

Polyetherimide-Modified Bismaleimide Resins. II. Effect of Polyetherimide Content

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ABSTRACT: A novel polyetherimide was prepared and used to improve the toughness of bismaleimide resin composed of bis(4-maleimidediphenyl) methane and O,O'-diallyl bisphenol A. The morphologies of the modified resins change from spherical particles to an inverted phase structure, depending on the modifier's content based on the scanning electronic microscopy results. Dynamic mechanical analysis is also used to characterize morphologies of the modified resins. The phase-separation process of the modified system is traced by time-resolved light scattering. The change in the light-scattering profile with curing time showed that the phase separation mechanism depended on the modifier concentration. Phase separation took place via the spinodal decomposition mechanism in the PEI 15-phr- and 20-phr-modified system. The fracture energy (G_{IC}) increased with PEI content in the modified system; in the PEI 15-phr-modified system, the G_{IC} value was three times greater than that of the unmodified BMI resin. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 350–358, 2001

Key words: polyetherimide; bismaleimide resin; morphology; fracture energy; phase separation

INTRODUCTION

In recent years bismaleimide (BMI) resins as high-performance thermosetting resins have been widely used as matrices for advanced composites. They possess many desirable properties, such as high tensile strength and modulus, excellent chemical and corrosion resistance, and hot/wet performance.^{1–3} However, the BMI resins are ex-

tremely brittle because of their highly crosslinked structure. Various attempts have been made to improve the impact and fracture toughness of BMI resins.^{1,4–9} One excellent modification is the use of a diallyl compound to copolymerize with BMI resins.² Yet its fracture toughness is not sufficient for use as a high-performance composite matrix.

In order to enhance the fracture toughness of the BMI resins, a good toughening approach is to use thermoplastics to serve as a toughness modifier for the thermosetting networks.^{10–19} The thermoplastic toughened systems display com-

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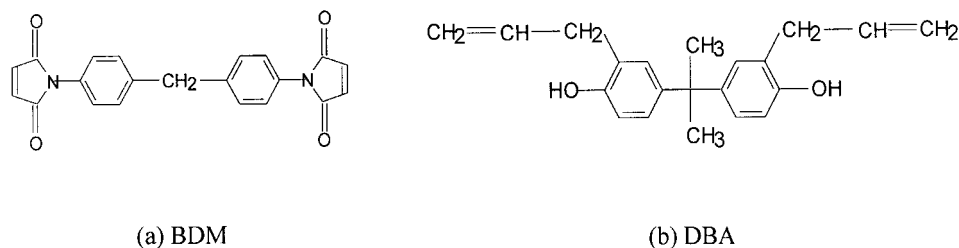


Figure 1 (a) Structure for bis(4-maleimidodiphenyl) methane. (b) Structure for O,O'-diallyl bisphenol A.

plex morphologies based on a number of the variables such as modifier content, molecular weight of the modifier, interactions between the modifier and the thermoset, reactive endgroups, viscosity, and even the method of mixing and the presence of fillers or fibers.¹⁹ The phase structure of the modified resin has a significant effect on fracture toughness. Thus, morphological control is very important in optimizing fracture toughness. Iijima^{11–13} carried out a series of modification research on the BMI resin. The morphologies of the modified resins depended on the modifier structure, molecular weight, and content. The most effective improvement of properties for the modified resins could be attained because of the co-continuous structure. Recker et al.¹⁸ reported the effect of weight percent (wt %) loading of modifier on the fracture toughness. At a 25% loading, they obtained co-continuous morphology, which achieved the optimum fracture toughness.

In a previous article,²⁰ we discuss the effect of polyetherimide (PEI) backbone chemistry on the modified systems. The degree of phase separation and the phase structure are important factors in the toughness of the modified system. The present article examines the effect of the modifier concentration on the toughening of PEI-modified BMI resins. In contrast to the numerous reports on phase-separation dynamics in modified epoxy systems, phase-separation studies on the toughened BMI resins were scarce. This article discusses the phase-separation mechanism in modified BMI systems.

EXPERIMENTAL

The BMI resin includes two components. Component A is bis(4-maleimidodiphenyl) methane (BDM), supplied by Hubei Fenguang Chemical Factory. Component B is O,O'-diallyl bisphenol A (DBA) supplied by Jianyou Electric Mechanical Material Factory (Fig. 1). PEI is synthesized in one step from bisphenol A dianhydride (BISA-DA), provided by Shanghai Institute of Synthetic Resin, and 4,4'-(1,3-phenylene-bis(isopropylidene) bisaniline (BISM), provided by Shanghai Institute of Synthetic Resin, in *m*-cresol at 200°C for 6 h.²⁰ The obtained PEI is characterized by GPC with a light-scattering detector of $M_n = 19,800$. The glass-transition temperature of PEI is 184°C, characterized by SETARAM differential scanning calorimetry (DSC) instrument at a heating rate of 10°C/min. The chemical structure of PEI is depicted in Figure 2.

The modified BMI resins containing 0–20-phr (per 100 BDM) PEI were prepared by the following procedure. PEI was dissolved in DBA by heating at 160°C. The mixture was then cooled to 150°C, and BDM was added to the mixture. The ratio of DBA to BDM was kept at 43:57 parts by weight (0.85:1 mole ratio). It was stirred continuously during the dissolving process. The resulting clear mixture was degassed *in vacuo* and poured into a mold, preheated at 150°C, to obtain a 3-mm-thick plaque. The curing cycle was 160°C/2 h + 185°C/2 h + 230°C/2 h.

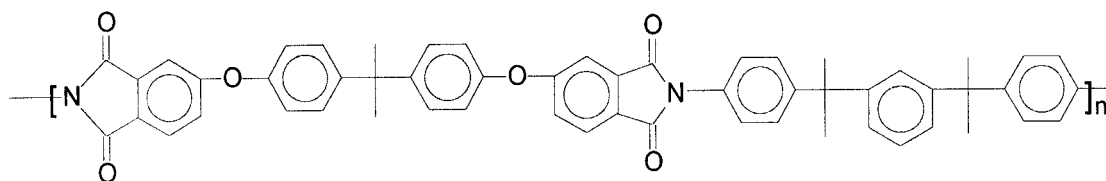


Figure 2 Scheme of polyetherimide (PEI) structure.

The phase-separation process during the curing reaction was observed at real time and *in situ* on self-made time-resolved light scattering (TRLS) with a controllable hot chamber. The TRLS technique has been described elsewhere.²¹ The change of the light-scattering profiles was recorded at appropriate time intervals during isothermal curing, i.e., 185°C. The blend of BMI resin with PEI for TRLS observation was prepared by solvent-casting film in CH₂Cl₂. The thin film of the blend was degassed for 2 days at room temperature to remove the solvent.

The fracture surface morphology of the modified resin was observed by scanning electron microscopy (SEM) (Hitachi S-520). The samples were fractured in liquid nitrogen.

A dynamic mechanical analysis was performed in the dual-cantilever bending mode between 50°C and 350°C, using a Netzsch DMA 242 apparatus at a heat rate of 3°C/min and a frequency of 10 Hz.

Fracture toughness was measured using the double torsion (DT) method at room temperature in the compressive mode with a cross-head speed of 0.5 mm/min, according to ASTM E-399. The fracture energy G_{IC} was calculated from

$$G_{IC} = K_{IC}^2 \times \frac{1 - \nu^2}{E}$$

where E is Young's modulus measured at the same temperature in which the double torsion test was performed, and ν is Poisson's ration, assumed to be 0.36 and 0.35, corresponding to the unmodified BMI resin and PEI-modified system.

RESULTS AND DISCUSSION

Morphology

The fracture surface of the unmodified BMI resin was demonstrated in a previous article.²⁰ The unmodified resin has only one phase, and the fracture surface is smooth and featureless. Inclusion of PEI leads to phase separation. The morphologies of the modified resins change drastically depending on the PEI content. In the 5-phr PEI-modified BMI resin [Fig. 3(a)], the PEI-rich phase (gray white part, call it, β phase) form small spherical domains randomly dispersed in BMI matrix (dark gray part, call it, α phase). When using 10-phr PEI, the modified system [Fig. 3(b)] shows a mixed structure, also called a "sand-

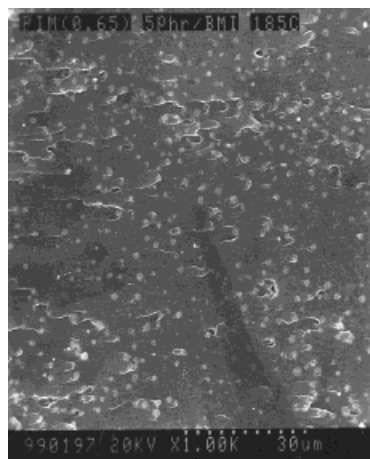
wich" structure. Both the BMI-rich phase and the PEI-rich phase form the continuous phase on a large scale, $\sim 150 \mu\text{m}$. In the BMI-rich phase [Fig. 3(c)], PEI forms small spherical domains dispersed in BMI matrix, as in the PEI 5-phr system, but the distance between the particles is increased. In the PEI-rich phase [Fig. 3(d)], the phase inversion has occurred. The BMI resins form spherical particles with PEI wrapped around them. When adding 15-phr PEI to the BMI resin, the morphology of the modified system is complete phase inversion [Fig. 3(e)]. The sizes of the BMI spherical particles are uniformly $6 \mu\text{m}$. The PEI 20-phr-modified system is also complete phase inversion [Fig. 3(f)], but the BMI spherical particles are smaller than those of the PEI 15-phr-modified system, $\sim 2 \mu\text{m}$.

Mechanical Properties of Modified BMI Resins

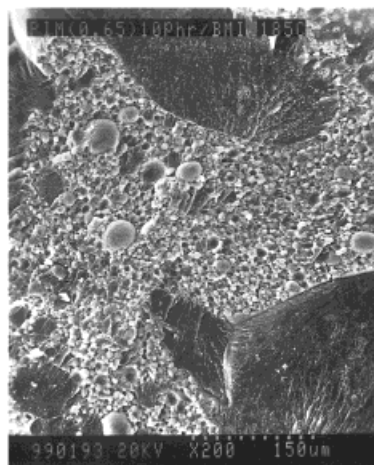
Table I lists the PEI content dependence of mechanical properties for the modified BMI resin. With increased PEI content, the fracture energy (G_{IC}) of the modified resin shows a considerable increase. For example, inclusion of 15-phr PEI results in a 300% increase in G_{IC} . The flexural moduli for the modified resins are slightly decreased. As considered with the SEM results, the fracture energy shows a strong relationship between structure and toughness. The toughening effect can be significantly improved in the modified system with the phase-inverted structure. By contrast, the size of BMI particles in the phase-inverted structure may affect the toughening effect with reference to the toughening effects of the PEI 15-phr system and PEI 20-phr system. Hourston and Lane²² reported the same results in the PEI Ultem-1000® modified trifunctional epoxy resin. The epoxy domains of the phase-inversion morphology gradually decrease with the increasing of PEI content and there is no further improvement in fracture properties.

Dynamic Mechanical Analysis of Modified BMI Resins

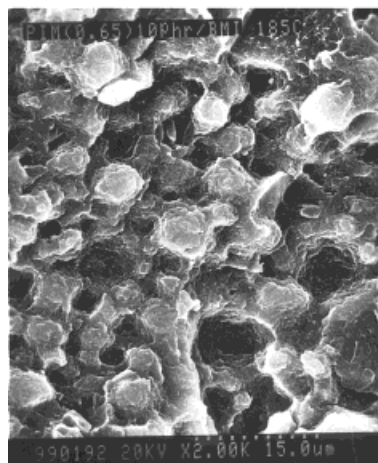
Figure 4(a) and (b) present dynamic mechanical data for the unmodified BMI resin and the pure PEI. The unmodified BMI resin and pure PEI give a single $\tan\delta$ peak at 293°C and 195°C, respectively. The effects of PEI content on the dynamic mechanical behavior of the modified resin are shown in Figure 5(a,b). With regard to the PEI-modified BMI system, two relaxation peaks can



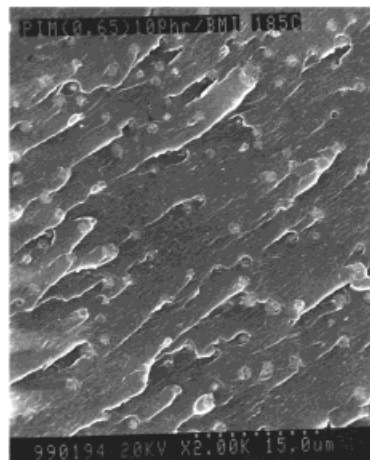
a) PEI 5phr system



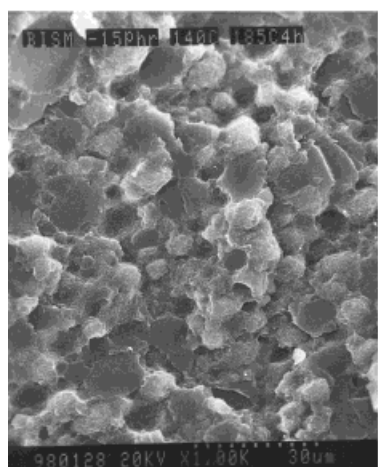
b) PEI 10phr system



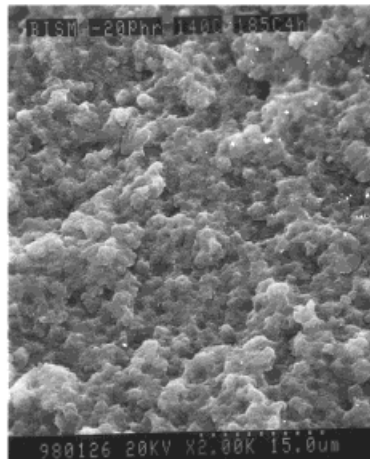
c) PEI rich phase of PEI 10phr system



d) BMI rich phase of PEI 10phr system



e) PEI 15phr system



f) PEI 20phr system

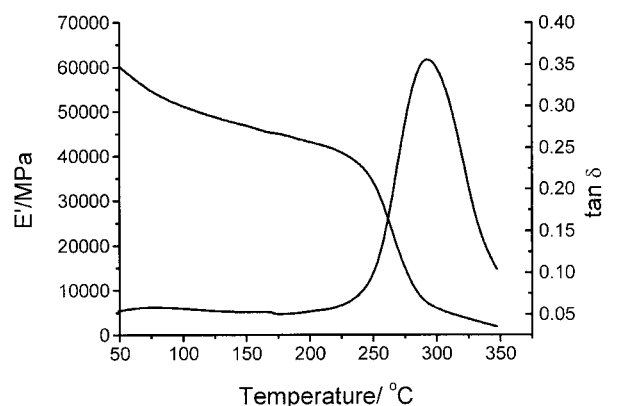
Figure 3 Scanning electron micrographs of fracture surfaces for the cured bismaleimide (BMI) resins, modified with polyetherimides (PEIs). (a) PEI 5-phr system; (b) PEI 10-phr system; (c) PEI-rich phase of PEI 10-phr system; (d) BMI-rich phase of PEI 10-phr system; (e) PEI 15-phr system; (f) PEI 20-phr system.

Table I Mechanical Properties and Fracture Toughness of the Modified Bismaleimide Resins

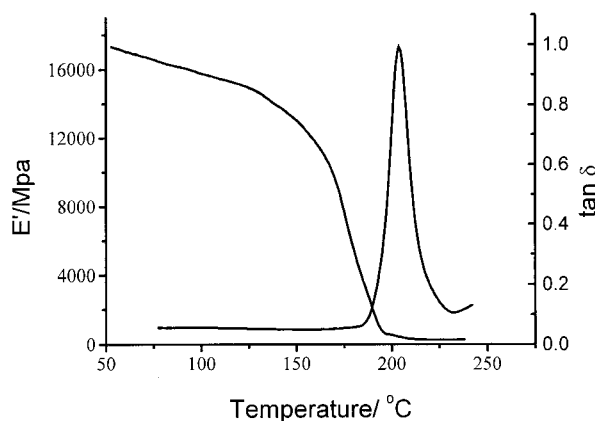
Sample	E (GPa)	K_{IC} (MPa m ^{1/2})	G_{IC} (J/m ²)
Unmodified BMI resin	3.94	0.970	210.0
PIM 5-phr modified	3.79	1.039	280.5
PIM 10-phr modified	3.63	1.260	386.8
PIM 15-phr modified	3.57	1.638	667.5
PIM 20-phr modified	3.55	1.560	602.0

BMI, bismaleimide; PIM, BISA-DA/BISM.

be clearly observed, which clearly indicates that phase separation has occurred during the curing process, in accordance with the SEM results. As

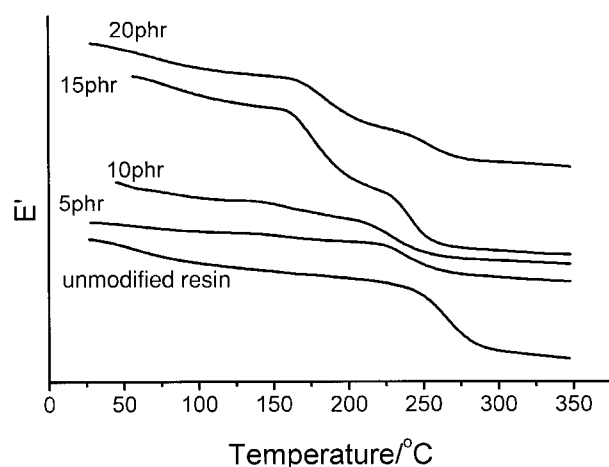


(a)

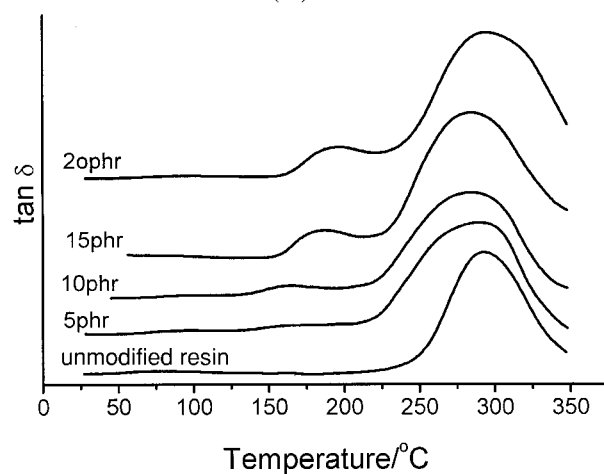


(b)

Figure 4 Dynamic mechanical spectra for (a) unmodified bismaleimide (BMI) resin, and (b) pure polyetherimide (PEI).



(a)



(b)

Figure 5 Dynamic mechanical data for unmodified and different content polyetherimide (PEI)-modified bismaleimide (BMI) resins: the storage moduli E' vs. temperature (a) and the loss factor $\tan\delta$ vs. temperature (b).

shown in Figure 5(a), the onset of decline in the storage modulus is controlled by the glass-transition temperature of the modifier.¹⁰ An additional important finding is that the degree of decrease might be associated with phase structure. In the PEI 5-phr-modified system, the decrease of the storage modulus within the range of the glass-transition temperature of PEI is slight because of the dispersed phase structure. In the case of the PEI 10-phr-modified system, the morphology of the modified resin is the “sandwich” structure. Although the PEI-rich phase becomes flexible, the continuous BMI-rich phase still can support the modulus of the materials within the range of the glass-transition temperature of PEI. However, in

Table II Peak Positions (T_α , T_β), Heights (H_α , H_β), and Ratio of Heights (H_β/H_α) for PEI-Modified System

Sample	Morphology	PIM-Rich Phase (β Phase)		BMI-Rich Phase (α Phase)		H_β/H_α
		H_β	T_β	H_α	T_α	
Unmodified BMI	—	—	—	0.346	293.2	—
Pure PIM	—	0.992	195	—	—	—
PIM 5-phr modified	Dispersed particles	0.073	—	0.330	289	0.221
PIM 10-phr modified	“Sandwich”	0.072	166	0.305	284	0.236
PIM 15-phr modified	Phase-inverted	0.111	187	0.405	284	0.274
PIM 20-phr modified	Phase-inverted	0.120	197	0.404	294	0.297

PEI, polyetherimide; PIM, BISA-DA/BISM; BMI, bismaleimide.

the PEI 15-phr-modified system, which is the complete phase inverted morphology, the continuous PEI-rich phase enters the rubber state, and the noninterconnect BMI spherical particle cannot support the modulus of the material, when the temperature reaches the glass-transition temperature of PEI. Thus, the modulus of the modified resin decreases sharply within the range of the glass-transition temperature of PEI, as does the PEI 20-phr system. In this respect, it suggests that most of the energy absorption occurs in the modifier. The ductile drawing of the thermoplastic-rich phase is the dominant toughening mechanism in the thermoplastic modified thermosetting resins.^{23,24}

Table II compares the magnitude and position of relaxation peak in modified systems with different PEI content. The magnitude of α -relaxation of PEI gradually increases with increasing of PEI content. The loss peak magnitude of the BMI-rich phase (H_α) does not change significantly with different PEI content. The value of H_β/H_α does not increase significantly, while the morphology changes from dispersed structure to phase inversion. It is different from the result reported by Girard-Reydet et al.,²⁵ in which the ratio of loss peak magnitude of the PEI-rich phase (H_β) to the epoxy-rich phase (H_α) is sensitive to the phase structures.

With the exception of the 20-phr PEI system, the loss peak position of PEI and BMI in PEI-modified systems both shift toward lower temperature in the modified system, and the peak became broader, as compared with the pure PEI and unmodified BMI resin. It is most likely a result of plasticization by the uncured low-molecular-weight monomers.

Phase Separation Observed by Light Scattering

Generally speaking, all the PEI-modified BMI blends were a single-phase system, and no apparent scattering light was detected after the temperature jumped from room temperature to the curing temperature 185°C. With the curing reaction between BDM and DBA, the blend became immiscible after a certain time lag. Phase separation took place, and the scattering light could be detected. There are different light-scattering profiles in the modified systems with different PEI content, indicating that they display different phase separation behaviors (Figs. 6–9).

The induced times of four PEI-modified BMI resins are 760s, 260s, 600s, and 1080s, respectively. The PEI 10-phr system has the shortest induced time. Because the phase diagram of the PEI/BDM/DBA ternary system is currently difficult to obtain, it would be arbitrary to make the assumption that the PEI 10-phr system is near the critical composition, whether it of the UCST or the LCST type phase diagram. Since it has been proved that the cure rate is not effected by different PEI content-modified BMI resin using the DSC method,²⁶ the PEI 10-phr system would be the first to enter the two-phase region during the cure reaction. Phase separation in all the other PEI content systems will begin later than that of the PEI 10-phr system.

The ring pattern appearing in the PEI 15-phr and 20-phr-modified system indicates the spinodal decomposition mechanism. However, the PEI 10-phr-modified system shows the interesting phase separation process: a ring pattern occurs after a certain time lag, becoming brighter, and gradually disappearing, and finally display-

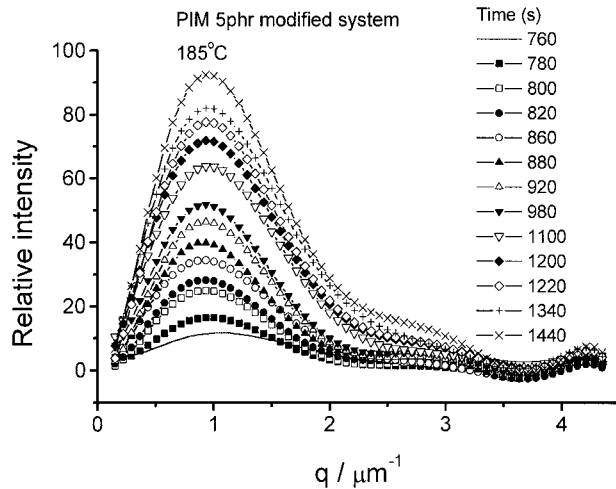


Figure 6 Time-resolved light-scattering profiles for the polyetherimide (PEI) 5-phr-modified bismaleimide (BMI) resin at 185°C.

ing the dispersed scattering light. This process is recorded in the time-resolved light-scattering profiles. After reaching the maximum [Fig. 7(a)], the intensity of scattering light begins to decrease gradually to zero [Fig. 7(b)]. However, the scattering light reappears and attains another maximum [Fig. 7(c)]. Such behaviors would suggest a new mechanism of phase separation. Detailed investigation of this phenomenon is continues.

The phenomenon of the time independence of q_m has been observed in PEI 5-phr, 15-phr, and 20-phr-modified systems (Figs. 6, 8, 9). In the early stage of phase separation, q_m value is determined by the thermodynamic driving force characterized by the quench depth. During the curing reaction, the quench depth increases continuously, which should cause a shift to a larger q_m . On the contrary, the phase-separated structure should be coarsened due to the interfacial instability, producing smaller q_m . In these PEI-modified BMI systems, the time independence of q_m may be due to a balance of both thermodynamic driving forces, namely the growth of the unstable concentration fluctuations is suppressed by an increase of the quench depth.²⁷ In the computer simulations using the Cahn–Hilliard nonlinear diffusion equation, it is found that the suitable quench rate can explain well the time independence of scatter vector q_m .²⁸

As compared with the thermal-induced phase separation (TIPS), studies on polymerization-induced phase separation (PIPS) remain limited, with many questions to be solved:

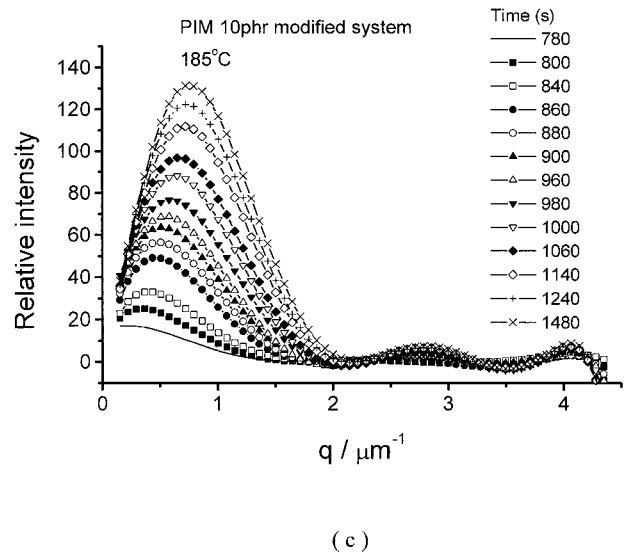
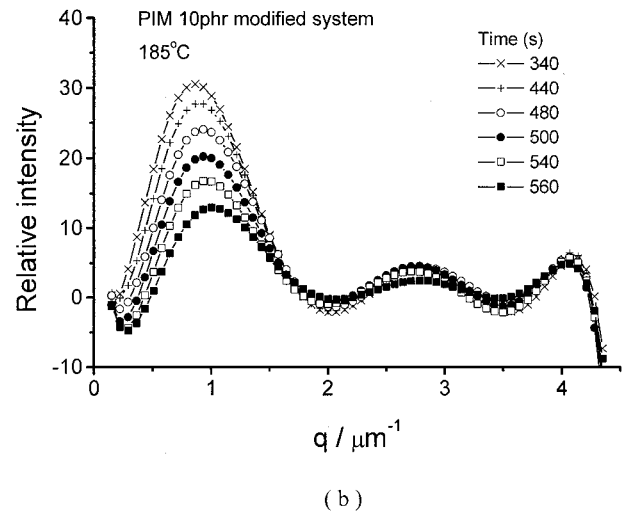
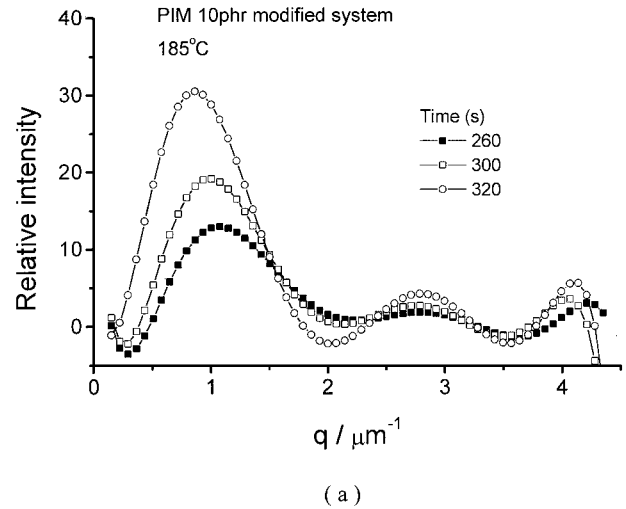


Figure 7 Time-resolved light-scattering profiles for the polyetherimide (PEI) 10-phr-modified bismaleimide (BMI) resin at 185°C.

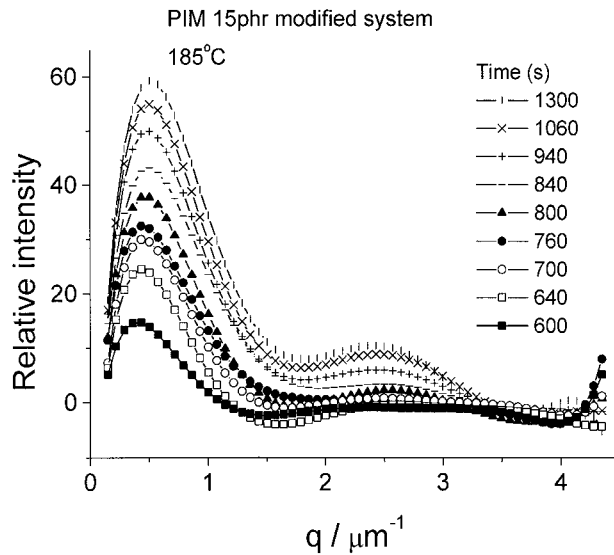


Figure 8 Time-resolved light-scattering profiles for the polyetherimide (PEI) 15-phr-modified bismaleimide (BMI) resin at 185°C.

1. How can we characterize the early stage of PIPS?
2. How can we modify the linearized Cahn–Hilliard theory on the early stage of phase separation, which is used to prove the spinodal decomposition nature in the TIPS system?
3. How can we explain the formation of “sandwich” morphology (Fig.10)?

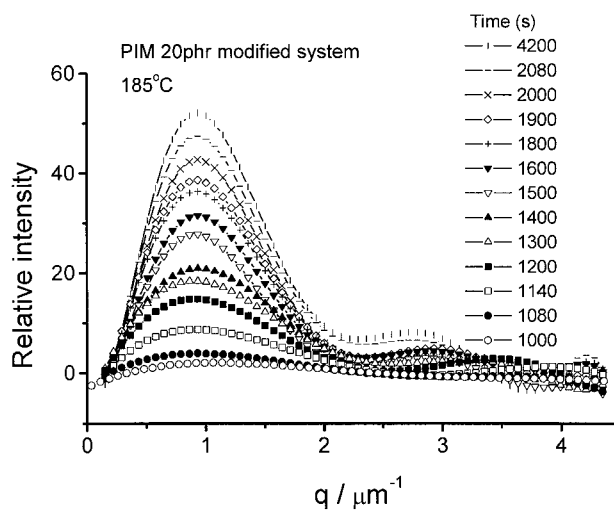


Figure 9 Time-resolved light-scattering profiles for the polyetherimide (PEI) 20-phr-modified bismaleimide (BMI) resin at 185°C.

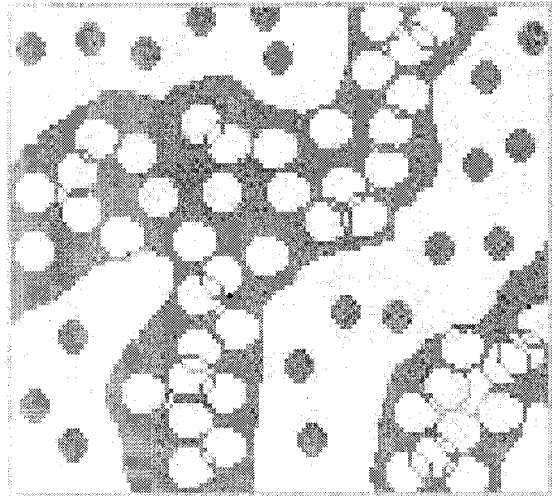


Figure 10 Schematic graph of “sandwich” morphology (the white part is thermosetting resin-rich phase; the black part is thermoplastic-rich phase).

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