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Synergistic effect of an aromatic boronic acid derivative and magnesium hydroxide on the flame retardancy of epoxy resin

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ABSTRACT

To develop new organic/inorganic flame retardants, the aromatic boronic acid derivative 2,4,6-tris(4-boronic-2-thiophene)-1,3,5-triazine (3TT-3BA) and magnesium hydroxide (MH) were selected. The two compounds were added to epoxy resin (EP) to investigate the flame retardant properties and mechanism. The mechanical, thermal, and flame retardant properties of the EP and flame retardant EP were investigated. The morphology of char was characterized by scanning electron microscopy. The results show that mixing EP with both 3TT-3BA and MH results in better thermal stability and flame retardant properties than mixing with only one of the compounds, indicating the synergistic effect of the two components. The elements in the char were investigated by elemental analysis to further investigate the flame retardant mechanism. The result of impact strengths shows that 3TT-3BA can inhibit combustion with MH effectively without decreasing the mechanical strength.

1. Introduction

Epoxy resins (EPs) are indispensable materials because of their excellent physical and chemical properties, but their flammability limits their application, such as for structural materials for electronic equipment, aircraft, and terrestrial vehicles [1–6]. Therefore, flame retardant materials are highly valued. Some traditional flame retardants are widely used in computers and other electronic equipment, such as organic bromine flame retardants. However, organic bromine flame retardants readily release toxic gases in the process of combustion, such as acid gases, and some other toxic compounds (such as polybrominated dibenzo-p-dioxins and dibenzofurans) can be released by polybrominated diphenyl ethers (PBDEs), European Union banned the use of PBBs and PBDEs on July 1, 2006 [7–9].

Magnesium hydroxide (MH) is a typical inorganic flame retardant. It has received increasing attention in recent years owing to its environmentally friendly advantages, low cost, and good smoke-suppressing properties [10–15]. The characteristics of endothermic decomposition and release of water above 300 °C reduce the heat of the flame retardant material. However, its relatively low flame retardant efficiency and poor compatibility with polymers decrease the mechanical strength of polymers. Superfine particle size and surface modification will overcome these drawbacks, but undoubtedly increase the cost. Therefore, finding a compounded system to reduce the dosage of MH is an important research issue.

It is well known that aromatic boronic acid releases water and forms boroxine or boronic acid anhydride by thermolysis. Thermolysis of boronic acids can be used to improve the flame retardancy of materials by diluting flammable volatile substances and cutting off the oxygen supply [16–24]. Triazine derivatives have received considerable attention because of their stable triazine rings and easy charring during combustion. Intumescent systems containing triazine derivatives as flame retardants are widely used in various polymers [25–27]. In addition, thiophene compounds have also been investigated as flame retardants, and they show good flame retardancy [28,29]. In a previous study, 2,4,6-tris(4-boronic-2-thiophene)-1,3,5-triazine (3TT-3BA) (Fig. 1), an organic boronic acid derivative containing thiophene and a triazine ring, was synthesized and the thermal and flame retardant properties were determined [30].

In this study, to investigate the synergistic flame retardant effect of 3TT-3BA and MH, the flame retardants were both added to EP

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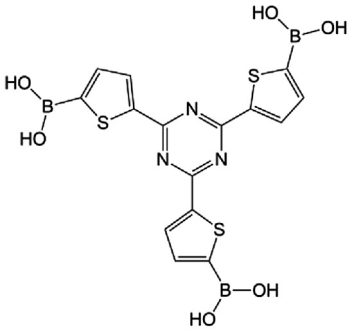

Fig. 1. Molecular structure of 3TT-BA.

and the flame retardant properties were investigated. The flame retardant mechanism is also discussed.

2. Experimental

2.1. Materials

Cyanuric chloride (99%), *trans*-dichlorobis(triphenylphosphine) palladium(II) (98%), triisopropyl borate (99%), and *n*-butyllithium (2.5 M in hexane) were obtained from Energy Chemical (Shanghai, China). Toluene (99.5%), diisopropylamine (99%), tetrahydrofuran (99%), dichloromethane (99.5%), and magnesium hydroxide (MH) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Epoxy resin (E-44, 6101) was supplied by Guangzhou Dongfeng Chemical industrial Co., Ltd (Guangdong, China), the epoxy value of the bisphenol A epoxy resin is 0.41–0.47.

Tetrahydrofuran was purified by distillation, the water was removed by metallic natrium.

2.2. Synthesis

In this work, the synthetic flame retardant prepared in our laboratories was also used, which had shown good flame retardancy when solvent blended with epoxy resin [30]. Its chemical structure is shown in Fig. 1.

Synthesis of 2,4,6-trithienyl-1,3,5-triazine (3TT): Yield: 4.2 g (84%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.29 (d, 3H), 7.63 (d, 3H), 7.22 (t, 3H). IR (KBr, cm^{-1}): 3097 ($\nu_{=C-H}$), 1650 ($\nu_{C=N}$), 1507 ($\nu_{C=C}$).

Synthesis of 2,4,6-tris(4-boronic-2-thiophene)-1,3,5-triazine (3TT-3BA): Yield: 5.8 g (83%). ^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.49 (s, 6H, −OH), 8.27 (d, 3H), 7.81 (d, 3H); ^{11}B NMR (193 MHz, DMSO-d_6) δ −11.28 (s, 3B). IR (KBr, cm^{-1}): 3391 (ν_{O-H}), 2974 (ν_{C-H}), 1730 ($\nu_{C=N}$), 1520 ($\nu_{C=C}$), 1378 (ν_{B-O}).

2.3. Preparation of samples

3TT-3BA dissolved in a small amount of dichloromethane was added to the EP. EP/3TT-3BA was then heated to 50 °C and sufficiently stirred to uniformly distribute 3TT-3BA and volatilize dichloromethane. MH was added to some of the samples at this point. After EP composites was cooled to room temperature, 7% ethylenediamine was added as a curing agent, and then the mixture was stirred for 10 min. Finally, the mixture was well blended through the use of ultrasonication. The mixture was cured at room temperature for 15 h and postcured at 60 °C for 2 h. The compositions of flame retardant samples are shown in Table 1.

Table 1
Compositions of flame retardant samples.

Sample	EP	MH	3TT-3BA	Ethylenediamine
EP	100	0	0	7
EP/MH[a]	100	20	0	7
EP/B[b]	100	0	20	7
EP/MH/B1[c]	100	10	5	7
EP/MH/B2[d]	100	10	10	7

[a] EP mixed with 20% MH.
[b] EP mixed with 20% 3TT-3BA.
[c] EP mixed with 10% MH and 5% 3TT-3BA.
[d] EP mixed with 10% MH and 10% 3TT-3BA.

2.4. Characterizations and tests

^{1}H-NMR spectra were recorded on a Bruker (Billerica, Massachusetts, USA) AVANCE-600 (MHz) NMR spectrometer and referenced to the solvent ($CDCl_3$, DMSO-d6). ^{11}B-NMR spectra were recorded at 193 MHz on the Bruker AVANCE-600 (MHz) NMR spectrometer.

Thermogravimetric analysis (TGA) and the derivative thermogravimetric (DTG) were performed with a Netzsch (Selb, Germany) 209 F3 thermal analyzer. The TGA tests were carried out under N_2 at a heating rate of 10 °C/min from 40 to 800 °C, the specimens were about 3 mg.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet (Madison, Wisconsin, USA) 6700 FTIR spectrometer with KBr pellets.

According to UL-94 test standard, the UL 94 vertical burning test was carried out with a Fire Testing Technology (FTT, East Grinstead, UK) UL94 instrument with a sample with dimensions of 127 mm × 12.7 mm × 3 mm. According to the ASTM D 2863 standard, the limiting oxygen index (LOI) was measured using an FTT instrument with a sample with dimensions of 80 mm × 10 mm × 4 mm. According to the ISO 5660 protocol, cone calorimeter (CONE) measurements were performed using a FTT CONE instrument at a heat flux of 35 kW/m^2 (the radiator temperature was about 740 °C). The sample dimensions used for the cone calorimeter test were 100 mm × 100 mm × 3.5 mm.

The residual char was observed with an EVO 18 special edition scanning electron microscope (Carl Zeiss, Germany) with an accelerating voltage of 10 kV. The elements of the residual char were determined using a Vario EL Cube elemental analyzer (Elementar, Germany).

According to the GB/T 1843–2008, the impact strengths of the EPs were measured with a ZCJ 1320 impact testing machine (Guangdong, China), the sample (10 samples of a group) dimensions were 80 mm × 10 mm × 4 mm, the gap depth of the samples was 2 mm.

3. Results and discussion

3.1. Characterization of flame retardant EP

3.1.1. TGA and DTG

Fig. 2 shows the TGA and DTG curves of the EP composites, and the characteristic thermal decomposition data is summarized in Table 2. The TGA and DTG curves suggest that decomposition of the EP and flame retardant EP involves two steps. The initial slight weight loss with a peak temperature at about 174 °C is because of a small amount of water released from the EP. Furthermore, 3TT-3BA releases water when it reacts to boroxine at about 147 °C [17–19,24,30], so the weight loss increases after 3TT-3BA is added. The next weight loss occurs from 300 to 420 °C, as shown in the