

Nitrile Functionalized Benzoxazine/Bismaleimide Blends and Their Glass Cloth Reinforced Laminates

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ABSTRACT: A novel high-performance resin blend composed of nitrile functionalized benzoxazine (CNBZ) and bismaleimide (4,4'-bismaleimidodiphenyl methane) (BMI) was prepared via solvent method. Its curing behaviors, thermal properties, and mechanical properties were studied by differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and universal testing machine, respectively. The results showed that the addition reaction between phenolic hydroxyl group and the double bond occurred except for the homopolymerization of CNBZ and BMI. When BMI content was more than 40%, the cured CNBZ/BMI blends exhibited higher glass transition temperatures (T_g s) than CNBZ and BMI homopolymers, which reached up to 334°C. Meanwhile, when BMI content was 40%, the tensile strength, flexural strength, and shearing strength reached up to 69, 235, and 12.9 MPa, respectively, which exhibited the comparable mechanical properties with BT resin. Furthermore, the glass cloth (GF) reinforced laminates based on these blends were prepared. The results showed that when BMI content was 40%, their tensile strength, flexural strength, and impact strength reached up to 334 MPa, 593 MPa, and 145 KJ m⁻², respectively. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41072.

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INTRODUCTION

Bismaleimide-triazine (BT) resin, derived from the blend of dicyanate ester (CE) and bismaleimide (BMI) resins, combined the advantages of CE and BMI resins. The triazine rings formed from cyclotrimerization reaction of cyanate groups offered the low dielectric constant and high heat resistance. BMI resin offered the excellent mechanical properties, thermal stability, and electrical insulation properties over a wide range of temperatures.¹⁻⁴ BT resin is widely applied in many fields such as circuit boards, engineering materials in aircraft, and semiconductor encapsulants, etc.^{5,6} However, it suffers from some limitations. The raw materials of CE have some drawbacks such as high-toxic and expensive.

As a new type of phenolic resin, benzoxazine resin has many attractive characteristics such as high heat resistance, flame retardancy, low toxicity, and low cost of raw materials.⁷⁻¹² Therefore, replacing CE with benzoxazine and blending with BMI has been explored recently. For example, Takeichi et al.¹³ reported the blending system of bisphenol-A based benzoxazine and BMI. Its T_g reached up to 268°C. Guo and Gu¹⁴ reported the blending system of 3,3'-phenylmethanebis (3,4-dihydro-2H-

1,3-benzoxazine) and BMI. The addition of BMI effectively enhanced the thermal and mechanical properties. Reghunadhan and coworkers¹⁵ studied the blending system of allyl-functionalized benzoxazine (Bz-allyl) and BMI. The curing temperature of the blend was lowered. However, the coreaction between Bz-allyl and BMI resulted in a decrease in the T_g s.

More recently, the nitrile functionalized benzoxazine (CNBZ) have attracted much attention.¹⁶⁻²³ This was because its nitrile groups produced the triazine ring during curing, which was similar to one formed from cyanate groups in CE resin. Therefore, CNBZ will improve the performance better than common benzoxazine when blending with BMI. However, to the best of our knowledge, there is no report on studying the nitrile functionalized benzoxazine/BMI (CNBZ/BMI) blends yet. Herein, The CNBZ was synthesized to blend with BMI. It was expected that this new heat-resistant resin exhibited the comparable properties with BT resin. The curing behaviors and the effects of BMI content on thermal properties and mechanical properties of CNBZ/BMI blends were investigated in detail. Furthermore, the glass fiber (GF) reinforced laminates based on CNBZ/BMI blends were studied as well.

Additional Supporting Information may be found in the online version of this article.

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EXPERIMENTAL

Materials

4,4'-Diamino diphenyl methane was purchased from J&K Scientific Ltd. and purified by recrystallization from ethanol. The monomer CNBZ was synthesized according to the procedure reported before.¹⁶ The product was a white powder with a yield of 87%. BMI was purchased from Huantai Chunguang. Glass cloth was purchased from Sichuan Glass Fiber. Other reagents were purchased from Tianjin Kermel Chemical Company and used as received.

Preparation of CNBZ/BMI Cured Blends

Various molar ratios of CNBZ/BMI blends were dissolved in DMSO and stirred for 30 min. The solution were cast on the corresponding mold and kept at 100°C to remove the solvent. The cure profile used was 150°C/2 h, 170°C/2 h, 190°C/2 h, 210°C/2 h, and 230°C/2 h, respectively.

Preparation of CNBZ/BMI/GF Laminates

Various molar ratios of CNBZ/BMI were dissolved in THF and a viscous solution was obtained. GF cloth (20 × 16 cm², 22 layers) was impregnated with the viscous solution and dried at room temperature for 24 h. The prepregs were baked for 20 min at 150°C to remove the residual solvent. The ratio was designed to give a prepreg of 40% blends and 60% GF by weight. After that, prepregs were compressed in a stainless steel mold and cured in steps of increasing temperature and pressure until pressure of 16 MPa at 230°C for 3 h.

Characterization

FTIR spectra was recorded on a Bruker Tensor27 FTIR spectrometer (Bruker, GM) in a range of 4000 to 500 cm⁻¹. Samples were prepared as KBr pellets.

Differential scanning calorimetry (DSC) thermogram was recorded with a Mettler-Toledo DSC822^e instrument (Mettler-Toledo, CH) at a heating rate of 10°C/min in nitrogen atmosphere.

Gelation time was tested on a gathered speed board from Gongyi Yuhua. About 2 g blends was put on the board at 180°C. The gelation time was calculated from the start to the moment that the blends did not flow.

Dynamic mechanical analysis (DMA) was performed on a Mettler-Toledo DMA/SDTA861^e instrument (Mettler-Toledo, CH). The specimen with dimensions of approximately 5.00 × 5.00 × 1.00 mm³ was tested by a shear mode with a frequency of 1 Hz, and the sample was heated at a rate of 3°C/min from 50°C to 350°C.

Thermogravimetric analysis (TGA) was performed using a TGA/DSC STAR^e instrument (Mettler-Toledo, CH). The cured blends were tested from 30 to 800°C at a heating rate of 10°C/min in nitrogen atmosphere.

Mechanical properties of the cured blends and laminates were measured using SANS UTM5105 Series Desktop Electromechanical Universal Testing Machine (Shenzhen SUNS Technology Stock, Ltd.). Shearing tests of cured CNBZ/BMI blends were measured according to the GB/T 7124-2008 with a crosshead displacement speed of 5 mm/min. Two pieces of treated stain-

less steel pieces were kept at 100°C for 1 h to remove solvent after CNBZ/BMI solution had been spread. The two pieces were jointed together at the curing stage. Ten samples were tested to obtain an average. Tensile tests and flexural tests of cured CNBZ/BMI blends were measured according to the GB/T 13022-1991, GB/T 9341-2000 standard test method with a crosshead displacement speed of 2 mm/min, 10 mm/min, respectively. Five samples were tested to obtain an average. Tensile tests and flexural tests of laminates were measured according to the GB/T 1447-2005, GB/T 9341-2008 with a crosshead displacement speed of 2 mm/min, 10 mm/min, respectively. Three samples were tested to obtain an average. Impact tests of laminates were measured according to the GB/T 1043-93 standard test method. Ten samples were tested to obtain an average.

The morphology of the fractured surfaces of CNBZ/BMI/GF laminates was observed by scanning electron microscope (SEM) (JEOL JSM6700F) operating at 5.0 kV. Microphotographs were taken on the surface, which was made by breaking the specimen by impact testing machine and then coating with gold. Microphotographs were taken at the magnification of 1000×.

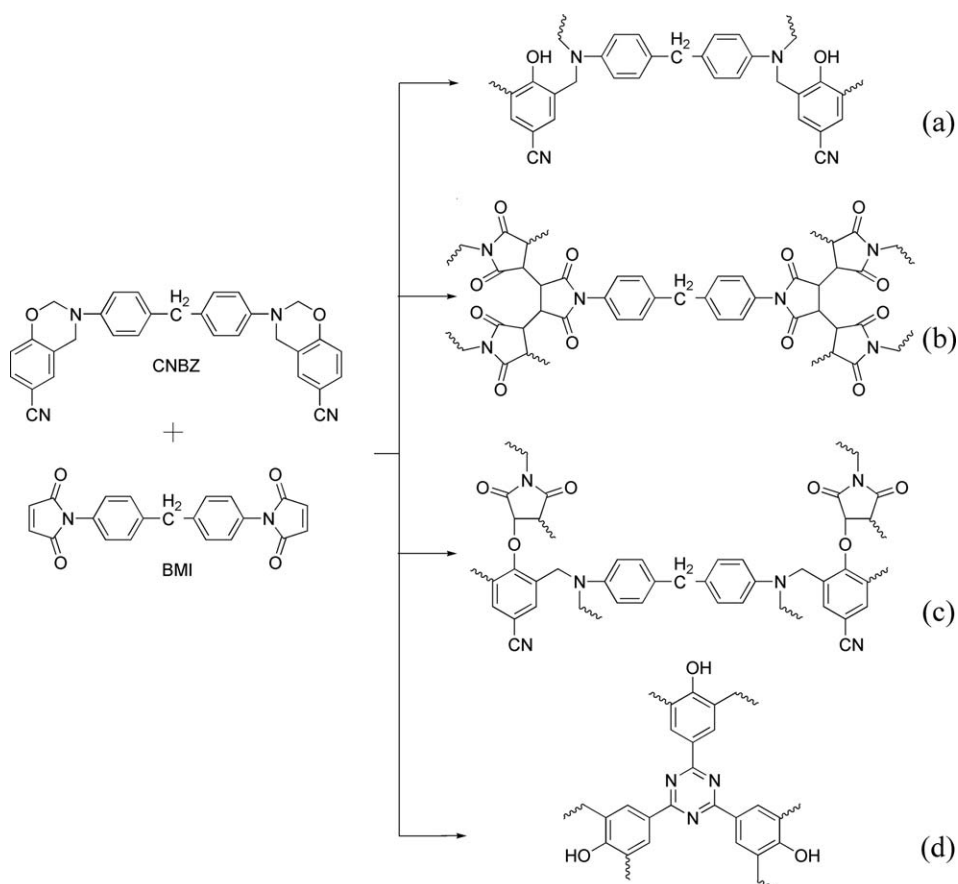
RESULTS AND DISCUSSION

Curing Reaction of CNBZ/BMI Blends

Scheme 1 illustrated the possible reactions occurred in the CNBZ/BMI blends. The CNBZ/BMI blends have three functional groups, including oxazine ring, double bond of maleimide, and nitrile groups. Four polymerization reactions may occur during the curing process. They are ring-opening polymerization of the oxazine ring [Scheme 1(a)], homopolymerization of double bond of maleimide [Scheme 1(b)], etherification reaction between phenolic hydroxyl group of polybenoxazine and the double bond of BMI [Scheme 1(c)], and cyclotrimerization reaction of nitrile groups [Scheme 1(d)]. These reactions finally lead to the formation of network structure.

Figure 1 showed IR spectra of CNBZ/BMI (6/4) blend before and after curing for 2 h at 230°C. The peaks of benzene ring attached with oxazine ring (940 cm⁻¹), nitrile groups (2220 cm⁻¹), and double bond of maleimide (831 cm⁻¹) were observed in Figure 1(a). After curing for 2 h at 230°C, the peak at 940 cm⁻¹ corresponding to benzoxazine nearly disappeared [Figure 1(b)], suggesting that the ring-opening reaction of the benzoxazine had completed. The peak at 831 cm⁻¹ due to double bonds of maleimide decreased mostly, indicating that the most double bonds of maleimide were consumed. Meanwhile, a new peak at 1203 cm⁻¹ corresponding to ether bond (C—O—C) appeared. This indicated that the phenolic hydroxyl group from polybenoxazine reacted with the double bond of BMI.¹³ In addition, the peak at 2220 cm⁻¹ corresponding to nitrile groups decreased about in half. A new characteristic peak at 1520 cm⁻¹ corresponding to the —C=N stretching vibration was observed, indicating the formation of triazine ring. The FTIR spectra confirmed the curing mechanism of CNBZ/BMI blends.

Figure 2 showed DSC curves of CNBZ/BMI blends with various ratios. The DSC curves of CNBZ and BMI were also taken for comparison. The peaks at 143 and 220°C assigned to the



Scheme 1. Possible reactions occurred in the CNBZ/BMI blends.

melting and polymerization peaks of CNBZ, respectively. The peaks at 153 and 247°C assigned to the melting and polymerization peaks of BMI, respectively. When BMI contents were 20%, 40%, and 50%, the melting peak shifted to 148°C. Meanwhile, two polymerization peaks were observed. The main polymerization peak shifted to a lower temperature at 200°C, and the shoulder polymerization peak centered at 230°C.

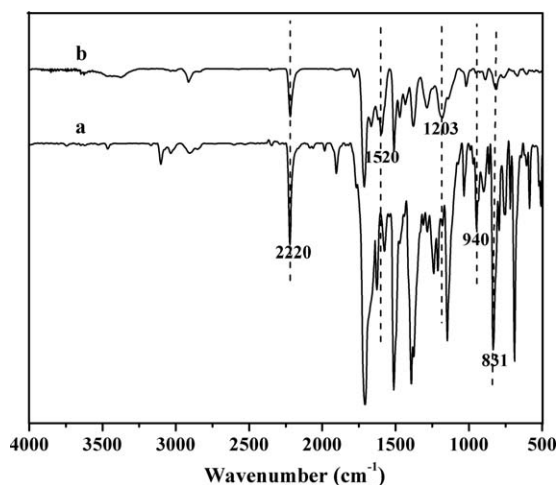


Figure 1. IR spectra of CNBZ/BMI (6/4) blend (a) before and (b) after curing for 2 h at 230°C.

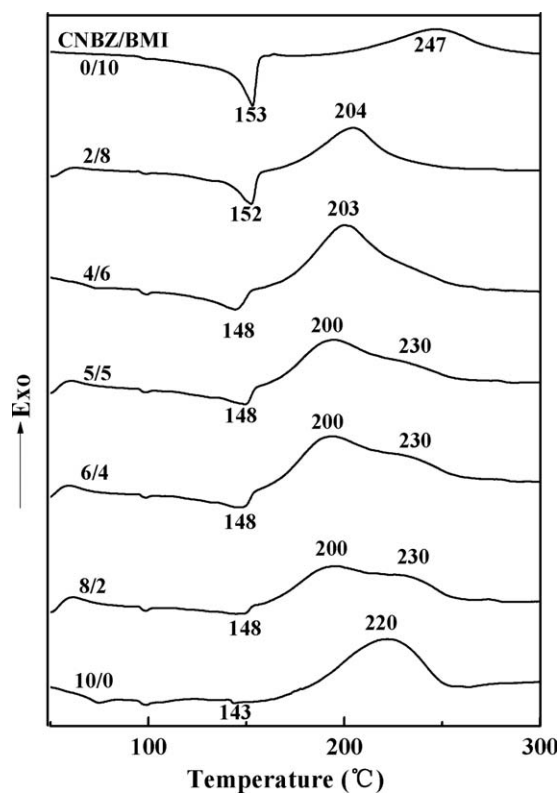


Figure 2. DSC curves of CNBZ/BMI blends with various ratios.

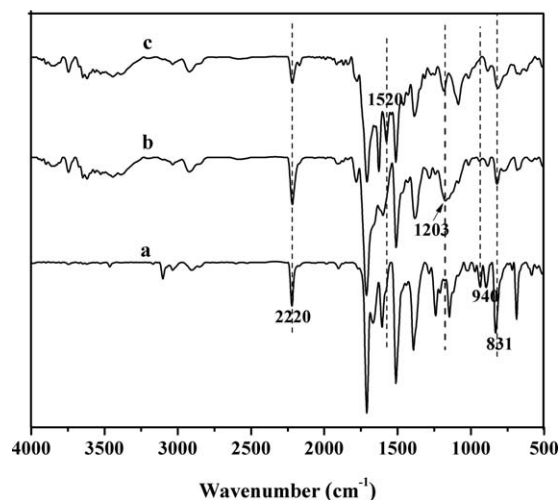


Figure 3. FTIR spectra of CNBZ/BMI (6/4) blend (a) before and (b) after curing from 50 to 215°C, and (c) from 50 to 260°C.

To confirm the assignment of two polymerization peaks, the FTIR analysis was used [Figure 3]. After curing from 50 to 215°C in N₂ with a heating rate of 10°C/min, the peaks at 940 and 831 cm⁻¹ assigned to benzoxazine and double bonds of maleimide respectively decreased [Figure 3(b)]. A new peak at 1203 cm⁻¹ assigned to ether bond (C—O—C) appeared. Therefore, we proposed that main exothermic peak at 200°C corresponded to the polymerization of oxazine ring and double bond. This polymerization temperature was lower than those of CNBZ and BMI. The reason might be that negative oxygen ions and amine groups from ring opening of benzoxazine had a catalysis effect on the polymerization of BMI.^{15,24} After curing from 50 to 260°C [Figure 3(c)], the peaks at 940, 831, and 1203 cm⁻¹ assigned to benzoxazine, double bond, and ether bond (C—O—C), respectively changed a little bit. However, the peak at 2220 cm⁻¹ assigned to nitrile groups decreased mostly. A new peak at 1520 cm⁻¹ assigned to the —C=N of triazine ring appeared. These results suggested that the shoulder exothermic peak at 230°C corresponded to the reaction of nitrile groups. When BMI content was 80%, the endothermic peak and exothermic peak shifted to a slight higher temperatures at 152 and 204°C, respectively.

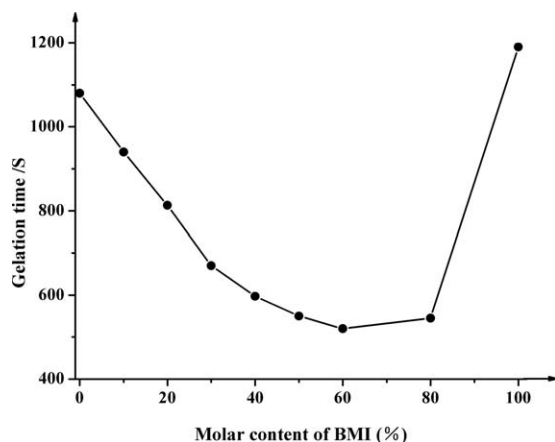


Figure 4. Gelation time of CNBZ/BMI blends at 180°C.

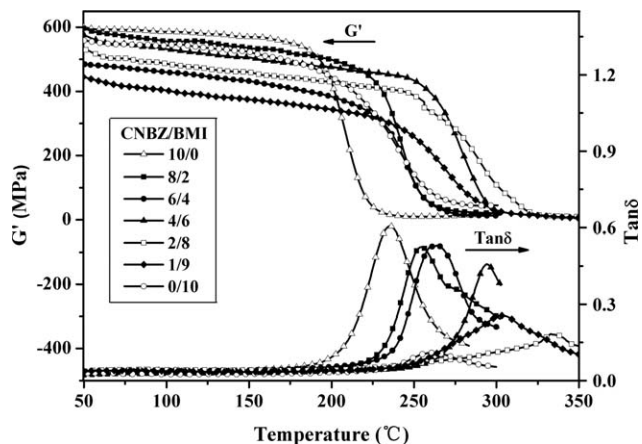


Figure 5. Tan δ and storage modulus (G') of cured CNBZ/BMI blends with various ratios.

Figure 4 showed gelation time of CNBZ/BMI blends at 180°C. The gelation time decreased with increasing BMI contents. This was because that negative oxygen ions and amine groups from ring opening of benzoxazine can catalyze the BMI polymerization, which caused the gelation time of the blending system to decrease. When BMI content was more than 60%, the gelation time increased. This was because that the polymerization of BMI played a dominant role at higher concentrations of BMI.

The Thermal Properties of Cured CNBZ/BMI Blends

Figure 5 showed tan δ and storage modulus (G') of cured CNBZ/BMI blends with various ratios. The analytical data was summarized in Table I. The influence of BMI content on T_g (from tan δ_{\max}) was shown in Figure 6. The T_g s estimated from the maximum of tan δ increased with increasing BMI. When BMI content was 80%, the T_g were up to 334°C, which was much higher than those of CNBZ and BMI homopolymers. The similar phenomenon was also observed in the bisphenol-A based benzoxazine and BMI blending system.¹³ The reason was that the addition reaction between phenolic hydroxyl group and the double bond afforded a higher crosslinking density, and the obtained T_g s of cured blends were higher than those of homopolymers. When BMI content was 90%, the T_g decreased to 303°C, which was still higher than those of CNBZ and BMI homopolymers.

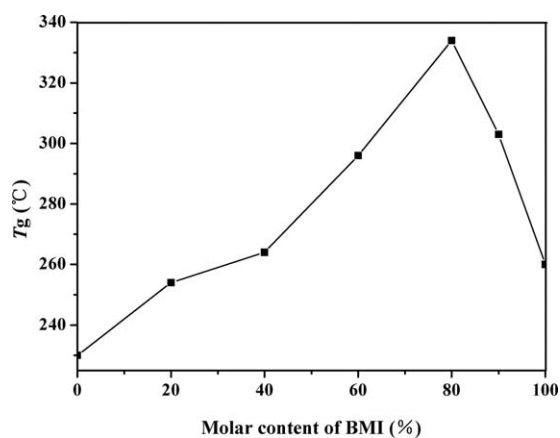
Figure 7 showed the TGA curves of cured CNBZ/BMI blends at various ratios. The typical results were summarized in Table I. The T_{d5} and T_{d10} of cured CNBZ resin were 351 and 382°C, respectively. For the cured CNBZ/BMI blends, the T_{d5} increased from 352 to 383°C, and the T_{d10} increased from 394 to 412°C. Those suggested that the addition of BMI effectively improved the thermal stability. Meanwhile, the char yields of cured CNBZ and BMI resins were 63.5% and 50.9%, respectively. For the cured CNBZ/BMI blends, the char yield decreased from 63.2% to 53.1%. It was attributed to the relatively low char yield of PBMI itself.

The Mechanical Properties of Cured CNBZ/BMI Blends

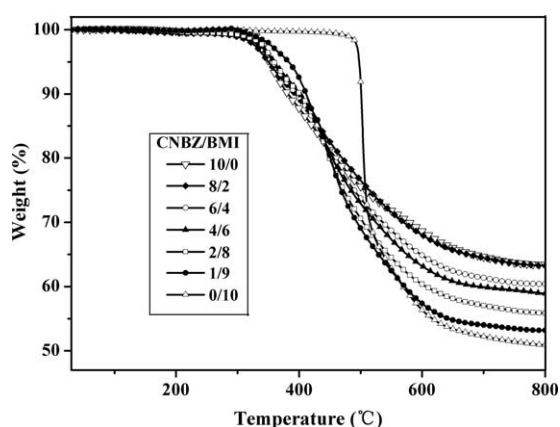
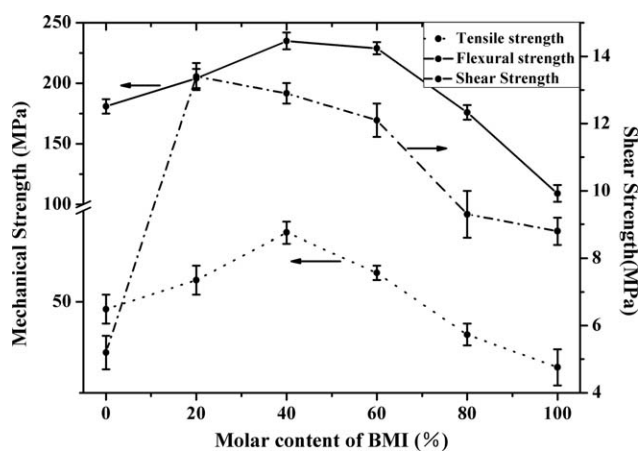
Figure 8 showed the tensile strength, flexural strength, and shearing strength of cured CNBZ/BMI blends. The analytical data was listed in Supporting Information (Table S1). The

Table I. Thermal Properties of Cured CNBZ/BMI Blends

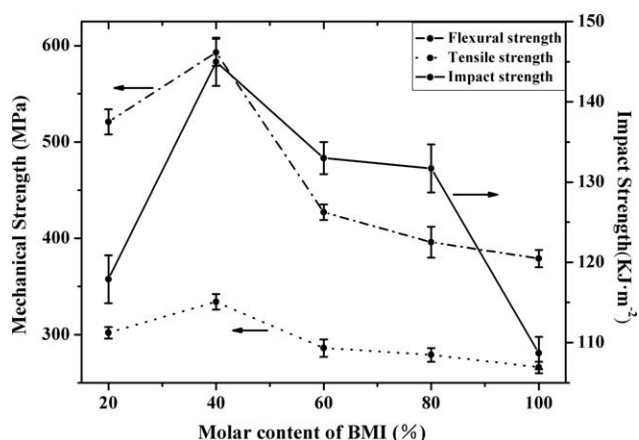
Cured samples	T_g			T_{d5} (°C)	T_{d10} (°C)	Char yield at 800°C (%)
	$\tan\delta_{\max}$ (°C)	G'' (°C)	G' (°C)			
CNBZ	230	212	195	351	382	63.5
CNBZ/BMI(8/2)	254	240	228	352	394	63.2
CNBZ/BMI(6/4)	264	248	230	358	396	60.4
CNBZ/BMI(4/6)	296	276	264	360	397	58.9
CNBZ/BMI(2/8)	334	297	273	362	402	56.0
CNBZ/BMI(1/9)	303	269	248	383	412	53.1
BMI	260	238	206	497	501	50.9

**Figure 6.** Influence of BMI content on T_g (from $\tan\delta_{\max}$).

tensile strength, flexural strength, and shearing strength of cured CNBZ/BMI blends increased with increasing BMI firstly and decreased afterward. When BMI content was 40%, the tensile strength, flexural strength, and shearing strength reached up to 69, 235, and 12.9 MPa, respectively. The tensile strength, flexural strength, and shearing strength of BT resin were 71, 117, and 13.9 MPa, respectively.^{25,26} Therefore, we thought the mechanical strength of cured CNBZ/BMI blends were comparable to that of BT resin.

**Figure 7.** TGA curves of cured CNBZ/BMI blends at various ratios.**Figure 8.** Tensile strength, flexural strength, and shearing strength of cured CNBZ/BMI blends.

When BMI contents were 20%, 40%, and 60%, the tensile strength, flexural strength, and shearing strength of cured CNBZ/BMI blends were even higher than those of CNBZ and BMI resin. The similar phenomenon was also observed in the benzoxazine and BMI containing allyl ether blending system.²⁷ The flexural strength of the benzoxazine/BMI containing allyl resins were higher than those of each homopolymer. When BMI

**Figure 9.** Tensile strength, flexural strength, and impact strength of CNBZ/BMI/GF laminates.

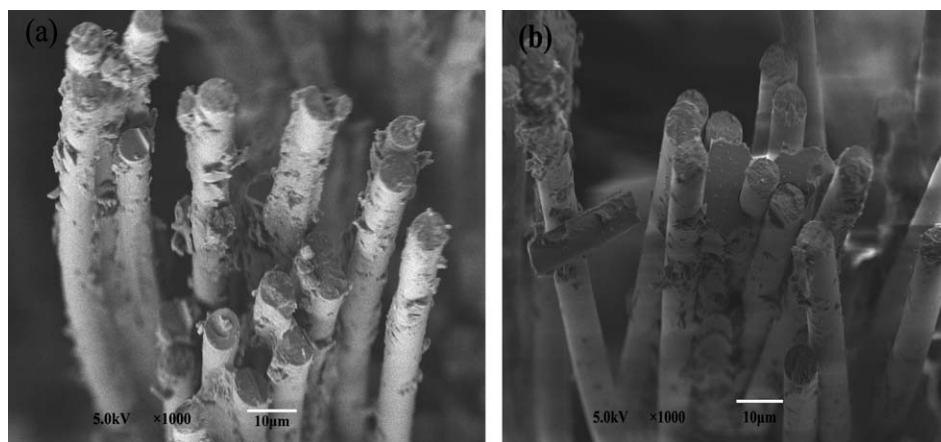


Figure 10. SEM images of fracture surfaces of (a) CNBZ/BMI/GF laminates with 40% of BMI and (b) CNBZ/BMI/GF laminates with 80% of BMI.

containing allyl was 15%, the flexural strength increased by 57% and 46% as compared with those of benzoxazine and BMI resin, respectively. We thought the reason was that the addition reaction between phenolic hydroxyl group and double bond contributed to increasing the crosslinking density of benzoxazine/BMI resin. The higher crosslink improved the mechanical strength of benzoxazine/BMI resin. Meanwhile, when BMI content was 40%, the elongation at break of cured CNBZ/BMI blends increased by 28% and 53% as compared with those of PCNBZ and PBMI, respectively (Supporting Information Table S1). This might be due to the formation of ether bond. The ether linkage had high rotational freedom and contributed to improving the toughness of the resin.

The Mechanical Properties of CNBZ/BMI/GF Laminates

When pure CNBZ was used to prepare CNBZ/GF laminate, severe foaming phenomenon was observed in the obtained CNBZ/GF laminates. Interestingly, we found this phenomenon was effectively suppressed when the CNBZ/BMI blends were used to prepare CNBZ/BMI/GF laminates. The addition of BMI helped to improve the processability. The reason needs to be investigated further.

Figure 9 showed the tensile strength, flexural strength, and impact strength of CNBZ/BMI/GF laminates. The analytical data was listed in Supporting Information (Table S2). As BMI content increased, the tensile strength, flexural strength, and impact strength of CNBZ/BMI/GF laminates increased firstly and decreased afterward. When BMI content was 40%, the tensile strength, flexural strength, and impact strength of the CNBZ/BMI/GF composites reached up to 334 MPa, 593 MPa, 145 KJ m⁻², respectively. The mechanical strength of CNBZ/BMI/GF laminates followed nearly the same trend as cured CNBZ/BMI blends. To further understand these results, fractured surface of CNBZ/BMI/GF laminates was observed by SEM. Figure 10 showed the SEM images of fracture surfaces of the CNBZ/BMI/GF laminates. When BMI content was 40%, the surface of GFs was covered by many matrices [Figure 10(a)], indicating strong interfacial adhesions between GFs and matrices. This was because that the addition of BMI contributed to increasing the fluidity of the resin,²⁸ which led to the increase of the fiber wetting. The

interfacial adhesion between fibers and matrices was enhanced. However, when BMI content was 80% [Figure 10(b)], the surface of GFs had a little remnant of matrices, indicating weak interfacial adhesions between GFs and matrices. This was because that at higher concentrations of BMI, the brittle nature of BMI dominated and led to an easy failure at the interphase.

CONCLUSIONS

CNBZ/BMI blends and CNBZ/BMI/GF laminates were successfully prepared. We found that the curing temperature of the blends was lowered and the gelation time was shortened. There existed the addition reaction between phenolic hydroxyl group and the double bond except for the homopolymerization of CNBZ and BMI.

The T_{gs} of the cured CNBZ/BMI blends increased firstly and then decreased. When BMI content was 80%, the T_g reached up to 334°C, which was much higher than those of CNBZ and BMI homopolymers. The cured CNBZ/BMI blends exhibited excellent thermal stability. The T_{d5} and T_{d10} were up to 383 and 412°C, respectively. They also exhibited excellent mechanical strength. When BMI content was 40%, the tensile strength, flexural strength, and shearing strength of cured CNBZ/BMI blends reached up to 69, 235, and 12.9 MPa, respectively.

The obtained CNBZ/BMI/GF laminates exhibited excellent mechanical strength. The tensile strength, flexural strength, and impact strength reached up to 334, 593, and 145 KJ m⁻², respectively. Therefore, the CNBZ/BMI blends and their glass cloth reinforced laminates can be one good candidate in some critical circumstances with requirements of high temperature resistance and excellent mechanical properties.

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