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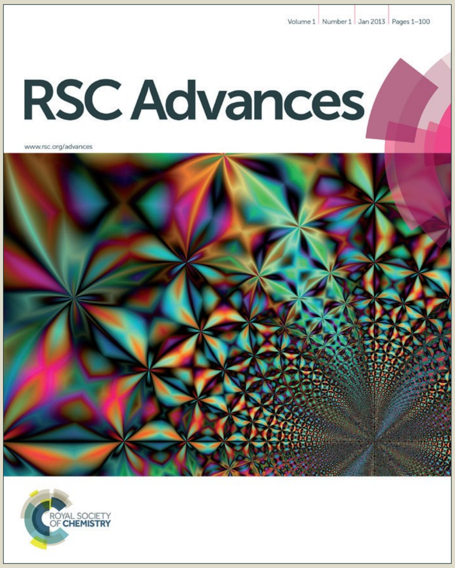

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Effect of functionalized benzoxazine with allyl groups on dielectric, mechanical and thermal properties of BMI/BADCy composites

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Abstract

Functionalized benzoxazine with allyl groups has recently attracted a great deal of attention due to its polymerizable group. In order to improve the properties of 4,4'-Bismaleimidodiphenyl methane (BMI)/cyanate ester (BADCy), benzoxazine (Boz) was added into the BMI/BADCy systems in this paper. Effect of functionalized Boz with allyl groups on dielectric, mechanical and thermal properties of BMI/BADCy composites were systematically investigated in details by mechanical measurement, scanning electron microscope (SEM), dynamic mechanical analysis (DMA) and thermo-gravimetric analysis (TGA). The results showed that formation of mannich bridge networks and Interpenetrating Polymer Network in the polymerizations of Bz-allyl and BMI/BADCy increased the cross-linking densities and thermal stability. Allyl-based polymers also exhibited high glass transition temperatures, and higher char yields. The dielectric constant values and the dielectric loss factor of BBz2 reached minimum value of 3.17 and 0.083 at 10^6 Hz respectivly. The mechanical properties (high flexural modulus of 4.18GPa and flexural strength of

120 MPa) of the BBz2 were superior. Scanning electron microscopy analysis showed distinct characteristics of ductile fracture of the blends.

Introduction

Bismaleimides (BMIs) are an important classes of addition-type polyimides which have gained much importance as a high-performance, thermoset matrix system. Their success in the areas of aerospace structural applications is mostly due to their flame retardation and oxidative stability, excellent thermal, low propensity to moisture absorption at elevated temperatures, especially in hot/wet environments[1-5]. Cyanate ester (BADCy) resin is a well-known thermosetting resin with outstanding thermal stability, moisture resistance, low dielectric constant and loss after being fully cured to form a triazine network[6-8].

Bismaleimide/cyanate ester (BMI/BADCy) resin is selected as the model for modification owing to its widespread use in electronics fields, such as circuit boards, interconnects, and adhesives for microelectronics applications (e.g., flexible and rigid dieattach adhesives)[9, 10]. However, there are also several problems with BMIs, high curing temperature, and brittleness. In addition, their relative high dielectric constants are not suitable for applications in electronic industries [11, 12]. Previous studies have showed that 2,2’-diallylbisphenol A (DBA) was one of the most effective modifier to improve their processibility and toughness. It can copolymerized with BMI through “Ene” and “Diels–Alder” reaction[13-15]. Another point is that the phenol groups in this allyl compound may act as catalyst to the cyclotrimerization of cyanate esters[16].

Polybenzoxazines possess typical characteristics of the traditional phenolic resins such as excellent flame retardance, heat resistanceand electronic properties. The major advantages of the typical polybenzoxazines are associated with the existence of inter- and intramolecular hydrogen bonds in the network structure[17-19]. Polymerizable group-containing monomers have attracted much attention because they can form the cross-linked network structure. Hence, it exhibit enhanced thermal and mechanical performance while preserving the beneficial properties of polybenzoxazine. Benzoxazine monomers (Boz) containing allyl can form highly cross-linked network structures after thermal treatment. Ishida groups[20] have synthesized an allyl-containing benzoxazine monomer by using allylphenol, aniline, and paraformaldehyde. Also, Tarek Agag[21] reported the preparation of a similar benzoxazine monomer from phenol, Bisphenol A with allylamine and formaldehyde. Therefore, it is of interest to study resin systems based on blends of Boz and BMI/BADCy resins. In such systems, Boz and BMI/BADCy are crosslinked through different reactions to form networks which interpenetrated each other in the cured resin[22]. This characteristic structure may result in synergistic effects on properties of the polymer networks, which are expected to couple the prominent dielectric properties of cyanate ester resin with the high temperature resistance and remarkable mechanical and processing behavior of the modified BMI resin.

Since the molecular structure of Boz can be designed[23], we synthesized several Boz monomers containing several allyl groups, which were used as new modifier for BMI/BADCy resin, and then a series of Boz modified BMI/BADCy resins were prepared. The focus of this paper is put on evaluating the effect of Boz and the content of allyl groups on the thermal and dielectric properties; and consequently, developing a new way for preparing high performance resins simultaneously with outstanding thermal and dielectric properties.

Experimental

Materials

Bisphenol A cyanate ester (BADCy) resins were purchased from Shangyu Shengda Biochemical Co. Ltd. (Shangyu, China). 4, 4'-Bismaleimidodiphenyl methane (BMI) was received from Hubei Fengguang Chemicals, China. Bz-a, Bz-allyl-1 and Bz-allyl-2 was prepared from bisphenol A, aniline and paraformaldehyde, diallyl bisphenol A, aniline and paraformaldehyde, diallyl bisphenol A, allylamine and paraformaldehyde, respectively, according to the method previously described[23]. The chemical structures of BADCy, BMI, Bz-a, Bz-allyl-1 and Bz-allyl-2 are shown in Fig. 1.

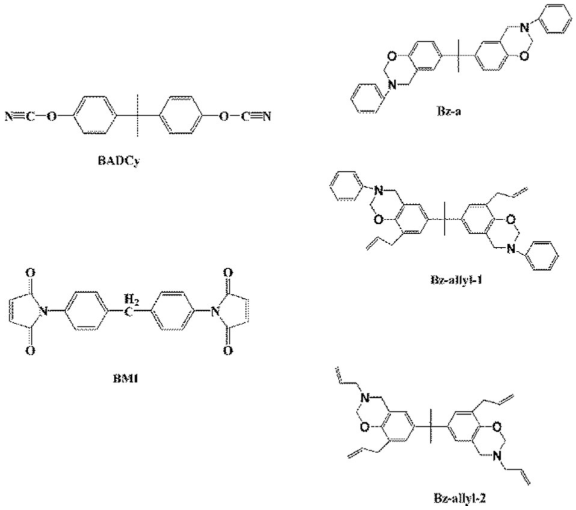


Fig.1 The chemical structures of BADCy, BMI and Bz-allyl

Preparation of the ternary blends

Appropriate quantities of BADCy and BMI were placed in a three-necked flask with a mechanical stirrer and a thermometer. The mass ratios of BADCy and BMI were 4:3. The mixture was heated to 160°C and maintained at that temperature with stirring until a homogeneous liquid was obtained. The liquid was maintained at that temperature for additional 0.5h, which is BMI/BADCy prepolymer. After that, cooling the mixture to 140°C the Boz was added, then, the ternary mixture was stirred for 20 min and a brown-red transparent liquid was obtained. Bz-a, Bz-allyl-1 and Bz-allyl-2 was blended with BMI/BADCy, respectively. The blends were noted as BBz, BBz1 and BBz2, respectively.

Preparation of cured resins

Firstly, the blends were poured into the preheated mold with silicone coating on the inner surface. Then, the blends were degassed in a vacuum oven (120°C for 0.5h in vacuum). Finally, the blends were cured following the procedures of 150°C/2h + 180°C/3h + 200°C/2h, and post-cured at 240°C/2h.

Characterization

Impact strength was performed according to GB/T2567-2008 on a testing machine (ZBC-50A Plastic Pendulum Impact Testing Machine, Shenzhen Sans Measurement Technology Co. Ltd, Shenzhen, China). The sample dimension was (50±0.02) × (7±0.02) × (4±0.02) mm^3. Flexural strength and modulus were performed according to GB/T2567-2008 on the testing machine (CMT-6303 Electronic Tensile Testing Machine, Shenzhen Sans Measurement Technology Co. Ltd, Shenzhen, China). The sample dimension was (80±0.02) × (10±0.02) × (4±0.02) mm^3. K_{IC} value was determined by three-point bending test on each precracked sample at room temperature according to STM Standard D 5528-01, using single edge notched bending tests measured in term of critical stress intensity factor (K_{IC}). Samples were tested to failure at a cross-head speed of 1 mm·min^{-1} at the loading point using the CMT-6303 Electronic Tensile Testing Machine. Density was performed according to GB 1033-1986 on a testing machine (JA2003J Electronic Analytical Balance, Shanghai Yueping scientific instrument Co. Ltd, Shanghai, China). Five samples were tested for each composition, and the results are presented as an average for tested samples.

DSC measurements were performed with a Q1000DSC thermoanalyzer system (USA) ranging from room temperature to 380°C under N^2 atmosphere at a heating rate of 10°C·min^{-1}. A dry nitrogen flow of 40 ml·min^{-1} was used as purge gas. Samples of about 10 mg were enclosed in aluminium DSC capsules. Dynamic mechanical analysis (DMA) was performed with a Switzerland Mettler-Toledo DMA with a sample size of 45 mm × 6 mm × 3mm. DMA tests were carried out from 25 to 380°C with a heating rate of 3°C·min^{-1} at 1Hz. TGA tests were performed by using a Netzsch STA 449C thermogravimetric analyzer (Germany) at a heating rate of 10°C·min^{-1} under N^2 atmosphere from 20 to 800°C.

The dielectric properties of composites were tested by using a broadband dielectric spectrometer (CONCEPE 80, Novocontrol Technology Company, Germany) with an Alpha-A high-performance frequency analyzer over the frequency range of 10^{-1} to 10^6 Hz.

Scanning electron micrographs (SEM) were performed on a TESCAN VEGA3 LMH instrument. SEM accelerating voltage was 20kv. The water absorption of a sample was determined by swelling in distilled water for 20h at 100°C. The sample dimension was (10±0.02) × (10±0.02) × (3±0.02) mm^3. FT-IR spectra were recorded on KBr pellets from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} on a Nicolet IS10 IR spectrometer (USA).

Results and discussion

DSC analysis for the curing reaction

The curing procedures for BMI/BADCy resin and the ternary blends were studied by DSC (Fig. 2). To BMI/BADCy resin, only one reaction exotherm was observed at the peak temperature of 305°C. BMI/BADCy resin is polymerized at a very high temperature, is usually required without catalyst. According to the figure, all of the exothermic peaks are single peaks, and the peak temperatures of the blends shift to lower temperatures as Boz adds. The curing reaction of BMI/BADCy is accelerated with the presence of Boz, because it can occur in the presence of phenolic hydroxyl, which can be obtained from Boz. As to BBz, BBz1 and BBz2 blends, the content of allyl groups in the Boz monomer increases, which makes BMI/BADCy react with allyl groups. The shift to a low temperature suggests that BMI/BADCy was induced to undergo a reaction in the presence of Boz and allyl groups.

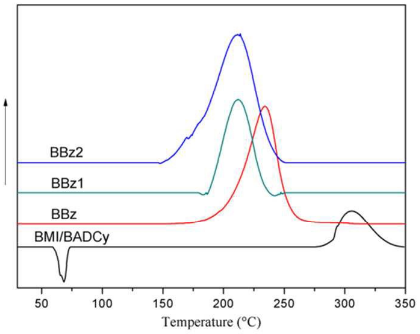


Fig.2 DSC curves of BMI/BADCy resin and the ternary blends

Mechanical properties of the ternary blends

The tensile strength, impact strength, flexural strengths, fracture toughness and density of the ternary blends are listed in Figures 3-4 and Table 1. The three-point bend test was used to determine the flexural strength and modulus of the ternary blends. It was observed from Fig.3 that the BBz2 had the maximum impact strength (18.4 kJ·m^{-2}), which is increased by 54 % compared with that of the BMI/BADCy resin. And our results show that flexural strength, flexural modulus as well as K_{IC} of the BBz2 can be enhanced by at least 41%, 14%, 30% compared with that of BMI/BADCy, respectively. Therefore, it can be concluded that the addition of Boz can efficiently improve the mechanical properties of BMI/BADCy resin. Especially the Boz has more allyl groups. The enhancement of impact and flexural strength may be attributed to the network structure of high crosslinking density and the flexible ether bonds in Boz/BMI/BADCy and aliphatic chain in BBz2.

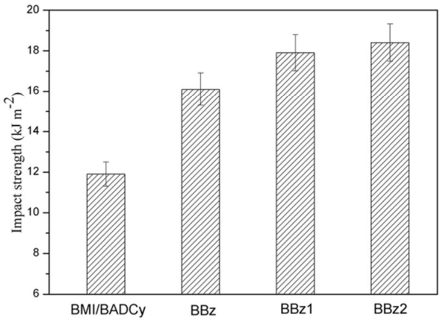


Fig.3 The impact strength of BMI/BADCy resin and the ternary blends

Table 1 The mechanical properties of BMI/BADCy resin and the ternary blends

Sample ID	**Impact strength (KJ m^{-2})**	**Flexural strength (MPa)**	**Flexural modulus (GPa)**	**Tensile strength (MPa)**	**Fracture toughness K_{IC} (MPa m$^{1/2}$)**	**Density (g cm^{-3})**
BADCy /BMI	11.9 (±0.2)	85 (±2)	3.65 (±0.05)	41.6 (±0.3)	0.91 (±0.02)	1.2656 (±0.0001)
BBz	16.1 (±0.1)	112 (±3)	4.15 (±0.09)	54.1 (±0.2)	1.04 (±0.04)	1.2499 (±0.0001)
BBz1	17.9 (±0.2)	118 (±3)	4.09 (±0.03)	61.8 (±0.5)	1.16 (±0.02)	1.2566 (±0.0001)
BBz2	18.4 (±0.2)	120 (±2)	4.18 (±0.06)	64.6 (±0.4)	1.19 (±0.01)	1.2563 (±0.0001)

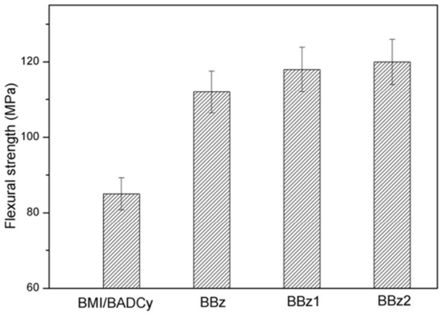


Fig.4 The flexural strength of BMI/BADCy resin and the ternary blends

To investigate the possible curing reactions of the ternary blends, FT-IR measurement was carried out. FT-IR spectra of the BMI/BADCy resin and ternary blends before and after cured are shown in Fig. 5. As a result, the absorption at 940 cm^{-1} assigned to oxazine ring in the benzoxazine ring structure disappeared after cured. And the absorptions at 2271 and 2236 cm^{-1} assigned to cyanate ester group also disappeared. The new absorptions at 1564 and 1371 cm^{-1} assigned to the triazine group appeared. The absorptions at 1638 cm^{-1} assigned to C=C decreased, which due to the the reaction between allyl groups. The appearance of absorption band at 1213cm^{-1} revealed the generation of ether bonds, which may due to the reaction between the BMI and PBoz as shown in scheme 2e.

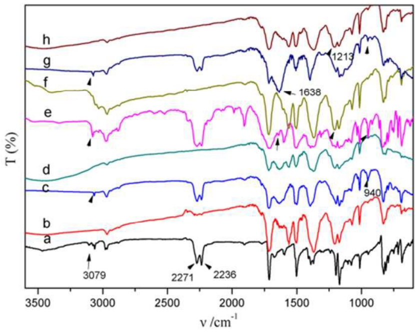
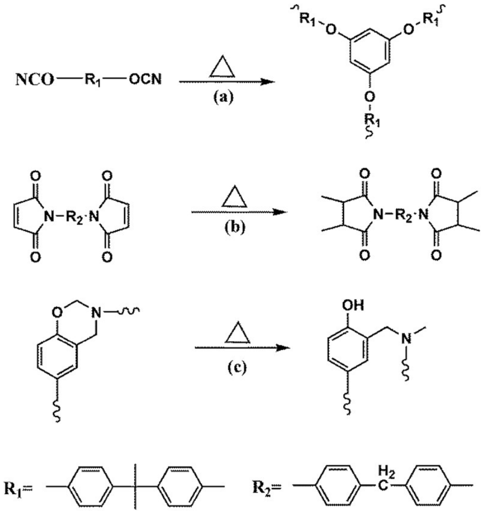


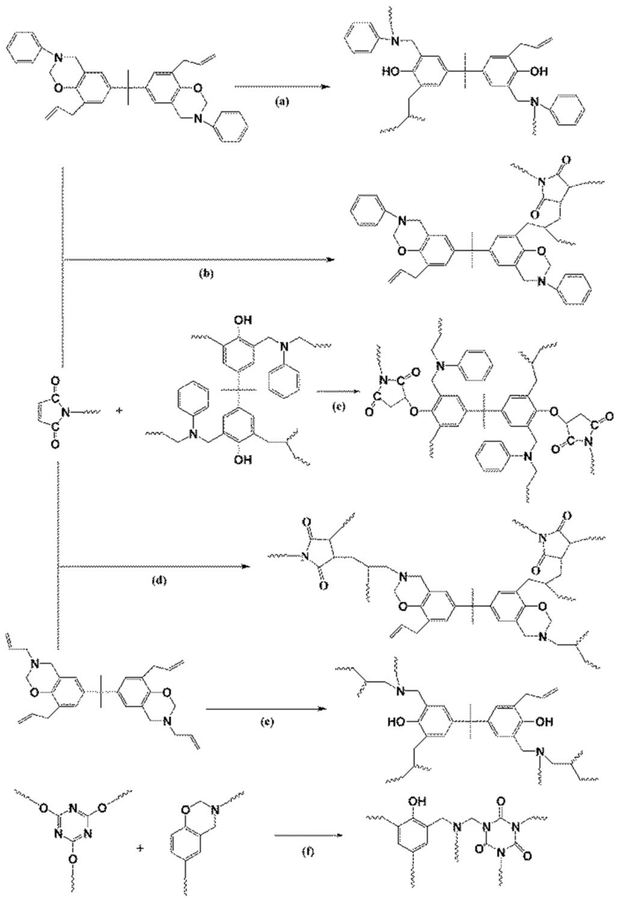
Fig.5 IR spectra of BMI/BADCy resin and the ternary blends before and after cured (a: uncured BMI/BADCy, b: cured BMI/BADCy, c: uncured BBz, d: cured BBz, e: uncured BBz1, f: cured BBz1, g: uncured BBz2, h: cured BBz2)

In the process of BMI and BADCy curing, the thermal reaction of the BMI and

BADCy can occur as shown in scheme 1a and 1b, respectively. However, the curing mechanism of the ternary blends is different from BMI/BADCy. Ene, Diels-Alder, homopolymerization, alternating copolymerization reactions are involved in BMI/BADCy modified with Boz[14, 24]. Ene reaction occurs at a lower temperature compared with that of other reactions (scheme 2(a,b,d,e)). The cure reactions of the blends of BADCy with BMI and Boz can occur (Scheme 1)[25]. Additionally, parts of Boz undergoes ring-opening polymerization to form polybenzoxazine and generate the phenolic hydroxyl group (scheme 1c), which can react with the BMI/BADCy (scheme 2(c,f)). By increasing the temperature, oxazine ring can react completely. allyl group oxazine ring can reacts completely (Scheme 2e). However, allyl group in benzene seldom reacts (Scheme 2a) because of the stability of the radical by resonance[26]. On one hand, the polymerization of the Boz/BMI/BADCy blends forms ether bonds, which results in good flexibility for the polymer. On the other hand, it may be attributed to the network structure of high crosslinking density formed in BBz2. Moreover, the hydrogen bonds can break and reform during the loading and unloading, thus increasing the energy dissipation in the materials. Also, the hydrogen bond is a physical interaction which will increase the impact strength and flexural strength of BMI/BADCy blends. Therefore, it can be concluded that the addition of Boz can efficiently improve the mechanical properties of BMI/BADCy resin, especially Bz-allyl-2.



Scheme 1 The curing procedure of BMI, BADCy and Boz, respectively



Scheme 2 The curing procedure of the ternary blends

Fracture surface of materials Bz-ally/BMI/BADCy resin system

In order to further confirm the effect of BOZ on the mechanical properties of BMI/BADCy resin, SEM images of the fracture surfaces of samples after impact tests are taken and shown in Figure 6. Fig. 6(a), (b), (c) and (d) presents SEM graphs of fracture surface of BMI/BADCy, BBz, BBz1 and BBz2, respectively. It can be observed that BMI/BADCy resin showing a smooth and riverlike fracture surface (Fig. 6a), exhibits a typical brittle feature. While with the addition of Bz-a into BMI/BADCy resin, the fracture surfaces become rougher and are accompanied with more ductile sunken areas, which is consistent with the improved impact strength of the composites. For the BBz1, as shown in Fig. 6c, the ductile sunken area is more than that of BBz. In the case of the BBz2, as shown in Fig. 6d, the fracture surface is much rougher than those of BMI/BADCy resin, BBz and BBz1, and there exist large amount of ductile sunken areas, which can absorb the energy of fracture and hinder the crack propagation, exhibits a typical rough feature. In summary, the BBz2 has a rough surface, more dimples and ductile sunken areas, and of high ductility and thus can absorb more energy during the impact process. The possible reason is that the co-curing of allyl groups and BMI/BADCy has largely enhanced the toughness of the resin. The features of the fracture surfaces of Boz/BMI/BADCy systems accord well with the mechanical properties.

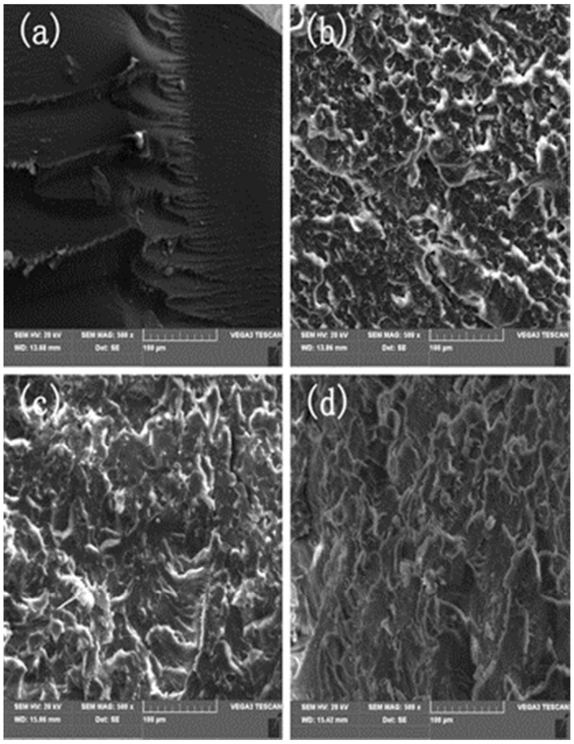


Fig.6 SEM of fracture surfaces of BMI/BADCy resin and the ternary blends

DMA properties of the ternary blends

The changes of T_g in composites are particularly important, not only because they yield insights into the fundamental changes in polymer chain dynamics, but also because the associated gains in thermal stability are critical for several applications. Determined from the midpoints of glass transition regions of the loss factor (tan δ) curves in Figures 7-8, the glass transition temperature (T_g) of various samples are listed in the Table 2. From the dynamic mechanical spectra, it is observed that the cured BMI/BADCy (Fig. 8) exhibits well-defined dynamic mechanical damping peaks centered at 245 and 308°C, which are ascribed to the glass transitions of polycyanurate and polybismaleimide, respectively[27]. However, it can be found that the T_g values for the composite with the different type of Boz are one single glass transition. Lin et al. reported that the alkyl isocyanurate and diphenyl ether linkages, which result from the coreaction of triazine and benzoxazine, randomly link the polycyanurate and polybenzoxazine domains, leading to a homogeneous thermosets between Boz and BADCy[28]. However, one single glass transition indicates that the ternary blends are a homogeneous network. There is only one single T_g existed so that we speculate further reactions between Boz and BMI/BADCy. The peak of tan δ for the cured ternary blends have shifted to a lower temperature compared with that of cured BMI/BADCy and increases with increasing content of allyl groups in Boz monomer. The increased allyl groups loading improves the cross-linking between BMI/BADCy and Boz containing allyl groups, and thus restricts the segmental movement of the polymer chains, which leads to a higher $T_{g[15,\ 16]}$. In fact, Boz containing allyl groups has two opposite influences on the improvement of T_g values of the composites. On one hand, the addition of Boz containing allyl groups can increase the cross-linking intensity of the cured system, which is beneficial to improve the T_g values of composites. On the other hand, the thermal stability of aliphatic chain is lower than that of rigid groups, which is a negative role on increasing the Tg value of composites.

Due to the strong interaction of intermolecular or intramolecular hydrogen bonds between the phenolic hydroxyl groups and the adjacent phenolic hydroxyl groups, or the N atoms on the Mannich bridges, or the π electrons on the benzene rings in the chemical structures of polybenzoxazine, copolymerizations of Boz with other resins have the higher initial modulus. With the increase of allyl groups in Boz, the initial storage modulus of the terpolymers improved. Based on the rubber elasticity theory and the following eqn (1)[29-31], we calculated the crosslinking densities of the different crosslinked systems and the data were shown in Table 1.

$$\boldsymbol{\rho = E/3\varphi RT} \qquad (1)$$

where ρ is the crosslinking density; E is storage modulus in the rubbery region(T_g+50°C); φ is the front factor, which is unity for ideal rubbers; R is the gas constant and T is absolute temperature[20]. It should be noted that this equation is applicable to polymer network that has a rubbery plateau region. So it is strictly valid only for lightly crosslinked materials and therefore is used only to qualitatively compare the level of crosslinking in the cast resins[32].

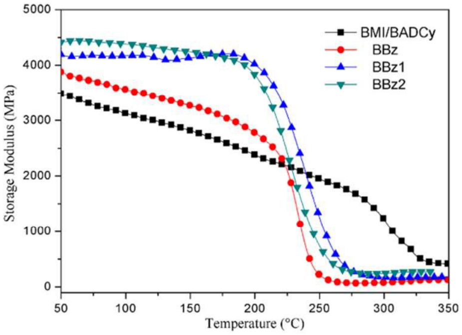


Fig.7 The storage modulus of BMI/BADCy resin and the ternary blends

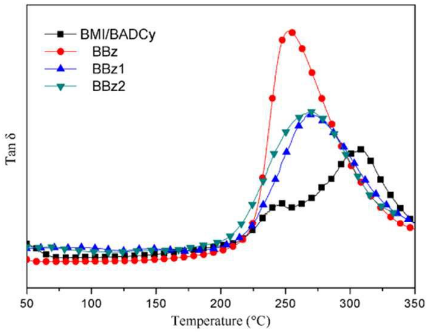


Fig.8 The tanδ of BMI/BADCy resin and the ternary blends

Compared to BMI/BADCy, the higher crosslinking density of Boz/BMI/BADCy led to the higher T_g. The formation of more crosslinked structure, and more rigid and stable triazine rings in the crosslinking network will increase the T_g and the retentions of the storage modulus of the terpolymers at high temperature. Therefore, the BMI/BADCy modified by Boz containing allyl groups have a higher initial storage modulus compared to BMI/BADCy; and BBz2 exhibit better thermal stabilities at high temperature than BBz.

Thermal properties of the ternary blends

The derivative curves of the TGA thermograms for the terpolymers reveal a great deal of information about the network structure of polybenzoxazine[33, 34]. In this work, we attempted to increase its crosslink density by adding Boz containing allyl groups. In an effort to explore the resulting improvement in thermal stability, the TGA thermograms and their derivative curves for the copolymers were obtained, and are presented in Fig. 9 and Fig. 10. The results for the decomposition temperatures and char yields of the copolymers were collected and are described in Table 2. As can be seen from Fig.10, different from an observable weight loss peak around 410°C on the differential curve of Boz/BMI/BADCy systems, there was no obvious weight loss of Boz/BMI/BADCy under 390°C. In Table 2, T_{d5} of BMI/BADCy is 441°C, while this of BBz2 is 426°C, respectively. The char yield at 800°C of BMI/BADCy is 35.8%, while this of BBz2 is 40.4%. The better thermal stability of BMI/BADCy than BBz2 may be attributed to the excellent thermal stability of BMI/BADCy, and more triazine rings in BMI/BADCy. And the addition of Boz will not significantly sacrifice the thermal resistance of BMI/BADCy. However, the thermal stability of the BBz systems may be attributed to the increased cross-linking degree of the Boz/BMI/ BADCy blends which results from the react between Boz undergoes ring-opening polymerization to form polybenzoxazine, ally groups react with BMI/CE resins and generate the phenolic hydroxyl group which is increased the interactions between molecules.

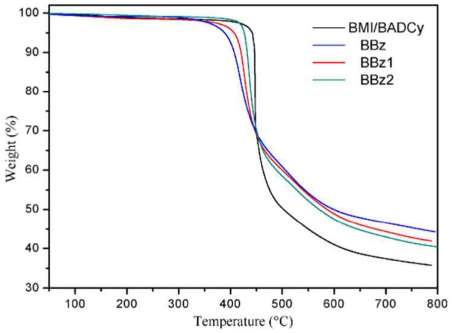


Fig.9 TGA curves of BMI/BADCy resin and the ternary blends

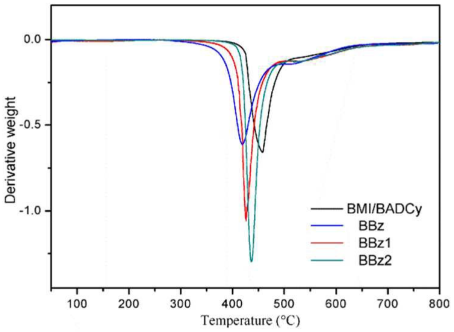


Fig.10 DTG curves of BMI/BADCy resin and the ternary blends

Table 2 Thermal Properties of BMI/BADCy resin and the ternary blends

Sample	BMI/BADCy	BBz	BBz1	BBz2
T_{d5} (°C)	441	388	406	426
T_{d10} (°C)	446	407	420	432
Char yield (%)	35.8	44.2	41.9	40.4
T_g	245, 308	252	271	268
Crosslinking density (mol m^{-3})	10^3	10^3	10^3	10^3

Dielectric properties of the ternary blends

The dielectric constant and dielectric loss factor of BMI/BADCy resin and other modified systems with different Boz are shown in Fig.11 and Fig.12, respectively. It can be seen that the dielectric constant values and the dielectric loss factor of Boz/BMI/BADCy blends are smaller than BMI/BADCy in a frequency band from 10^{-1} to 10^6 Hz. It indicates that the Boz/BMI/BADCy terpolymers have good dielectric stability.

It is known to all that polybenzoxazine possesses a lower electrical capacitance than other thermosetting materials but also is less sensitive to changes in frequency[20]. As the Fig.11 and Fig.12 show, it can be seen that the dielectric constant values and the dielectric loss factor of BBz system are bigger than those of BBz1 and BBz2, but smaller than that of BMI/BADCy. The dielectric constant values and the dielectric loss factor of BBz2 reached minimum value of 3.17 and 0.083 at 10^6 Hz, respectively. In addition, it can be seen that BBz2 possesses good dielectric stability over the testing frequency band from 10^{-1} to 10^6 Hz. There are three possible reasons. Firstly, the Boz have lower dielectric constant than the copolymer of BMI/BADCy, which can cause dielectric constant of the composites to become small. Secondly, it was due to the triazine rings and diphenyl ether with low the dielectric constant and the dielectric loss factor. Furthermore, the dielectric constant could be reduced by the decrease on the dipole polarization in higher crosslinked system. And the dielectric loss factor is also related to the crosslinking density based on its effect on the lagging of dipole polarization. But at high frequency there is no time for the polarization of dipoles. So the dielectric loss factor was insensitive to the crosslinking density at high frequency, which led to no obvious difference on the measured values of the dielectric loss factor. Shieh et al. reported that the high cross-linking density and high viscosity during the final curing stage of cyanate ester hindered the mobility of residual cyanate groups[35]. However, according to Shieh's conclusion, the network structure of high crosslinking density led to more free volume in the ternary blends, which reduced the dielectric constant of Boz/BMI/BADCy blends[36, 37]. Therefore, both the dielectric constant and loss factor of Boz/BMI/BADCy blends decrease compared with BMI/BADCy. It can be concluded that BBz2 has good dielectric properties and retain good dielectric stability.

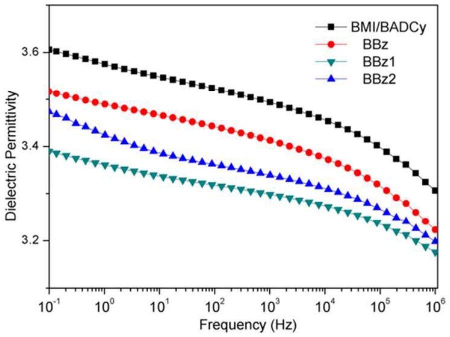


Fig.11 The dielectric constant of BMI/BADCy resin and the ternary blends

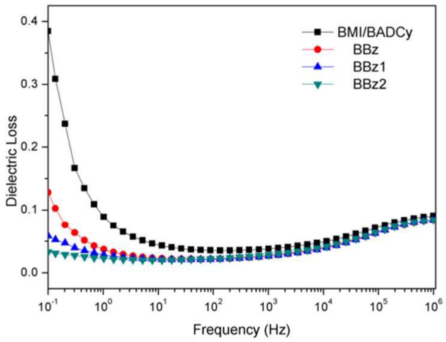


Fig.12 The dielectric loss factor of BMI/BADCy resin and the ternary blends

Conclusion

A kind of high-performance polymer composite has been fabricated using Boz/BMI/BADCy resin, in which the BMI/BADCy resin was modified with Boz containing allyl groups in order to improve its dielectric, thermal, mechanical properties and the cross-linking degree after curing. The incorporation of Boz can catalyze the reaction of BMI/BADCy resin and react with BMI/BADCy resin. BBz2 shows the maximum impact strength and flexural strength compared with BMI/BADCy, BBzand BBz1, which are 54% and 41% higher than that of BMI/BADCy resin, respectively. The T_g value of the BBz2 is 268°C. The BBz2 still shows good thermal resistance. And the addition of Boz containing allyl groups can not significantly sacrifice the thermal resistance of BMI/BADCy resin. Also, allyl groups can improve the dielectric properties of BMI/BADCy resin. The dielectric constant values and the dielectric loss factor of BBz2 reached minimum value of 3.17 and 0.083 at 10^6 Hz. In addition, the SEM analysis shows that BBz2 have a distinct characteristic of ductile fracture. The outstanding integrated properties of BBz2 blend can be attributed to mannich bridge networks and the network structure of high crosslinking density formed in BBz2 blends.

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Figure Captions:

Fig.1 The chemical structures of BADCy, BMI and Bz-allyl

Fig.2 DSC curves of BMI/BADCy resin and the ternary blends

Fig.3 The impact strength of BMI/BADCy resin and the ternary blends

Fig.4 The flexural strength of BMI/BADCy resin and the ternary blends

Fig.5 IR spectra of BMI/BADCy resin and the ternary blends before and after cured (a: uncured BMI/BADCy, b: cured BMI/BADCy, c: uncured BBz, d: cured BBz, e: uncured BBz1, f: cured BBz1, g: uncured BBz2, h: cured BBz2)

Fig.6 SEM of fracture surfaces of BMI/BADCy resin and the ternary blends

Fig.7 The storage modulus of BMI/BADCy resin and the ternary blends

Fig.8 The tanδ of BMI/BADCy resin and the ternary blends

Fig.9 TGA curves of BMI/BADCy resin and the ternary blends

Fig.10 DTG curves of BMI/BADCy resin and the ternary blends

Fig.11 The dielectric constant of BMI/BADCy resin and the ternary blends

Fig.12 The dielectric loss factor of BMI/BADCy resin and the ternary blends

Table Captions:

Table 1 The mechanical properties of BMI/BADCy resin and the ternary blends

Table 2 Thermal Properties of BMI/BADCy resin and the ternary blends

Scheme Captions:

Scheme 1 The curing procedure of BMI, BADCy and Boz, respectively

Scheme 2 The curing procedure of the ternary blends

Effect of functionalized benzoxazine with allyl groups on dielectric, mechanical and thermal properties of BMI/BADCy composites

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Incorporation of functionalized benzoxazine with allyl groups into BMI/BADCy composites can induce an interpenetrating network (IPN) structure. And the fracture surface will change from riverlike shape to ductile sunken shape.