

Phase Morphology and Mechanical Properties of a Poly(ether sulfone)-Modified Bismaleimide Resin

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Received 21 November 2006; accepted 28 February 2007

DOI 10.1002/app.26493

Published online 14 June 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The polymerization-induced phase-separation behavior of a thermoplastic [poly(ether sulfone) (PES)]-modified thermosetting bismaleimide resin during isothermal curing was investigated with differential scanning calorimetry, time-resolved light scattering, and scanning electron microscopy with various contents and molecular weights of PES. The results suggested that the phase structure changed from a dispersed structure to a bicontinuous structure to phase inversion with an increase in the PES content. Three kinds of PES with different molecular weights were used to study the effects of the molecular weight on the phase structure and mechanical properties

of modified systems. With higher molecular weight PES, a phase-inversion morphology could be obtained at lower PES contents. The curing conversion of bismaleimide was affected by the composition of the blend. The curing rate decreased with an increase in the PES content. A blend with 15 wt % PES of a suitable molecular weight had a higher tensile strength and elongation at break than that without PES. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 77–83, 2007

Key words: mechanical properties; morphology; phase separation; poly(ether sulfones); thermosets

INTRODUCTION

Bismaleimide resins, as high-performance thermoset materials, have attracted more and more interest because of their good thermal stability, low water absorption, and good retention of mechanical properties at high temperatures. However, the inherent brittleness is a major drawback with most cross-linked thermosetting materials, including highly crosslinked polybismaleimide.

Therefore, the toughening of polybismaleimide has been explored through physical blending with rubber,^{1,2} glycidyl ether of bisphenol A,³ polydimethylsiloxane,⁴ (meth)allyl,⁵ functionalized thermoplastics,⁶ and high-performance thermoplastics.^{7–15} The use of a high-performance thermoplastic has an additional advantage over rubber modification: there is no reduction in the thermal and mechanical properties of the bismaleimide matrix. The thermoplastics used have included high-modulus and high-glass-transition-temperature thermoplastics, such as poly(ether imide) (PEI),^{7–9} poly(arylene ether ketone)s,¹⁴ and polysulfone.¹⁵

Careful control of the morphological structure is necessary to achieve significant toughening. Therefore, the study of the phase separation of thermoset/thermoplastic blends is of great importance in toughening thermoset resins. Unlike thermoplastic/thermoplastic blends, phase separation is induced through an increase in the molecular weight of the thermoset resins in the thermoset/thermoplastic blends. Yamanaka and Inoue¹⁶ studied the structural development of an epoxy resin modified with poly(ether sulfone) (PES). They found that the morphology in a multicomponent thermosetting resin could be controlled through the contents of the thermoplastics and the curing conditions, which lead to a competition between the phase separation and the crosslinking reaction. Groeninckx et al.¹⁷ investigated the phase separation of crystallizable polyoxymethylene/epoxy blends and found that all blends demix according to a spinodal decomposition mechanism with a clear signature of viscoelastic effects at specific polyoxymethylene contents. Thomas et al.¹⁸ studied a poly(ether sulfone ether ketone) (PESEK)-modified epoxy system. Their blends revealed a homogeneous morphology due to the similarity in the chemical structures of the modifier and the epoxy and the hydrogen-bonding interactions between the blend components. The fracture toughness of the epoxy resin increased on blending with PESEK because of the increase in the ductility of the matrix.

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Contract grant sponsor: China Postdoctoral Science Foundation; contract grant number: 20060400626.

Journal of Applied Polymer Science, Vol. 106, 77–83 (2007)

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In our previous research,^{8,19} various phase morphologies for PEI-modified bismaleimide blends were obtained, such as cocontinuous and phase-inversion structures. We also reported that there experimentally existed a viscoelastic phase-separation behavior for a PES-modified bismaleimide system.²⁰ The objective of this study was to investigate the phase-separation behavior of blends based on bismaleimide resins and PES. In this study, phase separation during isothermal curing was studied with differential scanning calorimetry (DSC), time-resolved light scattering (TRLS), and scanning electron microscopy (SEM). Tensile tests were also carried out to investigate the relation between the mechanical properties and the blend morphologies.

EXPERIMENTAL

Materials

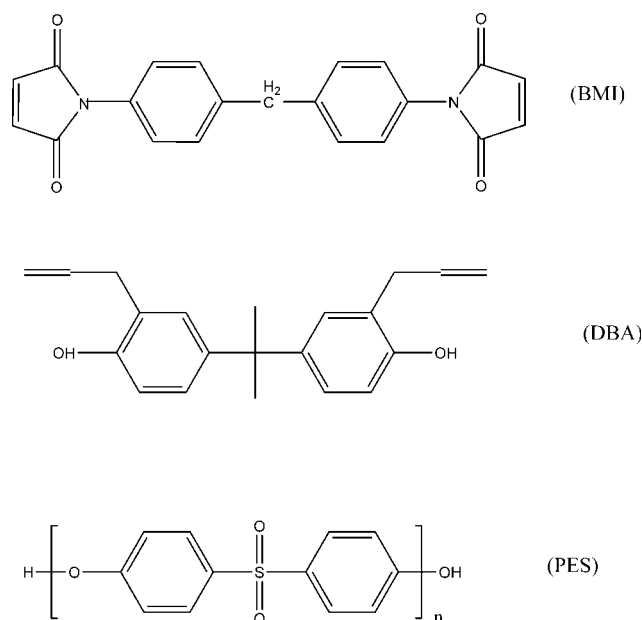
4,4'-Bismaleimidodiphenylmethane (BMI; Beijing Aeronautical Manufacturing Technology Research Institute, Beijing, China) was used. 2,2'-Diallyl bisphenol A (DBA; Sichuan Jiangyou Insulating Material Factory, Sichuan, China) was also used. Three kinds of PES, supplied by Jilin University (Jilin, China), were used [intrinsic viscosity = 0.22 dm³/kg (number-average molecular weight = 9.2×10^3 , weight-average molecular weight = 2.3×10^4), intrinsic viscosity = 0.36 dm³/kg (number-average molecular weight = 1.9×10^4 , weight-average molecular weight = 4.5×10^4), and intrinsic viscosity = 0.53 dm³/kg (number-average molecular weight = 3.1×10^4 , weight-average molecular weight = 6.7×10^4)]. The intrinsic viscosity was determined in *N,N*-dimethylformamide at 25°C. The molecular weight of PES was measured with a PerkinElmer (Waltham, MA) S-250 gel permeation chromatograph; polystyrene standards (Showa Denko, Ltd., Tokyo, Japan) were employed to make a calibration curve. The chemical structures of BMI, DBA, and PES are shown in Scheme 1.

Sample preparation

PES/BMI blends containing different contents and different molecular weights of PES were prepared as follows. PES was dissolved in DBA at 150°C under the protection of nitrogen. After the mixtures had cooled to 120°C, BMI was added. The weight-percentage ratio of BMI to DBA was kept at 57 : 43 (1 : 0.85 molar ratio). The mixture was stirred continuously until a transparent blend was obtained. Then, the blends were cooled and cured under different conditions.

Measurements

The scattering vector with the maximum scattering intensity (q_m) was obtained with a self-made TRLS



Scheme 1 Chemical structures of BMI, DBA, and PES.

instrument with a controllable hot chamber. The TRLS technique has been described elsewhere.²¹ The morphology of the fully cured blends was examined with SEM (Tescan, Czech) (model TS5136MM). The samples for SEM were cured at 160°C for 3 h. The cured samples were fractured in liquid nitrogen and coated with a layer of gold before observation. For measuring the reaction conversions of the blends, the samples were isothermally cured at 160°C with a PerkinElmer Pyris 1 differential scanning calorimeter. The curing conversion was calculated through the contrast of the residual exotherms, which were observed in scans over the temperature range of 50–350°C, with the total exotherms of the uncured samples. The specimens for mechanical property testing were cured at 160°C for 3 h and at 185°C for 2 h and then postcured at 220°C for 3 h. The testing of the mechanical properties of the blends was performed with an Instron (Instron Ltd., High Wycombe, Bucks, UK) model 1121 tensile tester at a constant temperature. A gauge length of 15 mm and a crosshead speed of 1 mm/min were used. All the reported results are averages of at least five specimens. The cloud-point times of the blends with different amounts of PES cured at 160°C were determined by transmission optical microscopy with a Leitz Orthoplan model (Leitz, Germany) with a heating device. The onset time at which the blend became cloudy was taken as the cloud-point time. Blends with different amounts of PES were taken from the oven at different curing times and dissolved in CH₂Cl₂. The onset time at which an insoluble fraction of the blend occurred was considered the gelation time. The conversions at the cloud point and gel point were determined by DSC.

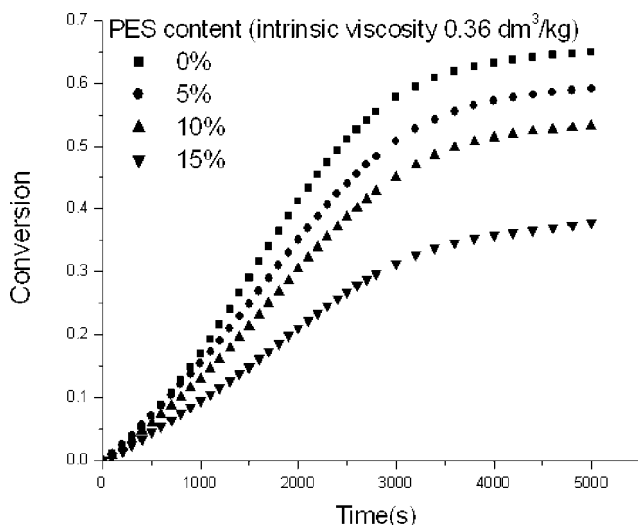


Figure 1 Curing conversion versus the curing time for PES/BMI blends cured at 160°C.

RESULTS AND DISCUSSION

Curing rate and conversion

To study the relation between the curing process and phase separation, the conversions of neat BMI and BMI/PES blends during isothermal curing were examined with DSC. As shown in Figure 1, the conversions of neat BMI and its blend were nearly the same at the early stage of the curing reaction. However, the final conversion of the BMI/PES blend decreased with the PES content. This could be attributed to the dilution effect usually seen for the thermoplastic modification of thermosetting resins.²² The final conversions of neat BMI and its blend were lower than 0.7 without postcuring. For further study, the cloud-point conversion and the gel conversion for blends with various PES contents and molecular weights cured at 160°C were also calculated and are summarized in Tables I and II. For all the blends, phase separation occurred at low conversions (0.12–0.16), and the gel conversions ranged from 0.53 to 0.56. Table II shows that the conversion at the offset of phase separation was in the range of 0.25–0.31, which was far lower than the conversion at the gel point. On the basis of Tables I and II and our previous study about the phase separation of thermoplas-

TABLE I
Conversions at the Cloud Point (χ_{cp}) and Gelation Point (χ_{gel}) for Blends Cured at 160°C

Composition (wt %)	χ_{cp}	χ_{gel}
95/5 BMI/PES	0.13	0.53
90/10 BMI/PES	0.12	0.56
85/15 BMI/PES	0.14	0.54

The PES intrinsic viscosity was 0.36 dm³/kg.

TABLE II
Conversions at the Cloud Point (χ_{cp}) and Offset of Phase Separation (χ_{offset}) Observed by TRLS for a 90/10 (wt %/wt %) BMI/PES Blend Cured at 160°C

Composition	χ_{cp}	χ_{offset}
BMI/PES (0.22 dm ³ /kg)	0.16	0.31
BMI/PES (0.36 dm ³ /kg)	0.12	0.27
BMI/PES (0.53 dm ³ /kg)	0.10	0.25

tic-modified epoxy resins, which found that phase separation occurred at the early stage of the curing reaction (normally, the cure conversion was less than 0.2),²³ the low conversion in this study had no effect on the phase separation.

In addition, the effect of the PES molecular weight on the curing process of the BMI/PES blends was studied. Figure 2 shows that the curing conversion of bismaleimide was also affected by the PES molecular weight. The curing rate of the blend with lower molecular weight PES was slightly slower than the blend with higher molecular PES. The reason might be that the phase separation of the blend with higher molecular weight PES was more complete; that is, in comparison with the blend with low-molecular-weight PES, the PES concentration in the bismaleimide-rich phase was lower in the blend with higher molecular weight PES modified systems during phase separation, and this reduced the dilution effect and thus accelerated the curing rate of bismaleimide.

Phase morphology

As we know, the properties of blends are related to the morphology of blends. Therefore, the fracture surfaces of the blends were examined by SEM to

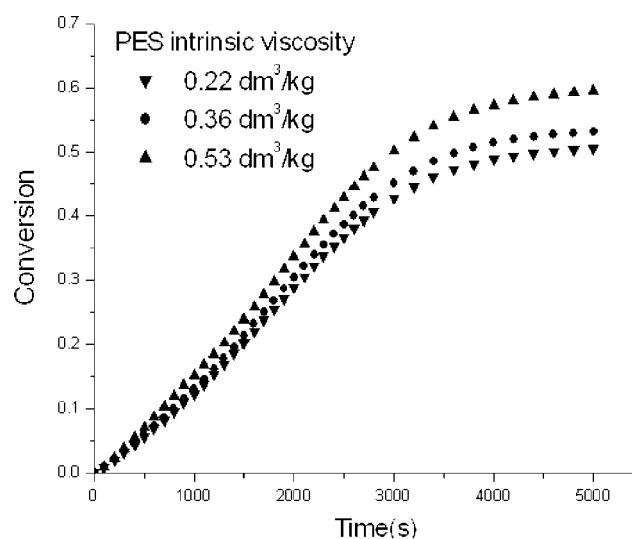


Figure 2 Curing conversion versus the curing time for PES/BMI blends (10 wt %/90 wt %) cured at 160°C with PES samples of different molecular weights.

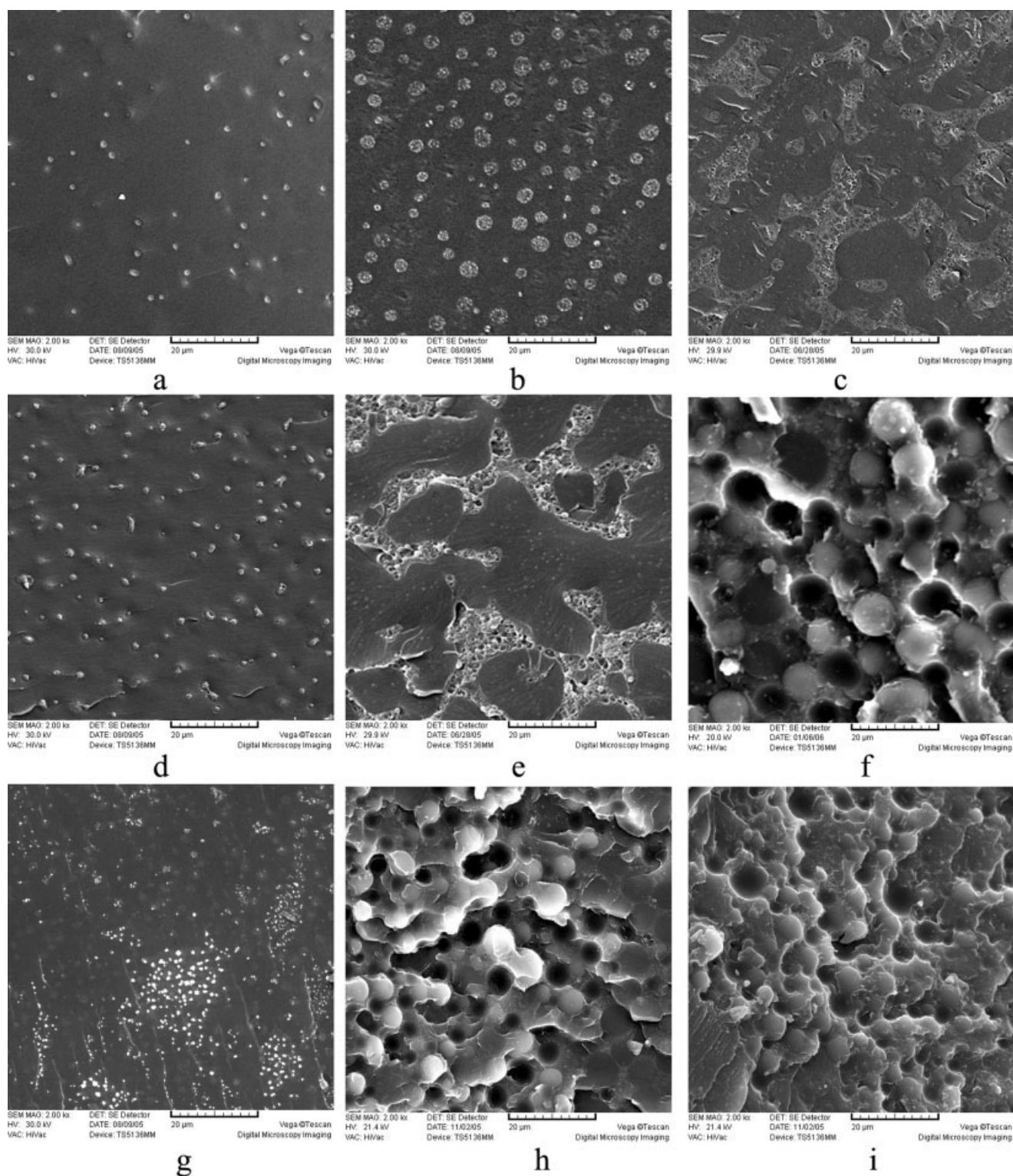


Figure 3 Morphologies of BMI/PES blends with various PES contents and molecular weights: (a,d,g) 5, (b,e,h) 10, and (c,f,i) 15 wt %. The PES intrinsic viscosities were (a–c) 0.22, (d–f) 0.36, and (g–i) 0.53 dm^3/kg .

evaluate the phase morphologies of the blends. The morphology changed drastically, depending on the PES content and molecular weight. The results are shown in Figure 3.

Figure 3(d–f) shows the typical morphologies of blends with a middle-molecular-weight PES (the intrinsic viscosity was 0.36 dm^3/kg). The blend with 5 wt % PES showed spherical domains around 1 μm

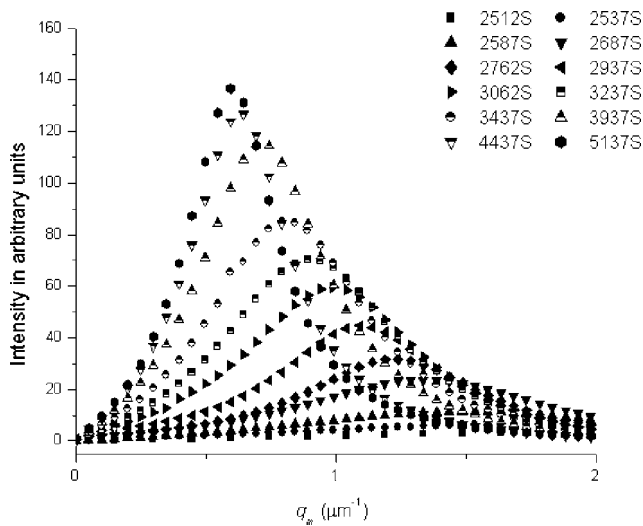


Figure 4 TRLS profiles of a PES/BMI blend (15 wt %/85 wt %) cured at 160°C.

in diameter dispersed in the BMI-rich matrix. A small number of PES particles broke off the matrix because the PES had no end functional groups to react with the bismaleimide and there were no chemical links between the two phases. In the case of 10% PES, the morphology of the blend was a bicontinuous phase structure. Small PES particles could be seen in the bismaleimide continuous phase; meanwhile, spherical particles of bismaleimide could also be found dispersed in the PES continuous phase. However, the size distribution of the bismaleimide particles in the PES continuous phase was not uniform, probably because of the high viscosity at the late stage of the curing reaction, which restricted the further development of the microstructure. The blend with 15 wt % PES showed complete phase inversion. The PES phase formed the matrix. Meanwhile, BMI appeared as big, interconnected spherical domains around 16 μm in diameter.

The effect of the PES molecular weight on the phase morphologies could also be observed through a comparison of Figure 3(a–i). As shown in Figure 3(a–c), when low-intrinsic-viscosity PES (0.22 dm³/kg) was used, the blends with 5 or 10 wt % PES showed a dispersed phase structure, whereas the blend with 15 wt % PES showed a bicontinuous phase structure. However, when high-intrinsic-viscosity PES (0.53 dm³/kg) was used, the blend with 10 wt % PES showed a complete phase-inversion structure. This means that a phase-inversion morphology could be obtained with less thermoplastic resin when a high-molecular-weight thermoplastic resin was used in the thermoplastic-modified thermoset system.

Phase separation observed by TRLS

To obtain clear knowledge of the phase-separation process and final phase structure, the phase-separa-

tion process of the blend was observed with TRLS. The scattered light intensity was shown as a function of the magnitude of scattering vector **q**, which is defined by $\mathbf{q} = (4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of light in the blend and θ is the scattering angle between the incident and scattered light.

As an example, a TRLS figure for the phase separation of the blend with PES with an intrinsic viscosity of 0.36 dm³/kg is shown in Figure 4. A light scattering peak first appeared in the profile at about 42 min. Then, the light scattering intensity, $I(\mathbf{q},t)$, increased rapidly with the curing time and reached the maximum value at about 86 min, and then $I(\mathbf{q},t)$ remained constant. Meanwhile, light scattering vector \mathbf{q}_m decreased rapidly with the curing time and remained constant at last (Fig. 5) at about 74 min.

According to the light scattering theory, $I(\mathbf{q},t)$ can be expressed by the following expression:

$$I(\mathbf{q}_m, t) \propto \langle \eta^2 \rangle \cdot \mathbf{q}_m(t)^{-3} \cdot S \left[\frac{\mathbf{q}(t)}{\mathbf{q}_m(t)} \right]$$

where $S[\mathbf{q}(t)/\mathbf{q}_m(t)]$ is a structure function corresponding to the character of the phase structure, \mathbf{q}_m is the position of the scattering vector related to the maximum lighting intensity in each light profile, and $\langle \eta^2 \rangle$ is the mean-squared fluctuation. The last can be expressed as follows:

$$\langle \eta^2 \rangle \propto \phi_1 \cdot \phi_2 \cdot (n_1 - n_2)^2$$

where ϕ_i and n_i are the volume fraction and refraction index of component i .

At the early stage of phase separation, both \mathbf{q}_m and $\langle \eta^2 \rangle$ changed, and they had a combined effect on the increase in the light scattering intensity. When the curing time was more than 74 min, $S[\mathbf{q}(t)/$

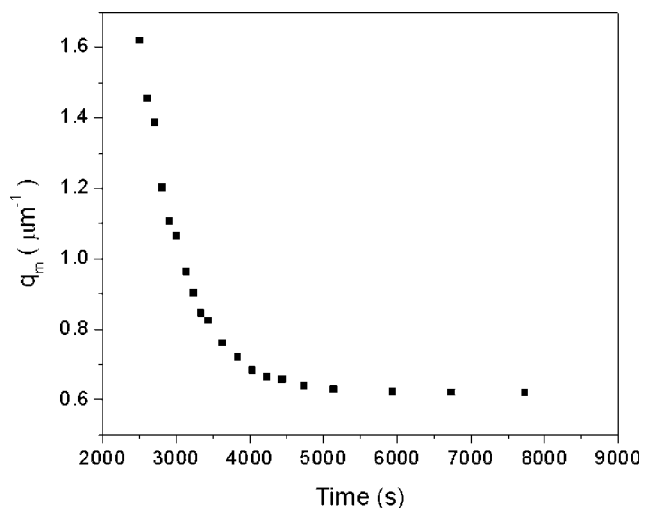


Figure 5 \mathbf{q}_m versus time for a PES/BMI blend (15 wt %/85 wt %) cured at 160°C.

TABLE III
Tensile Properties of Neat BMI and Its Blends with Various PES Contents

Composition (wt %)	PES intrinsic viscosity (dm ³ /kg)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
BMI	—	68.7	3.97	1.83
95/5 BMI/PES	0.22	67.5	3.16	1.87
	0.36	77.4	3.87	1.95
	0.53	68.4	3.93	1.81
90/10 BMI/PES	0.22	68.2	3.32	1.89
	0.36	72.5	3.82	1.83
	0.53	71.5	3.74	1.82
85/15 BMI/PES	0.22	73.1	3.35	2.02
	0.36	87.4	3.81	2.27
	0.53	74.3	3.78	1.88

$q_m(t)$] and q_m did not induce a change in $I(q_m, t)$ because q_m remained constant. $I(q_m, t)$ was proportional only to $\langle \eta^2 \rangle$. Therefore, the increase in the light scattering intensity at the latter stage of phase separation suggested that the diffusion of the BMI or PES molecules between two phases still continued after macroscopic phase separation was arrested.

As presented in Figure 5, light scattering vector q_m decreased with the curing time at the early stage of the curing reaction, and this indicated that the average distance between the same neighboring phases increased with the increase in the curing content of BMI. When the curing time was more than 74 min, the q_m value became constant, and this meant that the domain size in the blend was fixed. The distance between the same neighboring phases in the blend could be calculated according to the formula $2\pi/q_m$, and the results were in agreement with those obtained from the SEM micrograph.

According to these results, the phase separation in the blend with 15% PES followed a spinodal decomposition mechanism. The same mechanism was found in the phase-separation process of the blend with 10% PES and in the phase-separation process of the blend with PES samples of different molecular weights (the intrinsic viscosity was 0.22, 0.36, or 0.53 dm³/kg). Therefore, the phase morphology shown in Figure 3 is believed to have been formed by a spinodal decomposition mechanism. However, we did not find any light scattering ring for the blend with 5 wt % PES, no matter what the molecular weight of PES was. The reason was probably that the phase separation of the blend with 5% PES occurred as a nucleation and growth mechanism.

Mechanical properties

To understand the relation between the phase morphology and the mechanical properties, the tensile properties of neat BMI and its blends with PES were investigated. The results are listed in Table III. The

tensile strength and elongation at break of the BMI/PES blends increased; meanwhile, the tensile modulus decreased a little. The tensile strength and elongation increased obviously for the blends with 15 wt % PES. Therefore, the results further illustrate that the toughness could be dramatically improved when a bicontinuous or phase-inverted microstructure was formed.²⁴

Meanwhile, Table III shows that for the blends with the same PES content, the blend with the highest molecular weight PES had a lower tensile strength and elongation at break. The reason might be that in comparison with the blend with low-molecular-weight PES, the blend with high-molecular-weight PES had a worse interface between the PES-rich phase and the bismaleimide-rich phase. However, the tensile strength and elongation at break of the blend with the lowest molecular weight of PES were lower than those of other blends with the same PES contents. A possible reason is that the lowest molecular weight PES had the lowest modulus, and this made the modified systems show a particle structure; both weakened the effect of toughness.

In general, the introduction of PES could enhance the toughness of neat BMI with a slight loss of the material modulus.

CONCLUSIONS

A thermoplastic, PES, was employed to modify a bismaleimide. The conversion extent and curing rate of BMI were measured simultaneously with DSC. The results showed that the final conversion of BMI was affected by the composition in the blend, although the conversions of BMI for all the blends were nearly the same at the early stage of curing. The curing rate decreased with the increase in the PES content because of the dilution effect usually found in the thermoplastic modification of thermosetting resins. The PES molecular weight also had an

effect on the curing rate for the BMI/PES blends. The phase structure changed from a dispersed phase to a bicontinuous phase to phase inversion with the increase in the PES content. The blend with 5 wt % PES had a dispersed phase morphology that was probably formed by a nucleation and growth mechanism. The phase separation occurred through a spinodal decomposition mechanism for the blend with 10 or 15 wt % PES. The phase-inversion morphology could be obtained with less PES when a high-molecular-weight PES was used. The mechanical properties of the blends with various PES contents could be correlated with the corresponding morphology. The blend with 15 wt % PES of a suitable molecular weight had the highest tensile strength and elongation at break because of the PES continuous phase structure. In addition, an increase in the PES molecular weight did not always lead to an increase in the mechanical properties of the blend with the same PES content.

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