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# Production of nano zinc borate ($4ZnO{\cdot}B_2O_3{\cdot}H_2O$) and its effect on PVC

Ayhan Mergen [a,*], Yeliz İpek [b], Hülya Bölek [a], Mustafa Öksüz [c]

[a] *Marmara University, Engineering Faculty, Metallurgical and Materials Eng. Dept., Göztepe Kampusu, 34722 Kadıkoy, Istanbul, Turkey*
[b] *Marmara University, Chemical Engineering Dept., Göztepe Kampusu, 34722 Kadıkoy, Istanbul, Turkey*
[c] *Marmara University, Faculty of Technology, Metallurgy and Materials Eng. Dept. Göztepe Kampusu, 34722 Kadıkoy, Istanbul, Turkey*

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**Abstract**

In this study, nano sized zinc borate powder with a formula of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ was synthesized using $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ as a starting chemical which was produced using a wet chemical method. After dissolving $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ in an ammonia solution, the clear solution was boiled until a white powder formed. The resultant powder was characterized with XRD, FTIR, TGA and TEM. XRD, FTIR and TGA results proved that the powder was belonged to the $4ZnO{\cdot}B_2O_3{\cdot}H_2O$. Nano composites of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$–polyvinylchloride (PVC) were produced by injection moulding by adding 1 and 5 wt% zinc borate powders into PVC to enhance its flame retardancy. Limiting oxygen index (LOI) of virgin PVC increased from 41% to 47% and 54% for the 1 and 5 wt% zinc borate added PVC, respectively. Nano zinc borate addition into the PVC does not have considerable negative effect on the mechanical properties of zinc borate–PVC composites even at high amounts of 5 wt%.


*Keywords:* Powders-chemical preparation; Nanocomposite; Mechanical properties

## 1. Introduction

Nano flame retardants are new group of flame retardants in the vicinity of nanometer dimensions. These flame retardants form a layer of carbon during combustion. Nano-sized flame retardants are very special because of their physical effects that provides a very efficient combustion resistance even at very low rates. Functions of a flame retardant during combustion are summarized below.[1]

1 Loosing water of their bodies and decrease the temperature of the burning material due to an endothermic reaction,
2 By creating a protective layer on the surface of combustible material, they cut off contact with air or oxygen and stop the progress of combustion,
3 By releasing non-combustible gases ($H_2O$, $CO_2$) from their bodies, they dilute oxygen of the environment and slow down the combustion event.

Although different materials have been used as flame retardant in polymeric materials like zinc borate, aluminum trihydrate, magnesium hydroxide, antimony oxide, phosphorus and bromine compounds, the most widely used ones are halogenated products, antimony trioxide and phosphorous compounds. Nevertheless, due to their hazardous effects the use of some flame retardants like halogenated flame retardants and antimony trioxide will be restricted.[2] The other fire retardants like aluminum trihydrate is not as effective as the others, although it is cheap and non-toxic.[2] Zinc borates are so interesting comparing with other flame retardants since they are non-toxic, smoke suppressant, afterglow suppressant, and anti-tracking agent and they have also anti-bacterial property.

Zinc borates as flame retardant used in different application areas of commercial materials: plastics and tires, cables, fire resistant paints, fabrics, electrical/electronic components, fire-resistant coatings, carpets, car/aircraft interior materials, textile and paper industry.[3–5] Zinc borate can help to produce a porous carbon layer on char, and this layer can be stable by $B_2O_3$. Zinc borate' refraction index is in the spectrum of most of organics, so when it is used on resin to mould board, it can guarantee the board transparency. Zinc borate can not only prevent polymer to fire and release heat, but obviously suppress smog and toxic gases. Zinc borates have varieties of chemical formulas with different dehydration temperatures. But the most widely used zinc borate types are $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$, $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ and $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ due to their excellent flame retardant property[6] and also due to their high and different dehydration

* Corresponding author. Tel.: +90 216 348 02 92x603; fax: +90 216 345 01 26.
*E-mail address:* ayhan.mergen@marmara.edu.tr (A. Mergen).

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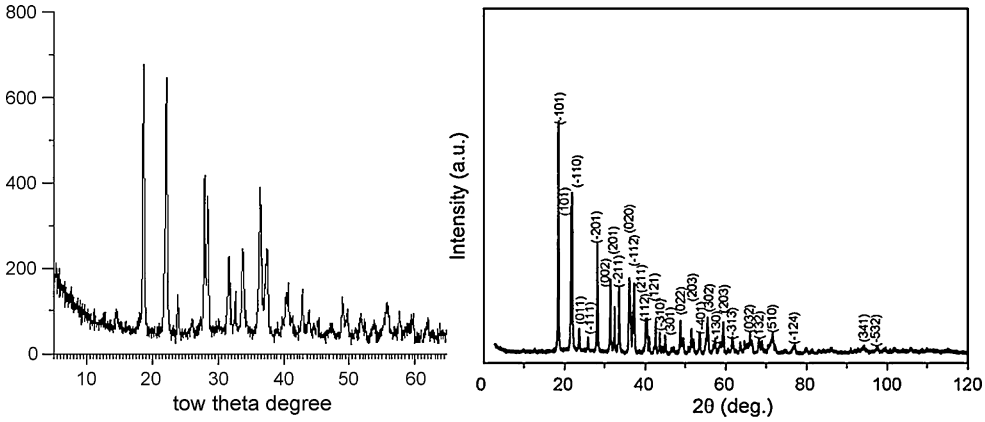


Fig. 1. (a) XRD pattern of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ powder synthesized in the present study and (b) XRD pattern of zinc borate given in the literature.[5,14]

temperatures which make them as attractive material in various polymeric systems. For example; $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ has a dehydration temperature of 290–300 °C while $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ has a dehydration temperature at 415–425 °C.[7] Such a high dehydration temperature makes these zinc borate compositions especially useful additive for polymers requiring high processing temperatures. In addition, $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ retains considerable translucency and allow the use of lower pigment loadings due to similar refractive index similar with most polymeric materials.

A few studies were performed to investigate into the flame retardancy effect of nano zinc borate on polymers. Li et al.[8] studied the flame retardancy effect of nanoflake zinc borate ($2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$) on polyethylene and explained that 2 wt% of zinc borate addition into polyethylene improved the flame retardancy significantly. Gao et al.[2] reported that nanozinc borate addition into polyurethane increased the thermal stability of polyurethane. Polyimide nano composites containing 1, 5 and 10 wt% nanometric zinc borate $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ increased the heat resistant properties of nano composite.[9]

It was reported that micronscale zinc borate can be used to partially or wholly replace antimony in PVC and halogenated flame retardant systems while maintaining flame retardant performance and reducing smoke evolution. Yıldız et al.[10] studied the effect of various amounts of zinc borate (Great Lakes Company (ZB 467)) on flame retardancy, oxidative stability and mechanical properties of polyurethane composite films containing 0.5, 1, 3, 5 and 7% zinc borate. Zinc borate increased the burning time and it was effective for flame retardancy, especially at higher concentrations. Polyurethane films containing zinc borate showed high oxidative stability. But mechanical properties slightly decreased with zinc borate.

Although zinc borates are used as flame retardants and smoke suppressants in various polymeric systems[2,7,11,12] no considerable study has been performed on the effect of nano zinc borates on polymers. As far as we are aware, no study was made on the flame retardancy of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$–PVC nano composite systems.

## 2. Materials and methods

Nano sized zinc borate powder with a chemical formula of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ was synthesized using $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ as starting material as middle product. Chemical precipitation method with ammonia was employed to synthesize the nano-sized $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ powder containing a single molecule of crystal water. Initially, zinc borate powder of $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ was produced by a wet chemical method using zinc nitrate ($Zn(NO_3)_2{\cdot}6.5H_2O$; Merck, >99%) and borax pentahydrate ($Na_2B_4O_7{\cdot}5H_2O$; supplied from Eti Mine Works, 99.9%) as starting materials.[13] After dissolving stoichiometric amounts of $Na_2B_4O_7{\cdot}5H_2O$ and $Zn(NO_3)_2{\cdot}6.5H_2O$ in water separately in a molar ratio of 1:8, they were mixed in aqueous ammonia solution ($NH_3$, Merck, 25%) at 45 °C. A white powder with a formula of $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ was produced which was then dried at 70 °C. $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ powder was dissolved in dilute ammonia solution. After obtaining a clear solution, it was boiled until all of the ammonia solvent was evaporated, during which a white powder was precipitated. 1 and 5 wt% of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ powders were added into PVC powder containing stabilizer and plasticizer and $4ZnO{\cdot}B_2O_3{\cdot}H_2O$–PVC nano composite material was produced using injection moulding technique.

X-ray diffractometer (XRD) measurements were carried out using a Rigaku X-ray diffractometer using Cu-Kα radiation and Ni filter at a scan rate of 2°/min between $2\theta$: 0° and 65°. In order to determine the percentage of weight loss, thermogravimetric analysis (TGA) was carried out using a Netzsch STA 449C with the heating rate of 10 °C/min between 25 and 800 °C under $N_2$. Fourier transform infrared (FT-IR) spectroscopy was performed to determine the O–H and B–OH interactions in the sample in the wave number ranging from 4000 to 450 $cm^{-1}$ using a THERMO (Nicolet) 6700 Model FTIR (Germany). Size of the zinc borate powders and their morphologies were examined using transmission electron microscopy (TEM, Jeol 200V; Japan). The fracture surfaces of zinc borate–PVC nano composites were characterized by means of scanning electron microscopy (SEM, JEOL,

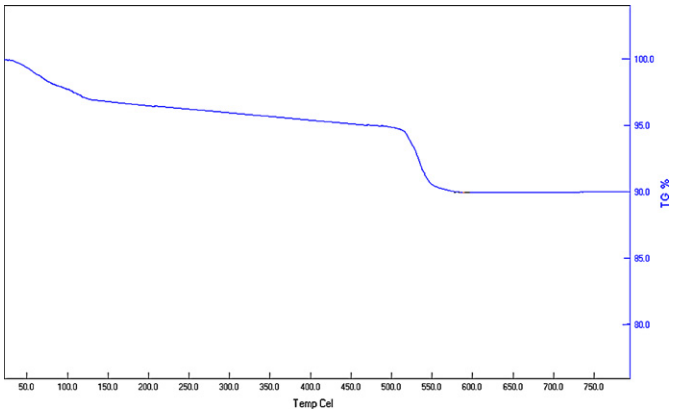


Fig. 2. TGA of synthesized zinc borate powder ($4ZnO{\cdot}B_2O_3{\cdot}H_2O$).

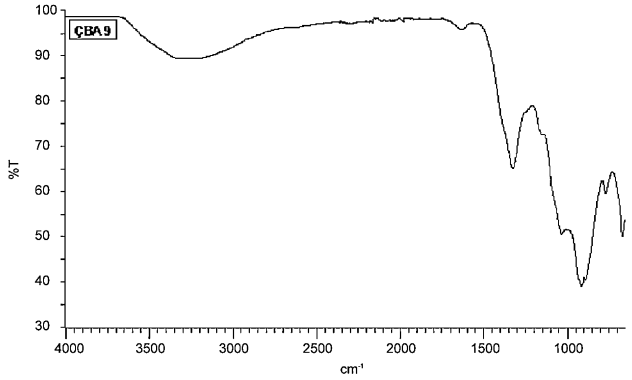


Fig. 3. FT-IR spectrum of 1 mol of hydrated zinc borate powder $4ZnO{\cdot}B_2O_3{\cdot}H_2O$.

JSM-5910LV; Japan). The flammability of the composites was determined by Limiting Oxygen Index (LOI). The effect of 1 and 5 wt% of zinc borate on mechanical properties of PVC nano composites was measured using a Zwick Universal Tensile Testing Machine Z010, according to ISO 37, Zwick Impact and hardness tester.

## 3. Results and discussion

### 3.1. Characterization of zinc borate powder

The XRD pattern of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ powder is fully overlaps with the XRD pattern in the literature[5,14] (Fig. 1). This implies that fast precipitation method successfully gives 1 mol of zinc borate with the formula of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$. TGA

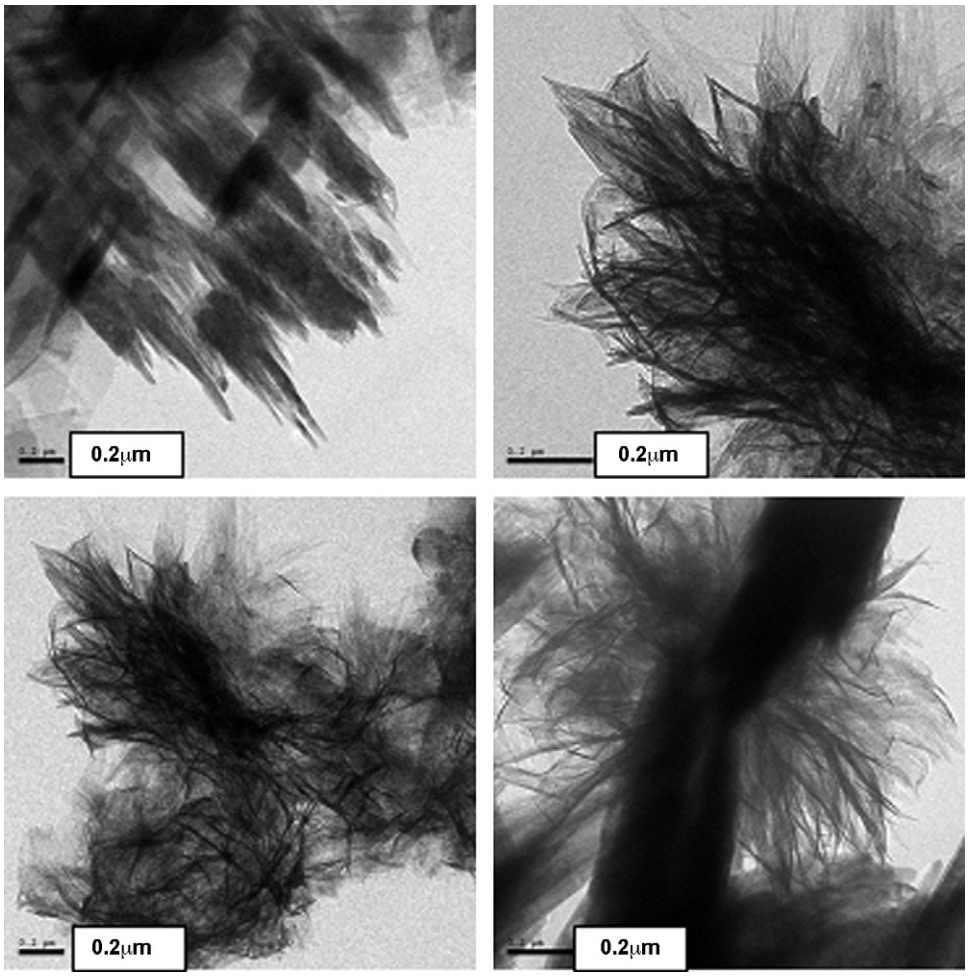


Fig. 4. TEM images of synthesized $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ powders.

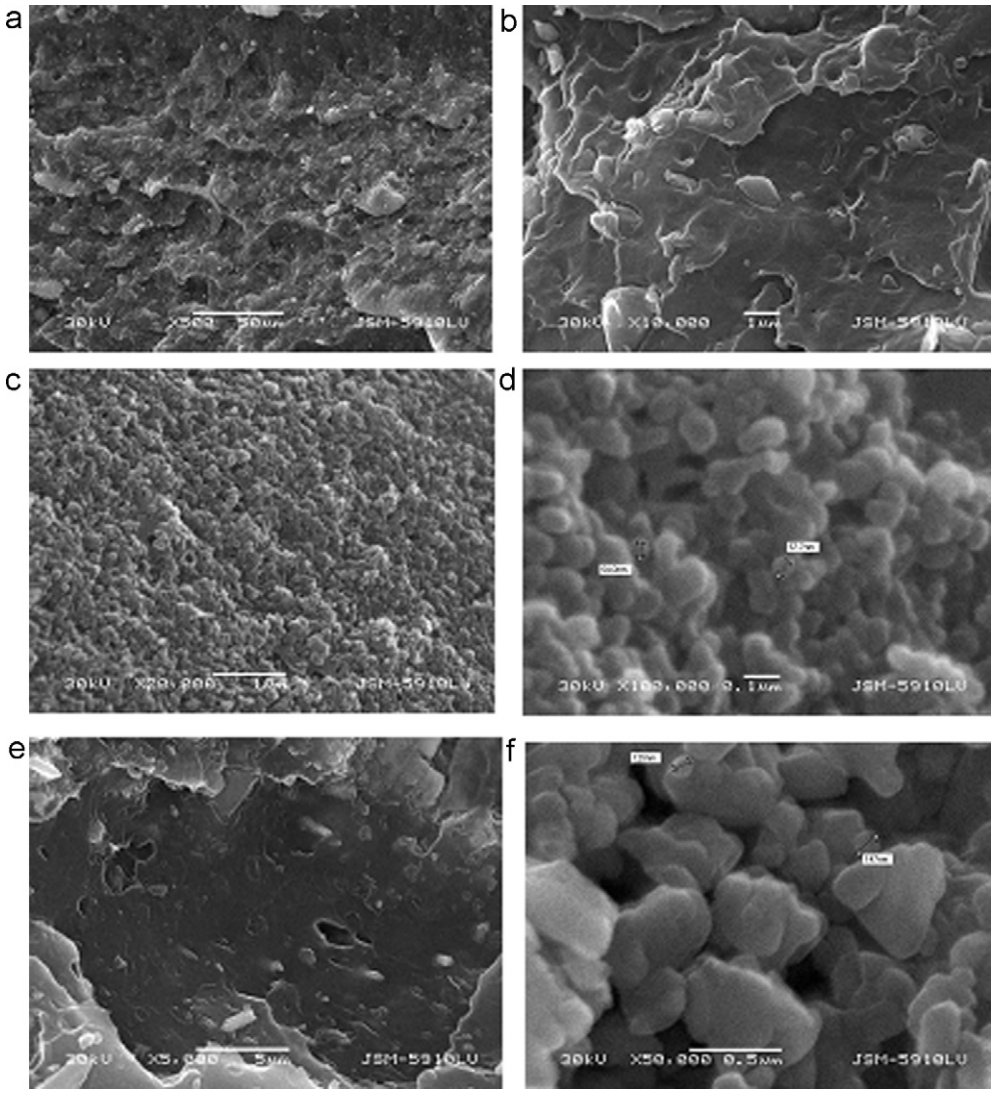


Fig. 5. SEM images of nano zinc borate ($4ZnO{\cdot}B_2O_3{\cdot}H_2O$)–PVC composites containing 1 wt% zinc borate (a, b, c, d) and 5 wt% zinc borate (e, f).

analysis of zinc borate containing a single molecule of crystal water ($4ZnO{\cdot}B_2O_3{\cdot}H_2O$) indicated that approximately 3 wt% of weight loss was observed up to 120 °C due to the evaporation of water adsorbed onto the surface of powder (Fig. 2). The powder was nearly stable up to around 520 °C and no considerable weight loss was detected. However, a sharp decrease in weight occurred between 520 and 560 °C. This weight loss of around 4.5 wt% was very near to the theoretical weight loss (4.4 wt%) of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$. These results confirmed the XRD results indicating that the appropriate chemical formula of zinc borate was $4ZnO{\cdot}B_2O_3{\cdot}H_2O$.

FT-IR analysis of zinc borate powder showed that there were hydroxyl and borate bonds in the synthesized powder and the results were identical with the literature[6,15] (Fig. 3). While the band at 3458 $cm^{-1}$ is the stretching of O–H, the band at 1634 $cm^{-1}$ is assigned to the H–O–H bending mode, which indicates that the compound containing the crystal water. The band at 1382 $cm^{-1}$ may be the asymmetric stretching of B(3)–O and the bands at 1100 and 788 $cm^{-1}$ are assigned as the asymmetric and symmetric stretching of B(4)–O, respectively. The band 608 $cm^{-1}$ is the symmetric pulse vibration of triborate anion indicating that the sample contains the $[B_3O_4(OH)_3]^{2-}$.

Morphology of powders, sizes and the degree of agglomeration was examined in TEM. The particles had a rod-shaped or acicular structure (Fig. 4). The thickness of the rods was between 5 and 50 nm, while the lengths of rod-shaped structures were above 1 μm. Zinc borate powders were partially agglomerated.

### 3.2. Characterization of zinc borate–PVC nano composites

LOI (Limiting Oxygen Index) measurement indicated that zinc borate addition into the PVC improved the flame retardancy

Table 1
% Limiting Oxygen Index (LOI) values of nanocomposites.

| Sample | LOI, % |
|---|---|
| PVC | 41 |
| 1 wt% $4ZnO{\cdot}B_2O_3{\cdot}H_2O$–PVC nanocomposite | 47 |
| 5 wt% $4ZnO{\cdot}B_2O_3{\cdot}H_2O$–PVC nanocomposite | 54 |

Table 2
Mechanical properties of virgin PVC and zinc borate (ZB) added PVC nanocomposites.

| Samples/mechanical properties | Tensile strength (MPa) | Impact strength (kJ/m$^2$) | Hardness (shore D) |
|---|---|---|---|
| Virgin PVC | 47.016 ± 0.691 | 13.38 ± 2.38 | 70 ± 1.0 |
| 1 wt%ZB–PVC | 46.446 ± 0.394 | 12.2 ± 1.04 | 69 ± 2.0 |
| 5 wt%ZB–PVC | 43.522 ± 0.431 | 9.65 ± 2.27 | 69 ± 1.5 |

of the composites. LOI gives very important information about relative flammability of polymeric materials. LOI is a percentage of oxygen in air mixture that is required for a material to burn. In other words, the LOI value is the oxygen/(nitrogen + oxygen) ratio. Flammability of the material decreases when this value increases. Table 1 gives the % LOI results for virgin PVC and zinc borate added PVC nano composites. Zinc borate addition increased the LOI value and as the zinc borate content increased, the LOI value also increased. The effect of flame retardancy of zinc borate is due to evaporation of crystal water and boron oxide that forms a strong protective layer against oxygen.

Fig. 5 shows the SEM micrographs of zinc borate–PVC nano composites. The distribution of zinc borate particles was nearly homogeneous. The size of zinc borate particles ranged between 50 and 120 nm and the distribution is relatively homogeneous, which indicates that no large agglomerates occurred during processing. The effects of nano zinc borate addition on mechanical properties of PVC composites were also investigated. Tensile and impact strengths and hardness results are given in Table 2. As the zinc borate content increased, the tensile and impact strengths and hardness of the PVC nano composites decreased but the decrease was not so significant. This reveals that the addition of nano zinc borate even at high amounts of 5 wt% did not have a considerable negative effect on mechanical properties.

## 4. Conclusion

Nano sized zinc borate powder with a chemical formula of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ was synthesized by a wet chemical method using $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ as a starting material. After dissolving the midproduct $2ZnO{\cdot}3B_2O_3{\cdot}3.0–3.5H_2O$ in ammonia solution, 1 mol of water containing zinc borate ($4ZnO{\cdot}B_2O_3{\cdot}H_2O$) was obtained by a fast evaporation of ammonia. XRD, FTIR and TGA analysis demonstrated that the chemical formula of zinc borate produced in this study belonged to the $4ZnO{\cdot}B_2O_3{\cdot}H_2O$. PVC nano composites containing 1 and 5 wt% zinc borate were produced by injection moulding. LOI and mechanical tests indicated that zinc borate addition significantly improved the flame retardancy of PVC nano composites without affecting the mechanical properties considerably.

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