



# The curing reaction of benzoxazine with bismaleimide/cyanate ester resin and the properties of the terpolymer



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## ARTICLE INFO

### Article history:

Received 17 July 2015

Received in revised form

12 September 2015

Accepted 23 September 2015

Available online 28 September 2015

### Keywords:

Benzoxazine

Cyanate ester

Thermal properties

Dielectric properties

Mechanical properties

## ABSTRACT

Thermosetting terpolymer composed of benzoxazine (BOZ), cyanate ester (BADCy) and maleimide resin (BMI) was prepared via co-curing reactions. The curing reaction of benzoxazine with bismaleimide/cyanate ester resin and the properties of the terpolymer were studied by differential scanning calorimetry (DSC) and Fourier transform-infrared spectroscopy (FT-IR), and the thermal, mechanical and dielectric properties of the terpolymer were also characterized. The FT-IR was applied to monitor the curing reactions of the reactive blends. Three reactions were observed in the curing reactions: the first is the polymerization of cyanate ester after oxazine ring opening, producing the triazine structure; the second is the coreaction between the triazine structure and benzoxazine, forming alkyl isocyanurate and diphenyl ether linkages, followed by the further reaction of the isocyanurate linkage; and the third is the self-polymerization of maleimide resin and benzoxazine, and coreaction with each other. Compared to the polybenzoxazine, the higher crosslinking density of the terpolymer led to the higher glass transition temperature ( $T_g$ ), as well as the 5% weight loss temperatures ( $T_{d5}$ ), indicating the better thermal stability of the terpolymer at service temperature. And the data for the mechanical and dielectric properties also showed that the terpolymer performs better than polybenzoxazine and the copolymer.

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## 1. Introduction

Benzoxazine resins are a new class of high performance polymers that are characterized by several unique properties such as near-zero volumetric shrinkage upon curing [1], flexibility in molecular design [2], minimal moisture absorption, excellent resistance to chemicals [3], and high glass transition temperature [4]. Additionally, polybenzoxazines are obtained by the ring-opening polymerization of monomers by thermal cure without any added initiator or catalyst [5]. Polybenzoxazines possess typical characteristics of the traditional phenolic resins such as good flame retardance, heat resistance and electronic properties. The major advantages of the typical polybenzoxazines are associated with the existence of inter- and intramolecular hydrogen bonds in the network structure [6–8].

Cyanate ester resin is a well-known thermosetting resin with

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high thermal properties, low dielectric constant and high glass transition temperature after being fully cured to form a triazine network [9–11]. Nair et al. reported that a copolymerization between the cyanate ester and benzoxazine resin and postulated a triazine–ether–benzoxazine network [12]. Lin et al. studied that the coreaction decomposes the polycyanurate structures and brings parts of the polycyanurate structures into the polybenzoxazine matrix [13]. Furthermore, Li et al. investigated the curing procedure of the benzoxazine–cyanate–epoxy system and the properties of the terpolymer [14]. The results showed that the higher crosslinking density of the terpolymer led to the higher glass transition temperature ( $T_g$ ), the better mechanical and dielectric properties. However, according to research on the bismaleimide–cyanate system [15,16], the copolymerization of bismaleimide with cyanate resin will result in an interpenetrating network (IPN) structure with high thermal and mechanical properties. So, the terpolymer composed of bismaleimide, cyanate ester and benzoxazine is expected to possess better composite performances.

Due to the complexity of the reactions, there is little research on the ternary system. As we all know, the polymer structures will

change in the curing procedure, which will affect the material properties. In this paper, the thermosetting blends composed of bismaleimide, bisphenol A dicyanate ester (BADCy) and benzoxazine were prepared. The curing process of the blends, microstructure, and thermal and dielectric properties of the terpolymers were investigated by differential scanning calorimetry (DSC), scanning electron microscope (SEM), Fourier transform-infrared spectroscopy (FT-IR) and dynamic mechanical analysis (DMA).

## 2. Experiment

### 2.1. Materials

Bisphenol A dicyanate (BADCy) ester (purity > 99.5%) white granular crystal was purchased from Shangyu Shengda Biochemical Co. Ltd. (Shangyu, China). 4,4'-Bismaleimidodiphenyl methane (BMI) was purchased from Hubei Fengguang Chemicals, China. Bisphenol A benzoxazine (BOZ) was synthesized from bisphenol A, aniline and paraformaldehyde according to procedures previously described [2]. The chemical structures of BADCy, BMI and BOZ are shown in Fig. 1.

#### 2.1.1. Preparation of BOZ/BMI/BADCy blends

The ternary blends were prepared by the following steps: firstly, the mass ratio of BMI and BADCy was 3:4 (molar ratio = 1:1.9), and BMI and BADCy prepolymer were thoroughly blended at 160 °C for 0.5 h with vigorous stirring; After that, cooling the prepolymer to 120 °C the BOZ was added, and then the ternary mixture was maintained with stirring for 0.5 h and a homogeneous liquid was obtained. BOZ was blended with BMI/BADCy in different mass ratios of 5%, 10%, and 15%. The blends were noted as PBOZ5, PBOZ10, and PBOZ15, respectively.

#### 2.1.2. Preparation of castings

Firstly, a preheated mold with silicone coating on the inner surface was heated at 120 °C for 1 h. The ternary blends were poured into the preheated mold with silicone coating on the inner

surface. Then, the ternary blends were degassed in a vacuum oven (120 °C for 0.5 h in vacuum). According to the DSC results, the curing cycles were determined by as follows: 150 °C/1 h + 180 °C/3 h + 200 °C/2 h, and post-cured at 220 °C/4 h.

### 2.2. Characterization

FT-IR spectra were recorded on KBr pellets from 400 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  on a Nicolet IS10 IR spectrometer (USA). DSC measurements were performed with a Q1000DSC thermoanalyzer system (USA) ranging from room temperature to 350 °C, at a heating rate of 10 °C  $\text{min}^{-1}$  under  $\text{N}_2$  atmosphere. TGA tests were performed by using a Netzsch STA 449C thermogravimetric analyzer (Germany) at a heating rate of 10 °C  $\text{min}^{-1}$  under  $\text{N}_2$  atmosphere from 20 to 800 °C. Dynamic mechanical analysis (DMA) was performed with a Switzerland Mettler-Toledo DMA with a sample size of 45 mm × 6 mm × 3 mm. The storage modulus  $E'$  and  $\tan\delta$  were determined as the sample was subjected to the temperature scan mode at a programmed heating rate of 3 °C  $\text{min}^{-1}$  at a frequency of 1 Hz. The flexural strength of the composites are measured by Electron Omnipotence Experiment Machine SANS-CMT5105 (Shenzhen New Sansi Corp., China) according to standard ASTM D 7264-2007 and ASTM D 2344-2000. Five samples were tested for each composition, and the results are presented as an average for tested samples. The dielectric constant and dielectric loss of the composites are measured using high frequency Q instrument (QBG-3D) and dielectric constant detector (S914) from Aiyi Electronic Equipment Co. (Shanghai, China).

## 3. Results and discussion

### 3.1. DSC analysis for the curing reaction

The curing procedures for BOZ, BMI, BADCy and their blend were studied by DSC (Fig. 2(a), (b)). The DSC thermogram for curing neat BADCy was shown in Fig. 2(a). Only one reaction exotherm was observed at the peak temperature of 315 °C. BADCy is polymerized at a very high temperature, is usually required without catalyst. Fig. 2(a) shows the exothermic peak temperatures of BOZ and BMI monomers were 227 °C and 210 °C, respectively. Shown in Fig. 2(b) is the DSC trace of PBOZ10 at a heating rate of 10 °C  $\text{min}^{-1}$ , which illustrates one exothermic peak lying between the peaks of its individual components. The onset and maximum temperatures of the exotherm were at 188 °C and 241 °C, respectively. The shift to a low temperature suggests that the BADCy component was induced to undergo a reaction in the presence of BOZ and BMI.

### 3.2. FT-IR analysis for the curing reaction

The FT-IR spectrum of PBOZ10 was recorded to investigate the reactions occurring at low temperature. The main characteristic absorptions in IR spectra are listed in Table 1. Shown in Fig. 3 are some crucial FTIR spectra of the ternary blends with different curing time at 140 °C. At the initial reaction stage, there were obvious characteristic peaks of oxazine rings (947  $\text{cm}^{-1}$ ), cyano groups (2236, 2271  $\text{cm}^{-1}$ ) and =C–H in the maleimide groups (691  $\text{cm}^{-1}$ ). With the prolongation of the curing time, the absorption peak of cyano groups decreased gradually followed by the appearance of the characteristic peaks assigned to triazine rings at 1371  $\text{cm}^{-1}$  (N=C–O) and 1564  $\text{cm}^{-1}$  (C=N–C), suggesting the polymerization of cyanate ester. At the same time, the characteristic absorptions of =C–H in the maleimide groups (691  $\text{cm}^{-1}$ ) no significantly change. It means that a small part of =C–H in the maleimide groups were consumed by its homopolymerization or

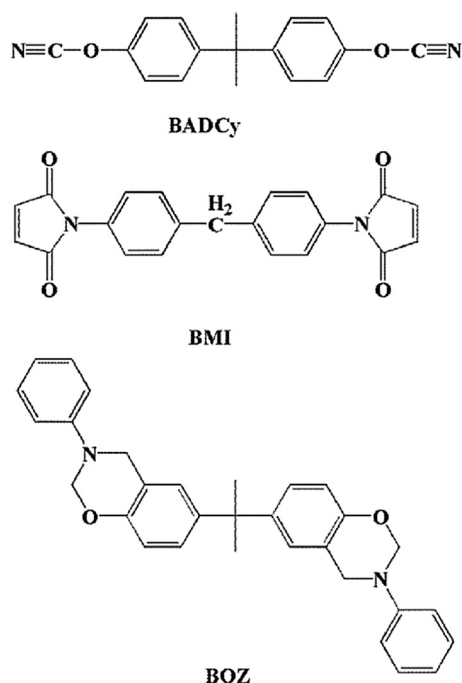


Fig. 1. The structures of BADCy, BMI and BOZ.

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