



An investigation on the effect of phenylboronic acid on the processibilities and thermal properties of bis-benzoxazine resins



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ARTICLE INFO

Article history:

Received 17 March 2015

Received in revised form 16 June 2015

Accepted 17 June 2015

Available online 21 June 2015

Keywords:

Benzoxazine resin

Thermal property

Char yield

Processibility

Phenylboronate

ABSTRACT

Benzoxazine resins (BZs) as a novel type of phenolic resin are high-performance matrix resin for advanced composites. Yet there still exist some deficiencies when used as ablative material in aerospace applications, such as high curing temperature and poor thermal stability. In the present study, the phenylboronic acid (PBA) modified BZs (PBBZs) exhibiting excellent processibilities and thermal properties were prepared by incorporating PBA into BZ. The viscosity, gel time and curing behaviors were examined to demonstrate that PBBZs possessed better processibilities than the BZ, representing the catalytic effect of PBA in this case. The incorporation of PBA accelerated the ring-opening polymerization of BZ, leading to the lower curing temperature. TGA results reveal that the cured PBBZs exhibit excellent thermal properties, where the char yield at 800 °C (nitrogen atmosphere) reaches 63.7% and is increased by 14.1 percentage points than that of BZ. The formed phenylboronates during curing act as additional cross-linking points and increase the cross-linking density of the cured resin, which results in the enhancement of the glass transition temperature of BZ ranging from 165 °C to 219 °C. This study provides a new vision for the preparation of high-performance matrix resin for ablative materials by introducing aryl-boron backbone.

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1. Introduction

Thermally stable polymers with outstanding performance have been developed in the last several decades to meet the crucial requirement for high-speed aircraft structures and as structural components of space vehicles. Benzoxazine resins (BZs), as a class of thermosetting phenolic resins (PRs) formed by the thermal ring-opening of the corresponding monomers without byproducts released or the need of any catalyst, have received drastically attention in the past several years [1,2]. BZs possess all the advantages of traditional PRs such as excellent mechanical and thermal properties along with the added unique advantages such as low melt viscosity, low water absorption, near-zero shrinkage upon curing, release of no by-products, and remarkable molecular design flexibility. The excellent performances of BZs make them promising matrices candidate over epoxies and PRs for high-performance composites, especially in microelectronics, aerospace, and other industries. Generally with excellent performance, the materials have the processing difficulty. Although BZs possess many advantages over other state-of-the-art thermosetting resins, their relatively high curing temperature as well as low char yield, inherent to the most thermosets, point to the need of modification to meet the

requirements of high-performance ablative materials [3–5]. Accordingly, recent research has focused on how to improve the processibilities and thermal resistance of BZs for various applications.

The extraordinarily rich molecular design flexibility coming from the usage of inexpensive and commercially available phenols, primary amines, and formaldehyde is one of the most important properties of BZs, which makes it possible for the resin to be tailored for a wide range of application and still offer all of the same chemical and processing advantages. Therefore, the approach of introducing additional polymerizable groups into BZ, such as acetylene [6], propargyl [7], nitrile [8], maleimide [9] or rigid groups such as aromatic amine [10], fluorenyl [11] and furan [12] has been reported to increase the cross-linking density and minimize the dangling side groups, thus, leading to the improvement of the thermal and mechanical properties. However, the processibilities of the above modified systems are deteriorated, such as the high viscosity and curing temperature. On the other hand, some thermosetting resins such as epoxy [13], PR [14] and polyimide resins have been blended with BZs to lower the curing reaction temperature or improve the toughness of BZs. Nevertheless, the improvement of the properties is limited because of the weak connection or no connection between BZ and thermosetting resin. Further improvements are achieved with the introduction of nanosize fillers (such as POSS, carbon nanotube, graphene oxide and montmorillonite) into BZs where substantial changes in thermal properties are obtained at very low loadings [15–17]. Unfortunately, the potential applications of such hybrid

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nanocomposites are hindered by manipulation difficulties due to their insolubility and poor dispersion in polymer matrix. Therefore, the above modification methods cannot give full consideration to the thermal resistance, toughness and processibilities. The design and creation of new BZ materials with high performance have become an extremely interesting field of research.

Boron-containing compounds have always been of significant interest to a wide range of chemists, because of the use of these compounds in organic synthesis. Boronic acids contain trivalent boron atoms bonded to one alkyl/aryl substituent and two hydroxyl groups ($\text{RB}(\text{OH})_2$). The discovery that boronic acids can be used in cross-coupling reactions for the construction of complex molecular architectures with interesting functions and properties is of particular importance [18]. Because these compounds are relatively nontoxic and thermally, air-, and moisture-stable, the exploitation of boronic acids' interactions has been an explosion of applied boronic acid based systems including, but not limited to, sensing, self-assembly, pharmaceutical, flame-retardants, self-healing, and electrolyte materials [19–21]. As a result of their unusual electronic structure, the empty p-orbital on boron leads to the Lewis acidity of boronic acids, which has gained tremendous interest as building blocks for the design of new electronic materials or for applications in Lewis acid catalysis. The results of Ishida et al. [22] showed that by adding certain Lewis acid catalyst, the induction time for the curing of benzoxazine precursor could be reduced and the reaction rate could be accelerated. Consequently, boronic acid may catalyze the ring-opening polymerization of BZs, which is conducive to reducing the curing temperature of the BZs.

The most important chemical characteristic that has led boronic acids to find utility in applications is their ability to form the boronate esters with diols. It is well known that BZs undergo thermally activated cationic ring-opening polymerization in the absence of a catalyst yielding a polymer backbone consisting of phenolic hydroxyl groups and Mannich bridge structures. Thus, the formation of the stable boronate ester network structure due to the condensation reaction of phenolic hydroxyl with B–OH during curing is quite possible, which is beneficial to enhance the thermal resistance of BZs. Our previous study has found that the phenylboronic acid (PBA) modified PRs (PBPRs) exhibits not only excellent processibilities such as low viscosity, and excellent mechanical properties, but also outstanding thermal resistance [23]. To the best of our knowledge, there is no report about PBA modified BZs (PBBZs). It is expected that combining BZ with PBA will generate the new material having the best attributes of them. A bis-benzoxazine named as 3-phenyl-6-[(3-phenyl(2H,4H-benzo[3,4-e]1,3-oxazin-6-yl)methyl)-2H,4H-benzo[e]1,3-oxazaperhydroine (Scheme S1) which exhibits good mechanical properties, low water sorption, dimensional stability, and flame resistance [24,25], is chosen to study the effect of PBA on the processibilities and thermal properties of BZ. We hope that this study will inspire others to continue the work on boronic acids and their application in thermosetting resin systems.

2. Experimental

2.1. Materials

Bis-benzoxazine was kindly donated by Sichuan University, China, and its structure was showed as Scheme S1; PBA with a high degree of purity (more than 99.0%) was purchased from TCI America (Portland, OR); Acetone was obtained from the Tianjin Chemical Reagent Co., China. All of the reagents used in these experiments were of analytical grade. Acetone was dried over calcium hydride and distilled prior to use.

2.2. Preparation of the PBBZs

PBBZs with differing PBA content were prepared by introducing PBA into BZ. First, a certain amount of PBA was dissolved in acetone to obtain a 30 wt.% solution, and the BZ was then added slowly with magnetic

stirring at 50 °C over 30 min. Lastly, PBBZs with 5, 10, 15 or 20 wt.% PBA which were named as PBBZ-a, PBBZ-b, PBBZ-c and PBBZ-d, respectively, were obtained. BZ without boron was prepared as a comparison.

2.3. Preparation of the cured PBBZs

The PBBZ solutions were poured into polytetrafluoroethylene moulds and the acetone was evaporated under reduced pressure at 50 °C in a vacuum drying oven. The samples were weighed every 30 min until a constant weight was maintained. PBBZs with different PBA content were subsequently cured step-wise at 140 °C for 2 h, 160 °C for 4 h, 180 °C for 4 h, 200 °C for 4 h and 220 °C for 4 h according to the DSC analyses. Lastly, the yellow-brown and optically transparent cured resins were obtained. The cured BZ without boron was prepared as a control.

Cured PBBZ-b was obtained at different curing temperatures (140 °C/2 h, 160 °C/2 h, 180 °C/2 h, 200 °C/2 h, and 220 °C/2 h) in a vacuum drying oven.

The castings of BZ and PBBZs were obtained at different curing temperatures (130 °C/1 h, 140 °C/1 h, 150 °C/1 h, 160 °C/1 h, 170 °C/1 h, 180 °C/1 h, 200 °C/1 h, or 220 °C/2 h) in a vacuum drying oven. When the PBA content is more than 10.0 wt.%, the castings of PBBZ resin have become difficult to prepare. Thus, we only prepare the castings of BZ, PBBZ-a and PBBZ-b.

2.4. Pyrolysis of the cured PBBZs

The cured resin was placed in graphite crucible and heated from room temperature to 700 °C for 2 h using a tube furnace at a heating rate of 10 °C/min under a nitrogen atmosphere (60 mL/min). The tube furnace was cooled from the setting temperature to the room temperature at approximately 2 °C/min using the same gas flow as heating.

2.5. Characterization

The Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} from KBr pellets using a Bruker Tensor 27 Spectrophotometer (Bruker Corporation, Germany). 32 scans were collected with a spectral resolution of 4.0 cm^{-1} . The X-ray photoelectron spectroscopic (XPS) measurements were obtained using a Perkin-Elmer PHI-5400 system (Mg Ka X-ray source, Perkin-Elmer Corp., USA) with a data acquisition system. The spectra were referenced to C1s peak at 284.5 eV. Viscosity analyses were conducted on an Anton Paar Rheometer (Model Physica MCR 501) using 25 mm disposable parallel plates at a constant frequency of 10 rad/s and a constant strain of 1% for all experiments. The gel time (t_{gel}) was tested using a knife flat method and defined as from heating to the beginning of drawing. The differential scanning calorimetry (DSC) analyses were performed on a NETZSCH DSC 200PC (NETZSCH Corporation, Germany) under a nitrogen atmosphere at a heating rate of 10 °C/min starting from room temperature and heating to 300 °C with an empty aluminum pan as the reference. The thermogravimetric analysis (TGA) diagrams were created using a NETZSCH TG 209C (Netzsch, Germany) and the samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. TGA-FTIR experiments were performed at a heating rate of 20 °C/min under a nitrogen flow of 60 ml/min using a TGA Netzsch TG209 which was connected to a Bruker Tensor 27 FTIR spectrometer. FTIR spectra were recorded in the spectral range of 4000–400 cm^{-1} with a 4 cm^{-1} resolution and sixteen scans. Dynamic mechanical measurement was conducted on a Perkin-Elmer Pyris Diamond DMA using a single cantilever bending mode at a frequency of 1 Hz with a heating rate of 3 °C/min from room temperature to 250 °C under a nitrogen atmosphere.

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