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ScienceDirect
Polymer 49 (2008) 1173–1179
polymer
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High-performance polymer alloys of polybenzoxazine and bismaleimide

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Received 9 November 2007; received in revised form 16 January 2008; accepted 17 January 2008
Available online 26 January 2008

Abstract

Two series of high-performance polymer alloys were prepared by mixing typical benzoxine monomers, 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a) or 6,6-(1-methylethyliden)-bis-(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine) (B-a), with a typical bismaleimide, 4,4-bismaleimidodiphenyl methane by various ratios followed by thermal treatment up to 240 °C. DSC and IR of the alloys were examined to follow the curing reaction. These analyses showed that the obtained polymer alloys are AB co-cross-linked polymer networks through the formation of ether linkage between the hydroxyl group of polybenoxazine and the double bond of bismaleimide. Viscoelastic analysis and softening temperature measurement revealed that the polymer alloys have much higher glass transition temperatures than those of each homopolymer. The thermal stability also increased with the increase of bismaleimide content as evidenced by TGA.
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Keywords: Polymer alloy; Polybenzoxazine; Bismaleimide

1. Introduction

Polybenzoxazines have been developed as a novel type of phenolic resins that can be afforded by the ring-opening polymerization of benzoxazine monomers [1,2]. Chemical structures of typical benzoxazine monomers, 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a) and 6,6-(1-methylethyliden)-bis-(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine) (B-a), and polymer of B-a (PB-a) are shown in Scheme 1. They have not only the characteristics of traditional phenolic resins such as good flame retardancy and chemical resistance, but also unique characteristics that are not found in the traditional phenolic resins such as molecular design flexibility, low moisture absorption, near-zero shrinkage upon polymerization, and low dielectric constant [2–6]. Furthermore, benzoxazines can be polymerized simply through heating without the need of strong acid catalyst, and without producing harmful byproducts during the cure process. Therefore, polybenzoxazines overcome the disadvantages of the traditional phenolic resins without sacrificing the advantages of the resins. However, it is reported that glass transition temperature (T_g) of PB-a is ca. 150 °C which is not high enough for the use in a harsh condition [7]. The approaches for improving the thermal properties of polybenzoxazine can be classified into two ways. One is the modification of the monomer structure [8–12] and the other is the alloys or hybrids with highly thermally stable materials, such as polyimide [13,14], multiwalled carbon nanotube [15], titania [16], silsesquioxane [17], and clay [18,19].

Bismaleimides, such as 1,1′-(methylenedi-4,1-phenylene)-bismaleimide (BMI, Scheme 1), offer excellent thermomechanical properties and withstand high stress at high temperatures at which typical phenol and epoxy resins as well as most high-performance plastics are no longer satisfactory. Thus, the maleimide structure has long been incorporated into many polymeric systems because it often yields thermally stable polymers with a high T_g and improved heat distortion temperature due to the rigid imide ring [20–22]. Recently, it was reported that incorporation of the maleimide group into benzoxazine monomer effectively improved the thermal property of its thermoset [23–25]. In this paper, we report thermal property enhancement of polybenzoxazine by alloying with

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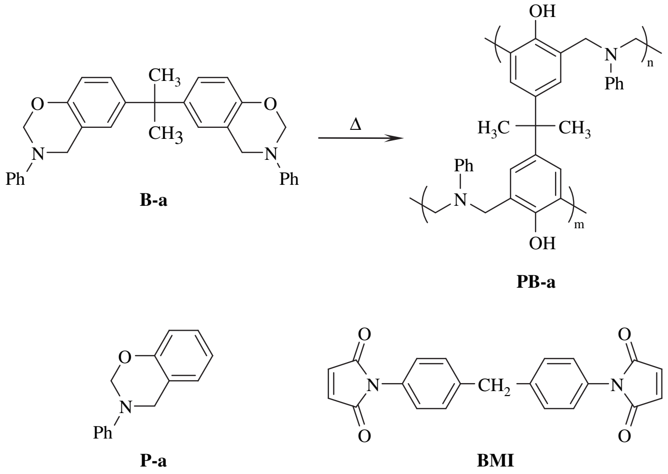
doi:10.1016/j.polymer.2008.01.041



Scheme 1. Chemical structure of B-a, PB-a, P-a and BMI.

BMI. The polymer alloys of polybenzoxazine and BMI resin were prepared by mixing benzoxazine and BMI monomers followed by curing. The curing behavior of the alloys and the effects of BMI content on thermal properties of the alloys are investigated.

2. Experimental

2.1. Materials

P-a and B-a were kindly supplied by Shikoku chemicals Co., Tokyo, Japan, and purified by washing with 3 N NaOH aq. BMI and *N*-phenylmaleimide were purchased from Tokyo Kasei, Tokyo, Japan. Phenol and dichlorodimethylsilane were used as-received from Kishida Chemicals Co., Japan.

2.2. Measurements

IR spectra were obtained with JASCO spectrophotometer model FT/IR-420. NMR spectra were recorded on a Varian Mercury 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C NMR) instrument. Differential scanning calorimetry (DSC) was conducted using Rigaku Thero Plus 2 DSC8230 at a heating rate of 10 °C/min under nitrogen. Thermogravimetric analysis (TGA) was performed with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of 5 °C/min under argon. Dynamic viscoelastic measurements were conducted on ORIENTEC automatic dynamic viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4 °C/min.

The softening curves (i.e., penetration depth *versus* scanning temperature) were measured by the penetration method under a constant indentation load for rising temperature scanning with the heating rate of 5 °C/min. A constant load during the penetration test was applied on a Vickers indenter made by silicon carbide through a load train using a mechanical lever. The penetration depth as a function of temperature was continuously detected by an electro-optical extensometer (Model 200X, Zimmer) with a precision of 0.5 μm by monitoring the gap made by a pair of silicon nitride tabs mounted at sample stage and indenter.

2.3. Preparation of benzoxazine/BMI polymer alloy

Benzoxazine and BMI monomers were mixed at various weight ratios in chloroform and stirred for 30 min. The blend solutions were cast on glass plates that were pre-treated with dichlorodimethylsilane, dried at 50 °C for 4 h, and then thermally treated at 100, 120, 160, 200, 240 °C for 1 h each to obtain the alloy films.

2.4. Model reaction of phenol and N-phenylmaleimide

Thermal reaction of phenol and *N*-phenylmaleimide was carried out as the model reaction between polybenzoxazine and bismaleimide. To phenol (9.411 g, 0.1 mol) was added *N*-phenylmaleimide (1.732 g, 0.01 mol) at room temperature and the mixture was refluxed at 170–180 °C for 8 h. Then, the unreacted phenol was removed by distillation. The crude product was purified by recrystallization from chloroform to obtain the reaction product as a white powder (0.67 g, 25.1% yield). Mp: 202–204 °C. Elem. Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24; O, 17.96. Found: C, 71.22; H, 5.03; N, 5.18; O, 18.57.

3. Results and discussion

3.1. Preparation of benzoxazine/BMI polymer alloy

Polymer alloys were prepared by blending BMI and benzoxazine followed by heat treatment. The blends of benzoxazine and BMI after drying at 50 °C for 4 h were yellow opaque. However, all the blend films became transparent after curing at 160 °C that is higher than the melting point of BMI. The color of the films after curing up to 240 °C was dark red at high benzoxazine content and became brown with the increase of BMI content. In addition, the alloy films obtained by casting on glass plates without surface treatment by dichlorodimethylsilane were difficult to peel off glass because of the very strong adhesive property and also high hydrophilicity of polybenzoxazine.

The obtained alloy films had improved toughness than the neat benzoxazine films and the toughness of alloy films increased with the increase of BMI content. The tendency of toughening by alloying with BMI was more remarkable in the case of monofunctional P-a than that of difunctional B-a.

3.2. Curing behavior of benzoxazine/BMI polymer alloy

The curing behavior of benzoxazine and BMI was investigated by DSC and IR measurements. Fig. 1 shows the DSC curves of blends of P-a and BMI with various blend ratios after removal of solvent at 50 °C for 4 h. Pristine P-a showed a sharp exothermic peak corresponding to the ring-opening polymerization of P-a, starting at ca. 198 °C with peak maximum at 222 °C and 57 cal/g as exothermic heat, while the

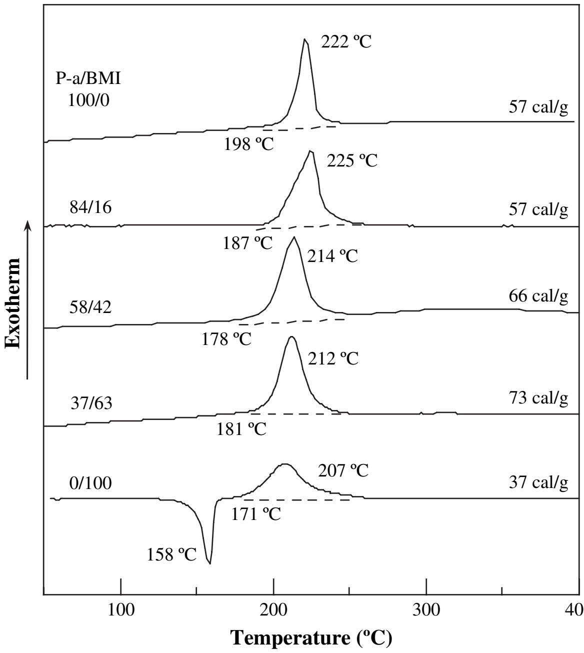


Fig. 1. DSC curves of P-a/BMI blends with various BMI wt% contents after removal of solvent at 50 °C for 4 h.

exotherm of pristine BMI started at ca. 171 °C with maximum at 207 °C and 37 cal/g of heat after endothermic peak corresponding to melting of BMI. Surprisingly, the exothermic heat of the blends was larger than those of P-a and BMI. The DSC result suggests that some kind of reaction was happening besides homopolymerizations of benzoxazine and BMI.

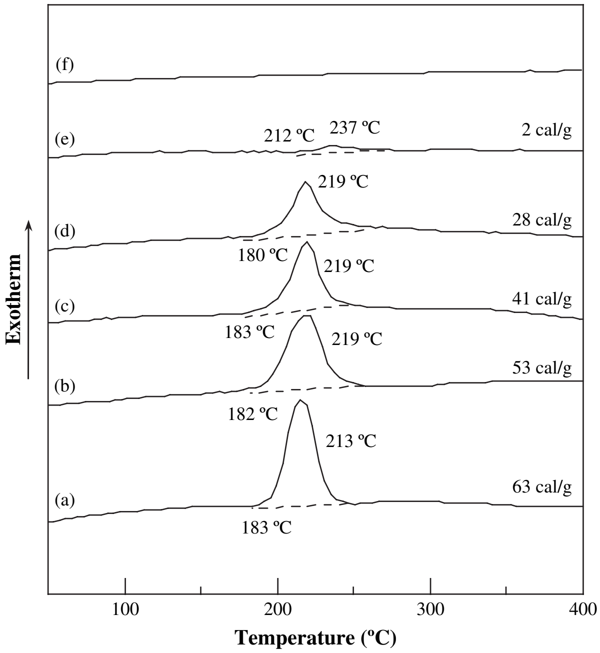


Fig. 2. DSC curves of P-a/BMI blend at 20 wt% BMI content after each cure stages at 50 (a), 100 (b), 120 (c), 160 (d), 200 (e) and 240 °C (f).

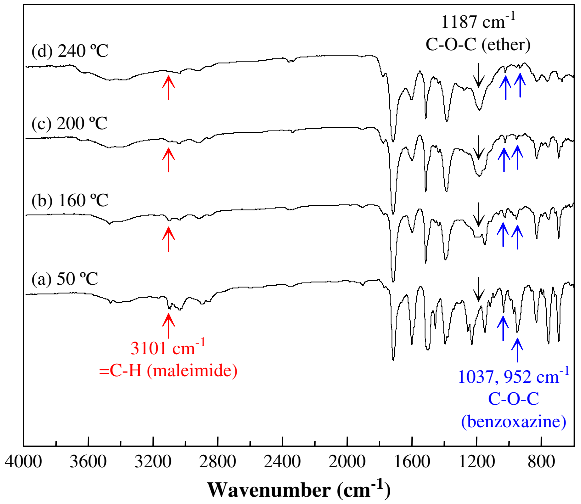


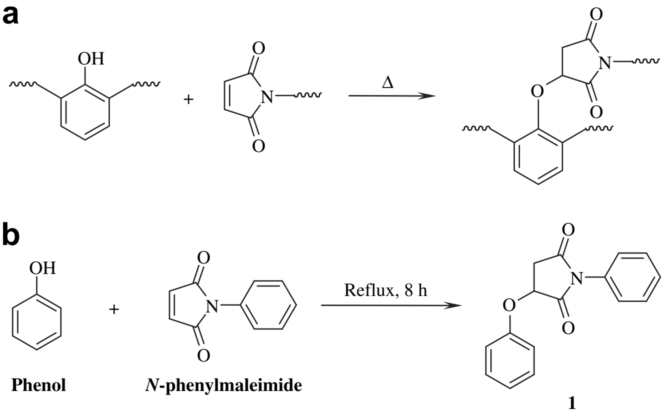
Fig. 3. IR spectra of P-a/BMI blend at 20 wt% of BMI content after each cure stages at 50 (a), 160 (b), 200 (c) and 240 °C (d).

DSC curves of P-a/BMI blend at 20 wt% BMI content after each cure stage are shown in Fig. 2. The DSC curve of blend after removal of solvent at 50 °C for 4 h revealed unimodal exothermic peak corresponding to the ring-opening polymerization of P-a and addition polymerization of BMI. The exothermic heat gradually decreased with the increase of heat treatment temperature and completely disappeared after heat treatment at 240 °C. These results indicate that the reactions of benzoxazine and BMI occurred simultaneously and finished at 240 °C.

The cure reaction was also investigated by IR. Fig. 3 shows the IR spectra of the alloy of P-a and BMI (BMI: 20 wt%). The characteristic absorptions of benzoxazine at 1037 and 952 cm^{-1}, and BMI at 3101 cm^{-1} were observed before curing (Fig. 3a). These characteristic absorptions simultaneously decreased with the progress of cure and disappeared after the cure at 240 °C, indicating that the reactions of double bond in BMI and ring opening of benzoxazine occurred simultaneously and finished at the temperature in good agreement with the DSC result. It is noteworthy that absorptions at 1187 cm^{-1} assignable to ether bond (C−O−C) increased with the progress of cure. This implies the possible chemical reaction between the hydroxyl group of polybenzoxazine and the double bond of BMI as described below.

3.3. Model reaction of phenol and N-phenylmaleimide

From the IR and DSC results, we expected that the reaction between the hydroxyl group of polybenzoxazine and the double bond of BMI occurred during cure as shown in Scheme 2a. In order to confirm the reaction, a mixture of phenol and *N*-phenylmaleimide was refluxed at 170−180 °C for 8 h as the model reaction (Scheme 2b). Fig. 4 shows IR spectra of the starting materials and product (**1**). The spectrum of *N*-phenylmaleimide showed the characteristic absorptions of double bond at 3093 cm^{-1}, and hydroxyl of phenol at 1374 and 815 cm^{-1}. In the spectrum of **1**, these absorptions were not



Scheme 2. Possible thermal reaction between polybenzoxazine and bismaleimide (a), and the model reaction of phenol and *N*-phenylmaleimide (b).

observed and, instead, an absorption at 1201 $\mathrm{cm^{-1}}$ attributed to ether bond was observed. These spectral changes were similarly observed in the case of polymer alloy. The chemical structure of **1** was confirmed by ^{1}H and ^{13}C NMR analyses (Fig. 5). From these results using model compounds, we confirmed that hydroxyl group of polybenzoxazine reacts with double bond of BMI by the heat treatment, affording a cross-link through ether bond.

3.4. Measurement of softening temperature of benzoxazine/BMI polymer alloy

Thermal properties of two series of polymer alloys were examined by measuring the softening temperature by indentation method. The softening curves of P-a/BMI alloys with various ratios are shown in Fig. 6. The pristine P-a and BMI resins expanded up to ca. 160 and 222 °C, respectively, and then the pin quickly inserted into the samples near glass transition temperature (T_g). The softening temperature shifted to higher temperature with the increase of BMI content. In the case of P-a/BMI alloy at 63 wt% BMI, pin did not insert so much into the sample. Furthermore, the softening temperature of P-a/BMI alloy with 73 wt% BMI was not observed up to 330 °C, which is the limitation of measurement. These results suggest that either T_g of the alloy having BMI content more than 50 wt% was higher than 330 °C or no softening flowability even over T_g.

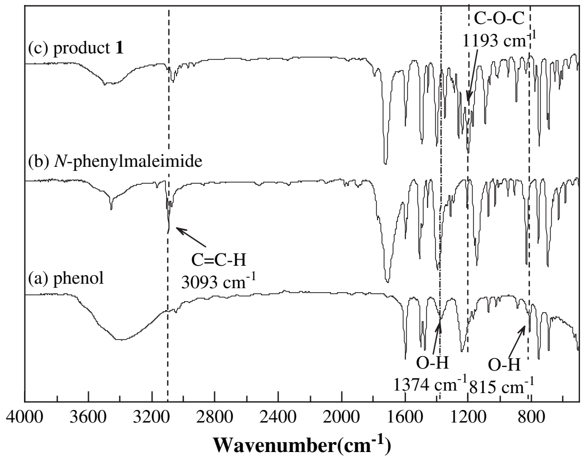


Fig. 4. IR spectra of phenol (a), *N*-phenylmaleimide (b) and product (**1**).

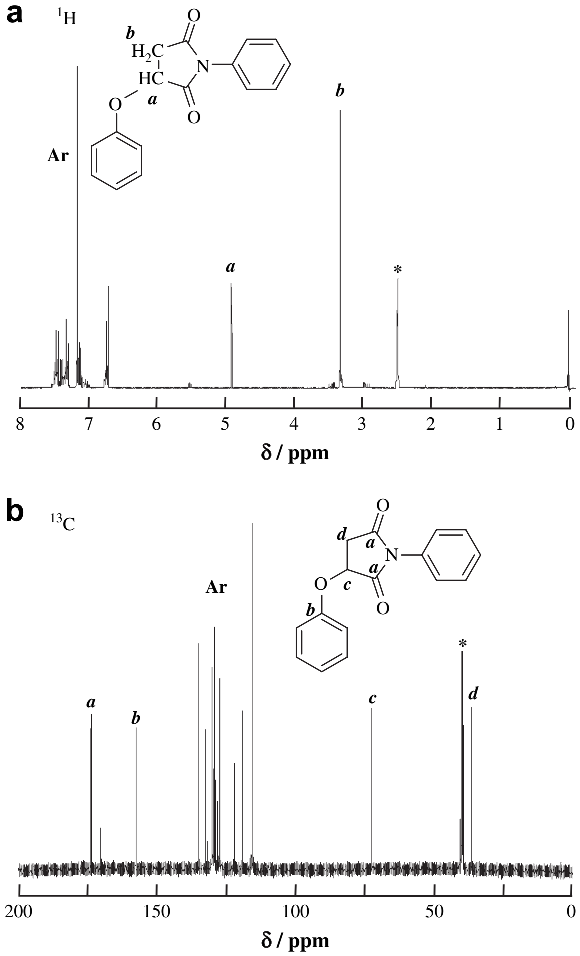


Fig. 5. ^{1}H (a) and ^{13}C (b) NMR spectra of **1** (DMSO-d_6, 25 °C). The asterisks denote the resonances from the solvent.

We also notice that thermal expansion of the alloys with higher content of polybenzoxazine is smaller than the thermal expansion of BMI-rich alloys, clearly showing the low coefficient of thermal expansion of polybenzoxazine.

Softening temperatures of two series of alloys are shown in Fig. 7 and summarized in Table 1. The softening temperature of the alloys shifted to higher temperature with the increase of BMI content. Interestingly, the softening temperatures of alloys at ratio of BMI more than 30 wt% were higher than that of pristine BMI resin, showing the formation of cross-linking between benzoxazine and BMI. Highly cross-linked AB co-cross-linked polymer alloy is considered to be formed in the present alloy system. Bifunctional B-a is more effective for the enhancement of softening temperature at low BMI content, probably due to the higher cross-link density than the monofunctional P-a.

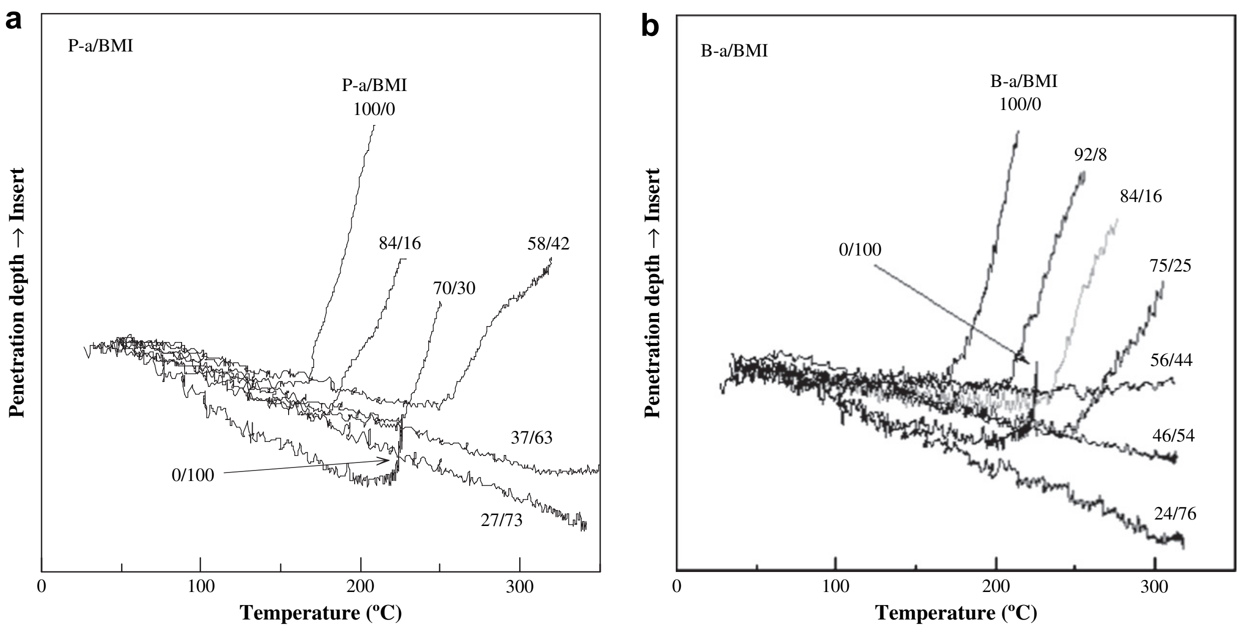


Fig. 6. Softening curves of P-a/BMI (a) and B-a/BMI (b) polymer alloys at various ratios.

3.5. Viscoelastic analysis of benzoxazine/BMI polymer alloy

The viscoelastic properties of benzoxazine/BMI alloys were studied using DMA. The temperature dependence of the storage modulus (E') and loss modulus (E'') of neat polybenzoxazines and the polymer alloys are shown in Fig. 8. The T_g estimated from the maximum of E'' is summarized in Table 1 and the shift of T_g against BMI content is plotted in Fig. 9.

Although, it is well known that most of the semi-interpenetrating polymer network (semi-IPN) or IPN systems tend to phase separate and show two T_gs [26], the appearance of only one T_g in all the alloy films suggests that the two

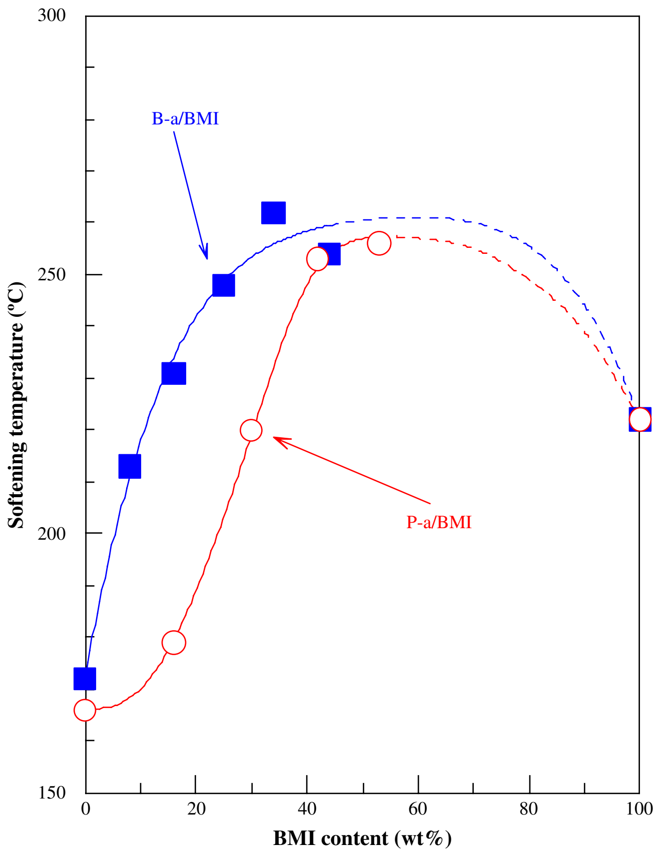


Fig. 7. Influence of BMI content on softening temperature.

Table 1
Thermal properties of benzoxazine/BMI polymer alloy

Benzoxazine	BMI content (wt%)	Softening temperature (°C)	DMA	TGA		
			T_g from E'' (°C)	T_5 (°C)	T_{10} (°C)	Char yield at 800 °C (%)
P-a	0	166	146	344	370	46
	16	179	167	352	381	49
	30	220	198	353	386	51
	42	253	211	363	396	52
	53	256	237	379	409	53
	63	–	244	386	414	54
	72	–	243	395	424	55
	80	–	240	421	431	55
	87	–	–	425	434	53
B-a	0	172	154	310	338	45
	8	213	214	315	342	47
	16	231	241	321	351	50
	25	248	250	327	360	51
	34	262	268	332	366	52
	44	254	272	333	367	53
	54	–	275	338	366	57
	64	–	275	351	379	57
	76	–	268	380	399	55
	87	–	–	428	435	53
–	100	222	222	477	482	51

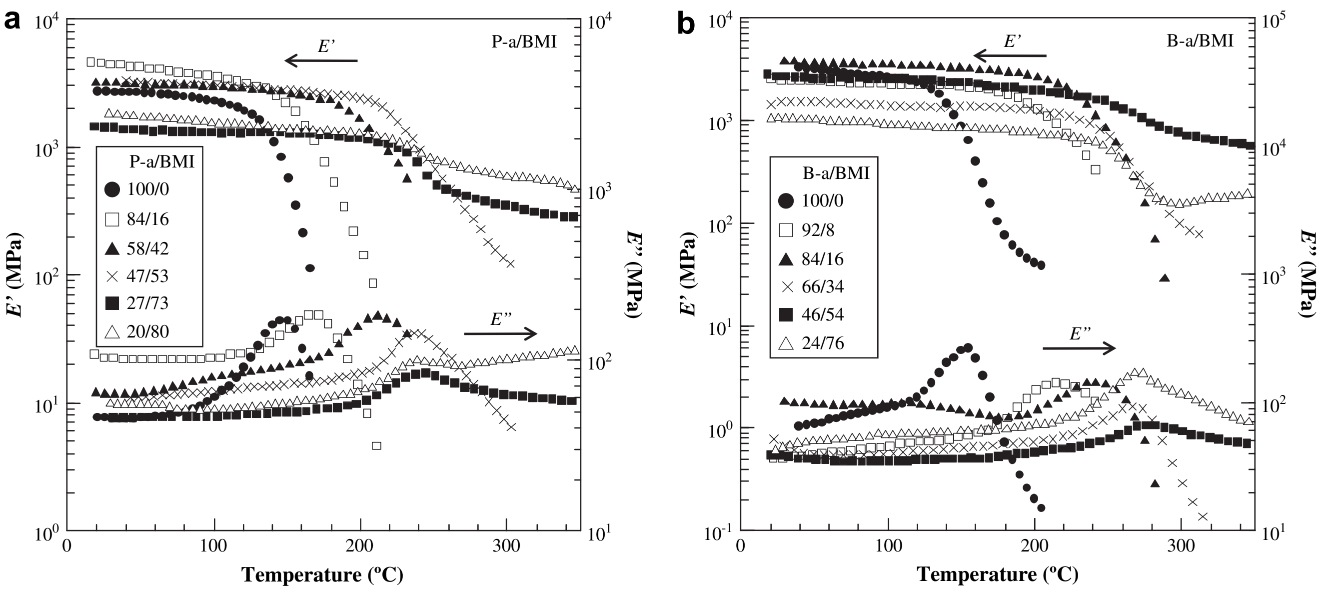


Fig. 8. Viscoelastic analysis of P-a/BMI (a) and B-a/BMI (b) polymer alloys at various ratios.

components in this study are well miscible or co-cross-linked. With the increase of BMI content, the T_g of polymer alloy shifted to higher temperature, suggesting that adding BMI to benzoxazine was effective for performance enhancement of polybenzoxazine. Moreover, the T_gs of the polymer alloys at high BMI contents were even higher than those of B-a and BMI homopolymers (Fig. 9). This is also another evidence indicating the formation of AB cross-linked structure.

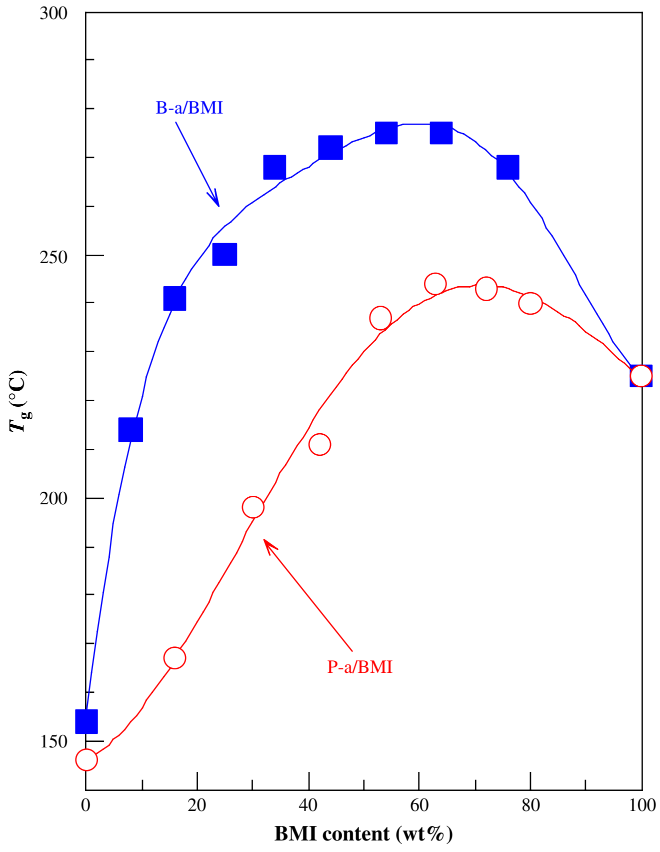


Fig. 9. Influence of BMI content on T_g (from E'').

3.6. Thermal stability of benzoxazine/BMI polymer alloy

The thermal stability of the two series of polymer alloys was investigated by TGA. The TGA profiles of alloys blended at various ratios are shown in Fig. 10. The values of 5 and 10% weight loss temperatures (T_5 and T_{10}) and the char yield at 800 °C are shown in Table 1. The T_5 and T_{10} gradually shifted to higher temperature with the increase of BMI content, indicating that the addition of BMI was effective for the improvement of the thermal stability of polybenzoxazine. Furthermore, the char yield of the polymer alloys increased as compared with the homopolymers, showing that the flame retardancy is also improved by alloying.

4. Conclusions

Polymer alloys were successfully prepared by mixing typical benzoxazine monomer, such as P-a and B-a, and bismaleimide followed by thermal cure. The obtained alloy films were transparent and the color changed from dark red to brown corresponding to the increase of BMI content. IR and DSC analyses of the cure stage revealed that the thermal reaction occurred between the hydroxyl group of polybenzoxazine and the double bond of BMI, forming an AB co-cross-linked structure as supported by the model reaction of phenol and *N*-phenylmaleimide. DMA measurement of the polymer alloys showed only one T_g, also suggesting the formation of the AB co-cross-linked structure. The T_g of the polymer alloys shifted to higher temperature by increasing the BMI content. In particular, the T_gs of the polymer alloys at high BMI contents were even higher than those of each resin due to the formation of

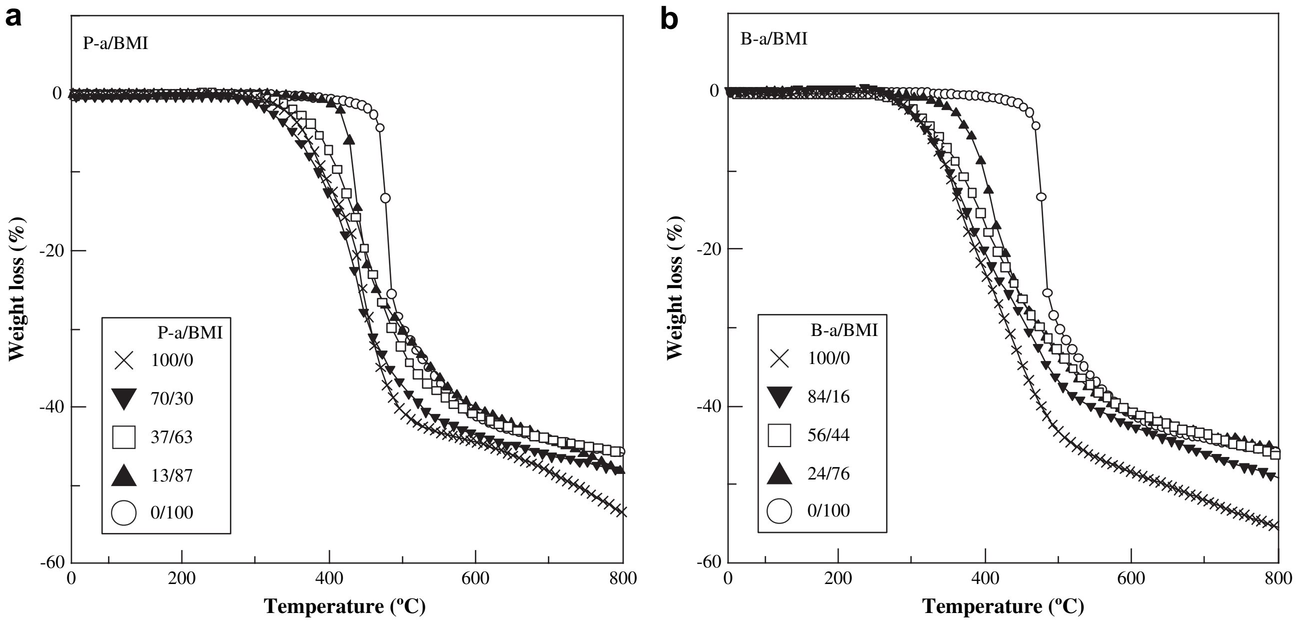


Fig. 10. TGA curves of P-a/BMI (a) and B-a/BMI (b) polymer alloys at various ratios.

AB co-cross-linking. The thermal stability also increased with the increase of BMI content as evidenced by TGA. The polymer alloys developed in this study can be good candidates for the matrix resin of advanced composite materials and also for the rigid printed circuits because of the excellent high temperature properties.

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