

Fabrication and characterization of poly (bisphenol A borate) with high thermal stability



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ARTICLE INFO

Article history:

Received 16 August 2016

Received in revised form

18 September 2016

Accepted 19 September 2016

Available online 20 September 2016

Keywords:

Poly (bisphenol A borate)

Thermal stability

High char yield

Borates

Boron oxide

ABSTRACT

In this work, poly (bisphenol A borate) (PBAB), which has excellent thermal resistance and a high char yield, was synthesized via a convenient $A_2 + B_3$ strategy by using bisphenol A (BPA) and boric acid (BA). The chemical reaction between BPA and BA and the chemical structure of PBAB were investigated. The results demonstrate that PBAB consists of aromatic, Ph–O–B and B–O–B structures, as well as a small number of boron hydroxyl groups and phenolic hydroxyl groups. The thermal properties of PBAB were studied by DMA and TGA. The results indicate that the glass transition temperature and char yield are gradually enhanced by increasing the boron content, where the char yield of PBAB at 800 °C in nitrogen (N_2) reaches up to 71.3%. It is of particular importance that PBAB show excellent thermal resistance in N_2 and air atmospheres. By analysing the pyrolysis of PBAB, the high char yield of PBAB can be attributed to the formation of boron oxide and boron carbide at high temperatures, which reduced the release of volatile carbon dioxide and improved the thermal stability of the carbonization products. This study provides a new perspective on the design of novel boron-containing polymers and possesses significant potential for the improvement of the comprehensive performance of thermosetting resins to broaden their applicability in the field of advanced composites.

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1. Introduction

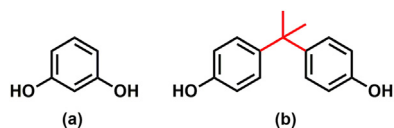
Over the last few decades, many types of high-performance resins have been explored, and they have extensive applications in aeronautics and astronautics [1]. Phenolic resins (PRs), as one of the most important thermosetting resins, have been studied for more than 100 years since they are first reported by von Bayer in 1872 [2,3]. PRs play a key role in high-performance composite

materials, especially for ablative composites, because of their excellent chemical resistance, dimensional stability, flame retarding property, mechanical strength, and adhesive strength [4]. Although PRs have a wide range of applications, their poor thermal resistance and low char yield at elevated temperatures are unsatisfactory for certain fields, especially for high-performance ablative and refractory materials. During pyrolysis at high temperatures, all non-carbon species in PRs will be eliminated and the majority of the polymer backbones form a char layer. However, drastic pyrolysis leads to the loss of volatiles, such as CO, CH₄, H₂O, and so on, whereas the disintegration and failure of the polymer structure occur at high temperatures [5]. If the char yield of PRs is improved, the manufacturing cost of the impregnation of carbon/carbon (C/C) composites and the binder of the refractory materials will be effectively reduced. Thus, the improvement in the thermal resistance of PR is very important and has long been the focus of many research investigations [5,6]. Extensive research has proved that the thermal properties of PRs can be improved remarkably by the incorporation of boron compounds, such as boric acid (BA) [7], phenylboronic acid (PBA) [8], boron carbide (B₄C) [9], zirconium boride [10], hafnium boride [11], and so on.

Abbreviations: PBAB, poly (bisphenol A borate); BPA, bisphenol A; BA, boric acid; N_2 , nitrogen atmosphere; PRs, phenolic resins; C/C, carbon/carbon; PBA, phenylboronic acid; B₄C, boron carbide; HBPs, hyperbranched polymers; PRB, poly(resorcinol borate); BZ, benzoxazine; Ph–OH, phenolic hydroxyl groups; NMR, nuclear magnetic resonance; FTIR, Fourier transform infrared; GPC, gel permeation chromatography; XPS, X-ray photoelectron spectroscopic; TGA, thermogravimetric analysis; XRD, X-ray diffraction; DMA, dynamic mechanical analysis; SEM, scanning electron microscope; B–OH, boron hydroxyl groups; ΔE , energy difference; B₂O₃, boron oxide; M_n , number-average molecular mass; PDI, polydispersity index; d_{002} , interlayer spacing; L_c , average crystallite size; T_g , glass transition temperature.

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Scheme 1. Structure of resorcinol (a) and BPA (b).

Hyperbranched polymers (HBPs) have received considerable attention because of their special structure and properties, such as a highly compacted semi-spherical shape, lack of entanglement, numerous functional terminal groups, and high solubility, as well as low solution and melt viscosities [12,13]. The terminal functional groups of HBPs endow them with excellent solubility in many common organic solvents and the ability to react with thermosetting prepolymers. HBPs have been shown to have a significant advantage in the modification of thermosetting resins. The results of Liu et al. [14] suggest that the heat-resistance and toughness performance of PR were significantly improved by the addition of an aromatic hyperbranched polyester. Cui et al. [15] conducted seminal work on the enhancement of the thermal and mechanical properties of epoxy resins by the addition of hyperbranched aromatic polyamide grown on microcrystalline cellulose fibre. Our previous work has demonstrated that poly(resorcinol borate) (PRB) can effectively improve the thermal resistance and mechanical properties of PR [16] and benzoxazine (BZ) resins [17], while still offering the same processing advantages. 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%.

PRB, as an ideal modifying agent, is synthesized from the esterification reaction of BA with resorcinol [18]. The char yield of PRB (800 °C, nitrogen atmosphere) reaches a value of 69.0%, which is also attributed to the excellent thermal stability of PRB-modified PR. However, the following deficiencies exist by using resorcinol as the phenol source when preparing PRB. First, the colour of the synthesized PRB is deeper because of the oxidation of resorcinol (Scheme 1a). Second, the structure of the PRB is not easy to control due to the low monomer conversion rate and synthesis yield. We attribute it to the oxidation of phenolic hydroxyl groups (Ph–OH), leading to a lack of Ph–OH and, at the same time, the formation of more B–O–B structures. Third, the molecular chain rigidity of PRB is strong, resulting in a poor solubility in organic solvents, which is unfavourable for the modification of thermosetting resins.

Considering the above factors, we report a one-pot $A_2 + B_3$ strategy to synthesize poly (bisphenol A borate) (PBAB) with a rigid backbone from the esterification reaction of the A_2 monomer of bisphenol A (BPA) (Scheme 1b) and the B_3 monomer of BA. Compared with resorcinol, BPA has a high stability and can effectively avoid the oxidation of dihydric phenol, leading to the lighter colour of the products. Because of the flexible isopropyl groups existing in BPA, the reaction of BPA with BA is easier to control, and the internal rotation of the molecular chain is substantially easier, which is conducive to improving the toughness of thermosetting resins. More interestingly, by controlling the molar ratio of A_2 and B_3 monomers, the elemental composition and molecular structures can be adjusted with the terminal tailoring strategy, which in turn determines and optimizes the solubility and reactivity of PBAB. This also provides a better way to tailor the miscibility and curing behaviours of thermosetting resins through the incorporation of PBAB. Thus, PBAB, which has a large number of aromatic rings and boron atoms, is effectively incorporated into thermosetting resins to give full consideration to the thermal resistance, toughness and processabilities.

In this contribution, PBAB was synthesized from BPA and BA. The chemical reactions that occurred in the system were studied, which was also the basis of understanding the relationship between the

Table 1
Composition of PBAB.

Resin	Molar ratio BPA/BA	Weight (g)		Atomic ratio ^a (%)		
		BPA	BA	C	B	O
PBAB-a	2:1	25.33	3.40	15	1.34	3.72
PBAB-b	1:1	59.85	16.23	15	9.59	11.89
PBAB-c	1:2	30.39	10.33	15	12.13	18.55

^a The relative content of BPA is calculated according to the relative content of carbon atoms from the XPS spectra, where a BPA molecule contains fifteen carbon atoms. Then the relative content of boron and oxygen atoms is calculated based on the relative content of BPA.

structure and performance of PBAB. Then, the chemical structure of PBAB was characterized by GPC, FTIR, XPS, NMR (¹H NMR and ¹³C NMR) and XRD. DMA and TGA were applied to demonstrate the excellent thermal properties of PBAB. Moreover, the structure of the carbonization products for PBAB was investigated to explain the reason for the high char yield of PBAB.

2. Experimental

2.1. Materials

BPA, 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 PBAB

PBAB was synthesized from BPA and BA according to the following steps. Under a nitrogen atmosphere, BPA, anhydrous ferric trichloride, cyclohexane, and NMP were added to 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 the gradual addition of a NMP solution of BA. The mixture was maintained at this temperature for 8 h. The cyclohexane was then replaced by xylene, and the temperature was then slowly raised to 165 °C. Finally, the reaction was refluxed for 8 h. The system was then heated to 200 °C with the 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 kept molten at 220 °C for 2 h to further increase the molecular mass. The heating was then stopped, and the resulting product was 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 colourless. The obtained filter cake was extracted with aether using a Soxhlet extractor for 48 h to remove the NMP residue and 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 PBAB with a red-brown colour was obtained. The obtained PBAB was further carbonized at different temperatures to investigate its thermal degradation behaviour.

By changing the molar ratio of BPA and BA, PBAB samples with different terminal groups were designed and synthesized, as shown in Table 1.

2.3. Pyrolysis of PBAB

The PBAB 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

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