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### POLYESTERIMIDE-MODIFIED BISMALEIMIDE RESINS. I. EFFECT OF POLYESTERIMIDE CONTENT

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## POLYESTERIMIDE-MODIFIED BISMALIMIDE RESINS. I. EFFECT OF POLYESTERIMIDE CONTENT

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### ABSTRACT

A novel polyesterimide (PEsI-M) was used to improve toughness of bismaleimide (BMI) resin composed of bis(4-maleimidediphenyl) methane (BDM) and O,O'-diallyl bisphenol A (DBA). Morphologies of modified resins changed from spherical particles to inverted phase structures, depending on PEsI-M's content based on the observation of scanning electronic microscopy (SEM). PEsI-M was an effective morphology modifier so that loading of 12 pbw resulted in a diverted phase structure. Dynamic mechanical analysis (DMA), rheometrics mechanical spectroscopy (RMS) and differential scanning calorimetry (DSC) were respectively used to investigate the dynamic mechanical behavior, and the gelation time and the curing extent of unmodified and modified BMI resins. The fairly uniform morphology in 15 pbw PEsI-M modified system cured at 180°C suggests that the phase separation might take place via a spinodal decomposition mechanism. The fracture energy ( $G_{IC}$ ) increased with the increase of PEsI-M content in the modified system.  $G_{IC}$  of 15 pbw PEsI-M modified system was 0.63 times larger than that of the unmodified BMI resin.

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*Key Words:* Polyesterimide; Bismaleimide resins; Phase separation; Morphology; Fracture energy

## INTRODUCTION

In recent years, BMI resins as high-performance thermosetting materials have been widely used as matrices for advanced composites. They possess many desirable properties, such as high tensile strength and modulus, excellent chemical resistance, corrosion resistance and heat resistance.<sup>[1–3]</sup> However, BMI resins are extremely brittle because of highly crosslinked structure. Many techniques have been used to improve the impact and fracture toughness of BMI resins.<sup>[1,4–9]</sup> A traditional modification is to employ a daillyl compound to co-polymerize with BMI resins.<sup>[2]</sup> However, its fracture toughness is not sufficient for a high-performance composite matrix.

In order to enhance the fracture toughness of the BMI resins, a good toughening means is to use thermoplastic to serve as a modifier among the thermosetting networks.<sup>[10–19]</sup> The thermoplastic-toughened system can produce complex morphologies depending on a number of variables such as modifier content, modifier molecular weight, interaction between modifier and thermoset, reactive end-group, blend viscosity, and even mixing method and interfused fillers or fibers.<sup>[19]</sup> The phase structure of the modified resin has a significant effect on fracture toughness. So, morphological control is very important for obtaining good fracture toughness. Iijima carried out a series of modification research on BMI resin and confirmed that morphologies of modified resins depended on the modifier structure, molecular weight, and content.<sup>[11–13]</sup> The effective improvement in the properties of modified resins could be seen when a co-continuous structure was achieved. Recker et al. reported the effect of the modifier content on the fracture toughness. When 25 pbw modifier was loaded into the modified system, a co-continuous morphology was obtained and the fracture toughness of the system was improved obviously.

In our previous research,<sup>[20–21]</sup> the co-continuous phase structure was obtained and the fracture toughness was improved, apparently when 15 pbw polyetherimide (PEtI) was used as a modifier in BMI resin. Since polyesterimides (PEsI) have higher  $T_g$  and higher modulus than those of polyetherimide (PEtI), it is an attempt to use organo-soluble polyesterimides as tougheners to modify BMI resin in order to further improve the thermal stability and flexural modulus of BMI resins. Recently, a novel polyesterimide was synthesized and used to modify BMI resin in our laboratory. This article will discuss the effects of PEsI-M contents on morphologies, also the phase-separating behavior and the mechanical properties of the modified BMI resin.

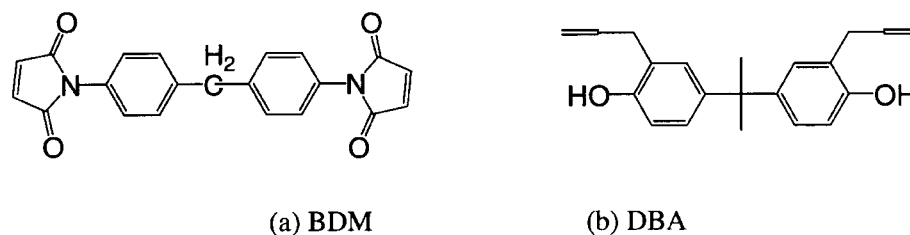
## EXPERIMENTAL

The BMI resin included two components. Component A was bis(4-maleimidodiphenyl) methane (BDM), purchased from Hubei Fengguang Chemical Factory. Component B was O,O'-diallyl bisphenol A (DBA) produced by Sichuan Jiangyou Insulating Material Factory (Fig. 1).

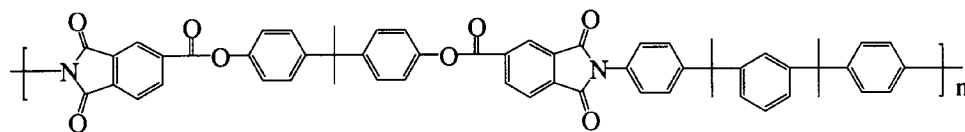
PEsI-M was prepared between 2,2'-bis(4-(3,4-dicarboxyphenoxy)phenyl) propane dianhydride (BTPDA) and 1,3-bis((4,4'-aminophenyl)isopropyl) benzene (BISM) in NMP at room temperature according to a similar synthesis route.<sup>[22]</sup> The  $M_w$  of PEsI-M was measured to be 31,000 g/mol by GPC with a light-scattering detector. Glass-transition temperature ( $T_g$ ) of PEsI-M was 211°C, measured by differential scanning calorimetry (DSC, Setaram 92) at a heating rate of 10°C/min. The chemical structure of PEsI-M is depicted in Fig. 2.

The modified BMI resins containing 5–20 pbw (parts by weight) PEsI-M were prepared by the following procedure. PEsI-M was dissolved in DBA at 150°C, and then BDM was added to the mixture. The ratio of DBA to BDM was kept at 43:57 pbw (0.85:1 mole ratio). The mixture was stirred continuously during the dissolving procedure. A dark-red transparent mixture was obtained and degased in vacuum, and then poured into a mold, preheated at 150°C, to obtain a 3 mm thick sheet for fracture toughness measure. The curing schedule was 160°C for 2 h, 185°C for 2 h and 200°C for 2 h.

The cured samples were fractured in liquid nitrogen and sprayed with a thin layer of gold. The fracture surface of the modified resin was observed by using SEM (Hitachi S-520).



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



**Figure 2.** Scheme of PEsI-M structure.

By using DSC, the curing extent of BMI resin was measured at 180°C. During isothermal reaction, the reaction heat ( $\Delta H_{iso}(t)$ ) was the function of time  $t$ . When the curve of  $\Delta H_{iso}(t)/t$  eventually leveled off, the isothermal reaction was considered to be finished and the area under the curve of  $\Delta H_{iso}(t)/t$  was integrated as the total isothermal reaction heat ( $\Delta H_{iso}$ ). The remain reaction heat ( $\Delta H_{rem}$ ) was measured by scanning the same sample from room temperature to 400°C. The curing extents,  $\alpha(t)$ , of unmodified and modified BMI resins at time  $t$  were calculated from the following equation:

$$\alpha(t) = \frac{\Delta H_{iso}(t)}{\Delta H_{iso} + \Delta H_{rem}}$$

Complex viscosity changes of the unmodified and modified BMI resins during isothermal curing were monitored by Rheometrics mechanical spectroscopy (RMS, Rheometrics Inc. ARES-4A) with two parallel stainless steel plates of 8 mm diameter, and the gap height between parallel plates was set to 0.5 mm. The RMS experiments were performed using a frequency of 1 rad/s and a strain of 1%.

A dynamic mechanical analysis (DMA, Netzsch 242) was used to study the dynamic mechanical behavior of modified BMI resins in a dual-cantilever bending mode between 50°C and 350°C, at a heating rate of 3°C/min and a frequency of 10 Hz.

According to ASTM E-399, fracture toughness ( $K_{IC}$ ) was measured by a double torsion (DT) method at room temperature in a compress mode with a cross-head speed of 0.5 mm/min. The fracture energy ( $G_{IC}$ ) was calculated from following equation:

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

Where  $E$  is Young's modulus measured at the same temperature by a double torsion test, and  $\nu$  is Poisson's ration, assumed to be 0.35 for the unmodified BMI resin and PEI-M modified system.

Tensile lap-shear strengths of polyesterimide-modified blends were measured according to ISO 4857:1995(e). 10% chloroform solutions of the uncured blends were brushed on several testing panels of aluminum. Chloroform was vaporized for 20 min at room temperature. The testing panels were overlapped in pairs, fixed with two steel clips and cured at 160°C for 2 h, at 185°C for 2 h and at 200°C for 3 h. Measurements were carried out with an autograph universal testing machine (Shimadzu, DDS-5000) at a cross-head speed of 5 mm/min.

To evaluate bond strengths of PEI-M modified blends in conjunction with bare aluminum wire substrates, 10% chloroform solutions of uncured

blends were used as impregnating agents. Helical coils, which had a mandrel diameter of 6.3 mm and a length of 75 mm, were immersed into the impregnating agents for 60s, drained for 20 min and then cured at 160°C for 2 hrs., at 185°C for 2 h and at 200°C for 3 h. Bond strengths were measured with an autograph universal testing machine (Shimadzu, DDS-5000) at a cross-head speed of 50 mm/min, according to IEC 1033:1991.

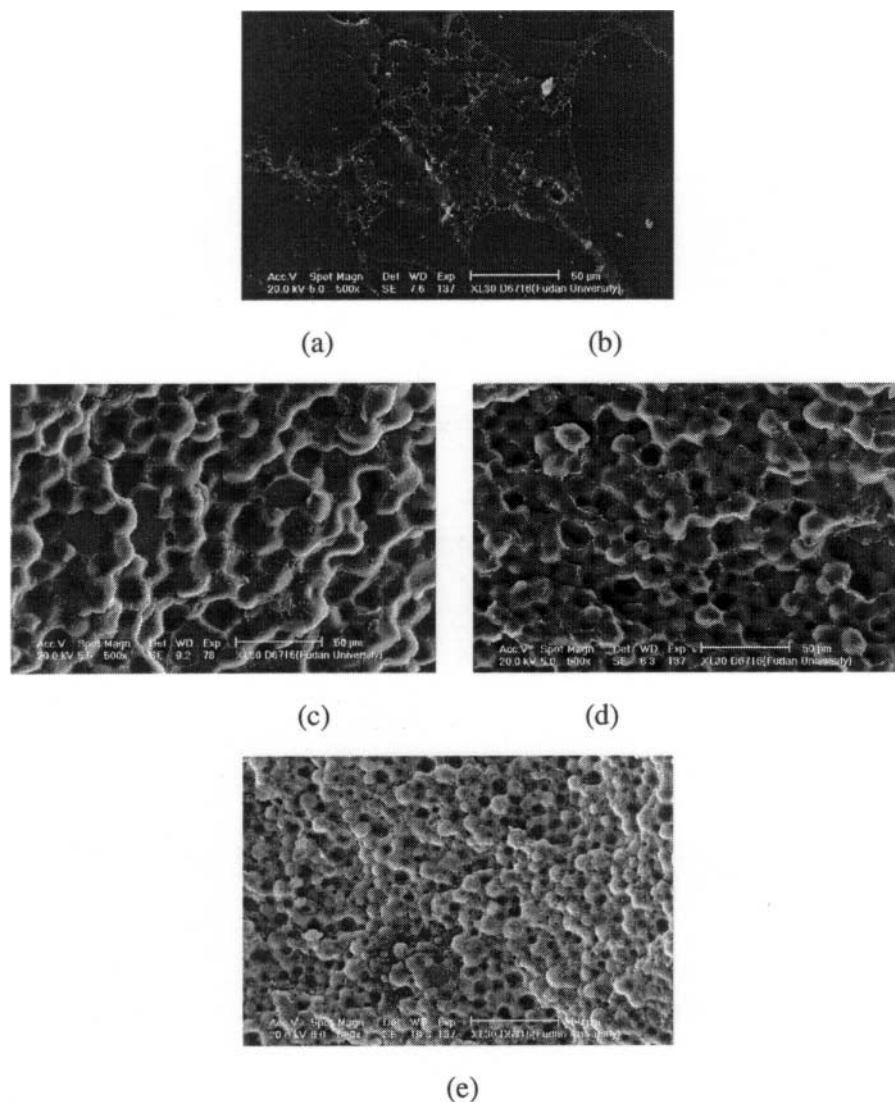
## RESULTS AND DISCUSSION

### Morphologies of Modified BMI Resins

The unmodified resin had only a single-phase structure, and the fracture surface was smooth and featureless.<sup>[20]</sup> Incorporation of PEsi-M into BMI resins led to a phase separation. The morphologies of the modified resins changed drastically depending on the PEsi-M content, Fig. 3(a–e). In the 5 pbw PEsi-M modified BMI resin, the PEsi-M-rich phase formed small spherical domains randomly dispersed in BMI matrix, Fig. 3(a). When 10 pbw PEsi-M being used, the modified system showed a mixed structure, also called a “sandwich” structure, Fig. 3(b). When 12 pbw or much PEsi-M was added to BMI resins, morphologies of modified systems were uniform diverted phase structure, Fig. 3(c–e). BMI-rich phase presented a dispersed phase structure and PEsi-M-rich phase formed a continuous one. With the increase of PEsi-M content from 12 pbw to 20 pbw, the sizes of BMI-rich phase globules decreased approximately from 17  $\mu\text{m}$  to 8  $\mu\text{m}$ . The reason for dwindling of BMI resin globules with the increase of PEsi-M content was that the same parts by weight of BMI resin were assigned to more parts by weight of PEsi-M. An interesting result was that the diverted phase structure was observed for 12 pbw PEsi-M blend. In comparison, the diverted morphology was only gained for the modified BMI of more than 15 pbw Polyetherimide.<sup>[20–21]</sup>

### Curing Extent of Modified System

Figure 4 demonstrated the effect of PEsi-M content on curing extents of the unmodified and modified systems at 180°C. The curing extents of all the systems increased rapidly with time at the early stage of curing and then leveled off at the final stage of curing. In unmodified and 5 pbw PEsi-M modified system, the curing extent leveled off at about 91%. In the case of 10 pbw or 15 pbw PEsi-M, the curing extent respectively leveled off at 78% and 62% due to high blend viscosity. It suggests that the curing time should be prolonged or the curing temperature should be lifted for a complete cure.



**Figure 3.** Scanning electron micrographs of fracture surfaces for the cured BMI resins modified with various contents of PEI-M. (a) 5 pbw PEI-M modified BMI resin; (b) 10 pbw PEI-M modified BMI resin; (c) 12 pbw PEI-M modified BMI resin; (d) 15 pbw PEI-M modified BMI resin; (e) 20 pbw PEI-M modified BMI resin.

### Complex Viscosity of Modified BMI Resin

By using RMS, changes in complex viscosity of the modified BMI resins were monitored during isothermal curing at 180°C. As shown in Fig. 5, complex viscosities of the BMI resins modified with various content of PEI-M increased slowly at the early stages of polymerization. After a certain

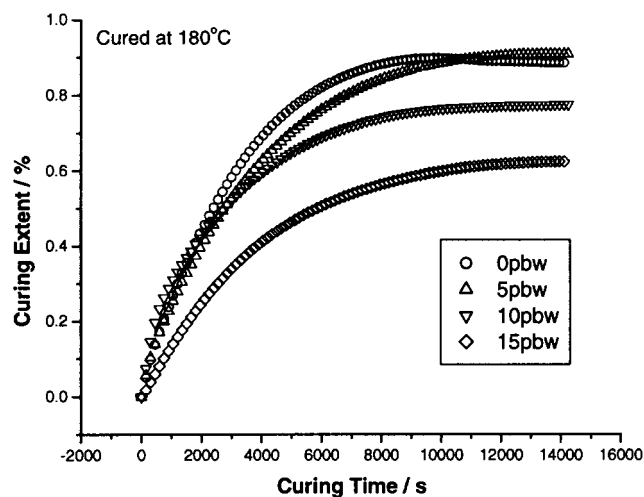


Figure 4. Effect of PESI-M content on curing extent of BMI resins at 180°C.

period, the complex viscosity abruptly increased. By extending the leveling part and the upraising part of the viscosity/time curve, the intersection was defined as gelling point of the blends. The time at the gelling point was called as gellation time ( $t_{gel}$ ).  $t_{gel}$  of the systems unmodified or modified with 5 pbw, 10 pbw and 15 pbw PESI-M were respectively 213s, 248s, 533s and, 775s and showed a dependence on PESI-M content. It was obvious that the high viscosity of PESI-M modified system slowed down the curing reaction.

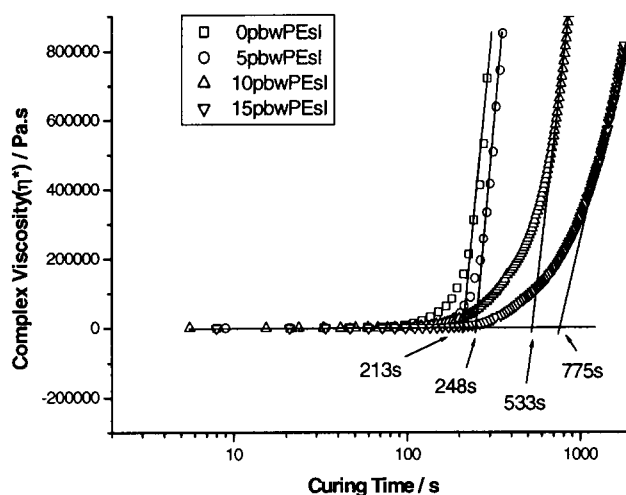


Figure 5. Dependence of PESI-M-modified BMI resin gelation time on PESI-M content.



### Dynamic Mechanical Analysis of Modified BMI Resins

Figure 6 presents the dynamic mechanical behaviors for the pure PEsi-M, the unmodified and the modified BMI resins. The pure PEsi-M and the unmodified BMI resin gave a single  $\tan \delta$  peak at 201°C and 299°C, respectively. When 10 pbw PEsi-M was loaded into BMI resin, a new  $\tan \delta$  peak appeared at 204°C and the  $\tan \delta$  peak of BMI-rich phase simultaneously moved to 297°C from 299°C. With the increase of PEsi-M content from 10 pbw to 15 pbw, the  $\tan \delta$  peaks of PEsi-M-rich phase and BMI-rich phase approached each other, as shown in Table 1. Approaching of the two  $\tan \delta$  peaks showed the slight difference of the phase-separating extent between two phases. The more the loading of PEsi-M, the higher the modified system complex viscosity. The increase of the blend viscosity resulted in an incomplete phase separation. The incomplete phase-separation was the reason that the PEsi-M-rich phase  $\tan \delta$  peak moved at a high temperature direction and the BMI-rich phase  $\tan \delta$  peak moved at a low temperature direction. In a word, the results of dynamic mechanical analysis coincided with the results of SEM.

### Mechanical Properties of Modified BMI Resins

Table 2 lists the dependence of mechanical properties of modified BMI resins on PEsi-M content. With the increase of PEsi-M content, the fracture energy ( $G_{IC}$ ), the bond strength ( $S_B$ ) and the tensile lap-shear strength ( $S_{TLS}$ ) of the modified BMI resins were improved significantly. The fracture energy

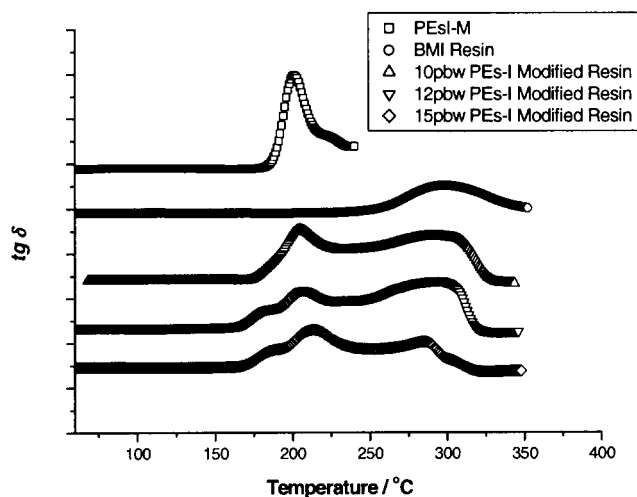


Figure 6. Dynamic mechanical data for modified BMI resins.

**Table 1.** Changes of  $\tan \delta$  Peak Temperature for PEsi-M-Rich Phase and BMI-Rich Phase in the Blends

Sample	Morphology	Temperature at $\tan \delta$ Peak for PEsi-M-Rich Phase ( $^{\circ}\text{C}$ )	Temperature at $\tan \delta$ Peak for BMI-Rich Phase ( $^{\circ}\text{C}$ )
Pure PEsi-M	—	201	—
Unmodified BMI resin	Single phase	—	299
10 pbw PEsi-M modified BMI resin	Co-continuous phase	204	297
12 pbw PEsi-M modified BMI resin	Phase-inverted phase	207	293
15 pbw PEsi-M modified BMI resin	Phase-inverted phase	212	284

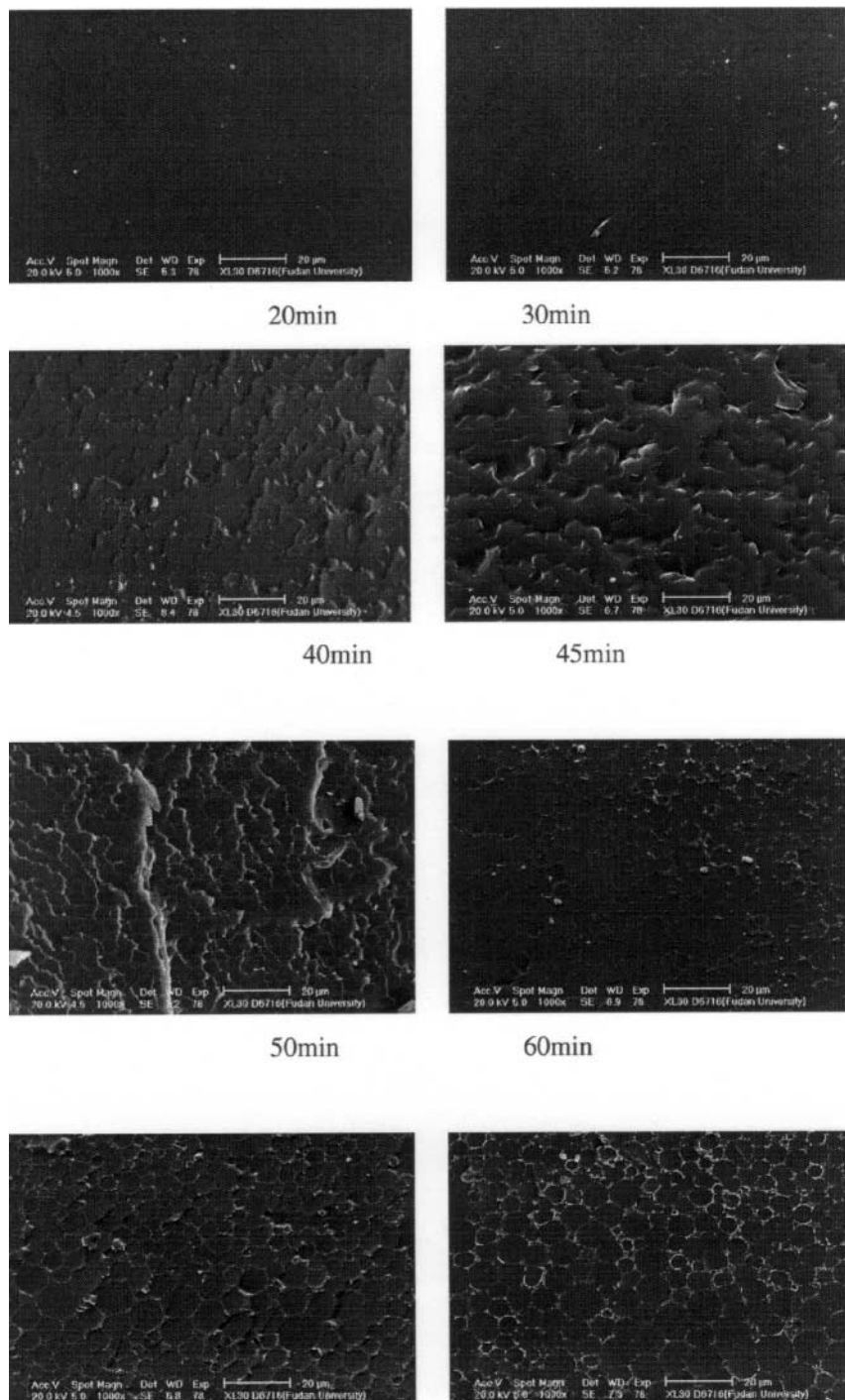
( $G_{IC}$ ) of 15PEsi-M modified BMI resin was 0.63 times larger than that of the unmodified BMI resin. The bond strength ( $S_B$ ) and the tensile lap-shear strength ( $S_{TLS}$ ) of the 15PEsi-M modified system were respectively 0.95 and 1.61 times larger than that of the unmodified BMI resin. In contrast with the SEM results, there existed a distinct relation between the mechanical properties and the morphologies of modified BMI resins. The fracture energy ( $G_{IC}$ ) was significantly improved in the modified systems with the phase-inverted structure.

### Evolution of Phase Structure in 15 pbw PEsi-M Modified System

The phase separation behavior of 15 pbw PEsi-M-modified BMI resin cured at  $180^{\circ}\text{C}$  was traced by using SEM. Figure 7 showed SEM micrographs of the fractured surface of the system containing 15 pbw PEsi-M at different times during curing. Before 30 min, the system presented a single phase. At 40 min, a thin two-phase structure was witnessed. At this moment, phase

**Table 2.** Mechanical Properties of Modified BMI Resins

Sample	E (GPa)	$K_{IC}$ (Mpam $^{1/2}$ )	$G_{IC}$ (J/m $^2$ )	$S_B$ (N)	$S_{TLS}$ (MPa)
Pure BMI resin	3.94	0.97	209	5.9	1.13
5 pbw PEsi-M-modified BMI resin	3.86	0.98	220	—	—
10 pbw PEsi-M-modified BMI resin	3.80	1.14	301	10.1	2.25
12 pbw PEsi-M-modified BMI resin	3.77	1.15	308	10.2	2.53
15 pbw PEsi-M-modified BMI resin	3.77	1.21	341	11.5	2.95



**Figure 7.** Evolution of phase structure of 15 pbw PEI-M blend cured at 180°C.

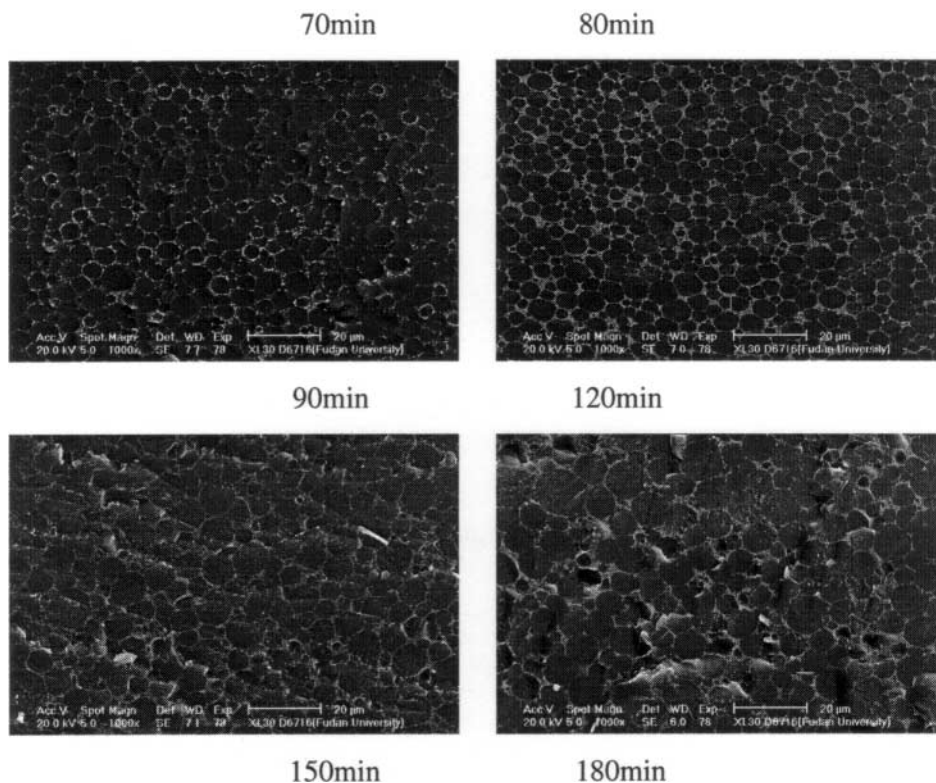


Figure 7. Continued.

separation proceeded fast. A clear two-phase structure was formed at 45 min. From 45 min to 180 min, the BMI-rich phase went on curing and the morphology of the system became more and more distinct. However, the size of the phase structure in the blend didn't change any more. The phase-separating behavior and the fairly uniform size of the modified system suggest that the phase separation may proceed via spinodal decomposition mechanism.<sup>[22]</sup>

## CONCLUSION

The morphologies of PEI-M-modified BMI resins changed from spherical particles to an inverted phase structure, depending on PEI-M content. The diverted morphology was produced in 12 pbw PEI-M-modified BMI resin. For 15 pbw PEI-M-modified system, the phase-separating behavior and the fairly uniform morphology suggests that phase separation at 180°C took place via a spinodal decomposition mechanism. The fracture energy ( $G_{IC}$ ) of 15 pbw PEI-M modified system was 0.63 times larger than that of the unmodified BMI resin.

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