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Polymerization induced phase separation in poly(ether imide)-modified epoxy resin cured with imidazole

Minghai Wang, Yingfeng Yu, Xianguo Wu, Shanjun Li*

Department of Macromolecular Science and the Key Laboratory of Molecular Engineering of Polymer, Ministry of Education, Fudan University, Shanghai 200433, China

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Abstract

This paper studies the phase separation in poly(ether imide) (PEI) modified epoxy resin using imidazole (C_{11}Z-CNS) as epoxy hardener to control its morphology. The sponge-like phase structures were founded at higher PEI concentration (10–25 phr), while homogeneous structures are formed at low PEI concentration (5 phr). The effects of PEI concentration on curing kinetics and phase structures were studied by differential scanning calorimeters (DSC) and scanning electron microscopy (SEM). It is shown that although the addition of PEI does not change the curing mechanism, the separated morphology becomes finer at high PEI concentration. The curing rate and conversion decrease with the increase of the content of PEI. The chain growth polymerization of these systems caused an early gelation (conversion $< 10\%$) and early freezing of morphologies. The evolution of phase separation in the early stage was monitored by synchrotron radiation small angle X-ray scattering (SR-SAXS) and transmission electronic microscopy (TEM). It is suggested that the formation of sponge-like phase structure could be attributed to the strong viscoelastic effects in the early stage of phase separation.

Keywords: Imidazole; Epoxy resin; Viscoelastic phase separation

1. Introduction

Epoxy resins have been widely used in the electronic industry and fiber-reinforced composites due to their superior thermal, mechanical and electrical properties such as high tensile strength and modulus, dimensional and thermal stability and excellent chemical and solvent resistance. Unfortunately, they tend to have a characteristic low resistance to brittle fracture. The improvements in fracture toughness of earlier rubber modified epoxies are invariably accompanied by a significant drop in stiffness, as a result, much work has been made to toughen highly crosslinked thermoset polymers with high modulus, high glass transition temperature thermoplastics, such as polyethersulfone (PES) [1,2], polysulfone (PSF) [3], poly (ether–ether ketone) (PEEK) [4] and polyether imide (PEI) [5,6].

Since the mechanical properties of the materials are determined by their final morphologies, much work has been focused on phase separation and morphology control. Pascault et al. [7] used PEI (Ultem 1000) to toughen epoxy resin and found that the effective improvement in toughness is only obtained at high fractions of the engineering thermoplastic, where the blends form sponge-like (a dispersion of thermoset-rich particles in a thermoplastic matrix) or sandwich-like (consisting of a dispersion of macroscopic irregular thermoplastic-rich domains showing a sponge-like structure in a thermoset-rich matrix exhibiting a dispersion of thermoplastic-rich particles) morphology. Similar results were also reported by other authors [8,9]. Thus it is essential to obtain a sponge-like or sandwich-like morphology for toughening purpose in material designing and property control.

In our previous works [10–13], a novel series of PEIs are synthesized and added into epoxy to study the phase separation process. Different morphologies are obtained by changing chain structure and molecular weight of PEI, varying curing temperatures and curing agents. And phase separation process is determined by the phase diagram and the ratio between fluctuation growth rate of phase structure

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* Corresponding author. Address: Macromolecular Science, Fudan, Lane 220, Handan RD, Shanghai 200433, China. Tel.: +86-2165642865; fax: +86-2165640293.

E-mail address: sjli@fudan.edu.cn (S. Li).

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and disentangle rate of polymer chain whatever phase separation mechanisms, i.e. SD and NG. However, thermoplastics-continuous phase structure can be obtained only when the content of PEI has high weight fraction ($\geq 15\%$).

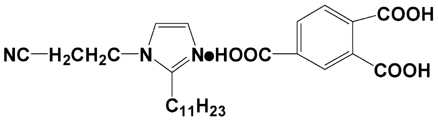
While it has been found recently [14–18] that abnormal phase structure with sponge-like (or network-like) morphology could be observed at even a minor polymer concentration in viscoelastic phase separation, which includes the category of phase separations with chemical reaction (thermoset/thermoplastic systems). The viscoelastic effect coming from very strong asymmetry in molecular dynamics such as polymer/solvent and polymer/polymer systems having a very large difference in glass transition temperature when the phase separation time is very short compared with the characteristic relaxation time of chain disentanglement, plays a dominant role in phase separation behavior [17]. Domains of a small molecular-rich phase appear in a polymer-rich matrix, and then sponge-like (or network-like) structures are formed by the domain growth. Finally, a continuous polymer-rich phase develops into a dispersed phase by shrinkage of the polymer-rich phase. In these systems, even a minor polymer component can provide sponge-like continuous phase structure in the early stage of phase separation.

As we know [13], PEI modified epoxy resins cured with imidazole have fast curing rate and well performance, aim of the present work is to achieve the PEI continuous phase structure at low PEI concentration based on strong viscoelastic effect and early vitrification owing to the fast chain growth polymerization by imidazole, and tries to describe the characteristic of the evolution process of phase separation in the early stage. It was hoped that these results would be helpful in material design by control of structure development in multicomponent thermoset resins with chain growth mechanism.

2. Experimental

2.1. Materials

The epoxy oligomer used in this study is a diglycidyl ether of bisphenol A (D.E.R.331, Dow Chemicals Company, USA) and was dried under vacuum at 80 °C before use. The hardener, 1-cyanoethyl-2-undecylimidazole trimellitate (C$_{11}$Z-CNS, 93% purity, mp 146.8 °C), was received from Shikoku Chemicals Corporation (Japan), and its structure is shown in Scheme 1. Poly(ether imide) was synthesized from bisphenol-A dianhydride (BISA-DA) and 4,4-[1,4-phenylene bis(1-methylethylidene)]bisaniline in *m*-cresol at 200 °C for 6 h. The number-average molecular weight is 2.9×10^4 g/mol and inherent viscosity is 0.9 dL/g (in 1-methyl-2-pyrrolidinone solvent at 30 °C) ($T_g = 218$ °C). The structure is depicted in Scheme 2.



Scheme 1. The structure of 1-cyanoethyl-2-undecylimidazole trimellitate (C$_{11}$Z-CNS).

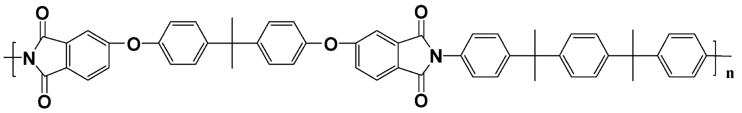
The modified epoxy resins containing 5–25 phr (per hundred DGEBA resin) PEI were prepared in two stage process: PEI was first dissolved in DGEBA at 150 °C, and the hardener (7 phr of C$_{11}$Z-CNS) was then added at 105 °C and stirred vigorously and degassed to attain a homogeneous mixture. The blend was cooled rapidly to room temperature and stored at < 0 °C to avoid further curing reaction. For comparison, four blends and neat epoxy cured by C$_{11}$Z-CNS studied in this work listed in Table 1.

2.2. Measurements

A Setaram 141 differential scanning calorimetry instrument was used for the isothermal and scanning curing experiments. The isothermal reaction was conducted at three temperatures (110, 120, and 130 °C) for 2 h and at 150 °C for 4 h for post curing. Measurements of the glass transition temperature (T_g) are at a rate of 10 °C/min under a nitrogen atmosphere. While a scanning electron microscope (Philips XL 30) was used to observe the morphology of the blends cured at three temperatures (110, 120, and 130 °C) for 2 h. The melt viscosity variations of the blends during cure reaction were recorded on an Ares-9A rheometry instrument: about 1 g of the blend was sandwiched between two circular plates and softened at 60 °C for 2 min. The plate distance was then adjusted to about 1.0 mm and the temperature was raised quickly at a rate of 100 °C/min to the preset curing temperature. All the blends were tested under a parallel plate mode with a controlled shear strain of 1% and test frequency of 1 rad/s to ensure that measurements were performed under dynamic equilibrium conditions. For transmission electronic microscopy (TEM) experiment, ultrathin (about 70–90 nm) sections of blend cured at 110 °C for different time were prepared and observed on a JEM-1200EX TEM instrument. SR-SAXS measurements were performed at the Beijing Synchrotron Radiation Facility. The wavelength of incident X-rays was 0.154 nm, and the camera length was 1510 mm. Scattering X-rays were detected by a photo imaging board with an effective length of 170 mm and the wave number (q) range was 0.1–1.5 nm^{-1}. The same specimen (DGEBA/PEI/C$_{11}$-

Table 1
The composition of epoxy blends (phr means per hundred DGEBA resin)

Blend code	DER 331 (phr)	PEI (phr)	C$_{11}$Z-CNS (phr)
Neat	100	0	7
PEI-5		5	
PEI-10		10	
PEI-18		18	
PEI-25		25	



Scheme 2. The structure of poly(ether imide) (PEI).

Z-CNS) was heated at a set temperature for a period of time and tested after being quenched in liquid nitrogen, then heated and quenched again for the next test to simulate the dynamic curing process. The relative scattering light intensity was obtained after attenuation, incident intensity fluctuation and air scattering corrections.

3. Results and discussion

3.1. Curing mechanism

Isothermal DSC curves of neat epoxy resin and DGEBA/PEI blends cured with C_{11}Z-CNS at various temperatures were shown in Figs. 1 and 2. Two exothermal peaks can be distinguished in both neat epoxy and modified systems as shown in Fig. 1(a). The first peak can be assigned to the adduct formation step and the second to the etherification reaction in which the reactive alkoxide anion is the propagating species [19]. This result implies that the introduction of PEI does not affect the reaction mechanism of this system. However, the addition of PEI delays the triggering time of the reaction and exothermal peak, and also prolongs the curing time; moreover, the higher concentration of PEI, the longer of curing time. Furthermore, the addition of PEI decreases isothermal conversion shown in Fig. 1(b). This could be attributed to two effects: the dilution effect and the early vitrification in the PEI system caused by the high T_g of the PEI. The former decreases the content of hardener in epoxy-rich phase, and the latter increases the viscosity of the blend and prevents molecules diffusing. Fig. 2 shows that increase of curing temperature improves the curing rate and conversion.

From the DSC result we can also see that the conversion grows quickly with time because of chain growth reaction. It means all the blends have fast curing rate and this shorten the time available for phase separation, which might be shorter than the characteristic relaxation time of chain disentanglement, thus influences the viscoelastic phase separation prominently.

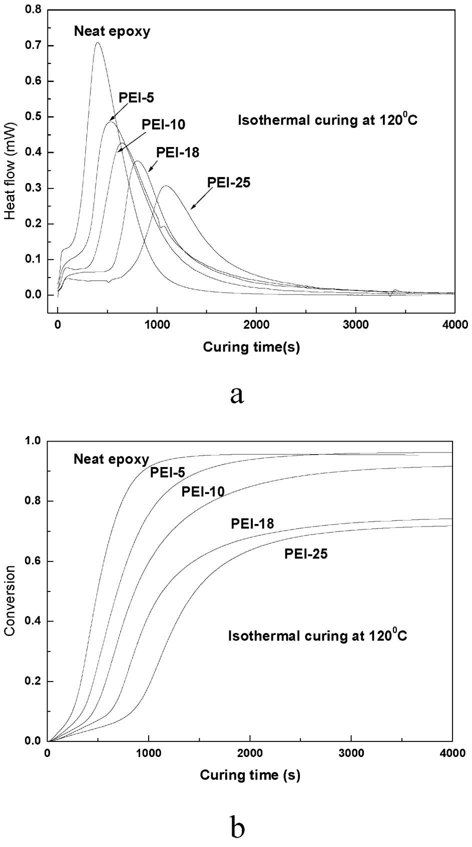


Fig. 1. Isothermal curing DSC curves of neat epoxy and modified systems with C_{11}Z-CNS at 120 °C. (a) Heat flow verse curing time; (b) conversion verse curing time.

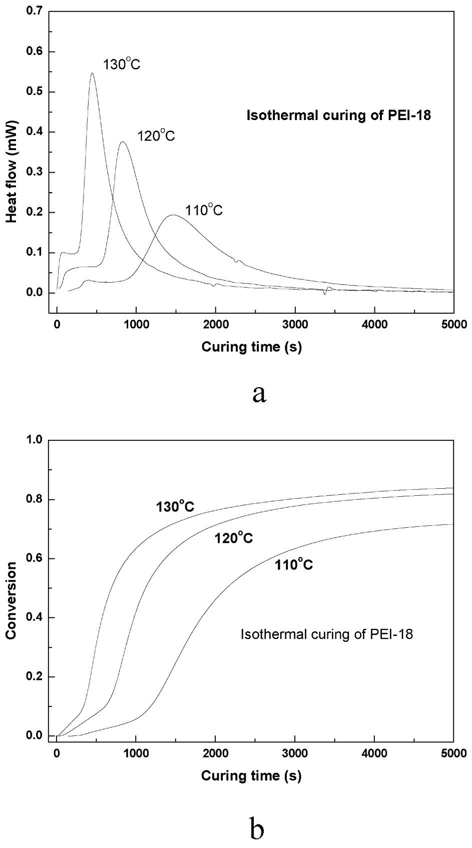


Fig. 2. Isothermal curing DSC curves of PEI-18. (a) Heat flow verse curing time; (b) conversion verse curing time.

3.2. Phase structures of cured blends

The SEM results shown in Fig. 3, at all curing temperature, PEI-5 has a homogenous structure. PEI-10 shows also a homogenous structure at 130 °C, however, forms sponge-like phase structure at lower curing temperature (110, 120 °C), in which uniform epoxy-rich globules with 0.2–0.5 μm diameter dispersed in the membrane-like PEI-rich phase. For PEI-18 and PEI-25, similar sponge-like phase structures were also observed, the diameter of epoxy-rich globules decreases with the increase of PEI concentration. Compared with other systems [10–12] the domain size of the present system is much smaller. This could be attributed to the strong viscoelastic effects and we will discuss in details later.

Table 2 shows T_gs of neat epoxy and modified systems after isothermal curing and post curing, respectively. For modified systems, both PEI-5 at all temperatures and PEI-10 cured at 130 °C show only one T_g, while others have two T_gs. The results indicate that PEI-5 and PEI-10 cured at 130 °C are homogenous but the others have two phases, which were proved by the SEM results. At same isothermal curing temperature, T_gs of both epoxy-rich phase and PEI-rich phase decrease with the increase of PEI concentration owing to the lowering the curing conversion of modified systems. But after post curing, all modified systems with sponge-like morphologies show about the same level of T_g. The result suggests that curing temperatures could control the phase structure, however, higher T_g could still be obtained by post curing for all blends.

Table 2
T_gs of isothermal cured and post cured epoxy and blends

Cure temperature	T_g	Neat epoxy	PEI-5	PEI-10	PEI-18	PEI-25
110 °C	T_{g1}	101	113	91	83	80
	T_{g2}			179	178	175
Post cured	T_{g1}	142	155	148	147	150
	T_{g2}			201	202	199
120 °C	T_{g1}	114	125	106	99	95
	T_{g2}			178	177	175
Post cured	T_{g1}	146	154	149	148	147
	T_{g2}			203	201	200
130 °C	T_{g1}	111	123	126	93	90
	T_{g2}				159	154
Post cured	T_{g1}	141	154	162	149	146
	T_{g2}				204	197

3.3. Rheological characterization during isothermal curing

The study of the rheological behavior provides information of the phase separation time and chain mobility of modified systems (Fig. 4). At the early stage of curing

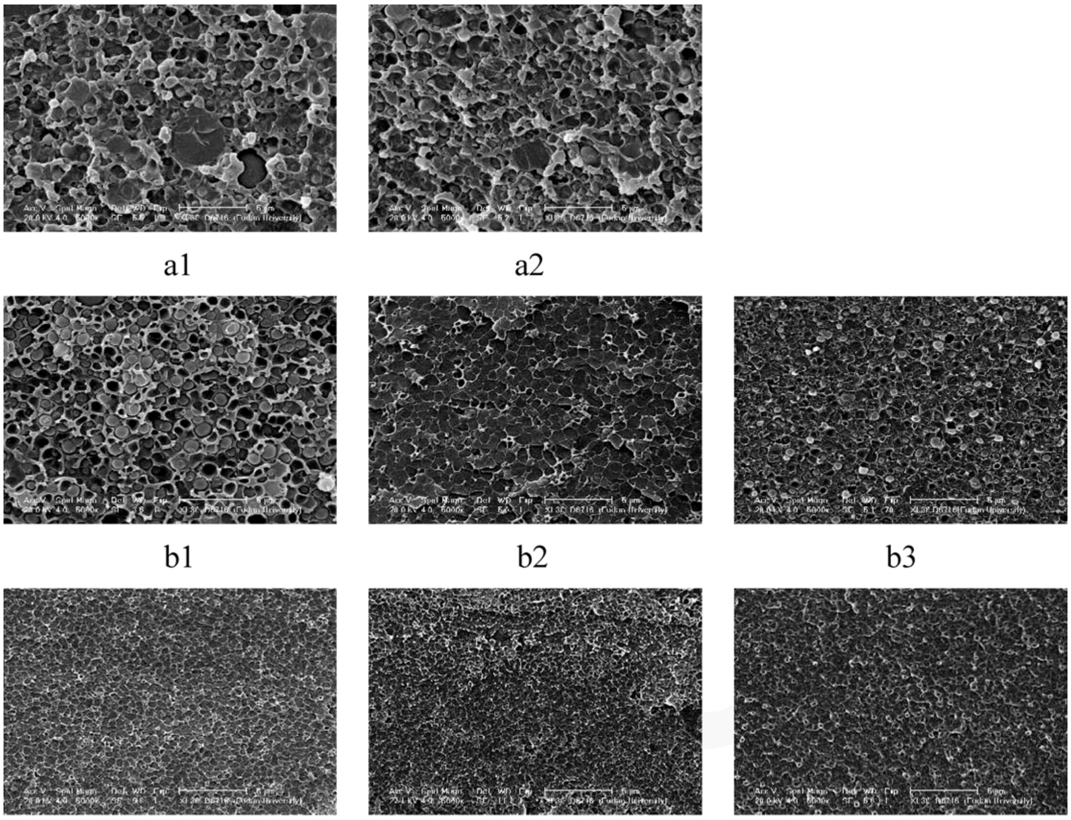

a1 a2
b1 b2 b3
c1 c2 c3

Fig. 3. Scanning electron micrographs of blends after curing 2 h at different temperatures. (a1) PEI-10 110 °C; (a2) PEI-10 120 °C; (b1) PEI-18 110 °C; (b2) PEI-18 120 °C; (b3) PEI-18 130 °C; (c1) PEI-25 110 °C; (c2) PEI-25 120 °C; (c3) PEI-25 130 °C.

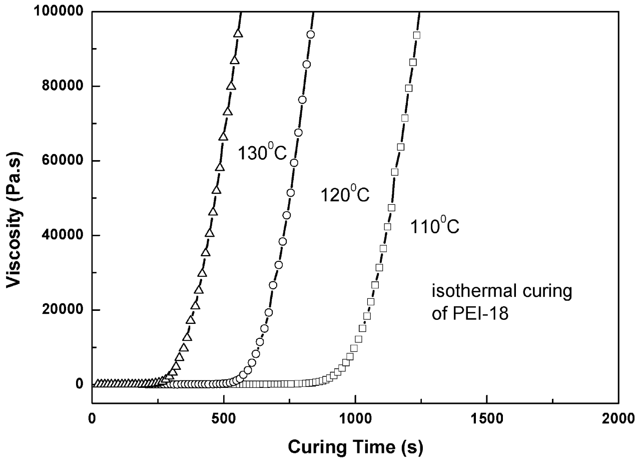


Fig. 4. Rheological behavior of PEI-18 at different temperatures.

reaction, the blends behave like viscoelastic liquid and have low viscosity (< 100 Pa s); after that, the viscosity grows abruptly at cure conversion of about 6–8% due to the chain growth reaction and the time interval between viscosity jumping and gelation is only about a 100 s. However, phase decomposition occurs just after the chain growth polymerization of epoxy resin, as shown in the result of morphology evolution study later. Thus, it indicates that the time available for phase separation is quite short since the holistic morphology could be frozen quickly by the network formation of epoxy matrix though the phase separation may be still in progress after gelation.

The relaxation time for a molecule in a viscous medium is directly proportional to the viscosity according to Debye

$$\tau = \frac{4\pi\alpha^3\eta}{kT}$$

where η is the viscosity of the medium, α is the molecular radius, k is Boltzmann's constant, and T is the absolute temperature. Based on this expression and rheological result, the characteristic relaxation time of chain disentanglement and viscosity increase rapidly at the conversion of about 6–8%. It means that in the early stage of phase separation the characteristic relaxation time of chain disentanglement is long and the diffusion is hard. As a result the morphology would not change apparently from the early stage of phase separation to the end.

3.4. Morphology evolution of phase separation

The chain-growth polymerization initiated by imidazole results in sponge-like structures with the minority volume fraction phase (PEI) as matrix, and similar results were also observed in other polymerization-induced phase separation systems with viscoelastic effects [20]. Viscoelastic effects coming from chain entanglements have so far believed to be important only in the very early stage where the phase separation time is shorter than the characteristic relaxation time representing the disentanglement time of a chain [17].

To get a better understand of phase separation mechanism, SR-SAXS and TEM were also used to study the early stage of phase separation in PEI-18 cured at 110 °C. Fig. 5 depicts a typical time evolution of scattered intensity versus scattering wave number (q), where q is defined as

$$q = (4\pi/\lambda)\sin\theta/2$$

where θ and λ are the scattering angle and the wavelength, respectively. Initially, a scattering maximum appeared in a large q_m at 900 s, that indicates phase separation of this system has occurred and the time is consistent with the beginning of propagation reaction based on DSC and rheology results (Figs. 2(a) and 4). Subsequently, the intensity of the scattering maximum (I_m) increased and the scattering maximum (q_m) decreased with time, which implies a typical SD mechanism of phase separation. From the equation of $\Lambda_m \cong 2\pi/q_m$, the characteristic length of this system cured from 900 to 2400 s is calculated to be 42–49 nm.

Fig. 6 is the TEM graphs of PEI-18 cured at 110 °C for different curing times. As one can see, a sponge-like phase structure formed from the very beginning of the phase separation, and the epoxy-rich particles grew from about 75 to 100 nm in diameter with time. The TEM results correspond well with results of SR-SAXS.

Two main factors affect the phase separation process, namely, strong dynamic asymmetry between PEI-rich and epoxy-rich and early gelation freezing phase structure at early stage of phase separation. Because the viscosity of the epoxy-rich medium is quite low whereas the PEI viscosity is too high to measure at experimental temperatures that are far below the glass transition temperature of PEI, strong dynamic asymmetry forms between PEI-rich and epoxy-rich. The phase structure was first strongly affected by the dynamic asymmetry in early stage and then frozen by the gelation. Since PEI-5 has the fastest curing rate than other

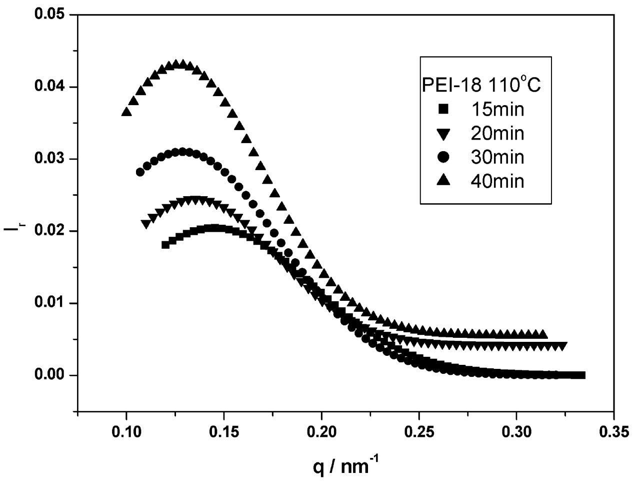


Fig. 5. Time evolution of scattering profiles for PEI-18 cured at 110 °C.

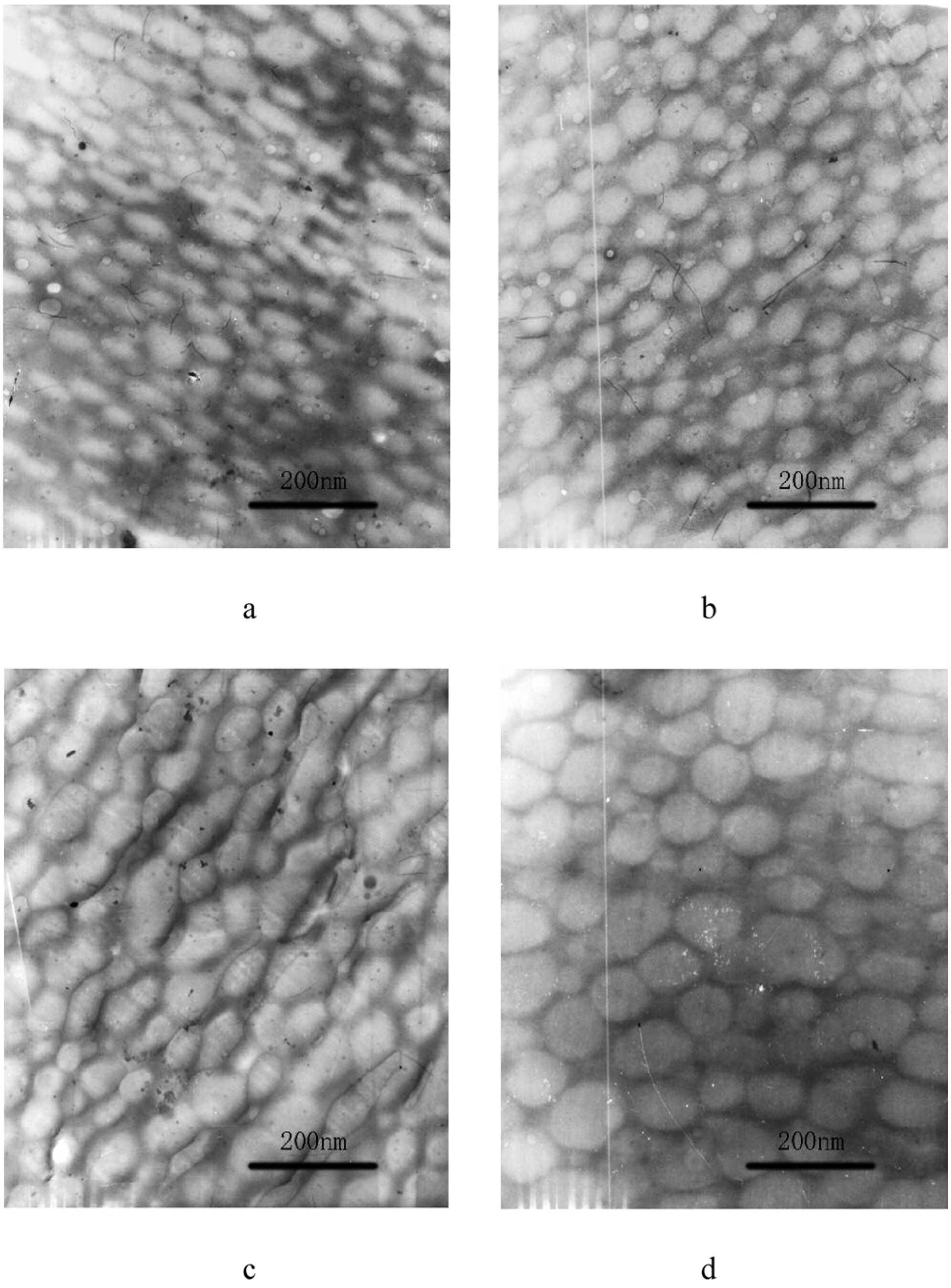


Fig. 6. Transmission electron micrographs of PEI-18 cured at 110 °C for different curing times. (a) 15 min; (b) 20 min; (c) 30 min; (d) 40 min.

three modified systems, i.e. deeper quench depth and early gelation, phase separation was hindered and homogenous structure was achieved because of the diffusion of epoxy molecules being prevented by the network formation of epoxy matrix. For PEI-10 cured at 130 °C, the better solubility at high temperature and faster curing rate shortens the time available for phase separation; as a result, PEI molecules are frozen in the epoxy network. While the lower curing rate of PEI-18 and PEI-25 extends the phase separation time but enhanced the characteristic relaxation time of chain disentanglement due to the increase of PEI volume fraction, as a result, sponge-like phase structure is formed.

4. Conclusions

PEI continuous phase structure can be achieved at low PEI fraction in the PEI modified epoxy systems cured with imidazole due to strong viscoelastic effect and early vitrification. The addition of PEI does not change the two steps curing mechanism, while curing rate and conversion decrease with the increase of the content of PEI. The chain growth polymerization of these systems caused an early gelation (conversion $<10\%$) and frozen morphologies at relatively early stage of phase separation. Morphology evolution of phase separation suggests that the formation of sponge-like phase structure could be attributed to the strong viscoelastic effects in the early stage of viscoelastic phase separation.

Acknowledgements

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