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Production and characterization of hydrophobic zinc borate by using palm oil

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Abstract: Zinc borate (ZB) was synthesized using zinc oxide, boric acid synthesized from colemanite, and reference ZB as seed. The effects of reaction parameters such as reaction time, reactant ratio, and seed ratio on its yield were examined. Then, the effects of palm oil with solvents (isopropyl alcohol (IPA), ethanol, and methanol) added to the reaction on its hydrophobicity were explored. Reactions were carried out under determined reaction conditions with magnetically and mechanically stirred systems. The produced ZB was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and measurements of contact angle identified hydrophobicity. The results showed that hydrophobic ZB was successfully produced under determined reaction conditions. The change of process parameters influenced its yield and the usage of palm oil provided hydrophobicity.

Keywords: zinc borate; hydrophobicity; seed; contact angle; palm oil

1. Introduction

Zinc borate (ZB) can be used as a multifunctional synergistic additive with flame-retardant additives in polymers to improve their flame-retardant performance [1-2] and to reduce smoke evolution [3-4]. ZB is a multifunctional fire retardant containing different proportions of zinc and boric oxides [5].

ZB, which is widely used, is a white, nonhygroscopic, viscose, and powder product. The most important properties of ZB are low solubility in water and high dehydration temperature. ZB dehydrates above 290°C, and the borate, which is known as anhydrous ZB, has a thermal resistance of about 400°C and hydrolyzes with a strong acid. By this way, extended fire is prevented and flame retardancy with this property is provided [6-10].

Studies on the preparation and the hydrophobic properties of ZB are relatively few. ZB particles are hardly dispersed in a polymer matrix. In order to improve the thermal stability and the dispersion of ZB in the polymer matrix and the compatibility between ZB particles and the polymer matrix, the particles were first modified with a modifying agent [11-14]. Tian *et al.* [11] prepared crystal and hydrophobic ZB ($Zn_2B_6O_{11}\cdot 3H_2O$) nanodiscs by a wet method using $Na_2B_4O_7\cdot 10H_2O$ and $ZnSO_4\cdot 7H_2O$ as raw materials and oleic acid (OA) as a modifying agent. The optimal amount of OA was 1.0% of the mass of $Zn_2B_6O_{11}\cdot 3H_2O$. Chen *et al.* [12] prepared nanoflake-like ZB $2ZnO\cdot 2.2B_2O_3\cdot 3H_2O$ via coordination homogeneous precipitation method using ammonia, zinc nitrate, and borax as raw materials. The products had excellent flame-retardant effect, and the carbon residue ratio increased to 75% when the product content was about 12wt%. According to Shi *et al.* [13], 2D and 3D nano/microstructures of $4ZnO\cdot B_2O_3\cdot H_2O$ with different morphologies have been successfully synthesized by a hydrothermal route in the presence of surfactant polyethylene glycol-300 (PEG-300). Li *et al.* [14] synthesized hydrophobic ZB ($2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$) nanoflakes by employing solid-liquid reaction of zinc oxide (ZnO) and boric acid (H_3BO_3) in the presence of OA. The products had an effect on flame retardant of polyethylene, especially when the ZB was modified by OA. The contact angle quickly increased from 109.27° to 129.02° with the mass ratio of OA/ZB increasing from 0.5wt% to 2.0wt%. Chen *et al.* [15] studied production of ZB nanoflakes ($2ZnO\cdot 2.2B_2O_3\cdot 3H_2O$) via coordination and homogeneous precipitation of ammonia, zinc nitrate, and borax. Specifically, with a ZB concentration of 12wt%, the carbon residue ratio of polypropylene

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increased to 75%. Tian *et al.* [16] produced hydrophobic $Zn_2B_6O_{11}\cdot 3H_2O$ nanoplatelets by using $Na_2B_4O_7\cdot 10H_2O$ and $ZnSO_4\cdot 7H_2O$ as raw materials through one-step precipitation reaction with OA as a modifying agent. The measurement of relative contact angle and active ratio indicated that $Zn_2B_6O_{11}\cdot 3H_2O$ samples were hydrophobic. When the OA (0.5wt%) was added into the preparation process of $Zn_2B_6O_{11}\cdot 3H_2O$, its wettability decreased, and the relative contact angle increased to 116°. When the amount of OA increased to 1.0wt%, the droplet placed on it remained spherical and the relative contact angle increased to 132°. Shi *et al.* [17] investigated $4ZnO\cdot B_2O_3\cdot H_2O$ nanorods that were synthesized by a hydrothermal route with a surfactant of PEG-300 as a template. The study on the flame-retardant property of $4ZnO\cdot B_2O_3\cdot H_2O$ nanorods is under way. Köytepe *et al.* [18] studied the structural properties of polymer nanocomposites-containing nanoparticles of ZB in a polyimide matrix. The compositions were synthesized by means of an original "*in situ*" method, which allows the polyimide films and different concentrations of ZB particles in the matrix to be obtained.

In this study, ZB was synthesized by using ZnO, H_3BO_3 synthesized from colemanite, and reference ZB as seed. The effects of reaction parameters such as reaction time, reactant ratio, seed ratio, and palm oil on its hydrophobicity and yield were examined. Reactions were carried out with magnetically and mechanically stirred systems. The produced ZB was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and measurements of contact angle identified hydrophobicity.

2. Experimental

2.1. Materials and methods

H_3BO_3 (99.9% pure) and reference ZB as seed were obtained from Eti Mine Works. ZnO (97% pure) was acquired from Colakoglu Chemicals Ltd. Palm oil was provided from Fluka (Analytical). Solvents (IPA, methanol, and ethanol) were supplied by Prolab.

2.2. Production of ZB

Reaction mixtures (ZnO, H_3BO_3, seed, and palm oil in various solvents) were stirred magnetically (in 25 mL solution) and mechanically (in 800 mL solution) in different systems by using H_3BO_3 and ZnO. The amounts of reactants were calculated for different capacities of reactors. In the magnetically stirred system, the reaction was conducted in a closed glass beaker at 95°C on a magnetic stir plate. A digital sensor was used for temperature control. Parameters such as reaction time, H_3BO_3/ZnO molar ratio (2:1-5:1), and seed (0wt%-1.5wt%) were varied. Palm oil used in reactions was between 1wt% and 6wt% for various solvents (ethanol, methanol, and IPA) (0-8 mL). The seed ratio was 0wt%-1.5wt% in terms of H_3BO_3. The initial reaction conditions were determined gradually for each parameter (Table 1). In the mechanically stirred system, the synthesis was carried out in a 1.5 L glass reactor (total reactor volume) under determined conditions. Fig. 1 displays the experimental setup used in the investigation. The products were filtered, rinsed with distilled water, and dried at 105°C for 20 h. The yield values were calculated on the basis of ZnO (g) consumed:

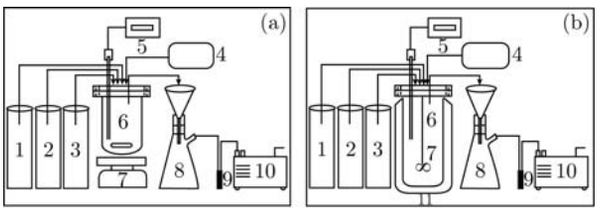

Fig. 1. Experimental setup: (a) magnetically stirred system; (b) mechanically stirred system. 1—H_3BO_3; 2—ZnO; 3—reference ZB; 4—palm oil + solvent; 5—digital temperature controller; 6—glass beaker (a) and reactor (b); 7—magnetic stir plate (a) and mechanical stirrer (b); 8—solid-liquid phase separation apparatus; 9—trap; 10—vacuum pump; 11—heating jacket (b).

Table 1. Experimental results of ZB production (reaction temperature 95°C, stirring rate 500 r/min, and seed 0.5wt% on the basis of H_3BO_3)

Concentration of H_3BO_3 / ($mol\cdot dm^{-3}$)	Reaction time / h	H_3BO_3/ZnO molar ratio	Reference ZB / wt%	Water volume / mL	Palm oil / wt%	Ethanol, Methanol, IPA / mL
120	1	2:1	0	**25**	1	0
	2	**3:1**	**0.5**		2	**2 (IPA)**
	3	4:1	1.0		**3**	4
	4	5:1	1.5		4	6
	5				5	8
					6	

Note: (1) The optimum parameters were determined in the magnetically stirred system. Then, the optimum points were iterated for the mechanically stirred system for 1.5 L volume (the available net volume of the reactor is 800 mL). (2) The concentration of H_3BO_3 in initial solution: 27.9wt%; H_3BO_3/ZnO: 3:1 (stoichiometric ratio, mole) (8.213/3.57 g).

$$2ZnO + 6H_3BO_3 = 2ZnO{\cdot}3B_2O_3{\cdot}3H_2O + 6H_2O \quad (1)$$

2.3. Analytical method

2.3.1. Analysis of ZnO

The amount of ZnO present in solid samples was determined by ethylenediaminetetraacetic acid (EDTA) titration. The sample (0.2-0.3 g) was dissolved in 37wt% hydrochloric acid (1 mL), and a solution of ammonia buffer (15-20 mL) was added into the dissolved sample solution to achieve a pH value of 9.5. The final solution was titrated with EDTA by adding a few drops of Erichrome black T indicator. The percentage of ZnO in the solid phase was calculated according to the following equation:

$$M = 0.408S \cdot \frac{E}{n} \quad (2)$$

where M, S, E, and n are the percentage of ZnO in the sample (wt%), the volume of EDTA (mL), the molecular weight of ZnO (g/mol), and the amount of the sample (g), respectively.

2.3.2. Analysis of B_2O_3

The sample (1 g) was dissolved in 37% hydrochloric acid. Then, 1 mL solution was added into 1 mL EDTA by using methyl orange indicator. This solution was titrated with 0.1 mol/m^3 NaOH. The titration proceeded by using mannitol and phenolphthalein. The percentage of B_2O_3 was calculated according to Eq. (3):

$$C = 56.36\% \times \frac{A}{B} \quad (3)$$

where A is the NaOH consumption (mL) for the ZB sample, B is the NaOH consumption (mL) for reference H_3BO_3,and C is the percentage of B_2O_3 (%).

2.4. Characterization

XRD, FT-IR, and SEM analyses were carried out by using Philips Panalytical-X'Pert Pro, Perkin-Elmer-Spectrum One instrument, and Cam Scan-Apollo, respectively. The hydrophobicity of ZB was determined with Contact Angle/Surface Tension Meter-Cam 200 to measure on a macroscopic level to characterize the average wettability of products. The samples were characterized by XRD to analyze the crystal structures of ZB with Cu K_α radiation at 45 kV and 40 mA. The registrations were mainly performed in the 2θ range of 0°–80°. The characteristic peaks of ZB were observed in the 2θ range of 15°-70° from XRD analysis as expected. In FT-IR analysis, the KBr disc method was used by mixing 4.0 mg ZB and 196 mg KBr to determine which functional groups were present in the samples. A pellet was obtained by pressing the powder mixture under a pressure of 7.85×10^4 Pa. SEM was used to determine the morphological structure of products and the samples were prepared with gold coatings for analysis. The results were consistent with the reference values.

3. Results and discussion

The synthesis of hydrophobic ZB was achieved by using H_3BO_3 produced from colemanite as a boron source and ZnO as a zinc source. Palm oil was used to produce hydrophobic ZB, and different solvents such as IPA, ethanol, and methanol were used to obtain homogenous phase. The results indicated that the addition of seed to the solution increased the yield of the reaction. In addition, the effects of reaction parameters such as reaction time, reactant ratio, and seed on the yield were examined by using a magnetic stirrer, and the results obtained by using a mechanically stirred glass reactor were compared at optimum reaction conditions. The yield calculated by using the mechanically stirred glass reactor was superior to the magnetic stirrer. The obtained products were characterized by XRD, FT-IR, and SEM. Contact angle measurements were carried out to determine the hydrophobicity of products. As a result, the change of process parameters influenced the yield and the usage of palm oil with different solvents provided hydrophobicity.

3.1. Effects of reaction parameters on yield

In this study, the yield of ZB was investigated as a function of various parameters and optimal parameters were determined. Thus, the effect of each parameter was investigated consecutively. The effect of reaction time on the yield is illustrated in Fig. 2(a). The temperature value selected was 95°C (up to 85°C) similar to a previous study [2]. If the option was to carry out the reactions at low temperatures, the reaction time would be longer [8].

Various ratios of H_3BO_3/ZnO (2:1-5:1) and reaction time intervals (1-5 h) were evaluated under otherwise identical conditions (reaction temperature 95°C, stirring rate 500 r/min, reference ZB 0.5wt%. The results revealed that the yield increased with an increase in reaction time from

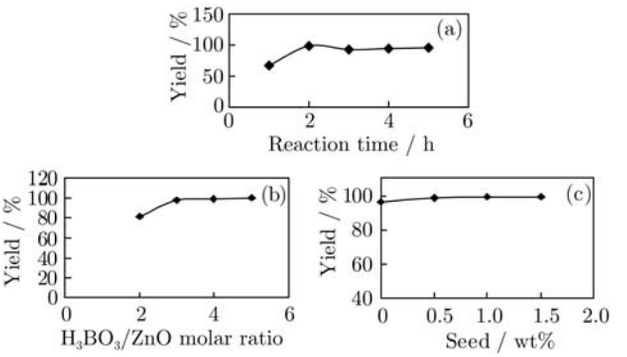

Fig. 2. Effects of reaction parameters on the yield: (a) reaction time (H_3BO_3/ZnO 3:1, reference ZB 0.5wt%, reaction temperature 95°C, and stirring rate 500 r/min); (b) H_3BO_3/ZnO (reaction time 2 h, reference ZB 0.5wt%, reaction temperature 95°C, and stirring rate 500 r/min); (c) seed content (H_3BO_3/ZnO 3:1, reaction time 2 h, reaction temperature 95°C, and stirring rate 500 r/min).

1 h to 2 h. However, an improvement in yield was not observed after 2 h. Thus, the optimal reaction time selected under the specified conditions was 2 h. The yield increased up to 98.56% for an H_3BO_3/ZnO ratio of 3:1 (Fig. 2(b)).

Reference ZB was used as a seed crystal to reduce the reaction time and to improve the quality of products. Alternatively, the yield increased with an increase in ZB concentration until the maximum value was obtained at 0.5wt% ZB. As shown in Fig. 2(c), the amount of seed greater than 0.5wt% did not alter the yield; thus, 0.5wt% of seed was selected for further studies.

First, the effect of palm oil on the yield was examined and IPA (2 mL) was determined as relevant solvent with respect to the yield (Fig. 3). The effect of palm oil on the yield was investigated in the range of 1wt%-6wt% (with respect to total mass). If palm oil was added without using any solvent into the mixture, palm oil could not be dispersed homogeneously in the solution.

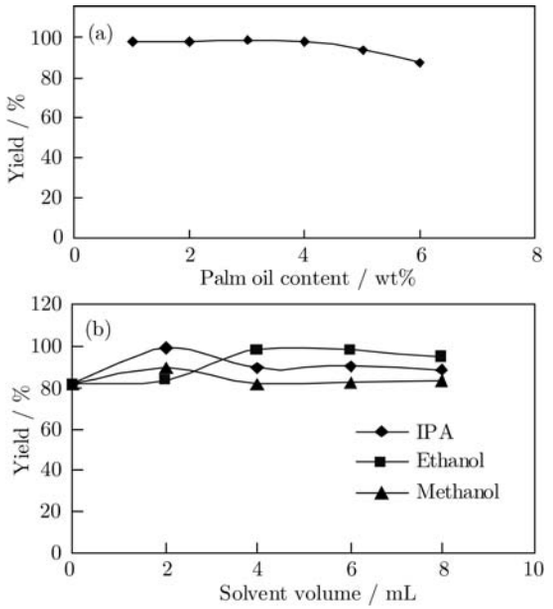

Fig. 3. Effects of palm oil and solvent amounts on the yield: (a) palm oil (reaction time 2 h, H_3BO_3/ZnO 3:1, reference ZB 0.5wt%, reaction temperature 95°C, and stirring rate 500 r/min); (b) solvent (reaction time 2 h, H_3BO_3/ZnO 3:1, palm oil 3wt%, reference ZB 0.5wt%, reaction temperature 95°C, and stirring rate 500 r/min).

Palm oil is ideally suited for use as an ingredient in different technologies, as it has 20%-22% solid fat content at 20°C, which helps in the formulation of products with a plastic range. It tends to crystallize in small β-prime crystals, a property desirable for various applications. Palm oil also has functional attributes that make it a valuable ingredient in formulations.

Palm oil (autoignition temperature: 316°C) is used in various applications as a wood preservative and flame retardant. In addition, palm oil is a relevant modifying agent due to its high autoignition temperature and providing high yield.

The yield values were obtained higher in the mechanically stirred system than the magnetically stirred system. The reactions were carried out in both the magnetically and mechanically stirred systems by using relevant solvent (2 mL IPA) and compared under identical optimum conditions. The findings were compared with small-scale reactor experiments in a literature and they are compatible to this work [19].

The optimum reaction conditions were the reaction time of 2 h, the H_3BO_3/ZnO of 3:1, the reaction temperature of 95°C, the stirring rate of 500 r/min, 3wt% palm oil, 2 mL IPA, and 0.5wt% reference ZB. The yield was determined as 98.56% in the magnetically stirred system and 99.98% in the mechanically stirred system.

3.2. Structure analysis of ZB

XRD analysis showed that the ZB peaks of products were similar to the peaks of reference ZB. The characteristic peaks of ZB were observed in the 2θ range of 15°-70° from XRD analysis as expected (Figs. 4 and 5). All diffraction peaks were quite similar to $Zn_2B_6O_{11}{\cdot}3H_2O$ (JCPDS File No. 32-1464) and earlier reports [19-20].

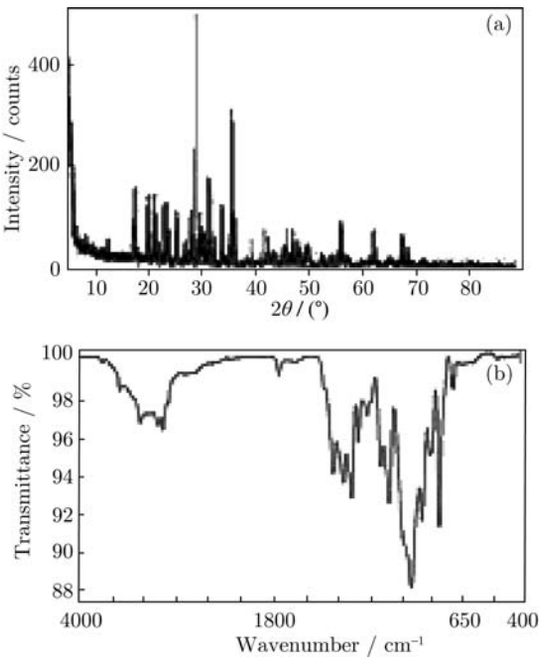

Fig. 4. Characterization of ZB under the optimum reaction conditions by using the magnetically stirred system: (a) XRD pattern; (b) FT-IR spectrum. Reaction time 2 h, H_3BO_3/ZnO 3:1, reaction temperature 95°C, stirring rate 500 r/min, palm oil 3wt%, IPA 2 mL, and reference ZB 0.5wt%.

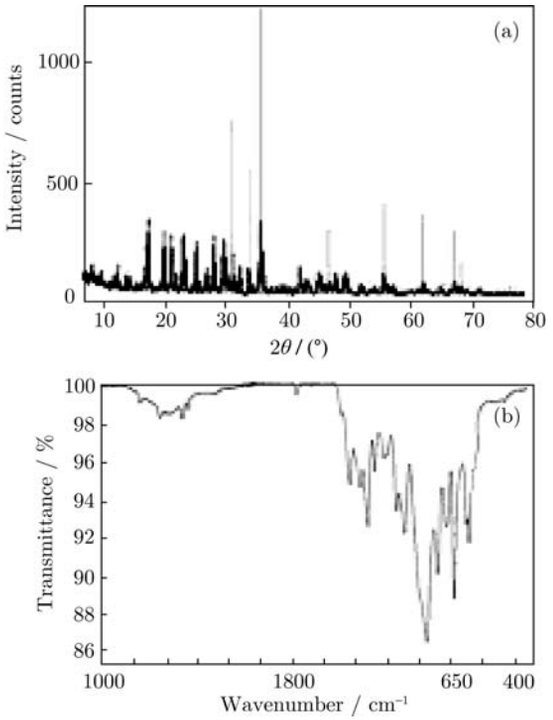

Fig. 5. Characterization of ZB under the optimum reaction conditions by using the mechanically stirred system: (a) XRD; (b) FT-IR. Reaction time 2 h, H_3BO_3/ZnO 3:1, reaction temperature 95°C, stirring rate 500 r/min, palm oil 3wt%, IPA 2 mL, and reference ZB 0.5wt%.

FT-IR analysis was carried out by using Perkin-Elmer, Spectrum One instrument. The band that indicates stretching vibrations of OtH is obvious between 3457 and 3460 cm^{-1}. The C=O vibration peak of palm oil is observed at 1743 and 1744 cm^{-1}. The HtOtH bending vibration is observed at 1600-1650 cm^{-1} as a broad peak. Also, the peaks observed at 2890 and 2900 cm^{-1} are due to vibrations of CH_2 groups of palm oil adsorbed on ZB crystals. The presence of the band between 1407 and 1408 cm^{-1} was assigned to asymmetric stretching vibrations of trihedral (BO_3) borate groups. The peaks in the range of 922-1063 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of tetrahedral (BO_4) borate groups. The peak observed between 751 and 650 cm^{-1} wavelength indicates in-plane bending vibrations of trihedral (BO_3) groups (Figs. 4 and 5). As a result, the usage of different stirred systems did not affect the structure as previous studies [12, 19].

SEM was used to determine the morphological structure of products. The particle size of reference ZB changed between 858 nm and 1.78 μm (Fig. 6(a)). The particle diameters of produced ZB in the magnetically and mechanically stirred systems were in the range of 919 nm-1.72 μm and 545 nm-4.13 μm (Figs. 6(b) and (c)), respectively. As it can be seen from Fig. 6, the usage of palm oil and different stirring systems significantly affected the morphology of ZB. The solution was seen to be more homogenous in the mechanically stirred system than that in the magnetically stirred system. For instance, irregular particles were formed in the magnetically stirred system and in the absence of palm oil whereas rod-like particles were formed in the mechanically stirred system.

3.3. Analytical method

As shown in Table 2 and Fig. 7, the content of ZnO and B_2O_3 was determined using analytical methods. H_2O was the remaining of 100%. The content of crystal water in ZB structure for the magnetically stirred system was alike as the mechanically stirred system and reference ZB (reaction time 2 h, H_3BO_3/ZnO 3:1, reaction temperature 95°C, stirring rate 500 r/min, palm oil 3 wt%, reference ZB 0.5wt%, and 2 mL IPA).

Table 2. Contact angle values under the optimum reaction conditions

Run No.	Solvent	Amount of solvent / mL	Contact angle/ (°)
Reference ZB	—	—	0
1	—	0	113.64
2	IPA	2	105.31
3	IPA	8	103.27
4	Ethanol	2	113.13
5	Ethanol	8	115.01
6	Methanol	2	101.69
7	Methanol	8	97.19

Note: Reaction time 2 h, H_3BO_3/ZnO 3:1, reaction temperature 95°C, stirring rate 500 r/min, palm oil 3wt%, and reference ZB 0.5wt%.

3.4. Hydrophobicity test results

Water drop contact angle is a measure of the surface wetting characteristic. If the contact angle is less than 90°, the surface is wettible or hydrophilic. If the contact angle is more than 90°, the surface is unwettible or hydrophobic [16, 19].

In order to improve the compatibility between ZB and the polymer system, OA was generally used as a modifying agent to transform the superficial features of ZB from hydrophilic properties to hydrophobic properties [14, 16]. The contact angles were determined in the range of 109.27°-129.02° with usage of OA as discussed by Ref. [14].

The contact angle of pure ZB powder was 0° and the product was hydrophilic. ZB was very easy to be wetted by water when the modifying agent was not used as previous study [16]. On the contrary, the relative contact angle was measured 97.51° when 1wt% palm oil was used. When palm oil (2wt%) was added into the preparation process of ZB, the wettability decreased, and the relative contact angle increased to 121.1°. Although the amount of palm oil was used in the range of 3wt%-6wt%, the relative contact

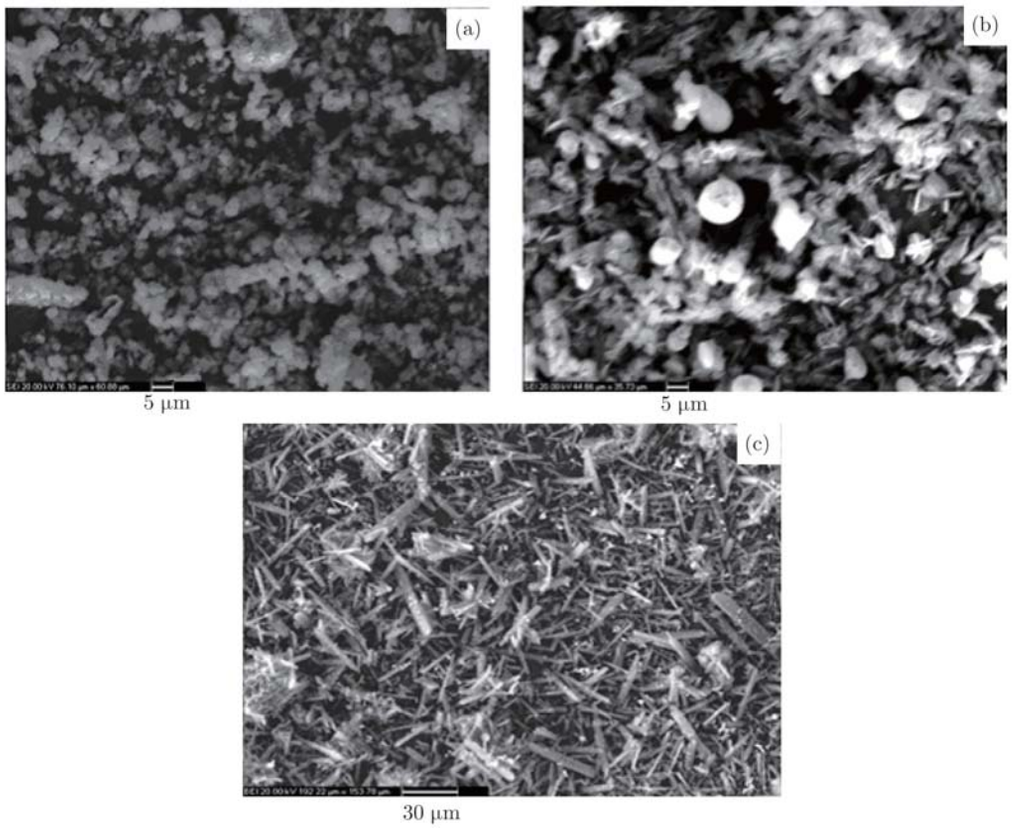

Fig. 6. SEM micrographs of samples: (a) reference ZB; (b) produced ZB with palm oil in the magnetically stirred system; (c) produced ZB with palm oil in the mechanically stirred system.

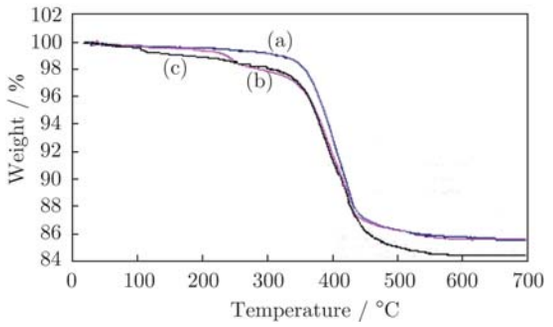

Fig. 7. TG curves of ZB: (a) reference ZB; (b) produced ZB with palm oil in the magnetically stirred system; (c) produced ZB with palm oil in the mechanically stirred system.

angle was higher than 100° (Fig. 8). 2 mL IPA was the relevant solvent amount to disperse palm oil. Ethanol was a convenient solvent to provide homogenous phase with palm oil. However, methanol was not proper solvent due to resulting in low hydrophobicity and yield.

When palm oil and OA were compared as a modifying agent, it was seen that the relative contact angle was determined as 115.01° (maximum) with using palm oil and ethanol. In a previous study [16], the relative contact angle increased to 132° as the OA amount increased to 1.0wt%.

Hydrophobic properties were improved by producing hydrophobic ZB depending on usage of palm oil. The analytical results (ZnO, B_2O_3) obtained under the optimum reaction conditions in different stirred systems were compared with the data of reference ZB (Table 3).

Table 3. Chemical composition and formulas of reference ZB and produced ZB under the optimum reaction conditions

Material	ZnO / wt%	B_2O_3 / wt%	H_2O / wt%	Formula
Reference ZB	39.21	47.46	13.33	$2.1ZnO{\cdot}3B_2O_3{\cdot}3.2H_2O$
ZB-magnetically stirred system	43.80	44.28	11.92	$2.6ZnO{\cdot}3B_2O_3{\cdot}3.1H_2O$
ZB-mechanically stirred system	35.22	49.02	15.76	$1.8ZnO{\cdot}3B_2O_3{\cdot}3.7H_2O$

Note: Reaction time 2 h, H_3BO_3/ZnO 3:1, reaction temperature 95°C, stirring rate 500 r/min, palm oil 3wt%, IPA 2 mL, and reference ZB 0.5wt%.

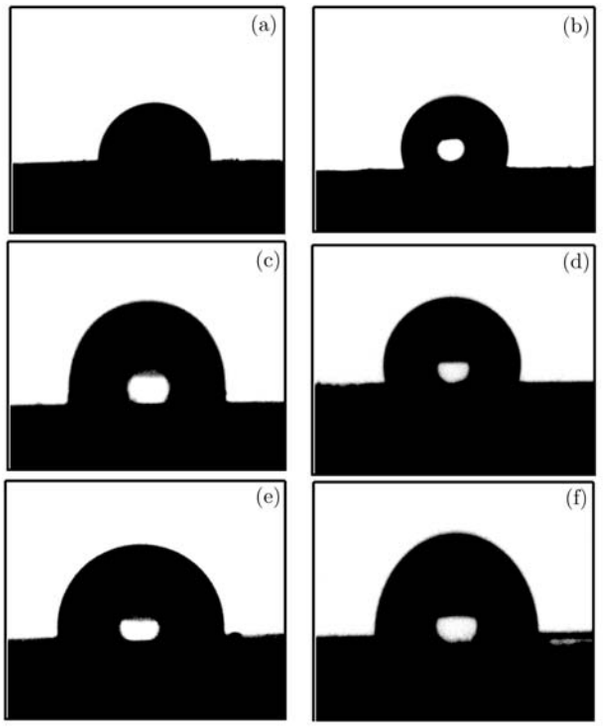

Fig. 8. Behavior of water droplets on thin pellets of ZB products with various amounts of palm oil (2 mL IPA): (a) 1wt%; (b) 2wt%; (c) 3wt%; (d) 4wt%; (e) 5wt%; (f) 6wt%.

The contact angles were 105.31° and 92.64° in the magnetically stirred and mechanically stirred systems for optimum reaction conditions, respectively (Fig. 9). The mechanical stirrer resulted in small droplets. Therefore, the contact angle in the mechanically stirred system was lower than that in the magnetically stirred system.

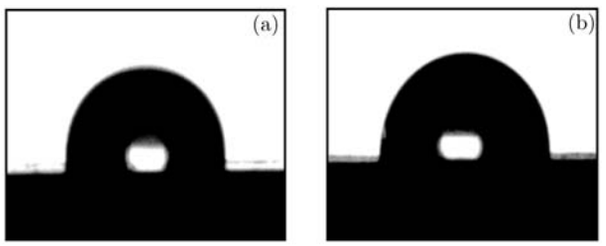

Fig. 9. Behavior of water droplets on thin pellets of ZB products under the optimum reaction conditions: (a) in magnetically stirred system; (b) in mechanically stirred system. Reaction time 2 h, H_3BO_3/ZnO 3:1, reaction temperature 95°C, stirring rate 500 r/min, palm oil 3wt%, IPA 2 mL, and reference ZB 0.5wt%.

4. Conclusion

XRD, FT-IR, and analytical results (ZnO, B_2O_3) showed that the synthesis of ZB was achieved and the usage of palm oil and different stirred systems did not affect the chemical structure. As a result of SEM analysis, it was observed that the morphological structure was changed by using different stirring systems. The contact angle of reference ZB was determined as 0°, which meant that reference ZB had a hydrophilic structure. Hydrophilic properties improved by producing hydrophobic ZB and using palm oil in various amounts. Reaction parameters and usage of palm oil with different solvents (IPA, ethanol, and methanol) affected the yield and hydrophobicity, respectively. Hydrophobic ZB with palm oil could be used as a proper flame retardant due to its high autoignition temperature (palm oil: 316°C) and ZB's flame-retardant property.

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