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Synergy effects of wood flour and fire retardants in flammability of wood-plastic composites

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Abstract

Addition of wood flour improve the mechanical properties of thermoplastics, on the other hand it increases the burning speed of the materials. To modify the flammability of wood-plastic composites(WPC), various fire retardants, such as ammonium polysphosphate (APP), melamine polyphosphate (MPP) and aluminum hydroxide were added to WPCs. Burning tests based on UL94 and cone calorimetry were conducted to evaluate a fire performance of WPCs with fire retardants. The addition of fire retardants could lead to self-extinguishing materials when 10 wt% of APP was used. However, in the case of pure polypropylene, addition of 10 wt% of APP did not improve the flammability. Wood flour accelerates the burning behavior of PP, but it can reduce the use of APP to achieve self-extinguishing materials. Synergy effects between wood flour and APP was confirmed. Wood flour facilitates the forming of foamed char layer by APP during the combustion. This protective char surface can reduce the heat and oxygen diffusion toward the WPCs. The effect of fire retardants of mechanical properties of WPCs was also investigated. Tensile strength and modulus of composites decreased with addition of fire retardants.

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Keywords: Fire retardants, Flammability, Heat release rate, Wood-plastic composite

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1. Introduction

Wood-plastic composites (WPC) combine the best properties of the neat components and can show outstanding performance. Wood flour is a readily available and relative inexpensive filler that can lower resin costs, improve stiffness, and act as an environmentally friendly way to reduce the use of petroleum-based plastics. In addition, WPCs have the advantages of good dimensional stability during lifetime, i.e. lower water uptake, and durability against fungi and insects compared with wood[1,2]. However, there are mainly two drawbacks for WPCs. Adhesion between wood flour and thermoplastics, especially for non-polar resin such as polypropylene (PP), is not enough to improve the mechanical properties [3-5]. The addition of MAPP can overcome the week adhesion property. The other disadvantage is that the WPCs show high flammability. High flammability of WPCs sets a limit to the application field of WPCs.

To modify the flammability of WPCs fire retardants are added during the compounding process[6]. Halogenated compounds based on chlorine and bromine are effective flame retardants. However, halogenated compounds produce toxic gases, so they should be avoided. Sainet et. al reported that the 25 % of magnesium hydroxide can effectively reduce the burning rate of WPCs to 50 % of composite without flame retardant [6]. They also confirmed a marginal reduction in the mechanical properties of the composites with addition of flame retardants. Graciaet. al found that the addition of fire retardants could lead to self-extinguish materials for polyethylene based composites when ammonium polyphosphate (APP) or aluminium hydroxide were used [7]. Stark et. al evaluated various fire retardants for use in wood flour-polyethylene composites[8]. Based on the investigation of cone calorimetry, magnesium hydroxide and APP improved the fire performance of WPCs the most in their study.

The evaluation of cone calorimetry can provide lots of information about the fire performance of WPCs, such as ignition time and (IT) and heat release rate (HRR). These data are key parameters for estimating the flammability of materials. However, in practices, the flammability of materials are evaluated based on UL94, which is a plastics flammability standard released by Underwriters Laboratories of the USA. In this standard, burning speed is measured from a practical standpoint. Both methods (cone calorimetry and UL94) are important to evaluate the flammability of the material. The results of UL94 should be considered based on the results of cone calorimetry to interpret the burning phenomenon.

In this study, we investigated the effective fire retardant to improve the flammability of PP/wood flour composites. Three types fire retardants; aluminium hydroxide, APP and melamine polyphosphate (MPP) were examined. The effects of wood flour on burning behavior of WPCs were also investigated. Addition of wood flour increased the burning speed of composites, however it couldreduce the amount of fire retardant that required for achievingself-extinguish property, owing to the synergy effect of wood flour and fire retardant. The strong synergy effect was observed for APP. The synergy effect between wood flour and APP will be discussed. We conducted the burning tests based on the UL standard to investigate the effective fire retardants and the minimum amount of fire retardant with respect to the improvement of fire performance. Cone calorimetry tests were also conducted to interpret the burning phenomenon of WPCs with fire retardant. Finally, tensile tests were performed to investigate the effect of fire retardants on the strength of WPC.

2. Experimental

2.1. Materials

High MFI PP is preferable with respect to flammability and processability of WPCs. High MFI PP (MFI=40g/min, J108M, Prime Polymer Co., Ltd.) was selected as matrix of WPCs. Wood flour (Lignoace□) was purchased from JUON in Japan. Lignin content of this wood flour is approximately 25 %. The other constituent of wood flour is cellulose and hemi-cellulose. Fire retardants used in this study are aluminum hydroxide (H-42M, Showa-Denko), APP (Kinseimatec Co., Ltd.) and MPP (MPP-A, SANWA Chemical Co., Ltd.). No halogen containing fire retardants was selected in order to use environmentally friendly materials. The weight ratio of fire retardants was varied between 5 to 10 wt%

To improve the dispersion and adhesion of the filler, MAPP (Youmex 1010, Sanyo Chemical) was used as a compatibilizer. If the wood ratio in WPCs increases, the surface area of wood flour increases. Therefore, the

effective amount of MAPP depends on the ratio of wood. We investigated the effective amount of MAPP to improve the mechanical properties of WPCs, and the optimal weight ratio of wood and MAPP was about 100:6.7. We added MAPP based on this result.

2.2. Preparation of wood flour/PP composites by twins screw extruder

A co-rotating twin-screw extruder (ZSK18, Coperion) with a screw diameter of 2 mm and a length-to-diameter ratio of 40 was used to compound PP/wood flour composites. The screw was composed of convey elements and kneading elements. The process temperature was set to 180 ˚C from the hopper to the die. The screw speed was 150 rpm and the throughput Q was 1 kg/h.

At first, wood flour and PP were dried in an oven at 80 ˚C for 24 h. Then, PP, MAPP, wood flour and fire retardant were dry mixed thoroughly before they were fed into the twin-screw extruder where they were compounded at the conditions mentioned above.

All specimens were injection molded into dumbbell-shaped tensile bars using a single screw injection-molding machine (PLASTR ET-40V, Toyo Machinery & Metal) with a barrel temperature of 210 ˚C. An end-gated mold was used for molding dumbbell-shaped samples according to the standard JIS K7113. The thickness and width of the specimens are 4 and 10 mm, respectively. Tensile test was conducted using this size of specimens. For specimens of flammability test, both ends of dumbbell-shaped samples were cut, and stripe specimens were prepared.

Table 1. Materials composition

No.	Composition based on weight (%)					
	PP	WF	MAPP	Fire retardants		
				APP	MPP	$Al(OH)_3$
1	100					
2	90			10		
3	90				10	
4	90					10
5	46.7	50	3.3			
6	41.7	50	3.3	5		
7	39.7	50	3.3	7		
8	36.7	50	3.3	10		
9	41.7	50	3.3		5	
10	36.7	50	3.3		10	
11	41.7	50	3.3			5
12	36.7	50	3.3			10
13	58	30	2	10		

2.3. Flammability test

The flammability test based on UL-94 is usually applied to evaluate and classify a fire performance of material. Therefore, a horizontal burning test and vertical burning test were conducted to investigate the effect of fire retardants on flammability of WPCs. In the horizontal burning test, the sample was held horizontally and a flame fuelled by natural gas was applied to light one end of sample for 20 sec. The height and angle of a flame against vertical direction were 10 mm and 30˚C, respectively. The time for the flame to reach from the first remark (20 mm from the end) to the second reference mark, which is 80 mm from the end in this study, was measured. The wire sheet was held under 10 mm of specimens to consider the effect of dripping, which is the falling of fire source. Prior to the test, the specimens were dried at 80 ˚C for 24 h. The tests were conducted at least three times for each

specimen. If the specimen showed incombustibility or self - extinguish in horizontal burning test, a vertical burning test was conducted. The sample was held vertically, and a flame with a 20 mm in height was applied to light one end of sample for 10 sec. The distance between the end of sample and burner was 10 mm. After that, the time of burning was measured. When the combustion of specimens stopped and a flame went out, the sample was ignited again for 10 sec. The combustion time, dripping of sample and burning state at fixing were investigated to determine the class of sample.

2.4. Cone calorimeter

Cone calorimeter test was performed on Cone III combustion analysis system (Toyo Seiki Seisaku-sho Ltd.). The boards were fabricated by hot press, and the samples were cut from the boards to a size of 100 mm x 100 mm. The sample thickness was at 3.3 mm. The sample were wrapped in aluminum foil and exposed in the horizontal orientation with the conical radiant electric heater located 25 mm above the samples. An external heat flux of 50 kW/m2 was applied to the samples. Several parameters are obtained from a cone calorimeter test, such as ignition time(IT), heat release rate (HRR), weight loss of sample. HRR is defined as the heat evolved from the specimens per unite time, and determined by the oxygen consumed during burning.Raman analysis

2.5. Tensile test

The tensile properties of the dumbbell PP/wood flour composite with fire retardants were measured using a universal testing machine (AG-100kN, Shimadzu) at a constant crosshead speed of 1 mm/min. The average value of tensile strength was calculated using at least five samples.

3. Results and discussions

3.1. Flammability of WPC with various fire retardant

Fig.1 shows the effect of wood flour content on the horizontal burning speed of WPCs. At low wood flour contents, the horizontal burning speed increased with increasing wood flour content. Therefore, the burning speed of WPC increased with the addition of wood flour. On the other hand, the heat release rate of wood is lower value compared to PP (shown in Fig. 2). The addition of wood decreases the heat release value. The burning speed of WPC might be decreased at high wood flour content (40-60 wt%) due to the reduction of heat release rate of WPCs. In any case, the burning speed of WPCs was higher than that of PP. Addition of wood flour accelerates the burning speed of PP.

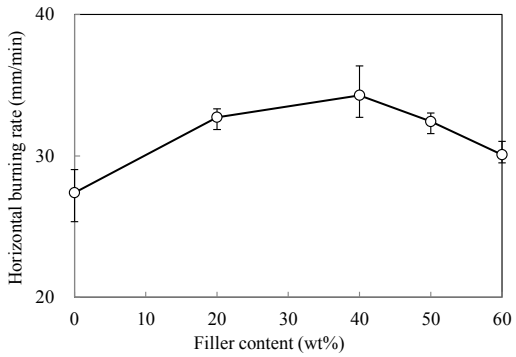

Fig. 1. Effect of wood flour content on horizontal burning rate of WPCs.

Table 2 summarizes the burning speed and flame classifications of PP and WPCs with fire retardants. The addition of fire retardant slightly decreases the burning speed of PP. Melting and dripping, which provide other ignition sources, were observed for all PP sample. Addition of 10 wt% of fire retardant cannot modify the fire performance of PP. In general, more than 30 wt% of fire retardant is required to provide self-extinguish property in thermoplastics [9,10]. In general, 10 wt% of APP or MPP is not enough to form char layer that can blockheat and oxygen from the combustion zone.

Table 2. Burning speed and flame classifications of PP and WPCs with fire retardants

No.	Test results	
	Average burning speed (mm/min)	Class Based on UL94
1	27.4	HB
2	22.7	HB
3	25.2	HB
4	27.5	HB
5	32.4	HB
6	22.2	HB
7	19.2	HB
8	Self-extinguish	V-0
9	22.5	HB
10	Self-extinguish	HB
11	22.2	HB
12	20.9	HB
13	21.2	HB

In the case of WPCs, the horizontal burning speed apparently decreased with the addition of fire retardants, and dripping of WPC was not observed. Especially for WPC with 10 wt% of APP or MPP, the flame did not spread and these materials showed self-extinguish property in horizontal burning test. We conducted vertical burning test with respect to WPCs with APP or MPP. All samples of WPC with APP showed self-extinguish property even though the samples were burn by a gas burner for 10 sec twice. No dripping was observed during the test. Therefore, this material is classified as V-0, which is the highest class in this test. In contrast, the flame of WPC with MPP was glowed to the clamp of sample. It could not satisfy the conditions of V-2, the lowest class in the vertical test. So, WPC with MPP was classified as HB. Both specimens created enough char during the test, however the expansion rate after the test was different. The expansion rate of WPC with APP after horizontal test was 90 %, and that with MPP was 78 %. APP showed better foaming property than MPP. It is presumed that the difference of foaming property generate the different flammability between APP and MPP. It is worth noting that addition of 10 wt% of APP did not improve the fire performance of PP, on the other hand it could give excellent fire performance for WPCs, though the addition of woof flour facilitate the burning speed. Synergy effects between wood flour and APP was apparently confirmed. As mentioned above, the 10 wt% of APP is not enough to form char layer in PP. In the case of WPC, there are lots source of char in wood flour. Therefore, 10 wt% of APP was enough to provide foaming layer of char, and this layer can restrain the spread of flame. APP is compatible to WPCs with respect to a fire performance. Stark et. al, Garcíaet. al and Li et al. also reported that APP showed better fire retardant property compared to other fire retardants, such as MPP, $Al(OH)_3$ and $Mg(OH)_2$ [11-13].

Owing to the synergy effect between wood flour and APP, addition of wood flour can reduce the minimum amount of APP required to give self-extinguish or V-0 class. Addition of 50 wt% of wood flour can reduce the required APP from 30 wt% to 10 wt%. This can contribute the mechanical properties and cost performance of WPCs. Note that in the case of WPC with 30 wt% of wood flour, addition of 10 wt% of APP could not improve the

fire performance class of WPC as shown Table 2 It indicates that the minimum amount of APP depends on the wood flour content in WPCs.

3.2. Cone calorimeter study

The cone calorimeter based on the oxygen consumption principle has been used to evaluate a fire performance of materials. The HRR measured by cone calorimeter is a very important parameter as it expresses the intensity of a fire. From the reaction-to fire point of view, such parameter as HRR after 1 or 3 min from ignition as well as peak HRR, and the time of ignition supply important information on the first stage of fire development [14,15]. We obtained these values and compared with the results of burning test (UL94).

Representative HRR versus time curves for PP, WPC and WPC with 10 wt% of fire retardants are shown in Fig.2. The HRR of PP gradually increased until a peak value, and then it sharply decreased due to the consumption of material. The HRR of WPCs reached a peak early during the test duration, then reached a second peak later in the test. All type of fire retardants reduced the peak HRR of WPCs without changing the tendency of HRR curves.

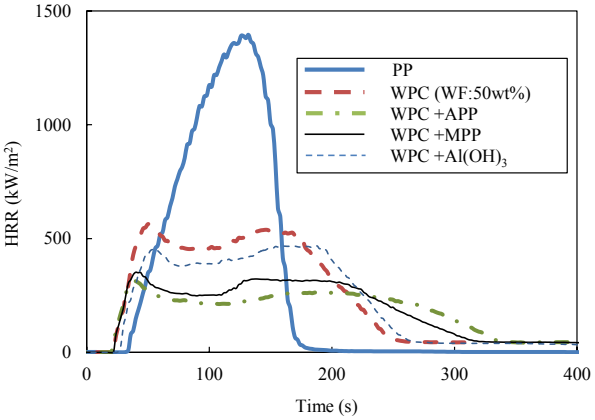

Fig. 2. HRR versus burning time for PP, WPC (WF = 50 wt%) and WPCs (WF = 50 wt%) with 10% fire retardant.

Cone calorimeter results for PP, WPC and WPC with fire retardants are shown in Table 3. Higher IT and lower HRR are preferable in a flammability of materials. The ignition time of WPC showed lower value compared to PP in spite of adding fire retardants. The lower specific heat of wood flour compared with PP means that less heat is required to start combustion of wood flour. In addition, decomposition temperature of wood is lower than that of PP as shown. These facts contribute the lower IT and higher burning speed of WPCs compared to PP. Peak HRR and average HRR were decreased with the addition of wood flour. This is because wood flour had the lower peak HRR and average HRR than PP, and fire performance of WPC fell between PP and wood flour [8].

Table 3. Burning speed and flame classifications of PP and WPCs with fire retardants

No.	Ignition time (S)	Peak Heat release rate (kw/m^2)	Total heat release (MJ/m^2)	Average HRR (kW/m^2)		
				60s	180s	Total
PP	31.6	1395	117	521	645	434
WPC (WF:50wt%)	21.4	563	93.4	416	456	336
WPC+APP	19.6	312	78.9	230	235	136
WPC+MPP	20.4	352	98.6	262	284	83.7
WPC+Al(OH)$_3$	24.8	467	99	341	400	96.5

Addition of fire retardant can reduce HRR and peak HRR of WPCs. Aluminum hydroxide increased the ignition time the most. This may be due to the high heat capacity of aluminum hydroxide. Reduced IT by aluminumhydroxide contributed the reduction of burning speed, however it cannot give self-extinguish property. In the view point of peak HRR and averave HRR, WPC containing APP preformed the best while WPCs containing aluminum hydroxide performed the worst. These results are consistent with the results of burning test based on UL 94. Synergy effect of wood flour and APP can form foamed char layer during combustion, thus APP can reduced HRR of WPC the most. With respect to WPCs, it seems that peak HRR and average HRR are dominate factors for determiningflammability as Babrauskaset. al indicated[14,15].

Fig. 3 shows the weight reduction behavior during cone calorimeter test. Fire retardants can be ordered in terms of reducing decomposition as follows: APP > MPP >Al(OH)3. This is the same relationships with reducing HRR and horizontal burning test. It is presume that investigation of weight reduction can be a brief indicator for flammability of materials.

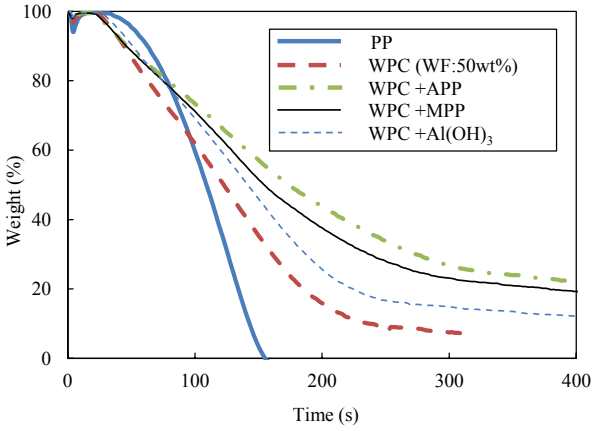

Fig. 3. Weight of sample versus burning time for PP, WPC (WF: 50 wt%) and WPCs (WF:50 wt%) with 10wt% fire retardant.

It is worth noting that thought the difference of HRR between WPC with APP and WPC with MPP was small as shown in Table 1, the difference of flammability class is significant (V-0 and HB). In this range of HRR (300-350 kW/m2), flammability of WPCs is sensitive to the value of HRR. It means a difference of few amount fire retardant considerably affects the fire performance of WPC in this range.

3.3. Mechanical performance

Figure 4, 5 show the effect of fire retardant on the tensile strength and elastic modulus of WPCs. About 50 % strength improvement was observed by adding 50 wt% of wood flour. We confirmed that if MAPP was not added to WPC, the strength of WPC was lower than the strength of PP. Therefore, interfacial adhesion is important in this material system. The addition of fire retardants decreased the tensile strength of WPC. Addition of 10 wt% of APP decreased the strength the most and the reduction ratio was approximately 14%. The results of elastic modulus showed the same results. Addition of APP decreased the modulus the most and the reduction ratio was 8 %. In summary, addition of 10 wt% APP can give self-extinguish properties to WPC with slight reduction of mechanical properties.

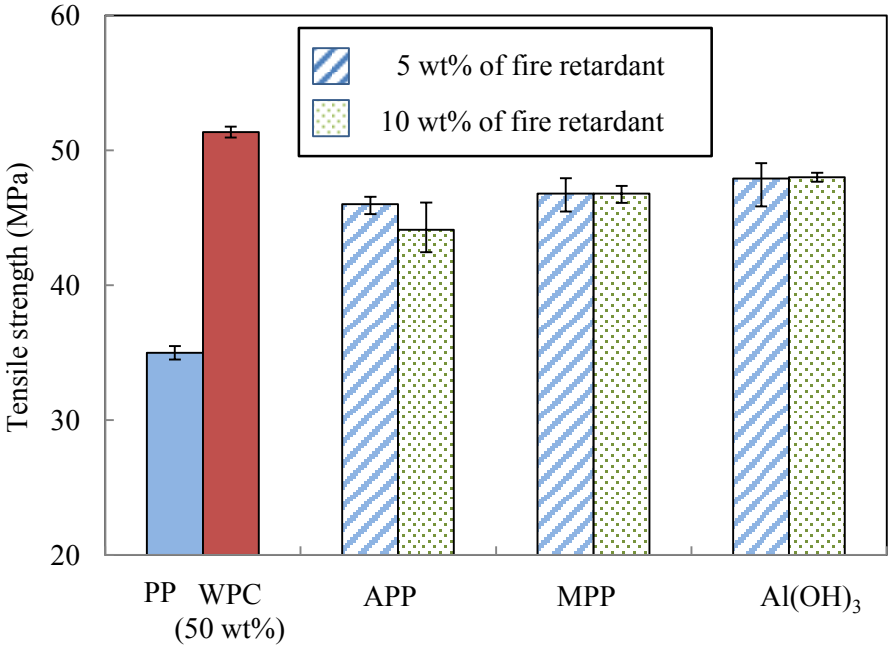

Fig. 4. Effect of fire retardants on the tensile strength of WPCs.

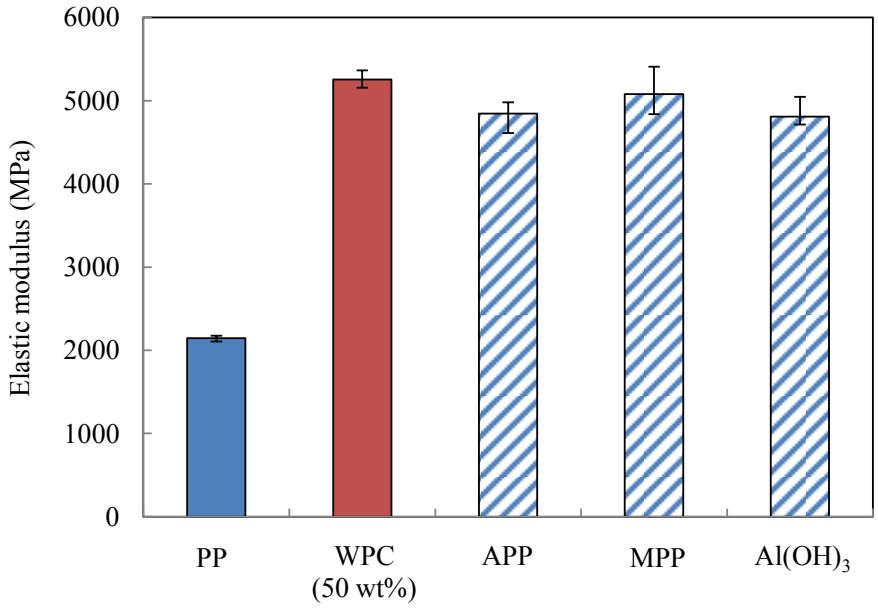

Fig. 5. Effect of fire retardants on the elastic modulus of WPCs.
Amount of fire retardant is 5 wt%.

4. Conclusion

The effective fire retardants and required amount of that to improve a fire performance of WPCs were investigated. Flammability of WPCs with various fire retardants were evaluated by burning tests based on UL94 and cone calorimeter. WPC with 10 wt % of APP showed the best fire performance, and flammability class was V-0, which means that it showed self-extinguish property at vertical burning test. In this study, 10 wt% was the minimum amount of fire retardants to satisfy V-0 class for WPCs with 50 wt% of wood flour. The minimum amount of APP for V-0 class depends on the amount of wood flour in WPCs. It indicates that the addition of wood flour can reduce the amount of APP. This is owing to the synergy effects between wood flour and APP. Addition of wood flour to plastics facilitates the forming of foamed char layer by APP. This barrier can block heat and oxygen from the combustion zone. It is presumed that the APP showed better performance than MPP, owing to its excellent intumescent property. Aluminum hydroxide showed the worst flammability, because there are no synergy effects considering the fire retardants mechanism of aluminum hydroxide. Consistent results were obtained with respect to flammability tests based of UL94 and cone calorimeter tests. Addition of 10 wt% fire retardants decreased the tensile strength of WPCs about 7 – 14%.

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