Studies of the Stability of Thermoplastic-Modified Bismaleimide Resin

KANCHENG MAI, JIANWEI HUANG, HANMIN ZENG

Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China

ABSTRACT: The stability of bismaleimide−o,o'-diallyl bisphenol A (BMI−DABA) blends modified with high-performance amorphous thermoplastic bisphenol A polysulfone (PSF), polyether ketone (PEK-C), and polyether sulfone (PES-C) bearing a phthalidylidene group has been studied by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The extent of stability of thermoplastic components has been compared with the area of the endothermic peak that appears within the glass transition region for thermoplastic component in cured blends aged at temperature below the glass transition temperature (T_g). The stability of thermoplastic can be improved by the formation of semi-interpenetrating polymer networks (semi-IPNs). The stability of thermoplastic with higher T_g is more easily controlled. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1965–1970, 1997

Key words: stability; bismaleimide; thermoplastics; semi-interpenetrating polymer networks

INTRODUCTION

Bismaleimide (BMI) possesses many desirable properties that are associated with thermoset networks. These include high tensile strength and modulus, excellent chemical and corrosion resistance, good dimensional stability, and good performances at elevated temperatures. However, one major disadvantage associated with many thermosetting networks is that it is inherently brittle. It exhibits poor fracture toughness and low resistance to crack propagation. Several approaches have been introduced to improve fracture toughness of BMI resin, as follows: (1) co-reacting BMI systems with diallyl compounds, which gives chain extension via the ene reaction of the allyl and the maleimide group[1–3]; (2) utilizing engineering thermoplastics to reduce the crosslink density as toughness modifiers[3–8]; (3)

combining methods (1) and (2).[1,4] The thermoset component crosslinks in the presence of linear polymers to produce microphase-separated semi-interpenetrating polymer networks (semi-IPN).[6,9,10] This approach offers the additional advantage, compared to rubber toughening, that other desirable properties of the matrix, such as modulus and glass transition temperature (T_g), are not adversely affected by the addition of the modifier.

Thermoplastic-modified BMI has found interest as matrix materials for advanced composites with improved damage tolerance. Most recently, the use of thermoplastic resin as a second-phase toughening agent in BMI has been explored.[1–8] By addition of thermoplastics and controlling the molecular weight, weight percent incorporation, and end group chemistry of modifier, the BMI fracture toughness may be enhanced while maintaining high-temperature performance. Phase separation of the thermoplastic modifiers occurs during network formation of the thermosetting component. The thermoplastic component can be incorporated within the thermoset network to pro-

Table I   DSC Results of BMI–DABA Blends

BMI : DABA (Mole Ratio)	T_m (°C)	ΔH_m (J/g)	T_r (°C)	ΔH_r (J/g)
1 : 0	159.8	86.8	222.3	−178.5
1 : 0.2	155.8	62.1	254.2	−272.2
1 : 0.4	144.3	48.1	253.6	−290.2
1 : 0.6	140.4	46.4	253.4	−316.4
1 : 0.8	130.1	32.7	252.6	−317.9
1 : 1	129.3	23.5	252.2	−320.7

duce microphase-separated semi-interpenetrating polymer networks (semi-IPN), or it can be simply mixed with the matrix. In such multiphase polymer blends, it is suggested that the physical and mechanical properties of polymer blends not only depend upon the morphology of the two phases in the blends, but also depend upon the stability of the morphology of two phases. The stability of morphology and mechanical properties depend upon the structural relaxation, which is a consequence of the nonequilibrium nature of the glassy state. Therefore, over the last decade, structural relaxation studies have been given greater importance because many high-performance polymer blends and composite materials are applied in the glassy state at a temperature below glass transition temperature.[11–13] In this article, the enthalpy relaxation of thermoplastic in BMI–diallyl compound blends modified with high-performance thermoplastics has been investigated. The extent of stability for thermoplastic components has been compared with the area of the endothermic peak, which appears within the glass transition region for the samples aged at temperature below the glass transition temperature of thermoplastics.

EXPERIMENTAL

Materials

BMI resin used in this study was 4,4′-bismaleimidodiphenylmethane from Fengguang Chemical Factory, Habai, China. $o,o′$-diallyl bisphenol A (DABA) was supplied by Jiangyou Electron Engineering Material Factory, Sichuan. The thermoplastic (TP) modifiers used throughout this work were amorphous bisphenol A polysulfone (PSF) from Shuguang Chemical Factory, Shanghai, and polyether ketone (PEK-C) and polyether sulfone (PES-C) bearing phthalidylidene groups from

Xuzhou Special Engineering Plastic Factory, Peoples Republic of China.

Preparation of Thermoplastic–BMI–DABA Blends

The BMI–DABA blends with different mole ratio of BMI–DABA were prepared by dissolving BMI in DABA at 140°C for 15 min, and a clear one-phase solution was obtained. For the TP–BMI–DABA ternary blends, the mole ratio of BMI to DABA was kept at 1 : 1. For the blends with low content of TP, thermoplastic was added for further mixing until fully dissolved at 140°C. For the blends with high content of TP, the blends were prepared by dissolving the thermoplastic and BMI–DABA blends in 1,2-dichloroethane to form a 20 wt % resin solution. The solvent was evaporated at room temperature for one day and dried at 100–120°C for 8 h. The TP–BMI–DABA ternary blends prepared from melt and solution mixing was degassed and precured at 140°C for 2 h in a vacuum oven, then cured at 300°C for 1 h. The cured BMI–DABA blends with PSF, PEK-C, and PES-C were aged at 175, 213, and 245°C for various times, respectively.

Differential Scanning Calorimetry

The aged samples were investigated by means of a differential scanning calorimetry (DSC) Perkin–Elmer DSC-2 under nitrogen at a 10°C/min heating rate from room temperature to 350°C.

Scanning Electron Microscopy

The fracture surface and the surface of etched specimens were coated with a thin layer of gold

Table II   Temperatures and Heats of Cure Reaction of Thermoplastic-Modified BMI–DABA (Mole Ratio = 1 : 1) Ternary Blends Precured at 140°C for 2 h

Thermoplastics	Content (wt %)	T_r (°C)	ΔH_r (J/g)
	0	252.5	−250.4
PSF	10	249.5	−242.4
PEK-C	10	246.4	−244.2
PES-C	10	246.2	−246.1
PSF	30	256.7	−244.7
PEK-C	30	252.7	−253.8
PES-C	30	255.5	−240.6
PSF	50	259.5	−239.4
PEK-C	50	259.1	−245.0
PES-C	50	255.5	−237.4
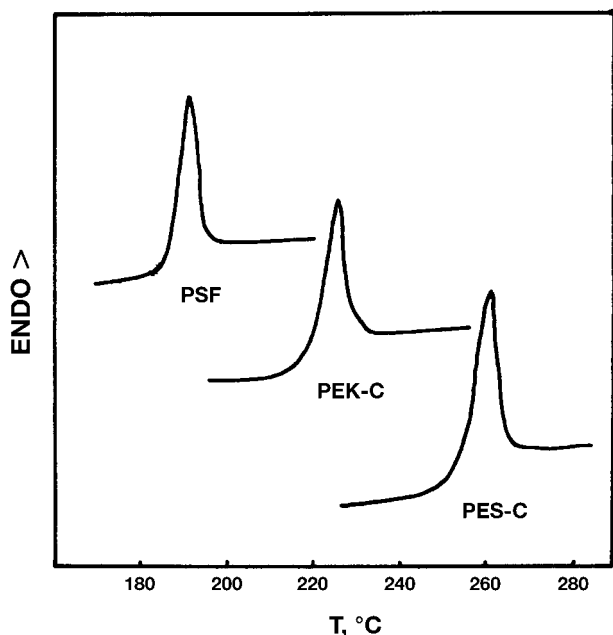
Figure 1 DSC thermograms of aged thermoplastics. Aging conditions: PSF aged at 175°C for 2 h; PEK-C aged at 213°C for 2 h; PES-C aged at 245°C for 2 h.

and examined using a HITACHI S-450 scanning electron microscope.

RESULTS AND DISCUSSION

Effect of Thermoplastics on Cure Reaction of BMI–DABA Blends

Table I presents DSC results of uncured BMI–DABA blends with various mole ratios. It can be seen that addition of DABA and increasing content of DABA resulted in a decrease in the melting temperature (T_m) and heat of fusion (ΔH_m) of BMI due to the coreaction of BMI with DABA in the preparation of BMI–DABA blends at 140°C. Because of the presence of copolymerization of BMI with DABA, the peak temperature of cure reaction (T_r) and heat of reaction (ΔH_r) increased with the addition of DABA. However, the peak temperature of cure reaction was independent of content of DABA, and the heat of reaction depended upon DABA content. An increase in DABA content resulted in an increase in the heat of reaction of BMI–DABA blends possibly because the heat of copolymerization of BMI with DABA is higher than that of homopolymerization of BMI.

The temperatures and heats of cure reaction of BMI–DABA blends modified with different con-

tent of thermoplastic are reported in Table II. In our case, we found that, by dissolving thermoplastic in BMI–DABA melt or dissolving thermoplastic and BMI–DABA blends in a common solvent, after the solvent removal, a clear, homogeneous mixture is obtained. However, both different thermoplastic resins and their contents have no effect on the temperatures and heat of cure reaction of BMI–DABA blends.

Stability of Thermoplastics in TP–BMI–DABA Ternary Blends

The morphology and mechanical properties of many multiphase polymer systems are usually unstable because of the nonequilibrium nature of the glassy state. The stability of polymers and multiphase polymer systems may been characterized by physical aging studies. For unstable systems, samples were aged at temperatures below T_g, and a endothermic peak within glass transition region was observed due to the structural relaxation.[11–13] The enthalpy relaxation was found to increase gradually with aging time to a limiting value at which structural equilibrium was reached. Therefore, the extent of stability of
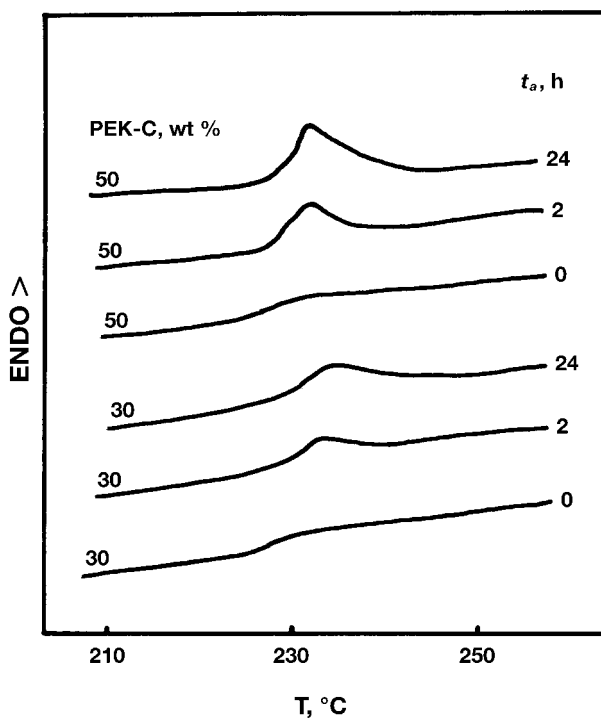
Figure 2 DSC thermograms of PEK-C–BMI–DABA ternary blends aged at 213°C for various times.
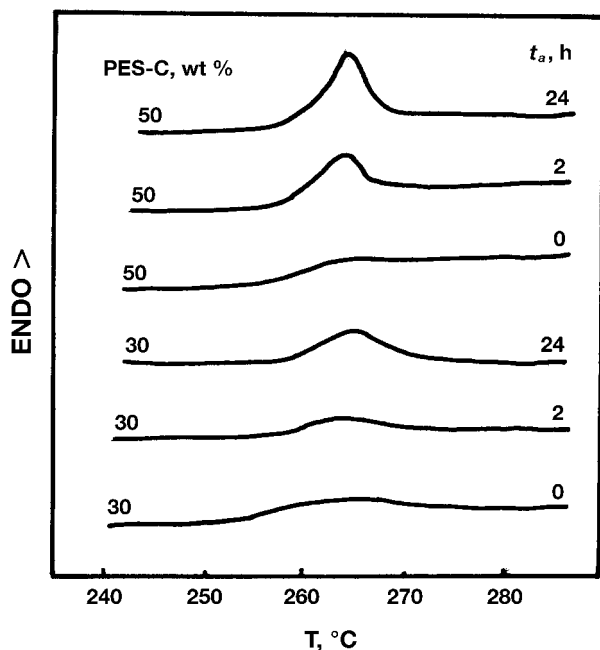
Figure 3 DSC thermograms of PES-C–BMI–DABA ternary blends aged at 245°C for various times.

polymer and multiphase polymer systems may be compared with the area of the endothermic peak, which appears within the glass transition region.

The DSC scans of PSF, PEK-C, and PES-C aged at 175, 213, and 245°C for 2 h, respectively, are shown in Figure 1. Three thermoplastics show the presence of the endothermic peak within their glass transition region. This behavior is in good agreement with other published results on thermoplastic polymers[12–15] and thermoset resin[11] and suggests that it is a general feature of the structural relaxation of glassy state.

The DSC scans of PSF, PEK-C, and PES-C-modified BMI–DABA cured blends are shown in Figures 2–4. It can be seen that the intensity and area of the endothermic peak of thermoplastic component in cured blends depend upon the nature of thermoplastics. For PEK-C ($T_g = 225°C$) and PES-C ($T_g = 260°C$) with high T_g, no endothermic peak was observed for aged blends containing thermoplastic of 30 wt % and was independent of the aging time. Even increasing the content of thermoplastic to 50 wt %, the intensity and area of the endothermic peak of thermoplastic component in aged blends is markedly depressed, as compared with neat thermoplastics. However, the presence of endothermic peak for aged blends containing PSF ($T_g = 190°C$) with lower T_g was observed, and the intensity and area of the peak

increases with increasing the aging time and content of the PSF component.

In the thermoplastic–thermoset multiphase polymer systems, the thermoset blend component crosslinks in the presence of linear polymers to produce a semi-interpenetrating polymer network (semi-IPN). Such a semi-IPN could be processed like a thermoset, possess good toughness like a thermoplastic, and show notable improvements in fracture toughness and microcracking resistance of fiber-reinforced composites over the unmodified thermosetting composites.[16,17] Synergisms in processability and properties have also been realized,[9,10,18] and interfacial adhesion has been improved between the fiber and matrix in fiber-reinforced composites.[19]

The structural relaxation process originates a simultaneous decrease of the free volume and segmental mobility. In the cured thermoplastic–BMI–DABA ternary blends, the semi-IPN can be formed during cure process. The formation of the thermoset network would restrict the segmental mobility of thermoplastic components. Therefore, the absence of endothermic peak or the decrease in the area and intensity of the endothermic peak
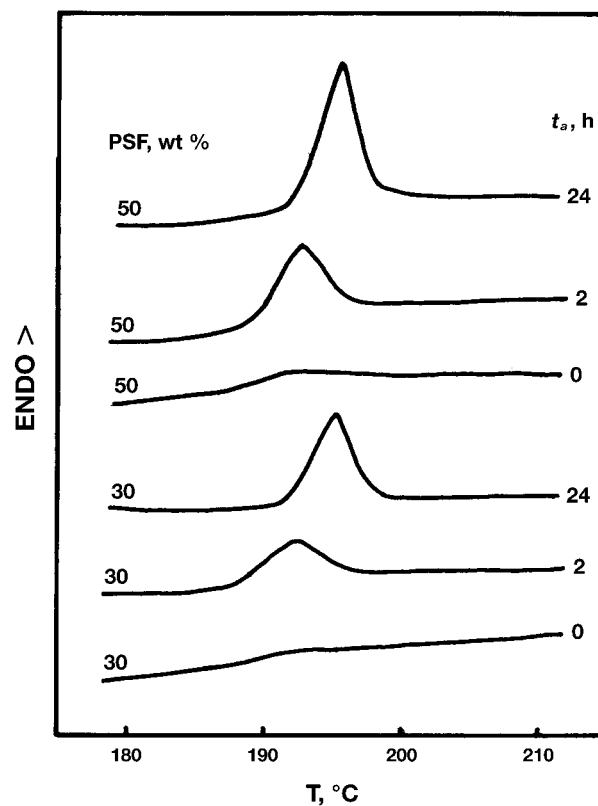

Figure 4 DSC thermograms of PSF–BMI–DABA ternary blends annealed at 175°C for various times.

of thermoplastic components in the aged blends was attributed to the formation of a semi-IPN to restrict the segmental mobility of the thermoplastic component. However, it is suggested that a competition of cure reaction and phase separation during cure process of thermoplastic–BMI–DABA blends exists. If the rate of phase separation is higher than that of cure reaction at cure conditions, the dispersed phase with large domain can be formed in some cases, and an endothermic peak can be observed due to the structural relaxation. For the BMI–DABA blends containing PSF with low T_g, the change of endothermic peak with a content of PSF and the aged time was attributed to a phase separation to form a large domain of PSF phase. The rate of phase separation is higher than the rate of cure reaction in the blends containing PSF component due to the lower T_g and melt viscosity, compared to the blends containing PEK-C and PES-C with a higher T_g at the same cure conditions. The enthalpy relaxation of a large domain of dispersed phase can take place at the age process, as neat thermoplastics.

Scanning electron microscopy (SEM) observation of fractured surface and the surface of etched specimens also indicates that the phase morphology of PSF blends differs from the PEK-C blends. Figure 5 shows scanning electron micrographs of the fractured-etched surface of the TP–BMI–DABA ternary blends. Because amorphous thermoplastic PSF, PEK-C, and PES-C are easily dissolved in dichloroethane, the remaining material is a crosslinked BMI–DABA-rich phase. For the PEK-C blends, fine particles of a few micrometers in diameter can be observed, and particles seen to be connected to each other. The connected particle structure implies a two-phase morphology of interconnected spherical domains of the BMI–DABA-rich phase dispersed in a matrix of the PSF-rich phase to obtain a cocontinuous two-phase structure. A similar morphology was obtained in the cured systems for thermoplastic-modified epoxy[20] and acetylene-terminated sulfone systems.[10] This morphology was not observed in the PSF–BMI–DABA ternary blends, indicating that the extent of phase separation of PEK-C blends is different from that of PSF blends. It is attributed to the difference of the extent of phase separation due to the difference of the T_g and melt viscosity of thermoplastics. For the PEK-C and PES-C blends, two-phase morphology could not develop well possibly because of the decrease in the extent of phase separation due to the restriction of thermoset networks.
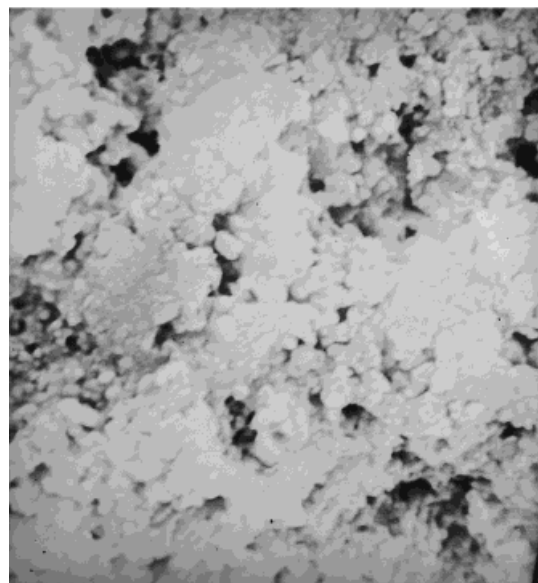
Figure 5 Morphology of fracture specimens of BMI–DABA blends with 50 wt % PSF (a) and 50 wt % PEK-C (b) after etching in 1,2-dichloroethane for 24 h.

CONCLUSION

The enthalpy relaxation of thermoplastic components in cured bismaleimide–o,o'-diallyl bisphenol A (BMI–DABA) blends modified with high-performance amorphous thermoplastics has been investigated by DSC. Three thermoplastics show the presence of the endothermic peak with the glass transition region. The intensity and area

of the endothermic peak of thermoplastic component in cured blends depend upon the nature of thermoplastics. The extent of stability of thermoplastics in BMI–DABA blends can be compared with the intensity and area of the endothermic peak that appears within the glass transition region of thermoplastic in blends aged at temperature below the glass transition temperature (T_g) of thermoplastic. The absence of endothermic peak or the decrease in the area of the endothermic peak of thermoplastic components in the aged blends was attributed to the formation of semi-interpenetrating polymer networks to restrict the segmental mobility of thermoplastic components. Therefore, it is suggested that the stability of phase morphology and mechanical property of multiphase polymer systems can be improved by the formation of semi-interpenetrating polymer networks.

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