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Investigation of the Fire, Thermal, and Mechanical Properties of Zinc Borate and Synergic Fire Retardants on Composites Produced with PP-MDF Wastes

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Synergic effects of different fire retardant compounds and zinc borate on wood-plastic composites filled with polypropylene (PP) and medium-density fiberboard (MDF) waste fibers were investigated. For this purpose, zinc borate, synergic compounds (antimony trioxide, ammonium phosphate, and magnesium hydroxide), and a coupling agent, *i.e.*, maleic anhydride-grafted polypropylene (MAPP), were used in the production of wood-plastic composites (WPCs). The composite samples were characterized in terms of the burning rate and limiting oxygen index (LOI) analyses, thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) along with mechanical tests, *i.e.*, flexural properties, tensile properties, elasticity modulus, and impact strength. It was found that the synergic influence of the combination of zinc borate, antimony trioxide, and magnesium oxide on WPCs increased the heat resistance according to the burning rate, LOI, TGA, and DSC tests. Also, the mechanical properties of the WPCs decreased slightly, but their elasticity modulus increased.

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INTRODUCTION

The WPCs have been used recently in different construction and building applications due to economic and environmental concerns. These fabricated materials have many advantages, such as lower resin costs, improved stiffness, and improved dimensional stability. Composites that are reinforced with lignocellulosic waste can reduce the use of petroleum-based plastics (Jeencham *et al.* 2014; Ozdemir *et al.* 2014).

In the production of WPCs the starting materials are wood and plastics, *i.e.*, thermoplastic and thermoset materials (Jeencham *et al.* 2014). Lignocellulose materials, such as sawdust, annual crops, and forest waste, can be used in the production of WPCs. Therefore, the use of WPCs has been increasing, and they consist of different lignocellulose wastes and plastics that provide positive performance and reduced cost (Faruk *et al.* 2007). Compatibilizers, such as maleic anhydride grafted polypropylene (MAPP), are often used in the production of composites to eliminate the incompatibility between wood and plastics (Kurt and Mengeloglu 2011). However, WPCs also have some disadvantages. One of the most serious disadvantages of using WPCs in houses is the high flammability of the lignocellulosic and plastic materials (Umemura *et al.* 2014). This is especially important because composite products used in such construction may be exposed to the fire hazards. However, the use of boron compounds, such as zinc borate

and boric acid, in the production of WPCs provides protection against fire. Boron compounds have been also used to protect wood from fungi and insects (Ayrilmis 2013; Turku *et al.* 2014). In addition, boron compounds have been used to reduce the thermal degradation of composite materials. Many fire-retardant compounds are available for polymer composites, including ammonium phosphate, diammonium phosphate, magnesium hydroxide, and aluminum trihydrate. Many studies have shown that the synergic effect between boron compounds, such as zinc borate, and other compounds, such as ammonium phosphate, diammonium phosphate, magnesium hydroxide, antimony trioxide, and aluminum trihydrate, provides a heat barrier for WPCs (Ning and Guo 2000; Kurt and Mengeloglu 2011; Arao *et al.* 2014; Jeencham *et al.* 2014; Turku *et al.* 2014; Umemura *et al.* 2014; Wu and Xu 2014). The amount of fire retardants used in the formulation of WPCs must be carefully controlled because the mechanical properties of composites may be adversely affected due to excessive usage of these compounds (Turku *et al.* 2014).

This research investigates the synergic effect between the zinc borate and various fire retardant compounds on the flammable properties of MDFw-filled PP composites. The relationship between zinc borate and MAPP was also investigated. A thermal gravimetric analyzer (TGA) and differential scanning calorimetry (DSC) were used to investigate the thermal resistance properties. Moreover, the horizontal burning rate and limiting oxygen index (LOI) tests of samples were carry out to determine the effects of the fire retardants on the stability of the fire properties. The effects of the fire retardants on the mechanical properties of the WPCs were also determined, including their tensile, flexural, and impact strengths, as well as their flexural and tensile modulus.

EXPERIMENTAL

Materials

The MDF particles were obtained from the Kastamonu Entegre Co. (Adana, Turkey). These fiber particles were separated into 60-mesh fibers using screens, and the fibers were oven-dried before the manufacturing process. Polypropylene (PP, density: 0.946 g/cm^3) and paraffin wax were provided by the Petkim Petrochemical Co. (Izmir, Turkey). Maleic anhydride grafted polypropylene, used as a coupling agent in some composite boards, was supplied by Clariant International Co. (Shanghai, China). Zinc borate ($ZnO•2B_2O_3•3.5H_2O$) was obtained from the Aromos Chemistry Co. (Izmir, Turkey). Antimony trioxide (Sb_2O_3), and ammonium phosphate ((NH_4)$_3PO_4$) were obtained from Tekkim Chemistry Co. (Istanbul, Turkey). Magnesium hydroxide ($Mg(OH)_2$) were obtained from the Zag Chemistry Co. (Istanbul, Turkey).

Methods

The oven-dried MDFw (103 °C), PP, MAPP, zinc borate (ZB), antimony trioxide (AT), ammonium phosphate (AP), and magnesium hydroxide (MH) were prepared according to Table 1 for the composite samples. Prepared materials were mixed with a high-speed mixer (speed range 5 rpm to 1000 rpm for 5 min) before the extrusion process. A twin-screw extruder was used to produce the composites; the temperatures of the extruder barrel were set at 175 °C, 180 °C, 185 °C, 190 °C, and 190 °C for the warm regions of the extruder: 1, 2, 3, 4, and 5, respectively. The temperature of the extruder die

zone averaged around 195 °C. The extruded composite products were sufficiently pelletized. The extruded composite pellets were first oven-dried until the moisture content of the pellets reached 1% to 2%. Then, the fabrication process of the composites was carried out using the hot press machine. These pellets were pressed for 10 min at 180 °C and 100 bar pressure. The specimens from the composite boards were sized and cut according to related ASTM standards for experimental examples and conditioned in respect to ASTM D618 (2013).

Table 1. Weight Percentages of WDFw Filled Wood Plastic Composites

Composition Based on Weight (%)								
Sample Code	MDF wastes	PP	MAPP	Zinc Borate	Ammonium Phosphate	Antimony Trioxide	Magnesium Hydroxide	Wax
Control	40	59						1
PP/MAPP	40	56	3					1
PP/ZB	40	47		12				1
PP/MAPP/ZB	40	44	3	12				1
PP/ZB/AP	40	47		6	6			1
PP/ZB/AT	40	47		6		6		1
PP/ZB/MH	40	47		6			6	1
PP/ZB/AP/AT	40	47		4	4	4		1

Flame retardancy and Limiting Oxygen Index (LOI) performance

The flame retardancy of composites was determined via horizontal burning tests according to ASTM D635 (2014). Composite samples with five replicates for each group were tested using an Atlas HVUL2 horizontal-vertical flame chamber. For the horizontal burning tests, the composite samples were horizontally held from one end and the free end of the composite sample was exposed to flame fueled by oxygen. The time needed for the flame to reach from the first reference point to the second reference point was measured. The distance between the two reference points is 75 mm.

The limiting oxygen index (LOI) test was performed according to ASTM D2863-10 (2000) using a limiting oxygen index chamber (Dynisco, Heilbronn, Germany). For LOI, the composite samples were vertically placed using a holder in the glass tube. The medium oxygen concentration was used to support combustion during the tests. The head of the composite sample was ignited and minimum oxygen concentrations which would support combustion were recorded as a percentage.

Thermal Gravimetric Analysis (TGA)

The TGA analyses were carried out to investigate the decomposition behavior of composite samples in this research. Powdered test samples were used for the thermogravimetric analysis. The analysis was performed using a Shimadzu TGA-50 thermal analyzer (Shimadzu, Tokyo, Japan) at a heating rate of 10 °C/min up to 800 °C under a nitrogen flow of 50 mL/min.

Differential Scanning Calorimetry Analysis

Powdered test samples were used for the DSC. The DSC analyses were performed in a Shimadzu DSC-60 differential scanning calorimeter (Shimadzu, Tokyo, Japan) at a heating rate of 10 °C/min up to 200 °C under a nitrogen flow of 100 mL/min according to

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ASTM D3418 (2008). For the samples, the melting temperature, the second melting enthalpy (ΔH_m), the crystallization peak temperature, and crystallization enthalpy were measured, and the degree of crystallinity (X_{cd}, %) was calculated using Eq. 1 (Joseph *et al.* 2003).

$$X_{cd} = \frac{\Delta H_m}{(1-x) - \Delta H_{pp}} \times 100 \qquad (1)$$

In this formula, ΔH_{pp} is the melting enthalpy (209 J/m) value of the 100% crystalline form of pure PP and (1-*x*) shows the weight ratio of PP in the composite examples.

Mechanical Properties

The tensile strength (TS) and modulus of elasticity were determined according to ASTM D638 (2007) with a crosshead speed of 5 mm/min and load cell of 0.1 kN. The flexural strength (FS) was determined according to ASTM D790 (2007) with a crosshead speed of 2 mm/min using a universal testing machine (Zwick/Roel, model Z010, Stuttgart, Germany) at room temperature. Impact testing was carried out with a pendulum impact tester (Zwick, HIT5.5P, Stuttgart, Germany), at room temperature, according to ASTM D256 (2007). The notches were made using a notching cutter (Ray-Ran Test Equipment, Ltd., Polytest; Nuneaton, UK). Eight samples were tested for the tensile, flexural, and impact tests.

Scanning Electron Microscopy (SEM) analysis of decayed composites

The morphological properties and the distribution of fire retardants in MDFw-filled PP composites was recorded using a JEOL Neo Scope JSM-500 (JEOL Co, Freising, Germany) scanning electron microscope under an acceleration voltage of 10 kV. The specimens were coated with gold (Cressington Scientific Instruments Co, Watford, England) under vacuum prior to scanning.

Statistical analysis

The statistical evaluation of the mechanical test results was performed using the SPSS 20.0 statistical analysis program. The data were subjected to ANOVA variance analysis at p≤0.05 confidence level, and significant differences between mean sample values were obtained according to the Duncan multiple range test. The significant differences between the groups are expressed in capital letters A, B, C and D.

RESULTS AND DISCUSSION

Flame Retardancy and Limiting Oxygen Index Results

Table 2 shows the burning rates of the composites, which ranged from 16 mm/min to 32 mm/min. The PP/ZB/AP/AT composite had the lowest burning rate. The burning rate of the PP/MAPP composite were reduced when compared the control group. Also, the burning rate of PP/MAPP/ZB was affected adversely in comparison with the PP/ZB because the addition of MAPP resulted in a tighter texture in the composite material. Various studies have shown that the addition of MAPP or MAPE into WPCs increased their burning rate (Sain *et al.* 2004; Kurt and Mengeloglu 2011; Cavdar *et al.* 2016).

The composites prepared by mixing zinc borate were compared to other fire retardant added samples to determine their synergic effect. Table 2 shows that the fire

resistances of PP/ZB/AP, PP/ZB/AT, and PP/ZB/MH had a synergic effect on the burning rate, decreasing it 55%, 44%, and 35%, respectively, compared to the control group. The lowest burning rate was observed when zinc borate, antimony trioxide, and ammonium phosphate were used together in the WPCs. Other studies have been conducted to reduce the burning rate related to the synergic effect in WPCs (Kurt and Mengeloglu 2011).

The LOI results of the WPCs were shown in Table 2. The highest values were obtained when using PP/ZB/AP and PP/ZB/AT. It was understood that the synergic compounds, such as antimony trioxide, ammonium phosphate, and magnesium hydroxide, have an effect on the LOI when they are used in the WPCs. Aluminum polyphosphate was used in an earlier study, and it was concluded that greater amounts of fire retardants improved the LOI results (Zhang *et al.* 2012). In another study about fire retardant added WPCs, it was found that addition of 10% aluminum polyphosphate to composite material resulted in self-extinguishing properties. The addition of aluminum polyphosphate to the composite material formed a layer on the composite surface. This layer prevented the passage of oxygen (Arao *et al.* 2014).

Table 2. Burning Rate and LOI Results of Composites

Sample Codes	Burning Rate (mm/min)	LOI (Oxygen %)
Control	30.5 (1.87*)	20% ± 0.2%
PP/MAPP	31.8 (2.24)	21% ± 0.2%
PP/ZB	18.5 (0.75)	21% ± 0.2%
PP/MAPP/ZB	26.7 (1.80)	21% ± 0.2%
PP/ZB/AP	22.6 (1.09)	22% ± 0.2%
PP/ZB/AT	16.9 (1.85)	22% ± 0.2%
PP/ZB/MH	19.9 (2.95)	22% ± 0.2%
PP/ZB/AP/AT	15.5 (0.83)	22% ± 0.2%

*Standard deviation

Thermal Gravimetric Analyze Results

The TGA results are given in Table 3, and they indicated that the degradation of all of the samples took place in two main steps. The first step was within the temperature range of 250 °C to 395 °C, and the second step was between 395 °C and 510 °C. It was concluded that the lignocellulosic material deteriorated in the first stage and the plastic material deteriorated in the second stage. Based on a comparison with the control group, it was apparent that all of the fire-retardant agents greatly improved the thermal characteristics of the composites. However, when MAPP was added alone into the formulation of the control, the thermal resistance of the composite material was diminished, and the residual amount of the material decreased approximately 30% in comparison with the control group. This result may have been due to the crosslinking of the MAPP with the polymer and MDFw, which produced a positive influence on the thermal conductivity of the composite. Lignocellulosic degradation in the temperature range of 200 °C to 350 °C was associated with to hemicellulose and cellulose, and the degradation of lignin occurred in the temperature range of 250 °C to 500 °C (Jeske *et al.* 2012; Arao *et al.* 2014).

The synergistic effect of zinc borate was mainly reflected in the first and second degradation stage. Moreover, according to the DTGA curve in Fig. 1, it was understood

that curves of composite samples with synergistically effective compounds had a lower peak area than that of control and PP/MAPP samples.

Table 3. Thermal Gravimetric Analyze Results of Composites

Samples	1st Degradation Stage Temperature Range (°C)	2nd Degradation Stage Temperature Range (°C)	Weight Loss (°C)		% Residue at 800 (°C)
			5%	50%	
Control	25 - 392	396 - 504	281	465	4.5
PP/MAPP	250 - 393	393 - 508	287	466	3
PP/ZB	262 - 394	406 - 509	289	476	16.5
PP/MAPP/ZB	261 - 394	403 - 512	274	477	17
PP/ZB/AP	262 - 379	411 - 500	290	475	13.5
PP/ZB/AT	255 - 386	399 - 509	282	478	20
PP/ZB/MH	255 - 285	396 - 509	281	477	17
PP/ZB/AP/AT	255 - 386	398 - 506	280	476	17.4

The combined usage of zinc borate and antimony trioxide was very effective to increase the thermal stability of the WPC sample, where the thermal degradation of the WPC samples was not initiated until the temperature reached the second degradation region. Compared to the control sample, it was clear that the addition of fire retardants in the formulations greatly reduced the total weight loss ratio and increased the residual amount at 800 °C. The best increase in fire resistance of the WPCs against thermal degradation occurred in the sample that contained zinc borate and ammonium phosphate. The weight loss ratio of PP/ZB/AT was reduced approximately 15% compared to the control sample. From the various fire-retardant chemicals used, zinc borate with MAPP and zinc borate in combination with ammonium phosphate and magnesium hydroxide had the most positive effect on the thermal resistance of the WPCs.
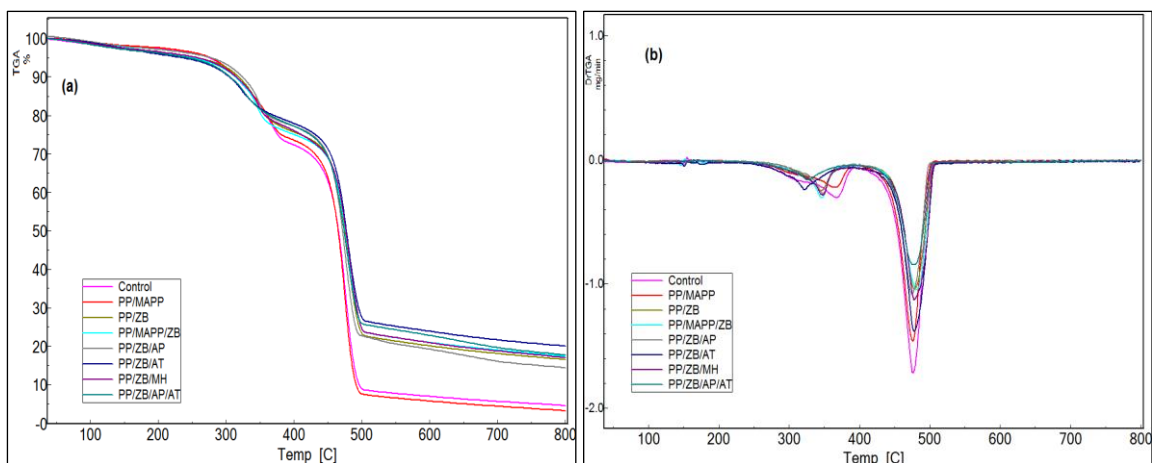

Fig. 1. TGA (a) and DTGA (b) Curves of Composite Samples

Differential Scanning Calorimetry (DSC) Results

The DSC results of the WPCs are presented in Table 4. The melting points of the WPCs that were filled with different fire retardants were lower than the melting point of the unfilled polypropylene composite. The WPC sample with the lowest melting point (*i.e.,* 161.7 °C) was PP/ZB/AT. The WPCs that contained fire retardants had higher peak crystallization temperatures than that of the control sample (116 °C) without fire

retardants. The peak crystallization temperature of the composites ranged from 116 °C to 119.5 °C. The crystallization enthalpy of the control samples was 50.6 J/g. The crystallization enthalpy of the composite samples ranged from 50.6 J/g to 39.5 J/g. These results indicated that the thermal stabilities of the composites varied, dependent upon the fire retardant. The PP/ZB/AT sample emitted more heat energy in the crystallization of the composites. The crystallization of the composite generally increased with the addition of the various fire retardants. It was assumed that this occurred due to the minor degradation of the polymer matrix. As the lengths of the polymer chains were reduced, the crystallization levels of the polymers increased (Ayadi *et al.* 2012; Akesson *et al.* 2016; Ichazo *et al.* 2001). The crystallites (X_{cd}) of the composite samples ranged frorm 33.7% to 50.1%. Fire retardants with synergistic effect added to composite samples generally increased the degree of crystallinity. The X_{cd} of the control sample was 35.8%, while the highest X_{cd} was found as 50.1% for PP/ZB/AT sample.

Table 4. Differential Scanning Calorimeter Results of Composites

| Samples	1st Melting Temperature (°C)	2nd Melting Temperature (°C)	2nd Melting Enthalpy (J/g)	Crystallization Temperature (°C)	Crystallization Enthalpy (J/g)	X_{cd} (%)
Control	163.8	163.1	44.1	116	50.6	35.8
PP/MAPP	163.1	162.1	46.6	115.8	48.1	39.8
PP/ZB	163.5	162.9	39.3	117.5	42.3	40.0
PP/MAPP/ZB	162.5	162.4	41	117.3	47	44.6
PP/ZB/AP	162	161.8	45.5	118.5	47.1	46.3
PP/ZB/AT	161.8	161.7	49.2	117.5	50.8	50.1
PP/ZB/MH	161.9	161.8	33.1	119.5	39.5	33.7
PP/ZB/AP/AT	162.8	162.6	43.7	117.9	45.3	44.5
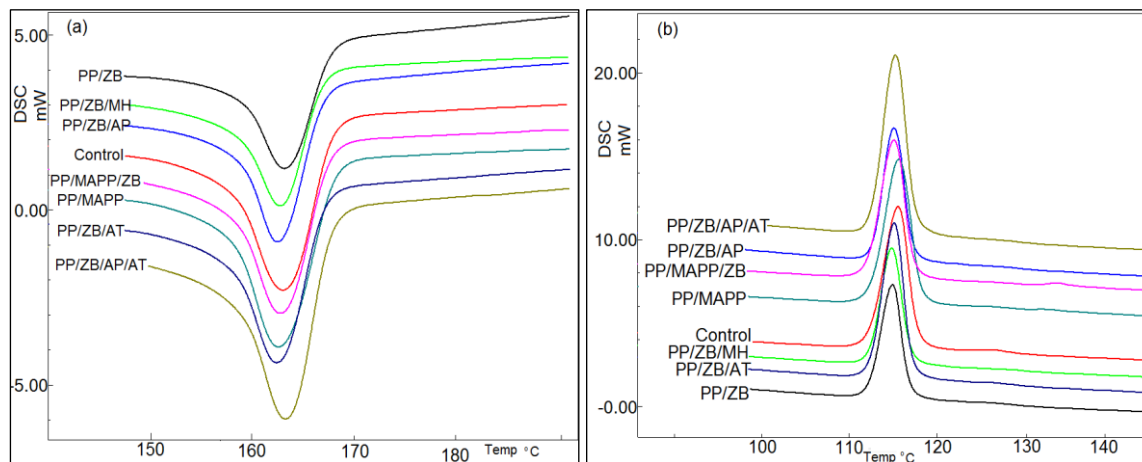
Fig. 2. DSC results of the composites: a) Melting, b) Crystallization Temperature

Results of the Mechanical Analysis

Table 5 shows the tensile strengths and elastic modulus of the composite samples. The effects of the fire retardants and MAPP on the tensile strengths and elasticity modulus of the composite samples are demonstrated in Fig 3. The addition of zinc borate as a fire retardant slightly reduced (11%) the tensile strength (13.22 MPa) but increased the elasticity modulus (909.7 MPa) of the PP/ZB composite. The addition of only 3%

MAPP in the composite sample increased the tensile strength (16.59 MPa) and elasticity modulus (842.89 MPa) of PP/MAPP. Moreover, using both 3% MAPP and zinc borate increased the tensile strength and the elasticity modulus in comparison with the control sample. It was determined that, without the addition of MAPP, the tensile strength and elasticity modulus of PP/MAPP/ZB were lower than those of the control group. It was reported that adding high levels of fire retardants, such as zinc borate, magnesium hydroxide, and ammonium phosphate, into polymer composites has a negative effect on the tensile strength (Arao *et al.* 2014; Umemura *et al.* 2014). The addition of various synergic fire retardant compounds with zinc borate to the WPCs generally reduced the tensile elastic modulus (TEM). When antimony trioxide, ammonium phosphate, and magnesium hydroxide were added separately to the WPCs, the strengths of the WPCs decreased 30%, 41%, and 6%, respectively. However, the addition of magnesium hydroxide increased the elasticity modulus (12%) of PP/ZB/MH sample according to the control sample. In a study, the fire retardant properties of composite samples with aluminum polyphosphate at different ratios were examined. Consequently, it was reported that the usage of fire retardants adversely affected the mechanical properties of composites (Arao *et al.* 2014).
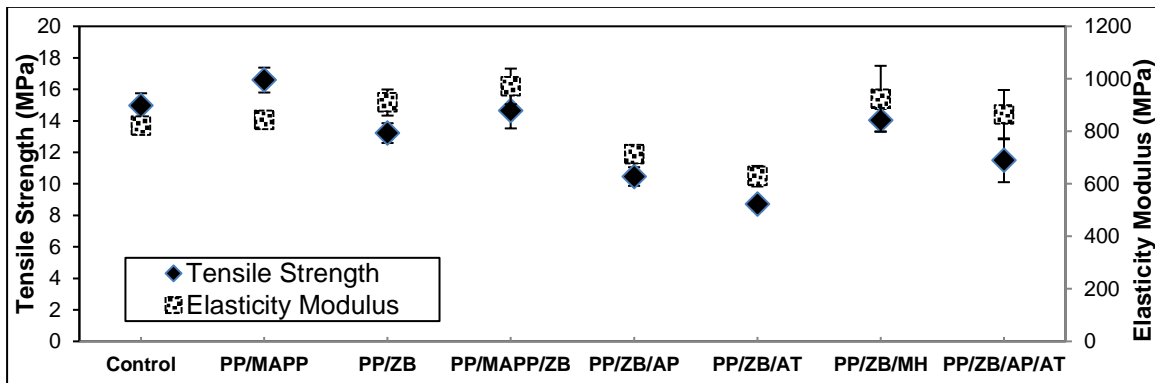

Fig. 3. Tensile strength and elasticity modulus of composite samples

Table 5. Mechanical Tests Results of Composites

Samples	Tensile Properties				Flexural Properties				Impact Strength	
	TS (MPa)	Sd[a]	TEM (MPa)	Sd	FS (MPa)	Sd	FEM (MPa)	Sd	IS (J/m)	Sd
Control	14.96[E,b]	0.79	821.29[C]	31.9	37.37[E]	2.1	2158.6[C]	162.7	22.6[D]	1.7
PP/MAPP	16.59[F]	0.79	842.89[CD]	32.0	38.84[E]	3.2	2216.1[C]	113.8	20.9[CD]	1.1
PP/ZB	13.22[D]	0.63	909.70[DE]	49.7	29.31[D]	1.8	2297.4[CD]	140.7	23.4[D]	2.4
PP/MAPP/ZB	14.64[E]	1.12	970.90[E]	68	32.01[C]	1.5	2442.4[D]	96.8	22.3[D]	1.5
PP/ZB/AP	10.46[B]	0.59	712.12[B]	25.3	22.42[A]	1.8	1579.4[A]	108.8	18.8[BC]	1.9
PP/ZB/AT	8.70[A]	0.42	629.13[A]	39.1	21.65[A]	2.4	1705.9[A]	128.1	14.3[A]	2.3
PP/ZB/MH	14.04[DE]	0.72	922.63[DE]	128.8	30.79[CD]	1.1	2159.3[C]	200.6	21.8[D]	1.1
PP/ZB/AP/AT	11.50[C]	1.39	863.60[CD]	93.8	25.13[B]	2.4	1945.3[B]	73.3	17.7[B]	0.9

[a]Standard deviation, [b]Homogeneity groups with superscripts were given from lowest to highest in the order letter (A-F) and those around it (α<0.05). The Superscripts indicate the statistical differences between properties of composite samples by Duncan' mean separation test.

Table 5 shows the flexural strengths and elastic modulus of the WPCs samples. Comparisons of flexural strengths and elasticity modulus of composite samples are given Fig. 4. The results indicated that the addition of zinc borate as a fire retardant material to the PP/ZB composite reduced flexural strength (21%) but increased its elastic modulus (6%) according to control sample. However, the addition of only 3% MAPP to the WPC increased the flexural strength and elastic modulus of PP/MAPP. In addition, the using both 3% MAPP and zinc borate reduced the tensile strength and increased the elastic modulus (13%) compared to the control sample. The addition of different fire retardant compounds with zinc borate in the composite samples generally reduced their flexural strengths and elastic modules according to Fig. 4. The lowest tensile strength and elastic modulus were obtained for the PP/ZB/AT composite, and there were two possible reasons for these effects. The first reason was the formation of a fragile surface between the polymer and zinc borate. The second reason was due to the structural incompatibility between the polymer and the fire retardant (Suppakarn and Jarukumjorn 2009; Ayrilmis 2013; Arao *et al.* 2014; Turku *et al.* 2014; Cavdar *et al.* 2016).
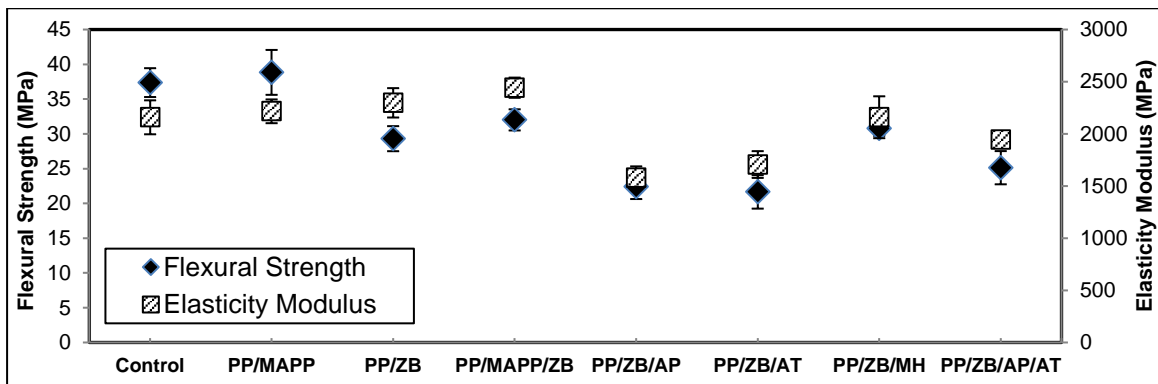

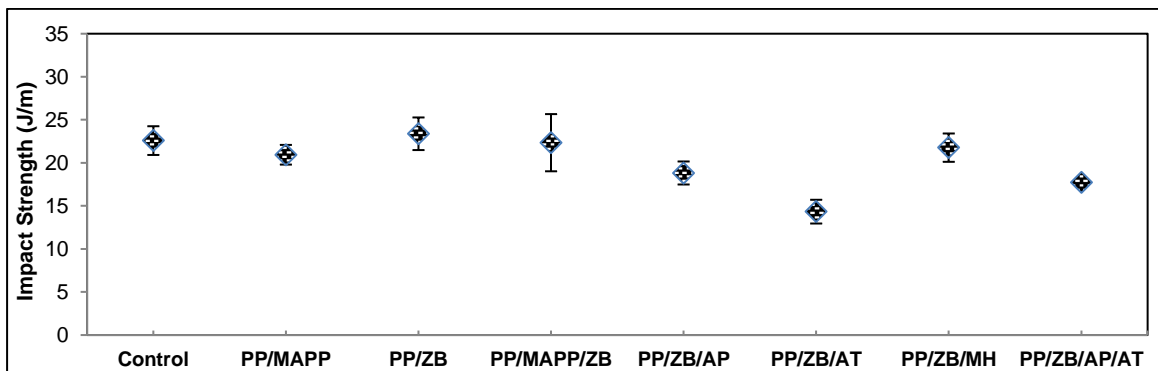**Fig. 4.** Flexural strength and elasticity modulus of composite samples

Fig. 5. The impact strengths of composite samples

Table 5 shows the impact strength of the composite samples. The mean values of the composite samples ranged from 14.3 MPa to 23.4 MPa. Figure 5 shows the impact strengths of composite samples. The impact strengths of the composites decreased slightly after addition of the zinc borate and various fire retardants. The lowest impact strength was obtained for the PP/ZB/AT composite. This reduction in impact resistance was mainly due to the distribution of energy by fire retardants, which are very rigid (Pan

*et al.*2012). Different studies have reported that the addition of fire retardants to a composite material generally reduces the impact strength (Suppakarn and Jarukumjorn 2009).

Scanning Electron Microscopy Results

Figure 6 shows the micrographs of the same composite samples with different fire retardants at fiber loading 40%. The control sample showed a tighter texture than that of the composite samples with zinc borate and other fire retardants. This situation was explained the decrease in the strength properties of composite samples with fire retardant. In a study on wood plastic composites, the reason for the decrease in the mechanical properties of the composite material with fire retardant was explained due to porous formed in structures (Mattos *et al.* 2014).
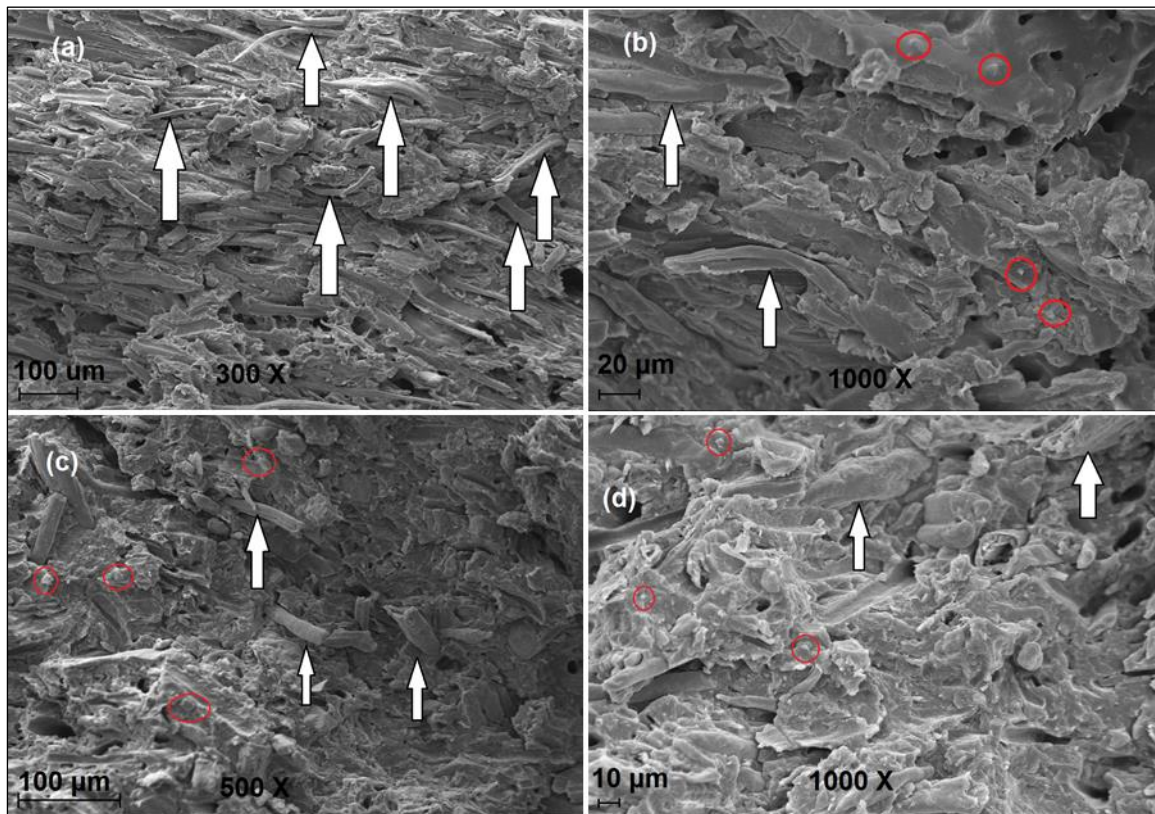

Fig. 6. SEM images of the composite samples a): Control; b): PP/MAPP/ZB; c): PP/ZB/AP and d): fibers in composites; b and d): PPP/ZB/AP/AT

CONCLUSIONS

1. The burning rate and limiting oxygen index properties of the composites were improved with the use of fire retardants. Coexistence of zinc borate, antimony trioxide, and ammonium phosphate in the composite created a synergistic effect and had the lowest burning rate.

2. The burning rates of composites with only zinc borate and together with zinc borate and antimony trioxide were fairly low in comparison to the control sample.

3. The highest limiting oxygen index results were obtained from the composite materials with synergistic effect.

4. According to the thermal gravimetric analyze results, both fire retardants postponed thermal degradation and increased the amount of charring residue at 800 °C. The composite materials with synergistic effect had the higher thermal degradation temperatures.

5. According to the DSC results, zinc borate and various fire retardants reduced the peak melting temperature and increased the peak crystallization temperature. The addition of fire retardants with synergistic effect to composites generally increased the degree of crystallinity.

6. The flexural and tensile strengths of the composites decreased when the fire retardants were used. However, the elastic modulus of the composites with fire retardants was generally affected positively.

7. The use of MAPP increased the tensile strength, flexural strength, and elastic modulus of the samples. The impact strengths of composites negatively affected when the zinc borate and synergistically effective compounds were used together.

ACKNOWLEDGMENTS

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