

Curing Behavior and Properties of the Cured Resin Based on Bismaleimide, Bisoxazoline, and Oleic Acid Ternary Copolymer

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ABSTRACT: The curing behavior and properties of bismaleimide (BMI), bisoxazoline (1,3-PBO), and oleic acid ternary copolymers are investigated. It is found that the cure temperature of BMI/1,3-PBO or BMI/1,3-PBO/oleic acid could be lowered, compared with that of BMI. The reason lies in the copolymerization reaction between BMI, 1,3-PBO, and oleic acid. SEM results confirm that 1,3-PBO and oleic acid could toughen BMI system because of the formation of

ester–amide bonds and the long fat chain of oleic acid. The cured resins from BMI/1,3-PBO or BMI/1,3-PBO/oleic acid have superior heat resistance and water resistance. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2321–2327, 2008

Key words: bismaleimide; 1,3-phenylene bisoxazoline; curing behavior; properties; copolymerization; FTIR; gelation; resins

INTRODUCTION

Bismaleimide (BMI) resins are one of the most important thermosetting polymers for high performance resin matrix because of their high heat resistance, thermal oxidative stability, and outstanding mechanical properties.¹ However, unmodified BMI resins suffer from brittleness and poor processability because of their high crosslinking densities after curing, poor solubility, and narrow processing window.^{2–4} To overcome the shortcomings, many modification methods have been reported to improve the processability and toughness of BMI in the published literature. These modified methods mainly include (1) synthesis of BMI with flexible or long segments in the backbone,^{5,6} (2) aromatic diamine reaction with BMI via the Michael addition reaction,^{7–9} (3) copolymerization of BMI with allyl compounds,^{10–12} (4) blending BMI with epoxy,^{13–15} aromatic dicyanate ester,^{16,17} and unsaturated polyester,¹⁸ and (5) copolymerization of BMI with olefinic compounds through Diels–Alder reaction.^{19,20} In the above methods, the reactions of BMI with other reactive monomers (for example, allyl amine, diallyl bisphenol A, styrene, and so on) were investigated in detail. The spontaneous reaction between BMI and 2-ethyl-2-oxazoline

also has been reported by Wilson and Huang.^{21–23} It was found that the initiation is spontaneous due to the formation of zwitterions by interaction of two monomers as shown in Figure 1.

However, this reaction has not so well been investigated for improving the processability and toughness of BMI by the addition of bisoxazoline. 2,2'-(1,3-Phenylene)-bis (4,5-dihydro-oxazolines) (i.e., 1,3-PBO), a member of oxazoline family, has a aromatic structure with two oxazoline rings. The aromatic structure of 1,3-PBO is propitious to retain the heat resistance of the modified system, and two oxazoline rings of 1,3-PBO are used to extend chain or crosslink due to high activity. It has been reported that 1,3-PBO can decrease the melt viscosity of benzoxazine or its oligomers system, increase the heat resistance of the system, and improve the toughness of the cured resin.^{24–26}

Because there was spontaneous reaction between BMI and oxazoline, introduction of flexible linkage or chain into BMI can be achieved by the addition of 1,3-PBO to BMI. Oleic acid, which presents long flexible chain and reactive groups (C=C double bond and –COOH), can copolymerize with BMI or 1,3-PBO. Our attempt is to improve the processability and toughness of BMI by ternary copolymerization of BMI, 1,3-PBO and oleic acid although keeping their good heat resistance. The present article focuses on the curing behavior of BMI with 1,3-PBO and oleic acid. Some properties were also investigated.

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EXPERIMENTAL

Materials

N,N'-bismaleimido-4,4'-diaryl methane (BMI) was supplied by HuBei Fengguang Chemicals (China). Ethanolamine, zinc acetate, 1,3-dicyanobenzene, ammonia, ethanol were purchased from Shanghai First Reagent Company, China. All chemicals were AR grade and used without further purification.

Synthesis of 1,3-PBO

Synthesis of 1,3-PBO was carried out according to the method described by Li and Wang²⁶ as shown in Figure 2. The product was recrystallized from ethanol (with a yield of about 90%). The structure of 1,3-PBO was confirmed by NMR: δ 8.42, 8.03–8.05, 7.41–7.46 (Ar–H); δ 4.39–4.45 (O–CH₂); δ 4.02–4.08 (N–CH₂).

Preparation of cured resin

Appropriate amounts of BMI and 1,3-PBO were placed in a flask equipped with a mechanical stirrer and thermometer. The mixture was heated to 90–120°C and maintained in this temperature range with stirring till a clear brown homogeneous liquid was obtained. Then the molten mixture was variously step post cured at 170°C for 2 h, 190°C for 2 h, 220°C for 2 h, 250°C for 2 h.²¹

Measurements

Viscosities of samples were measured with a Brookfield model DV-II Viscometer with the thermal furnace and temperature controller, spindle 21#, variable speed dependent of the viscosity to ensure that the digit reader was in effective range. Gel time was measured with a spatula on a heated steel plate. The steel plate and spatula were heated to a controlled temperature. Approximately 1 g of sample was put on the steel plate and spread to a disk with the spatula. Then, the sample was kneaded by pressing it uniformly about every second until the sample was no longer stuck to the spatula, and the time was measured and taken as the gelation time of the resin. The structure of the cured resin was analyzed using

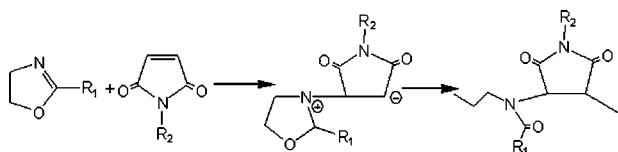


Figure 1 The spontaneous reaction between maleimide and oxazoline.

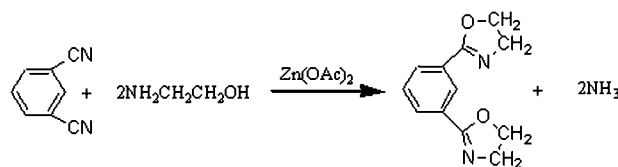


Figure 2 Synthesis of 1,3-PBO.

an FTIR spectrometer. FTIR spectra were obtained on a Perkin–Elmer-2 spectrometer (KBr pellet). Differential scanning calorimetry (DSC) was measured with a heating rate of 10°C/min under N₂ atmosphere on a Perkin–Elmer DSC6 apparatus. Dynamic scans of the samples were recorded. Thermogravimetric analyses (TGA) were performed on a DuPont 2000 Thermogravimetric Analyzer. Cured samples were weighed in the sample pan and then heated in the TGA furnace at a heating rate of 10°C/min. The resulting thermograms were recorded. Fracture surfaces of the cured resin were carried out using scanning electron microscopy (Quanta 200 FEI ESEM). Water absorption was conducted by putting samples into distilled water at 25°C for 100 h, then measuring the weight of the sample, and calculating the water absorption by the following equation

$$\text{Water absorption (\%)} = (M_2 - M_1)/M_1 \times 100$$

where M_2 is the weight of the sample after it was maintained in the distilled water at 25°C for 100 h, M_1 is the original weight of the sample before water absorption.

RESULTS AND DISCUSSION

Curing reaction of 1,3-PBO, BMI, and oleic acid

FTIR characterization

Figure 3 shows FTIR spectra of 1,3-PBO, BMI, and 1,3-PBO/BMI copolymer. As a result of the curing reaction of BMI with 1,3-PBO, the absorption at 1601 cm⁻¹ assigned to C=C of BMI monomer disappeared, along with the disappearance of the absorption at 1656 cm⁻¹ assigned to C=N, 1237, 1194, and 1170 cm⁻¹ assigned to C–O–C of 1,3-PBO monomer. The intensities of the absorption at 1701 and 1784 cm⁻¹ (νC=O symmetrical and asymmetrical, respectively) corresponding to the imide ring coming from BMI are increased, being accompanied by the appearance of the 1621 cm⁻¹ band assigned to the νC=O of the amide coming from the oxazoline ring. This demonstrates that oxazoline ring opened and reacted with the C=C of BMI by spontaneous reaction, and is indicative of the reaction mechanism is shown in Figure 4 (1).

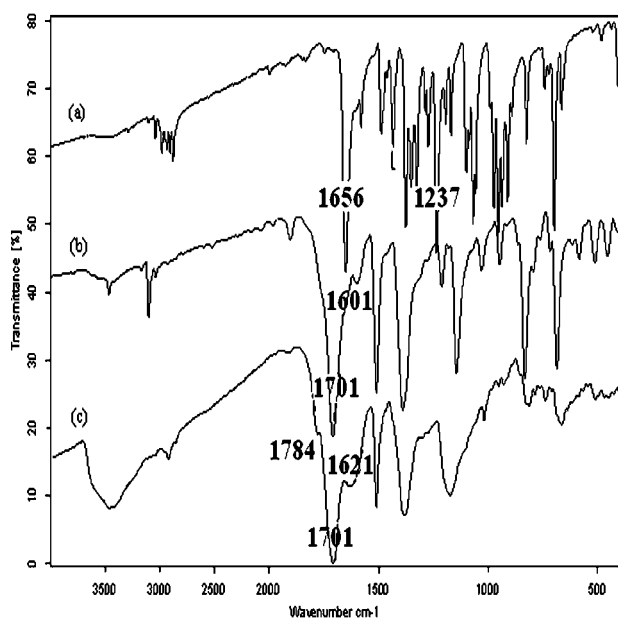


Figure 3 FTIR spectra of 1,3-PBO (a), BMI (b), and 1,3-PBO/BMI copolymer (c).

From the FTIR spectra of oleic acid (Fig. 5), it can be seen that the broad bands around 2926, 1463, and 939 cm^{-1} are assigned to the absorption of hydroxyl group of carboxyl. The peak at 1771 cm^{-1} is the absorption of carbonyl. The band at 1605 cm^{-1} is the characteristic absorption of C=C stretching. Figure 6 shows the FTIR spectra of BMI/1,3-PBO/oleic acid ternary copolymer. Comparing with the spectrum of BMI, 1,3-PBO and oleic acid, the change of absorption peak is also the same as that in Figure 3. This also indicates that BMI is copolymerized with 1,3-PBO. However, the peak of 1605 cm^{-1} also disappeared and there is a new absorption peak at 3423 assigned to the absorption of amide. It is because oleic acid reacted with BMI and oxazoline ring

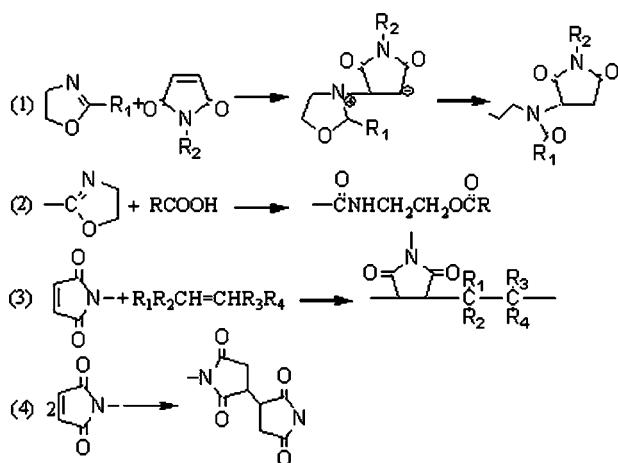


Figure 4 Reaction of BMI/1,3-PBO/oleic acid system.

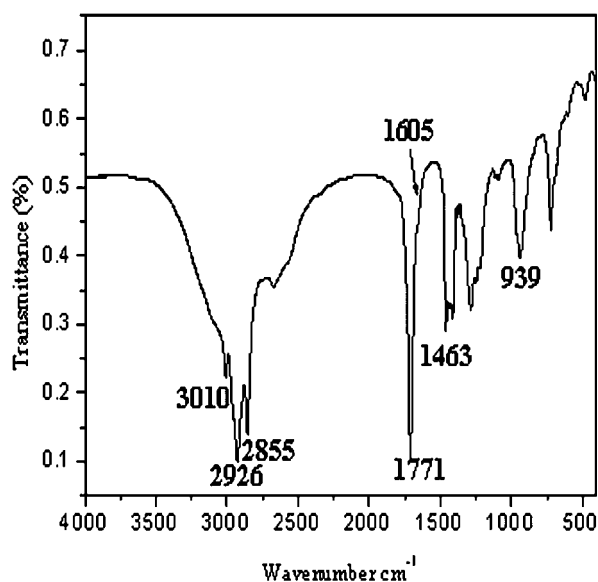


Figure 5 FTIR spectra of oleic acid.

opened. The reaction of BMI/1,3-PBO/oleic acid system was shown in Figure 4.

Viscosities

The viscosity of resin is a key factor in the process. Figure 7 shows that the viscosity–temperature relation for BMI/1,3-PBO and BMI/1,3-PBO/oleic acid systems. The viscosity of all systems decreases with temperature's increasing from 90 to 140°C. The viscosity of the resins at 140°C follows the following order: BMI/1,3-PBO/oleic acid (1 : 1 : 0.2, mol %) <

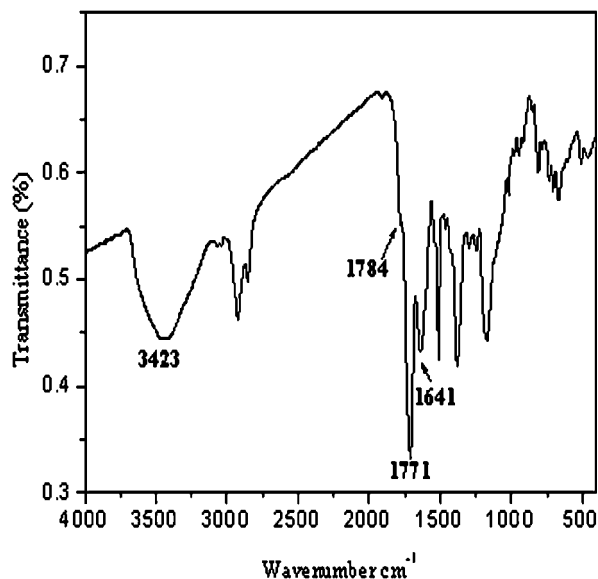


Figure 6 FTIR spectra of BMI/1,3-PBO/oleic acid copolymer.

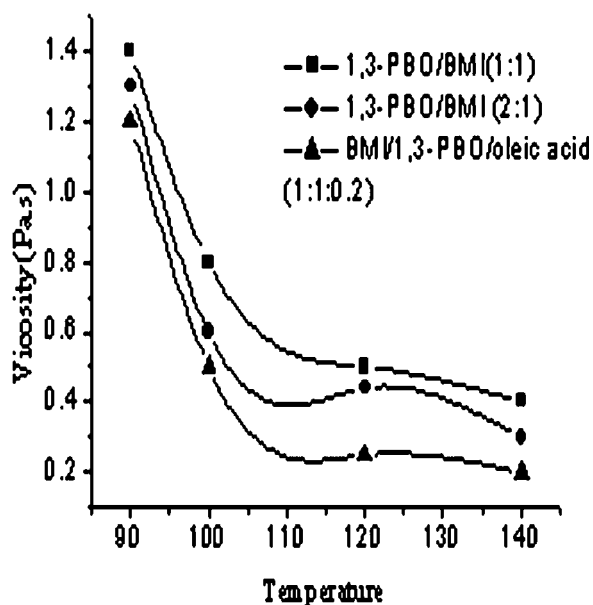


Figure 7 Viscosity-temperature plots for BMI/1,3-PBO and BMI/1,3-PBO/oleic acid systems.

1,3-PBO/BMI (mol %) (2 : 1, mol %) < 1,3-PBO/BMI (1 : 1, mol %). This indicates that 1,3-PBO and oleic acid play a role in dilute agent to BMI at low temperature. The viscosity of resin can be adjusted and controlled through various ratio of BMI, 1,3-PBO, and oleic acid.

Gelation time

Table I shows the gelation time of the molten mixtures from BMI/1,3-PBO and BMI/1,3-PBO/oleic acid. The gelation occurs at a critical extent of reaction. As the gel point is reached, the average molecular weight of the branched molecules becomes infinity, and viscosity increase very rapidly. At 120°C, the gel time of 1,3-PBO/BMI(1 : 1) and BMI/1,3-PBO/oleic acid (1 : 1 : 0.2) are very long. It indicates the 1,3-PBO/BMI(1 : 1) and BMI/1,3-PBO/oleic acid (1 : 1 : 0.2) systems are stable at lower temperatures. They have long pot life at lower temperatures. However, the gel time decreases rapidly. This means that the 1,3-PBO/BMI (1 : 1) and BMI/1,3-PBO/oleic acid (1 : 1 : 0.2) systems have higher reactivity at high temperature.

In addition, the gel time of 1,3-PBO/BMI(1 : 1) at 180°C is 3 min. But the gel time of 1,3-PBO/BMI(2 : 1) and BMI/1,3-PBO/oleic acid (1 : 1 : 0.2) are 4.5 min and 8 min, respectively. It is obvious that 1,3-PBO and oleic acid were used as a dilute agent to BMI as stated above.

DSC characteristics

DSC traces of 1,3-PBO on heating are shown in Figure 8. The endothermic peak at 151°C is attributed

to melting of 1,3-PBO. No exothermic peak from 151 to 250°C indicates that ring-opening thermohomopolymerization of 1,3-PBO is negative in the temperature range studied. In the DSC trace of BMI, a sharp endotherm indicating melting is observed at 162°C. Then a broad and small exotherm was observed, which was attributed to the double bond self-polymerization and a glass transition temperature of the polymer.

DSC curves of BMI/1,3-PBO and BMI/1,3-PBO/oleic acid are shown in Figure 9 and the characteristic parameters are listed in Table II. The exothermal peak of copolymerization reaction of BMI/1,3-PBO (mol ratio 1 : 1) starts at 153°C, reaches the maximum at 218°C, and stops at 260°C. The amount of exothermic enthalpy is 210 J/g. Although the double bond self-polymerization reaction of BMI starts at 196°C, reaches the maximum at 221°C, and stops at 245°C. The amount of exothermic enthalpy is 107 J/g. This indicates that there is an increase in ΔH values and a decrease in curing temperature range due to the addition of 1,3-PBO to BMI. Similarly, the exothermal peak of copolymerization of BMI/1,3-PBO (mol ratio 1 : 2) starts at 147°C, reaches the maximum at 210°C, and stops at 272°C. The amount of exothermic enthalpy is 141 J/g. In other words, with the increase of 1,3-PBO content, the curing temperature and exothermic enthalpy of copolymer resins is decreased. Moreover, there is a broader exotherm between onset temperature (131°C) and maximum temperature (224°C) with the addition of oleic acid to the BMI/1,3-PBO system. This could result from the reaction of oleic acid and 1,3-PBO. Nery et al.²⁷ also reported that the COOH-oxazoline reaction proceeds readily in bulk at 140–220°C. However, the higher maximum temperature (224°C) is attributed to the copolymerization reaction of the C=C double bond in BMI and oleic acid.¹⁸ The amount of exothermic enthalpy is 122 J/g, which is smaller comparing with BMI/1,3-PBO(1 : 1) system. From onset curing temperature and peak temperature of above curing systems, it can be seen that the curing temperature of BMI/1,3-PBO could be lowered due to the addition of 1,3-PBO and oleic acid. With the

TABLE I
Gelation Time of BMI/1,3-PBO and BMI/1,3-PBO/Oleic Acid Mixture

Temperature (°C)	1,3-PBO/BMI (mol %) (1 : 1)	1,3-PBO/BMI (mol %) (2 : 1)	BMI/1,3-PBO/oleic acid (mol %) (1 : 1 : 0.2)
120	>60	>60	>60
160	7	15	25
180	3	4.5	8
190	2	2.5	5
200	1	1.5	3

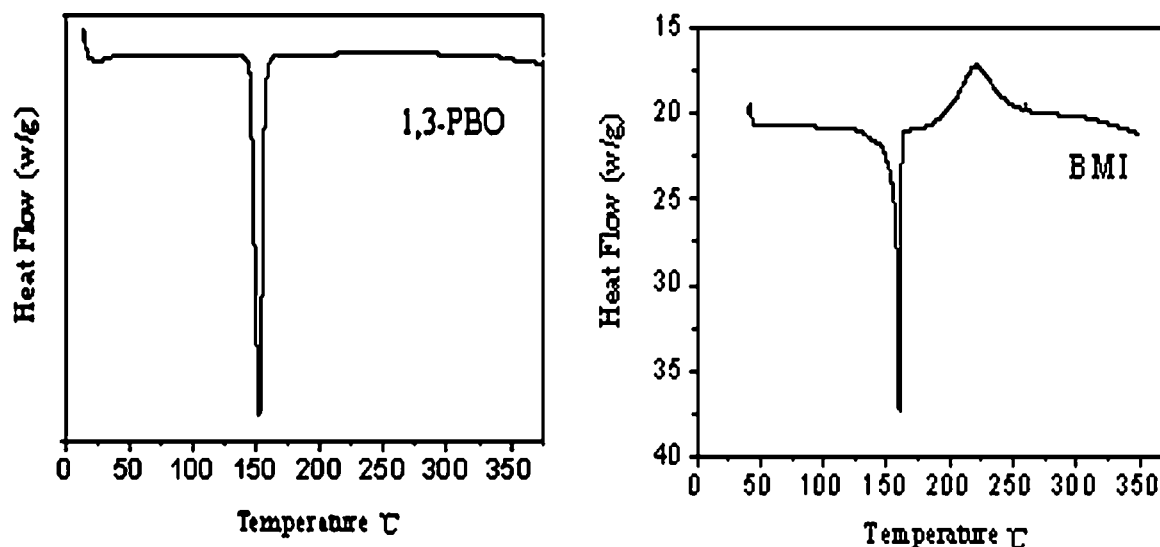


Figure 8 DSC curves of 1,3-PBO and BMI.

increase in 1,3-PBO and oleic acid content, the curing exothermic enthalpy of the blend decreased from 210 J/g for BMI/1,3-PBO (mol ratio 1 : 1) to 141 J/g for BMI/1,3-PBO (mol ratio 1 : 2), to 122 J/g for BMI/1,3-PBO/oleic acid (mol ratio 1 : 1 : 0.2), thus the small curing exothermic made the curing process more moderate. This means that the processability of BMI can be improved markedly by the addition of 1,3-PBO because of the lower curing temperature and moderate curing reactions.

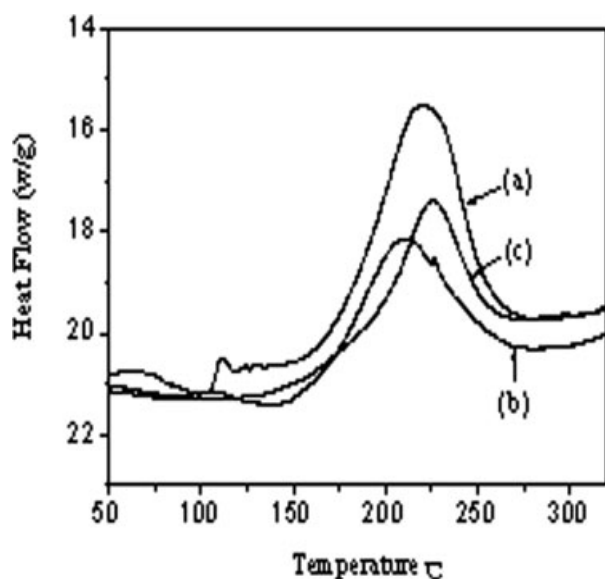


Figure 9 DSC curves of BMI/1,3-PBO and BMI/1,3-PBO/oleic acid. (a) BMI/1,3-PBO (mol ratio 1 : 1); (b) BMI/1,3-PBO (mol ratio 1 : 2); (c) BMI/1,3-PBO/oleic acid (mol ratio 1 : 1 : 0.2).

Properties of the cured resin

The thermal stability of the cured resins was evaluated by DSC test (Fig. 10). An increased molar ratio of 1,3-PBO in the mixture decreases T_g of the cured resin. More bisoxaoline in the mixture produces materials with more flexible fat linkage units in the crosslinking network, lowering the T_g of the material. The T_g of cured resin from BMI/1,3-PBO/oleic acid also decreases. The reason also lies in the long flexible chain of oleic acid. On the other hand, the copolymerization such as BMI and oleic acid, 1,3-PBO, and BMI, 1,3-PBO and oleic acid enhances the crosslinking density. As a result, the cured resin still has high T_g . The other possibility is a result of homopolymerization reaction of BMI.²⁸

The thermal stability of the cured resins also was characterized by TGA. Figure 11 shows the TGA curves of cured resins from BMI/1,3-PBO or BMI/1,3-PBO/oleic acid and the results were listed in Table III. It can be seen that the three resins show similar decomposition curves, but the difference was that the 5% mass loss temperature of BMI/1,3-PBO(1 : 2) is 231, being lower than that of BMI/1,3-PBO (1 : 1).

TABLE II
DSC Characteristics of BMI, BMI/1,3-PBO,
and BMI/1,3-PBO/Oleic Acid Mixtures

Sample name	T_1 (°C)	T_2 (°C)	T_3 (°C)	ΔH (J/g)
BMI	196	221	245	107
BMI/1,3-PBO (1 : 1)	153	218	260	210
BMI/1,3-PBO (1 : 2)	147	210	272	141
BMI/1,3-PBO/oleic acid (1 : 1 : 0.2)	131	224	258	122

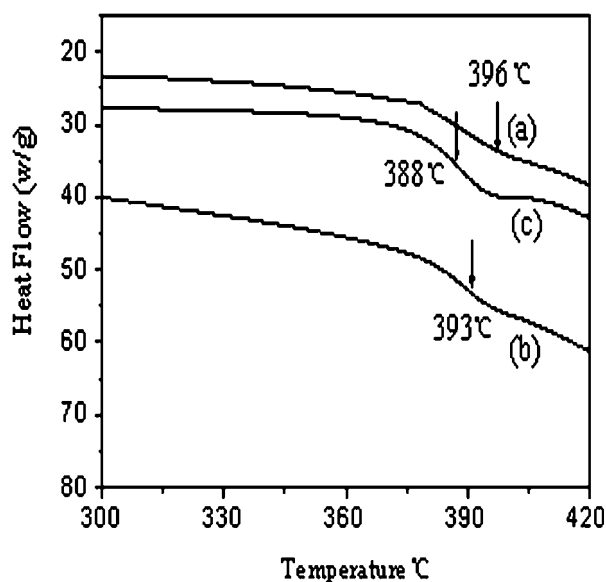


Figure 10 DSC curves of cured resin from BMI/1,3-PBO and BMI/1,3-PBO/oleic acid. BMI/1,3-PBO (mol ratio 1 : 1); (b) BMI/1,3-PBO (mol ratio 1 : 2); (c) BMI/1,3-PBO/oleic acid (mol ratio 1 : 1 : 0.2).

This indicates that the cured resin from BMI/1,3-PBO(1 : 1) presents better heat resistance than the cured resin from BMI/1,3-PBO (1 : 2). Owing to higher concentration of 1,3-PBO, BMI/1,3-PBO (1 : 2) would possess higher concentration of fat linkage coming from ring opening of 1,3-PBO. Thus, higher concentration of fat linkage leads to a decreased thermal stability of the cured resin. The 5% mass

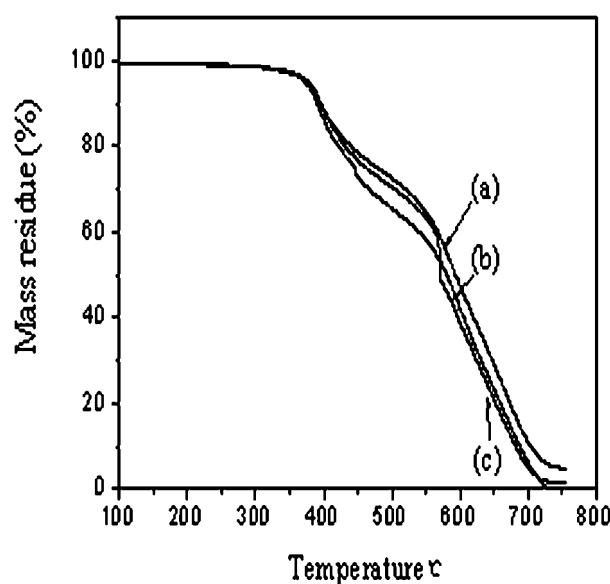


Figure 11 The TGA profiles of cured resin (heat rate 10/ min, N_2 50 mL/min). (a) BMI/1,3-PBO (mol ratio 1 : 1); (b) BMI/1,3-PBO (mol ratio 1 : 2); (c) BMI/1,3-PBO/oleic acid (mol ratio 1 : 1 : 0.2).

TABLE III
Thermal Resistance of BMI, BMI/1,3-PBO, and BMI/1,3-PBO/Oleic Acid Resin Measured by TGA

Resin sample	Inflection temperature (°C)	Temperature at 5 wt % loss (°C)	Temperature at 15 wt % loss (°C)
BMI/1,3-PBO (1 : 1)	365	376	417
BMI/1,3-PBO (1 : 2)	362	370	415
BMI/1,3-PBO/oleic acid (1 : 1 : 0.2)	355	365	410

loss temperature of BMI/1,3-PBO/oleic acid (1 : 1 : 0.2) is lower than that of BMI/1,3-PBO(1 : 1). The results reveal that the introduction of oleic acid decreases the thermal stability of the system. Although the copolymerization of BMI and oleic acid (C=C double linkage) causes higher crosslinking density, the longer fat linkage of oleic acid decreases the thermal decomposition temperature. The partial ester–amide linkage coming from the copolymerization of 1,3-PBO and oleic acid also decreases the thermal stability of the system.

Water absorption of the cured resin from BMI/1,3-PBO(1 : 1), BMI/1,3-PBO (1 : 2), and BMI/1,3-PBO/oleic acid (1 : 1 : 0.2) are 1.01%, 1.64%, and 1.84% respectively. The cured resin from BMI/1,3-PBO/oleic acid(1 : 1 : 0.2) are slightly higher than that cured resin from BMI/1,3-PBO(1 : 1 or 1 : 2). This could be attributed to the formation of hydrophilic ester–amide bonds. Figure 12 shows the SEM photographs of fractured surfaces of cured resin from BMI/1,3-PBO or BMI/1,3-PBO/oleic acid. It is clear that 1,3-PBO could toughen BMI resin. Oleic acid also can improve toughness of BMI/1,3-PBO system because of the formation of ester–amide bonds²⁷ and the long fat chain of oleic acid. When the molar ratio of BMI/1,3-PBO/oleic acid is 1 : 1 : 0.4, the cured resin indicates a remarkable tough fracture surface [Fig. 12(d,e)].

CONCLUSIONS

The curing behavior of the BMI, bisoxazoline, and oleic acid ternary copolymers are investigated. The results indicate that 1,3-PBO and oleic acid play a role in diluting to BMI at lower temperatures. At higher temperatures, the copolymerization between BMI, oleic acid, and 1,3-PBO increases the crosslinking density in the resultant materials. The cured resin still remains high T_g . SEM results confirm that 1,3-PBO and oleic acid could toughen BMI system because of the formation of ester–amide bonds and the long fat chain of oleic acid. The cured resin from BMI/1,3-PBO or BMI/1,3-PBO/oleic acid have superior heat resistance and water resistance.

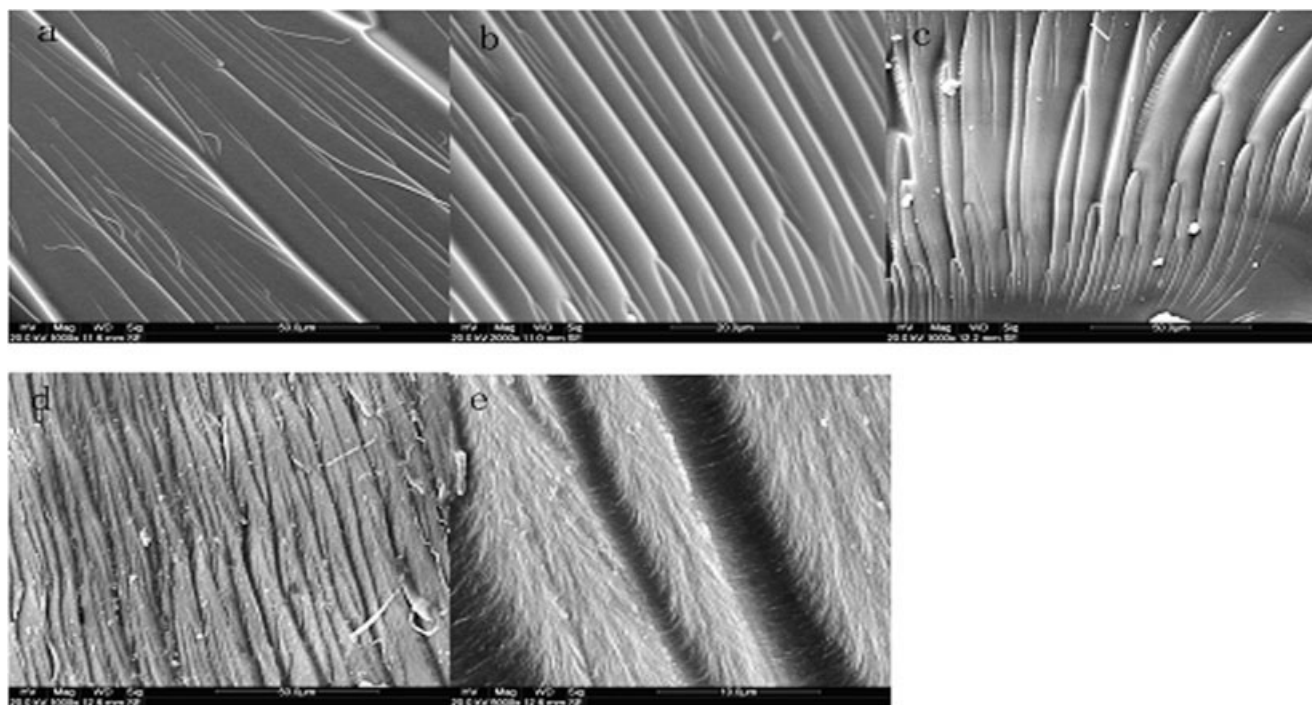


Figure 12 ESEM photographs of fractured surfaces of cured resin from BMI/1,3-PBO or BMI/1,3-PBO/oleic acid. (a) BMI/1,3-PBO (mol ratio 1 : 1), (b) BMI/1,3-PBO (mol ratio 1 : 2), (c) BMI/1,3-PBO/oleic acid (mol ratio 1 : 1 : 0.2), (d) BMI/1,3-PBO/oleic acid (mol ratio 1 : 1 : 0.4), (e) BMI/1,3-PBO/oleic acid (mol ratio 1 : 1 : 0.4). The magnification was $\times 1000$ for a–d, and $\times 5000$ for e, respectively.

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