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Preparation and characterization of bismaleimide-triazine/epoxy interpenetrating polymer networks

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ABSTRACT

In this paper, we reported the preparation of the bismaleimide-triazine/epoxy interpenetrating polymer networks using 4,4′-bismaleimidodiphenymethane (BMI), bisphenol A dicyanate (BADCy) and 4,5-epoxycyclohexane 1,2-dicarboxylic acid dilycidyl (TDE-85) epoxy resin. The non-isothermal curing kinetics of TDE-85/BMI/BADCy copolymer was studied by the differential scanning calorimetry (DSC) at various heating rates. Kissinger equation and Ozawa equation were used to describe the apparent activation energy of the modified system. Compared to unmodified BMI/BADCy resins, the TDE-85/BMI/BADCy copolymer exhibited excellent mechanical properties and stable thermal properties when the content of TDE-85 epoxy resin was 20 wt%. The dielectric properties of TDE-85/BMI/BADCy copolymer such as dielectric constant and dielectric dissipation factor remained the good stability over a wide frequency from 10 MHz to 60 MHz.

1. Introduction

Cyanate ester resins possess a series of great properties, such as low shrinkage during cure, high thermal property, excellent chemical resistance, and excellent mechanical and dielectric property [1]. Thanks to their various great properties, they are widely used as adhesives, matrixes for composites and high performance matrixes for printed circuit board [2–4]. Due to the high crystalline degree and large portion crosslink density of CEs, they exhibit high brittleness after curing. The brittleness makes their broad application limited. So, the toughening modification of CEs was crucial. The current methods of toughening modification of CE resins contained rubber modification, copolymerization modification, blending modification and IPNs modification [5–8].

BMI possesses a series of great properties, such as their excellent mechanical properties, thermal stability, solvent resistance, and electrical insulation properties over a wide range of temperature. So, blending of BMI with other reactive comonomers had been reported [9–15]. In order to improve the toughness of CEs, BMI with functional group of bi-functional compounds was added into the CEs. CE functional group (—OCN) could react with unsaturated double bond in the active hydrogen of maleimide ring, known as bismaleimide-triazine (BT) resins. A lot of researches had been carried out to develop modified BT resins for adapting various applications [16–19]. Owning to a variety of attractive properties, they were preferred in circuit boards and semiconductor encapsulations.

In order to further improve the toughness of CEs, the TDE-85 epoxy resin which possesses good processability and high resistance to heat, was incorporated into the BT resin systems and IPNs were formed. IPNs were one of the important methods in modified thermosetting resin, which was an effective method of developing polymers performances [20–23].

In this study, the modification of BT resins by TDE-85 was reported. The non-isothermal curing kinetics of TDE-85/BMI/BADCy copolymers was studied by the differential scanning calorimetry (DSC). The effect of the amount of TDE-85 on the toughness of the resultant blends was examined. The mechanical, dielectric properties and thermal properties of the blends were studied by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) in detail.

2. Experiment

2.1. Materials

White granular bisphenol A dicyanate (BADCy) ester crystal, purity >99.5%, cyanate equivalent of 139 g/eq, was purchased from Shangyu Shengda Biochemical Co. Ltd. (Shangyu, China). 4,4′-Bismaleimidodiphenyl methane was purchased from Hubei Shuangfeng Chemicals (Honghu, China). BMI was commercial-grade yellow power containing more than 85% of maleimide

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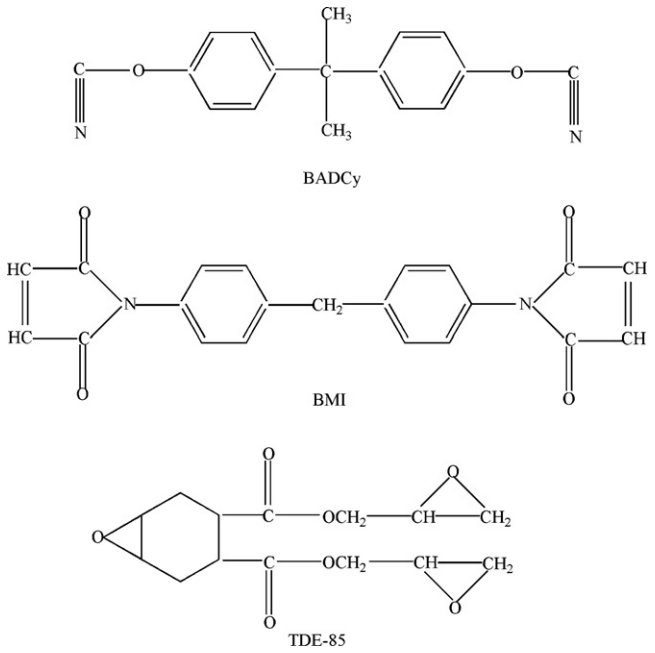

Fig. 1. Chemical formulae of BADCy, BMI and TDE-85.

double-bond structure. 4,5-Epoxycydohexane 1,2-dicarboxylicacid diglycidyl ester (TDE-85) was purchased from Tianjin Jindong Chemicals (Tianjin, China). The chemical structures of BADCy, BMI and TDE-85 are represented in Fig. 1.

2.2. Preparation of TDE-85/BMI/BADCy resins

The BADCy/BMI/TDE-85 blends were prepared by the following steps: firstly, BADCy and BMI prepolymer were thoroughly blended at 170 °C for 1 h with vigorous stirring, in which the mass ratio of BMI and BADCy was 1:2. Then, TDE-85 was added into it after the temperature was lower than 120 °C, and the ternary mixture was stirred to form homogeneous liquid.

2.3. Preparation of cured TDE-85/BMI/BADCy resins

Firstly, the prepolymer of what was poured into a preheated mold with silicon coating on the inner surface. Secondly, the prepolymer was degassed at 120 °C for 30 min in a vacuum oven. Finally the prepolymer was cured via the following curing procedure: 150 °C/3 h + 180 °C/3 h, and post-cured at 220 °C/4 h.

2.4. Measurements of the properties of TDE-85/BMI/BADCy resins

About 5 mg of the sample was weighed in hermetic aluminum pan. The curing thermal data were obtained using a TA Instruments DSC Q1000, the temperature ranged from 25 °C to 300 °C with different heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 30 °C/min, in a nitrogen atmosphere.

The unnotched impact and bending strength of what were tested by an Instron universal testing apparatus according to GB/T2571-1995 and GB/T2570-1995 test standard, respectively. At least five specimens for each system were tested.

The fractured surfaces of samples were observed by Quanta 200 SEM at an accelerated voltage of 20 kV. Samples were coated with a thin layer of Au and all the samples were dried at 120 °C for 3 h before test.

DMA scans were performed with a single-cantilever blending mode using TA DMA Q800 apparatus from TA instruments. DMA of cured resin was measured from room temperature to 300 °C with a heating rate of 3 °C/min at 1 Hz. The sample dimension was (35 ± 2) mm × (13 ± 0.05) mm × (4 ± 0.02) mm.

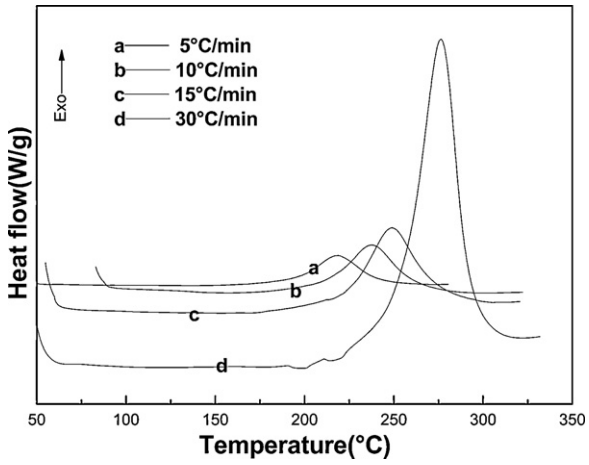

Fig. 2. DSC curves of TDE-85/BMI/BADCy copolymer at different heating rates.

The dielectric properties of what were tested by a S914 broadband dielectric spectrometer (QBG-3D) at the frequency between 10 MHz and 100 MHz. The test temperature was at 25 °C.

The thermal properties of what were tested by a thermal analyzer (TA instruments, Q600SDT). The cured resins were placed in a Pt cell and tested from 25 °C to 800 °C at a heating rate of 20 °C/min in nitrogen atmosphere.

3. Results and discussion

3.1. DSC analysis and non-isothermal curing kinetics

DSC curves of TDE-85/BMI/BADCy resin system at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 30 °C/min are shown in Fig. 2. From Fig. 2, it indicated that the position of the exothermic peak was different. After reaching a minimum, the heat flow started to increase due to the curing of resin system. As expected, the TDE-85/BMI/BADCy resin system showed an exothermic peak. With the increase of the heating rate, the exothermic peaks moved toward high temperature. This result was due to a thermal lag between the programmed heating rate and the real temperature in the furnace, which made it possible to calculate the apparent activation energy of polymerization of TDE-85/BMI/BADCy resin systems by applying different methods.

Various models had been proposed for analyzing the non-isothermal curing behavior of polymer [24–27]. In this work, Kissinger method and Ozawa method were adopted. The temperatures gotten from the DSC curves are listed in Table 1.According to the relationship between heating rates and the variety of temperature of DSC curves, the calculation of apparent activation energy of polymerization of TDE-85/BMI/BADCy resin systems at different values of α were calculated.

The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exothermic. They

Table 1
Exothermic peak temperatures of TDE-85/BMI/BADCy resins system at different heating rates.

Heating rate (°C/min)	Onset temperature(°C)	Peak temperature (T_m) (°C)	Ending temperature (°C)
5	149.34	193.47	232.33
10	157.88	217.10	263.45
15	164.09	238.64	292.69
30	178.44	252.10	300.00