

## Curing Behaviors and Thermal Properties of Benzoxazine and *N, N'*-(2, 2, 4-Trimethylhexane-1, 6-diyl) Dimaleimide Blend

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**ABSTRACT:** A blend of bisphenol-A based benzoxazine (BA-a)/*N, N'*-(2, 2, 4-Trimethylhexane-1, 6-diyl) dimaleimide (TBMI) with the ratio of 1:1 was prepared and its curing behaviors were studied by differential scanning calorimetry (DSC), Fourier Transform Infrared (FTIR). The curing mechanism was proposed based on the semiquantitative analysis from FTIR spectra. The model compound was used to study the catalysis effect of BA-a on the curing reaction of TBMI. It was found the curing reactions of BA-a and TBMI not only proceeded simultaneously, but their coreactions also occurred. The research further indicated that negative oxygen ions from ring opening of benzoxazine mainly promoted the polymerization of maleimide groups, even though the amine group of benzoxazine had a positive effect on the reaction of maleimide groups. Besides, BA-a and TBMI blends showed improved thermal properties based on the results from DMA and TGA. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1124–1130, 2013

**KEYWORDS:** blends; thermal properties; catalysts; copolymers; ring-opening polymerization

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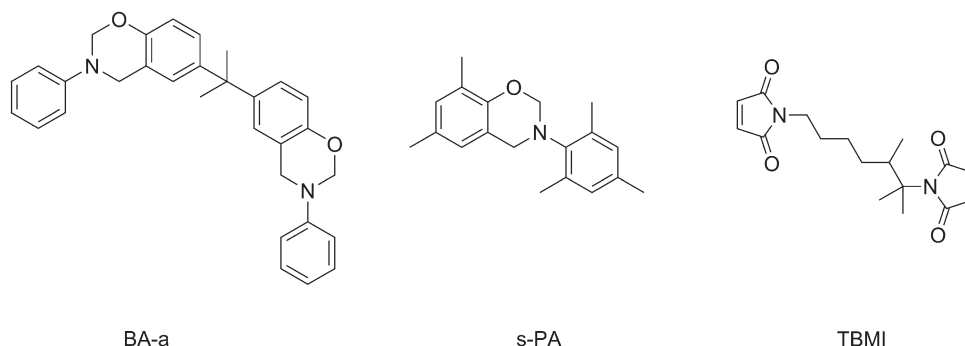
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### INTRODUCTION

High-performance thermosets have received plenty of attention for their wide applications in aircraft, electronics, space transport, and other industrials. Polybenzoxazines, a novel class of phenolic resins, have attractive characteristics, including small shrinkage during curing, low water absorption, high thermal stability, self-extinguishing, good mechanical properties, and excellent electrical properties.<sup>1–5</sup> Among the studies on benzoxazines, enhancing the performance of polybenzoxazine in harsh environment is mainly focused on. Introducing other polymerizable groups into benzoxazine monomers is an effective method to improve the mechanical and thermal properties of polybenzoxazines. Preparing polymer alloys with other resins is another relatively simple approach to get desired properties.<sup>6–12</sup> For example, benzoxazine-bismaleimide alloys have been studied widely. Maleimide precursors can undergo self-addition reactions and generate cross-linked polymers whose thermomechanical properties are good enough to meet the requirements in the aerospace industry.

Many studies focus on the catalysis effects, curing mechanisms of benzoxazine/bismaleimide (BMI) blends, and the relationships between crosslinked structures and properties.<sup>13,14</sup> Especially, catalysis effect between benzoxazine and BMI has been discussed widely about their curing mechanism and curing process. Liu

and Yu<sup>15</sup> studied the catalysis effect between benzoxazine and bismaleimide using 3-Phenyl-3,4-dihydro-2H-1,3-benzoxazine (P-ABz), *N*-Phenylmaleimide (MI-H), 4-hydroxyphenylmaleimide (MI-OH), and 4-maleimidobenzoic acid (MI-COOH). The results showed that the acidic MI-OH and MI-COOH promoted the polymerization of P-ABz, and MI-H did not promote the polymerization of P-ABz because MI-H did not possess acidic groups. On the other hand, the amine group from the ring opening of benzoxazine catalyzed the crosslink reactions of maleimides. Agag and Takeichi<sup>16</sup> also observed the curing reactions of benzoxazines and maleimides shifted to low temperatures. They believed it should be attributed to the residual phenolic OH in blend system. Furthermore, Kumar et al.<sup>17</sup> studied the curing behavior of bis allyl benzoxazine and bismaleimide blends using bisphenol A based benzoxazine (BA-a) as the model material. It was also found that the amine group from the ring opening of benzoxazine can catalyze the reaction of BMI. However, in reported papers, the curing peak temperatures of the P-ABz or BA-a in the DSC curves are 220 and 218°C, respectively. These DSC results showed that the purity of P-ABz or BA-a was not high enough. The residual phenolic OH in impure benzoxazine can catalyze the reaction of benzoxazine and affect the reaction of BMI. Furthermore, all reporters used triethylamine as model material to illustrate the catalysis effect of amine group from ring opening of benzoxazine on BMI. However, the structure of



**Scheme 1.** The structures of BA-a, s-PA and TBMI.

triethylamine as a kind of aliphatic amine is different from the amine group from benzoxazine, especially the different alkaline amines may have different effect on the curing reaction of BMI. Furthermore, Takeichi et al.<sup>18</sup> reported their studies on the curing behavior of the mixture of P-ABz and MI-OH. Meanwhile, the peak temperature of P-ABz was 222°C meaning its purity was also not high. Ishida et al.<sup>19</sup> synthesized a series of benzoxazines containing maleimide group. These polybenzoxazines showed excellent thermal properties and flame retardancy. Their research results showed the ring opening of benzoxazine occurred before the crosslink reaction of maleimide and there was no reaction between the oxazine ring and maleimide.

There are some deficiencies in previous researches about the curing mechanism of benzoxazine and BMI blends. First, the benzoxazine which was chosen as the model material is not enough purity so that the phenolic hydroxyl groups from benzoxazine can catalyze the curing reaction of benzoxazine, which has an influence on studying the curing mechanism. Second, the triethylamine as the model material may not completely imitate the catalysis effect of benzoxazine on BMI. Third, whether the cocuring reaction between benzoxazine and BMI exists or not is still unclear. So, the study on the curing mechanism of benzoxazine and BMI blends without the disturbing of impurities needs to be done and more real model materials should be used.

In this article, bisphenol-A based benzoxazine (BA-a) and low viscosity *N,N'*-(2, 2, 4-Trimethylhexane-1, 6-diyl) dimaleimide (TBMI) were chosen to study the curing mechanism of their blends. To avoid the side reactions caused by the impurities, BA-a and TBMI were purified by recrystallization for several times. The results showed that the negative oxygen ion and amine group from the ring opening of benzoxazine can catalyze the curing reaction of TBMI, and the negative oxygen ion played a main role. Furthermore, the research about the curing mechanism of the blends further proved that the cocuring reactions between BA-a and TBMI really existed besides their respective self-polymerizations.

## EXPERIMENTAL

### Materials

Aniline, aqueous formaldehyde solution, toluene, acetone, maleic anhydride, triethylamine, *N,N*-dimethylaniline, bisphenol A, 2,4-Xylenol, 2,4,6-Trimethylaniline, Sodium acetate trihydrate, tetrahydrofuran (THF), and ethyl alcohol were provided by Chengdu Kelong Chemical Reagents, China. Toluene sulfonic acid was supplied by Shanghai QianFeng Chemical, China. Trimethylhexamethylenediamine was purchased from Shanghai BaoMan biotechnology, China. All reagents were used without further purification.

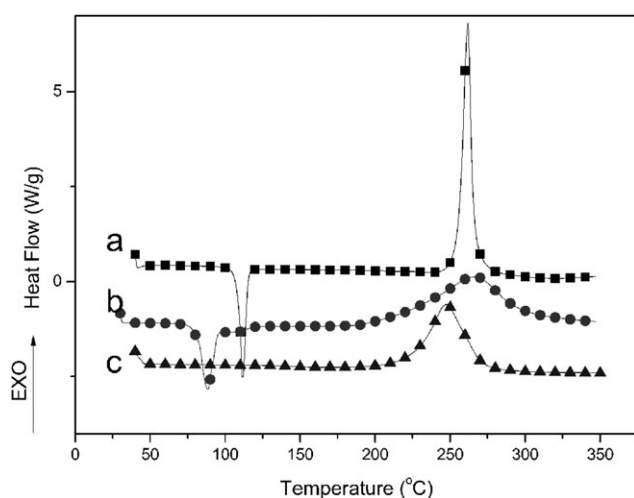
Bisphenol A based benzoxazine (BA-a) (mp, 111°C) and 2,4-xylenol-based benzoxazine (s-PA) were synthesized and characterized according to previous reports from our group.<sup>20</sup> *N,N'*-(2, 2, 4-Trimethylhexane-1, 6-diyl) dimaleimide (TBMI) (mp 88°C) was synthesized and purified following the reported procedure.<sup>21</sup> Their structures are shown in Scheme 1.

### Measurements

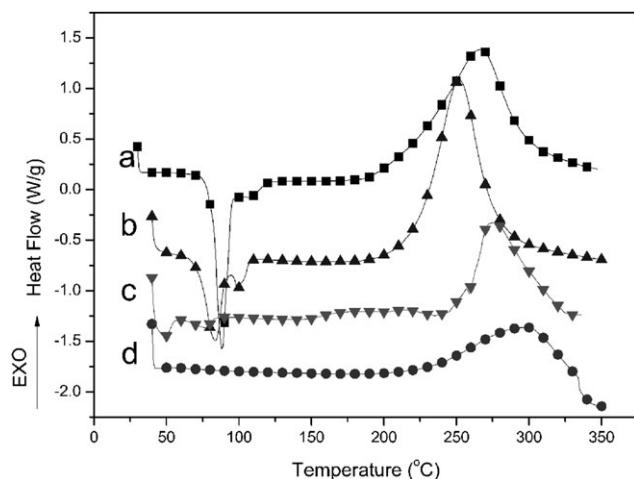
TA Instrument DSC model Q20 was used with heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min for nonisothermal tests.

Fourier transform infrared (FTIR) spectra were taken by using a Nicolet 5700 FTIR spectrometer. Coaddition of 32 scans was recorded at a resolution of 4 cm<sup>-1</sup>. FTIR spectra were obtained using the KBr pellet technique.

Dynamic mechanical analysis (DMA) was performed by using a TA Instruments DMA Q800 at a frequency of 1Hz and a heating rate of 5°C/min in a bending mode under N<sub>2</sub>.



**Figure 1.** DSC curves of BA-a (a), TBMI (b), and BT11(c).



**Figure 2.** DSC curves of TBMI (a), TBMI/triethylamine (b), TBMI/*N,N*-dimethylaniline (c) and TBMI/bisphenol A (d).

Thermo Gravimetric Analyzer (TGA) was carried out using TA Instruments TGA2950 analyzer with a heating rate of 10°C/min and a nitrogen flow rate of 40 mL/min.

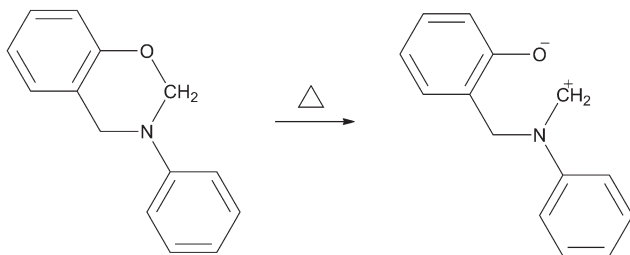
#### Preparation of BA-a/TBMI Blend and Copolymer

The binary blend of BA-a/TBMI with the molar ratio of 1:1 was prepared by melting at 115°C. This blend was named as BT11. The blend was put in a vacuum oven at 115°C for 1 h to remove the bubbles. Subsequently, a cure profile (140°C/2 h, 160°C/2 h, 180°C/2 h, 200°C/2 h) was applied. The transparency and amber castings were obtained.

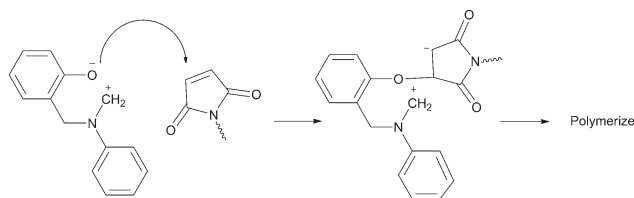
## RESULTS AND DISCUSSION

### Curing Behavior of BA-a/TBMI

The curing behavior of BT11 was studied by DSC as shown in Figure 1. The DSC curves of BA-a and TBMI were also taken for comparison. A single exothermic peak centered at 261°C was observed for BA-a. Its onset temperature was 241°C and the enthalpy was 149.3 KJ/mol. This result is very different from those of Refs. 11 and 12, in which the onset and peak temperatures of BA-a are much lower. This different may lead to the differences in proposed mechanism in following part. For TBMI, the onset and maximum temperatures of the exothermic peak were 182 and 267°C, respectively. The total amount of exotherm of TBMI was 139.2 KJ/mol. BT11 had a single exotherm with an onset temperature of 194°C and a peak temperature of 247°C. The enthalpy of BT11 was 121.1 KJ/mol. If there are only the self-polymerizations of two resins, the theoretic en-



**Scheme 2.** Ring-opening of benzoxazines.



**Scheme 3.** The proposed catalyzing mechanism of benzoxazine and maleimide.

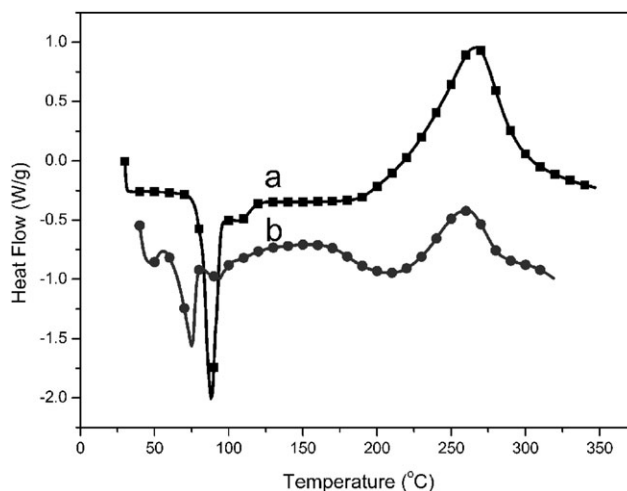
thalpy value of the blend should be 144.2 KJ/mol which is larger than the tested result implying more reactions occurred in BT11. Moreover, compared to the each component, the exotherm peak temperature of BT11 was lower, which may be caused by the catalysis effect. Besides, the curing onset temperature of BT11 was located between that of two monomers. It can be proposed that a part of TBMI cured firstly and followed by the cure of a little benzoxazine.

To prove the existence of the catalysis effect in the blend, the gelation times of TB11, BA-a, and TBMI were examined at 160°C. The gelation times of BA-a and TBMI exceeded 9500s while the gelation time of TB11 was 7681s. This short gelation time suggests that the catalysis effect indeed exists in the curing process of TB11.

### The Catalysis Effect in BA-a/TBMI

TBMI has no catalysis effect on BA-a,<sup>15</sup> while the possible catalysis effect comes from BA-a on TBMI in the blend. To study the catalysis mechanism in BT11, the model reactions were done in this work. Triethylamine and *N,N*-dimethylaniline were used to test whether the amine group from ring opening of BA-a can decrease the curing reaction temperature of TBMI. Bisphenol A was used to test whether the -OH from ring opening of BA-a can catalyze the reaction of TBMI.

DSC curves of TBMI/triethylamine, TBMI/*N,N*-dimethylaniline, and TBMI/bisphenol A at 1/1 were taken. As shown in Figure 2(b), TBMI/triethylamine showed an exotherm with onset at 181°C and max at 252°C. The peak temperature shifted 15°C to



**Figure 3.** DSC curves of different systems (a, TBMI; b, TBMI/s-PA).

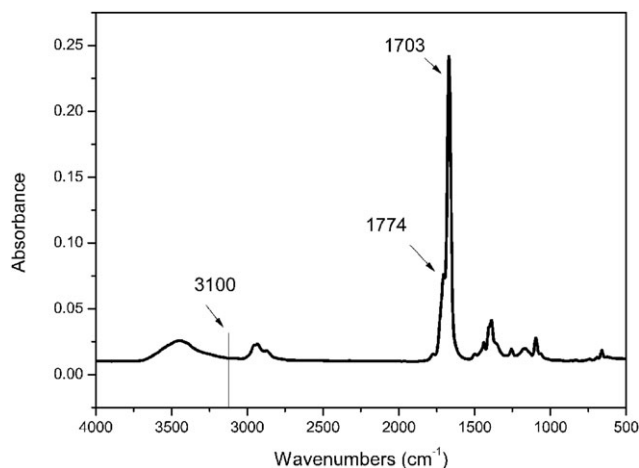


Figure 4. FTIR spectra of TBMI/CH<sub>3</sub>CHOONa after curing in 110°C.

a lower temperature compared to that of TBMI. Therefore, the triethylamine can catalyze the maleimide polymerization. For TBMI/*N,N*-dimethylaniline, it should be noted that there was a small curing reaction peak in the range of 150–240°C with an enthalpy of 7.1 kJ/mol. It is proposed that the amine group from the ring opening of benzoxazine has a catalysis effect on the reaction of TBMI based on these phenomena. TBMI/bisphenol A showed an exotherm with onset at 198°C and max at 297°C. Compared with that of TBMI, the peak temperature of TBMI/bisphenol A moved to the higher temperature, which means that the bisphenol A has no catalysis effect on TBMI.

The maleimide double bonds of TBMI are electron deficient by the electron withdrawing nature of the adjacent carbonyl groups, so alkaline amines can catalyze the reaction of TBMI. Comparing the  $pK_b$  values for *N,N*-dimethylaniline ( $pK_b = 8.9$ ) and triethylamine ( $pK_b = 3.2$ ), the basicity of the aromatic amine is significantly weaker meaning triethylamine has a more obvious catalysis effect on TBMI than *N,N*-dimethylaniline. One can easily find that the structures of *N,N*-dimethylaniline

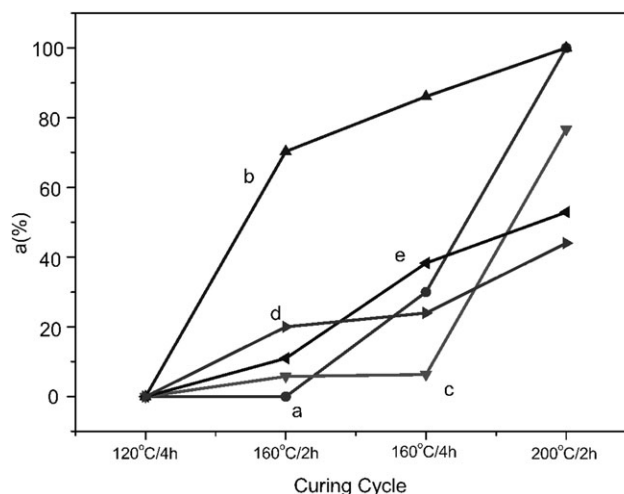


Figure 6. The reaction degree of different groups vs. temperatures: oxazine ring in BT11 (a); [dbons]C–H of TBMI in BT11 (b); =C–H of TBMI (c); =C–H of TBMI in the blend of TBMI/9 wt % s-PA (d); =C–H of TBMI in the blend of TBMI/bisphenol A (1/1) (e).

and ring opening of BA-a is more alike than that of triethylamine. As seen in the DSC curve, the catalysis effect of *N,N*-dimethylaniline on TBMI made the whole system has a new reaction peak at 150–240°C. So, it can be concluded that the catalysis effect of BA-a on TBMI partly comes from the amine group of ring opening of benzoxazine. This result is coincidence with other researches.<sup>15,16</sup>

Furthermore, study on the ring opening of benzoxazine showed that the ring opening of benzoxazine under heat would form carbonium ion and the negative oxygen ion as shown in Scheme 2. Negative oxygen ion is a strong nucleophilic reagent which can attack maleimide double bonds of TBMI easily. So the main catalysis effect of BA-a on TBMI is proposed as Scheme 3. The negative oxygen ion from partial ring opened benzoxazine mainly catalysis the reaction of TBMI.

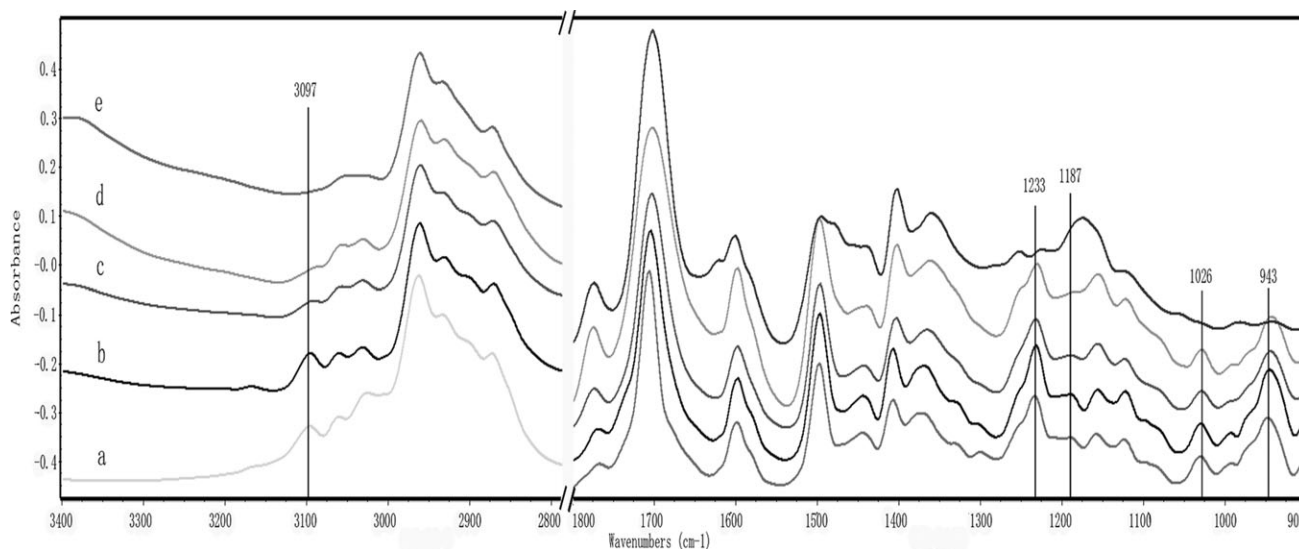
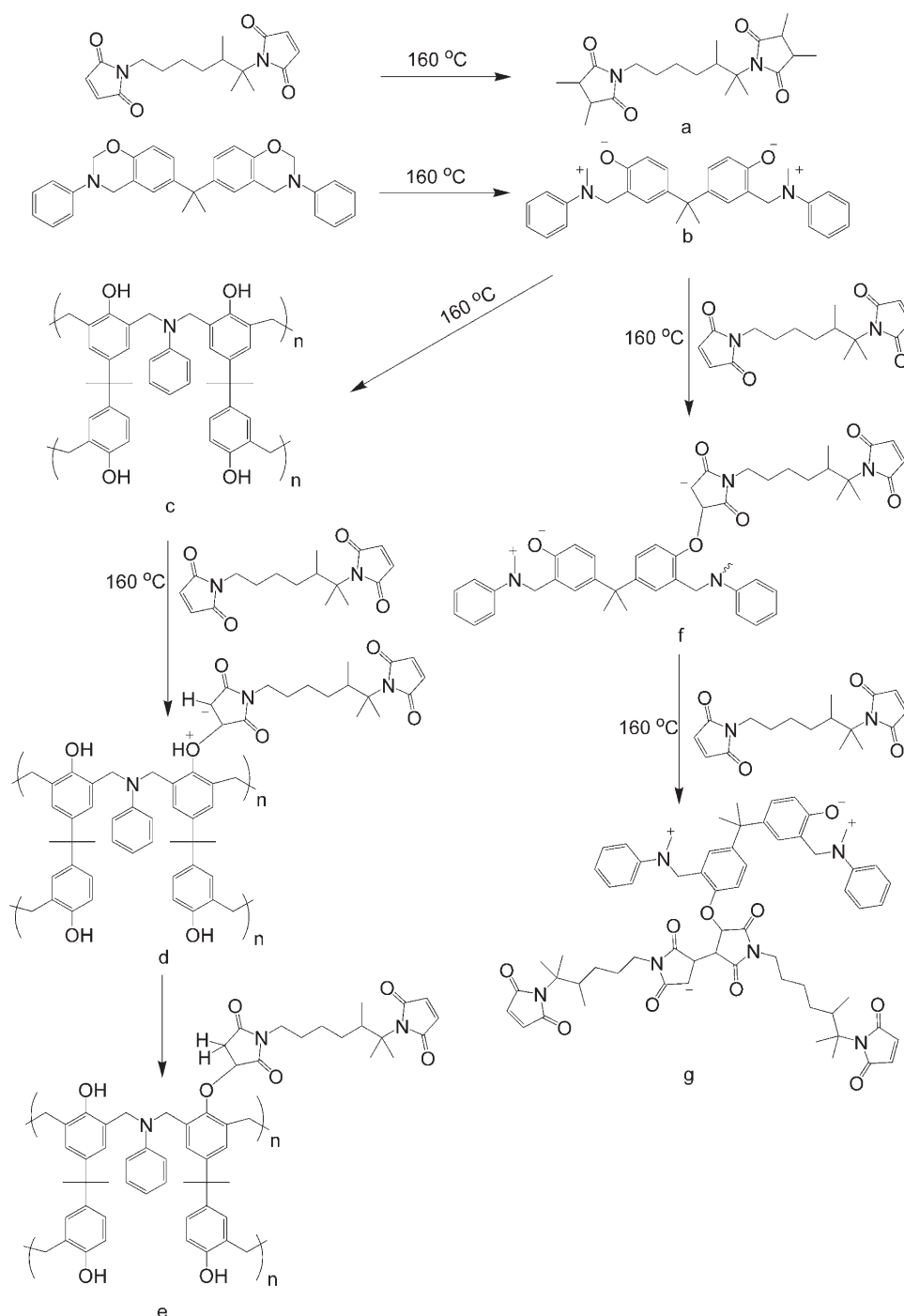


Figure 5. FTIR spectra of BT11 at room temperature (a) and after cure at 120°C/4 h (b), 160°C/2 h (c), 160°C/4 h (d), 200°C/2 h (e).



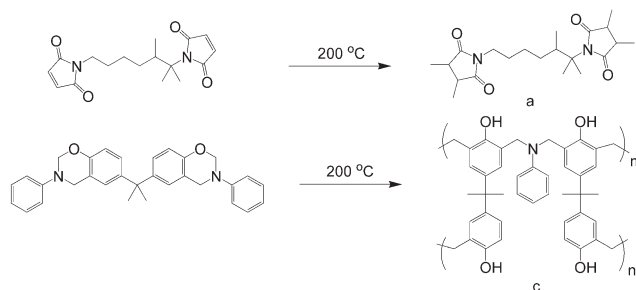
**Scheme 4.** The proposed curing mechanisms for BT11 at 160°C.

To prove the negative oxygen ion from the ring opening of benzoxazine can catalyze the reaction of TBMI, *s*-PA was chosen to model the reaction between BA-a and TBMI. The *s*-PA was blended with TBMI with a mol ratio of 1:1. Their DSC curves are shown in Figure 3. The blend showed the onset temperature was 101°C and followed by the two peak temperatures at 150 and 267°C, respectively. Compared with the DSC curve of TBMI, both onset and peak temperatures were lower. Besides, the peak at the low temperature was significantly larger than

that of TBMI/*N,N*-dimethylaniline. So, it can be proven that the negative oxygen ion from the ring opening of benzoxazine can greatly catalyze the curing reaction of TBMI.

To further prove the negative oxygen ion can catalyze the curing reaction of TBMI, study on the catalysis mechanism was done using CH<sub>3</sub>COONa as the model material. Totally, 5 wt % CH<sub>3</sub>COONa was blended with TBMI in DMF. The blend was stirred at 110°C for 2 h and the system became gel. Then, the gel was put in a vacuum oven for 1 week at room temperature





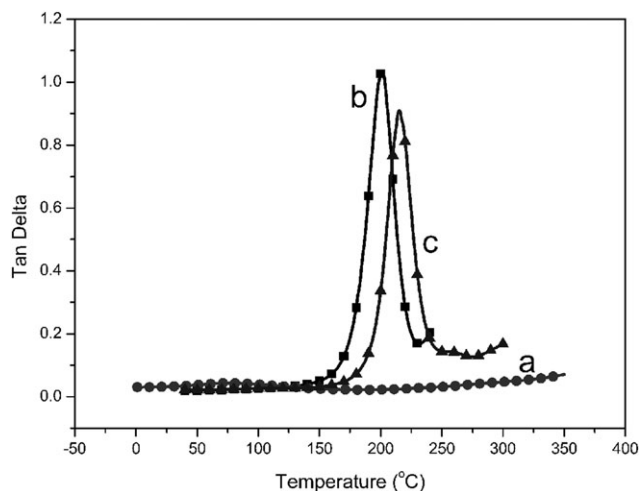
**Scheme 5.** The proposed curing mechanisms for BT11 at 200°C.

and was investigated by FTIR. As seen in Figure 4, after curing at 110°C for 2 h, the C=O absorption band at 1703 and 1774  $\text{cm}^{-1}$  was not changed, and the band due to =C—H at 3100  $\text{cm}^{-1}$  disappeared. The phenomenon implied the occurrence of curing reaction of TBMI. Thus, this result illustrates that the negative oxygen ion can effectively catalyze the reaction of TBMI.

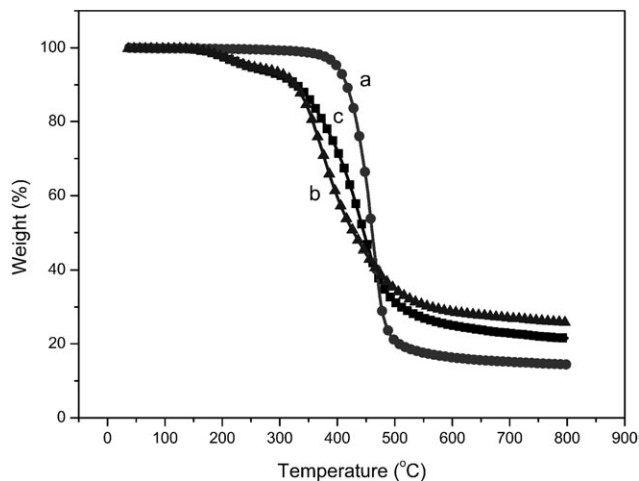
#### Curing Reaction of BA-a/TBMI Studied by FTIR

To make clear the curing mechanism of BA-a/TBMI blend, the half-quantity analysis of FTIR was used. Figure 5 shows the FTIR spectra of cured BT11 at different cure cycles.

The bands at 944  $\text{cm}^{-1}$  for the oxazine ring, at 1026 and 1224  $\text{cm}^{-1}$  for C—O—C of benzoxazine and at 3097  $\text{cm}^{-1}$  for =C—H of TBMI were observed before curing [Figure 5(a)]. Changes of these absorption peaks cannot be seen after curing at 120°C for 4 h [Figure 5(b)]. It means the curing reaction of BT11 does not occur at this condition. The intensity of these bands gradually decreased with cure [Figure 5(c–e)] and disappeared after curing at 200°C for 2 h [Figure 5(e)]. However, the characteristic absorption of TBMI at 3097  $\text{cm}^{-1}$  decreased more obviously than that of BA-a at 943  $\text{cm}^{-1}$  at early curing stage [Figure 5(c)], indicating that the reaction rate of TBMI is faster than that of BA-a and in good agreement with DSC results. It is notable that the band at 1187  $\text{cm}^{-1}$  assignable to the C—O—C



**Figure 7.** Tan Delta vs. temperature of different systems: PTBMI (a), PBA-a (b), and BT11(c).



**Figure 8.** TG curves of different systems(a, PTBMI; b, PBA-a; c, BT11).

appeared after curing at 160°C for 2 h [Figure 5(c)] and increased with curing process. This means the existence of cocuring reaction of benzoxazine and TBMI.<sup>18</sup>

To make the curing mechanism more clearly, the reaction degree were calculated from the change in the area of different absorbance bands. The band at 1700  $\text{cm}^{-1}$  assigned to the C=O in TBMI was chosen as the internal standard sign. Changes in concentration of BA-a and TBMI can be directly determined from the integration of bands at 943  $\text{cm}^{-1}$  and at 3097  $\text{cm}^{-1}$ , respectively. The relationship of reaction degree versus temperature obtained from FTIR spectra is expressed as

$$a = \left[ 1 - \frac{A(T)/A'(T)}{A(120)/A'(120)} \right] \times 100\% \quad (1)$$

where  $A(T)$  and  $A(120)$  are the integrated areas of the characteristic bands at 943  $\text{cm}^{-1}$  and 3097  $\text{cm}^{-1}$  in Figure 3 at a given temperature of  $T$  and 120°C, respectively.  $A'(T)$  and  $A'(120)$  are the integrated areas of C=O band at 1700  $\text{cm}^{-1}$  at a given temperature of  $T$  and 120°C, respectively. The reaction degree vs. temperature curves of different groups are shown in Figure 6. Curve c, d, and e mean the reaction degree of TBMI in pure TBMI, TBMI/9 wt % s-PA blend and TBMI/bisphenol A (1/1) blend, respectively (the FTIR of TBMI is not shown).

In the initial reaction stage, the reaction degree of BA-a in BT11 [Figure 6(a)] was low and reached 4 and 27% after curing at 160°C for 2 and 4 h, respectively. After curing at 200°C for 2 h, BA-a reacted completely. However, the reaction degree of =C—H of TBMI in BT11 [Figure 6(b)] reached 70% at the initial curing stage. Then the reaction degree increased with the increase of the curing temperature and reached 100% finally. Different from TBMI in BT11, the reaction degree of =C—H of pure TBMI [Figure 6(c)] was only 6% after curing at 160°C for 4 h and the ultimate reaction degree after curing cycle was 77%. It can be found that the reaction degree of pure TBMI is low at low temperature and cannot react completely at 200°C. This is because the high crosslink density limits the movement of TBMI. To further improve catalysis effect of BA-a on TBMI, 9 wt % s-PA was added [Figure 6(d)]. The reaction degree of

TBMI in blend of TBMI/9 wt % s-PA was 20% after curing at 160°C for 2 h. This value was higher than that of pure TBMI. Combined with the results of DSC in Figure 3, we can conclude that the catalysis effect of BA-a on TBMI exists and the main catalysis effect comes from the negative oxygen ion of ring opening of BA-a. Meanwhile, the reaction degree of =C—H of TBMI in TBMI/bisphenol A (1/1) [Figure 6(e)] reached only 11% after curing at 160°C for 2 h. This value is much lower than that of BT11 and higher than that of pure TBMI. This is because in bisphenol A, —O<sup>−</sup> from —OH reacts with TBMI and —H from —OH transfers to the other side of TBMI at the same time, which makes TBMI react a little and has no further curing reaction as shown in Scheme 4 (c d e) procedures. The whole process is different from the negative oxygen ion catalysis process as shown in Scheme 4 (b f g) procedures. In this process the lack of —H make TBMI can be further cured following the anionic polymerization mechanism.

The probable reaction mechanism of BA-a and TBMI blend was proposed as shown in Schemes 4 and 5. TBMI and BA-a can occur self-polymerization partly at low temperature and form Scheme 4(a,c) partly. The ring opening of a little BA-a can generate amine group and negative oxygen ion. These ions can catalyze the reaction of TBMI abundantly and the negative oxygen ion [Scheme 4(b)] plays a principal role. Meanwhile, the —OH [Scheme 4 (c)] comes from the ring opening of benzoxazine can coreact with TBMI. After the system reaches the elevated temperature (200°C), the self-polymerization of monomer occurs (Scheme 5).

#### Thermal Properties of Cured Blends

The thermal properties of the cured blends were studied by DMA. Temperature dependence of the  $\tan \delta$  of different systems is shown in Figure 7. The  $T_g$ s were estimated from the maximum of  $\tan \delta$ . As seen, cured TBMI (after post curing at 220°C) has no obvious  $\tan \delta$  peak in the entire testing range because of the high crosslink density of PTBMI. The  $T_g$  of cured TBMI was 215°C, which is higher than that of cured BA-a (201°C) obviously. This implies the BT11 has improved thermal property.

The thermal stability of three polymers was studied by TGA. The results are shown in Figure 8. As shown, the BT11 has better thermal property than PBA-a at intermediate temperature (around 400°C). The char yield of blend is located between that of PBA-a and PTBMI.

#### CONCLUSIONS

A polymer alloy was prepared based on two heat-resistant resins, BA-a and TBMI. The amine groups and negative oxygen ion from the BA-a have a catalytic effect on the polymerization of TBMI. The negative oxygen ion plays a main role. The curing

mechanism of blend was investigated carefully. The results showed that a little BA-a and TBMI occur self-polymerization first, then the BA-a catalyze the reaction of TBMI abundantly. After that, remained monomer occur self-polymerization at high temperature. The thermal property of blend improved compared with PBA-a, so the polymer alloys prepared in this study can be excellent candidates for the composite materials.

#### ACKNOWLEDGMENTS

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