

# Preparation and Characterization of High Char Yield Polybenzoxazine/Polyarylacetylene Blends for Resin-Transfer Molding

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**ABSTRACT:** Benzoxazine precursors (BOZP), 6,6'-bis(2,3-dihydro-3-(3-ethynylphenyl)-4H-1,3-benzoxazinyl)-ketone and 6,6'-bis(2,3-dihydro-3-(3-ethynylphenyl)-4H-1,3-benzoxazinyl)ether were synthesized and characterized by Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) and Fourier transform infrared spectroscopy (FTIR). The polyarylacetylene (PAA) was synthesized through thermal polymerization of diethynylbenzene, and characterized by  $^1\text{H-NMR}$ , FTIR, and Differential Scanning Calorimetry (DSC). The BOZP/PAA blends were prepared with different contents

of PAA, and their viscosity was measured using NDJ-79 rotating visometer. The curing behavior of BOZP/PAA blends was characterized by DSC. The thermal stability of cured BOZP/PAA blends was studied using Thermogravimetric Analysis, the results show char yield at 800°C was in the range of 78–84%. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3026–3033, 2009

**Key words:** polybenzoxazine; polyarylacetylene; resin transfer molding; char yield

## INTRODUCTION

Resin transfer molding (RTM) is a well-established technique for production of automotive and aerospace components. It is an environmentally friendly process, which offers good reproducibility combined with low costs and the ability to manufacture complex shapes parts. Therefore, many efforts have been made to develop high performance RTM matrices for advanced polymeric composites and some resins systems have been successfully developed.<sup>1–6</sup> For RTM, the resins should generally have low viscosity and sufficient pot-life at injection temperature, cure fast at processing temperature, and have no volatile molecules released in the course of curing.<sup>5,7</sup>

Phenolic resins have been widely used as matrix in composites for thermal protection due to their thermal stability, high char yields, and low flammability. However, the drawbacks of phenolics are volatiles which may be produced during curing, residual catalyst, and other reactants retained in the resins.<sup>8–10</sup> Polybenzoxazines, as a novel class of thermosetting phenolic resins, are useful as precursors for high char yielding materials, and offer a number

of attractive properties, including high glass transition temperature, high thermal stability, good mechanical properties, and flexibility in molecular design.<sup>11–15</sup> In addition, they do not produce byproducts during curing and no catalysts are needed. The additional reactive acetylene group increases the glass transition temperature and thermal stability of polybenzoxazine, for example, the char yields of polybenzoxazine based on 3-aminophenylacetylene significantly improved compared with the corresponding aniline-based polybenzoxazine.<sup>16–18</sup> However, much of benzoxazines are solid at room temperature and have high melt viscosity. Many studies have been made to utilize reactive diluents to lower liquefying temperature as well as to further reduce melt viscosity of the benzoxazine resins. Ishida and Allen<sup>19</sup> reported that addition of liquid epoxy (EPON825) to a polybenzoxazine could significantly lower liquefying temperature and greatly increased a crosslink density of the thermosetting matrix. Rimdusit et al.<sup>20</sup> showed that toughness of polymer alloys of rigid polybenzoxazine and low viscosity flexible epoxy (EPO732) systematically increased with the amount of the epoxy due to an addition of more flexible molecular segments in the polymer hybrids. Jubsilp et al.,<sup>21</sup> Dansiri et al.,<sup>31</sup> and Gu et al.<sup>32</sup> reported that to utilize liquid monofunctional benzoxazine as reactive diluents to reduce melt viscosity of bifunctional benzoxazine resin.

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However, the addition of the diluents into the solid benzoxazines was reported to lower a crosslink density of the polymer network and led to the decrease in thermal degradation temperature and char yield of the polymer hybrids.<sup>21,22</sup>

Polyarylacetylene (PAA) is a resin which could form a highly crosslinked aromatic polymer that contains only carbon and hydrogen, it is extremely attractive as a carbon precursor because of its very high carbon content, which results in a high char yield, and used as a resin matrix for C/C composites.<sup>23</sup> Polydiethynylbenzene is a typically PAA, which was prepared from diethynylbenzene (DEB) polymerization, if the reaction is allowed go to completion, the product is a highly crosslinked, insoluble, infusible material. However, the reaction is generally stopped at a monomer conversion above about 30% and below about 90%, it is possible to produce a prepolymer with low average molecular weight, the prepolymer are viscous liquids, and have low melt viscosity which enables easy impregnation of carbon fiber, and undergo thermal polymerization to yield a highly crosslinked structure.<sup>24</sup>

The objective of our work was to develop a resin matrix with high char yield, a blend of benzoxazine precursors (BOZP) with PAA, is a viscous liquid at room temperature or has low viscosity, and has potential application for manufacturing of advanced polymer composites with RTM process. In this article, the preparation and miscibility of BOZP and PAA were described, and the viscosity, curing and char yield of the BOZP/PAA blends were also investigated.

## EXPERIMENTAL

### Materials

Formaldehyde (37%), all solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. 4,4'-Dihydroxydiphenylether (99%) were purchased from Wuxi Shengan Chemical Co. Ltd. 4,4'-Dihydroxybenzophenone (99.0%) were purchased from Hubei Kexing Medical & Chemical Co. Ltd. All the chemicals were used without further purification. 3-aminophenylacetylene (99%) was prepared and supplied by the fine-chemical laboratory in our university. Diethynylbenzene (DEB, purity 90%, which contains 31% *p*-DEB and 59% *m*-DEB, others like monoethynylbenzene-derived compounds) was prepared by our laboratory.

### Synthesis of benzoxazine precursors

The BOZP, as-synthesized 6,6'-bis(2,3-dihydro-3-(3-ethynyl-phenyl)-4H-1,3-benzoxazinyl)ketone, abbreviated as 44K-eP, and as-synthesized 6,6'-bis(2,3-dihydro-3-(3-

ethynylphenyl)-4H-1,3-benzoxazinyl)ether, abbreviated as 44E-eP, were synthesized using the following procedure.<sup>25</sup> Formaldehyde (36%) 33.3 g (0.4 mol) and 50 mL toluene was added in 500 mL three-neck flask equipped with a stirrer, thermometer and reflux condenser, 3-aminophenylacetylene 23.4 g (0.2 mol) was added dropwise, and the mixture was cooled by ice-bath to keep the temperature below 4°C with stirring. After the addition was over, 4,4'-dihydrodiphenylether 20.2 g (0.1 mol) or 4,4'-dihydroxybenzophenone 21.4 g (0.1 mol) was added to the system. Then the mixture was heated to 80°C and kept this temperature for 6 h. The products were washed with 1 mol/L NaOH solution three times and then washed with distilled water until the mixture was neutral. The solvents were removed by reduced pressure distillation. The structure of the products was characterized by Fourier transform infrared spectroscopy (FTIR), Proton nuclear magnetic resonance (<sup>1</sup>H-NMR).

The benzoxazine precursor 44E-eP was obtained as an orange-colored solid with a melting range of 105–125°C, the oxazine ring content of 67.2%. FTIR(cm<sup>-1</sup>): 3440, 3280, 2890, 2110, 1600, 1570, 1490, 1430, 1270, 1250, 1230, 1210, 1170, 945, 779, 694, 646, 629. <sup>1</sup>H-NMR (ppm): 7.25–6.62(14H, Ar-H), 5.31(4H, -N-CH<sub>2</sub>-Ph), 4.92–4.80(H, -CH<sub>2</sub>-N-CH<sub>2</sub>-), 4.56(4H, -N-CH<sub>2</sub>-O), 3.04(2H, -C≡CH).

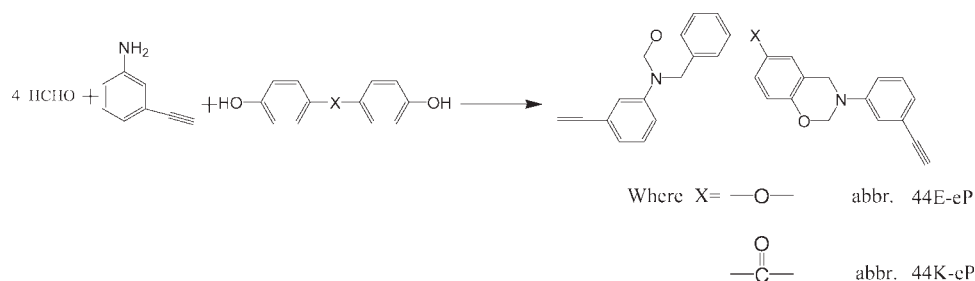
The benzoxazine precursor 44K-eP was obtained as a pale yellow powder with a melting range of 72–91°C, the oxazine ring content of 77.3%. FTIR (cm<sup>-1</sup>): 3440, 3280, 2910, 2100, 1650, 1600, 1570, 1490, 1370, 1330, 1310, 1240, 1120, 935, 789, 687, 656, 633. <sup>1</sup>H-NMR (ppm): 7.55–6.84(14H, Ar-H), 5.41(4H, -N-CH<sub>2</sub>-Ph), 5.18–4.80(H, -CH<sub>2</sub>-N-CH<sub>2</sub>-), 4.66(4H, -N-CH<sub>2</sub>-O), 3.05(2H, -C≡CH).

### Synthesis of polyarylacetylene

PAA was prepared from thermal polymerization of diethynylbenzene. Diethynylbenzene 126 g (1 mol) was charged into a 250 mL three-necked flask equipped with stirrer, thermometer, and reflux condenser, and heated to 110°C and kept stirring at 110°C for 16 h. The system was cooled to room temperature. The product, PAA resin, was brown viscous liquid prepolymer with the viscosity of about 800 mPa s at 30°C. PAA resin was characterized by FTIR and <sup>1</sup>H-NMR.

### Preparation of BOZP/PAA blends

The blends of BOZP and PAA (BOZP/PAA) were prepared with different contents of PAA, by using solution blending method. 44E-eP, 44K-eP precursors, and PAA were dissolved into acetone separately, the solutions of them were mixed and a



**Scheme 1** Synthesis of benzoxazines.

transparent brown solution was obtained. The solvent in the blended mixture was evaporated in an ambient environment until most of the solvent was driven off, and then the residual solvent was removed in a vacuum oven at 60°C for at least 2 h.

### Measurements and characterization

FTIR spectra were obtained on Thermo Electron Corp. Nicolet5700 spectrometer in the range of 4,000–500  $\text{cm}^{-1}$  wavenumber. The BOZP were cast from a tetrahydrofuran solution onto KBr plates, and PAA was coated directly.  $^1\text{H-NMR}$  spectrum was recorded with a Bruker DRX500 spectrometer at 500MHz with deuterated chloroform as the solvent for BOZP, and deuterated acetone for PAA. Thermogravimetric analysis (TGA) was performed with a WIT-I TGA thermograms at heating rates of 10°C/min over the temperature range of room temperature to 800°C in a nitrogen atmosphere. Viscosity was determined with NDJ-79 rotating viscometer. Differential scanning calorimeter (DSC) analyses are performed on NETZSCH200 with a heating rate of 10°C/min using a nitrogen purge and empty aluminum pan as a reference. Dynamic Mechanical Analysis (DMA) spectra were recorded with Rheogel-E4000FDAI Dynamic Mechanical Spectrometer. Specimens, with dimensions of  $30 \times 4 \times 2 \text{ mm}^3$ , were tested in flexural mode, and the test frequency was 1 Hz and at a heating rate of 5 K/min for temperature sweep tests. Flexural and compressive strength were measured according to GB/T 9341-2000 (People's Republic of China National

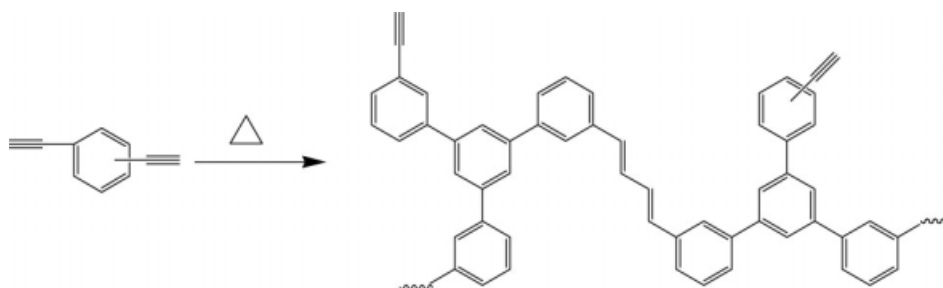
Standard Methods) on AG-2000A universal testing Instrument.

## RESULTS AND DISCUSSION

### Synthesis and characterization of BOZP and PAA

Benzoxazine monomers, 44E-e and 44K-e, were reported firstly by Ishida and coworkers,<sup>16</sup> their chemical structures are shown in Scheme 1. For practical application, the as-synthesized mixture, BOZP, which consists of monomer and oligomers that contain phenolic groups, is good enough, but for controlled structure and properties, the monomer is freed of the oligomers.<sup>26</sup> In our work, the BOZP was synthesized and confirmed by FTIR and  $^1\text{H-NMR}$ .

According to literature acetylene can react under cationic, coordination, free radical, photolytic. Thermal polymerization of model diethynyl compounds in the literature showed reaction paths forming Strauss coupling, Diels-Alder products, trimers, tetramers, naphthalenes, and conjugated polymers.<sup>27</sup> One study of acetylene terminated imide reported 30% of the acetylenic groups underwent cyclotrimerization while the remainder was consumed by other reactions.<sup>28</sup> In our work, PAA was prepared by thermal polymerization of diethynylbenzene as shown in Scheme 2. Polymerization was carried out under 110°C for 16 h to achieve conversion of about 30% calculated by  $^1\text{H-NMR}$  (Fig. 1) and 34.5% calculated by DSC of DEB and PAA (Fig. 2). The prepolymer had a viscosity of about 800 mPa s at 30°C.  $^1\text{H-NMR}$  spectrum of PAA was shown in Figure 1, the signals



**Scheme 2** Thermal polymerization of diethynylbenzene.

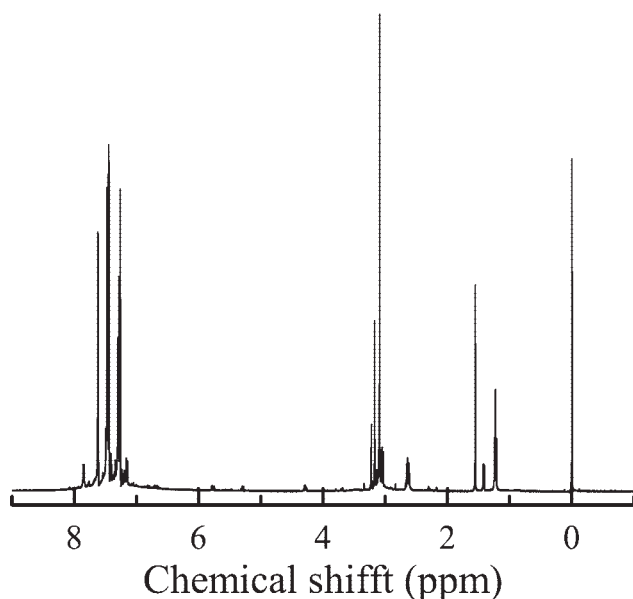


Figure 1  $^1\text{H-NMR}$  spectrum of PAA.

at 7.14–7.86 ppm due to aromatic protons, 3.03–3.22 ppm due to the protons of free terminal acetylene with different aromatic ring. The infrared spectrum of PAA was shown in Figure 3. The acetylene group showed characteristic IR absorption band at 3290 and 621  $\text{cm}^{-1}$  correlated with the carbon(sp)-hydrogen stretching and bending vibrations, the  $\text{C}\equiv\text{C}$ -stretching at 2110  $\text{cm}^{-1}$ . The absorption peak at 3290  $\text{cm}^{-1}$  reveals the present of free terminal  $\text{C}\equiv\text{CH}$  groups, and the absorption peaks at 1700–2000  $\text{cm}^{-1}$  indicate that PAA has the alternating double bond structure ( $\text{—CH=CPh—}$ ).

#### Miscibility of BOZP with PAA

The miscibility of BOZP with PAA plays an important role in influencing the properties of cured BOZP/PAA blends. Polymer–polymer and polymer–

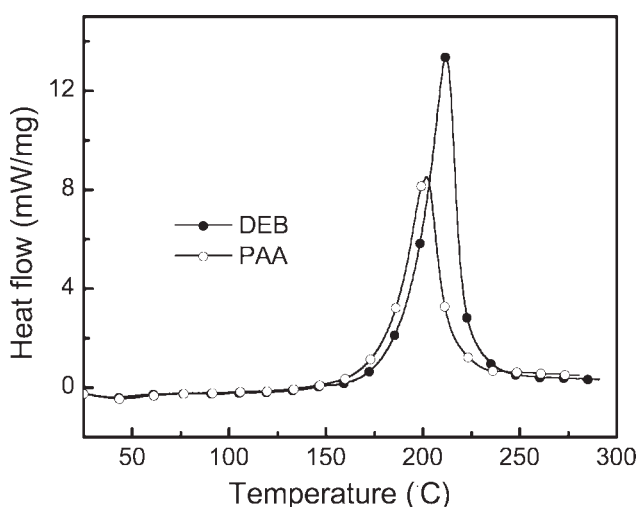


Figure 2 DSC thermograms of PAA and DEB.

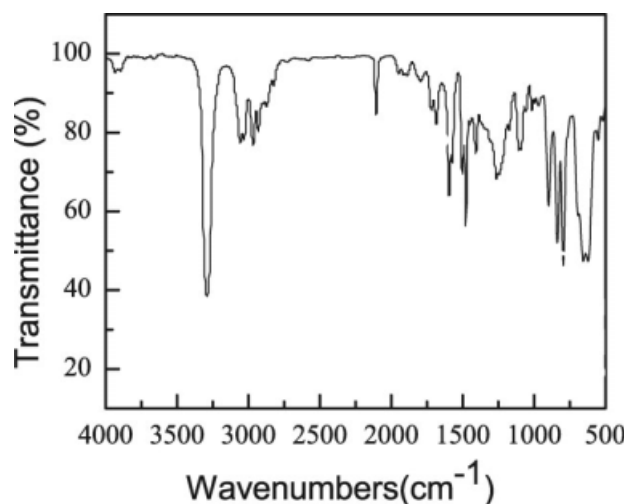


Figure 3 FTIR spectra of PAA.

solvent compatibility are very often approached qualitatively by a comparison of the solubility parameters ( $\delta$ ). However, the solubility parameter of 44E-eP, 44K-eP, and PAA resin have not been reported in literature. In this study, the group contribution method was employed to estimate the solubility parameter for 44E-eP, 44K-eP, and PAA resin. Fedors method<sup>29,30</sup> describes that

$$\delta = \left( \frac{\sum \Delta E_i}{V} \right)^{1/2} \quad (1)$$

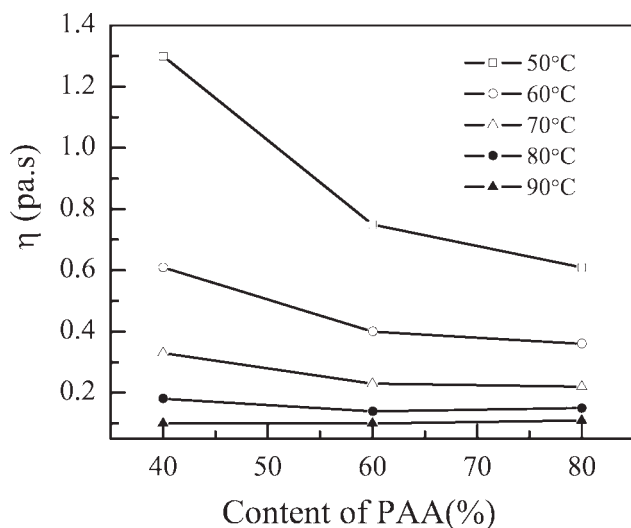
where  $\Delta E_i$ , energy of vaporization;  $V$ , molar volume. For various groups, the values of  $\Delta E_i$  and  $V$  are given in literature.<sup>28</sup>

The calculated solubility parameters for 44E-eP, 44K-eP and PAA resin according to Fedors method are 25.1, 25.8, and 24.9  $\text{MPa}^{1/2}$ , respectively. The literature has shown that the differences in solubility parameters of less than 7.0  $\text{MPa}^{1/2}$  between materials were considered being miscible system. So it was proposed that the BOZP and PAA have good intermiscibility. When heated up to 50°C, all the BOZP/PAA blends were transparent, and the clarity can be reserved until 90°C for ca. 3 h, these suggest that the BOZP/PAA blends were miscible, no phase separation occurred at the scale under visible lights.

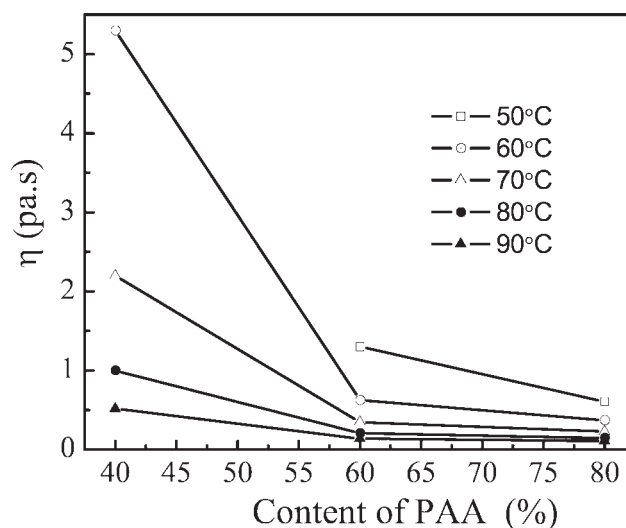
#### Characterization of PAA/BOZP blends

BOZP, 44E-eP and 44K-eP, and PAA (BOZP/PAA) blends were preparation with different weight fractions of PAA, 40, 60, and 80%. All BOZP/PAA blends are miscible giving homogenous and viscous liquid. The viscosity of BOZP/PAA blends as a function of PAA content under different temperature were exhibited in Figure 4 and 5. It can be seen from both figures, first, the viscosity of BOZP/PAA





**Figure 4** Viscosity–temperature for 44E-eP/PAA blends with different content of PAA.



**Figure 5** Viscosity–temperature for 44K-eP/PAA blends with different content of PAA.

blends decreased with increasing the content of PAA from 40 to 80%; second, the viscosity of 44E-eP/PAA blends was much lower than that of 44K-eP/PAA blends; and third, the viscosity of BOZP/PAA blends decreased rapidly with increasing the temperature from 50 to 90°C, especially, when the content of PAA was less than 60%.

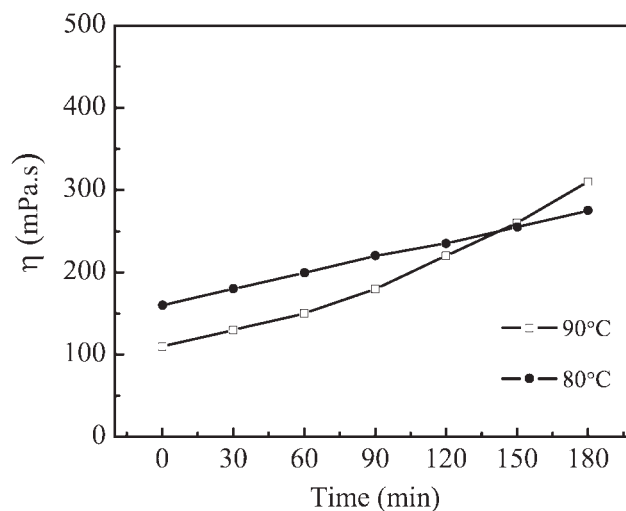
For 44E-eP/PAA blends, the viscosity is quite low when the content of PAA was more than 40% by weight, at temperature above 70°C, the viscosity was less than 0.5 Pa s, which was an advantage for RTM process, when temperature was above 90°C, the viscosity was less than 0.1 Pa s, such low viscosity tends to form turbulence in the RTM process. For 44K-eP/PAA blends, the viscosity was higher than 0.5 Pa s, when the content of PAA was less than 50% by weight at temperature below 90°C. Therefore, when the content of PAA was more than 50% by weight, the viscosity was low enough for RTM processing.

The viscosity–time curves of 44K-eP/PAA blend with 60% PAA at both 80°C and 90°C was shown in Figure 6, The viscosity of 44P-eP/PAA blend remains low and fairly constant up 180 min in the experimental temperature which was an advantage for RTM process. Therefore, the BOZP/PAA blends were recommended to retain its low viscosity with suitable period of time, which was sufficient for RTM process.

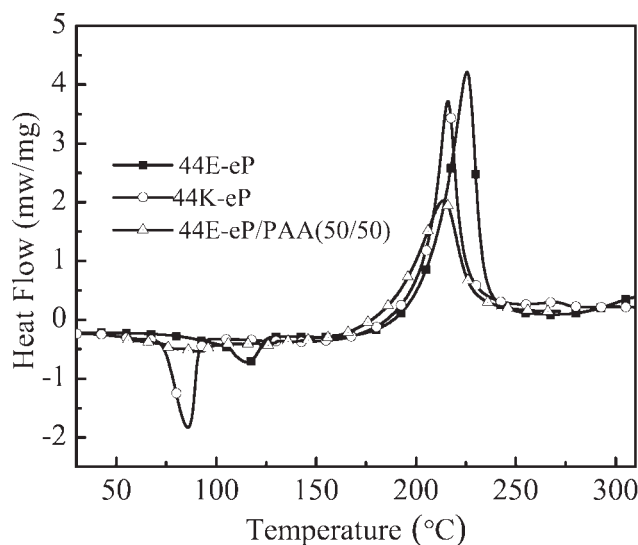
#### Curing behavior of BOZP/PAA blends

The curing characteristics of BOZP/PAA blends were investigated by DSC analysis, as comparison, 44E-eP and 44K-eP was also included. The nonisothermal DSC thermograms of 44E-eP, 44K-eP and 44E-eP/PAA (50/50 wt %) were shown in Figure 7

and the feature data were summarized in Table I. 44E-eP and 44K-eP have shown melting transition peak in the range of 105–125°C and 71–92°C, respectively. 44E-eP, 44K-eP and 44E-eP/PAA blends have a single exothermic (polymerization reaction) peak at approximately 226, 216, and 214°C, respectively. The exothermal peak of crosslinking reaction of 44E-eP starts at 169°C, goes through the onset at 193°C, reaches the maximum at 226°C, and stops at 249°C, the amount of exothermic enthalpy is 456 J/g, and for PAA/44E-eP was 158°C, 182°C, 214°C, 262°C and 520 J/g, respectively. The results suggest that ring-opening polymerization reaction of oxazine ring and crosslinking reaction of acetylene group to form a network structure took place simultaneously at almost the same temperature range. On the other hand, the cure reaction started temperature of 44E-



**Figure 6** Viscosity–time curves of 44K-eP/PAA(40/60) blend at 80°C and 90°C.



**Figure 7** DSC thermograms of 44E-eP, 44K-eP and 44E-eP/PAA(50/50) blend.

eP/PAA blends was observed a slight shift toward a lower temperature than 44E-eP, and the cure exotherm appeared in a broad range from 158 to 262°C, due to the effect from the presence of PAA which polymerization temperature started at 113°C (Fig. 2). Generally, decreasing in cure temperature was an advantage for RTM process.

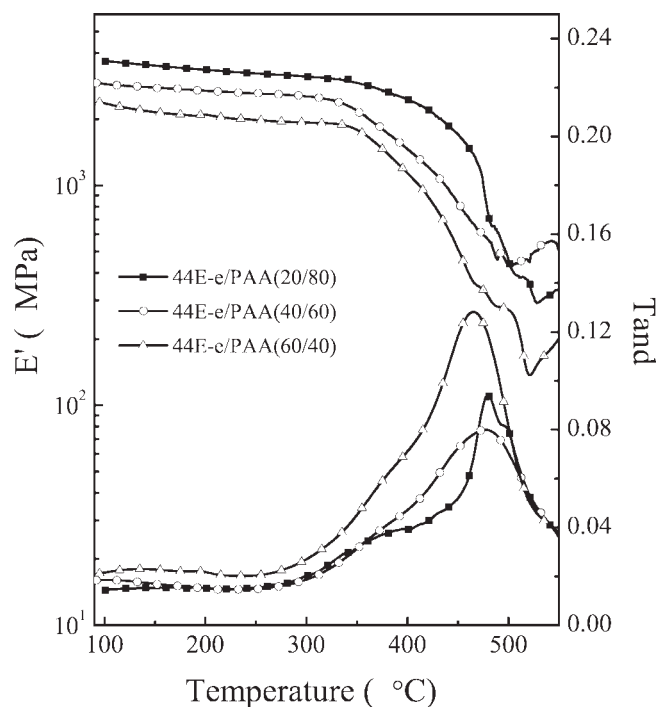
On the basis of dynamic DSC analysis of BOZP/PAA blends and PAA, the cure reaction of PAA started at 113°C, and cure heat was 1167 J/g, the cured schedule of BOZP/PAA blends were given as follow: 110°C/4h, 120°C/2h, 140°C/2h, 160°C/2h, 180°C/2h, 200°C/2h, and post cured 250°C/4h in an oven.

#### Mechanical properties of cured BOZP/PAA blends

The effect of PAA content on the dynamic mechanical properties of cured BOZP/PAA blends was depicted in Figure 8. From this figure, it was

**TABLE I**  
Cure Characteristics of 44E-eP, 44K-eP, and 44E-eP/PAA Blend

Feature temperature (°C)	44E-eP	44K-eP	PAA	44E-eP/PAA (50/50)
Melting peak	105–125	71–92	/	/
Start cure temperature	169	170	113	158
Onset temperature	193	190	181	182
Peak temperature	226	216	202	214
Stop temperature	249	245	268	262
Exothermic enthalpy(J/g)	456	529	1167	520



**Figure 8** Dynamic mechanical spectrum of cured 44K-eP/PAA blends.

observed that the storage modulus and glass transition temperature of cured BOZP/PAA blends were found to systematically increase with PAA content increasing, as a result of the addition of the higher crosslink density and more rigid molecular segments of PAA into the network. For BOZP/PAA(60/40) blends, The storage modulus ( $E'$ ) is 3.2 GPa at 25°C, and the storage modulus retention is over 80% at 200°C, over 70% at 300°C, indicating that the cured BOZP/PAA blends offer excellent thermomechanical properties.

The glass transition temperature ( $T_g$ 's) of cured BOZP/PAA blends were determined as the peak of the  $\tan \delta$  in dynamical mechanical thermograms as seen in Figure 8 and summarized in Table II, the  $T_g$ s of cured BOZP/PAA blends were expectedly found to increase with PAA content. Again, only a single  $\tan \delta$  peak was observed in each cured BOZP/PAA blends suggesting the presence of a single phase network in the blends, which is in good agreement with the miscibility result. The maximum amplitude of the  $\delta$ -relaxation peak was found to decrease with PAA content increasing. The behavior suggests the higher crosslinking density of cured BOZP/PAA blends when PAA content increases thus limiting greater segmental mobility in the network.

The flexural and compression strength of the cured BOZP/PAA blends was shown in Table II. Cured BOZP/PAA blends present the characteristic mechanical behavior of a brittle solid, with

**TABLE II**  
**Mechanical Properties and Char Yield of Cured BOZP/PAA Blends**

Samples	Composition		$T_{d5}$ (°C)	$T_g^*$ (°C)	Char yield at 800°C (%)	Strength (MPa)	
	BOZP	PAA				Flexural	Compression
1	44E-eP 100	0	398	/	73.6	/	/
2	60	40	414	465	78.8	68.7	111.1
3	40	60	406	477	81.4	48.3	87.3
4	20	80	453	479	81.9	39.2	20.0
5	0	100	567	/	87.4	/	/
6	44K-eP 100	0	400	/	71.6	/	/
7	60	40	428	424	77.9	63.1	147.6
8	40	60	442	452	81.3	44.2	125.8
9	20	80	490	485	84.2	31.9	23.2

\*The glass transition temperatures ( $T_g$ ) of cured BOZP/PAA blends were determined from the  $\tan\delta$  peak in dynamic mechanical thermograms.

practically linear stress-strain curves in which all the deformation is elastic. On the other hand, the flexural and compression strength of cured BOZP/PAA blends decrease with PAA content increasing.

#### Char yield of cured BOZP/PAA blends

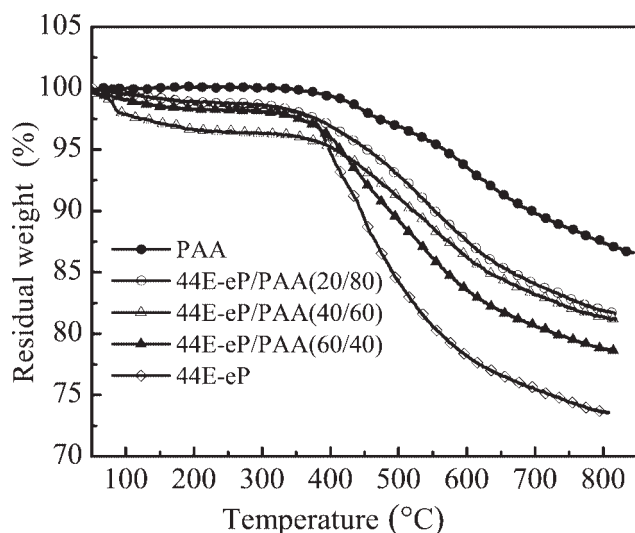
The cured BOZP/PAA blends were analyzed for their thermal stability and char yield by TGA which were shown in Figures 9 and 10 for cured 44E-eP/PAA and 44K-eP/PAA blends with different content of PAA. For comparison, the TGA of cured 44E-eP, 44K-eP and cured PAA were also included, and the details of decomposition including  $T_{d5}$  (temperature at 5% weight loss) and char yield were summarized in Table II. The thermal stability was dependent on the compositions of BOZP/PAA blends, apparently, the thermal stability increase with content of PAA increasing. Thus, the PAA results in an increase in

the overall thermal stability of cured BOZP/PAA blends.

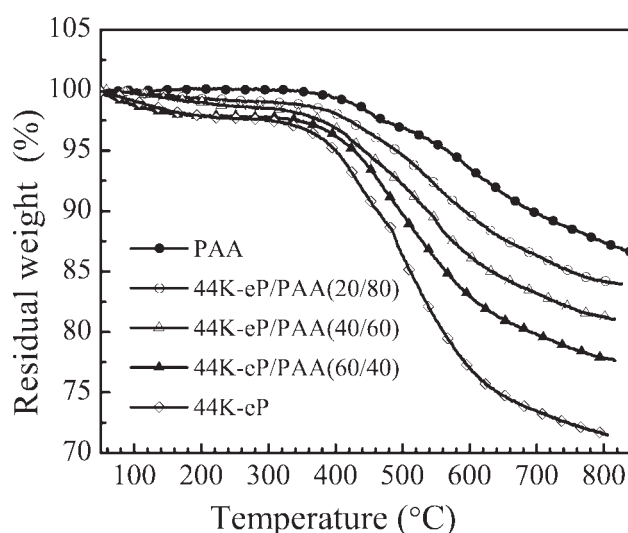
#### CONCLUSIONS

Low-viscosity binary blends of PAA and benzoxazine have been developed. The blends render homogeneous and void-free cured specimens with high char yield which are strongly dependent on the combined amount of PAA and benzoxazine in the blends. Benzoxazine resins imparts thermally curable, high char yield, and mechanical strength to the material, whereas PAA is used mainly to reduce the viscosity of the mixture, besides the function as a diluent, PAA also gives higher char yield material.

The blends showed excellent processing properties for RTM. The TGA thermograms of cured blends showed char yield at 800°C and  $T_{d5}$  were in the range of 79.1–82.0% and 419.7–460.2°C for cured 44E-eP/PAA blends; 78.2–84.2% and 431.2–492.2°C for



**Figure 9** TGA thermograms of cured 44E-eP/PAA blends.



**Figure 10** TGA thermograms of cured 44K-eP/PAA blends.

cured 44K-eP/PAA blends. The BOZP/PAA blends could be deemed as a high-char-yield resin and will be a good candidate for the matrix of ablative composite with RTM process.

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