

## HIGH PERFORMANCE COMPOSITES BASED ON PHENOLIC / BENZOXAZINE BLENDING MATRIX

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### Abstract

*In this study, a binary matrix system was prepared to investigate the effect of interaction between phenolic (PF) and benzoxazine (BOZ) resin on the processability, mechanical and thermal properties of chopped polyvinyl alcohol (PVA) fibre reinforced composites. A single-ring BOZ resin was synthesized to produce the phenolic / benzoxazine (PF-BOZ) blending matrix used in this composite system. The structure of BOZ monomer was confirmed by FTIR and <sup>1</sup>H-NMR. The results of DSC and resin gelation time measurements revealed that the addition of phenolic resin into benzoxazine resin can lower the curing temperature of the binary systems and reduce distinctly the vitrification time, which indicated a better processability for the blending matrix. In addition, with increasing the concentration of BOZ up to 40 wt.% in the blending matrix, the moulding shrinkage of composites showed a significant decline from 0.79% to 0.60%, and the impact and flexural strength of composites were increased by 74.6% and 13.2%, respectively.*

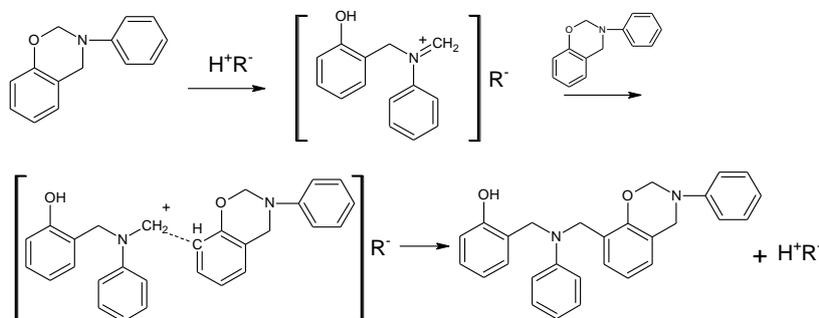
### 1 Introduction

Phenolic (PF) composites present many advantages, such as high adhesive strength, high carbon residue rate, low smoke, low toxicity, flame retardance, good thermal stability and chemical inertness, and have been widely applied a myriad of industrial products, particularly as the ablative composite material in the aviation industry [1,2]. However, applications are limited by such deficiencies as brittleness, short storage duration and release of small molecules during curing period of PF matrix [3, 4]. To overcome these weaknesses, many studies reported PF resins were blended with modifier agents, e.g. rubber, boric acid, molybdic acid, cashew nut-shell oil, curing agent and inorganic nanoparticles [1-4].

In recent years, the development of the benzoxazine-based class of phenolic resins has attracted significant attention [5]. Benzoxazine (BOZ), as a class of thermosetting phenolic resins, can provide attractive material properties such as high glass transition temperature (T<sub>g</sub>), high thermal stability, fire retardance, good mechanical properties, wide design flexibility of molecular architectures, low water adsorption, low cost and near-zero volumetric change upon curing [6-11]. Conventionally, BOZ monomers are synthesized from a phenolic

derivative, a primary amine, and formaldehyde [12]. However, Shen and Ishida [8] found that the melting points of the pure BOZ were too high and were close to their curing temperatures. Therefore, BOZ monomers need to be modified and/or blended with other polymers to improve the processability in terms of melting point and solubility.

Although the polymerization of BOZ monomers occurs through a heterocyclic ring opening at high temperatures without generating any by-products, a strong acid has to be used as a catalyst, as shown in Fig.1 [13,14]. However, Ishida and Rodriguez [15] surveyed potential polymerization catalyst systems ranging from strong carboxylic acids to weak carboxylic acids to phenols and realized that BOZ cured with strong carboxylic acids was inferior to that cured with weak carboxylic acids. Moreover, Dunkers and Ishida [13] claimed that BOZ cured with phenols as a catalyst resulted in the ring opening faster than when cured with weak carboxylic acids. Therefore, selection of appropriate catalysts for BOZ resin determines the processability and performance of the composites.



**Figure 1.** Mechanism of BOZ monomers curing ( $H^+R^-$  acts as a catalyst).

In order to overcome the weaknesses of PF resin and to improve processability and to catalyze polymerization of BOZ monomers, a new approach with desired mutual benefit was developed by Jubsilp et al. [16]. The processability, mechanical and thermal characteristics such as the flexural modulus and the glass transition temperature of the resulting wood composites were effectively enhanced with increasing benzoxazine fraction in the ternary system of benzoxazine/epoxy/phenolic resin. The aim of this study was to understand the interaction between PF and BOZ resin in a binary matrix system. The processability and polymerization of BOZ monomers were investigated in the addition of PF resin as a catalyst. The mechanical and thermal properties of PF composites were also tested at various ratios of PF and BOZ matrix.

## 2 Materials and testing methods

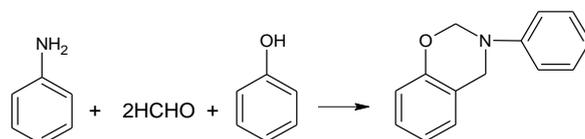
### 2.1 Materials

AR grade phenylamine, formaldehyde and phenol was purchased from Tianjin Hongyan Chemical Reagent Company, China; technical grade thermoplastic phenolic resin was from Xi'an Resin Company, China; AR grade hexamethylene tetramine was obtained from Tianjin Fuchen Chemical Reagent Company, China; cure accelerator, releasing agent, ethanol, acetone and talcum powder was used as received. PVA fibre was kindly provided by Fujian Chemical Fibre Group, China.

### 2.2 Synthesis of benzoxazine

Formaldehyde and phenylamine were put into a three-neck flask in water bath by a molar

ratio of 2:1 with stirring at room temperature for 1 hour. After heating up to 60°C, phenol was added into the flask with same molar weight of phenylamine. The mixture was kept refluxing at 105°C for 1 hour. After that, a dehydration process was performed at a low pressure condition by a vacuum pump until no bubble generated from the mixture. A single-ring BOZ resin were formed after cooling at room temperature and ground to fine powder to kept in a refrigerator prior to use. The reaction mechanism of BOZ resin synthesis is shown in Fig.2.



**Figure 2.** Reaction mechanism of BOZ resin synthesis.

### 2.3 Resin characterization

Fourier transform infrared spectra (FTIR, WQF-310, Beijing Ruili Analysis Instruments Company, China) were analyzed in respect to the structure of synthetic BOZ resin in KBr pellet. <sup>1</sup>H-NMR spectrum was recorded on a JEOL-FX-90Q spectrometer. Curing behavior of BOZ resin was studied by Differential Scanning Calorimetry (DSC, MDSC2910, TA, US) with heating rate of 10°C/min and a nitrogen flow rate of 50 ml/min for all tests. The resin gelation time was measured by metal plate method [1].

### 2.3 Preparation of prepreg

The blending matrix with different ratios shown in Table 1 was dissolved into a mixed solvent of acetone and ethanol to obtain resin solutions. The cure accelerator, releasing agent and talcum powder were added as fillers in the solutions. After stirring solutions to homogeneous suspensions, the dried and chopped PVA fibres were immersed gradually into resin solutions and kept mixing uniformly. the suspensions were dried at 40°C for 5 hours and then, the prepreg were prepared and sealed for the further usage. The parameters of prepreg are shown in Table 2.

Sample codes of blending matrix	Ratios (wt.%)	
	PF	BOZ
PF-BOZ-1	90	10
PF-BOZ-2	80	20
PF-BOZ-3	70	30
PF-BOZ-4	60	40

**Table 1.** Blending matrix with different ratios.

<b>Solid content</b>	<b>Fibre length</b>	<b>Fibre orientation</b>	<b>Volatile content</b>
56 %	36 mm	astatic	< 5 %

**Table 2.** Prepreg parameters.

### 2.4 Compression molding and post cure

Prepreg with different matrix blend ratios was placed rapidly into the preheated mould. The quantity of prepreg and the size of mould cavity were dependent on various test standards. Then, the mould was pressurized by a hot press up to 40MPa for 30 min at 180°C. During the pressing process, the mould was decompressed for 3 times to release small molecular volatiles. The post cure process for each prepreg was conducted in an oven by the procedure of 90°C for 1 h, 130°C for 2 h, 160°C for 2 h and 180°C for 1 h.

### 2.5 Characterization of PF-BOZ composites

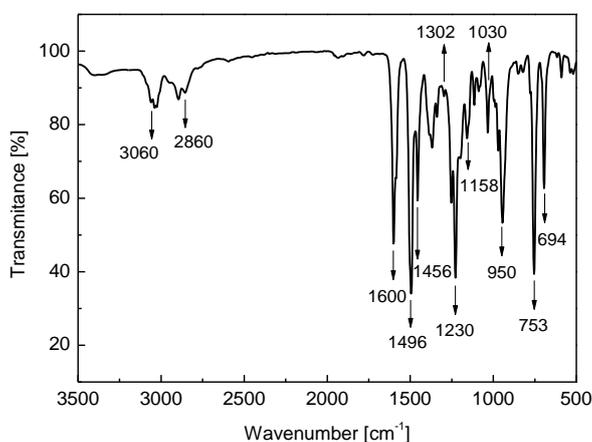
The moulding shrinkage measurement was performed under GB/T 1404.2-2008 standard. Thermal stability of composite samples was determined by 110A Matin heat resistance test device (NWPU, China) under GB 1035-70 standard. Unnotched impact strength and flexural behavior were tested by under GB/T 1451-2005 and GB/T 1449-2005 standards, respectively. In each measurement, 3 samples with each type of blending matrix were measured to determine statistically average values and their standard deviations were used as error bars.

## 3 Results and discussion

### 3.1 Analysis of synthesized BOZ

#### 3.1.1 FTIR spectra

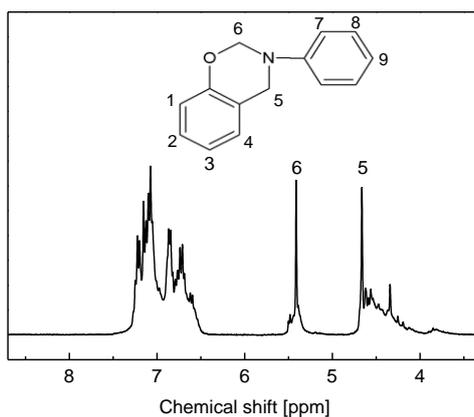
As can be seen in Fig. 3, the transmission FTIR spectra of synthesized BOZ are shown. The C–H stretching vibration in benzene ring is observed at the peaks from 2860 to 3060  $\text{cm}^{-1}$  [17,18] and the characteristic peaks of stretching vibration of benzene framework C=C are presented at 1600  $\text{cm}^{-1}$ , 1496  $\text{cm}^{-1}$  and 1456  $\text{cm}^{-1}$ , respectively [16-18]. A low intensity peak at 1302  $\text{cm}^{-1}$  is assigned to the rocking vibration of CH<sub>2</sub> bond in oxazine ring [18]. The peaks corresponding to the asymmetrical and symmetrical stretching vibration of C–O–C bond is observed at around 1230  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$ , respectively [18-21]. The peak at 1158  $\text{cm}^{-1}$  indicates the asymmetrical stretching vibration of C–N–C bond [18,19] and the characteristic peak of vibration of benzene with an attached oxazine ring is located at 950  $\text{cm}^{-1}$  [20]. The appearance of these bands demonstrates the formation of oxazine ring in BOZ monomer. In addition, the C–H out-of-plane bending of benzene ring is confirmed by the presented peaks at 753  $\text{cm}^{-1}$  and 694  $\text{cm}^{-1}$  [18,19].



**Figure 3.** FTIR spectra for synthesized BOZ resin.

#### 3.1.2 <sup>1</sup>H-NMR spectra

The structure of BOZ as shown in Fig. 2 is verified by <sup>1</sup>H-NMR spectroscopies and the corresponding spectra are shown in Fig. 4. In <sup>1</sup>H-NMR, The characteristic signals of oxazine ring are assigned to the -Ar-CH<sub>2</sub>-N- (5) and -O-CH<sub>2</sub>-N- (6) methylene protons appeared as two singlets at 4.665 and 5.411 ppm [18-20]. The intensity ratio of the protons (5) and (6) is determined roughly to be 1 : 1, which is well coincident with the theoretical protons ratio based on the chemical structure [18]. The prominent resonance from 6.573 to 7.275 ppm in the aromatic frequency corresponds to the hydrogen in the benzene ring [20,21].

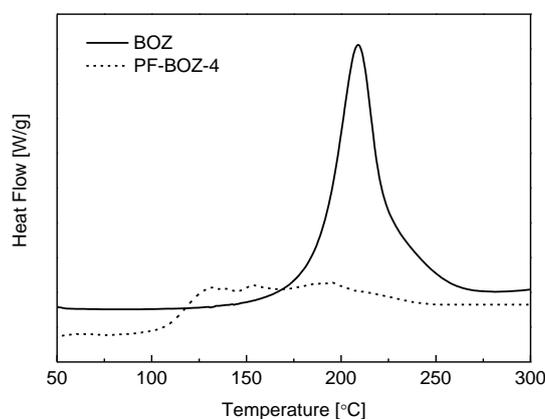


**Figure 4.** <sup>1</sup>H-NMR spectra for synthesized BOZ resin.

### 3.2 Blending matrix characterization

#### 3.2.1 DSC analysis

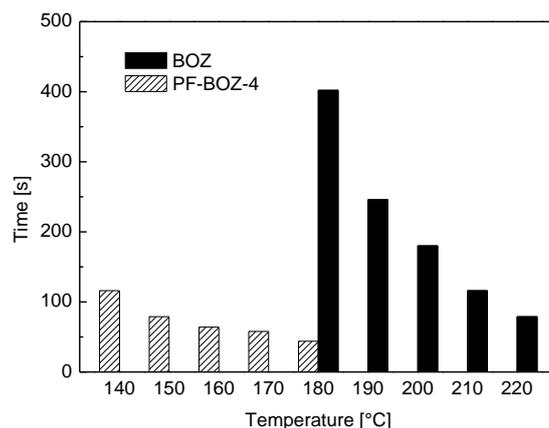
The polymerization reaction of BOZ resin and PF-BOZ-4 blending matrix were studied by DSC as shown in Fig. 5. The pure BOZ resin shows only one exothermic peak at 208°C, corresponding to the ring-opening polymerization reaction of the benzoxazine ring. As compared with the curve of PF-BOZ-4 blending matrix, the polymerization reaction of pure BOZ shows more concentrated exothermic process. As can be seen in Fig. 5, there are three exothermic peaks in the PF-BOZ-4 curve. The first peak is located at around 130°C, which is assigned to the exothermic polymerization reaction of PF resin. The second peak at 153°C corresponds to the BOZ ring-opening polymerization reaction catalyzed by phenol groups in PF resin [14,16]. The last peak, which indicates the shift of thermally activated ring-opening polymerization reaction temperature, is observed at about 190°C in the PF-BOZ-4 curve. The presence of the latter two peaks can be explained by the existence of phenolic hydroxyl groups and active hydrogen in ortho- and para-position of PF resin in the PF-BOZ-4 blending matrix. Therefore, the oxazine ring is catalyzed to open and polymerize at lower temperature, which leads to a reduction of polymerization reaction temperature of BOZ resin. Meanwhile, temperature range and heat release of exothermic reaction are increased.



**Figure 5.** DSC thermograms of BOZ resin and PF-BOZ-4 blending matrix.

#### 3.2.2 Resin gelation time

Resin gelation time, as a parameter of resin processibility, indicates the transformation process rate of thermoset polymer from a linear structure to a dendritic or reticular macromolecular structure. As can be seen in Fig. 6, the gelation time is significantly dependent on gel temperature and the obtained gelation time of pure BOZ resin is much longer than that of PF-BOZ-4 blending matrix at various temperatures. It is due to the catalysis of PF resin on the ring-opening polymerization reaction of BOZ monomer, which is consistent with the DSC result. That means PF content in the PF-BOZ-4 blending matrix changes significantly the kinetics of the gelation process. Furthermore, from the point of resin process, characteristics of high activity, low gelation temperature and short gelation time make PF-BOZ-4 blending matrix have better processibility.



**Figure 6.** Resin gelation time of BOZ resin and PF-BOZ-4 blending matrix at different temperatures.

### 3.3 Characterization of composites

#### 3.3.1 Moulding shrinkage

The moulding shrinkage of PVA fibre reinforced composites was studied at various ratios of PF and BOZ matrix as shown in Table 3. There is an approximately linear decrease of moulding shrinkage with increasing the BOZ concentration in the composite blending matrix. This is caused by the almost zero shrinkage and no release of small molecular volatiles during the ring-opening polymerization reaction of BOZ monomers, which results in a densified macromolecular structure of matrix.

	PF	PF-BOZ-1	PF-BOZ-2	PF-BOZ-3	PF-BOZ-4
<b>Moulding shrinkage [%]</b>	0.79 ± 0.02	0.72 ± 0.01	0.68 ± 0.006	0.66 ± 0.012	0.6 ± 0.008

**Table 3.** Moulding shrinkage of composites with various blending matrix.

#### 3.3.2 Thermal stability

As can be seen in Table 4, the Martin heat resistance temperature ( $T_M$ ) of composites reduces slightly with the addition of BOZ resin in matrix, however, followed by a gradual raise with an increase in the BOZ concentration of blending matrix. It is due to the restriction of molecular chain movement and the obstruction of macromolecular structure expansion caused by the intense association of hydrogen bond in BOZ resin [22]. Apart from that, the high ring-opening polymerization temperature of BOZ resin is also a reason which leads to a decline in degree of resin cure with the presence of BOZ in matrix system. However, due to the high glass transition temperature of BOZ resin, the thermal stability of composites is improved slightly as the BOZ content increased in matrix.

	PF	PF-BOZ-1	PF-BOZ-2	PF-BOZ-3	PF-BOZ-4
$T_M$ [°C]	121.8 ± 1.1	114.5 ± 1.0	117.4 ± 0.8	120.1 ± 1.2	123.8 ± 0.9

**Table 4.** Matin heat resistance temperature of composites with various blending matrix.

### 3.3.3 Impact and flexural properties

Table 5 shows that the mechanical properties of PVA fibre reinforced composites with different ratios of PF and BOZ matrix were investigated by impact and flexural tests. For the composites containing pure PF matrix or low content of BOZ in blending matrix, the impact and flexural strength are only 19.7 kJ·m<sup>-1</sup> and 86.9 MPa, respectively. This is associated to the high brittleness of PF resin caused by its self-polymerization dominated in the period of matrix curing. With increasing the concentration of BOZ up to 40 wt.% in the blending matrix, the impact and flexural strength of composites are increased by 74.6% and 13.2%, respectively. It is likely that the copolymerization of PF and BOZ led to an increase in the number of flexible molecular chains in the blending matrix thereby decreasing the brittleness of composites. Due to there was almost no shrinkage of resin volume and release of small molecules during the ring-opening polymerization of BOZ, a dense structure of blending matrix was formed to increase the flexural strength and to retain the flexural modulus and moulding shrinkage of composites.

	PF	PF-BOZ-1	PF-BOZ-2	PF-BOZ-3	PF-BOZ-4
<b>Impact strength (unnotched) [kJ·m<sup>-1</sup>]</b>	19.7 ± 1.1	19.0 ± 2.4	20.5 ± 1.5	30.3 ± 2.1	34.4 ± 1.7
<b>Flexural strength [MPa]</b>	86.9 ± 2.2	89.0 ± 1.5	93.0 ± 1.8	96.0 ± 1.1	98.4 ± 0.9
<b>Flexural modulus [GPa]</b>	5.5 ± 0.2	5.2 ± 0.1	5.0 ± 0.05	5.2 ± 0.1	5.3 ± 0.1

**Table 5.** Impact strength, flexural strength and modulus of composites with various blending matrix.

## 4 Conclusions

The effect of interaction between PF and BOZ resin on the processability, mechanical and thermal properties of PVA fibre reinforced composites was investigated in this study. A single-ring BOZ resin was synthesized and confirmed by the analysis of FTIR and <sup>1</sup>H-NMR. The DSC curves showed that the ring-opening polymerization temperature of BOZ resin was higher than that of PF-BOZ blending matrix; moreover, the resin gelation time results indicated the latter had better processability. For the chopped PVA fibre reinforced composites, the moulding shrinkage of composites declined from 0.79% to 0.60% with increasing the concentration of BOZ up to 40 wt.% in the blending matrix. Meanwhile, the impact and flexural strength of composites with PF-BOZ-4 blending matrix were increased by 74.6% and 13.2%, respectively. This can be explained by the increased number of flexible molecular chains in the blending matrix after the copolymerization of PF and BOZ, and almost no shrinkage of resin volume and release of small molecules during the ring-opening polymerization of BOZ. Therefore, a dense structure of blending matrix was formed to improve the mechanical and thermal properties of composites.

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