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Catalytic effect of sulfonated poly (styrene-divinylbenzene) microspheres on the thermal curing behavior of benzoxazine

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ABSTRACT

In this study, the effects of sulfonated poly (styrene-divinylbenzene) (SP(St-DVB)) microspheres on the thermal curing of bisphenol A-based benzoxazine (Ba) was studied by preparing resin systems consisting of Ba and SP(St-DVB) microspheres. The thermal curing behavior and mechanism of Ba/SP(St-DVB) systems were investigated by differential scanning calorimetry and *in situ* Fourier transform infrared spectroscopy. The curing kinetics of Ba and Ba/SP(St-DVB) systems were investigated by non-isothermal DSC. The apparent activation energy of Ba and Ba/SP(St-DVB) systems gradually increased with the reaction extent (α). The dynamic mechanical analysis indicated that the glass transition temperatures of PBa/SP(St-DVB) composites did not decrease. The improved thermal stability of PBa/SP(St-DVB) composites was investigated by thermogravimetric analysis in the air and nitrogen atmosphere, respectively. The images of the fracture surfaces for PBa and PBa/SP(St-DVB) composites were investigated by scanning electron microscopy, demonstrating improved toughness of PBa/SP(St-DVB) composites.

1. Introduction

Polybenzoxazine resins are novel types of phenolic resins formed by the cationic ring-opening polymerization of benzoxazine monomers [1–3]. Polybenzoxazine resins, the newly developed heat-resistant resins, overcome the shortcomings of traditional phenolic resins while retaining their original advantages [4]. In recent years, polybenzoxazine has attracted wide attention from scientific researchers owing to their intriguing properties such as molecular design flexibility [5,6], near-zero shrinkage upon curing [7,8], high glass-transition temperature (T_g), low moisture absorption [9], high char yields, low surface energy, and good thermal stability [5–11]. Therefore, polybenzoxazine resins are widely applied in electronics, aerospace, and other fields [3,12].

However, the high curing temperature and the brittleness of polybenzoxazine resins restrict their application [3,10–12]. A number of studies have been focused on decreasing their curing temperature. Various catalytic systems including organic acids, such as phenols, carboxylic acids, and phosphonic acids [13–15], metal halides [16], metal complexes [17,18], nucleophilic catalysts [3,19], thiols [20], primary amine salts [21], imidazoles, and primary amine compounds [22,23] have been employed. Nevertheless, the thermostability of polybenzoxazine resins deteriorates, because these catalysts keep polybenzoxazine resins in the form of micro-molecules or form weak bonds in the cross-linked structures. The Brønsted acid [3] has also been reported to decrease the curing temperature of polybenzoxazine resins. The donated protons initiate the well-known acid-catalyzed ring-opening polymerization of benzoxazine. Then, the zwitterionic intermediates further react with the benzoxazine monomers affording a network of polybenzoxazine resins [24]. Sulfonated poly (styrene-divinylbenzene) (SP(St-DVB)) is a type of Brønsted acid and has been not fully explored yet, indicating that investigating a wide range of Brønsted acids would be a promising strategy to develop highly efficient catalysts that may drastically decrease the curing temperature of polybenzoxazine resins. Moreover, toughening polymer matrix has been rarely taken into consideration in SP(St-DVB). Polybenzoxazine-based composites have attracted significant interest of researchers during the last decade owing to the superior properties of polybenzoxazines [25]. Some studies on these composites resulted in increased toughness of polybenzoxazine [25–28]. Hou et al. [29] investigated the toughness of polymers by adding microspheres, and their results showed that the toughness improved obviously. Zhao et al. [30] prepared PBa/Nylon12 composites based on bisphenol-A type benzoxazine and Nylon12 microspheres, and the combined analysis of mechanical properties and crack propagation process confirm that the Nylon12 microspheres exhibited a synergistic toughening mechanism

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of crack ground-anchor and crack deflection in the PBa matrix. Commonly, microspheres can increase the toughness effects for thermosetting resins owing to their special physical structure [29].

Inspired by microspheres toughening mechanism and acid catalytic effects on PBa, in this study, SP(St-DVB) microspheres were successfully synthesized and introduced into the PBa matrix. The main aim of this study was to investigate the thermal curing behavior of the resulting SP (St-DVB) microspheres as the catalysts on the thermal curing of bisphenol A-based benzoxazine (Ba) and evaluate the toughness of the resulting polybenzoxazine resins. The curing behavior and curing kinetics of benzoxazine monomers with and without the SP(St-DVB) microspheres catalysts were investigated by differential scanning calorimetry (DSC). *In situ* Fourier transform infrared (FTIR) spectra of the pristine Ba and Ba/SP(St-DVB) systems were recorded for further understanding the reaction progress and mechanism based on the changes in the functional groups during the curing process. With the aim to establish the polymerization mechanism of the curing process, Ba containing Ba/SP(St-DVB) microspheres were prepared herein, and their curing kinetic parameters were calculated by non-isothermal DSC at different heating rates. The thermal stability and the toughening properties of PBa/SP(St-DVB) composites were also investigated.

2. Experimental

2.1. Materials

Bisphenol A-based benzoxazine (Ba) was provided by Polyris Technology Co., Ltd (Sichuan, China) and used as received. Anhydrous ethanol, polyvinylpyrrolidone K30 (PVP), azobisisobutyronitrile (AIBN), styrene (St), divinylbenzene (DVB), concentrated sulfuric acid, acetone, and potassium persulfate ($K_2S_2O_8$) were purchased from Chengdu Kelon Chemical Reagent Factory (Sichuan, China).

2.2. Synthesis and preparation

2.2.1. Synthesis poly (styrene-divinylbenzene) (P(St-DVB))microspheres

P(St-DVB) microspheres were prepared by suspension polymerization [31]. First, 0.4 g of PVP was dissolved in 125 mL of anhydrous ethanol in a three-neck reaction flask equipped with a condenser. After the formation of a homogeneous solution at room temperature, the flask was placed in a 70 °C oil bath and stirred mechanically at 100 rpm. Second, 0.2 g of AIBN, 2.27 g (2.5 mL) of DVB, and 10.88 g (12 mL) of St were weighed successively and mixed in a beaker under stirring, and then, this mixture was added to the PVP solution in the first step. Third, the crude reaction mixture obtained after 6 h of reaction was cooled to room temperature, and the product was washed twice with anhydrous ethanol and deionized water. Finally, the resulting product was collected and dried at 60 °C for 8 h in a conventional oven and 60 °C for 8 h in a vacuum oven.

2.2.2. Sulfonation of P(St-DVB) microspheres

The P(St-DVB) microspheres were sulfonated in a 100 mL single-necked flack. A mixture of 0.5 g P(St-DVB) microspheres and 20 mL concentrated sulfuric acid was dispersed for 1 h using an ultrasonic cleaner (40 Hz, 100 W). Then, the mixture was slowly heated to 40 °C at a magnetic stirrer speed of 300 rpm and retained at that temperature for 20 h. Next, the crude mixture was dispersed in anhydrous ethanol and washed with deionized water, until the supernatant titrated with barium chloride solution showed no white precipitate. Finally, the resulting products were dried at 60 °C in vacuum for 12 h and labeled as SP (St-DVB) microspheres.

2.2.3. Preparation of Ba/SP(St-DVB) systems and PBa/SP(St-DVB) composites

A hybrid Ba resin containing various levels of SP(St-DVB) (i.e., 5, 10, and 15 wt%) was prepared. Taking 5 wt% as an example, 5 g SP(St-DVB), 95 g Ba, and 50 mL acetone were added to a round-bottom flask, and the resulting mixture was stirred for 30 min to obtain a homogeneous solution. Then, the acetone was removed under reduced pressure using a rotary evaporator. The resulting dark-red, viscous product was degassed and labeled as Ba/SP(St-DVB)-5%. The viscous product was poured into a vertical glass mold. A sequential heating process was employed for curing at 180 °C/2 h and 200 °C/2 h in a programmed oven to produce a PBa/SP(St-DVB) composite cured plate. The final composite plate was marked as PBa/SP(St-DVB)-5%. Ba/SP (St-DVB)-10%, Ba/SP(St-DVB)-15%, PBa/SP(St-DVB)-10%, and PBa/SP (St-DVB)-15% were prepared by the same procedure by adjusting the weight proportion.

2.3. Instruments and characterizations

2.3.1. Scanning electron microscopy (SEM) images

The morphology of the microspheres and the section obtained by the single notch three-point bend (SEN-3PB) test of PBa and PBa/SP(St-DVB) composites was investigated using a ZEISS EV0 MA15 SEM at an accelerating voltage of 15.0 kV. Prior to the SEM morphology imaging, the microspheres and brittle fracture of the samples were sputtered with a thin layer of gold to provide conductive surfaces.

2.3.2. Fourier transform infrared spectroscopy

FTIR spectra were recorded using a Nicolet 6700 apparatus (Thermo Electric Corporation, USA) using a width ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The microspheres were prepared on the thin potassium bromide (KBr) pellets by the tableting method, and the thin film was prepared using a sample to KBr ratio of 1:100 by mass.

2.3.3. In situ fourier transform infrared spectroscopy (In situ FTIR)

Time-dependent FTIR absorbance spectra were recorded using a Frontier PerkinElmer FTIR spectrometer. Spectra of the pristine Ba and Ba/SP(St-DVB) systems were recorded every 18 s from 100 to 250 °C at a heating rate of 2.5 °C/min.

2.3.4. Differential scanning calorimetry analysis

The non-isothermal DSC curing of the pristine Ba and Ba/SP(St-DVB) blends (approximately 5 mg of sample contained in aluminum pans) were monitored from 25 to 300 °C at different heating rates of 2.5, 5, 10, and 20 °C/min. A DSC Q20 equipment from TA instruments was used at a constant flow rate of 50 mL/min under nitrogen for all the DSC studies. An empty aluminum pan was used as the reference for DSC measurements.

2.3.5. Dynamic mechanical analysis (DMA)

DMA was conducted to obtain the storage modulus and glass transition temperature (T_g) of the pristine PBa and PBa/SP(St-DVB) composites using a Q800 analyzer (TA Instruments) in a three-point bending mode with the sample dimensions of 40 × 10 × 3.2 mm^3, and with a span of 20 mm, a frequency of 1 Hz in the air, and a heating rate of 5 °C/step range from 40 to 300 °C.

2.3.6. Thermogravimetric analysis (TGA)

The thermal characteristics of the pristine PBa and PBa/SP(St-DVB) composites were investigated by TGA using a STA 6000 (PerkinElmer, USA) under nitrogen atmosphere at a flow rate of 50 mL/min. The samples with a mass of 5.0 mg were heated from 40 to 800 °C at a heating rate of 20 °C/min.