

# Preparation and Properties of High Performance Phthalide-Containing Bismaleimide Modified Epoxy Matrices

Xuhai Xiong,<sup>1</sup> Ping Chen,<sup>1,2</sup> Jinxiang Zhang,<sup>1</sup> Qi Yu,<sup>2</sup> Baichen Wang<sup>2</sup>

<sup>1</sup>State Key Laboratory of Fine Chemicals, Department of Polymer Science and Materials, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

<sup>2</sup>Liaoning Key Laboratory of Advanced Polymer Matrix Composites Manufacturing Technology, Department of Polymer Science and Engineering, Shenyang Aerospace University, Shenyang 110136, China

Received 15 June 2010; accepted 20 October 2010

DOI 10.1002/app.33588

Published online 6 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A series of intercrosslinked networks formed by diglycidyl ether of bisphenol A epoxy resin (DGEBA) and novel bismaleimide containing phthalide cardo structure (BMIPP), with 4,4'-diamino diphenyl sulfone (DDS) as hardener, have been investigated in detail. The curing behavior, thermal, mechanical and physical properties and compatibility of the blends were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), notched Izod impact test, scanning electron microscopy (SEM) and water absorption test. DSC investigations showed that the exothermic transition temperature ( $T_p$ ) of the blend systems shifted slightly to the higher temperature with increasing BMIPP content and there appeared a shoulder on the high-temperature side of the exothermic peak when BMIPP content was above

15 wt %. TGA and DMA results indicated that the introduction of BMIPP into epoxy resin improved the thermal stability and the storage modulus ( $G'$ ) in the glassy region while glass transition temperature ( $T_g$ ) decreased. Compared with the unmodified epoxy resin, there was a moderate increase in the fracture toughness for modified resins and the blend containing 5 wt % of BMIPP had the maximum of impact strength. SEM suggested the formation of homogeneous networks and rougher fracture surface with an increase in BMIPP content. In addition, the equilibrium water uptake of the modified resins was reduced as BMIPP content increased. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3122–3130, 2011

**Key words:** epoxy resin; bismaleimide; blends; thermal properties; fracture toughness

## INTRODUCTION

Epoxy resins, one of the most important classes of high-performance thermosetting polymers, present the attractive characteristics of high mechanical strength, excellent chemical and corrosion resistance, good dimensional stability, and high service temperature. They are widely used in such diverse applications, which range from laminated circuit boards, electronic component encapsulations, surface coatings, rigid foams, structural adhesives, and fiber-reinforced composites.<sup>1–6</sup>

However, the highly crosslinked microstructure leads to low fracture toughness and poor resistance to crack propagation. In addition, the relatively high

moisture absorption also seriously affects their mechanical and dielectric performances.<sup>7–10</sup> To meet many end-use applications, the modification of epoxy resins has become increasingly important. The conventional techniques of improving the toughness of epoxy resins are to incorporate a second microphase of dispersed elastomers or thermoplastics.<sup>4–6,11–14</sup> Unfortunately, the incorporation of reactive low molecular weight elastomers into epoxy resin may effectively improve impact strength at the expense of tensile strength and flexural modulus. The addition of engineering thermoplastics has been demonstrated to yield improved toughness of epoxy without a loss in modulus or strength, but increases the viscosity of mixture system, resulting in a processability penalty.<sup>15</sup> Recently, it is found the formulation of thermoset-thermoset blends may be promising approach, which could balance the advantages and disadvantages of both components. For example, the incorporation of a bismaleimide (4,4'-bismaleimidodiphenylmethane) into epoxy (tetraglycidyl diaminodiphenyl methane) system may reduce its water uptake at equilibrium and enhance hygrothermal and thermomechanical properties, especially, resulting polymer "alloy" may have a higher

Correspondence to: P. Chen (chenping\_898@126.com).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50703024.

Contract grant sponsor: Liaoning Provincial Science and Technology Plan Project; contract grant number: 2007403009.

Contract grant sponsor: Innovative Research Team Program (University of Liaoning Education Department); contract grant number: LT2010083.

fracture toughness than individual components owing to possible formation of interpenetrating or interlocking networks.<sup>10,16,17</sup>

Bismaleimide (BMI) resins, an important class of addition polyimides, possess an advantageous combination of properties. They can provide a higher service temperature than epoxies, while maintaining epoxy-like processing. Many efforts have been devoted to incorporating bismaleimide into various epoxy systems to obtain improved matrices. Chandra et al.<sup>18</sup> investigated the effect of bismaleimide on the curing kinetics of epoxy-amine system. Vanaja and Rao<sup>19</sup> found the introduction of BMI into novolac epoxy could enhance the glass transition and thermal stability for their composites. Kumar et al.<sup>20</sup> developed intercrosslinked network of siliconized epoxy-1,3-bis(maleimido)benzene and found that incorporation of BMI into epoxy resin improved stress-strain properties with lowering of toughness. Mahesh et al.<sup>21</sup> synthesized a chain-extended bismaleimide containing ester linkage and added it into epoxy resin and polyurethane modified epoxy resin, resulting in the thermal stability and both tensile and flexural properties of the blends increased with increasing BMI content, but the impact strength and glass-transition temperature decreased. Dinakaran et al.<sup>22</sup> prepared bismaleimide/cyanate ester (CE)/epoxy ternary blend system and observed that the moisture resistance increased with increasing CE and BMI content.

In this study, modified epoxy matrices were developed by blending the epoxy resin (DGEBA) with a thermosetting bismaleimide containing phthalide cardo structure (BMIPP), using DDS as hardener. The curing characteristic, thermomechanical behavior, thermal stability, water uptake behavior, compatibility, and fracture toughness of the DGEBA/BMIPP/DDS blends were investigated.

## EXPERIMENTAL

### Materials

Commercially available diglycidylether of bisphenol A (DGEBA)-based epoxy resin, with an epoxy equivalent of about 185–210, was supplied by Wuxi Resin Works, China. The hardener used was 4,4'-diaminodiphenylsulfone (DDS) provided by Shanghai Huifeng Science and Trading Company (Shanghai, China). 3,3-Bis[4-(4-aminophenoxy)phenyl]phthalide (BAP) and its precursor were synthesized according to the reported procedure.<sup>23</sup> All other chemicals were of reagent grade and used directly.

### Preparation of 3,3-Bis[4-(4-maleimidophenoxy)phenyl]phthalide (BMIPP)

BMIPP was prepared as per reported method with some modifications.<sup>24</sup> To a solution of BAP

(0.06 mol) in acetone (150 mL) was added dropwise a solution of maleic anhydride (0.132 mol) in acetone (100 mL) in 1 h under stirring. After the addition, the reaction solution was stirred at room temperature for another 4 h to complete the reaction. And then the triethylamine (3.9 mL), sodium acetate (0.57 g) and acetic anhydride (13.4 mL) were added in sequence into the reaction vessel and the entire mixture was heated slowly to reflux. When the reaction system became transparent, gentle reflux was continued for an additional 6 h. The mixture was cooled to room temperature with stirring constantly and then poured into ice-water, stirring for 2 h. The precipitate was collected by suction filtration, dissolved in hot toluene and washed with a dilute solution of sodium bicarbonate. The organic layer was dried with anhydrous calcium chloride and then evaporated in a rotary evaporator. The resulting light yellow precipitate was obtained; 36.7 g (yield 88%).

IR (KBr,  $\text{cm}^{-1}$ ): 3097 (= C-H, maleimide ring), 1765 (C=O, lactone), 1716 (C=O, imide), 1396, 1145 (C-N-C, maleimide ring), 692 (C=C, maleimide ring). <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d, 1H,  $J = 7.6$  Hz, ArH), 7.74 (t, 1H,  $J = 7.5$  Hz, ArH), 7.58 (m, 2H, ArH), 7.30 (m, 8H, ArH), 7.09 (d, 4H,  $J = 8.9$  Hz, ArH), 7.01 (d, 4H,  $J = 8.8$  Hz, ArH), 6.85 (s, 4H, H-C = C-H).

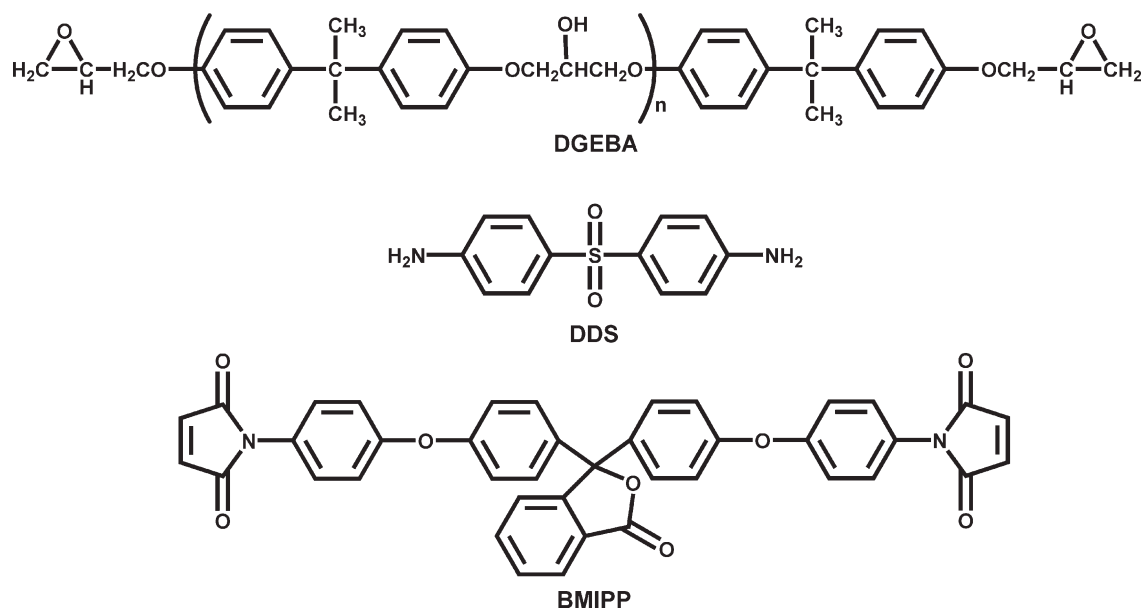
### Preparation of DGEBA/BMIPP/DDS blends

The structures of DGEBA, DDS and BMIPP are shown in Scheme 1. Cured DGEBA/BMIPP/DDS blend resins were prepared as follows: an appropriate amount of BMIPP was dissolved in an epoxy resin at 80°C, under vigorous stirring. After complete dissolution of BMIPP, stoichiometric amounts of DDS (with respect to epoxy) were thoroughly blended at 130°C for 15 min. All the mixtures was degassed at 130°C under vacuum to remove trapped air, and then poured directly into preheated (130°C) Teflon molds and thermally cured in an air convection oven at 150°C for 1 h, 180°C for 2 h, 200°C for 4 h plus a postcure period at 220°C for 2 h. Finally, the castings were removed from the mold and characterized. The compositions of the investigated mixtures are reported in Table I.

### Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-20DXB IR spectrophotometer using 32 scans at a resolution of 4 wave numbers. The prepolymers were prepared from solution as a film on a NaCl pellet and the cured samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks.

<sup>1</sup>H NMR were recorded on 400 MHz Varian INOVA NMR spectrometer, using deuterated chloroform as



Scheme 1 Chemical structures of DGEBA, DDS, and BMIPP.

the solvent with tetramethylsilane (TMS) as an internal reference. Chemical shifts ( $\delta$ ) are reported in ppm scale.

Differential scanning calorimetry (DSC) measurements were conducted with an NETZSCH DSC 204 instrument. The calorimeter was calibrated with indium metal (99.99% pure) as a standard. About 5–7 mg samples were used at a heating rate of 10°C/min under a flow of nitrogen (20 mL/min).

Dynamic mechanical analysis (DMA) was done on a TA Instruments Q800 DMA with an amplitude of 20  $\mu$ m, driving frequency of 1.0 Hz, and a temperature ramp rate of 3°C/min in nitrogen atmosphere. The specimens were cut to dimensions of 35 mm  $\times$  6 mm  $\times$  2.5 mm for the single cantilever mode.

Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA-7 thermal analyzer in purified nitrogen and all samples (around 5 mg) were heated from 25 to 600°C at a heating rate of 20°C/min, under the gas flow rate of 60 mL/min.

The fracture toughness of the cured epoxy resins was evaluated from the impact strength according to the GB/T 1843-1996. The tests were performed on the Izod impact testing machines (XJ-40A).

The fracture surfaces of impact specimens were analyzed by SEM (QUANTA200, FEI). The specimens were adhered to a SEM mount with conductive adhesive. The microscope was operated under 60 Pa with accelerating voltage of 25 kV.

The water absorption rates were measured as follows: the sample, in the form of disk (20 mm in diameter and 2.5 mm in thickness), was dried *in vacuo* at 130°C until constant weight. Then the dried sample was immersed in a jar full of deionized water at desired temperature and periodically

removed from the water, wiped down, and quickly weighed to an accuracy of 0.1 mg. The percentage of water absorbed by the specimens is calculated using the equation given below:

$$\% \text{ Increase in weight} = (W_t - W_0)/W_0 \times 100 \quad (1)$$

where  $W_0$  is the weight of the dry specimen and  $W_t$  is the weight of the wet specimen at time  $t$ .

## RESULTS AND DISCUSSION

### FTIR spectral analysis

Figure 1 shows the FTIR spectra of prepolymer mixtures with 0 and 20 wt % of BMIPP. In comparison

TABLE I  
Composition and Thermal Properties of DGEBA/BMIPP/DDS Blends

BMIPP content (wt %)	Code	$T_i^a$ (°C)	$T_{p1}^b$ (°C)	$T_{p2}^b$ (°C)	$\Delta H_1^c$ (J/g)	$\Delta H_2^d$ (J/g)	$T_{g1}^e$ (°C)	$T_{g2}^f$ (°C)
0	P-0	178	223	–	331	–	217	228
5	P-5	181	227	–	321	–	206	–
10	P-10	183	229	–	244	–	202	–
15	P-15	184	230	326	258	4.0	199	–
20	P-20	187	231	320	309	9.1	189	213

<sup>a</sup> The initial curing temperature.

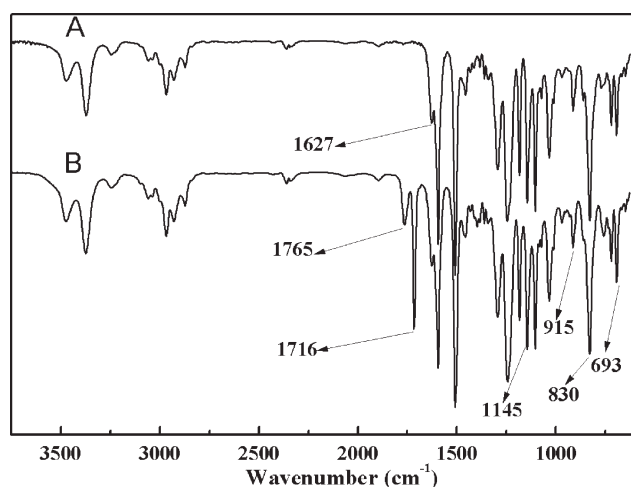
<sup>b</sup> The exothermic transition temperature.

<sup>c</sup> Total heat of cure reaction of the prepolymers.

<sup>d</sup> Total heat of cure reaction of the cured resins.

<sup>e</sup> Glass transition temperature of the cured resins by from DSC.

<sup>f</sup> Glass transition temperature of the cured resins (post-cured at 220°C for 10h) from DSC.



**Figure 1** IR spectra of DGEBA/BMIPP/DDS prepolymers with 0 wt % (curve A) and 20 wt % (curve B) of BMIPP.

with curves A, the remarkable difference of curves B is the appearance of new absorption bands at 1765 and 1716  $\text{cm}^{-1}$ , which are associated with the carbonyls of lactone group and of maleimide group, respectively. These peaks provide strong evidence for the presence of bismaleimide containing phthalide structure.

As shown in Figure 2, the typical infrared spectra of cured resins exhibit several distinctive differences from that of the corresponding prepolymer resins. In the wave-number range 4000–3200  $\text{cm}^{-1}$  the well resolved doublet at 3475 and 3375  $\text{cm}^{-1}$ , which is due to the asymmetric and symmetric stretching vibration of the  $\text{NH}_2$  group, respectively, is replaced by a broad absorption band in the range 3600–3200  $\text{cm}^{-1}$  maybe due to the formation of hydroxyl group after curing. Especially, the first overtone of the  $\delta$  ( $\text{NH}_2$ ) fundamental at 1627  $\text{cm}^{-1}$ , which appears as a shoulder of the aromatic absorption at 1612  $\text{cm}^{-1}$ , completely disappears thus confirming that the primary amine groups reacts to full conversion.<sup>10</sup>

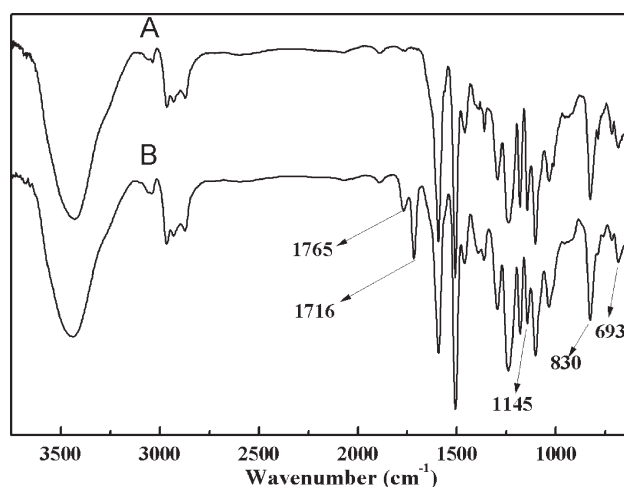
The medium peak at about 915  $\text{cm}^{-1}$  is considered as the characteristic absorption band of oxirane ring.<sup>10</sup> Compared with traces A and B in Figure 1, two curves in Figure 2 show the intensity of characteristic peak for the epoxy group decreases sharply and becomes negligible after curing thermally. This fact verifies that epoxy groups in both neat epoxy and blend systems almost completely react.

Although there are some diagnostic absorption bands which are often employed to monitor the BMI polymerization, it is still difficult to determine the conversion of unsaturated bond of bismaleimide in the systems under consideration by FTIR. Because the weak peak at around 3097  $\text{cm}^{-1}$ , ascribed to the C–H stretching mode of the double bond of the bismaleimide, appears as a shoulder of the aromatic C–H absorption at 3035 and 3057  $\text{cm}^{-1}$  and is

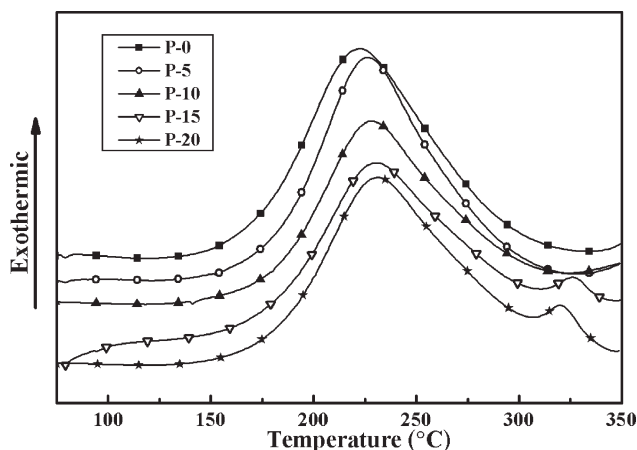
poorly resolved from the complex profile (see Fig. 1). The sharp and medium intensity peaks at 830 and 693  $\text{cm}^{-1}$ , attributable respectively, to the out-of-plane bending of the C–H of maleimide unit and in-plane deformation vibration of maleimide ring, are apparently ideal objects investigated.<sup>10</sup> Unfortunately, based on a comparison of traces A and B (Figs. 1 and 2), we found that unmodified epoxy system also has absorption at around 829 and 693  $\text{cm}^{-1}$ , whose intensity undergoes a dramatic decrease upon curing. Thus both are overlapping bands and can not be used directly to analyze the conversion of double bond. Another peak located at 1145  $\text{cm}^{-1}$ , attributed to the asymmetric stretching the C–N–C of the maleimide group, is also suitable for polymerization investigation for its perfect profile. However, it suffers from the interference of a strong absorption at 1147  $\text{cm}^{-1}$  produced by sulfonyl group. But the DSC scans of all cured blend resins do not exhibit obvious exothermic transition, indicating the almost complete conversion of the unsaturated bond.

### DSC analysis

DSC is an important thermal analysis technique that measures the heat flow change of a material as a function of temperature or time, and is widely used in investigating curing behavior of thermosetting resin.<sup>1</sup> Herein, the reactivity of the DGEBA : DDS (1 : 1 stoichiometry)/BMIPP blending systems, containing five different concentrations (0–20 wt %) of BMIPP, were characterized by DSC at a heating rate of 10°C/min under a nitrogen atmosphere. The DSC traces are shown in Figure 3 and analytical results are tabulated in Table I. There is only one exothermic transition associated with curing when the BMIPP content varies from 0 to 10 wt %. However, with increased BMIPP content above 15 wt %,



**Figure 2** IR spectra of cured DGEBA/BMIPP/DDS resins with 0 wt % (curve A) and 20 wt % (curve B) of BMIPP.



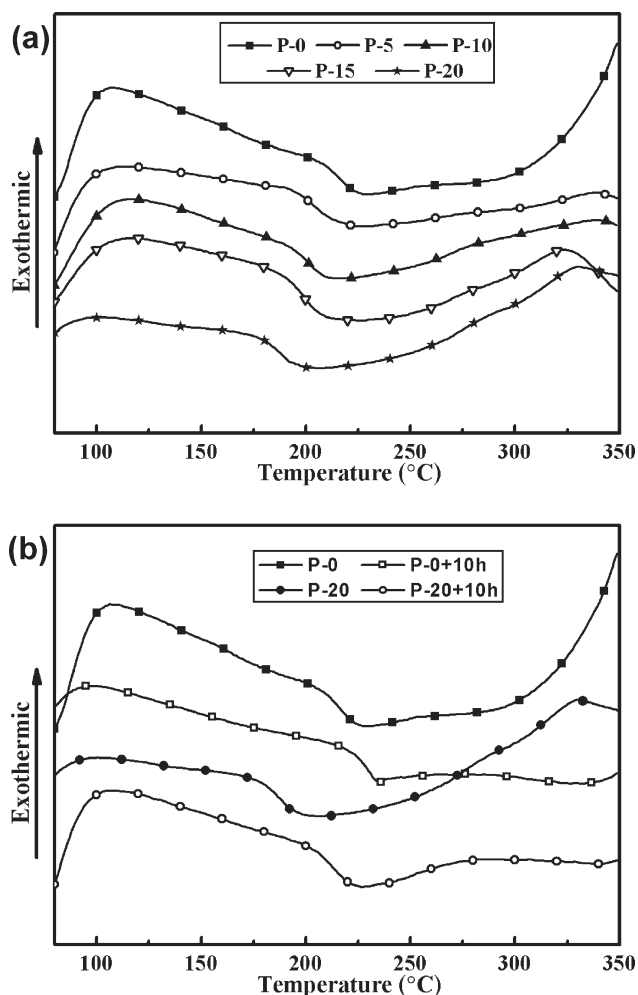
**Figure 3** DSC traces of DGEBA/BMIPP/DDS prepolymers (10°C/min, N<sub>2</sub>).

a shoulder is formed on the high-temperature side of the exothermic peak, indicating that the sample experiences a two-stage exothermic reaction. In contrast with that of blending system at 15 wt % BMIPP content, the second exothermic peak of the blending with 20 wt % BMIPP content can occur at relatively lower temperature. Another, as the amount of BMIPP increases, the main exothermic peaks shift slightly toward a higher temperature. On the other hand, the enthalpy of reaction initially decreases, passes through a minimum and then increases with increasing BMIPP concentration.

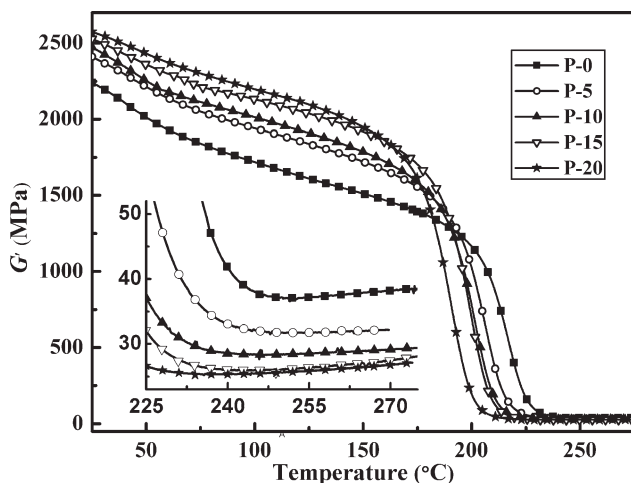
To study the reason for the aforementioned phenomena, it is important to understand what types of chemical reaction occur in the cure process. As is well known, there are usually five types of reactions in the epoxy/amine/bismaleimide system including reactions between the epoxy ring and primary amines for producing chain growth and secondary amines for building chain branches, etherification of epoxy rings in the absence of active *N*-H functionality, homopolymerization of bismaleimides and Michael-addition reaction between diamine and bismaleimide.<sup>18–20</sup> The shoulders, presented on the DSC traces of blend system with higher BMIPP concentration, may be ascribed to the occurrence of etherification reaction when BMIPP reacts with DDS leading to the deficiency of hardener.<sup>3</sup> The higher content of BMIPP results in the more deficiency of *N*-H functionality and the etherification reaction shall take place at relatively lower temperature. The phenomena for the enthalpy of reaction, which shows vee-shaped trace with increasing BMIPP concentration, may be because that heats of reaction between epoxy group and primary or secondary amine and etherification of epoxy ring are larger than that of Michael-addition reaction between diamine and bismaleimide and homopolymerization of bismaleimides.<sup>1,16</sup> When the BMIPP content is

below 10 wt %, the homopolymerization and Michael-addition reaction of BMIPP decrease the enthalpy of the overall reaction; however, when BMIPP content exceeds 10 wt %, the heat generated by etherification of epoxy rings becomes prominent and it drives a rapid increase in the total enthalpy. This assumption was confirmed by the observation that the heat of reaction of the blend system containing 20 wt % of BMIPP decreased when DDS content was increased.

The glass transition temperature ( $T_g$ ) is one of the most important structural and technical characteristics of amorphous solids.<sup>2</sup> The DSC scans of the cured networks can provide the information about the glass transition temperature ( $T_g$ ) which is determined from the characteristic discontinuity in heat capacity.<sup>1</sup> From Figure 4(a) and Table I, a single  $T_g$  is obtained for each cured blend and shifts to lower temperatures with increasing BMIPP content. Generally, the observation of a single  $T_g$  indicates the existence of a unique amorphous phase. In addition,



**Figure 4** DSC traces of cured DGEBA/BMIPP/DDS resins: (a) comparison of  $T_g$ s for various cured resins; (b) comparison of  $T_g$ s for cured resins untreated and treated by post-cure treatment at 220°C for another 10 h.



**Figure 5** Storage modulus for various cured DGEBA/BMIPP/DDS resins.

when the amount of BMIPP is more than 15 wt %, there appears a small exothermic peak in the high-temperature region which may be attributed to the reaction of residual unreacted group such as epoxy group trapped into the glassy polymeric network. The residual heat of reaction (listed in Table I) was calculated from the area under the residual exotherm of the cured samples, and the state of cure,  $\alpha$ , was assessed according to the following equation:<sup>25</sup>

$$\alpha = \frac{H_t - H_r}{H_t} \quad (2)$$

where  $H_t$  is the total heat of reaction for uncured samples and  $H_r$  the residual heat of reaction of cured samples. The systems modified with 15 and 20 wt % of BMIPP reach respectively, 97 and 98% of conversion. This indicates presence of tiny amounts of unreacted groups in networks with higher BMIPP content, which may be responsible for the marked decrease in  $T_g$  values. To elucidate whether above-mentioned phenomenon is only factor which decreases the  $T_g$ , the cured samples with 0 wt % and 20 wt % BMIPP content (P-0 and P-20) were post-cured at 220°C for another 10 h (code: P-0 + 10h and P-20 + 10, respectively) and then the  $T_g$ s thereof were measured [Fig. 4(b)] and listed in Table I. Compared with that of the corresponding untreated cured resins, the  $T_g$ s of network containing 0 wt % and 20 wt % BMIPP increase from 217 to 228°C and from 189 to 213°C, respectively. The increase in  $T_g$  of unmodified cured epoxy resin may be due to some reorganization of the glassy network and of 20 wt % BMIPP cured blend resin may be mainly ascribed to the increase of the crosslink density resulting from reaction of residual reactive groups as well as network regulation.<sup>2</sup> Observably,  $T_g$  of completely cured resin with 20 wt % of BMIPP is still lower

than that of unmodified epoxy resin. This undoubtedly implies that addition of BMIPP reduces the crosslink density of the blend resins.

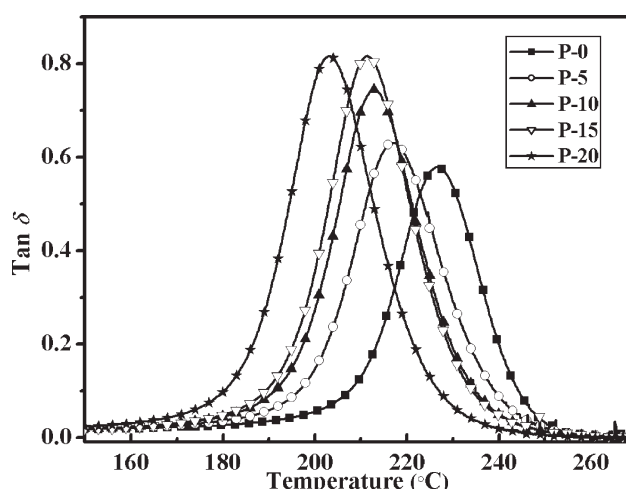
### DMA studies

The load capacity of polymeric materials at elevated temperature is one of the key aspects of high performance material. In this study, dynamic mechanical analysis (DMA) was employed to monitor the temperature dependence of the stiffness and mechanical damping of cured networks with various BMIPP concentrations, and the dynamic mechanical spectra in terms of storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) are reported in Figures 5 and 6, respectively.

The  $G'$ - $T$  plot offers a valuable insight into the stiffness of the sample as a function of temperature. From Figure 5, it can be seen that all composites exhibit only one-step decrease in storage modulus, indicating occurrence of just one physical transition in polymers. The  $G'$ s in the glassy region increase with the increased BMIPP content. This may be attributed to the special features in the chemical structure of BMIPP, which contains bulky phthalide moiety and imide ring. The incorporation of rigid heterocyclic structure into the crosslinked network leads to an increase in segment stiffness and packing density, thus increasing the modulus. Additionally, the  $G'$ s in the rubbery plateau region, which do not vary with temperature, decrease as BMIPP content in the networks is increased. The crosslink density of polymer network ( $\rho$ ) is calculated according to the rubber elasticity theory as follows<sup>26</sup>:

$$\rho = G'/3RT \quad (3)$$

where  $G'$  is the storage modulus at  $T_g + 50^\circ\text{C}$ ,  $R$  is the gas constant,  $T$  is the absolute temperature at



**Figure 6** Damping factors ( $\tan \delta$ ) for various cured DGEBA/BMIPP/DDS resins.

**TABLE II**  
DMA and TGA Measurement Results of DGEBA/  
BMIPP/DDS Blends

Code	Storage modulus (Mpa)		$T_g^c$ (°C)	$\rho \times 10^3$ (mol/cm <sup>3</sup> )	tan $\delta^d$	$T_{5\%}$ (°C)	RW <sup>e</sup> (%)
	Glass Region <sup>a</sup>	Rubber region <sup>b</sup>					
P-0	2201	38.2	227	2.77	0.58	372	11.8
P-5	2372	32.1	217	2.38	0.63	391	13.2
P-10	2431	28.9	214	2.16	0.74	393	14.7
P-15	2496	26.9	212	2.02	0.82	395	17.6
P-20	2548	25.8	203	1.97	0.82	396	20.4

<sup>a</sup> Storage modulus at 30°C.

<sup>b</sup> Storage modulus at  $T_g + 50$  °C

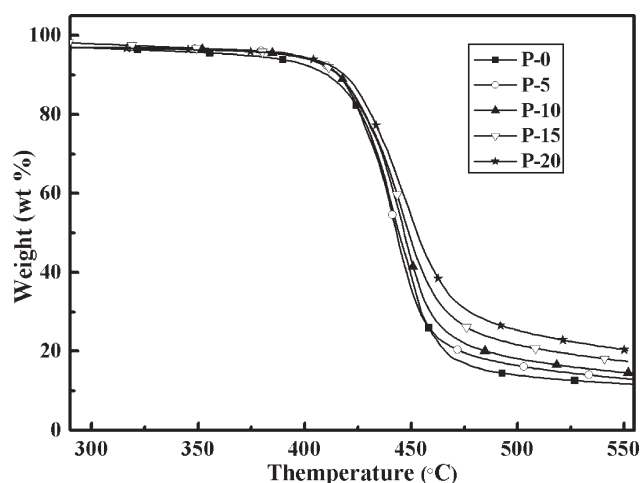
<sup>c</sup> Glass transition temperature from DMA.

<sup>d</sup> Maximum value of tan  $\delta$ .

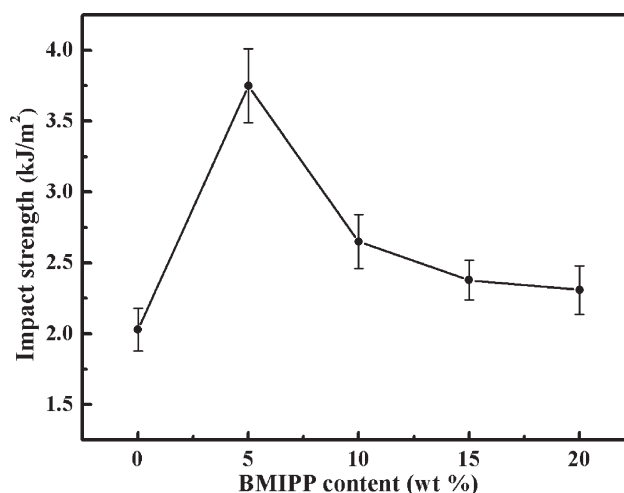
<sup>e</sup> RW refers to the residual weight percentage at 550°C.

$T_g + 50$ °C. The results of  $T_g$ s, storage modulus at both below and above  $T_g$ , and crosslink density are summarized in Table II.

Figure 6 shows the temperature dependence of tan  $\delta$  for all cured resins. There is a single, sharp, and symmetrical relaxation peak for each trace, suggesting homogeneity of all epoxy-bismaleimide networks. Providing the temperature at the maximum of tan  $\delta$  peak is identified as the glass transition temperature ( $T_g$ ),  $T_g$ s decrease with an increase in the concentration of BMIPP. The 20% blend system exhibits the lowest value (203°C) and 24°C lower than unmodified epoxy system. These observations are in contradiction with that reported previously in the literature, where the  $T_g$  increases with the bismaleimide content.<sup>19,20</sup> The reported explanation is that the enhanced  $T_g$  is attributed to the homopolymerization of BMI, which produces higher crosslink density network. However, we speculate Michael addition reaction of BMIPP with DDS may



**Figure 7** Dynamic TGA behavior for various cured DGEBA/BMIPP/DDS resins (20°C/min, N<sub>2</sub>).



**Figure 8** Impact strength of cured DGEBA/BMIPP/DDS resins versus BMIPP concentration.

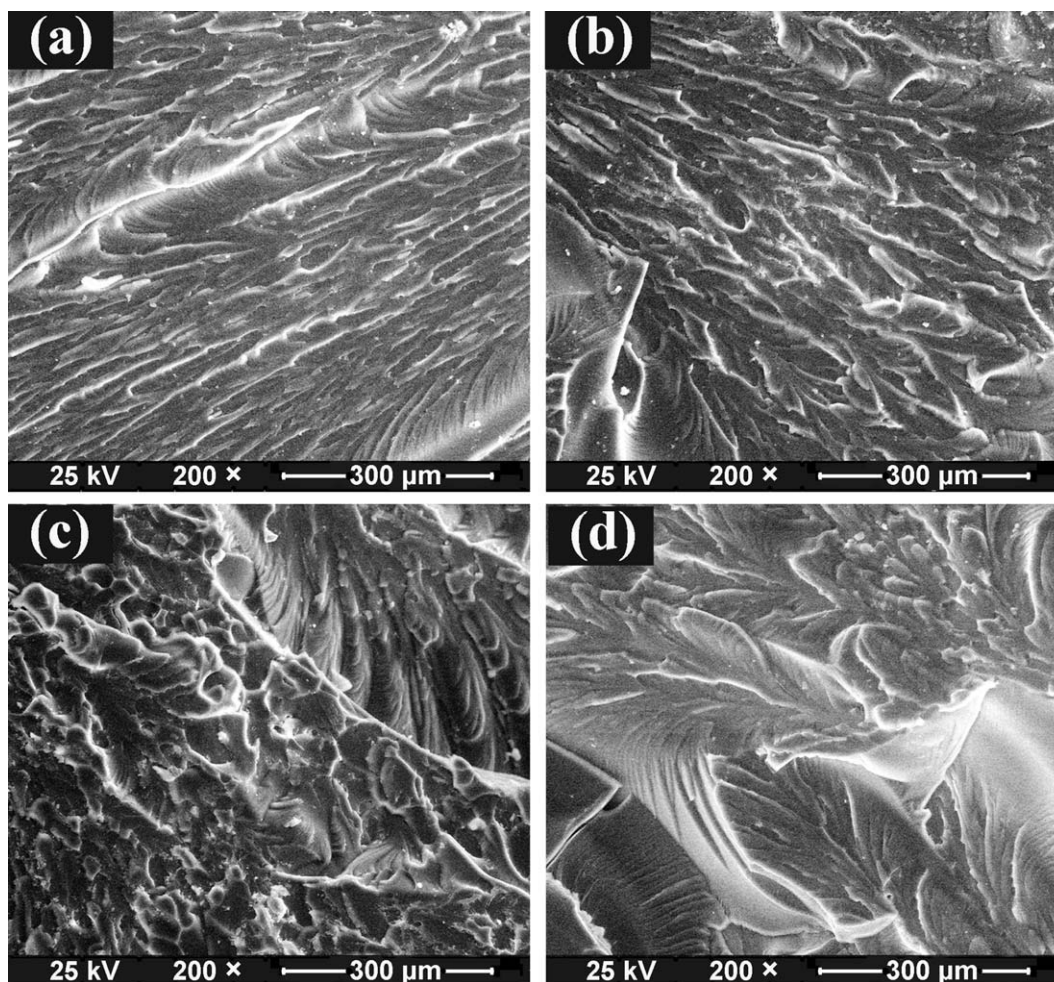
be prevailing in the blend systems investigated, due to lower reactivity for homopolymerization of BMIPP, longer curing time at low-temperature and bulky molecular structure restricting motion of the reactive site. Three factors disfavor radical polymerization of BMIPP double bond. On the other hand, the Michael addition reaction can lead to a decrease in crosslink density, which is consistent with the calculated results based on the theory of rubber elasticity.

### TGA results

The thermal stability of DGEBA/BMIPP/DDS blends was investigated by TGA (see Fig. 7). The thermogravimetry curves of these resins were characterized in terms of onset decomposition temperature ( $T_{5\%}$ ) and char yield at 550°C. The results of TGA are summarized in Table II. From an inspection of the TGA thermograms in Figure 7, the  $T_{5\%}$  values for the cured blends are all above 390°C and higher than that for the neat DGEBA/DDS resin (372°C) and the char yield at 550°C increase with increasing BMIPP concentration in the blending system. These demonstrate the incorporation of BMIPP into epoxy-amine system can improve thermal stability of the resultant cured products. Evidently, the strong heat-resistant phthalide cardo and cyclic maleimide structures of BMIPP are responsible for the increased thermal degradation temperature.

### Fracture toughness and morphology investigation

The fracture toughness is the resistance of a material to crack initiation and propagation. In the present case, the fracture toughness of the blends, expressed as notched impact strength, is plotted in Figure 8 as the function of the BMIPP concentration. It can be seen that the addition of BMIPP can moderately



**Figure 9** SEM of the fracture surface of DGEBA/BMIPP/DDS resins: (a) 0 wt % BMIPP; (b) 5 wt % BMIPP; (c) 15 wt % BMIPP; (d) 20 wt % BMIPP.

enhance the toughness of cured epoxy resin and the maximum impact strength value of modified epoxy resins appears at 5 wt % of BMIPP. The phenomena may be explained in term of the crosslink density. Generally, the crosslink density has a great influence on the toughening, and the toughness shows a maximum for intermediate crosslink density.<sup>27</sup> The result of fracture toughness also testify the main reaction associated with the BMIPP is Michael addition reaction which may reduce the crosslink density of the cured networks due to chain extension. Moreover, fracture initiation in glassy networks is in some way connected with the concentration of chemical defects (unreacted groups), which are likely to take part in embrittlement of the glassy polymers.<sup>2</sup> In sum, compared with the other modified epoxy systems, the 5 wt % BMIPP modified system should have a moderate crosslink density and less chemical defects.

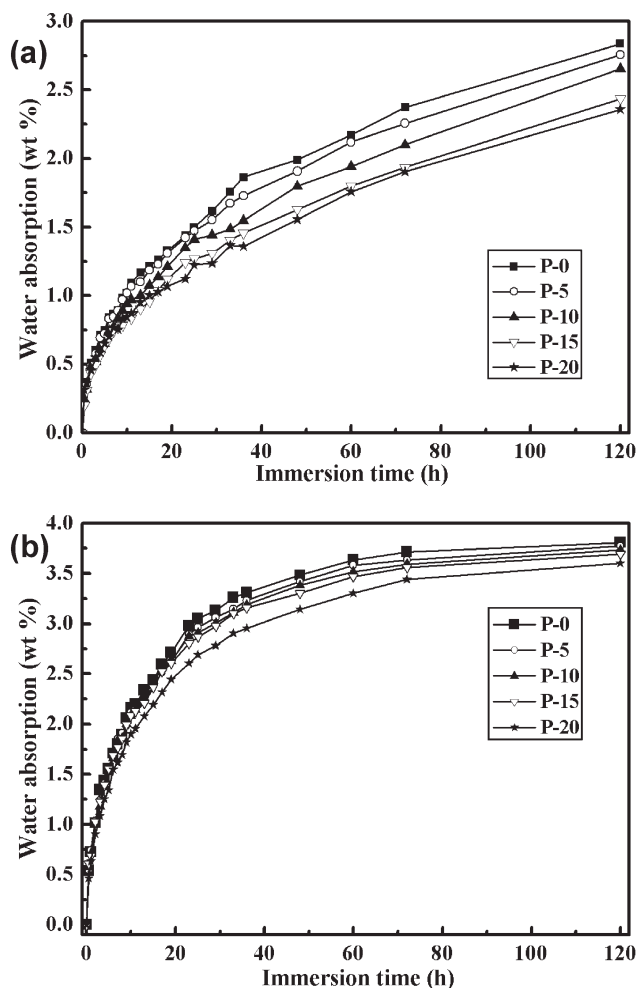
The morphologies of the impact fracture surface of blend systems (Fig. 9) were examined using the scanning electron microscope (SEM). As shown in

Figure 9(a), the SEM image of the fracture surface of the unmodified epoxy system reveals a glass, homogeneous microstructure without any plastic deformation. By comparison, the BMIPP-modified epoxy systems [Figure 9(b-d)] exhibit rougher fracture surface with increasing BMIPP content, indicating the transition to ductile fracture. But no phase domains of two components are observed in the SEM micrographs of all formulation, which indicates that the various networks derived from BMIPP are compatible with epoxy system.

#### Water absorption behavior

The absorption and diffusion of water in epoxy resin has been the focus of interest, because the absorbed water has a profound impact on the properties of cured products. It was reported that the absorbed moisture, acting as a very effective plasticizer, decreased the strength and elastic modulus, substantially lowered the glass transition point and strongly deteriorated the dielectric properties.<sup>28</sup> Therefore,





**Figure 10** Water absorption curves against time at 50°C (a) and 100°C (b) for cured DGEBA/BMIPP/DDS resins.

extensive research effort has been dedicated to the modification of epoxy resins to reduce their water uptake.<sup>10,22,29</sup> The water absorption curves of the cured blend resins, tested at 50°C and 100°C, are presented in Figure 10 as a function of immersion time. As seen from both Figure 10(a,b), the equilibrium water content and the initial rate of water absorption decrease as BMIPP content is increased. Furthermore, water absorption at 100°C varies slightly with BMIPP content, while for water absorption at 50°C the variation is much more evident. This suggests the incorporation of BMIPP may enhance hydrophobic nature of epoxy resin, especially at lower temperature.

## CONCLUSIONS

Phthalide-containing BMIPP-modified epoxy resins with various concentrations of BMIPP were developed. DSC investigations of the blend prepolymers revealed that exothermic transition temperature ( $T_p$ )

slightly increased as the weight ratio of BMIPP increased. When the weight ratio of BMIPP rose above 15 wt %, a shoulder appeared on the high-temperature side of the main exothermic peak. On the other hand, only one obvious glass transition ( $T_g$ ) was observed from DSC scan of the resulting cured resin in the temperature range from 50 to 350°C, indicating the formation of highly crosslinking homogeneous networks, and the  $T_g$ s decreased with the content of BMIPP, possibly suggesting that the main reaction which BMIPP participated in was Michael addition reaction rather than homopolymerization. Dynamic mechanical analysis of the cured DGEBA/BMIPP/DDS blends exhibited that the glassy modulus increased as the BMIPP content increased. TGA investigations showed thermal stability of the cured blend resins was improved markedly in the presence of BMIPP. Microscopy investigation also revealed BMIPP modified networks showed homogeneous morphology and the fracture surface became rougher with increasing BMIPP content. The water absorption measurements conducted at 50°C and 100°C showed that the presence of the BMIPP component decreased the equilibrium water content.

## References

- Barton, J. M. *Adv Polym Sci* 1985, 72, 111.
- Oleinik, E. F. *Adv Polym Sci* 1980, 80, 49.
- Dyakonov, T.; Chen, Y. *Polym Degrad Stabil* 1996, 53, 217.
- Ratna, D.; Banthia, A. K. *Polym Eng Sci* 2007, 47, 26.
- Shukla, S. K.; Srivastava, D. *J Mater Sci* 2007, 42, 3215.
- Ben, S. A. B.; Mohd, I. Z. A. *J Phys Sci* 2009, 20, 1.
- Glaskova, T.; Aniskevich, A. *Compos Sci Technol* 2009, 69, 2711.
- Shenoy, M. A.; Patil, M.; Shetty, A. *Polym Eng Sci* 2007, 47, 1881.
- Lin, Y. C.; Chen, X. *Chem Phys Lett* 2005, 412, 322.
- Musto, P.; Martuscelli, E. *J Appl Polym Sci* 1998, 69, 1029.
- Francis, B.; Thomas, S. *Colloid Polym Sci* 2006, 285, 83.
- Parzuchowski, P. G.; Rokicki, G. *Polymer* 2007, 48, 1857.
- Pasquale, G. D.; Motta, O. *Polymer* 1997, 38, 4345.
- Cherian, A. B.; Varghese, L. A. *Euro Polym J* 2007, 43, 1460.
- Robeson, L. M. *Polymer Blends*; Carl Hanser Verlag: Munich, 2007; Chapter 4, p.188.
- Woo, E. M.; Chen, L. B. *J Mater Sci* 1987, 22, 3665.
- Lin, K. F.; Chen, J. C. *Polym Eng Sci* 1996, 36, 211.
- Chandra, R.; Rajabi, L. *J Appl Polym Sci* 1996, 62, 661.
- Vanaja, A.; Rao, R. M. V. G. K. *Euro Polym J* 2002, 38, 187.
- Kumar, A. A.; Alagar, M. *Polymer* 2002, 43, 693.
- Mahesh, K. P. O.; Alagar, M. *J Appl Polym Sci* 2003, 87, 1562.
- Dinakaran, K.; Alagar, M. *Euro Polym J* 2003, 39, 2225.
- Yang, C. P.; Tang, S. Y. *J Polym Sci A: Polym Chem* 1999, 37, 455.
- Xiong, X. H.; Chen, P. *Polym Int* 2010, 59, 1665.
- Huang, M. L.; Williams, J. G. *Macromolecules* 1994, 27, 7423.
- Zhang, B. F.; Wang, Z. G. *Polymer* 2009, 50, 817.
- He, S. J.; Shi, K. Y. *Polymer* 2001, 42, 9641.
- Musto, P.; Ragosta, G. *J Polym Sci Part B: Polym Phys* 2002, 40, 922.
- Abdelkader, A. F.; White, J. R. *J Appl Polym Sci* 2005, 98, 2544.