

Research Article

Synthesis and Characterization of Zinc Borate Nanowhiskers and Their Inflaming Retarding Effect in Polystyrene

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Zinc borate nanowhiskers $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ were in situ successfully synthesized via one-step precipitation reaction. A set of experiments was performed to evaluate the influence of reaction temperature. Increasing the temperature up to 70°C led to the high purity of zinc borate nanowhiskers with a monoclinic crystal structure measuring 50 nm to 100 nm in diameter and approximately $1\ \mu\text{m}$ in length. However, higher temperature decreases the crystallization due to the emergence of other styles of zinc borate. Flame-resistant nanocomposites of polystyrene and zinc borate nanowhiskers were also successfully synthesized. The samples were investigated by XRD, FESEM, FTIR, and TG. The mechanical properties of the composites were also tested. The incorporation of zinc borate nanowhiskers improved the thermal and mechanical properties for polystyrene. FESEM images show that zinc borate nanowhiskers increased the smoothness of composites. The composites presented good responsive behavior in relation to LOI (limiting oxygen index) allowing them to be suitable for green flame retardants.

1. Introduction

Zinc borate is a commonly used material in a variety of industries. It is used as a lubricating oil additive and in refractory ceramic materials, nonlinear optical materials, and solid electrode materials, but its use in fire retardants is its most typical application [1–3]. Zinc borate is naturally occurring but it is also easily synthesized and is used as an inorganic fire retardant material because of its high surface area and its good mechanical properties.

The addition of zinc borate has been demonstrated to improve the fire retardant properties of polymers [4]. The effect of zinc borate has been attributed to the formation of a glassy char at the polymer surface which protects the bulk from the combustion zone. In addition, zinc borate has been recognized for its ability to suppress smoke and afterglow, which often occur during the burning of a polymer composite or wood [5, 6]. The compounds $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$, $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$, and $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ are widely used as fire retardants. Among these, $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ is the most important as it can be incorporated into polymers at much

higher temperatures due to its exceptionally high dehydration temperature (about 415°C).

Nanomaterials have unique properties due to their small size and as a result they have found applications in many industries [7, 8]. Researchers have become increasingly interested in nanoreinforcement of polymer matrices as it has been suggested that in general nanocomposites show improved properties when compared to similar microsized systems [9]. Nanowhiskers in particular have enhanced performance resulting from their high surface area and good mechanical properties [10–15]. Thus, there has been a growing interest in synthesizing nanowhiskers as nanoreinforcement for polymer matrices [16]. In these studies, fire retardant performance and mechanical properties of polymer matrices are improved by controlling the morphology and size of nanowhisker additives.

Recently, Zheng et al. [17] synthesized $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ nanowhiskers and demonstrated their ability to increase the thermal stability of polyethylene. However, the application of zinc borate nanowhiskers to other polymers has not been explored. In this study, zinc borate nanowhiskers

($4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$) were synthesized and their flame retardant behavior in polystyrene matrix was characterized. The effect of reaction temperature on the nanowhiskers formation is investigated by XRD and FESEM. The effects of the nanowhiskers on the thermal stability and mechanical performance of the polymer matrix were also evaluated. These results and the LOI provide information which allow for promising applications of this material.

2. Experimental Procedure

2.1. Materials. All chemicals in the synthesis process of this experiment, namely, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (99.5 wt.% purity), $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ (99.5 wt.% purity), sodium dodecylbenzenesulfonate (SDBS) (99.5 wt.% purity), polystyrene, NaOH (96 wt.% purity), absolute ethanol, and cyclohexane, were bought from Tianjin Reagent Factory (Tianjin, China) and used as reactants without further purification. Distilled water was used during the treatment and synthesis processes.

2.2. Synthesis of Zinc Borate Nanowhiskers. In a typical procedure, 1.91 g of $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ and 0.5 g of sodium dodecylbenzenesulfonate (SDBS) are dissolved in 50 mL of distilled water at room temperature in a 1 L constant temperature water bath reactor equipped with a reflux condenser and a mechanical stirrer operating at 300 rpm. The reactor is placed in a water jacket to control the reaction temperature. The slurry is then heated at constant temperature for 30 min. Subsequently, a solution of 5.95 g $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 10 mL of distilled water is added and stirred at 600 rpm. NaOH solution is used to adjust the pH to 7.0. The resulting solution is stirred for 7 h. The resulting precipitate is separated via centrifugation, washed with absolute ethanol and distilled water to remove adsorbed ions, and dried in a vacuum oven at 80°C for 12 h giving zinc borate nanowhiskers as a white powder.

2.3. Synthesis of Polystyrene/Zinc Borate Nanowhiskers. 15 g polystyrene is dissolved in 100 mL of cyclohexane in a 250 mL three-neck round-bottom flask equipped with a mechanical stirrer. The solution is stirred at 800 rpm until homogeneous. Zinc borate nanowhiskers are then added to polystyrene solution over the course of 2 h. Pouring the mixture onto a piece of clean glass gives the final polystyrene/zinc borate nanowhiskers composites.

2.4. Characterizations. Powder X-ray diffraction (XRD) measurements were carried out using a Bruker AXS GmbH Bruker D8 FOCUS automatic X-ray diffractometer to identify the crystal structure of the samples using Ni-filtered and graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, and 40 mA) with a step size of 0.02° . The registrations were performed in the 5° – 80° (2θ) range. HITACHI X-650 field-emission scanning electron microscope (FESEM) was used to characterize the morphology and size of the product (before SEM imaging, the sample was coated with thin layers of gold). Fourier transform infrared (FT-IR) spectroscopy of the samples as powder-pressed KBr pellets was examined

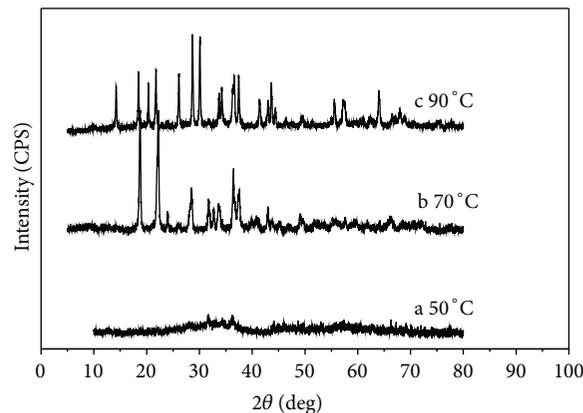


FIGURE 1: XRD patterns of samples obtained at different reaction temperature. (a) Reaction temperature: 50°C . (b) Reaction temperature: 70°C . (c) Reaction temperature: 90°C .

in the wave number range from 4500 to 400 cm^{-1} with a PerkinElmer 2000 spectrophotometer. The thermal gravimetric analysis (TG) was carried out on NETZSCH STA 409 instruments under N_2 atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. Mechanical property of composite samples was studied in a AG-10KNA Material Machine and the method was followed ASTM638 standard. LOI data of all products were obtained at room temperature with an oxygen index instrument (DRK304) (Jinan Drick Instruments Co., Ltd., China) produced by Jinan Drick Instruments Co., Ltd., according to ASTM D2863-77 standard. The dimensions of all samples are $120 \text{ mm} \times 7.0 \text{ mm} \times 3.0 \text{ mm}$.

3. Results and Discussion

3.1. XRD Spectra of Zinc Borate. The samples with a sort of stable white powders were obtained at room temperature. The XRD of zinc borate synthesized at different reaction temperature (50°C , 70°C , and 90°C) is illustrated in Figure 1. The data reveal that as the reaction temperature increases the resulting nanowhiskers become more crystalline. When the reaction temperature is set to 50°C , XRD of the resulting product shows only low intensity reflections demonstrating that the sample is largely amorphous (Figure 1, a). In contrast, when the reaction temperature is increased to 70°C , high-intensity peaks are observed at $2\theta = 16.40^\circ$, 20.35° , and 36.35° (Figure 1, b), indicating that the organized microporous framework in the sample is composed of a structure which is in good agreement with the crystal structure of zinc borate [18]. Additionally, when compared to the sample synthesized at 50°C , the microporous ordering is significantly improved in samples synthesized at 70°C . Increasing the reaction temperature to 90°C , however, results in the observation of many extra peaks (Figure 1, c). Some of the peaks, at about 34.45° and 56.63° , correspond to pure zinc oxide and other peaks to a different structure of zinc borate. This result indicates that when the reaction temperature is too high, zinc oxide reacts incompletely and can generate an undesirable form of zinc borate. Therefore, the optimal reaction temperature for $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ nanowhiskers is 70°C .

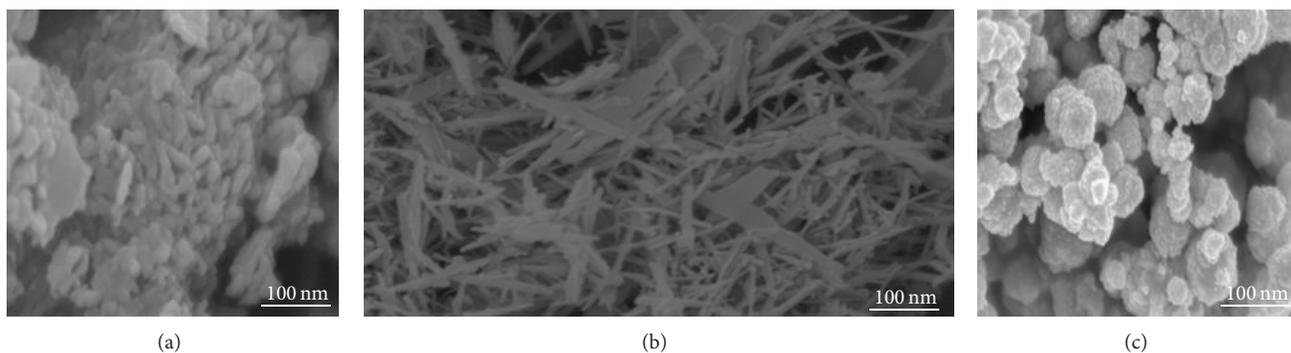


FIGURE 2: FESEM images of samples obtained at different reaction temperature. (a) Reaction temperature: 50°C. (b) Reaction temperature: 70°C. (c) Reaction temperature: 90°C.

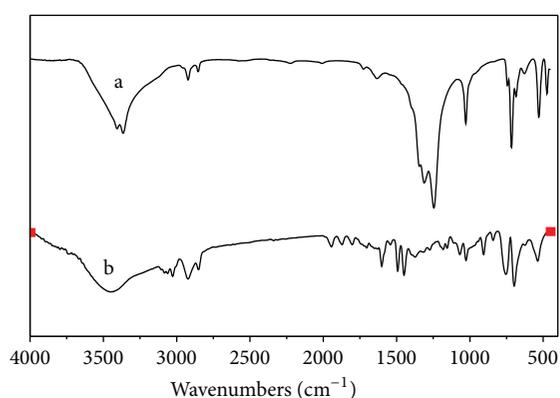


FIGURE 3: FT-IR images of the samples. (a) Zincborate nanowhiskers. (b) Polystyrene/zinc borate nanowhiskers composite materials.

3.2. FESEM Micrograph of Zinc Borate. The effects of reaction temperature on the zinc borates morphology were evaluated using SEM. Figure 2 shows the SEM images of zinc borate synthesized at 50°C, 70°C, and 90°C. The material synthesized at 50°C has small-sized whiskers with many disordered blocks. In contrast, the material synthesized at 70°C is composed of relatively uniform whiskers which are 50–100 nm in diameter, demonstrating that increased reaction temperature can promote the formation of ordered whiskers with regular morphology. However, when the temperature was further increased to 90°C, the sample consisted of several tiny-sized particles with irregular morphology. These experimental results show the effects of reaction temperature on the morphology of zinc borate nanowhiskers which are likely caused by changes in growth mechanisms and rates of crystallization.

3.3. FT-IR Spectrum of the Samples. The FTIR spectra of zinc borate nanowhiskers and of polystyrene/zinc borate nanowhiskers composites are shown in Figures 3-a and 3-b, respectively. The intensity of the absorption band at 3480 cm^{-1} , corresponding to the bending vibration of -OH, increases in the spectrum of polystyrene/zinc borate

nanowhiskers composite relative to that of the nanowhiskers alone. Additionally, absorption bands at 3200 cm^{-1} and 3000 cm^{-1} emerge in the composite, implying that the -OH groups in zinc borate nanowhiskers interact with the polystyrene matrix. The absorption band at 1630 cm^{-1} also indicates interaction between the nanowhiskers and polystyrene. The absorption bands at 1605 cm^{-1} and 1541.87 cm^{-1} in the composite can be attributed to the $\nu\text{C}=\text{C}$ (benzene) and result from the presence of polystyrene. In addition, the absorption at 2922.54 cm^{-1} corresponds to the B-H stretching mode and the peaks at 1213.84 cm^{-1} , 718.26 cm^{-1} , and 537.57 cm^{-1} can be attributed to the B(3)-O stretching vibrations indicating the presence of zinc borate in the composite. Together, the FTIR results show that zinc borate nanowhiskers have been successfully introduced into the framework of the polystyrene.

3.4. FESEM Micrograph of the Composites. Many properties of polymers can be improved by adjusting their morphologies through the use of additives. The effects of the addition of zinc borate nanowhiskers on the morphology of polystyrene were evaluated using SEM. Figure 4 shows the FESEM micrographs of the fractured surface of pure polystyrene (Figure 4(a)) and the polystyrene/nanowhisker composite material (nanowhisker content is 7 wt. % (Figure 4(b))). In the pristine material, there are a number of discontinuous blocks of polymer mixed with large voids, which is undesirable in the macromolecule materials (Figure 4(a)). In comparison, the micrograph of the composite shows a fracture surface which is more homogeneous and continuous (Figure 4(b)). In the composite, no voids or blocks of polystyrene were observed and, interestingly, the interface between the polymer and nanowhiskers is not clear, suggesting that a protective layer has been formed in the composite which could protect the polymer from burning during the combustion process and improve the flame retardant behavior of the composite. This result is consistent with analysis of LOI.

3.5. TG of the Samples. TG is a widespread method used to investigate the thermal decomposition of polymers.

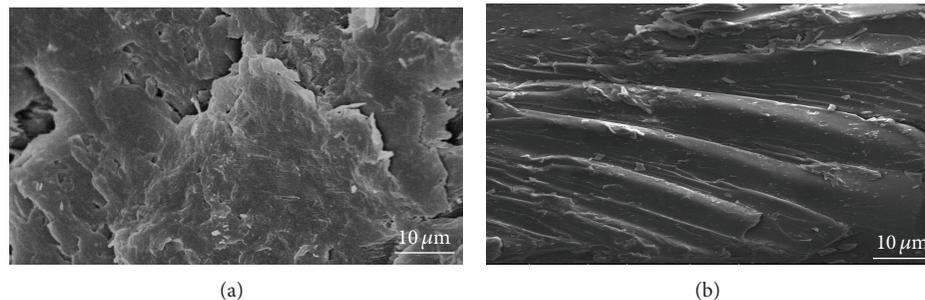


FIGURE 4: FESEM images of the products: (a) pure polystyrene and (b) polystyrene/zinc borate nanowhiskers composite materials (zinc borate nanowhiskers $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ content is 7 wt.%).

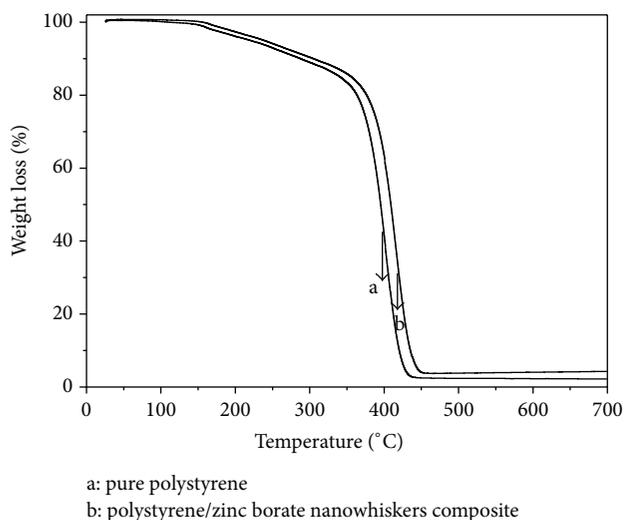


FIGURE 5: TG of the samples: (a) pure polystyrene and (b) polystyrene/zinc borate nanowhiskers composite materials (zinc borate nanowhiskers $4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$ content is 7 wt.%).

Figure 5 shows the degradation curves of pure polystyrene (Figure 5, a) and the polystyrene/nanowhiskers composite (nanowhisker content is 7 wt.% (Figure 5, b)). The TG curve of pure polystyrene shows that its weight changes from 200°C to 500°C while the TG curve of the composite shows that dehydration occurs between 220°C and 530°C. The mass remainder ratios of polystyrene and the composite at 350°C were 83.4% and 86.2%, respectively. The difference between the two is probably caused by a few low molecular weight polymers which are less volatile in the polystyrene/zinc borate nanowhiskers composite. Additionally, because they release water into the vapor phase, the zinc borate nanowhiskers can effectively dilute the volatile species emanating from polymer degradation. A notable mass loss was observed when the temperature increased to 400°C, indicating that the nanocomposite has a higher decomposition temperature than pure polystyrene. It is reasonable to assume that the collapse of the nanocomposite structure during combustion forms a phosphate carbonaceous structure on the surface, which acts as a barrier to mass transport and insulates the underlying

polystyrene. Through this mechanism, the addition of zinc borate can improve the thermal stability of polystyrene.

3.6. Mechanical Property of Composite Samples. Figures 6(a) and 6(b) show the effects of zinc borate nanowhiskers loading on the mechanical properties of the composite. These results were obtained from the tensile test on the composites. The trends show that the tensile strength and tensile strain at break both increase with increased loading of zinc borate nanowhiskers until they reach a maximum and decrease with further addition of zinc borate nanowhiskers. When the content of the zinc borate nanowhiskers is 7 wt.%, the tensile strength reaches a maximum with a tensile strain at break of 26.4 MPa. These results indicate that the introduction of zinc borate nanowhiskers improves the tensile properties of polystyrene. The result may be due to the small size of the zinc borate nanowhiskers, resulting in a high surface-to-volume ratio and a large aspect ratio and thus a high-energy surface. The enhanced bonding between the polymer matrix and the nanoparticles with high interfacial energy is the cause of improved mechanical properties in these composites. The decrease in mechanical strength when zinc borate nanowhiskers content is too high probably results from the aggregation of zinc borate nanowhiskers which inhibits the bonding between the polymer matrix and the nanowhiskers.

3.7. LOI of the Composite Samples. Comparison of polystyrene/zinc borate nanowhiskers and polystyrene/commercial ZB2335 composites was accomplished by LOI as shown in Figure 7. The LOI of polystyrene was dramatically enhanced as zinc borate nanowhiskers were loaded up to 7%. It was shown that zinc borate nanowhiskers for polystyrene have a remarkable resistance characteristic. With the filler content improved to 9%, the reduction of LOI is tender. The probable reason is that zinc borate nanowhisker particles do not satisfactorily disperse. The curves show that the flame retardation of polystyrene/zinc borate nanowhiskers composites is exceedingly excellent compared with that of ZB2335 for polystyrene. This result shows that the optimum content of zinc borate nanowhiskers in the nanocomposites had the outstanding capability of flaming retarding.

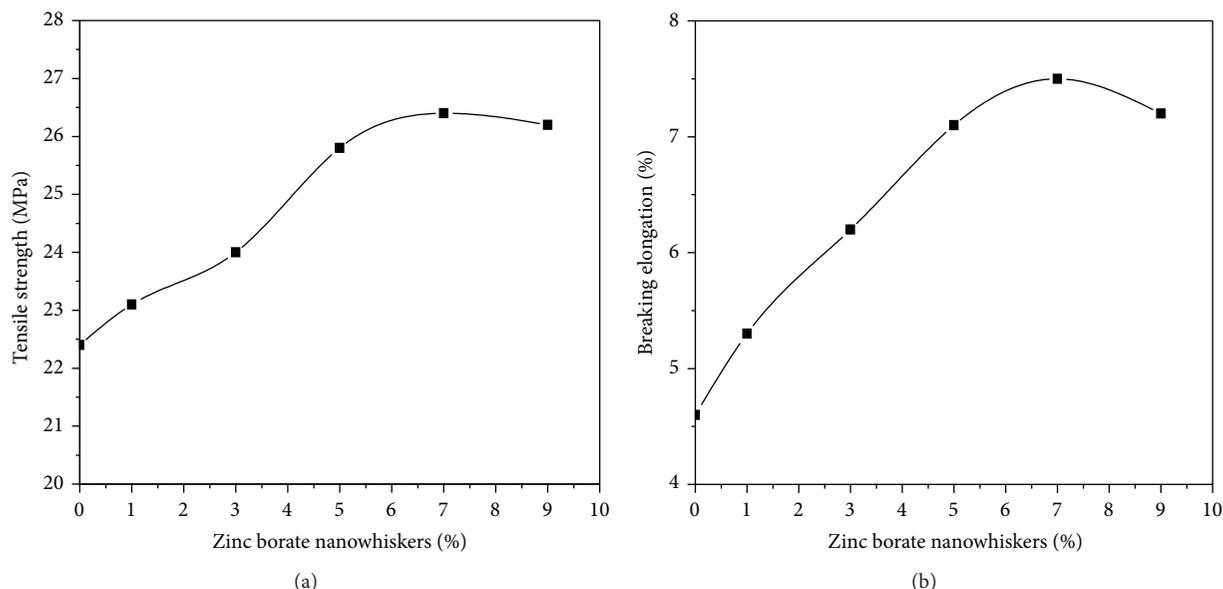


FIGURE 6: Effect of zinc borate nanowhiskers loading on mechanical properties of polystyrene/zinc borate nanowhiskers composites. (a) Effect of zinc borate nanowhiskers loading on tensile strength of polystyrene/zinc borate nanowhiskers composites. (b) Effect of zinc borate nanowhiskers loading on tensile strain at break of polystyrene/zinc borate nanowhiskers composites.

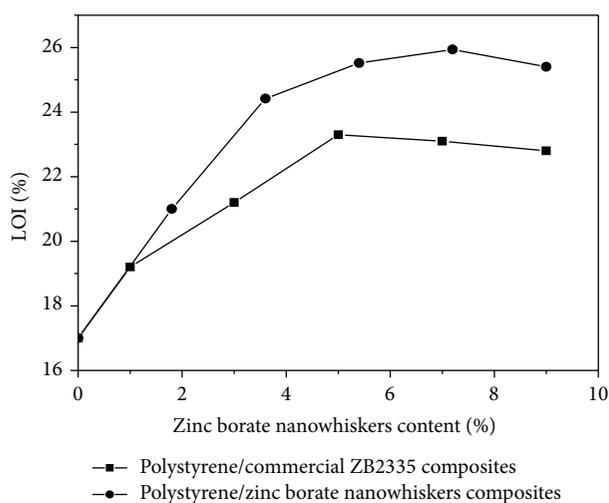


FIGURE 7: LOI of the composites.

4. Conclusions

Zinc borate nanowhiskers were successfully synthesized using the one-step precipitation method with zinc nitrate and borax as raw materials under the optimum temperature (70°C). The morphological analyses results revealed that zinc borate exhibited nanowhiskers morphology with particle sizes of 50 nm to 100 nm. The formed polystyrene/zinc borate nanowhiskers composite was confirmed by FTIR and FESEM data. The TG curve results indicate that the thermal stability of the polystyrene/zinc borate nanowhiskers composite is better than that of pure polystyrene. Improved bonding between the polymer matrix and the reinforcing phase results

in improved mechanical properties. Moreover, zinc borate nanowhiskers mainly improve the flame retardant property of polystyrene. When the dosage of zinc borate in polystyrene reached 7 wt.%, the LOI of the composite was the highest, indicating that the composite has the best flame retardant performance. Therefore, zinc borate nanowhiskers as green flame retardant have wide application in material industry.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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