

Research on curing mechanism and thermal property of bis-allyl benzoxazine and *N,N'*-(2,2,4-trimethylhexane-1,6-diyl) dimaleimide blend

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ABSTRACT

A blend of 2,2'-bis(8-allyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane (Bz-allyl) and *N,N'*-(2,2,4-trimethylhexane-1,6-diyl) dimaleimide (TBMI) was prepared. The curing mechanism and thermal property of the cured blend were studied with Differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR) and Dynamic mechanical analysis (DMA). It was found that in BzT11 the thermal polymerization reaction of TBMI, the reaction of TBMI catalyzed by Bz-allyl, Ene reaction between TBMI and allyl groups occurred at a low temperature (160 °C) simultaneously. About 20% of TBMI was consumed by Ene reaction. Besides, seldom oxazine ring of Bz-allyl polymerized at a low temperature (160 °C) and most oxazine ring of Bz-allyl reacted at a high temperature (over 160 °C). The T_g of cured blends was increased with the increment of the proportion of TBMI in the blends.

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1. Introduction

Polybenzoxazines, a novel class of phenolic resins, have been gained a lot of attention because of its attractive characteristics, including small shrinkage during curing, low water absorption, high thermal stability, self-extinguishing, good mechanical properties and excellent electrical properties [1–5]. However, the performance of polybenzoxazine cannot satisfy the application in harsh environment. Preparing polymer alloys with other resins is an effect approach to get desired properties, which is also an easier method than introducing other polymerizable groups into benzoxazine monomers [6–10]. One example is benzoxazine/BMI alloys. Lots of reports showed their mechanical and thermal properties have been improved greatly. Nevertheless, the improvement of the properties is limited because of the weak connection [11] or no connection [12,13] between benzoxazine and BMI.

On the other hand, bismaleimide precursors can undergo a self-addition reaction and generate cross-linked polymers whose thermomechanical properties are good enough to fulfill the requirements of aerospace industry. However, the cured resins are brittle because of the high crosslinking density of the network, which limits their application. The compounds containing allyl group have been used to modify bismaleimides successfully

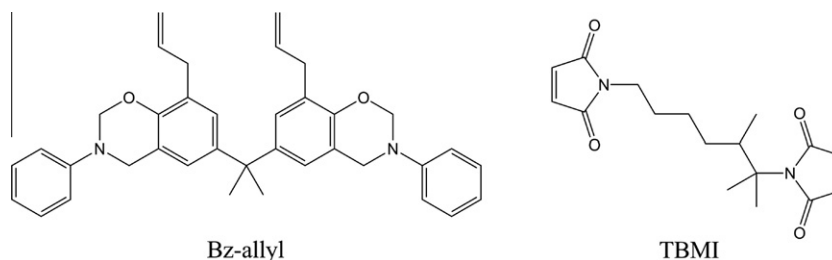
[14,15]. Many studies on allyl-modified bismaleimides have been reported and the reaction between allyl groups and maleimides has been known. However, the thermal and mechanical properties of those modified systems were deteriorated.

There was a report about benzoxazine monomer containing imide and allyl unites [16]. The reaction mechanism and properties were investigated. The reaction between maleimides and allyl groups occurred before oxazine ring opening reaction. A polymer alloy of polybenzoxazine containing allyl unites and bismaleimide was reported by Kumar et al. [17,18]. The properties of the alloy were studied and the possible cured structures were proposed. They thought the reaction between bismaleimide and allyl group was the same as the literature [14,15] and there was no catalytic effect of 2,2'-bis(8-allyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane (Bz-allyl) on curing reaction of bismaleimide. Because the reaction of allyl groups and maleimide occurred firstly and little maleimide was left to be catalyzed by Bz-allyl. However, Gu et al. [19] found that a little negative oxygen ion and N atoms from ring opening of oxazine ring can effectively catalyze the reaction of TBMI.

In this paper, TBMI, which has a broad processing window, was chosen to study the curing mechanism of Bz-allyl/TBMI blend. The structure is showed in Scheme 1. Compared with previously reports, some different results were gotten. It was found that only 20% of TBMI can react with allyl groups, some TBMI reacted through thermal reaction and others were catalyzed by Bz-allyl. Besides, improved thermal property was obtained in cured blends.

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Scheme 1. The structures of Bz-allyl and TBMI.

2. Experimental

2.1. Materials

Ortho-diallyl Biaphenol A (O-DABPA) was provided by Qinyang Company of Henan province. Aniline, aqueous formaldehyde solution, toluene, acetone, maleic anhydride, triethylamine and ethyl alcohol were provided by Chengdu Kelong Chemical Reagents Corp. (China). Toluene sulfonic acid was supplied by Shanghai QianFeng Chemical co. Ltd. (China). Trimethylhexamethylenediamine was purchased from Shanghai BaoMan biotechnology Corp. (China).

The monomer 2,2'-bis(8-allyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane (Bz-allyl) was synthesized and purified according to previous reports from our group [20]. TBMI (mp 88 °C) was synthesized and purified following the reported procedure [21].

2.2. Measurements

TA Instrument Differential scanning calorimetry (DSC) model Q20 was used with heating rate of 5, 10, 15, and 20 °C/min. A nitrogen flow rate of 50 mL/min for non-isothermal tests was used in all tests. The Kissinger [22,25] and Ozawa [26] methods were used when calculated the activation energy for polymerization. The original Kigginger's relation is

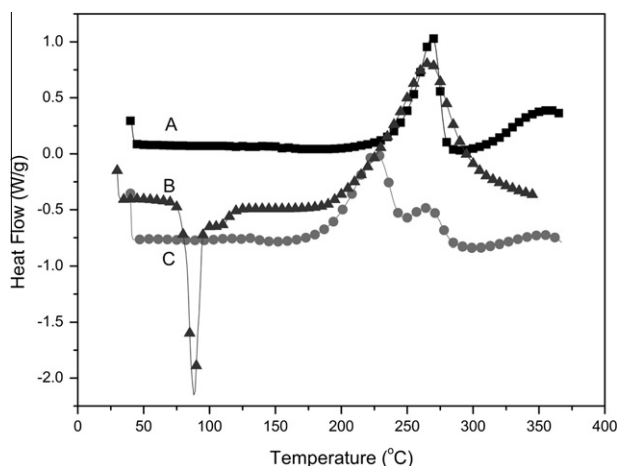


Fig. 1. DSC thermograms of Bz-allyl (A), TBMI (B) and BzT11(C).

Table 1

The activation energy of each peak obtained by Kissinger and Ozawa methods.

	Activation energy of the first peak (E_{a1} , kJ/mol)	Activation energy of the second peak (E_{a2} , kJ/mol)	Activation energy of the TBMI (E'_a , kJ/mol)	Activation energy of the Bz-allyl (E_a , kJ/mol)
Kissinger	66	119	90	113
Ozawa	76	121	94	116

$$\frac{d \ln \left(\frac{T_p^2}{\alpha} \right)}{d \left(\frac{1}{T_p} \right)} = E_a/R \quad (1)$$

and the Ozawa's relation gives

$$\frac{d \ln(\alpha)}{d \left(\frac{1}{T_p} \right)} = -E_a/R \quad (2)$$

where α is the heating rate, T_p is the peak temperature and R is the gas constant.

Fourier transform infrared (FT-IR) spectra were taken by using a Nicolet 5700 FT-IR spectrometer. Co-addition of 32 scans was recorded at a resolution of 4 cm^{-1} . FT-IR spectra of the samples were obtained using the KBr pellet technique.

Dynamic mechanical analysis (DMA) was performed by using a TA Instruments DMA Q800 at a frequency of 1 Hz and a heating rate of 5 °C/min in a bending mode under N_2 . From the theory of rubber elasticity, the crosslink density of a cured polymer can be determined by the following equation [22]:

$$\rho(E') = E'/3\phi RT \quad (3)$$

where E' is the storage modulus of the cured polymer in the rubbery plateau region above $T(T_g + 50 \text{ K})$, ϕ is the front factor, R is the gas constant, and ρ is the crosslinking density. For most cross-linked polymers, the value of ϕ is in the range of 0.5–2.0 and is usually assumed to be unity. It is also treated as unity in this study.

2.3. Preparation of Bz-allyl/TBMI blends and their co-polymers

Bz-allyl was blended with TBMI in different mole ratios of 1/2, 1/1 and 2/1. The blends were prepared by melting method and were noted as BzT12, BzT11 and BzT21, respectively. The blend was put in beaker and stirred at 120 °C until the transparent liquid was obtained (the totally time is at 15–20 min). Then, the blends were put in vacuum oven at 110 °C for 1 h to remove the bubbles. Subsequently, a cure profile (140 °C/2 h, 160 °C/2 h, 180 °C/2 h, 200 °C/2 h) was applied to get the copolymers.

3. Results and discussion

3.1. Curing behavior of BzT11

The curing behavior of BzT11 was examined by DSC. The DSC curves of Bz-allyl and TBMI were also taken for comparison. A peak centered at 276 °C was observed for the reaction of benzoxazine

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