

# Synthesis, Characterization of New Carboxylic Acid-Containing Benzoxazine and Its Curing Behaviors with Bisoxazoline

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Received 14 February 2011; accepted 20 March 2011

DOI 10.1002/app.34535

Published online 9 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A new benzoxazine-benzoic acid (BBA) was synthesized and the structure was confirmed by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FTIR, etc. The cure behavior of BBA and cure behavior of BBA with phenylene bisoxazoline (1,3-PBO) were investigated by differential scanning calorimetry (DSC). It was found that BBA showed a single curing exothermic peak at about 217°C. However, all BBA/1,3-PBO systems exhibited two exothermic peaks. One may be attributed to the reaction between carboxyl groups of BBA and 1,3-PBO. And the other was attributed to the ring-opening polymerization of oxazine rings and the reaction between phenolic hydroxyl groups generated by the ring

opening of benzoxazine ring and 1,3-PBO. The curing temperature of benzoxazine containing carboxyl groups could be lowered by the copolymerization of 1,3-PBO. Thermogravimetric analysis showed that the incorporation of ester-amide groups had a significant effect on decreasing thermal stability and char yield of the cured resin. SEM results indicated that 1,3-PBO could toughen BBA benzoxazine resin. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 922–928, 2012

**Key words:** benzoxazine; 1,3-PBO; carboxylic; thermal properties

## INTRODUCTION

Phenolic resin is one of the earliest synthetic resins and widely used in the construction and electrical industries because of superior mechanical strength, heat resistance, dimensional stability, and chemical resistance. However, the traditional phenolic resin has many shortcomings. For example, they release by-products such as water and ammonia compounds during the curing process, which sometimes reduce the properties of cured resins due to the formation of micro voids. The addition coreaction of novolac phenolic resin with phenylene bisoxazoline (1,3-PBO) has been explored to overcome this shortcoming.<sup>1</sup> Phenol-bisoxazoline resin had a character of low shrinkage, excellent toughness, high  $T_g$ , low flammability, and low smoke emission. Bisoxazolines were used to chain extend and/or crosslink phenolic resin. There were no volatiles byproducts produced in the reaction of novolac phenolic resin and bisoxazoline.

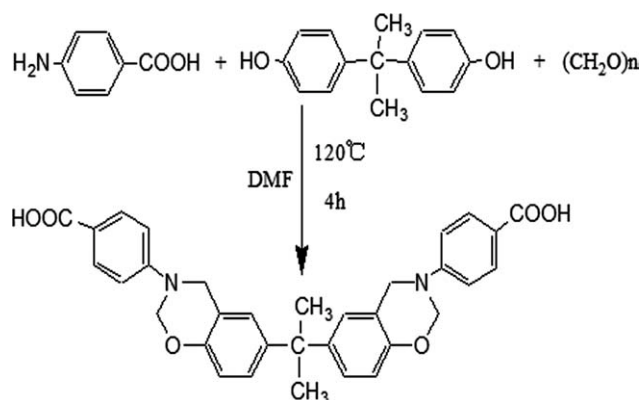
In recent years, Ishida and coworkers<sup>2–8</sup> synthesized various types of benzoxazine and studied their cured kinetics and mechanical properties. Benzoxazine ring has to be stable at low temperature, but a ring-opening reaction occurs at high temperature, when both the phenolic hydroxyl group and tertiary amine group are produced.<sup>9</sup> High curing temperature and brittleness are limited to the application of benzoxazine. Using the phenolic hydroxyl groups, benzoxazine have been successfully modified with epoxy,<sup>8,10–12</sup> ATBN or CTBN,<sup>13</sup> poly(imide-siloxane),<sup>14</sup> polyurethane,<sup>15</sup> and bisoxazoline.<sup>16–21</sup> In our previous research,<sup>22</sup> 4,4'-diaminodiphenyl methane-based benzoxazine and its oligomers (Oligo-Da) were synthesized and the curing behavior and properties of the Oligo-Da/1,3-PBO copolymer resins were investigated. We found that the cure induction time and cure time of the molten mixture from Oligo-Da/1,3-PBO could be reduced, especially above 175°C. The toughness of Oligo-Da could be improved. In addition, we also investigated the curing behavior and properties of ternary copolymer from bismaleimide (BMI), bisoxazoline (1,3-PBO), and oleic acid. We found that the curing temperature of BMI could be lowered and the toughness of BMI system could be improved because of the reaction between 1,3-PBO and carboxylic groups.<sup>23</sup>

Andreu et al. reported that the presence of carboxyl groups influenced thermal curing and the

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Contract grant sponsor: Science and Technology Bureau of Huangshi, China; contract grant number: 2010A1019-4.

Contract grant sponsor: National Postdoctoral Science Foundation of China; contract grant number: 20100471162.



**Figure 1** Synthesis of benzoxazine containing carboxylic groups.

processing temperatures were lower.<sup>24–26</sup> Since carboxylic acid can effectively catalyze the thermal curing of benzoxazine at lower temperature and reacted with 1,3-PBO,<sup>24–26</sup> a new benzoxazine-benzoic acid (BBA) was synthesized and coreacted with 1,3-PBO in this study. We expected that incorporation of the carboxylic moieties into benzoxazine could lower the curing temperature and improve the properties of the benzoxazine/1,3-PBO copolymer. The cocuring behavior of the benzoxazine/1,3-PBO and the properties of the cured resins were also discussed in detail.

## EXPERIMENTAL

### Materials

Bisphenol A, 4-amiobenzoic acid, ethanolamine, zinc acetate, ammonia, ethanol paraformaldehyde, *N,N'*-dimethylformamide, and 1,3-dicyanobenzene were purchased from Shanghai First Reagent Company, China. All chemicals were AR grade and used without further purification. Phenylene bisoxazoline (1,3-PBO) (Fig. 2) was prepared according to our earlier report.<sup>22</sup> The yield was about 90% and the structure was confirmed by NMR:  $\delta$ 8.42, 8.05–8.03, 7.46–7.41 (Ar–H);  $\delta$ 4.45–4.39 (O–CH<sub>2</sub>);  $\delta$ 4.08–4.02 (N–CH<sub>2</sub>).

### Measurements

The structure of the cured resin was analyzed using a FTIR spectrometer. FTIR spectra were obtained on a Perkin-Elmer-2 spectrometer (KBr pellet). <sup>1</sup>H (300 MHz) and <sup>13</sup>C (100.5 MHz) NMR spectra were obtained with a Bruker spectrometer with Fourier transform, with CDCl<sub>3</sub> as a solvent, and TMS as an internal standard. Elemental analysis was performed with a VARIO EL III rapid elemental analyzer. Differential scanning calorimetry (DSC) was measured with a heating rate of 10°C/min under N<sub>2</sub> atmosphere on Perkin-Elmer DSC6 apparatus. Dynamic scans of the samples were recorded. Thermogravi-

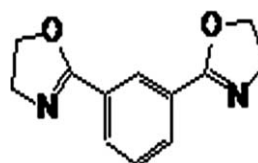
metric analyses (TGA) were performed on a DuPont 2000 thermogravimetric analyzer. Cured samples were weighed in the sample pan and then heated in the TGA furnace at a heating rate of 5°C/min. The resulting thermograms were recorded. The resulting thermograms were recorded. Fracture surfaces of the cured resin were carried out using scanning electron microscopy (Hitachi ISI-SX-40 SEM). 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

$$\text{Water absorption(\%)} = (M_2 - M_1)/M_1 \times 100 \quad (1)$$

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.

### Synthesis of benzoxazine-benzoic acid

As shown in Figure 1, the mixtures of bisphenol A (3.7 g, 20 mmol), 4-amiobenzoic acid (5.5 g, 40 mmol), and paraformaldehyde (2.6 g, 86 mmol) were placed in a 500-mL round-bottom flask and dissolved with 200 mL of *N,N'*-dimethylformamide (DMF). The mixtures were heated at 100°C for 1 h, dissolved completely, and then the reaction was kept at 120°C for 4 h. After cooling at room temperature, the mixtures were dissolved in dichloromethane. The resulting solution was filtered and washed with deionized water and the solvent was removed by rotary evaporation at reduced pressure. The product was dried at reduced pressure and room temperature to provide an orange powder. The yield was 75%; m.p.: 51–52°C; Anal. C<sub>33</sub>H<sub>28</sub>O<sub>6</sub>N<sub>2</sub>; C 72.26%; H 5.11%; N 5.11%; found: C 71.18%; H 5.36%; N 5.02%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS,  $\delta$  ppm): 7.38 (4H, ArAH), 7.12–7.01 (2H, ArAH), 7.00–6.87(2H, ArAH), 7.00–6.87(4H, ArAH), 6.84–6.76(2H, ArAH), 5.45 (4H, ArOCH<sub>2</sub>N), 4.68 (4H, ArCH<sub>2</sub>N), 4.68 (6H, CCH<sub>3</sub>). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, TMS,  $\delta$  ppm): 161.0 (COOH), 153.4 (CAO), 152.7(CAN), 142.0 (CH), 130.1 (C), 129.4 (C), 128.2 (C), 126.9 (C), 125.0 (C), 118.4 (C), 79.1 (OCN), 49.2(ACN), 38.2 (C), 40.0 (CH).



**Figure 2** The chemical structure of 1,3-PBO.

TABLE I  
Formulations of BBA/1,3-PBO Resins

Resin code	Mass ratio (BBA/1,3-PBO)
BBA	1/0
BP1-1	1/1
BP1-2	1/2
BP1-2.5	1/2.5

### Blending sample preparation

Blends of BBA/1,3-PBO were prepared with molar ratios of 1 : 1, 1 : 2, and 1 : 2.5 for DSC, FTIR, and thermal property studies. The formulations of BBA and BBA/1,3-PBO Resins are shown in Table I. The two materials were weighed and dissolved in tetrahydrofuran together. The solution was placed onto a piece of metal plate. After most of the solvent was removed under ambient atmosphere at 60°C, the metal plate was placed into a vacuum oven at 60°C for 24 h to remove the residual solvent. After that, the vacuum oven was subjected to a step curing procedure as follows: 100°C (2 h), and 130°C (2 h), 170°C (2 h), 190°C (2 h), 210°C (2 h) 250°C (2 h). The step cure procedure was according to the DSC studies of the materials. Then the samples were slowly cooled to room temperature over several hours.

## RESULTS AND DISCUSSION

### Preparation and characterization of BBA

BBA was prepared using bisphenol A, 4-amiobenzoic acid, and paraformaldehyde as raw materials (Fig. 1). The yield of BBA was 75%. BBA was yellow

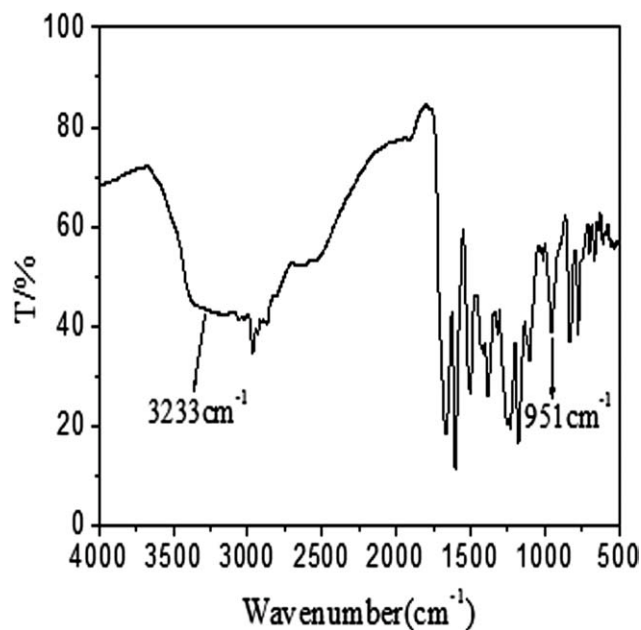


Figure 3 FTIR spectra of BBA.

powder at room temperature and soluble in common solvent such as toluene, tetrahydrofuran, ethylacetate, acetone, butanone, chloroform, and dichloromethane, indicating their good processing properties in solution processes.

The chemical structure of the obtained BBA was further confirmed by FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectra. As shown in Figure 3, the characteristic absorption band of benzoxazine for BBA appeared at 951 cm<sup>-1</sup>. In addition, the band at around 1226 and 1015 cm<sup>-1</sup> were assigned to asymmetric stretching of C—O—C and the band at 1326 cm<sup>-1</sup> was assigned to wagging of CH<sub>2</sub>. Another characteristic

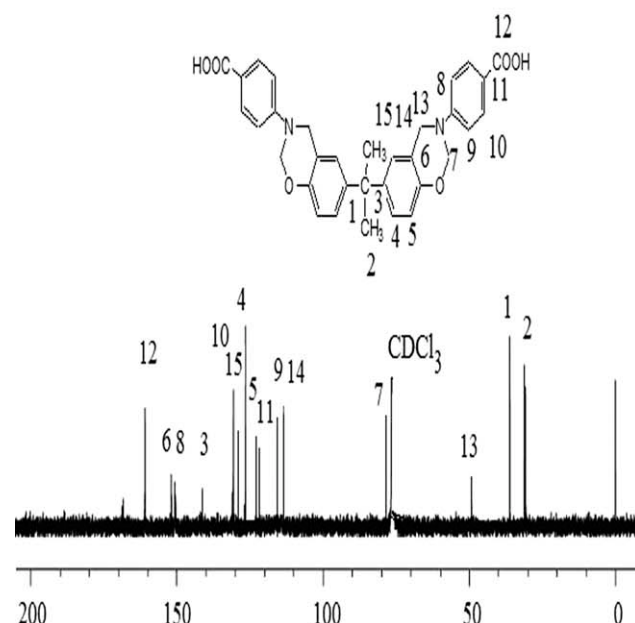
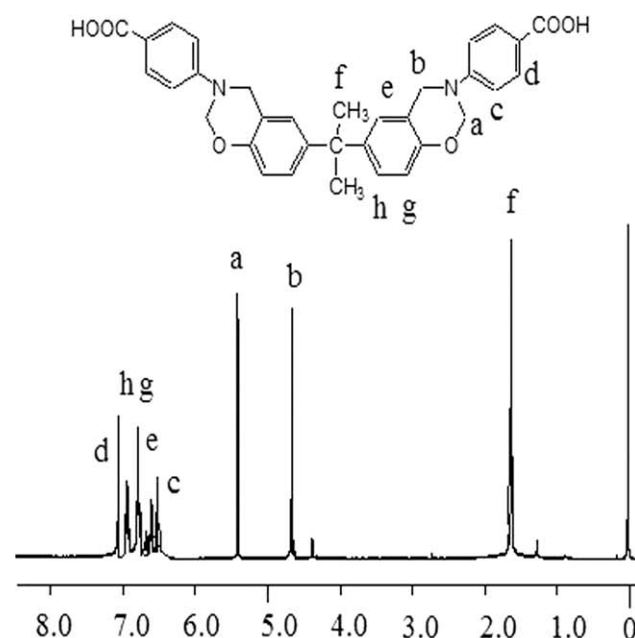
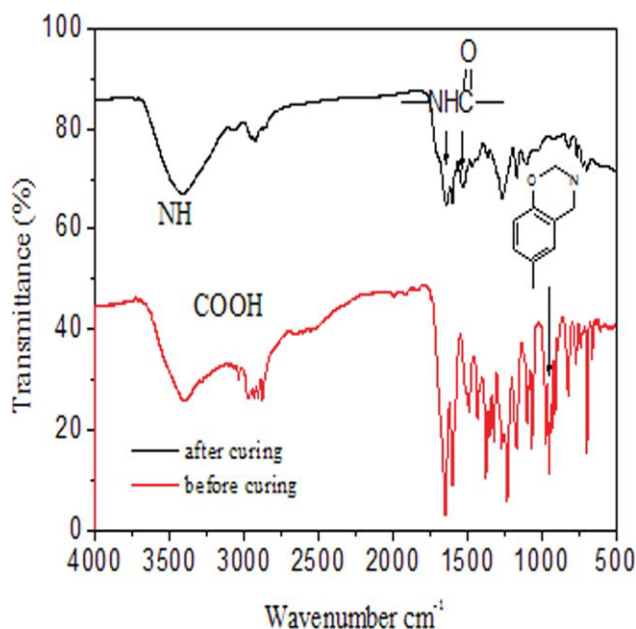


Figure 4 <sup>1</sup>H and <sup>13</sup>C-NMR spectra of BBA.



**Figure 5** FTIR spectra of BBA/1,3-PBO before (a) and after (b) curing. [Color figure can be viewed in the online issue, which is available at [www.onlinelibrary.wiley.com](http://www.onlinelibrary.wiley.com).]

band at around  $1463$  and  $1495\text{ cm}^{-1}$  was assigned to multisubstituted benzene ring. And the broad band assigned to functional carboxylic groups appeared at  $3233$  to  $2500\text{ cm}^{-1}$ .

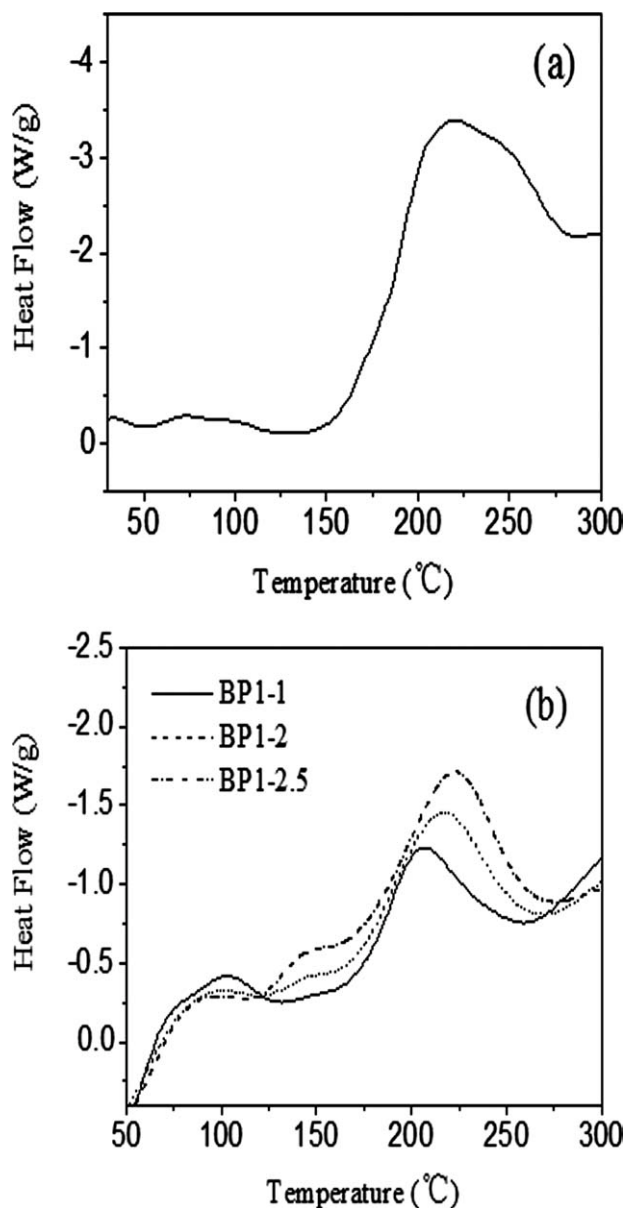
Figure 4 shows the  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of BBA with the main assignments. The typical characteristic protons of oxazine ring appeared at  $5.28$  and  $4.85$  ppm assigned to  $-\text{O}-\text{CH}_2-\text{N}-$  and  $\text{Ar}-\text{CH}_2-\text{N}-$  in  $^1\text{H}$  spectra, respectively. The carboxyl groups were characterized with absorption peaks at  $170$  ppm in  $^{13}\text{C}$ -NMR spectra. All the absorption peaks were accordant with the structure of BBA.

#### Cure behavior of BBA and BBA/1,3-PBO

The curing reactions of BBA and 1,3-PBO were further confirmed by FTIR analysis. Figure 5 shows the FTIR spectra of the BBA and 1,3-PBO before and after the polymerization reaction. As a result, the absorption at  $951\text{ cm}^{-1}$  assigned to trisubstituted benzene ring with benzoxazine ring attached disappeared. It suggested that the ring opening reaction of benzoxazine have occurred in BBA. In addition, the broad absorption at  $2850\text{ cm}^{-1}$  assigned to the carboxyl groups disappeared, indicating the reaction of carboxyl groups and oxazoline rings. Moreover, the broad absorption at  $3360\text{ cm}^{-1}$  assigned to the secondary amine group appears. And the absorption at  $1520\text{ cm}^{-1}$ ,  $1620\text{ cm}^{-1}$  assigned to the amide group also appeared. This means that the ring opening reaction of benzoxazine ring had occurred, and then the phenolic hydroxyl groups generated by the ring opening of benzoxazine rings reacted with oxa-

zoline rings. The possible reaction mechanism of BBA/1,3-PBO system including the reaction between carboxyl groups, oxazoline, and phenolic hydroxyl groups generated by the ring opening of BBA are shown in Figure 7.

The polymerization behavior of BBA and BBA/1,3-PBO were studied with DSC at heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere from room temperature to  $300^\circ\text{C}$ . Figure 6 shows the DSC thermograms of BBA and BBA/1,3-PBO and the results were listed in Table II, respectively. As shown in Figure 6, an endothermic peak centered at ca.  $51^\circ\text{C}$  was attributed to the melting points of BBA. Then an exothermic behavior observed at high temperature region associates to the ring-opening



**Figure 6** DSC profiles of BBA (a) and BBA/1,3-PBO system (b).

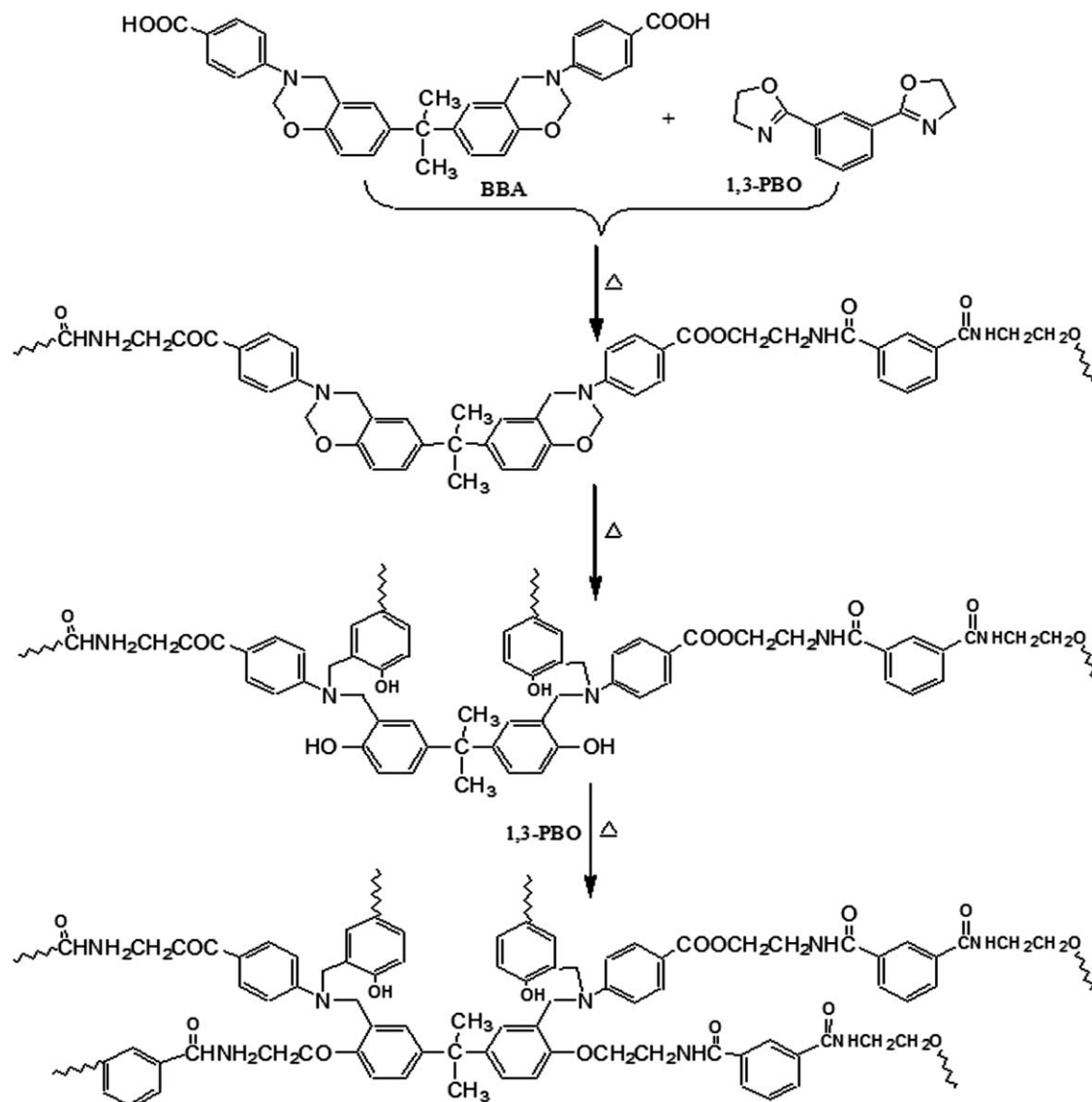


Figure 7 Possible reaction mechanism of BBA/1,3-PBO system.

polymerization of oxazine rings. The exothermic peak temperatures of BBA are 217°C, which is comparable to the polymerization temperatures of other benzoxazine compounds.

As it can be seen in Figure 6, all BBA/1,3-PBO systems exhibited two exothermic peaks, which was different from BA-a (benzoxazine prepared by bisphenol-A and aniline)/1,3-PBO. BA-a showed only a single exothermic peak, which is assigned to the ring-opening polymerization of oxazine rings and the reaction between phenolic hydroxyl groups generated by the ring opening of benzoxazine ring and 1,3-PBO.<sup>16</sup> For BP1-1, one exothermic peak was centered at 100°C and the other at 208°C. For BP1-2 and BP1-2.5, both exothermic peaks were also observed (for BP1-1, 150°C and 217°C; for BP1-2.5, 150°C and 222°C, respectively.). Nery et al.<sup>27</sup> also reported that the COOH-oxazoline reaction proceeds readily in

bulk at 140–220°C. Thus, for all BBA/1,3-PBO systems, the first exothermic peak may be attributed to the reaction between carboxyl groups of BBA and 1,3-PBO. The second exothermic peak was attributed to the ring-opening polymerization of oxazine rings

TABLE II  
DSC Characteristics of BBA and BBA/1,3-PBO System

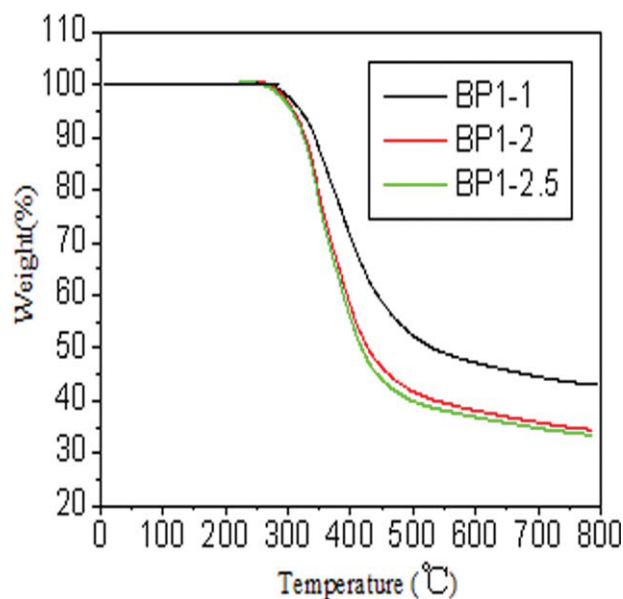
Sample name	$T_{1-2}$ (°C) <sup>a</sup>	$T_{1-2}$ (°C) <sup>b</sup>	$T_{2-2}$ (°C) <sup>c</sup>	$T_{3-2}$ (°C) <sup>d</sup>
BBA	–	153	217	279
BP1-1	100	151	208	254
BP1-2	150	160	217	265
BP1-2.5	150	162	222	269

<sup>a</sup> Peak temperature of the first exothermic peak.

<sup>b</sup> Onset temperature of the second exothermic peak.

<sup>c</sup> Peak temperature of the second exothermic peak.

<sup>d</sup> Stop temperature of the second exothermic peak.



**Figure 8** TGA thermograms of BBA/1,3-PBO copolymer. [Color figure can be viewed in the online issue, which is available at [www.onlinelibrary.wiley.com](http://www.onlinelibrary.wiley.com).]

and the reaction between phenolic hydroxyl groups generated by the ring opening of benzoxazine ring and 1,3-PBO. This was accordant with FTIR results as stated above.

Furthermore, it can be seen in Table II that the onset curing temperature and peak temperature (the second) of BP1-1 were 151°C and 208°C, respectively. While for BBA were 153°C and 217°C, respectively. In other words, the curing temperature of BBA could be lowered due to the addition of 1,3-PBO. This also indicated that the processability of BBA could be improved by the addition of 1,3-PBO. The main reason may that the carboxylic groups of BBA could effectively catalyze the thermal curing of benzoxazine at lower temperature.<sup>24–26</sup> Thus, the temperature of the curing reaction between BBA and 1,3-PBO could be lowered when the ratio of BBA/1,3-PBO was 1/1. However, the curing temperature increased gradually when the ratio of BBA/1,3-PBO increasing from 1/1 to 1/2 or 1/2.5, again. This could be attributed to the fact that superfluous 1,3-PBO acted as reactive diluents for

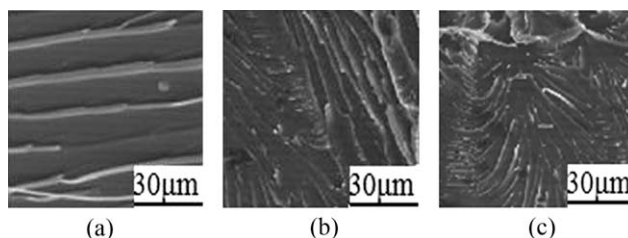
BBA benzoxazine resin when the ratio of BBA/1,3-PBO increased from 1/1 to 1/2 or 1/2.5. Therefore, the catalyst effect of carboxylic groups of BBA on the thermal curing of benzoxazine was weakened in these cases.

### Properties of the cured resin

To investigate the thermal stability of cured resin from BBA/1,3-PBO, TGA for cured products from BP1-1, BP1-2, and BP1-2.5 were recorded under N<sub>2</sub> and air atmosphere at 5°C/min to 800°C, respectively. Figure 8 shows the TGA curves for BBA/1,3-PBO after curing. The results are summarized in Table III.

From Table III, it can be seen that all cured resins showed fairly good thermal stability, which was approximately stable up to 300°C in air or nitrogen. For BP1, the 5 and 15% weight loss temperatures (Td5 and Td15) were 310°C and 375°C, whereas for BP1-2 and BP1-2.5, Td5 and Td10 decreased to 303°C and 350°C, 301 and 346°C, respectively. Moreover, the char yields of BP1-1, BP1-2 and BP1-2.5 at 800°C were 42.5%, 34.6%, and 33.2%, respectively, which were the same as the results of Td5 and Td15. These results indicated that ester–amide groups incorporation had a significant effect on decreasing thermal stability and char yield of cured resin due to the formation of linkages between carboxyl groups of BBA. Similar results were also previously reported.<sup>23</sup>

Water absorption of the cured resin from BP1-1, BP1-2, and BP1-2.5 was 0.32%, 0.38%, and 0.42%, respectively. This could be attributed to the formation of hydrophilic ester–amide bonds. Figure 9 shows the SEM photographs of fractured surfaces of the cured resin BP1-1, BP1-2, and BP1-2.5. Compared with the BP1-1, BP1-2 and BP1-2.5 showed much rougher fracture surfaces with massive plastic deformation. The increased surface roughness implied that the path of the crack tip is distorted, making crack propagation more difficult. These results illustrated that 1,3-PBO could toughen BBA resin to some degree. The other toughness testing on mechanical properties is in progress and will be reported in the future.



**Figure 9** SEM photographs of fractured surfaces of cured resin from BBA/1,3-PBO. (a) BP1-1, (b) BP1-2, and (c) BP1-2.5.

**TABLE III**  
Thermal Resistance of BBA and BBA/1,3-PBO System

Resin sample	Temp. at 5 wt % loss (°C)	Temp. at 15 wt % loss (°C)	Char yield (%) (800°C)
BP1-1	310	375	42.5
BP1-2	303	350	34.6
BP1-2.5	301	346	33.2

## CONCLUSIONS

In this work, a new benzoxazine containing carboxylic moieties (BBA) was synthesized to show attractive processing and thermal properties when cocured with 1,3-PBO. BBA showed a single curing exothermic peak at 217°C but decreased to 208°C when cocured with 1,3-PBO in the molar ratio of 1 : 1. FTIR and DSC showed that the reaction had occurred between carboxyl groups of BBA, phenolic hydroxyl groups generated by the ring opening of benzoxazine ring and 1,3-PBO. Using 1,3-PBO as modifier, the curing temperature of as-synthesized benzoxazine could be lowered and the toughness could be improved.

## References

1. Culbertson, B. M. *Prog Polym Sci* 2002, 27, 579.
2. Ning, X.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1994, 32, 921.
3. Ning, X.; Ishida, H. *J Polym Sci Part A: Polym Chem* 1994, 32, 1121.
4. Ishida, H.; Rodriguez, Y. *Polymer* 1995, 36, 3151.
5. Ishida, H.; Allen, D. J. *J Polym Sci Part B: Polym Phys* 1996, 34, 1019.
6. Ishida, H.; Rodriguez, Y. *J Appl Polym Sci* 1995, 58, 1751.
7. Shen, S. B.; Ishida, H. *J Appl Polym Sci* 1995, 61, 1595.
8. Ishida, H.; Allen, D. J. *Polymer* 1996, 37, 4487.
9. Ishida, H.; Sanders, D. P. *Macromolecules* 2000, 33, 8149.
10. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1998, 68, 1903.
11. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1999, 74, 2266.
12. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 2001, 79, 555.
13. Jang, H.; Seo, D. *J Appl Polym Sci* 1998, 67, 1.
14. Agag, T.; Takeichi, T. *Polym Prepr Jpn* 1998, 47, 2922.
15. Takeichi, T.; Guo, Y.; Agag, T. *J Appl Polym Sci* 2000, 38, 4165.
16. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Fukuda, A. *J Appl Polym Sci* 1999, 72, 1551.
17. Kimura, H.; Hasegawa, K.; Matsumoto, A. *J Appl Polym Sci* 2001, 79, 2331.
18. Kimura, H.; Matsumoto, A.; Ohtsuka, K. *J Appl Polym Sci* 2009, 112, 1762.
19. Kimura, H.; Matsumoto, A.; Ohtsuka, K. *J Appl Polym Sci* 2008, 107, 710.
20. Chen, Q.; Xu, R.; Yu, D. *J Appl Polym Sci* 2006, 100, 4741.
21. Chen, Q.; Xu, R.; Zhang, J.; Yu, D. *Macro Rapid Commun* 2005, 26, 1878.
22. Shengfang, L.; Luoli, W. *J Appl Polym Sci* 2006, 99, 1359.
23. Youqing, L.; Shengfang, L.; Heqing, T. *J Appl Polym Sci* 2008, 108, 2321.
24. Andreu, R.; Reina, J. A.; Ronad, J. C. *J Polym Sci Part A: Polym Chem* 2008, 46, 6091.
25. Kiskan, B.; Demirel, L.; Kamer, O.; Yagci Y. *J Polym Sci Part A: Polym Chem* 2008, 46, 6780.
26. Lin, C. H.; Lin, H. T.; Chang, S. L.; Hwang, H. J.; Hu, Y. M.; Taso, Y. R.; Su, W. C. *Polymer* 2009, 50, 2264.
27. Nery, L.; Lefebvre, H.; Fradet, A. *Macromol Chem Phys* 2003, 204, 1755.