blend was cooled rapidly and kept in a refrigerator where no significant reaction took place over periods of several months.

Monitoring phase separation

The phase separation process taking place during the isothermal curing reaction was observed in real time and in situ on the self-made TRLS instrument with controllable hot chamber. The light source is a 15-mW plane-polarized He–Ne laser with a wavelength of 632.8 nm. The sample sandwiched between two cover glasses was inserted into a heating chamber kept at a constant temperature. The chamber was set horizontally on the light-scattering stage. Radiation from the He–Ne gas laser was applied vertically

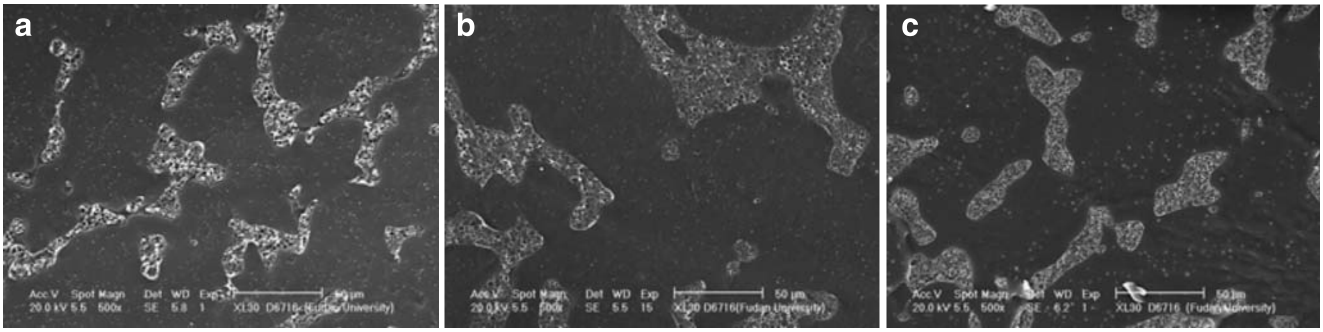

Fig. 1 Scanning electron micrographs of fracture cross-sections views of three blends cured at 150 °C for 5 h. **a** P720, **b** HP720, **c** NP720

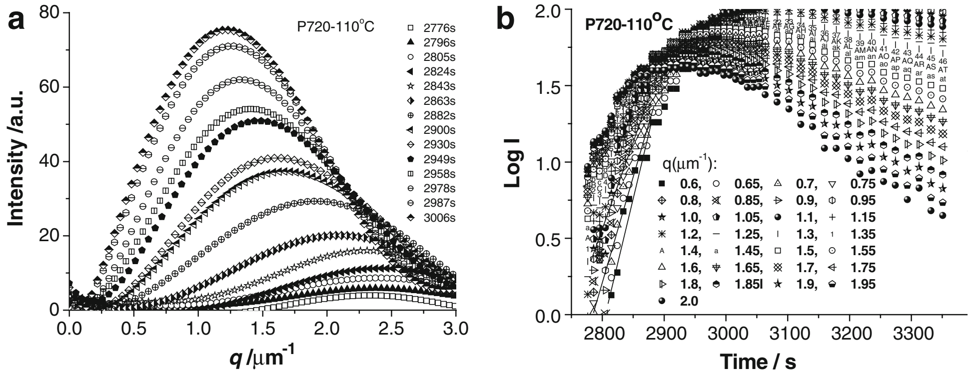

Fig. 2 The results of TRLS of blend P720 cured at 110 °C. **a** TRLS profiles at the early stage of SD. **b** Semilogarithmic plot of $I(q,t)$ versus time t at various fixed q

to the specimen. The scattered light intensity distribution $I(q)$ was determined using a two-dimensional CCD camera detector [23]. The change in the light-scattering profiles was recorded at appropriate time intervals during isothermal curing. The film sample for TRLS observation was prepared by melt-pressing with a thickness of about 20 μm.

Measurements

The calorimetric measurements were made on Perkin Elmer Pyris 1 DSC in a dry nitrogen atmosphere. The T_g of PEI was determined by DSC from room temperature to 300 °C at a heating rate of 10 °C/min. To examine the cure kinetics, the dynamic measurement was performed at five different heating rates of 5, 10, 15, 20, and 25 °C/min for all three uncured blends. Study of conversion of the two blend systems was also carried out on the DSC apparatus.

Molecular weight and molecular weight distribution of PEI and epoxy–anhydride mixture were measured by GPC relative to a polystyrene standard with tetrahydrofuran being used as eluent.

Results and discussion

Morphologies observed by SEM

The morphologies of cured blends were observed with scanning electron microscopy (SEM). As shown in Fig. 1, the morphologies of the three blends consist of large PEI-rich domains exhibiting irregular shapes and dispersed in an epoxy-rich continuous phase which is very close to the cocontinuous-type phase structure [19]. Meanwhile, the morphologies obtained at different temperatures are almost the same.

Evolution of $q(t)$ during the isothermal process

Figure 2a–b gives a typical example of time evolution of a scattering peak for the blend P720 cured at 110 °C isothermally. The observed scattered light intensity I was corrected by subtracting the background intensity acquired at the onset of phase separation. The scattering maximum first appears at a large q, and the peak position remains invariant for a short period depending upon the curing temperature. As the curing temperature increases, the time period for this stage became shorter. At a later time, the scattering vector with maximum scattering intensity, q_m, decreases with time and then leveled off until fixed to a certain value, while the relative intensity of scattered light increased continually. It indicates the development of a regularly phase-separated morphology by SD [24]. It is consistent with the result of SEM above. The morphologies generated after 5 h cure are similar regardless of different curing temperature and all consist of large irregular PEI-rich domains dispersed in an epoxy-rich continuous phase (not being showed here). It suggests that the composition of

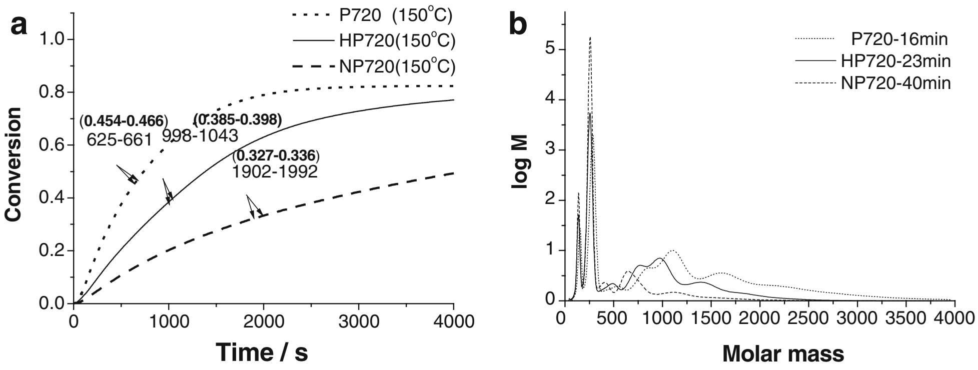

Fig. 3 **a** Time–conversion curves of epoxy resin at 150 °C for different blends. **b** GPC results for different blends

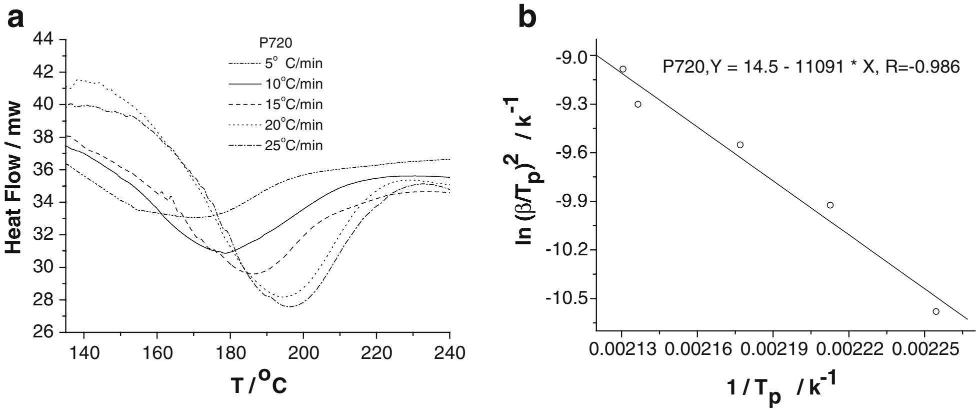

Fig. 4 **a** Heat flow measured by DSC during cure at different heating rates for blend P720. **b** Kissinger plot for blend P720

the blend (20 pbw of PEI) is near the critical point of phase separation at the different experimental temperatures. The experiments gave evidence for SD and became dominant during the PIPS.

Notably, similar characteristics are displayed at all the temperatures investigated for the three blends, including temperatures such as 100, 110, 120, 130, 140, and 150 °C. This feature indicates that typical SD took place over the temperature investigated in the PEI-modified blend.

Figure 2b depicts the plots of the corrected intensity log $I(q,t)$ versus time t for different scattering vectors q ranging from 0.6 to 2.0 μm^{-1} at 110 °C is shown in Fig. 2b. The time dependence of log $I(q,t)$ versus time t satisfactorily appears quasilinear at the early stage of phase separation.

The validity of Cahn–Hilliard–Cook linearized theory

The Cahn–Hilliard–Cook equation is strictly valid at the early stage of SD. At this stage, the concentration fluctuations grow exponentially, but the characteristic length scale of the fluctuation remains almost constant or varies only very slowly. Experimentally, these features manifest themselves in the exponential growth of the peak intensity (the effect has been observed especially at lower temperatures or lower concentrations of accelerator BDMA) with the peak position remaining almost fixed. Though this situation occurs in a small fraction of the period in Fig. 2a and b, the very beginning data as showed were used to fit linear.

Theoretically, Cook treatment for a simple thermal quenching system must be modified for such chemically reacting system. However, as shown above, the experimental data of the three blends all fit the linearized Cahn–Hilliard–Cook theory well. It can be associated with the fact that the lower conversion of epoxy curing reaction and the degree of polymerization at the early stage of phase separation for the epoxy–anhydride *n*-mers are still very small and hardly change at the early stage of SD investigated. The blends during phase separation at the early stage can still be regarded as concentrated PEI–solvent (low molecular weight of epoxy–anhydride *n*-mers). The ranges of time and conversion of the three blends cured at 150 °C are shown in Fig. 3a. The arrows indicate the range of time and conversion at the early stage of phase separation, respectively. It appears that the time ranges become longer at lower concentration of BDMA because of the lower reaction rate and phase separation rate; however, the corresponding conversion ranges at 150 °C are all about 0.01 (showed in the bracket in Fig. 3a). The change of conversion in this study is so small, and the epoxy–anhydride *n*-mers, which take diffusion movement, are in fact dimers or even trimers.

It was approved by GPC experiments (Fig. 3b, the time were delayed considering the dilution effect of PEI in the blends in order to make sure the molecular weight is close or more than of that at the early stage of phase separation) showing the molecular weight were about 500 to 1,500 (are 2-mers and 3-mers, much less than that of PEI) during the early stage of phase separation, although the curing mechanism of blends with accelerator are different with the blend without accelerator [25–28]. But in our systems, the amount of BDMA is very little(0.1 and 0.2 pbw, the mole ratio of BDMA to epoxy group is about 0.0015 and 0.0031). The increase of molecular weight for blend P720

Table 2 The relationship between heating rate (β) and maximum temperature of exothermic peak (T_p) for blend P720

Heating rate β (°C/min)	5	10	15	20	25
Peak temperature T_p (°C)	170	179	186	195	196
$1/T_p$ $(1/k)$	0.00225	0.00221	0.00218	0.00214	0.00213
$\ln\left(\beta/T_p^2\right)$	−10.6	−9.92	−9.55	−9.30	−9.08

and blend HP720 is not so fast as in the chain reaction. There exist different molecular weight epoxy–anhydride oligomers, in particular, at the early stage of phase separation. The PEI/epoxy blend could still be considered as concentrated solution of thermoplastic and it is reasonable that the three blends cured at different temperatures fitted the Cahn–Hilliard–Cook linearized theory well at the early stage of phase separation.

Then, apparent diffusion coefficients D_{app} can be estimated using the Cahn-Hilliard-Cook theory and apparent activation energy of diffusion at the early stage of spinodal decomposition can be obtained from D_{app} at different temperature by Arrhenius equation. They are 64.9, 50.9 and 46.1 kJ/mol for blends P720, HP720 and NP720 respectively.

Activation energy of curing reaction of the blends

As the presence of accelerator BDMA, the curing mechanism of blends P720 and HP720 is different with the blend NP720 [29–32]. Figure 4a is the heat flow curves of blend P720 at different heating rate.

According to the Kissinger equation:

$$\frac{d\left(\ln\beta / T_{\mathrm{p}}^{2}\right)}{d\left(l / T_{\mathrm{p}}\right)} = -\frac{E}{R} \tag{1}$$

where T_p, β, and E are the peak temperature of different heating rate, heating rate, and activation energy, respectively. From Eq. 1, the activation energy of curing reaction can be calculated [29–30].

Table 2 is the DSC results obtained from Fig. 4a. As shown in Fig. 4b, the linear plot of $\ln(\beta/T_{\mathrm{n}})^2$versus $1/T_{\mathrm{p}}$ is obvious and the slope is 1.11×10^4, thus the activation energy of curing reaction for blend P720 is calculated as 92.3 kJ/mol. Similarly, the activation energies of blend HP720 and blend NP720 are 89.8 and 67.4 kJ/mol, respectively. To contrast with results in the literature [30], the activation energies of the three blends investigated are all about 10 kJ/mol less, it might be caused by the dilution effect of PEI [31].

The apparent activation energy of relaxation movement at the later stage of the phase separation are 69.9 [19], 60.0, and 51.4 kJ/mol. It is clear that the activation energy of curing reaction for the three blends is much bigger than that of relaxation movement. Then, in the course of PIPS, it implies that as soon as a curing reaction takes place further, the relaxation movement can catch up without delay.

In PIPS blends, the polymerization reaction leads to the increase of quench depth due to the increase of molecular weight of epoxy resin. It has been shown similar feature experiments with the continuous cooling-induced decomposition [32]. As it has been discussed above, the PEI/epoxy blend can still be considered as concentrated solution of thermoplastic–epoxy owing to the lower molecular weight of epoxy–anhydride *n*-mers. In the three blends investigated, the curing reaction is a slower reaction, respectively, due to its larger activation energy. Obviously, the curing reaction might be the dominant factor to affect the rate of phase separation at the early stage of SD. The further the curing reaction proceeds, the deeper the quench is. Meanwhile, the phase separation (early by diffusion movement and later by relaxation movement) should catch up with the chemical reaction.

Conclusion

The phase separation of PEI/epoxy blends took place by SD mechanism. At the early stage of SD of the three blends investigated, since the changes of conversion were very small, the PEI/epoxy blends could still be considered as concentrated solutions of thermoplastic, and it is reasonable that the three blends cured at different temperatures fitted the Cahn–Hilliard–Cook linearized theory well at the early stage of phase separation.

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