



Structure and thermal pyrolysis mechanism of poly(resorcinol borate) with high char yield



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ABSTRACT

Boron-containing organic polymers have excellent thermal stability and flame retardancy. Hyperbranched polymers, in which boron atoms are introduced in the form of borates, exhibit superior performance and have more applicability. This work focuses on the boron-containing polymer poly(resorcinol borate) (PRB). The chemical structure of PRB and its structural evolution at high temperatures are investigated in order to clarify the reason for its high char yield. The results indicate that the molecular skeleton of PRB mainly consists of aromatic structures, borates, B–O–B structures, and a small number of boron hydroxyl groups and phenolic hydroxyl groups. During pyrolysis, boron oxide is formed by the cleavage of borate O–C bonds at about 400 °C. This process effectively avoids the formation and release of volatile carbon dioxide, reducing carbon loss. A large fraction of the carbon from aromatic rings is converted to amorphous carbon via pyrolysis, which possesses higher thermal stability. These results can guide the design and synthesis of novel boron-containing polymers and can provide a strategy for modifying the thermal properties of phenolic resins in order to broaden their applicability in the field of ablative-resistant composites and coatings.

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1. Introduction

During the past decade, hyperbranched polymers with a compacted sphere-like structure have attracted a lot of scientific interest because of their unique topology and advantages over their linear analogues, such as excellent solubility in organic solvents, low melt viscosity, versatility of end groups, and a quick and convenient method of synthesis. The most significant benefits of hyperbranched polymers are that they are highly processable and that the mechanical properties (such as toughness) of thermosetting resins can be significantly improved [1,2]. Our previous work demonstrated that poly(resorcinol borate) (PRB) synthesized from the esterification reaction of boric acid (BA) with resorcinol exhibits a high thermal decomposition temperature and char yield. The TGA results indicate that the char yield of PRB (800 °C, nitrogen atmosphere) reaches a value of 69.0% [3], which cannot be matched by any thermoplastic polymers. More importantly, PRB can be effectively incorporated into phenolic resin (PR) or benzoxazine resin to

enhance their thermal resistance properties, especially the char yield, as well as their process abilities and mechanical properties [4,5]. For example, an addition of 10 wt% of PRB increases the char yield of the PRB-modified PR (800 °C, nitrogen atmosphere) to 75.1%. This value is close to the char yield for polyarylacetylene resin, which is known for its high char yield (80%, nitrogen atmosphere) [6], and is higher than that of PR (63.8%, nitrogen atmosphere). It is worth noting that the char yield of the PRB-modified resin is not simply determined in an additive manner by the char yields of each component. The synthesis and development of PRB and its applications for modifying thermosetting resins are greatly impeded due to the lack of a definitive investigation of the high char yield and pyrolysis mechanism of PRB.

A large amount of research has been devoted to investigating the effect of boron on thermal resistance, providing a valuable theoretical foundation for understanding the high char yield of PRB. The results of Wang et al. [7] suggested that in the reaction between boron carbide (B₄C) and oxygen-containing volatiles, carbon was partially converted and remained in the resin matrix in the form of amorphous carbon, resulting in the improved char yield of B₄C-modified PR. Liu et al. [3] proposed that the excellent thermal stability of PRB could be attributed to the large number of aromatic

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rings in PRB. Xu et al. [8,9] stressed that borates, formed by the reaction of boron hydroxyl groups in PRB with phenolic hydroxyl groups in PR, were the main reason for the high char yield of PRB-modified PR. Gao et al. [10] proposed that the formation of borates reduced the number of ether linkages; B–O bonds, with a higher bond energy (561 kJ/mol) than that of the C–O bond (384 kJ/mol), would require higher temperatures for breaking, thus improving the thermal stability of boric acid-modified PR. The research of Wang et al. [11] revealed that the phenylboronates formed during the curing of phenylboronic acid-modified PR promoted char-formation during pyrolysis, which in turn increased the char yield.

It is commonly known that chemical reactions occurring during the pyrolysis of resins require higher temperatures. Thus, a better understanding of the thermal pyrolysis mechanism in PRB is imperative, not only for improving the thermal resistance of PRB but also as a basis for developing novel structured polyborates. The current understanding of the structure of PRB is very limited, which is the motivation behind this study and the accompanying investigation of the high char yield of PRB. The first part of this paper involves a study of the PRB structure. The pyrolysis of PRB, especially its structural evolution at high temperatures, is researched in order to completely reveal the effect of structure on the thermal stability of PRB. These results are significant for understanding the effect of bonding styles of boron atoms on the thermal resistance of the polymer and on the chemistry of the boron-containing polymer.

2. Experimental

2.1. Materials

Resorcinol, BA, *N*-methyl-2-pyrrolidone (NMP), anhydrous ferric trichloride, cyclohexane, xylene, acetone, and aether were supplied by Tianjin Chemical Reagent Company. All of the reagents used in these experiments were of analytical grade.

2.2. Preparation of PRB

PRB was synthesized from boric acid and resorcinol according to the following steps. Under nitrogen atmosphere, resorcinol (1.1 g, 0.5 mmol), anhydrous ferric trichloride (0.081 g, 0.5 mmol), cyclohexane, and NMP were added into a four-necked round bottom flask equipped with a magnetic stirrer, a thermometer, a reflux condenser, and a Dean-Stark trap. The temperature was gradually raised to 95 °C, and this was followed by a gradual addition of NMP solution of BA (0.62 g, 10 mmol). The mixture was maintained at this temperature for 8 h. The cyclohexane was then replaced by xylene, following which the temperature was slowly raised to 165 °C, at which temperature the reaction was refluxed over 8 h. The system was then heated to 200 °C with concurrent removal of xylene and was refluxed at this temperature until no water was observed in the Dean-Stark trap. The residual solvents were removed under reduced pressure, after which the collected brown liquid oil was molten at 220 °C for 2 h to further increase the molecular weight. The heating was then stopped, and the resulting products were poured into a polytetrafluoroethylene beaker. The crude product was dissolved in acetone and precipitated three times. The precipitated product was collected by filtration, and the filter cake was washed with aether several times until the filtrate was colorless. The obtained filter cake was extracted with aether using a Soxhlet extractor for 48 h to remove the NMP residue and the unreacted reagents. Finally, the purified product was collected and dried at 160 °C in a vacuum drying oven for 12 h, and the powder sample of PRB with a red-brown color was obtained. The obtained PRB sample will be further carbonized at different

temperatures to investigate the thermal degradation behaviour of PRB.

In order to identify the effect of destruction of borates on the thermal stability of PRB, the PRB was extracted with water using a Soxhlet extractor, and the obtained sample was denoted by A. The method for the preparation of A was presented in the Supporting Information (page 2, line 2).

2.3. Pyrolysis of PRB

The PRB sample as mentioned in Section 2.2 was placed in a graphite crucible and heated from room temperature to the target temperature for 2 h using an SGM6812B5 tube furnace at a heating rate of 10 °C/min and under a nitrogen atmosphere (60 mL/min). In order to investigate the thermal degradation behaviour of PRB, the PRB was carbonized at 400 °C for 2 h, at 600 °C for 2 h, and at 800 °C for 2 h. The tube furnace was cooled from the set temperature to room temperature at approximately 2 °C/min using the same gas flow rate as that used for heating. The PRB after treated at 400 °C for 2 h, 600 °C for 2 h, and 800 °C for 2 h, are represented by B, C, and D, respectively.

2.4. Characterisation

X-ray photoelectron spectroscopic (XPS) measurements were obtained using a Perkin-Elmer PHI-5400 system (Mg K α X-ray source, Perkin-Elmer Corp., USA) attached to a data acquisition system. Nuclear magnetic resonance (NMR) spectra were acquired using a Bruker (Avance III) 400 MHz spectrometer with deuterated dimethylsulfoxide-d₆ as the solvent and tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm⁻¹ from KBr pellets using a Bruker Tensor 27 Spectrophotometer (Bruker, Karlsruhe, Germany) with a resolution of 1.0 cm⁻¹. The base vacuum of this system was 6.0 × 10⁻⁸ Torr. Spectra were referenced to the C1s peak at 284.5 eV. Thermogravimetric analysis (TGA) diagrams were created using a NETZSCH TG 209C (Netzsch, Germany), and the samples were heated from room temperature to 1000 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Solid-state NMR experiments were performed on a Bruker Avance III NMR spectrometer (500 MHz, Bruker GmbH., Karlsruhe, Germany) equipped with a Varian/Chemagnetics 4 mm magic angle spinning (MAS) probe, and a 14.1 T Oxford magnet at the Larmor frequency of 192.5 MHz for ¹¹B and 100.61 MHz for ¹³C. The powdered sample weighing 200 mg was packed into 4-mm ZrO₂ rotors in an Ar atmosphere and sealed with airtight Teflon caps to minimize the possibility of oxygen and moisture contamination. The sample was spun at the magic angle of 54.7° at a frequency ($\omega_r/2\pi$) of 15 kHz during measurements. 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 connected to a Bruker Tensor 27 FTIR spectrometer. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance (Bruker AXS, Germany) with Cu K α radiation ($\lambda = 0.154$ nm, 40 kV and 40 mA). Data were collected between 10° and 80° with a scanning speed of 2°/min. Pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) was employed to separate and identify the pyrolysis volatiles. For this purpose, a frontier PY-2020s pyrolysis device (Shimadzu, Japan) was directly attached to a QP2010 GC-MS (Shimadzu, Kyoto, Japan) system. Pyrolysis temperatures of 300, 500, and 700 °C were used for characterisation. Chromatographic separation of the volatile products was performed using an Agilent HP-5 quartz capillary column (30 mm × 0.25 mm × 0.25 μ m film thickness), following which the volatiles were analysed by MS. The temperature of the column was increased from 40 to 260 °C at a heating rate of 5 °C/min and

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