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Controllable synthesis of three kinds of zinc borates and flame retardant properties in polyurethane foam

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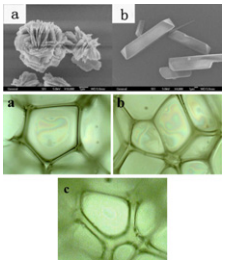
HIGHLIGHTS

- A new method for preparing $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ has been proposed.
- The morphologies of three types of zinc borates are peculiar.
- Zinc borates transform with each other by appropriately controlled.
- Polyurethane/zinc borate materials have excellent retardant properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Depending on the molar ratios of $ZnO{:}B_2O_3{:}H_2O$, zinc borates can be classified into many kinds of categories. In this paper, we successfully synthesized three kinds of zinc borates ($2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$, $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $3ZnO{\cdot}3B_2O_3{\cdot}5H_2O$) by controlling the reaction conditions, using $Na_2B_4O_7{\cdot}10H_2O$, H_3BO_3 and $Zn(NO_3)_2{\cdot}6H_2O$ as the reactants. These three zinc borates transform with each other if the reaction conditions were appropriately controlled. The morphologies of three products are peculiar. The synthesized $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ is anomalous spheric-like or flaky, $3ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ is flower-like, and $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ is club-shaped. According to the thermodynamic performance of three kinds of zinc borates, we selected $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ which had the best flame retardant properties, then doped it into the polyurethane to synthesize polyurethane/zinc borate materials. The maximum decomposition temperature of the polyurethane foam doped with zinc borate was increased by 54 °C before 300 °C. Furthermore, the maximum decomposition temperature was increased by 104 °C after 400 °C.

1. Introduction

Zinc borates are usually used as flame retardant, afterglow suppressant, smoke suppressant, and antitracking agent in both halogen-containing and halogen-free polymers [1–6]. Depending on the reaction conditions, a host of zinc borates with different molar ratios of $ZnO{:}B_2O_3{:}H_2O$ can be produced [7–15]. The most widely used zinc borates have the molecular formula as follows: $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$, $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$, $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ [16,17], $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ [7,18]. The dehydration temperatures of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ and $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ are 410 °C and 290 °C, respectively, which enable them to prefer in the polymers that require high processing temperature [19]. Compared with $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$, $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ is not stable in higher temperature, but it is economical while the processing conditions allow. Zinc borate ($2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$) in general is produced with the reaction between zinc oxide and boric acid, with high reaction temperature and high reaction concentration.

In our study, we got $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ by reacting between $Na_2B_4O_7{\cdot}10H_2O$, H_3BO_3 and $Zn(NO_3)_2{\cdot}6H_2O$ for the first time. We also synthesized the other two zinc borates, that is, $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ and $3ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ through the fine tuning of the reaction conditions. According to the knowledge we have learned, the reports of the composition preparation of

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Table 1
Summary of the reaction conditions of some representative experiments in the first reaction system at 80 °C with pH 5–6.

Sample	Time (h)	n(B)/n(Zn)	n(Zn)/V(H_2O) (mol/mL)	Products
1	1	3:1	0.02/15	ZB237, ZB335
2	2	3:1	0.02/15	ZB237, ZB335
3	3	3:1	0.02/15	ZB335
4	4	3:1	0.02/15	ZB237
5	5	3:1	0.02/15	ZB237, ZB2335
6	7	3:1	0.02/15	ZB2335

$3ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ have not seen up to now. We are sure that these three zinc borates transform with each other if the reaction conditions are reasonably controlled.

The dehydration temperatures of as-synthesized three zinc borates, that is, $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$, $3ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ and $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ are 170 °C, 210 °C and 290 °C, respectively, which allow them to be used in the flame retardant of polymers having different decomposition temperatures. The morphologies of three products are peculiar. The synthesized $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ is anomalous spheric-like or flaky, $3ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ is flower-like, and $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ is club-shaped.

The polyurethane rigid foam is a new generation of synthetic polymer material, which provides with the excellent heat insulation and the flame retardant performance. According to the thermodynamic properties of zinc borate tests, we conclude that zinc borate is an excellent thermal retardant additive. Yıldız et al. [20] have studied the properties of polyurethane film adding zinc borate, in which zinc borate was used for improvement of flammability and oxidative stability of polyurethanes produced for application as artificial leather. In this paper, we added the zinc borate as an inorganic flame retardant into the polyurethane foams. The maximum decomposition temperature of the polyurethane foam doped with zinc borate was increased by 54 °C before 300 °C. Furthermore, the maximum decomposition temperature was increased by 104 °C after 400 °C. The products' flame retardant properties were more superior. In addition, the zinc borate improved the mechanical properties of polyurethane foam simultaneously. This polyurethane foam can be applied in the thermal insulation and sealant products.

2. Experimental

2.1. Materials

All reagents were from Beijing Chemicals Co. Ltd. with analytical purity and employed without any further treatments. Distilled water was used for all synthesis and treatment processes.

2.2. Synthesis of samples

In a typical procedure for sample 1 (S1, as shown in Table 1), 15 mL of distilled water, 2.48 g boric acid (H_3BO_3) and 1.91 g borax ($Na_2B_4O_7{\cdot}10H_2O$) were mixed in a 250 mL three-neck round-bottom flask equipped with a thermometer, reflux condenser, and mechanical stirrer, heated at 80 °C to get the clear solution (pH 5–6). We added 5.95 g zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) into above solution, kept the temperature and stir sped steady for 1 h, then we obtained the final white zinc borate powders. In the first reaction system, we got samples 1–6 (S1–S6, as reported in Table 1) by varying the reaction time. Changing the temperature to 90 °C, we got samples 7–13 (S7–S13, as shown in Table 2) by varying the reaction time in the second reaction system. Keeping the temperature at 80 °C and altering the molar ratio of H_3BO_3 with $Na_2B_4O_7{\cdot}10H_2O$ to 2:1 (pH 7–8), we got samples 14–19 (S14–S19, as seen in Table 3) by varying the reaction time in the third reaction system. With the molar ratio of H_3BO_3 with $Na_2B_4O_7{\cdot}10H_2O$ being 2:1 (pH 7–8) and alter the temperature to 90 °C, we got the samples 20–24 (S20–S24, as shown in Table 4) by varying the reaction time in the fourth reaction system.

Table 2
The contents of zinc oxide, boron trioxide and water of sample S3.

ZnO/wt.%	B_2O_3/wt.%	H_2O/wt.%
45.53	38.04	16.43

Table 3
Summary of the reaction conditions of some representative experiments in the first reaction system at 90 °C with pH 5–6.

Sample	Time (h)	n(B)/n(Zn)	n(Zn)/V(H_2O) (mol/mL)	Products
7	0.25	3:1	0.02/15	–
8	0.5	3:1	0.02/15	ZB237
9	0.75	3:1	0.02/15	ZB335
10	1	3:1	0.02/15	ZB335
11	3	3:1	0.02/15	ZB335
12	4	3:1	0.02/15	ZB237
13	5	3:1	0.02/15	ZB2335

We used the two-step foaming method to synthesize the polyurethane foams. In the first step, 15 g polyether polyol, 0.08 g dibutyltin dilaurate, 0.75 g water, 0.3 g foam stabilizer and $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ were mixed in a plastic cup, which were called as the white material. The mass fractions of the added zinc borate were 0%, 1% and 2%, respectively. Then we mixed the white material and 24 g polyisocyanate which was used as the black material together with stirring. After the foam reaction we got the polyurethane rigid foams at last. This reaction was performed at room temperature.

2.3. Characterization of the samples

The crystallinity and the composition of as-prepared composites were analyzed by X-ray powder diffraction (XRD) (SHIMADZU XRD-6000 diffractometer employing Ni-filtered Cu Kα radiation, at a scanning rate of 6°/min with 2θ ranging from 5° to 45°).

The morphology and the size of the samples were observed using a Hitachi H-800 transmission electron microscope (TEM), at an accelerator voltage of 200 kV and a Hitachi scanning electron microscope (SEM) with a field-emission-scanning electron microscope (JEOL JSM-6700F, 5.0 kV). The samples used for SEM and TEM characterization were dispersed in absolute ethanol and were ultrasonicated before observation. The microscopic structures of polyurethane foams doped with zinc borate were observed by an Olympus XC21 optical microscope. The magnification is 10 times.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) are valuable techniques for studying the thermal properties of various compounds, which were carried out by means of a DTG-60H analyzer (SHIMADZU). Tests were performed with

Table 4
Summary of the reaction conditions of some representative experiments in the first reaction system at 80 °C with pH 7–8.

Sample	Time (h)	n(B)/n(Zn)	n(Zn)/V(H_2O) (mol/mL)	Products
14	1	3:1	0.02/15	–
15	2	3:1	0.02/15	ZB335, ZB237
16	3	3:1	0.02/15	ZB335
17	5	3:1	0.02/15	ZB335
18	6	3:1	0.02/15	ZB237, ZB335
19	7	3:1	0.02/15	ZB2335