Thermochimica Acta 559 (2013) 86–91

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Preparation and characterization of novel dicyanate/benzoxazine/bismaleimide copolymer

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ARTICLE INFO

Article history:
Received 24 December 2012
Received in revised form 25 February 2013
Accepted 26 February 2013
Available online 13 March 2013

Keywords:
Bisphenol A dicyanate
Bismaleimide
Bisphenol A benzoxazine
Copolymers
Differential scanning calorimetry (DSC)
Mechanical properties
Thermal properties
Moisture absorption

ABSTRACT

In this paper, we reported the dicyanate/benzoxazine/bismaleimide copolymers using bisphenol A dicyanate (BADCy), 4,4′-bismaleimidodiphenyl methane (BMI) and bisphenol A benzoxazine (BOZ). BOZ/BMI was copolymerized with BADCy to improve toughness and processability. The non-isothermal curing kinetics of BADCy/BOZ/BMI copolymer was studied by the differential scanning calorimetry (DSC) at various heating rates, and the isoconversional method was used to describe the apparent activation energy of the modified system. The properties of BADCy/BOZ/BMI copolymers, such as mechanical properties, thermal properties and moisture absorption, were systemically investigated in detail by mechanical measurement, scanning electron microscope (SEM) and thermo-gravimetric analysis (TGA). The results showed that the addition of the appropriate amount of BADCy could improve the impact strength and the flexural strength of the BADCy/BOZ/BMI copolymer, which could form an interpenetrating polymer network in the system. The thermal stability of the blends was found to be higher than that of the BOZ/BMI system, and the moisture absorption of the blends was found to be lower than that of the BOZ/BMI system.

1. Introduction

BMI is well known for their excellent mechanical properties, thermal stability, solvent resistance, and electrical insulation properties over a wide range of temperature [1]. BMI resins are widely used in some of the most important and complex high performance applications, circuit boards, semiconductor encapsulations and ranging from military programs such as the Air Force to electronic engineering [2,3]. However, BMI possesses the poor processability and the poor toughness. There are many reports on modification of BMI to improve its toughness [4,5]. So, blending of BMI with other reactive comonomers had been reported [6–10]. In order to improve the toughness of BMI, BOZ, which possesses excellent glass transition temperature, high module, low water absorption values, good dielectric properties in addition to zero shrinkage and a slight expansion upon cure [11–15], was introduced into the BMI resin system, forming BOZ/BMI copolymer. In order to further improve the toughness of BOZ/BMI copolymer, the cyanate ester resin (CE) which possessed low shrinkage during cure, high thermal property, excellent chemical resistance, and excellent mechanical and dielectrical property [16] was introduced into the BOZ/BMI copolymer forming BADCy/BOZ/BMI copolymer.

The following work investigated the possibilities of BADCy/BOZ/BMI copolymer from a practical perspective. It would be shown that the copolymerization could in fact produce thermosetting materials with quite favorable characteristics. The non-isothermal curing kinetics parameter, a variety of mechanical properties, thermal properties and moisture absorption would be studied for a series of BADCy/BOZ/BMI compositions and would be compared to the BOZ/BMI blends in order to determine the effect of BADCy concentration on the copolymer properties.

2. Experimental

2.1. Materials

Bisphenol A dicyanate (BADCy) ester (purity > 99.5% and cyanate equivalent of 139 g/equiv.) 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. BMI was commercial-grade yellow power containing more than 85% of maleimide double-bond structure. Bisphenol A benzoxazine (BOZ) ester (purity > 95%) reddish brown was purchased from Shandong Yineng Polymer Materials Co. Ltd. (Laiwu, China). The chemical structures of BADCy and BMI as well as BOZ were represented in Fig. 1.

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http://dx.doi.org/10.1016/j.tca.2013.02.030

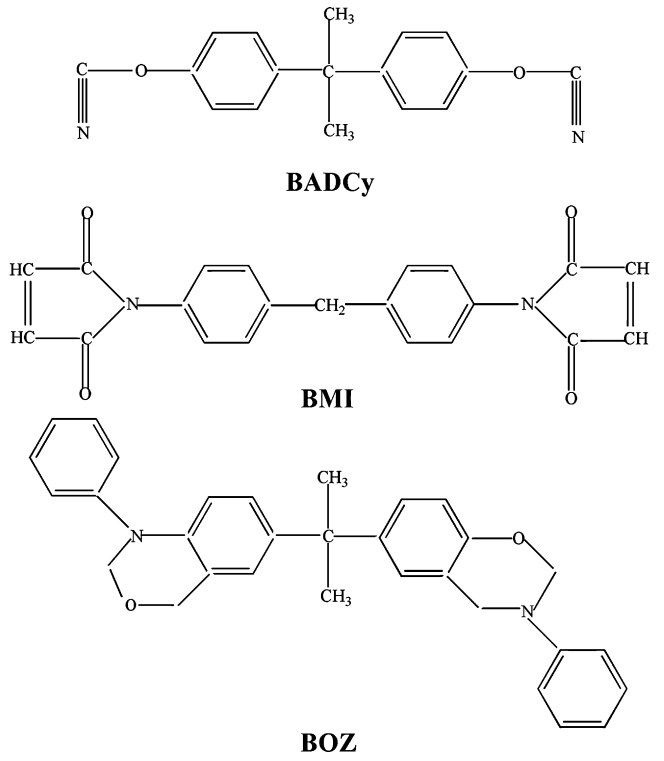

Fig. 1. Chemical formulae of BADCy, BMI and BOZ.

2.2. Preparation of BADCy/BOZ/BMI prepolymer

The BADCy/BOZ/BMI blends were prepared by the following steps: firstly, the mass ratio of BMI and BOZ was 2:1, and BOZ and BMI prepolymer were thoroughly blended at 140 °C for 1 h with vigorous stirring; Secondly, after cooling the prepolymer to 100 °C, the BADCy was added, and then the ternary mixture was maintained with stirring for 0.5 h and a homogeneous liquid was obtained.

2.3. Preparation of cured BADCy/BOZ/BMI copolymers

Firstly, a preheated mold with silicon coating on the inner surface was heated at 110 °C for 1 h. The prepolymer was poured into the preheated mold with silicon coating on the inner surface. Secondly, the prepolymer was degassed at 110 °C for 0.5 h in a vacuum oven. Finally the prepolymer was cured in the high oven via the following curing procedure: 150 °C/2 h + 180 °C/2 h + 200 °C/2 h, and post-cured at 220 °C/4 h.

2.4. Characterization

About 5 mg of the sample was weighed in hermetic aluminum pan. The curing thermal data were obtained using a Q1000 DSC System (TA Instruments, DE, USA), which was heated from 25 to 350 °C with different heating rates such as 5, 10, 15 and 30 °C/min, in a nitrogen atmosphere.

An Instron universal testing apparatus was used to test the mechanical properties of the resultant resins. The unnotched impact strength and bending strength were carried out according to GB/T2571-1995 and GB/T2570-1995, respectively. At least five specimens for each system were tested.

Scanning electron microscope (SEM) observations were performed on the fractured surfaces of samples. Samples were coated with a thin layer of Au and observed under Quanta 200 SEM, at an accelerated tension of 20 kV. All the samples should be dried at 120 °C for 3 h before test.

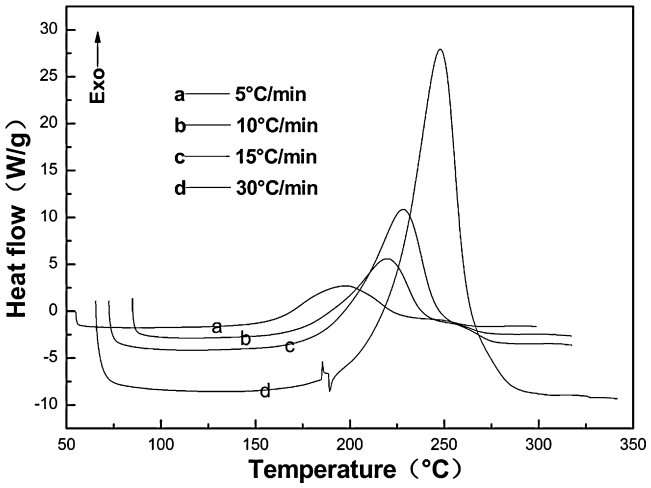

Fig. 2. DSC curves of BADCy/BOZ/BMI copolymer at different heating rates.

TGA analysis of cured BADCy/BOZ/BMI resins was performed using a TA Instruments Q600SDT simultaneous DSC/TGA analyzer. The cured resins were placed in a Pt cell and tested from 25 to 800 °C at a heating rate of 20 °C/min in nitrogen atmosphere.

Long-term water uptake studies were performed at two different temperatures (20 and 50 °C). Polymer samples (approximately 20 mm × 10 mm × 2 mm) were post-cured at 220 °C and dried to constant weight in a vacuum oven at 100 °C. They were then immersed in water and stored at the appropriate temperature for the duration of the study. For weighing, samples were removed and their surfaces dried.

3. Results and discussion

3.1. DSC analysis and non-isothermal curing kinetics

DSC curves of BADCy/BOZ/BMI resin systems at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 30 °C/min were shown in Fig. 2. With the increasing of the heating rate, the exothermic peaks moved toward high temperature. The shifting of the exothermic peak temperature as a function of the heating rate is due to the kinetics of the reaction. The higher the heating rate was, the more serious the phenomenon was.

Various models had been proposed for analyzing the non-isothermal curing behavior of polymer [17–19]. In this work, the isoconversional method was adopted [20–23]. According to the relationship between heating rates and the variety of temperature of DSC curves, apparent activation energy of polymerization of BADCy/BOZ/BMI copolymer at different values of α was calculated.

The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exothermic. They were processed further to obtain a fractional conversion (α) and the rate of the reaction $d\alpha/dt$.

The rate of the kinetic process could be described by Eq. (1).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where, $k(T)$ is a temperature-dependent reaction rate constant, and $f(\alpha)$ is assumed to be independent of temperature.

The temperature dependence was assumed to reside in the rate constant through an Arrhenius relationship given by Eq. (2):

$$k(T) = A \ \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where A is the pre-exponential factor or Arrhenius frequency factor (s^{-1}), E_a the apparent activation energy (J/mol), R the gas constant