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## Zinc borate production with boron mineral source: effect of process parameters on yield and hydrophobicity

### Introduction

In recent years increasing amounts of boron compounds are being used as flame retardant additives (Genovese and Shanks 2007) in plastic materials. Zinc borates (Shete et al. 2004) are commonly used in rubber, plastic, ceramic, paint, glass (Gaafar et al. 2009), electric insulation, wood applications, cement, medicine and flame retardants (Igarashi et al. 2002; Sawada et al. 2004). Zinc borates (Eltepe et al. 2007) have been used as flame retardant (Giúdice and Benítez 2001), smoke suppressant, afterglow suppressant, and anti tracking agent in both halogen-containing and halogen-free polymers. Furthermore, zinc borates (Schubert et al. 2003) have been used as a preservative in wood (Garba 1999) composites, as anticorrosive pigments in coatings and as polymers (Yıldız et al. 2009) additives to promote char formation, to suppress smoke and to retard combustion (Shi et al. 2008; Tian et al. 2008).

Surface modification of zinc borate (Gürhan et al. 2009; Chang et al. 2006) with hydrophobic properties lead to a great expansion of its applications. Zinc borate (Ting et al. 2009) particles are hardly dispersed in a polymer matrix. In order to improve thermal stability and

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the dispersion of zinc borate in polymer matrix and the compatibility between zinc borate particles (Tian et al. 2006) and polymer matrix, particles were firstly modified with modifying agent (Shi et al. 2009).

Koytepe et al. (2009) studied the structural properties of polymer (Li et al. 2010) nanocomposites-containing nanoparticles of zinc borate in a polyimide matrix. The compositions were synthesized by “in situ” preparation method obtaining the polyimide films and different concentrations of zinc borate particles in the PI matrix. SEM–EDX studies showed the homogenous dispersion of zinc borate in the polyimide matrix with an increase in the thermal steadiness of the composite films on zinc borate loadings.

Tian et al. (2008) produced hydrophobic  $\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 3\text{H}_2\text{O}$  nanoplatelets in situ successfully obtained by  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  as raw materials through one-step precipitation reaction, and modifying agent. The measurement of the relative contact angle and the active ratio indicated that  $\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 3\text{H}_2\text{O}$  samples were hydrophobic.

In this study, zinc borate was synthesized by using zinc carbonate (Tuğrul et al. 2014; Tuğrul et al. 2010, 2011; Baran et al. 2010), reference boric acid, reference zinc borate as seed and to investigate effects of modifying agents and reaction parameters on hydrophobicity and yield, respectively. The effects of different modifying agents (PG, kerosene and OA) with solvents (IPA, ethanol, methanol) added to reaction on hydrophobicity were compared and the effects of reaction parameters on yield and different modifying agents (propylene glycol, kerosene, oleic acid) with solvents (isopropyl alcohol, ethanol, methanol) added to reaction on hydrophobicity were investigated comparingly. Furthermore, reactions were carried out under determined reaction conditions in both magnetically and mechanically stirred systems. Zinc borate produced was characterized by analytical methods, XRD (X-ray Diffraction), FT-IR (Fourier Transform Infrared Spectroscopy) techniques and measurement of contact angle which identified hydrophobicity was carried out. In conclusion, it was observed that zinc borate was synthesized successfully. Reaction parameters, usage of modifying agent with solvent affected the yield and hydrophobicity, respectively.

## 1. Experimental

### 1.1. Materials

Reference boric acid (molecular formula:  $\text{B}(\text{OH})_3$ , 99.9% pure) and reference ZB were obtained from Eti Mine Works. Zinc carbonate (96% pure) was acquired from Kadim Chemistry Ltd. Propylen Glycol was provided from Solventas A.S; Kerosene, Oleic Acid and Solvents were supplied by Prolab.

## 1.2. Methods

The synthesis of zinc borate was carried out by the reaction of zinc carbonate, reference boric acid and reference zinc borate by using Propylene Glycol (PG), Kerosene, and Oleic Acid (OA) in various solvents. Reference zinc borate was used as a seed crystal to reduce reaction time and to improve the quality of the product. Reactions were stirred magnetically and mechanically in different systems by using reference boric acid and zinc carbonate. In magnetic system, the reaction was conducted in a closed glass beaker at 368 K on a magnetic stir plate. The experiments were carried out by dissolving of reference boric acid in a glass beaker in distilled water. Temperature is controlled using a digital temperature sensor and magnetic stirrer provides constantly stirring during the reaction. In mechanic system, the synthesis was carried out in a 1.5 L glass reactor by using heating jacket under determined conditions. Fig. 1 displays the experimental set up used in the investigation. The products were dried at 378 K for 20 h. Dry, fine powdered zinc borate particles were produced. The yield values were calculated in grams of zinc carbonate consumed. The XRD and FT-IR analysis results showed that zinc borate was synthesized successfully. It was determined by contact angle tests that usage of different modifying agents with various solvents affected the hydrophobicity of zinc borate.

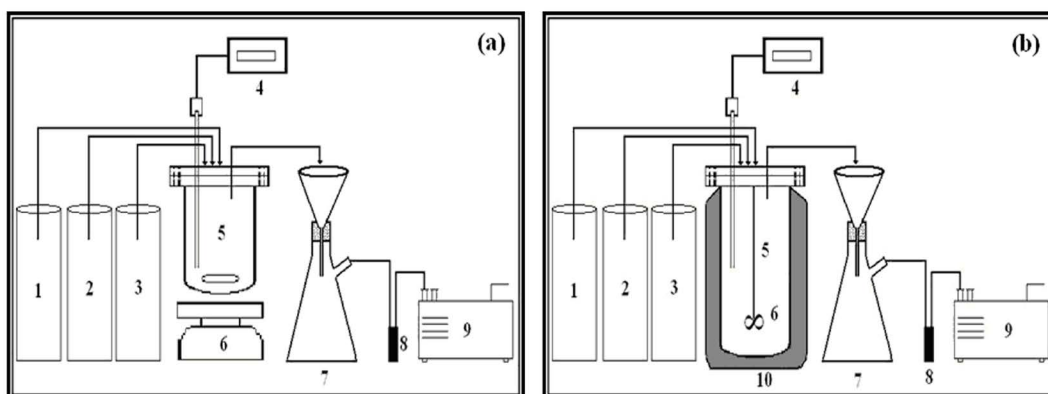


Fig. 1. Experimental set up

(a) Magnetic stirred system, (b) Mechanic stirred system: 1 – Reference boric acid, 2 – Zinc carbonate, 3 – Reference zinc borate, 4 – Digital temperature controller, 5a – Glass beaker, 5b – Reactor, 6a – Magnetic stir plate, 6b – Mechanic stirrer 7 – Solid-liquid phase separation apparatus, 8 – Trap, 9 – Vacuum pump, 10b – Heating jacket

Rys. 1. Stanowisko doświadczalne

a – system mieszania magnetycznego, b – system mieszania mechanicznego,  
 1 – kwas borowy (referencyjny), 2 – węgiel cynku, 3 – boran cynku (referencyjny),  
 4 – cyfrowy sterownik temperatury, 5a – zlewka, 5b – reaktor,  
 6a – płyta mieszadła magnetycznego, 6b – mieszadło mechaniczne,  
 7 – urządzenie (aparatura) do rozdzielania fazy stałej i ciekłej, 8 – pułapka, 9 – pompa próżniowa,  
 10b – urządzenie grzewcze

### 1.3. Analytical method

#### 1.3.1. Analysis of ZnO

The amount of zinc oxide present in solid samples was determined by the following Na<sub>2</sub>-EDTA titration. The sample (0.2–0.3 g) was dissolved in 37% hydrochloric acid (1 ml), and a solution of ammonia buffer (0.5 ml) was added into dissolved sample solution to achieve a pH of 9.5. The final solution was titrated with Na<sub>2</sub>-EDTA by adding a few drops of erichrome black-t indicator. The percentage of zinc oxide in the solid phase was calculated according to Eq. (1):

$$M = 0.408 \cdot S \cdot E/n \quad (1)$$

Where  $M$ ,  $S$ ,  $E$  and  $n$  were the percentage of ZnO in the sample (%), the volume of Na<sub>2</sub>-EDTA (ml), the molecular weight of ZnO (g/mol) and the amount of sample (g), respectively.

#### 1.3.2. Analysis of B<sub>2</sub>O<sub>3</sub>

The sample (1 g) was dissolved in 37% hydrochloric acid. 1 ml of solution was added into 1 ml of Na<sub>2</sub>-EDTA by using methyl orange indicator. This solution was titrated with 0.1 N NaOH. The titration was preceded by using mannitol and phenolphthalein. The percentage of B<sub>2</sub>O<sub>3</sub> was calculated according to Eq. (2):

$$B_2O_3(\%) = 56.36 \cdot A/B \quad (2)$$

$A$  and  $B$  are consumption of NaOH (ml) for sample and reference boric acid, respectively.

### 1.4. Characterisation

All products were characterised by XRD (Philips Panalytical, Xpert-Pro). Furthermore, FT-IR (Perkin Elmer, Spectrum One) was used to identify the functional groups present in the products. Measurement of contact angle which identified hydrophobicity was determined by Optical Contact Angle (Cam 200).

### 1.5. Hydrophobicity

Contact angle is a measure of static hydrophobicity, and contact angle hysteresis and slide angle are dynamic measures. Contact angles have great potential utility. They can

be measured on a macroscopic level to characterize the average wettability of a materials system. Contact angles can be of great value; however, making meaningful contact angle measurements and interpreting those measurements is complex.

Water drop contact angle is a measure of the surface wetting characteristics. If contact angle is less than  $90^\circ$ , it can be said wettible surface or hydrophilic. If contact angle is more than  $90^\circ$ , it can be said unwettable surface or hydrophobic.

Hydrophobic substances do not typically dissolve in water, due to the polar nature of water. These substances have a negligible solubility in water.

Propylene glycol provides hydrophobicity due to physico-chemical mechanisms. Kerosene is less hydrophobic and low surface polarity. OA is a surface modifying agent with carboxyl group, long alkyl chain and unsaturated bond. Oleic acid is a substance with one hydrophobic and one hydrophilic end. When a small amount of oleic acid is placed on the surface of water, it stands on end with the hydrophilic end towards the water and the hydrophobic end away.

## 2. Results and Discussion

### 2.1. The effect of process parameters on yield

In this study, optimal points were determined, and the yield of zinc borate was investigated as a function of various parameters. Thus, the effect of each parameter was investigated consecutively. The effect of reaction time and  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$  on yield is illustrated in Fig. 2.

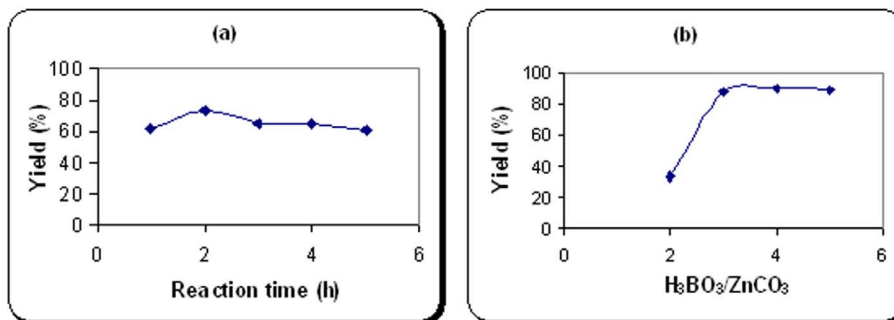


Fig. 2. The effect of process parameters on yield  
(a) Reaction time (h) ( $\text{H}_3\text{BO}_3/\text{ZnCO}_3$ : 3:1), (b)  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$  (reaction time: 2 h)  
(Reaction conditions: 0.5% of seed,  $95^\circ\text{C}$ , 500 rpm)

Rys. 2. Wpływ parametrów procesu na wydajność (uzysk)  
a – czas reakcji (h) ( $\text{H}_3\text{BO}_3/\text{ZnCO}_3$  – 3:1), b – ( $\text{H}_3\text{BO}_3/\text{ZnCO}_3$  – 3:1) (czas reakcji 2 h)  
(warunki reakcji: udział zarodków krystalizacji 0,5%,  $95^\circ\text{C}$ , 500 obr./min)

Various ratios of  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$  (2:1–5:1) and reaction times (1–5 hours) were evaluated under otherwise identical conditions (368 K, 500 rpm, reference ZB: 0.5%, PG: 3%, IPA: 2 ml).

The results revealed that the yield increased with an increase in reaction time; however, an improvement in yield was not observed after 2 h (Fig 2a). Thus, the optimal reaction time point selected under the specified conditions was 2 h. The yield increased up to 89.71% for 4:1 of reactant ratio and did not change after this point (Fig 2b).

Reference ZB was used as a seed crystal to reduce reaction time and to improve the quality of the product. As discussed in the previous study, the reaction of boric acid and zinc oxide (Kılınc et al. 2010) does not yield ZB product if ZB crystals are not added to the solution as seed. Alternatively, the yield increased with an increase in ZB concentration until a maximum value was obtained at 0.5% ZB (w/w).

As shown in Fig. 3a, amount of seed greater than 0.5% (w/w) did not alter the yield; thus, 0.5% (w/w) of seed was selected for further studies. The experiments were carried out between 400–700 rpm to determine optimum stirring rate and the optimum value was 500 rpm (Fig 3b).

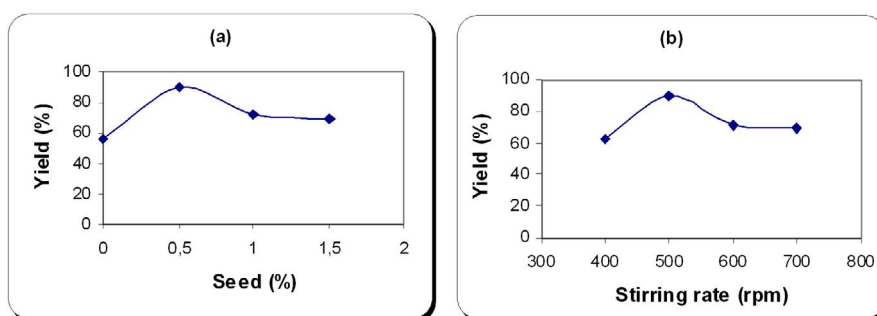


Fig. 3. The effect of process parameters on yield  
(a) Seed (%) (95°C, 500 rpm,  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$ : 4:1, 2 h), (b) Stirring rate (rpm) (seed: 0.5%)  
(2 h,  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$ : 4:1, 95°C, 500 rpm)

Rys. 3. Wpływ parametrów procesu na wydajność (uzysk) wytwarzania boranu cynku  
a – udział zarodków krystalizacji (%), (warunki reakcji: 95°C, 500 obr./min,  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$  – 4:1, 2 h),  
b – szybkość mieszania (obr./min)  
(warunki reakcji: udział zarodków krystalizacji 0,5%, 2 h,  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$  – 4:1, 95°C, 500 obr./min)

The synthesis of zinc borate was conducted between 323 and 393 K (2 h,  $\text{H}_3\text{BO}_3/\text{ZnCO}_3$ : 4:1, reference ZB: 0.5%, 500 rpm, PG: 3%, IPA: 2 ml) The results of the temperature studies indicated that the yield of the reaction increased dramatically with an increase in temperature until a maximum yield was obtained at 368 K. At temperatures greater than 368 K, the yield of the reaction remained constant. Thus, at 368 K, the reaction was fully complete, and an optimum reaction temperature was obtained as 368 K (Fig. 4a). The system was cooled to a variety of temperatures between 353–283 K. Cooling the reaction to temperatures greater than 323 K caused a significant decrease in yield (Fig. 4b).

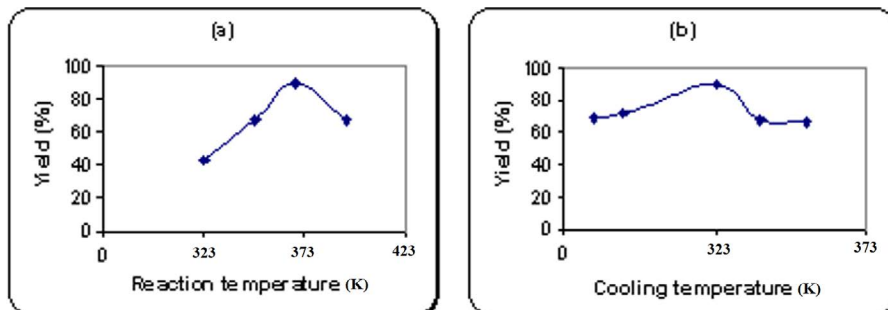


Fig. 4. The effect of process parameters on yield:  
 (a) Reaction temperature ( $^{\circ}\text{C}$ ) (cooling temperature:  $50^{\circ}\text{C}$ ), (b) Cooling temperature ( $^{\circ}\text{C}$ )  
 (reaction temperature:  $95^{\circ}\text{C}$ ) (2 h, 0.5% of seed, 500 rpm,  $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  : 4:1)

Rys. 4. Wpływ parametrów procesu na wydajność (uzysk)  
 a – temperatura reakcji ( $^{\circ}\text{C}$ ) (temperatura chłodzenia:  $50^{\circ}\text{C}$ ), b – temperatura chłodzenia ( $^{\circ}\text{C}$ )  
 (temperatura reakcji:  $95^{\circ}\text{C}$ ), (warunki reakcji: 2 h, udział zarodków krystalizacji 0,5 %, 500 obr./min,  
 $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  – 4:1)

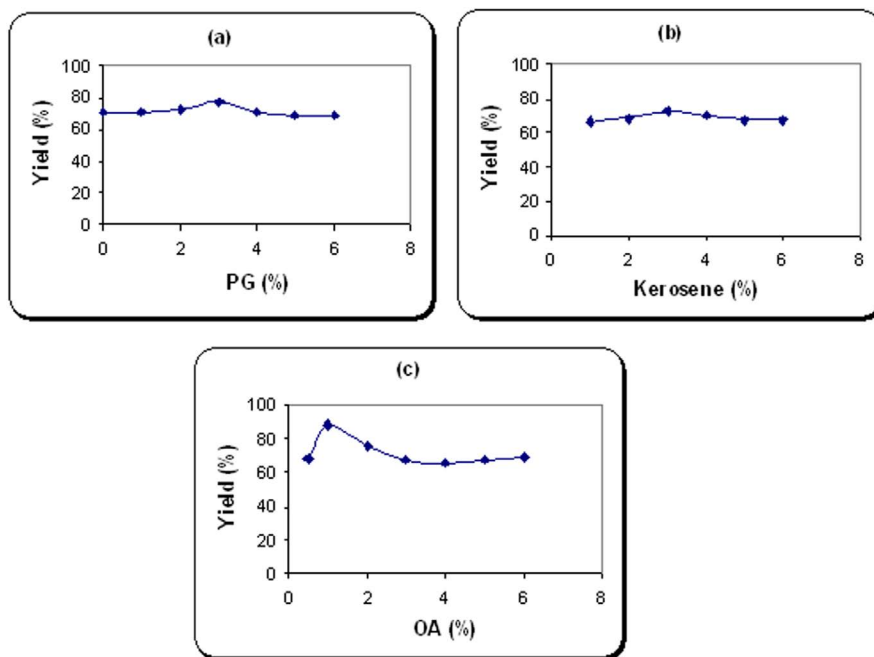


Fig. 5. The effect of modifying agent (%) on yield  
 (a) PG (2 h,  $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  : 4:1, 0.5% of seed, IPA: 2 ml,  $95^{\circ}\text{C}$ , 500 rpm),  
 (b) Kerosene (2 h,  $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  : 4:1, 0.5% of seed, IPA: 2 ml,  $95^{\circ}\text{C}$ , 500 rpm),  
 (c) OA (2 h,  $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  : 4:1, 0.5% of seed, IPA: 2 ml,  $95^{\circ}\text{C}$ , 500 rpm)

Rys. 5. Wpływ odczynnika modyfikującego na wydajność (uzysk) wytwarzania boranu cynku  
 a – PG (2 h,  $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  – 4:1, udział zarodków krystalizacji 0,5%, IPA: 2 ml,  $95^{\circ}\text{C}$ , 500 obr./min),  
 b – kerozyna (2 h,  $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  – 4:1, udział zarodków krystalizacji 0,5%, IPA: 2 ml,  $95^{\circ}\text{C}$ , 500 obr./ min),  
 c – OA (2 h,  $\text{H}_3\text{BO}_3:\text{ZnCO}_3$  – 4:1, udział zarodków krystalizacji 0,5%, IPA: 2 ml,  $95^{\circ}\text{C}$ , 500 obr./min)

The effects of modifying agents (%) on yield were investigated in range of 0–6% (w% with respect to total weight) (Fig. 5). Optimum PG (%), Kerosene (%) and OA (%) were determined as 3 (yield: 76.86%), 3 (yield: 72.98%) and 1 (yield: 88.32%), respectively. The usage of PG and OA which have 644 K and 636 K of autoignition temperature are an advantage to use in various applications as wood preservative and flame retardant. Hence, this modifying agents are relevant modifying agents in consideration of their high yields and autoignition temperatures. In contrast, kerosene which has 311 K of autoignition temperature with lower yield is not a relevant modifying agent.

Firstly, the effect of OA on yield was examined and IPA (2 ml) was determined as relevant solvent with respect to yield (Fig. 6). The relevant solvent for usage of PG and Kerosene was ethanol (6 ml). The reactions were carried out and compared in both magnetically and mechanically stirred systems by using relevant solvents under identical optimum conditions. The yields were 85.59%, 89.37% for PG in magnetic and mechanic stirred systems, respectively and 88.32% for OA in magnetic stirred system. The solution was viscous due to usage of OA. Thus, it would be a problem for mechanic stirred system and OA was not used for this system. In addition, the yields were 85.73% and 69.47% for Kerosene in magnetic and mechanic stirred systems, respectively.

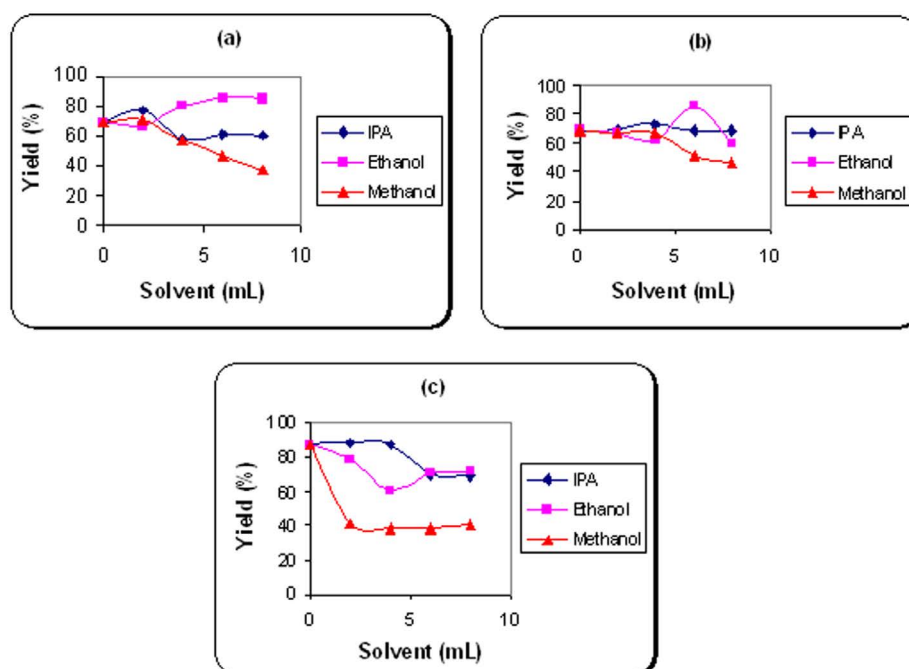


Fig. 6. The effect of various solvents on yield by using different modifying agents (2 h,  $H_3BO_3:ZnCO_3$  : 4:1, 0.5% of seed, 95°C, 500 rpm): (a) PG (3%), (b) Kerosene (3%), (c) OA (1%)

Rys. 6. Wpływ różnych rozpuszczalników modyfikowanych odczynnikami na wydajność procesu wytwarzania boranu cynku (2 h,  $H_3BO_3:ZnCO_3$  : 4:1, udział zarodków krystalizacji 0,5%, 95°C, 500 obr./min); a – PG (3%), b – kerozyzna (3%), c – OA (1%)



## 2.2. Characterization

Reaction conditions for zinc borate produced under optimum conditions are shown in Table 1. The usage of different modifying agents did not affect the structure of ZB. Thus, experiments which were carried out in magnetic system are just given in Fig. 7 and Fig. 8 for citation to show the characterization of products.

Table 1. Reaction conditions for zinc borate produced under optimum conditions

Tabela 1. Warunki reakcji boranu cynku wytwarzanego w optymalnych warunkach

Run no	Reaction conditions	Modifying agent	Solvent	Stirred system
1	Reference ZB	–	–	–
2	Reaction time: 2 h $H_3BO_3/ZnCO_3$ : 4:1 Seed: 0.5% Stirring rate: 500 rpm, Reaction temperature: 368 K	PG (3%)	Ethanol (6 ml)	Magnetic
3		Kerosene (3%)	Ethanol (6 ml)	Magnetic
4		OA (1%)	IPA (2 ml)	Magnetic
5		PG (3%)	Ethanol (6 ml)	Mechanic
6		Kerosene (3%)	Ethanol (6 ml)	Mechanic

## 2.3. FT-IR analysis

FT-IR (Fourier Transform Infrared Spectroscopy) analysis was carried out by using Perkin-Elmer, Spectrum One instrument. The band which indicates stretching vibrations of

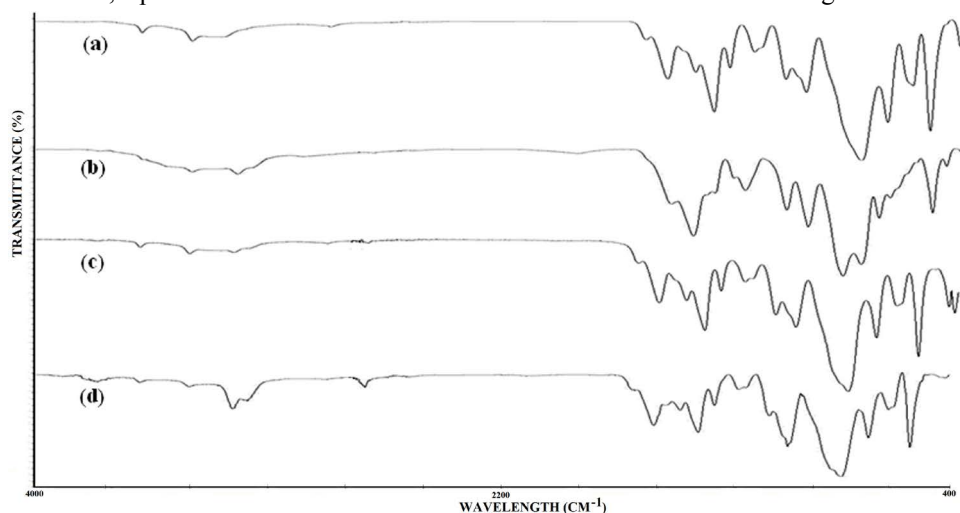


Fig. 7. FT-IR spectrum of ZB: (a) Reference ZB, (b) Run no 2, (c) Run no 3, (d) Run no 4

Rys. 7. Widmo FT-IR boranu cynku (ZB)

a – boran cynku (ZB) odniesienia (referencyjny), b – próbka nr 2, c – próbka nr 3, d – próbka nr 4

O-H is obvious between 2500–3500  $\text{cm}^{-1}$ . Bending vibrations of H-O-H band which are due to crystal water included in compound is slightly seen between 1600–1700  $\text{cm}^{-1}$ . The presence of the band between 1300–1450  $\text{cm}^{-1}$  assigned to asymmetric stretching vibrations of trihedral ( $\text{BO}_3$ ) borate groups. The peaks in range of 1000–1150 and 700–900  $\text{cm}^{-1}$  are assigned to asymmetric and symmetric stretching vibrations of tetrahedral ( $\text{BO}_4$ ) borate groups. The peak observed between 650–750  $\text{cm}^{-1}$  wavelength indicates in plane bending vibrations of trihedral ( $\text{BO}_3$ ) groups (Fig. 7).

As a result, the usage of different modifying agent and stirred system did not affect the structure and it was similar with reference zinc borate. Reaction conditions for zinc borate produced under optimum conditions (Table 1) and FT-IR spectrums of the product show the formation of zinc borate (Fig. 7) (Piskin et al. 2011).

## 2.4. XRD analysis

XRD (X-Ray Diffraction) (Philips Panalytical, X'Pert Pro) analysis showed that zinc borate peaks were similar to reference zinc borate with peaks. The characteristic

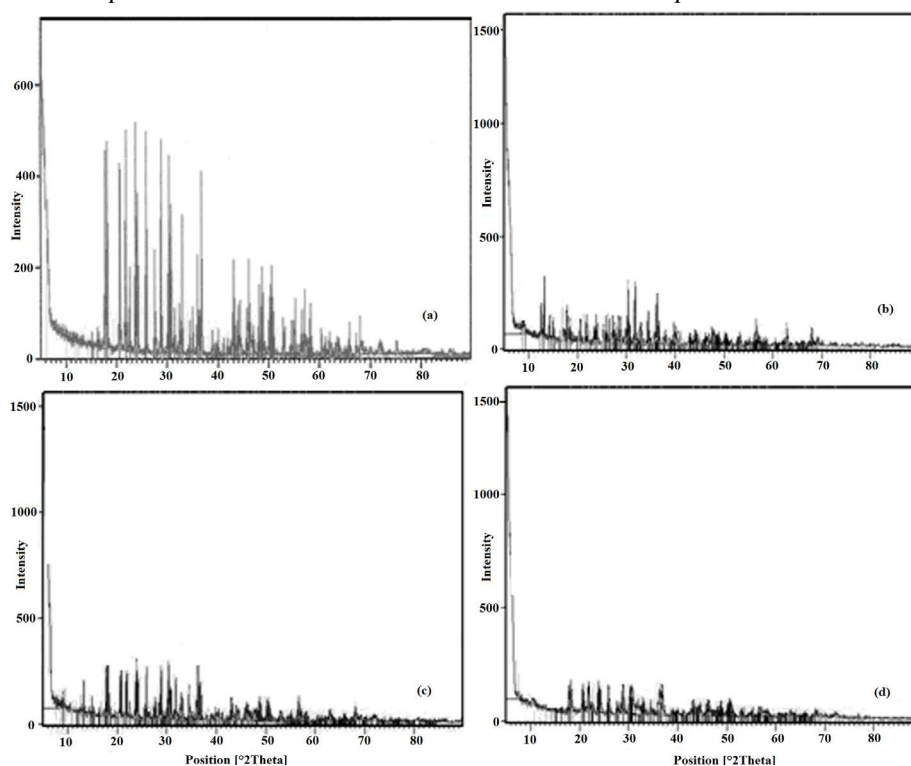


Fig. 8. XRD diagrams of ZB: (a) Reference ZB, (b) Run no 2, (c) Run no 3, (d) Run no 4

Rys. 8. Diagramy XRD boranu cynku (ZB)

a – odniesienia (referencyjny), b – próbka nr 2, c – próbka nr 3, d – próbka nr 4

peaks of zinc borate were observed in range of  $15\text{--}70^\circ 2\theta$  from XRD analysis as expected (Fig. 8).

## 2.5. Analysis results

As shown in Table 2, the content of ZnO (%),  $B_2O_3$  (%) were determined using analytical methods,  $H_2O$  (%) was the remaining of 100 (%), respectively. The content of crystal water in ZB structure for kerosene was higher when the results were compared with PG and OA system. The use of a magnetically or mechanically stirred system caused the various structure formations (Gönen et al. 2011). In addition, the structures and formulas of ZB produced are similar to ZB which are used in industry for various applications.

Table 2. Chemical composition and formulas of ZB produced under optimum reaction conditions ( $H_3BO_3$ :  $ZnCO_3$ : 4:1, 2 h, Seed: 0.5%, 500 rpm,  $95^\circ C$ )

Tabela 2. Skład chemiczny i wzory chemiczne boranu cynku (ZB) wytwarzanego w optymalnych warunkach ( $H_3BO_3$ :  $ZnCO_3$ : 4:1, 2 h, udział zarodków krystalizacji 0,5%, 500 obr./min,  $95^\circ C$ )

No	Reaction conditions	$B_2O_3$ (%)	ZnO (%)	$H_2O$ (%)	Formulas
1	Reference ZB	39.21	47.46	13.33	$2.1ZnO \cdot 3B_2O_3 \cdot 3.2H_2O$
2	PG: % 3, Ethanol: 6 mL (magnetic stirring)	47.25	34.71	18.04	$2.2ZnO \cdot 3B_2O_3 \cdot 4.4H_2O$
3	Kerosene: 3%, Ethanol: 6 mL (magnetic stirring)	47.38	26.97	25.65	$1.5ZnO \cdot 3B_2O_3 \cdot 6.3H_2O$
4	OA: 1%, IPA: 2 mL (magnetic stirring)	44.37	33.58	22.05	$1.9ZnO \cdot 3B_2O_3 \cdot 5.8H_2O$
5	PG: % 3, Ethanol: 6 mL (mechanic stirring)	41.44	48.15	10.41	$2.2ZnO \cdot 3B_2O_3 \cdot 2.5H_2O$
6	Kerosene: 3%, Ethanol: 6 mL (mechanic stirring)	37.16	49.85	12.99	$1.9ZnO \cdot 3B_2O_3 \cdot 3H_2O$

## 2.6. Hydrophobicity test results

The contact angle (Optical Contact Angle/Surface Tension Meter, Cam 200) test results for optimal points were shown as Table 3.

There is improvement from hydrophilic to hydrophobic due to usage of modifying agent and when these results were compared with reference ZB. Hydrophobicity is important to use zinc borate produced on wood surfaces. Zinc borate produced protects wood surfaces against to insects. Therefore, hydrophobicity tests were performed in detail. In conclusion, it was seen that changing modifying agents affected the hydrophobicity of zinc borate (Fig. 9). In mechanic stirred system, stirrer causes forming the big droplets. Therefore, the contact angle values in mechanic system are higher than when it is compared with magnetic stirred system.

Table 3. Contact angle values under optimum reaction conditions

Tabela 3. Wartość kąta zwilżania w optymalnych warunkach reakcji

No	Reaction conditions	Contact angle (°)
1	Reference ZB	0
2	PG: % 3, Ethanol: 6 mL (magnetic stirring)	21.66
3	Kerosene: 3%, Ethanol: 6 mL (magnetic stirring)	17.95
4	OA: 1%, IPA: 2 mL (magnetic stirring)	103.19
5	PG: % 3, Ethanol: 6 mL (mechanic stirring)	29.20
6	Kerosene: 3%, Ethanol: 6 mL (mechanic stirring)	27.22

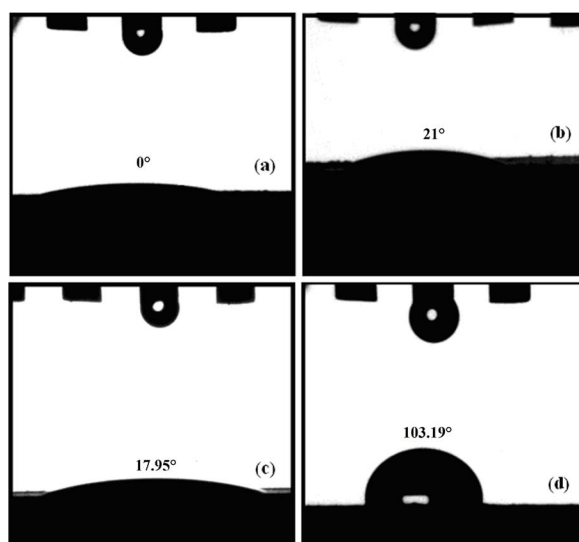


Fig. 9. Hydrophobicity test results:(a) Reference ZB, (b) Run no 2, (c) Run no 3, (d) Run no 4

Rys. 9. Wyniki testu hydrofobowości boranu cynku (ZB)

a – odniesienia (referencyjny), b – próbka nr 2, c – próbka nr 3, d – próbka nr 4

## Conclusion

The analysis results (XRD, FT-IR), analytical methods showed that the synthesis of zinc borate was achieved and the usage of different modifying agents (PG, Kerosene, OA) with various solvents (IPA, ethanol, methanol) did not affect the structure. Optimum points for each modifying agent were determined. The yields were 85.59%, 89.37% for PG in magnetic and mechanic stirred systems, respectively and 88.32% for OA in magnetic stirred system.

The solution was viscous due to usage of OA. Therefore, it would be a problem for mechanic stirred system and OA was not used for this system. In addition, the yields were 85.73% and 69.47% for kerosene in magnetic and mechanic stirred systems, respectively. The contact angle of reference ZB was determined as 0° which means the reference ZB had a hydrophilic structure. There was improvement from hydrophilic properties to hydrophobic properties when modifying agents were used. In conclusion, it was seen that reaction parameters, usage of modifying agents with solvents affected the yield and hydrophobicity, respectively.

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**WYTWARZANIE BORANU CYNKU Z SUROWCÓW MINERALNYCH BORU:  
WPLYW PARAMETRÓW PROCESU NA WYDAJNOŚĆ I HYDROFOBOWOŚĆ**

Słowa kluczowe

hydrofobowość, wydajność, boran cynku, węglan cynku

Streszczenie

Celem tego artykułu jest synteza boranu cynku przy użyciu węglanu cynku, kwasu borowego, referencyjnego boranu cynku (ZB) jako substancji aktywnej oraz badanie efektywności tego procesu modyfikowanego odczynnikami i parametrami reakcji na hydrofobowość i wydajność syntezy boranu cynku. Dotyczy to działania różnych czynników modyfikujących hydrofobowość i parametry reakcji: glikol propylenowy (PG) (0–6%, kerozyna 1–6%, kwas oleinowy (OA) 1–6% oraz rozpuszczalniki: alkohol izopropylowy (IPA), etanol i metanol. Po pierwsze, badano jak wpływają następujące parametry reakcji na uzysk boranu cynku: czas reakcji (1–5 h), wskaźnik reaktywacji ( $H_3BO_3 : ZnO$ ), (2–5), udział zarodków krystalizacji (0–1,5%) w odniesieniu do kwasu borowego, temperatura reakcji (50–120°C), temperatura chłodzenia (10–80 °C), szybkość mieszania (400–700 obr./min). Ponadto, reakcje były przeprowadzone w określonych warunkach mieszania mechanicznego i magnetycznego. Wytwarzany boran cynku ze względu na hydrofobowość badano metodami: dyfrakcji rentgenowskiej XRD, spektroskopii FT-IR oraz pomiarami kąta zwilżania. Reasumując, stwierdzono, że boran cynku można otrzymać z powodzeniem z różnymi rozpuszczalnikami wpływającymi na jego hydrofobowość.

**ZINC BORATE PRODUCTION WITH BORON MINERAL SOURCE:  
EFFECT OF PROCESS PARAMETERS ON YIELD AND HYDROPHOBICITY**

Keywords

hydrophobicity, yield, zinc borate, zinc carbonate

Abstract

The aim of this study was to synthesize zinc borate by using zinc carbonate, boric acid, reference zinc borate (reference ZB) as seed and to investigate effects of modifying agents and reaction parameters on hydrophobicity and yield, respectively. Different from the studies available in the

literature, the effects of different modifying agents (propylene glycol (PG) (0–6%), kerosene (1–6%), oleic acid (OA) (1–6%)) with solvents (isopropyl alcohol (IPA), ethanol, methanol) added to reaction on hydrophobicity were investigated comparably. Firstly, the effects of reaction parameters such as reaction time (1–5 h), reactant ratio ( $\text{H}_3\text{BO}_3/\text{ZnO}$ ) (2–5), seed ratio (0–1.5%, in terms of boric acid, w/w), reaction temperature (323–393 K), cooling temperature (283–353 K) and stirring rate (400–700 rpm) on yield were investigated. Furthermore, reactions were carried out under determined reaction conditions in both magnetically and mechanically stirred systems. The product, zinc borate, was characterized by analytical methods, XRD (X-ray Diffraction), FT-IR (Fourier Transform Infrared Spectroscopy) techniques and measurement of contact angle which identified hydrophobicity was carried out. In conclusion, it was observed that zinc borate was synthesized successfully and different modifying agents with various solvents affected the hydrophobicity of zinc borate.

