

Designing a Phthalonitrile/Benzoxazine Blend for the Advanced GFRP Composite Materials

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Abstract High performance resin must be used in the high performance glass fiber-reinforced plastic (GFRP) composites, but it is sometimes difficult to balance the processabilities and the final properties in the design of advanced thermoset GFRP composites. In this study, a phthalonitrile/benzoxazine (PPN/BZ) blend with excellent processability has been designed and applied in the GFRP composite materials. PPN/BZ blend with good solubility, low melt viscosity, appropriate gel condition and low-temperature curing behavior could enable their GFRP composite preparation with the prepreg-laminate method under a relatively mild condition. The resulted PPN/BZ GFRP composites exhibit excellent mechanical properties with flexural strength over 700 MPa and flexural modulus more than 19 GPa. Fracture surface morphologies of the PPN/BZ GFRP composites show that the interfacial adhesion between resin and GF is improved. The temperatures at weight loss 5% ($T_{5\%}$) and char residue at 800 °C of all PPN/BZ GFRP composites are over 435 °C and 65% respectively. PPN/BZ GFRP composites with high performance characteristics may find applications under some critical circumstances with requirements of high mechanical properties and high service temperatures.

Keywords Phthalonitrile; Benzoxazine; High performance composite; GFRP composites

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INTRODUCTION

Due to their superior strength/stiffness-to-weight, fatigue damage resistance, outstanding corrosion resistance, glass fiber-reinforced plastic (GFRP) composites have been widely used in the fields of buildings, sport goods and automotive industries^[1–6]. In some special areas such as aerospace, aircraft and military^[7–9], however, high performance GFRP materials are pursued with some strict requirements. Except for high strength and modulus, these GFRP materials should withstand high temperature.

In the design of advanced GFRP composites, glass fiber (GF), matrix and interface are three important factors^[9, 10]. Generally, mechanical properties of GFRP composites are mainly determined by the choice of GF, which is known as the primary load bearing constituent^[11]. The service temperatures of GFRP composites, however, are dominated by the matrix. The interface between matrix and GF also depends largely on the intrinsic properties of matrix such as the wetting abilities and polar functional groups^[12]. The choice of an appropriate matrix herein is very important to prepare the advanced GFRP composites. High performance matrix resin must be set on the advanced GFRP composites,

as the right saddle must be set on the right horse.

Phthalonitrile (PPN) resin, as a candidate to meet the US Navy specification (MIL-STD-2031)^[13–18], can be an ideal polymer matrix to design the advanced GFRP composites. PPN resins, due to their highly aromatic and rigid structures, exhibit comprehensive properties such as excellent mechanical performances, high thermal and thermo-oxidative stabilities, superior flame-retardant abilities and outstanding chemical resistances. The strong polar crosslinkable nitrile groups on the aromatic ring in PPN molecular structure may promote the interfacial property between matrix and GF^[19]. On the other hand, such unique aromatic and rigid structure of PPN also leads to high melt point (> 190 °C), insoluble in common solvents (*e.g.* acetone), high curing temperature (up to 375 °C) and long curing time (> 16 h). These characteristics make the traditional dry or wet prepreg method and the real industrial manufacturing for GFRP composite impossible. To cater for classical prepreg method, some researchers^[14–16, 20] were dedicated to designing new PPN monomers; others^[17, 18, 21] copolymerized or blended PPN with other resins. Unfortunately, the limited processability was realized either with multiple rigid chemical steps or at a cost of sacrificing the desirable properties. For example, Zhang *et al.*^[20] have reported a silicon-containing PPN monomer with excellent solubility in strong polar solvent. The synthesis process was rather complex while the satisfied properties was realized by a top curing temperature up to 375 °C with a total

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curing time for 17 h. Guo *et al.*^[21] have prepared PPN/epoxy blend and their GFRP composites; the preparation condition was mild but the mechanical properties, especially thermal properties were not satisfying. At the present, in the PPN research, a balance between the desired processabilities and final properties of composites is a challenge.

Recently, a new kind of novolac benzoxazine (BZ) has attracted significant attention. BZ not only maintains the excellent heat resistance and flame resistance of traditional phenolic resins, but also exhibits good processabilities like low volumetric shrinkage and no release of by-products upon curing^[22–26]. During the ring-opening polymerization of BZ, the chain transfer usually leads to large numbers of intramolecular and intermolecular hydrogen bonds (OH—N and OH—O)^[22, 25, 27]. As a result, BZ usually shows a low molecular weight, low crosslinking degree and thus low decomposition temperature, which is detrimental to final mechanical and thermal properties of GFRP composites. Those active hydrogen groups that should be avoided in ring-opening polymerization of BZ, however, are just what is required in the ring-form of PPN resin. Previous researches^[13, 18, 21] have proved that active hydrogen bonds, especially phenolic hydroxyl groups are relatively effective curing agent for PPN resins. Herein, blending PPN with BZ may integrate good processabilities of BZ and comprehensive properties of PPN. To promote the compatibility and optimize the blend structure, the backbone of both PPN and BZ type can be chosen to be bisphenol A-based. The PPN/BZ blend with balanced processability and final properties can be an ideal matrix for preparing advanced GFRP composite materials.

The objectives of this work are: (i) to design a PPN/BZ blend with good processabilities to cater for wet prepreg method; (ii) to understand curing behaviors of PPN/BZ blend to get effective mould procedures for preparing its advanced GFRP composites; (iii) to investigate the final (mechanical, thermal and morphological) properties of PPN/BZ GFRP composites.

EXPERIMENTAL

Materials

The off-white bisphenol A-based phthalonitrile monomer (PPN), with a density of 1.2 g/cm³ and a melting point about 195 °C, was kindly supplied by Guangdong Shunde Great New Materials Co., Ltd. Its chemical structure is shown in Scheme 1(a). The yellow bisphenol A-based benzoxazine monomer (BZ), with a density of 1.0 g/cm³ and a softening point about 90 °C, was purchased from Sichuan Dongfang Insulating Material Co., Ltd. The chemical structure is given in Scheme 1(b). High strength glass fiber fabric (GF,

SW180D-90a), with a thickness of 0.18 mm and a specific weight of 180 g/m², was obtained from Nanjing Fiberglass Institute. Diamino diphenyl sulfone (DDS), *N*-methyl pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), 1,4-dioxacyclohexane (DOC), methyl ethyl ketone (MEK), and acetone (AC) were all analytical grade and obtained from Tianjin BODI chemicals.

Preparation of PPN/BZ Blend

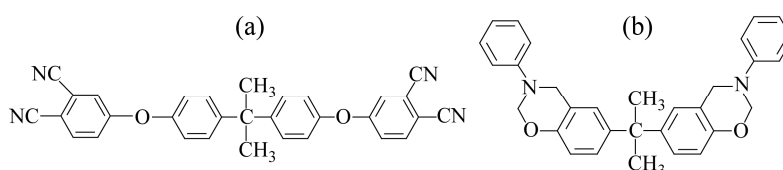
PPN/BZ blends were prepared as follows. First, a measured weight of PPN monomer and DDS was added in NMP. The weight ratio of PPN/DDS was 100/2, while the mass of the solid and the solvent was controlled as 100/100. Second, the above mixture was refluxed at 200 °C for 60 min, and a dark green PPN prepolymer solution was obtained. Then it was cooled to 140 °C, and a weight-measured amount of BZ (0 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%) was added and reacted for 60 min. The mixture was then precipitated with water and washed three times. After drying in a vacuum at 100 °C overnight, a green solid powder of PPN/BZ blend was finally obtained.

Preparation of PPN/BZ GFRP Composites

Various PPN/BZ blends obtained above were dissolved in the acetone and a green solution was obtained. Then, GF fabric (16 cm × 16 cm) was infiltrated with the solution and dried at 60 °C for 30 min. The PPN/BZ blend GF prepreg was obtained. The ratio was designed to give a prepreg of 38 wt% blend and 62 wt% GF theoretically. Fifteen layers of prepreg were hot-pressed under a pressure of 10 MPa with a procedure according to processability and curing behavior studies (190 °C/2h; 220 °C/2h; 250 °C/2h; 280 °C/2h, respectively). After gradually cooling to room temperature, the black PPN/BZ GFRP composite laminates were obtained.

Characterizations

Solubilities of PPN/BZ blends were tested at room temperature (about 25 °C) in various solvents. Dynamic rheological analysis (temperature and time scan) of PPN/BZ blends was performed using TA Instruments Rheometer AR-G2 with a frequency of 1 Hz at different temperatures in air. The samples (0.9–1.0 g) were melted between 25 mm diameter parallel plates with an environmental testing chamber of the rheometer. Differential scanning calorimetry (DSC) measurement was carried out on TA Instruments Modulated DSC-Q100 at a heating rate of 10 K/min and a nitrogen flow rate of 50 mL/min. The flexural tests of the PPN/BZ GFRP composites were performed with a SANS CMT6104 series desktop electromechanical universal testing machine at room temperature. Flexural tests (three-point bending mode) were held according to the GB/T 9341-2008/ISO 178 standard test method with a crosshead



Scheme 1 The structures of (a) phthalonitrile monomer (PPN) and (b) benzoxazine monomer (BZ)

displacement speed of 10 mm/min and the test fixture was mounted in a 10 kN capacity^[28]. The samples (dimension: 80 mm × 15 mm × 2 mm) were tested with a support span/sample thickness ratio of 15:1, and gained as an average value for every five samples. The fracture surface morphologies of PPN/BZ GFRP composites were observed by scanning electron microscopy (SEM, JSM2 5900LV) operating at 20 kV. Thermal gravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 with a heating rate of 20 K/min under nitrogen with a purge of 40 mL/min.

RESULTS AND DISCUSSION

Processability of the PPN/BZ Blends

The processability of a thermoset is decisive to the manufacturing process and application prospect of its GFRP composite. To cater for classical wet prepreg-laminate processing method of GFRP composite preparation, generally, good solubility, low melt viscosity and appropriate gel condition are three basic requirements to thermoset blends.

Solubilities of PPN/BZ blends in various solvents at room temperature are given in Table 1. PPN can only be dissolved in the high boiling point polar solvents. In fact, a high boiling point solvent should be avoided as likely as possible during the wet prepreg process. It is well known that, the residue of high boiling point solvent leads to cavitation defect, weak interface interaction and poor comprehensive properties in the final GFRP composites. Encouragingly, the solubility of PPN/BZ blend with only 10 wt% BZ content has been obviously improved. It can be dissolved in the common solvents such as butanone that wet prepreg process always employs. The possible reason is that the rigid molecules of PPN has been rearranged in the existence of BZ. In addition, the polar hydroxyl groups formed during the BZ ring-opening can enhance the interactions between PPN/BZ blends and solvent molecules. Good solubilities of PPN/BZ blends in the low point solvents provided possibilities for GFRP composite preparation through the traditional wet prepreg method.

Table 1 Solubilities of PPN/BZ blends in various solvents

Sample	AC	MEK	DOC	DMF	NMP
0 wt%	—	—	+-	++	++
10 wt%	+-	++	++	++	++
20 wt%	++	++	++	++	++
30 wt%	++	++	++	++	++
40 wt%	++	++	++	++	++

Note: ++, soluble; +-, partially soluble; —, insoluble

Melt complex viscosity (η^*) curves of various PPN/BZ blends as a function of temperature from 100 °C to 300 °C are shown in Fig. 1. Overall, with increasing temperature, the η^* of both PPN and PPN/BZ blends first decrease dramatically and fluctuate gently, then increase abruptly, and finally maintain constant. These changes correspond to gradual softening, complete melting, gel occurring and curing reaction. During these processes, the state of the resins transformed from solid, liquid, rubber to solid again. There are, however, some obvious differences between PPN and PPN/BZ blends. In the softening region, the η^* of PPN/BZ blends is lower than that of PPN; and more obvious is in the

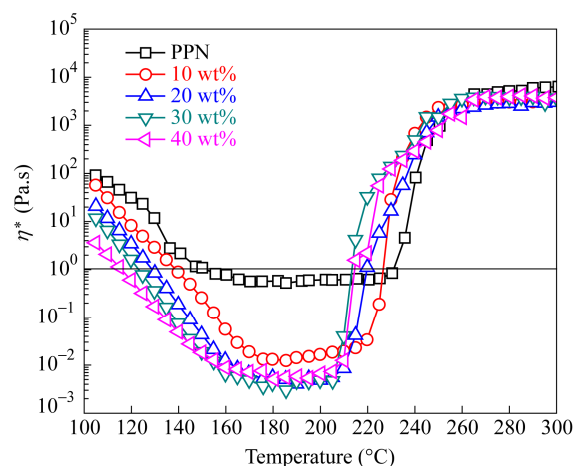


Fig. 1 η^* curves of various PPN/BZ blends as a function of temperature

melting region. This can be attributed to the low η^* of BZ itself. Nevertheless, when BZ content is over 20 wt%, no further decrease in η^* PPN/BZ blends could be observed. This manifests that the low η^* of BZ itself is not the main reason. Several references^[13, 18, 21] have reported that the active hydrogen could catalyze the curing reaction of PPN. The active hydroxyl groups from BZ ring-opening have participated in the triazine and phthalonitrile ring-forming of PPN, and the rigid prepolymer molecules of PPN are disturbed and rearranged. Herein, the inner molecular change of PPN/BZ blends is responsible for the η^* decrease. Generally, the processability of a prepreg depends largely on the η^* in softening and melting region. Herein, the lower η^* of the PPN/BZ blend can help the resin to wet the GF adequately.

With increasing the BZ content, the gel occurring temperature becomes lower. For example, the temperature in abrupt η^* increase for PPN is about 240 °C, but that for PPN/BZ blend is about 220 °C. These results once again suggest that BZ could catalyze PPN curing reaction. To further access the dependence of gel occurring, the η^* curves of the PPN/BZ blend with 20 wt% BZ content as a function of time at various temperatures are given in Fig. 2. At 170 °C, no obvious change η^* in the given time indicates that the curing reaction ran very slowly. At 210 °C, on the contrary, curing reaction was carried out so fast that the η^* increase took a rather short time about only 240 s. Comparatively, the temperature at 190 °C balanced the curing reaction rate and the resin viscosity. From the aspect of GFRP composite preparation, the long-time low η^* at 170 °C means good liquidity and thus is helpful to wet the GF, but it is hard to control resin flow. The detention time of low η^* at 210 °C is too short to promote resin-GF wetting and it is unfavorable to exhausting residue solvent of the prepreg. The appropriate detention time of low η^* at 190 °C is favorable for the resin-controlling, resin-GF wetting and bubble-exhausting. Herein, the processability of PPN/BZ blend is dependent on the temperature and the preferred processing temperature for composite preparation is about 190 °C.

The preferred temperature of 190 °C, therefore, was selected to further investigate the rheological behaviors of

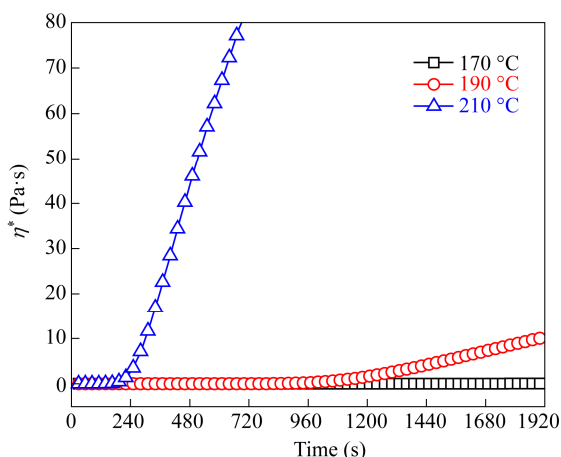


Fig. 2 η^* curves of the PPN/BZ blend with 20 wt% BZ content as a function of time at various temperatures

PPN/BZ blend with 20 wt% BZ content, and plots of storage modulus (G') and loss modulus (G'') as a function of time are given in Fig. 3. According to classical rheological theory, dynamic rheological analysis is of basic and practical importance since it is related to composite processing, dynamics, structure-property relationship^[29–32]. The storage modulus (G') represents the elastic melt properties and provides a measure of composite ‘stiffness’, while the loss modulus (G'') stands for viscous melt properties and reveals the information of ‘softness’^[32]. Thus G' and G'' dependence on time can characterize the state transform of the blend and thus guide the final GFRP composite preparation. The trend in Fig. 3 can be divided into three regions. (1) $G'' > G'$ (0–960 s): The blend is mainly in the liquid-like state and the curing reaction proceeds gradually. During this period, the resin is wetting GF and exhausting bubbles. (2) $G'' = G'$ (960–1080 s): The blend is neither in the liquid-like state nor in the solid-like state; it is close to rubber state. In the composite preparation process, it is just the right time to keep up the pressure without gummosis. (3) $G' > G''$ (over 1080 s): The resin is in the solid-like state and curing procedure can be conducted. Herein, at the preferred temperature of 190 °C, the appropriate pressure-keeping time is 960–1080 s.

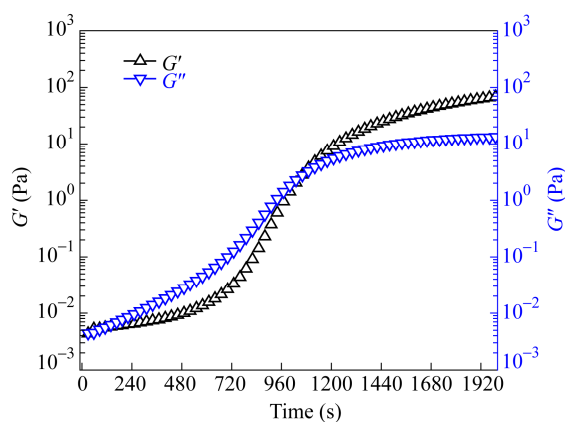


Fig. 3 G' and G'' of the PPN/BZ blend with 20 wt% BZ content as a function of time at the preferred temperature of 190 °C

Curing Behaviors of the PPN/BZ Blends

Studies on the processability of the PPN/BZ blend above have proved that the wet prepreg method was feasible, and also provided the key processing parameters (temperature and time) for GFRP composite preparation. Investigating curing behaviors of the PPN/BZ blends could offer the appropriate curing procedure for final composite laminating.

The DSC curves in Fig. 4 show the effect of various BZ ratios on the curing behavior of the PPN/BZ systems. PPN prepolymer only shows a small endotherm peak at about 160 °C corresponding to the melting behavior, which is in good agreement with rheological results in Fig. 1. No curing peak could be observed, suggesting that it is hard to cure PPN without any outside help. Apart from the melting endotherm peak, PPN/BZ blend with only 10 wt% BZ content exhibits an obvious exothermic peak at about 260 °C. These results indicate that the addition of BZ could effectively catalyze the curing of PPN^[13, 18, 21]. During the oxazine ring-opening process, the chain transfer usually leads to plenty of intramolecular and intermolecular hydrogen bonds (OH—N and OH—O)^[22, 25, 27]. The active hydroxyl groups could react with nitrile groups of PPN and finally form the triazine and phthalonitrile ring^[13, 18, 21]. However, when BZ content is over 20 wt%, PPN/BZ blend shows double exotherm peaks. The first peak is about 230 °C while the second one is around 270 °C. The curing peak of BZ itself overlaps with the first exotherm peak, thus it can be attributed to the oxazine ring-opening polymerization of BZ itself while the second peak is mainly due to copolymerization of PPN and BZ. In addition, it is easy to understand that the first oxazine ring-opening becomes obvious. However, it is confusing that the second peak corresponding to copolymerization of PPN and BZ is observed to be shifted to higher temperature. The oxazine ring can be opened up by the heat and result in active hydroxyl groups. The active hydroxyl groups can further speed up the oxazine ring-opening. Since the temperature for oxazine ring-opening is lower than that for phthalonitrile ring-forming, most of the active hydroxyl groups are consumed by oxazine ring-opening rather than phthalonitrile ring-forming. When the BZ content is lower than 20 wt%, perhaps PPN acts as diluents that retards the polymerization of BZ. However, when BZ content is over 20 wt%, this kind

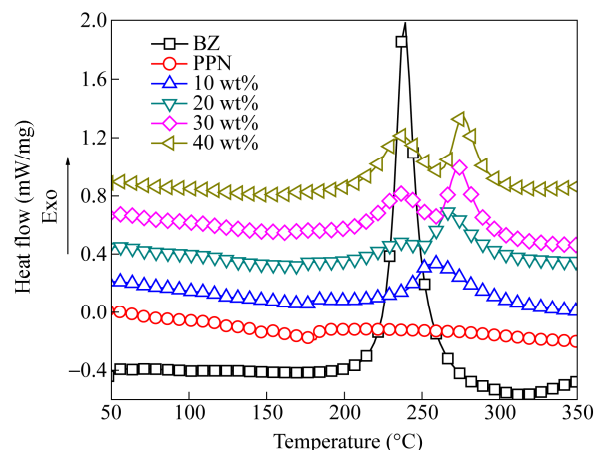


Fig. 4 DSC curves of the PPN/BZ systems

of diluent effect is limited and most of the active hydroxyl groups is consumed by oxazine ring-opening, and relatively, the number of active hydroxyl groups that can help cure nitrile is reduced. As a result, the copolymerization peak is shifted to higher temperature.

DSC curves of PPN/BZ blend with 20 wt% BZ content were chosen to investigate curing behaviors after being cured at different temperatures, as shown in Fig. 5. It can be seen that after being cured at 190 °C for 2 h, the peaks of the oxazine ring-opening polymerization and phthalonitrile ring-forming copolymerization still exist. After being further cured at 220 °C for 2 h, the oxazine ring-opening polymerization has finished and phthalonitrile ring-forming copolymerization can still be observed. After being further cured at 250 and 280 °C for 2 h, both oxazine ring-opening and phthalonitrile ring-forming polymerization are completed. Herein, combined with the rheological results, the appropriate curing procedure for PPN/BZ blends can be settled as 190 °C/2h; 220 °C/2h; 250 °C/2h; 280 °C/2h.

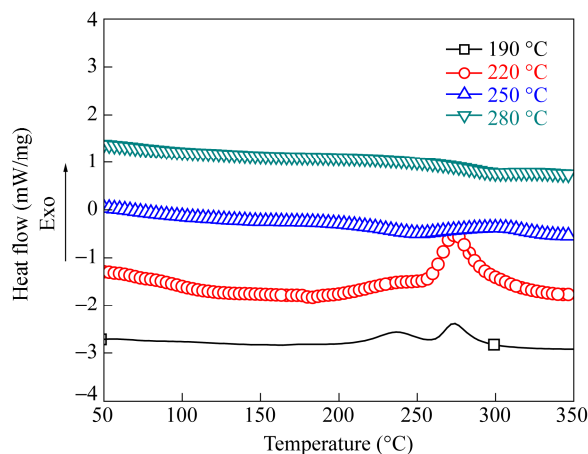


Fig. 5 DSC curves of PPN/BZ blend with 20 wt% BZ content after different curing procedures

Mechanical Properties of the PPN/BZ GFRP Composites

The main goal of this paper is to design PPN/BZ blend for GFRP composites. Investigations on the processability and curing behaviors of PPN/BZ blend have provided the processing method and preparation parameters for their GFRP composite. PPN/BZ GFRP composite laminates were finally realized by the wet prepreg and hot-pressed method. Expect for the use as high performance materials, their mechanical properties and service temperature were essentially concerned.

Figures 6 and 7 display flexural strength and flexural modulus of the final PPN/BZ GFRP composite. Flexural strength and flexural modulus of the PPN-only GFRP composite are 616 MPa and 18.17 GPa, respectively. With an addition of 10 wt% BZ, flexural strength and flexural modulus of PPN/BZ GFRP composite are 700 MPa and 19.24 GPa, which are increased by 84 MPa and 1.07 GPa respectively, compared with those of PPN GFRP composites. Then, mechanical properties of PPN/BZ GFRP composites steadily increase with the BZ content and reach their maximums when BZ content is 40 wt%. At that point, flexural

strength and flexural modulus increase from 616 MPa and 18.17 GPa in PPN GFRP composite to 762 MPa and 20.84 GPa in PPN/BZ GFRP composite, leading to 23.7% and 14.7% increase, respectively. To conclude, with increasing BZ content, both flexural strength and flexural modulus of PPN/BZ GFRP composite have been obviously improved.

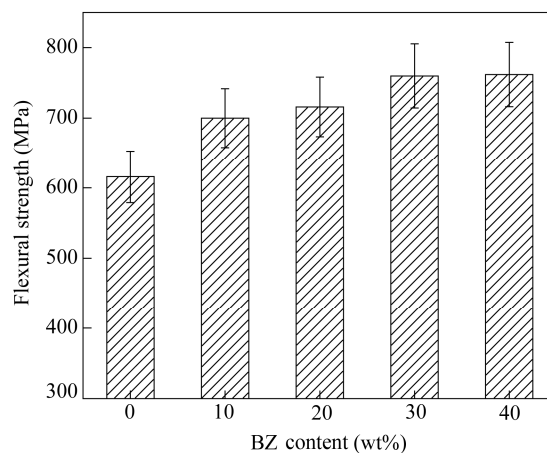


Fig. 6 Flexural strength of the final PPN/BZ GFRP composite

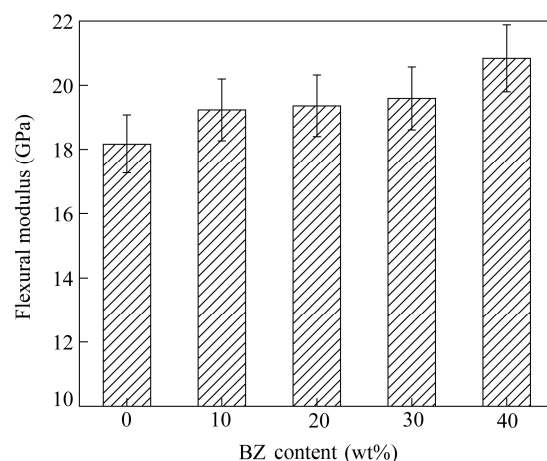


Fig. 7 Flexural modulus of the final PPN/BZ GFRP composite

In this paper, all PPN/BZ GFRP composites exhibit excellent mechanical properties with flexural strength over 700 MPa and flexural modulus more than 19 GPa. As far as we know, this is the first time that excellent mechanical properties of PPN-based GFRP composite are realized under a mild preparation condition. On one hand, the flexural strength of PPN-based GFRP composites reported by most references^[21, 33, 34] is lower than 700 MPa and hard to be called high performance GFRP materials. On the other hand, Sastr *et al.*^[35] have prepared 4,4'-dihydroxybiphenyl-based PPN GFRP composites with comprehensive properties and its flexural strength was as high as 819 MPa. However, solution prepreg process involved high boiling point solvent NMP around 200 °C, and GFRP composites needed a top curing temperature as high as 375 °C and a total curing time as long as 21 h. These process conditions and efficiency are too rigid to realize the industrial manufacture and application.

Fracture Surface Morphology of the PPN/BZ GFRP Composites

Mechanical enhancement mechanism of GFRP composites is really complicated and it relates with matrix, GF and matrix-GF interaction. Fracture surface morphologies of the PPN/BZ GFRP composites are displayed in Fig. 8 to help illustrate the improvement of mechanical properties. Figure 8(a) shows fracture surface morphology of PPN GFRP composites. It can be seen that PPN GFRP composites have little remnant of resins on the GF, and a lot of grooving and crevices of bare GF exist. The small resin shaving after fracture can be observed. These results indicate that PPN has poor wetting properties with GF and weak interfacial adhesion strength between PPN and GF. The fracture surface morphology of PPN/BZ GFRP composites with 20 wt% BZ content is changed, as shown in Fig. 8(b). It can be seen that the degree of resin coverage on the surface of GF is improved, and the grooving and crevices of bare GF is reduced. The fracture surface morphology of PPN/BZ GFRP composites with 40 wt% BZ content in Fig. 8(c) shows that the whole composite structure is rather compact and resin adheres to most of the GF surfaces. From the cross-section images in Fig. 8(d), no obvious caves or defects could be observed and the composite structure is very dense. These structures could lead to effective stress transfer and prevent crack initiation and propagation^[36]. Thus, mechanical enhancement of PPN/BZ GFRP composites may be due to the improved processabilities of PPN/BZ blend. During prepreg and laminate process, good solubilities and low melt viscosity can help resins wet GF adequately. In addition, the large number of polar hydroxyl groups generated by the ring-opening of BZ may not only increase cure degree, but also improve the interfacial interaction.

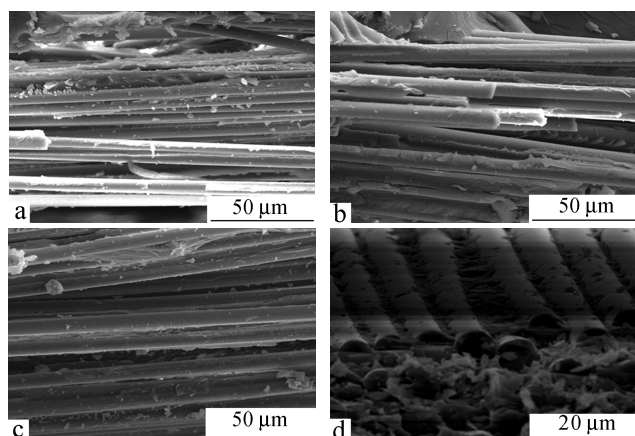


Fig. 8 SEM images of fracture surface of (a) PPN GFRP composites, (b) PPN/BZ GFRP composite with 20 wt% BZ content, (c) PPN/BZ GFRP composite with 40 wt% BZ content and (d) its cross-section

Thermal Properties of the PPN/BZ Composites

High performance GFRP composites should also have high service temperature, which is generally decided by the thermal stabilities of resin matrix. Thermal properties of the PPN/BZ composites are summarized in Table 2, in which the temperatures at weight loss 5% ($T_{5\%}$), 10% ($T_{10\%}$) and char residue at 800 °C (R) are displayed.

Table 2 Thermal stabilities of PPN/BZ composites

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	R
0 wt%	430.8	456.8	61.4%
10 wt%	444.4	468.7	65.2%
20 wt%	454.8	478.8	68.4%
30 wt%	440.9	469.9	70.5%
40 wt%	439.3	468.4	68.1%

Note: $T_{5\%}$, weight loss at 5%; $T_{10\%}$, weight loss at 10%; R , residue at 800 °C

With the increasing BZ content, the $T_{5\%}$, $T_{10\%}$ and char residue of PPN/BZ composites increased and reached to the maximum values when BZ content was 20 wt%. At that point, the $T_{5\%}$, $T_{10\%}$ and char residue of PPN/BZ composites are 454.8 °C, 478.8 °C and 68.4%, which are increased by 24.8 °C, 16.0 °C and 7.3% compared with those of PPN-only composites, respectively. Then, thermal properties of the PPN/BZ composites decreased with the increasing BZ content, but they are still higher than those of neat PPN. This suggests that the introduction of BZ does not deteriorate thermal properties of PPN, which is unexpected. The char yield at 800 °C of PPN/BZ composites is all higher than 65%. Combined with DSC studies, these results indicate that the crosslinking units formed by the addition reaction of PPN groups and the BZ structure are directly responsible for excellent thermal stabilities as well as for high char yields. It should be noted that PPN itself shows excellent thermal stabilities, but a rather strict curing procedure (over 350 °C/20 h or even more) is needed. Herein, in terms of excellent mechanical and thermal properties to relatively mild preparation condition, PPN/BZ blend designed for advanced GFRP composite materials turns out to be successful in this study.

CONCLUSIONS

A phthalonitrile/benzoxazine (PPN/BZ) blend has been designed and applied in the GFRP composite materials. The PPN/BZ blend with excellent processabilities (good solubility, low melt viscosity and appropriate gel condition) and low-temperature curing behavior enables PPN/BZ GFRP composites to be realized by prepreg-laminate method under a relatively mild condition (top curing temperature is 280 °C and total time is 8 h). The resulted PPN/BZ GFRP composites exhibit excellent mechanical properties with flexural strength over 700 MPa and flexural modulus more than 19 GPa. The temperatures at weight loss 5% ($T_{5\%}$) and char residue at 800 °C are over 435 °C and 65% respectively. To our knowledge, this is the first time that high performance PPN-based GFRP composite is obtained under a mild preparation condition. High performance PPN/BZ GFRP composites may find applications under some critical circumstances with requirements of high mechanical properties and high service temperatures.

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