



Synthesis of hydrophobic zinc borate nanoflakes and its effect on flame retardant properties of polyethylene

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ABSTRACT

Zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) has relatively high dehydration on-set temperature which property permits processing in a wide range of polymer system. But zinc borate particles are hardly dispersed in a polymer matrix so that they prevent their using in industry. To address this problem, we synthesized hydrophobic zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) nanoflakes by employing solid–liquid reaction of zinc oxide (ZnO) and boric acid (H_3BO_3) in the presence of oleic acid. This method does not bring pollution. By conducting morphological and microscopic analyses, we found that this compound displayed nanoflake morphology with particle size of around 100–200 nm, thickness less than 100 nm and there were uniform mesopores with the diameter about 10 nm within the particles. Furthermore, our products had an effect on flame retardant of polyethylene, especially when the zinc borate was modified by oleic acid.

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1. Introduction

Zinc borates have been used as flame retardant, smoke suppressant, afterglow suppressant, and antitracking agent in both halogen-containing and halogen-free polymers [1–8]. The most widely used ones are zinc borates with compositions $3\text{ZnO} \cdot 2\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and anhydrous $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3$. Previous work about the synthesis methods of zinc borates contained reaction of zinc oxide and boric acid, and reactions of zinc salts and borate salts in hot water ($\geq 60^\circ\text{C}$) or using the ethanol supercritical fluid drying technique [9]. In these methods, the process using zinc oxide and boric acid as the raw materials was more preferable for that the by-product of the reaction was water with no contaminants.

The procedure of synthesizing zinc borates is as follows: two products $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ and $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, dehydrating at around 130°C with 1–27% mass loss and at around 350°C with 10–12% mass loss, have been obtained at 60°C and further heated at 90°C , respectively [10]. Gürhan and his colleagues had synthesized fine zinc borate particles using seed crystals with the average particle sizes between 4.3 and $16.6\ \mu\text{m}$ [11]. Chen et al. obtained a new netlike nano zinc borate $\text{ZnO} \cdot y\text{B}_2\text{O}_3 \cdot z\text{H}_2\text{O}$ ($y=0.3\text{--}0.4$, $z=1.0\text{--}1.4$) with amorphous phase via coordination homogeneous precipitation method [12]. Shi et al. reported an industrially important zinc borate, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, by a

rhological phase reaction method using zinc oxide and boric acid as starting materials. Furthermore, the main factors that affected the formation of zinc borate were water volume, sealing state, reaction time and temperature [13]. However, they reported these synthesizing zinc borates which were not modified and particle size was larger.

In order to improve the compatibility between zinc borate and polymer system, we have tried to transform the superficial features of zinc borates, using oleic acid (OA) as the modifying agent, from hydrophilic properties to hydrophobic properties [9]. We obtained the hydrophobic zinc borate ($\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 3\text{H}_2\text{O}$) nanoplatelets, using $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as the raw materials. Here, we report a new method for synthesizing zinc borate. Zinc oxide and boric acid are also employed as the raw materials. Our products have an effect on flame retardant of polyethylene, especially when the zinc borate is modified by oleic acid. Therefore, the procedure reported here is a new method for synthesizing hydrophobic zinc borate nanoflakes as flame retardants of polyethylene with the meet of green chemical synthesis.

2. Experimental

2.1. Materials

All reagents were from Beijing Chemicals Co. Ltd. with analytical purity and employed without any further treatments.

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Distilled water was used for all synthesis and treatment processes.

2.2. Synthesis of samples

In a typical procedure for sample 1 (S1), 25 ml of distilled water, 7.50 g boric acid (H_3BO_3), 2.846 g zinc oxide (ZnO), 7 ml absolute ethanol and a certain amount of oleic acid were mixed in a 250 ml three-neck round-bottom flask equipped with a thermometer, reflux condenser, and mechanical stirrer were heated to 95 °C for 4 h with stirring. The white product S1 was obtained and then filtered, washed repeatedly with absolute ethanol and distilled water to remove unreacted reactants and oleic acid, and finally dried in the oven at 80 °C to obtain the final white zinc borate (ZB) powders. Samples 2–10 (S2–S10) were obtained under different conditions listed in Table 1.

Afterwards, 10 g polyethylene (PE) was dissolved in 50 ml cyclohexane in another 250 ml three-neck round-bottom flask equipped with a mechanical stirrer. A certain amount of synthesized products were then added to the dissolved PE over 1 h. The mixture was finally poured on a piece of clean glass to form the film [14].

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 $K\alpha$ radiation, at a scanning rate of 6°/min with 2θ ranging from 15° to 55°) and an energy-dispersive X-ray spectrometer (EDS) (JEOL-6700F, Hitachi) attached to the SEM, respectively.

The morphology and the size of the samples were observed using a Hitachi H-800 transmission electron microscope (TEM), at an accelerator voltage of 100 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.

Simultaneous thermogravimetry (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 about 10 mg of sample on alumina crucibles with the heating rates of 20 °C/min in air atmosphere and using tabular $\alpha\text{-Al}_2\text{O}_3$ as reference weight losses were calculated from the TGA.

Water contact angles of samples were measured by using a JC2000C2 contact angle goniometer (Shanghai Zhongchen Power-each Company, China) by the sessile drop method with a microsyringe at 25 °C.

3. Results and discussion

3.1. X-ray diffraction diagrams of zinc borates

Our synthesized product is stable white powder at room temperature. All diffraction peaks are quite similar to those of bulk $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ and the diffraction data are in good agreement with earlier reports [10,11], which indicate the particles are crystals (Fig. 1a). No characteristic peaks of other zinc borates and other unreacted compounds are observed. Chemical analysis using EDS taken from the as-prepared pure zinc borate particles (Fig. 1b) indicates the presence of Zn, B and O (elements of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ and element H was not analyzed), no other elements exist in Fig. 1b. Furthermore, the quantification of the peaks give that the atomic ratio of Zn:B:O is

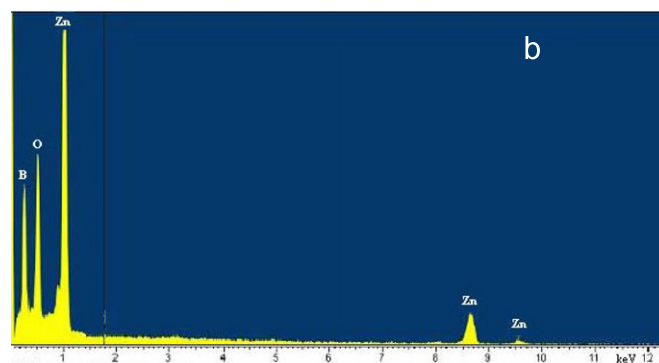
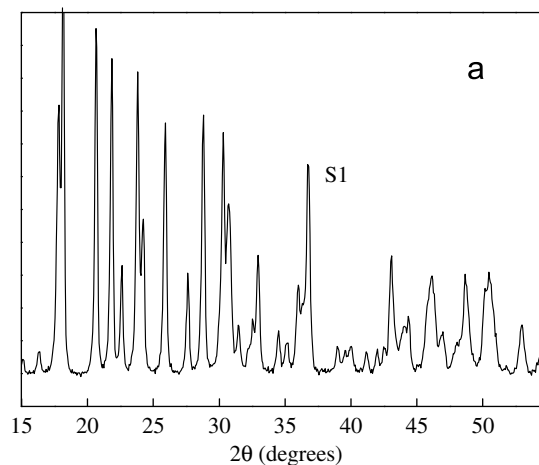


Fig. 1. (a) XRD of hydrophobic $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ nanoflakes (sample S1, Table 1) and (b) typical EDS spectrum of the as-prepared sample (sample S8, Table 1).

Table 1

Summary of the reaction conditions of some representative experiments.

Samples	$n(\text{H}_3\text{BO}_3):n(\text{ZnO})$	Temperature (°C)	Mass fraction of oleic acid added (%)	Reaction time (h)	Did zinc oxide react completely?
1	4:1	95	1.0	4	Yes
2	2:1	95	1.0	4	No
3	3:1	95	1.0	4	Yes
4	4:1	75	1.0	4	No
5	4:1	85	1.0	4	Yes
6	4:1	95	1.0	2	Yes
7	4:1	95	1.0	6	Yes
8	4:1	95	0.0	4	Yes
9	4:1	95	0.5	4	Yes
10	4:1	95	2.0	4	Yes

2:6.02:14.51, which is very close to the stoichiometric $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$.

Fig. 2 presents the XRD patterns of the samples with the molar ratios of boric acid and zinc oxide being 2:1 (S2), 3:1 (S3) and 4:1 (S1), respectively. The XRD pattern of the as-synthesized sample S1 can be in good agreement with the pure phase of the crystal structure of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$. From the comparison of Fig. 2, it can be deduced that there are extra peaks in Fig. 2-S2. The extra peaks, as indicated as arrows in Fig. 2, at about 31.7° , 34.4° , 36.2° and 47.5° 2θ values are identical to the peaks of pure zinc oxide. It reveals that ZnO does not react completely with the molar ratio of boric acid and zinc oxide being 2:1, which further testifies that the stoichiometric ratio of boric acid and zinc oxide is 3:1. Fig. 3 presents the XRD patterns of the samples reacting at 75°C (S4), 85°C (S5) and 95°C (S1), respectively. We obviously find that these three patterns are similar to each other, but S4 has many extra peaks (Fig. 3). Some of the peaks at about 31.7° , 34.4° , 36.2° and 47.5° 2θ values belong to the peaks of pure zinc oxide, and the residuary peaks apparently index to another structure of zinc borate, suggesting that if the reaction temperature is lower

than 85°C , zinc oxide reacts incompletely, meanwhile it can generate another style of zinc borate. Fig. 4 presents the XRD patterns of the samples reacting for 2 h (S6), 4 h (S1) and 6 h (S7), respectively. Furthermore, the three patterns are identical to each other, that is, when the products are obtained at 95°C for 2 h, with the molar ratio of boric acid and zinc oxide being 4:1, we can get pure $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$.

3.2. TGA of the powders

To further testify that the products are the configuration of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ crystals, the products S1 and S8 are tested by TGA. The weight loss is 14.39% from 180 to 450°C , which corresponding to the loss of 3.5 molar equivalent of the crystal water (Fig. 5a). The result is comparable with calculated value of 14.46%, which proves that the product is $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$. The TGA data are consistent with the XRD results. However, the weight loss is 16.92% when the temperature is raised from 180 to 700°C (Fig. 5b). Obviously, the two samples have the different

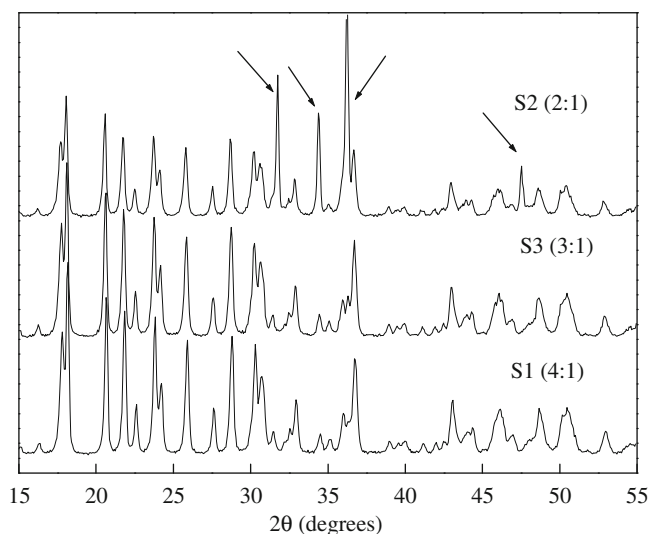


Fig. 2. XRD of products obtained at different molar ratio of boric acid and zinc oxide: sample S1 (4:1), sample S2 (2:1) and sample S3 (3:1).

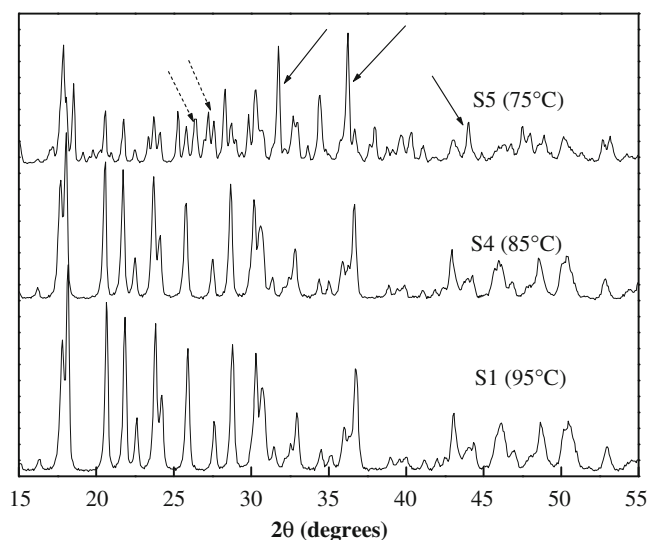


Fig. 3. XRD of products obtained at different temperature: sample S1 (95°C), sample S4 (85°C) and sample S5 (75°C).

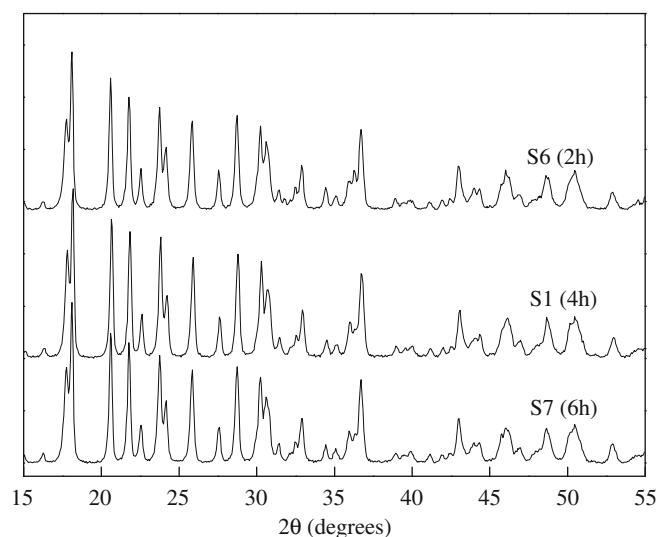


Fig. 4. XRD of products obtained at different reaction time: sample S1 (4h), sample S6 (2h) and sample S7 (6h).

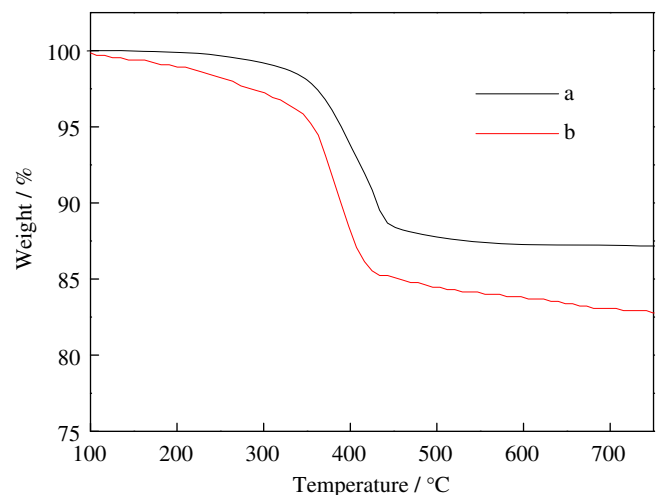


Fig. 5. TGA of the (a) pure $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ powders (sample S8, Table 1) and (b) hydrophobic $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ nanoflakes (sample S1, Table 1).

weight loss. The weight loss of hydrophilic zinc borate is due to the dehydration of zinc borate, whereas the weight loss of hydrophobic zinc borate is not only due to the dehydration of zinc borate but also the degradation of OA.

3.3. Micrograph of the powders

Fig. 6 shows the SEM images of the obtained products S1 and S8. The product S1 is obtained using oleic acid as the modifying agent. Previous works showed that, using $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as the raw material, zinc borate nano-/microstructure with different morphologies had successfully been fabricated through a facile surfactant-assisted method [9,14–17]. Our SEM images show that the morphology and the size of the samples S1 and S8 are similar. It accounts for that oleic acid does not affect the morphology and the size of zinc borate that using zinc oxide and boric acid as the reactants because of the high initial supersaturation. Despite that, the images show that $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ is irregular nanoflakes flocking together with the particle size of around 100–200 nm and the thickness less than 100 nm. As will be discussed in the following section, the product S1 obtained through this method can be well dispersed into PE.

Fig. 7 shows the internal framework of the obtained products S1 and S8, which are in good agreement with the results of SEM. The particle size is between 100 and 200 nm. Furthermore, there are some uniform mesopores in the particles and the diameter of the cavities is about 10 nm. These regions appear brighter because they have absorbed fewer electrons than their surroundings. Judat and Kind investigated the inorganic particle morphology and internal structure (the cavities contained within the particles). The pore size increased with increasing supersaturation in the ethanol and water solution [18]. In the present work, we also prepare the zinc borate nanoflakes using ethanol and water solution as solvent and the initial supersaturation is very high so that zinc borate particles have the porous structure.

3.4. Water contact angle of composites

The water contact angle is widely used as a criterion for evaluating surface hydrophobicity [19]. In order to study the surface characteristics, the zinc borate powders are analyzed to measure the relative water contact angle. Fig. 8 presents the changes of the contact angles containing the unmodified zinc borates (without added oleic acid) and the modified zinc borates (with added different amount of oleic acid). In the process of testing, when a drop of water falls onto squeezed unmodified zinc borate flakes, the water immerses into the unmodified zinc borate flakes immediately, which shows that unmodified zinc borate is

hydrophilic (shown in Fig. 8a). The contact angle quickly increase from 109.27° to 129.02° with the weight ratio of OA/ZB increasing from 0.5 to 2.0 wt% (shown in Fig. 8b–d). It demonstrates that the hydrophobicity of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ nanoflakes has been improved when the weight ratio of OA/ZB increased from 0.5 to 2.0 wt%.

3.5. Thermal analysis of the zinc borate/PE compounds

TGA is widely used to investigate the thermal decomposition of polymers. Fig. 9 shows the degradation curves of pure PE, unmodified zinc borate/PE (the mass fraction of ZB was 5%), and hydrophobic zinc borate/PE (the mass fraction of hydrophobic ZB was 5%), respectively. It clearly indicates that the decomposition on-set temperature of PE has been enhanced with adding zinc borate. The function of zinc borate is as follows: the TGA curve of pure PE shows that its weight loss ranges from 320 to 510°C , and zinc borate is dehydrated ranging from 310 to 510°C . As for the ZB/PE composite, when the temperature reaches the decomposition on-set temperature of PE, zinc borate has begun to dehydrate and released water into the vapour phase. The dehydration of zinc borate is endothermic process, so that heat is absorbed in the conversion, resulting in the increase of the decomposition on-set temperature of PE. In addition, because of the releasing of water into the vapour phase, it can effectively dilute the volatile species emanation from polymer degradation.

Fig. 9 also shows that the decomposition on-set temperature of hydrophobic zinc borate/PE is higher than that of zinc borate/PE and pure PE. It means that hydrophobic zinc borate has an edge than unmodified zinc borate in improving the flame retardant of

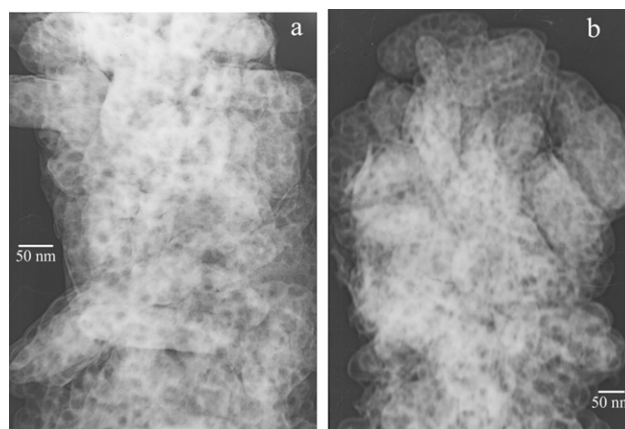


Fig. 7. TEM images of the products: (a) without oleic acid (sample S8, Table 1) and (b) with oleic acid (sample S1, Table 1).

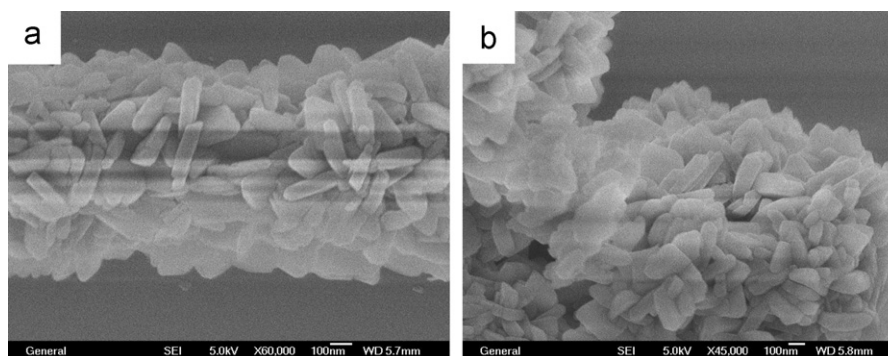


Fig. 6. SEM images of the products: (a) without oleic acid (sample S8, Table 1) and (b) with oleic acid (sample S1, Table 1).

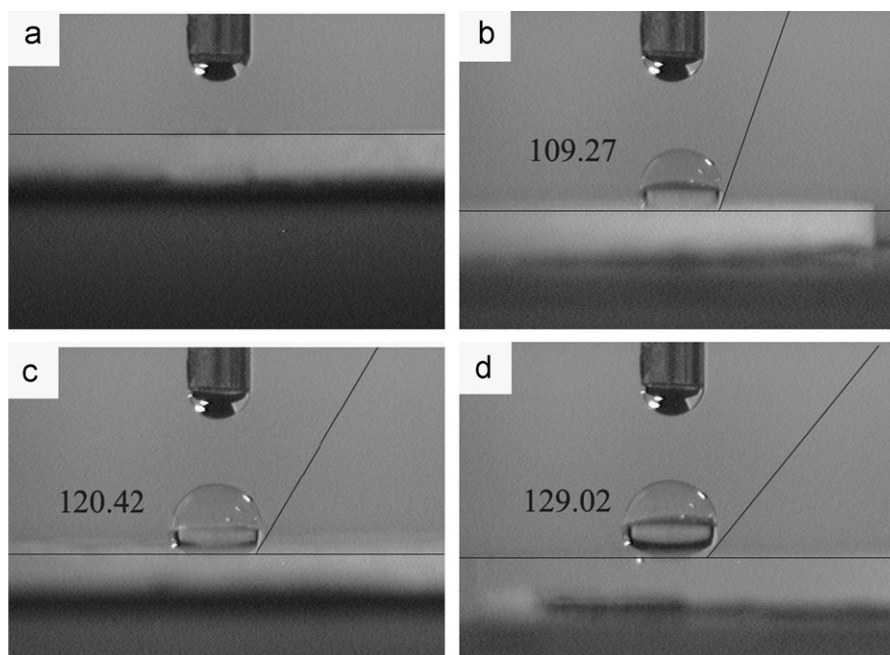


Fig. 8. Contact angle of samples using different amount of OA as modifying agent: (a) (sample S8, 0%), (b) (sample S9, 0.5%), (c) (sample S11, 1%) and (d) (sample S10, 2%).

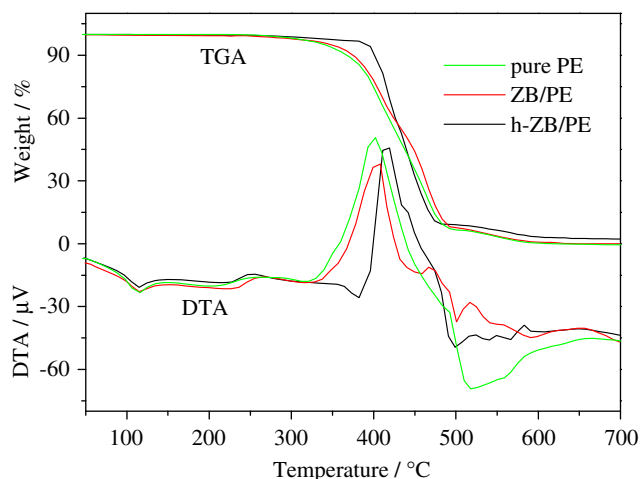


Fig. 9. (a) TGA and (b) DTA of the pure PE, zinc borate/PE (5.0 wt% of zinc borate added) and hydrophobic zinc borate/PE (5.0 wt% of hydrophobic zinc borate added).

organic polymers. We believe that the hydrophobic zinc borate can be better dispersed in the polymers than unmodified inorganic particles, and the unmodified zinc borate particles tend to aggregate together while mixed with PE. The wonderful compatibility between hydrophobic zinc borate and polymer effectively avoids the reduction of mechanical properties. It indicates that the addition of hydrophobic zinc borate has improved the thermal stabilities of PE.

From the corresponding DTA analysis, the endothermic peaks of three samples between 50 and 180 °C correspond to evaporation of residual water and solvents (Fig. 9-DTA). The big on-set exothermic decomposition temperature of pure PE is 320 °C, while the big on-set exothermic decomposition temperature of hydrophobic zinc borate/PE rises to 380 °C compared with the 330 °C of the big on-set exothermic decomposition of zinc borate/PE (Fig. 9-DTA), which is in good agreement with TGA analysis (Fig. 9-TGA). The results show that the addition of hydrophobic zinc borate nanoflake can improve the degraded temperature of polyethylene from 320 to 380 °C.

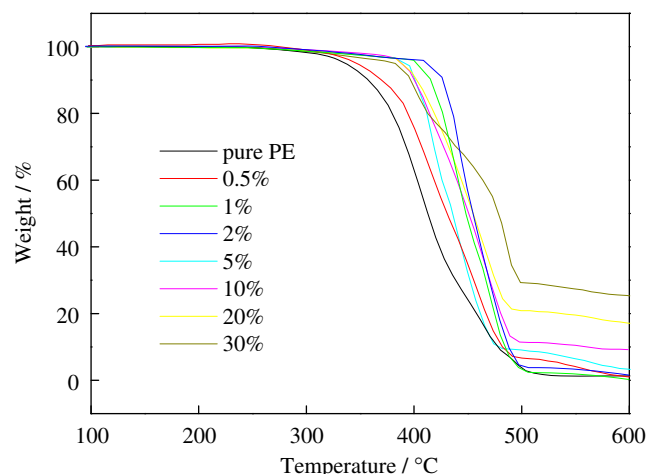


Fig. 10. TGA of PE with various amount of the hydrophobic zinc borate.

Fig. 10 shows the degradation curves of pure PE and hydrophobic zinc borates/PE (the mass fraction of hydrophobic zinc borate range from 0.5% to 30%), respectively. While the dosage of hydrophobic $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ nanoflakes reaches 2%, the decomposition on-set temperature gets to the highest value. The decomposition on-set temperature of PE falls to 382 °C with adding the zinc borate, and then the decomposition on-set temperature remains unchanged. Large amount of inorganic filler can lead to the reduction of polymer's mechanical properties. In our work, we can clearly see that the doping of just 2.0 wt% of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ nanoflakes in PE provides the best flame retardant performance.

4. Conclusions

Hydrophobic zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) nanoflakes were successfully synthesized via solid-liquid reaction of zinc

oxide (ZnO) and boric acid (H_3BO_3) with oleic acid as the modifying agent. A series of XRD patterns of the obtained products show that, in order to get pure $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$, the reaction temperature should be higher than 85°C ; and the molar ratio of boric acid and zinc oxide should be higher than 3:1; the reaction time should be longer than 2 h. By conducting morphological and microscopic analyses, we found that zinc borate displayed nanoflake morphology with particle size of around 100–200 nm, thicknesses less than 100 nm and there were uniform mesopores with the diameter about 10 nm within the particles. The contact angle test shows that the modifying agent oleic acid changes the superficial features of the zinc borate nanoflakes from hydrophilic properties to hydrophobic properties. The $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ nanoflakes largely improve the flame retardant of PE, especially when the zinc borate is modified by OA. When the dosage of hydrophobic zinc borate in PE reaches 2.0 wt%, the composite has the best flame retardant performance.

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