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Effect of Bis allyl benzoxazine on the thermal, mechanical and dielectric properties of bismaleimide-cyanate blend polymer

Yiqun Wang\textsuperscript{1}, Kaichang Kou\textsuperscript{1}, Guanglei Wu*\textsuperscript{1,2}, Ailing Feng\textsuperscript{3}, Longhai Zhuo\textsuperscript{1}

1. The Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education and Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi’an 710129, P.R. China

2. Center of Nanomaterials for Renewable Energy (CNRE), State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi’an Jiaotong University, Xi’an 710049, P.R. China

3. Institute of Physics & Optoelectronics Technology, Baoji University of Arts and Sciences, Baoji 721016, P.R. China

*Corresponding author: Guanglei Wu

Tel./fax: +86 29 8339-5372

E-mail address: wuguanglei@mail.xjtu.edu.cn

Abstract

Thermosetting terpolymer composed of Bis allyl benzoxazine (Bz-ally), cyanate ester (BADCy) and 4, 4’-Bismaleimidodiphenyl methane (BMI) was prepared via co-curing reactions. The curing kinetics of Bz-ally/BMI/BADCy was investigated via non-isothermal DSC at different heating rates by Flynn-Wall-Ozawa method. The dielectric, thermal and mechanical properties of Bz-ally/BMI/BADCy terpolymers
were systemically investigated in detail by mechanical measurement, scanning electron microscope (SEM), dynamic mechanical analysis (DMA) and thermo-gravimetric analysis (TGA). The results show that a suitable addition of Bz-allyl can enhance the impact strength and flexural strength as well as reduce the dielectric constant and the dielectric loss of BMI/BADCy. The dynamic mechanical analysis reveals that the cross-link density of the blend is higher than BMI/BADCy. The higher crosslinking density of the terpolymer led to the good thermal stability of the terpolymer. Scanning electron microscopy analysis shows distinct characteristics of ductile fracture of the blends. All these changes in properties are closely correlated to the copolymerization between Bz-allyl and BMI/BADCy, which could form an interpenetrating polymer network in the system.

**Keywords:** Benzoxazine; Cyanate ester; Dielectric properties; Thermal properties; Mechanical properties

**Introduction**

Polybenzoxazines have evinced significant interest as a class of high performance phenolic resin. Compared with traditional phenolic resin, polybenzoxazine possesses several superior properties[1,2]. Such as near-zero shrinkage during polymerization, high thermal stability, flame retardancy, good mechanical strength, low dielectric constant, cured without any added initiator or catalyst and good reactivity and compatibility with other polymers[3,4]. In addition, with the molecular design flexibility, polybenzoxazine precursors can be prepared, which makes the tailoring of
well-defined molecular structures for specific applications possible[5]. The major advantages of the typical polybenzoxazines are associated with the existence of inter- and intramolecular hydrogen bonds in the network structure[6-8]. Therefore, benzoxazine resin is widely used in the modification of thermosetting resin.

Polycyanurates derived from the thermal cure of cyanate ester possess high thermal properties, low dielectric constant and mechanical properties after being fully cured to form a triazine network[9-13]. However, the thermal characteristics are inferior to those of conventional bismaleimide systems. Blends of cyanate ester and bismaleimide have been realized to derive systems bearing good physicochemical attributes of the two components, i.e. the heat resistance and of bismaleimide and the mechanical properties of polycyanurates[14-18]. Some blend systems were investigated by the addition polymerization of bisphenol A dicyanate (BADCy) and 4,4’-bismaleimido diphenylmethane[19], and also BADCy and 2,2’-bis[4-(4-maleimido phenoxy)propane][20,21]. Commercial blend formulations of bismaleimide-cyanate known as B-T resins are available, which is extensively used as materials for engineering materials in aircrafts, reinforced plastics, and injection-molding powders, as well as materials in electric motor coil windings, etc. [22] However, according to research on the bismaleimide-cyanate system[23,24], the copolymerization of bismaleimide with cyanate resin will result in an interpenetrating network (IPN) structure with high thermal and mechanical properties. Some novel allyl-functionalised aryl cyanate esters were developed to be incorporated into cyanate
ester/bismaleimide blend [25-29]. The addition of a small amount of allyl-functionalised aryl cyanate esters may increase the $T_g$ of the overall network by linking the polycyanurate network to the poly-bismaleimide network. So, Bis allyl benzoxazine, which has allyl groups, is selected to modify bismaleimide-cyanate ester, and is expected to possess better composite performances.

In this work, Bis allyl benzoxazine (Bz-ally) are performed to modify BMI/BADCy resins, aiming to regulating its dielectric, heat resistance, and mechanical properties. The effects of Bz-ally on the moisture resistance, mechanical, dielectric and thermal properties of Bz-ally/BADCy/BMI composites were investigated to develop high performance materials.

**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. Bis allyl benzoxazine (Bz-ally) was synthesized from diallyl bisphenol A, aniline and paraformaldehyde according to procedures previously described[5]. The chemical structures of BADCy, BMI and Bz-allyl are shown in Fig. 1.
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 the 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 Bz-allyl was added, and then the ternary mixture was maintained with stirring for 20 min and a brown-red transparent liquid was obtained. Bz-allyl was blended with BMI/BADCy in different mass ratios of 3%, 6%, 9% and 12%. The blends were noted as BBz3, BBz6, BBz9 and BBz12, respectively.

**Preparation of cured resins**
Firstly, the blends were poured into the preheated mold with silicon 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) mm³. 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) mm³. 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 N₂ atmosphere. 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 N₂ atmosphere from 20 to 800°C.

The dielectric constant ε and loss factor tanδ were measured by a high-frequency QBG-3 Gauger and a S914 dielectric loss test set (Shanghai AE Electron Equipment Co. Ltd., Shanghai, China) at a frequency between 10 and 60MHz. The sample dimension was (25±0.02) × (25±0.02) × (3±0.02) mm³.

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) mm³. 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

Curing behavior of BBz9 resins

To explain the high thermal properties of Bz-ally/BADCy/BMI, it is necessary to study the curing behavior of the BBz9 in order to establish the curing kinetic parameters and offer a better knowledge of curing process and an improvement of the quality of high performance materials. The curing behaviors of the BBz9 were studied by differential scanning calorimetry.

The non-isothermal DSC thermograms at the heating rates of 5°C·min⁻¹, 10°C·min⁻¹, 15°C·min⁻¹, 20°C·min⁻¹ and 25°C·min⁻¹ were shown in Fig.2. Obviously, the heating rate showed a great influence on the curing process. With increasing the heating rate,
exothermic curing peaks were shifted to a higher temperature. Information about the nature of the curing reaction such as onset temperature ($T_i$), peak temperature ($T_p$), and endset temperature ($T_e$) at different heating rates could be derived, which are listed in table 1.

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>Onset temperature ($T_i$) (°C)</th>
<th>Peak temperature ($T_p$) (°C)</th>
<th>Endset temperature ($T_e$) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>112</td>
<td>195</td>
<td>251</td>
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<td>10</td>
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<td>25</td>
<td>128</td>
<td>226</td>
<td>291</td>
</tr>
</tbody>
</table>

Various models had been proposed for analyzing the non-isothermal curing behavior of polymer [30-32]. According to the relationship between the peak temperature and heating rate ($\beta$), the apparent activation energy ($E_a$) of the curing reaction of the terpolymer was 101.9 and 104.7 kJ·mol$^{-1}$, respectively, calculated by Kissinger and Ozawa methods [33,34] (Fig. 3). The $E_a$ values from Kissinger and Ozawa methods were quite close to each other and their differences may be caused by the different of assumptions.
The reaction active energy also could be calculated by the Flynn-Wall-Ozawa (FWO)\([35]\) (eq 1) multheating rate methods at different values of conversion.

\[
\log\beta = \log\left(\frac{AEa}{RG(\alpha)}\right) - 0.4567Ea/RT - 2.315
\]

where \(\beta\) is the rate of temperature increase, \(\alpha\) is the degree of curing reaction, \(A\) is a constant, \(Ea\) is the reaction active energy, \(R\) is the gas constant, and \(G(\alpha)\) is the integral form.

For a constant conversion \(\alpha\), the plot of \(\log\beta\) versus \(1/T\) obtained from DSC
thermograms using various heating rates should render a straight line, where the slope allows the determination of the apparent activation energy. According to Flynn-Wall-Ozawa method, linear relationships of logβ versus 1/T at various degrees of conversion were established in Fig.4. Fig.5 presented activation energy as a function of conversion. It could be seen that the activation energy values tended to increase with the degree of conversion.

Fig.4 Flynn-Wall-Ozawa plots at various degrees of curing of the BBz9

Fig.5 Variation of Ea versus conversion

**Mechanical properties of Bz-ally/BMI/BADCy resin system**

The impact strength of the BMI/BADCy resin and the blends with the different
contents of Bz-ally is shown in Fig. 6. The three-point bend test was used to determine the flexural strength and modulus of the Bz-ally/BMI/BADCy blends. The composition effects on flexural strength and flexural modulus of Bz-ally/BMI/BADCy blends are depicted in Fig.7. It is observed from Fig.6 that the BBz9 system has the maximum impact strength (17.9 kJ·m⁻²), which is increased by 50 % compared with that of the BMI/BADCy resin. The BBz9 system has the maximum flexural strength (128MPa) and flexural modulus (4089MPa), which is increased by 41% and 13% compared with that of BMI/BADCy, respectively. Therefore, it can be concluded that the addition of Bz-ally can efficiently improve the mechanical properties of BMI/BADCy resin. The enhancement of impact and flexural strength may be attributed to the network structure of high crosslinking density formed and the flexible ether bonds in Bz-ally/BMI/BADCy.

Fig.6 The impact strength of Bz-ally/BMI/BADCy systems
To investigate the possible curing reactions of BBz9, FT-IR measurement was carried out. FT-IR spectra of BBz9 before and after cured are shown in Fig. 8. As a result, the absorption at 947 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 appearance of absorption band at 1213 cm\(^{-1}\) revealed the generation of ether bonds, which may due to the reaction between the BMI and PBz-ally as shown in scheme 2d.
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 Bz-allyl/BMI/BADCy blends is different from BMI/BADCy. Ene, Diels-Alder, homopolymerization, alternating copolymerization reactions are involved in BMI/BADCy modified with Bz-allyl [36]. Ene reaction occurs at a lower temperature compared with that of other reactions as shown in scheme 2c. The cure reactions of the blends of BADCy with BMI can occur as shown in Scheme 1[37]. Additionally, parts of Bz-allyl undergoes ring-opening polymerization to form polybenzoxazine and generate the phenolic hydroxyl group as shown in scheme 2a, which can react with the BMI/BADCy as shown in scheme 2(d,e). With increasing temperature, Bz-allyl can react completely, but allyl group seldom reacts (Scheme 2b) because of the stability of the radical by resonance[38]. On one hand, the polymerization of the Bz-allyl/BMI/BADCy blends forms ether bonds, which results in good flexibility of the polymer. On the other hand, it may be attributed to the network structure of high crosslinking density formed in Bz-allyl/BMI/BADCy blends. Moreover, the hydrogen bond is a physical interaction which will increased the impact strength and flexural strength of BMI/BADCy blends. Therefore, it can be concluded that the addition of Bz-allyl can efficiently improve the mechanical properties of BMI/BADCy resin.
Scheme 1 The curing procedure of BMI and BADCy, respectively
Scheme 2 The curing procedure of Bz-ally/BMI/BADCy
Fracture surface of materials Bz-allyl/BMI/BADCy resin system

To research the effect of Bz-allyl on the mechanical properties of BMI/BADCy resin, SEM images of the fracture surfaces of samples after impact tests are taken and shown in Fig. 9.

Fig. 9(a), (b), (c), (d) and (e) presents SEM graphs of fracture surface of BMI/BADCy, BBz3, BBz6, BBz9 and BBz12, respectively. It can be observed that BMI/BADCy resin has a smooth and riverlike fracture surface (Fig.9a), exhibiting a typical brittle feature. While with the addition of Bz-allyl 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 BMI/BADCy resin, BBz3 and BBz6, as shown in Fig.9(a-c), with the content of the Bz-allyl increased, the riverlike fracture surface becomes more concentrated can be observed. The aspect ratios of cracks on the river region of the blend (Fig.9c) are smaller than that of BMI/BADCy resin (Fig.9a), and the ductile sunken areas is more than that of BMI/BADCy resin. In the case of the BBz9 system, as shown in Fig.9d, the fracture surface is much rougher than those of BMI/BADCy resin, BBz3 and BBz6 system, and there exist large amount of ductile sunken areas, which can absorb the energy of fracture and hinder the crack propagation, exhibiting a typical rough feature. In addition, BBz12, as shown in Fig.9e, has large ductile sunken areas in the matrix, and the surface scaly roughness is more obvious. In summary, the Bz-allyl/BMI/BADCy blend 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 Bz-allyl and BMI/BADCy has largely enhanced the toughness of the resin. Therefore, the impact strength of the composite with high Bz-allyl content is increased. The features of the fracture surfaces of Bz-allyl/BMI/BADCy systems accord well with the mechanical properties.

![Fig.9 SEM of fracture surfaces of Bz-allyl/BMI/BADCy systems](image)

**Dynamic mechanical analysis of Bz-allyl/BMI/BADCy resin system**
The DMA curves of the temperature dependence of tan δ and storage modulus of the cured blends of BMI/BADCy, BBz3, BBz6, BBz9 and BBz12 are shown in Figures (10-11). From the dynamic mechanical spectra, it is observed that the cured BMI/BADCy (Fig.11) 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 [21]. Corresponding temperatures for BBz3 are 246 and 371°C in Fig.11. In contrast, only one dynamic mechanical damping peak at about 262°C is observed in cured BBz9 (Fig.11). Two glass
transitions undoubtedly confirmed that the cured BMI/BADCy and cured BBz3 included two kinds of network. However, one single glass transition indicates that BBz6, BBz9 and BBz12 are a homogeneous network. There is only a single $T_g$ existed so that we speculate further reactions between Bz-allyl and BMI/BADCy.

As can be seen, all composites exhibit slightly higher storage modulus than BMI/BADCy resin in the glassy state. This result may be attributed to the higher modulus of PBz-allyl. So the initial modulus of Bz-allyl/BMI/BADCy blends was increased by the increase of Bz-allyl content. The $T_g$ of the Bz-allyl/BMI/BADCy blends is summarized in Table 2. With the increase of Bz-allyl content, the $T_g$s of the cured blends shifted to the higher temperature. Based on the rubber elasticity theory and the following eqn (1) [39], we calculated the crosslinking densities of the different crosslinked systems and the data were shown in Table 2.

\[
\rho = \frac{E}{3\varphi RT}
\]

(1)

where $\rho$ is the crosslinking density; $E$ is storage modulus in the rubbery region($T_g+40^\circ C$); $\varphi$ is the front factor, which is unity for ideal rubbers; $R$ is the gas constant and $T$ is absolute temperature[28]. 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.[40] It indicates that the addition of Bz-allyl into BMI/BADCy resin leads to increased $T_g$ because of the increased crosslinking degree of the Bz-allyl/BMI/BADCy blends. The crosslink density increased with the increase proportion of Bz-allyl may be attributed to the reaction
between Bz-allyl and BMI/BADCy. However, the Bz-allyl/BMI/BADCy terpolymers still have high $T_g$. Therefore, a conclusion can be drawn that the Bz-allyl/BMI/BADCy terpolymers show good heat resistance.

**Dielectric properties of Bz-allyl/BMI blends**

The dielectric constant and dielectric loss factor of BMI/BADCy resin and other modified systems with different contents of Bz-allyl are shown in Fig.12 and Fig.13, respectively. It can be seen that the dielectric constant values and the dielectric loss factor of Bz-allyl/BMI/BADCy blends are smaller than BMI/BADCy in a frequency band from 10 to 60 MHz. It indicates that the Bz-allyl/BMI/BADCy terpolymers have good dielectric stability.

![Fig.12 The dielectric constant of Bz-allyl/BMI/BADCy systems](image-url)
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\cite{41}. As the Fig.12 and Fig.13 show, it could be seen that the dielectric constant values and the dielectric loss factor of Bz-allyl/BMI/BADCy resins system decreased with the content of Bz-allyl firstly. Then the dielectric constant values and the dielectric loss factor slightly increased with further addition of Bz-allyl into the BMI/BADCy resin system. When the Bz-allyl content in cured Bz-allyl/BMI/BADCy resins was 9wt\%, the dielectric constant values and the dielectric loss factor of the blends reached minimum value of 3.02 and 0.0158 at 10 MHz, respectively. On one hand, it was due to the triazine rings and diphenyl ether with low the dielectric constant and the dielectric loss factor. On the other hand, 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. Wang 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[42]. However, according to Wang’s conclusion, when Bz-allyl increased, the network structure of high crosslinking density formed by Bz-allyl/BMI/BADCy hindered the curing of BMI/BADCy, which incurred the increase of the dielectric constant and the dielectric loss factor. Therefore, both the dielectric constant and loss factor of Bz-allyl/BMI/BADCy blends decrease compared with BMI/BADCy. It can be concluded that the suitable content of Bz-allyl in Bz-allyl/BMI/BADCy blends have good dielectric properties and retain good dielectric stability.

**Thermal properties of Bz-allyl/BMI/BADCy resin system**

![TGA curves of Bz-allyl/BMI/BADCy systems](image)
The derivative curves of the TGA thermograms for the terpolymers reveal a great deal of information about the network structure of polybenzoxazine [43,44]. In this work, we attempted to increase its crosslink density by adding Bz-allyl. The TGA and their derivative curves are shown in Fig. 14 and Fig. 15. Table 2 summarizes the results.

As can be seen from Fig. 15, different from an observable weight loss peak around 420°C on the differential curve of Bz-allyl/BMI/BADCy systems, there was no obvious weight loss of Bz-allyl/BMI/BADCy blends under 350°C. In Table 2, $T_{d5}$ of BMI/BADCy is 441°C, while this of BBz9 is 387°C, respectively. The char yield at 800°C of BMI/BADCy is 35.8%, while this of BBz9 is 43.1%. The better thermal stability of BMI/BADCy than BBz9 may be attributed to the excellent thermal stability of BMI/BADCy, and more triazine rings in BMI/BADCy. And the addition of Bz-allyl can 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 Bz-allyl/BMI/CE blends which results from the react between Bz-allyl 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.

### Table 2 Thermal Properties of BOZ/BMI/BADCy Thermosets

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{d5}$ (°C)</th>
<th>$T_{d10}$ (°C)</th>
<th>Char yield (%)</th>
<th>$T_g$ (°C)</th>
<th>Crosslinking density $(10^3 \text{ mol} \cdot \text{m}^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI/BADCy</td>
<td>441</td>
<td>446</td>
<td>35.8</td>
<td>245, 308</td>
<td>1.83</td>
</tr>
<tr>
<td>BBz3</td>
<td>427</td>
<td>433</td>
<td>46.6</td>
<td>246, 271</td>
<td>1.92</td>
</tr>
<tr>
<td>BBz6</td>
<td>405</td>
<td>415</td>
<td>45.2</td>
<td>248</td>
<td>2.15</td>
</tr>
<tr>
<td>BBz9</td>
<td>387</td>
<td>406</td>
<td>43.1</td>
<td>262</td>
<td>2.28</td>
</tr>
<tr>
<td>BBz12</td>
<td>379</td>
<td>401</td>
<td>43.3</td>
<td>267</td>
<td>2.32</td>
</tr>
</tbody>
</table>

**Water absorption of Bz-ally/BMI/BADCy resin system**

It is well recognized that BMI/BADCy is considered as a matrix for high-temperature aerospace structural applications and expected to experience extreme environmental conditions for a prolonged period of time. Outstanding moisture resistance is a very important property of a material, especially those requiring stably high performance [45], because in general absorbed water will decline almost all properties of the original material including thermal, glass transition temperature, mechanical and dielectric properties, etc [38]. Therefore, less water absorption is one important target of developing new BMI/BADCy composites with high performance. Water absorption of Bz-allyl/BMI/BADCy systems is presented in Fig.16. At the initial reaction stage, water absorption values of Bz-allyl/BMI/BADCy
systems are increased fast with the increasing immersing time. With the prolongation of the immersing time, water absorption values are increased slowly. It also can be seen that the water absorption decreases from 2.52 to 2.28 wt% with the small addition (3wt%) of Bz-allyl into BMI/BADCy resin, and which continually decreases with the continuous increase of Bz-allyl content in BMI/BADCy systems. In the case of BBz9 system, its water absorption is only 1.77 wt%, which is much lower than those of BMI/BADCy resin. However, the addition of Bz-allyl tends to increase the water resistance property. Apicella et al.[46] propose that there may be three ways for epoxy resins to absorb water: (1) formation of polymer-diluent solution; (2) adsorption at hydrophilic sites; (3) adsorption on the surface of free volume elements. The improvement of water resistant property of Bz-allyl/BMI/BADCy systems may be due to the more perfect network structure. Compared with BMI/BADCy, Bz-allyl has the phenolic hydroxyl groups, which catalyzed the reaction between BMI with BADCy; Bz-allyl also has ally groups, which reacted with BMI/BADCy and formed a perfect network structure after cured. Therefore, the Bz-allyl/BMI/BADCy systems have less free volume elements, which results in lower water absorption values of Bz-allyl/BMI/BADCy systems.
Conclusion

A kind of high-performance polymer composite has been fabricated using Bz-allyl/BMI/BADCy resin, in which the BMI/BADCy resin was modified with Bz-allyl in order to improve its dielectric, thermal, mechanical properties and the cross-linking degree after curing. The curing kinetics of Bz-allyl/BMI/BADCy was investigated via non-isothermal DSC at different heating rates by Flynn-Wall-Ozawa method. The incorporation of Bz-allyl can catalyze the reaction of BMI/BADCy resin and recat with BMI/BADCy resin. BBz9 shows the maximum impact strength and flexural strength, which are 50% and 41% higher than that of BMI/BADCy resin, respectively. The $T_g$ value of the BBz9 is 262°C. The Bz-allyl/BMI/BADCy blend with a suitable addition of Bz-allyl still shows good thermal resistance and moisture resistance. And the proper addition of Bz-allyl can not significantly sacrifice the thermal resistance of BMI/BADCy resin. Also, Bz-allyl can improve the dielectric properties of BMI/BADCy resin. The dielectric constant and loss of the BBz9 are 2.95-3.02 and 0.0148-0.0158 over a relatively wide frequency band from 10 to 60
MHz, respectively. In addition, the SEM analysis shows that the Bz-allyl/BMI/BADCy systems have a distinct characteristic of ductile fracture. The outstanding integrated properties of the Bz-allyl/BMI/BADCy blend can be attributed to the network structure of high crosslinking density formed in Bz-allyl/BMI/BADCy blends.

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Figure Captions:

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

Fig.2 DSC curves of the BBz9 at different heating rates

Fig.3 Representations of Kissinger and Ozawa methods to calculation activation energy from non-isothermal data for the copolymer

Fig.4 Flynn-Wall-Ozawa plots at various degrees of curing of the BBz9

Fig.5 Variation of Ea versus conversion

Fig.6 The impact strength of Bz-allyl/BMI/BADCy systems

Fig.7 The flexural strength and flexural modulus of Bz-allyl/BMI/BADCy systems

Fig.8 IR spectra of BBz9 before and after cured

Fig.9 SEM of fracture surfaces of Bz-allyl/BMI/BADCy systems

Fig.10 The storage modulus of Bz-allyl/BMI/BADCy systems

Fig.11 The tanδ of Bz-allyl/BMI/BADCy systems

Fig.12 The dielectric constant of Bz-allyl/BMI/BADCy systems

Fig.13 The dielectric loss factor of Bz-allyl/BMI/BADCy systems

Fig.14 TGA curves of Bz-allyl/BMI/BADCy systems

Fig.15 DTG curves of Bz-allyl/BMI/BADCy systems

Fig.16 Water absorption of Bz-allyl/BMI/BADCy systems

Table Captions:

Table 1 Exothermic peak temperatures of the BBz9 at different heating rates

Table 2 Thermal Properties of BOZ/BMI/BADCy Thermosets
Scheme Captions:

Scheme 1 The curing procedure of BMI and BADCy, respectively

Scheme 2 The curing procedure of Bz-ally/BMI/BADCy