

# The Effect of Fire Retardants on the Flammability, Mechanical Properties, and Wettability of Co-Extruded PP-Based Wood-Plastic Composites

Irina Turku,\* Marina Nikolaeva, and Timo Kärki

In this work, fire retardants (FRs) such as aluminum trihydroxide (ATH), zinc borate (ZB), melamine, graphite, and titanium oxide (TiO<sub>2</sub>) were loaded into the shell layer of a co-extruded polypropylene (PP)-based wood-plastic composite (WPC). The incorporated retardants reduced the peak of the heat release rate by 8 to 22%, depending on the type of FR. Other studied parameters, such as ignition time and mass loss rate, were improved after the FR loading. The total heat release decreased slightly (except for the graphite-WPC). The effective heat of combustion was independent of the presence of the FR or, in the case of graphite, slightly increased. Carbon monoxide production increased (ZB, graphite) or was not changed significantly (ATH, melamine, and TiO<sub>2</sub>). It was also observed that the tensile strength improved after the FR loading; however, the tensile modulus decreased, except for the graphite-WPC. The impact strength improved or was independent of the FR loading, as in the case of the sample with ATH. The wettability of the composites decreased with filler loading, except for ZB, which showed the highest water absorption value among the studied composites.

*Keywords:* WPC; Co-extrusion; Flammability; Mechanical properties; Wettability

*Contact information:* Department of Mechanical Engineering, Lappeenranta University of Technology, P. O. Box 20, Lappeenranta, 53851 Finland; \*Corresponding author: irina.turku@lut.fi

## INTRODUCTION

Wood-plastic composites (WPCs) represent a new class of materials capable of combining the useful properties of both wood and plastic. The manufacturing of WPCs can be classified as ‘green technology’ due to the possibility of using waste wood and recycled plastic. WPCs are used in a great number of applications in different fields, including building, infrastructure, and transportation (Klyosov 2007). Due to the organic nature of the main constituents of WPCs, one of the critical drawbacks of WPCs is their flammability, which can limit their use. The traditional method of reducing the flammability of composites is using fire retardants (FRs). However, the amount of FR required is often so high that they can reduce the mechanical properties of the composite (Klyosov 2007). Another aspect is that some retardants, *e.g.*, ones containing halogen, are not environmentally friendly. Despite the importance of the flammability issue, research in this area is limited.

Metallic hydroxides, such as aluminum trihydroxide (ATH) and magnesium hydroxide, have been found to be effective FRs. They are also inexpensive, non-toxic, and environmentally friendly. At enhanced temperatures, starting from 220 °C, ATH decomposes to metal oxide and water ( $2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ ). The reaction is endothermic, taking about 1 kJ/g of heat from the system, releasing water as a cool-down

material and diluting combustible gases at the same time. The metal oxide can form a protective non-flammable layer on the polymer surface, which protects the material from further thermal decomposition and toxic gases release (Rakotomalala *et al.* 2010). It has been reported that ATH is effective in the reduction of the heat rate release (HRR) and smoke propagation for (poly(ethylene-co-vinyl acetate) (EVA) polymer alone or in combination with zinc borate (ZB), showing a synergistic effect (Bourbigot *et al.* 1999). Also, a mixture of ZB and ATH has shown a good synergistic effect on the flame retardancy and smoke suppression of PVC; thermal stability was significantly improved (Ning and Guo 2000). ATH has been found to be effective in the burning speed reduction of WPCs (García *et al.* 2009). As has been frequently reported, a common disadvantage of FRs is that they have to be used in large amounts. However, a combination of ATH with a small amount of a nanofiller, *e.g.*, montorillonite, could reduce ATH loading (Beyer 2001).

Zinc borates are multifunctional additives in WPC manufacturing. Along with the FR function, they are used as a wood preservative, as they are effective against fungal decay, for example. ZBs are low-cost materials and are known to be stable. ZBs are hardly soluble in water, which prevents their leaching from the composite material (Klyosov 2007). They are also thermally stable, having a decomposition temperature of approximately 300 °C. During combustion, ZBs release water vapor, thereby diluting the volatiles and decreasing the temperature in the system. They also form a glassy layer after the decomposition, which is a barrier for heat and volatiles transfer. ZB can be used alone or in combination with other retardants, supposing a synergistic effect (Ning and Guo 2000). Partial replacement of sisal by ZB or/and Mg(OH)<sub>2</sub> in a sisal/PP composite reduced the burning rate and increased the thermal stability; however, no synergistic effect was observed when Mg(OH)<sub>2</sub> and ZB were incorporated together (Suppakarn and Jarukumjorn 2009). Also, the addition of flame retardants did not deteriorate the mechanical properties of the composite. Another study showed the absence of a synergistic effect between Mg(OH)<sub>2</sub> and ZB; Mg(OH)<sub>2</sub> (25%) alone decreased the burning rate of a sawdust/PP composite to a greater extent than its combination with ZB or boric acid (Sain *et al.* 2004). Their paper also reported that the mechanical properties of composites with flame retardants were lower than those of the pure composite. This was attributed to poor compatibility of the flame retardants with the polymer. It has also been reported that the incorporation of ZB with WPCs in amounts of 1 to 3 wt.% did not affect the flexural strength and increased the flexural modulus slightly (Klyosov 2007). However, water adsorption increased with ZB incorporation. Stark *et al.* (2010) reported that ZB (10%) improved the oxygen index (OI), reduced the HRR, and lowered the total heat release (THR) and mass loss rate (MLR) of a PE-based WPC. Also, the studied flexural properties of the composite improved significantly after the retardant incorporation.

Melamine is a nitrogen-based flame retardant. At high temperatures, melamine and melamine derivatives are decomposed endothermically and produce inert N-based gases, which dilute oxygen and fuel gases. Also, melamine does not sublime completely in fire; a portion of un-sublimed melamine undergoes self-sublimation with the release of ammonia and formation of melamine derivatives, such as melam, melem, and melon. The derivatives play the role of char formers in the composite (Lowden and Hull 2013). In general, char acts as a mass or heat barrier and protects the underlying material from burning. Stark *et al.* (2010) reported that melamine phosphate (10%) improved the OI, reduced the HRR, and lowered the THR and MLR of a PE-based WPC. Also, the studied

flexural properties of the composite did not suffer after the retardant incorporation. However, García *et al.* (2009) report that melamine cyanurate enhanced the burning speed of an HDPE-based WPC.

As mentioned above, conventional FRs usually work at a high loading amount, which can have a negative impact on the mechanical performance of the composite. In this context, nano-sized particles are of interest due to their potential as reinforcing fillers, including their anti-flammable properties at very small loading amounts (Turku and Kärki 2014). Layered nanofillers such as clays and graphite have high aspect ratios (length-to-thickness) and large surface areas, as well as some specific mechanical and physical properties, which make them suitable for improving both the mechanical and barrier properties. Nanofillers mostly play the role of passive retardants due to the fact that they do not release water and inflammable gases, as is the case with conventional FRs (see above). During burning, they can facilitate char formation. Graphite, mainly expandable graphite, has been found to be an effective flame retardant in composites (Schartel *et al.* 2003; Seefeldt *et al.* 2012; Naumann *et al.* 2012). Graphite does not produce fire during oxidation; in addition, graphite consumes oxygen during oxidation, thereby reducing the flame in the system (Schartel *et al.* 2003). Nano-sized particles can act as FRs alone, as well as in combination with flame retardants, *e.g.*, clay combined with ATH (Beyer 2001). Nano-sized titanium oxide together with nanoclay has shown thermal barrier properties to oxygen and heat transfer throughout the composite (Deka and Maji 2011). It has also been reported that the mechanical properties of the WPC were improved in the presence of nanofillers.

One of the ways to facilitate WPC performance is using recently developed co-extrusion techniques (Stark and Matuana 2007; Jin and Matuana 2008; Jin and Matuana 2010). Co-extrusion means extrusion of the composite from the materials with different properties as a single array. Co-extrusion involves at least two extruders, which form layered or encapsulated material. With the co-extrusion method, it is possible to design materials with target mechanical, barrier, and aesthetic properties in a cost-saving manner. It has been shown that a surface layer that consists of pure polymer or polymer reinforced with different fillers can improve the water resistance properties (Stark and Matuana 2007; Jin and Matuana 2008; Jin and Matuana 2010), increase the flexural strength (Jin and Matuana 2008; Jin and Matuana 2010; Kim *et al.* 2013) and impact strength (Kim *et al.* 2013), and regulate the thermal expansion coefficient (Huang *et al.* 2012; Kim *et al.* 2013).

The aim of this work is to investigate the impact of three conventional flame-retardants, namely ATH, melamine, and zinc borate, and two nano-sized fillers, namely graphite and TiO<sub>2</sub>, on the flammable properties of a co-extruded composite. The filler was loaded only into the shell layer of the composite, and its amount was 10 wt.% of the shell layer. In addition, the influence of the fillers on the mechanical characteristics (tensile properties and impact strength) as well as the wettability of the composites was studied.

## EXPERIMENTAL

### Materials

A polypropylene (PP), Eltex P HY001P (Ineos), density 0.910 g/cm<sup>3</sup> and melt mass-flow rate 45 g/10 min (230 °C/2.16 kg), was used in the experiments. The coupling

agent was maleated anhydride PP (MAPP), Orevac ® CA 100 (Arkema). Struktol TPW 113 was used as the lubricant. Pulp cellulose (PC) was delivered by UPM, Finland. Zinc borate,  $4ZnO \cdot 6B_2O_3 \cdot 7H_2O$ , particle size  $d_{average}=5 \mu m$ , 99% less than  $25 \mu m$ , was obtained from Chemtura, Switzerland. Melamine with particle size  $d_{50}=10-15 \mu m$  was obtained from EcoChem Technologies, Belgium. Aluminum trihydrate (ATH) with particle size  $d_{50}=1.3$  to  $2.3 \mu m$ ,  $d_{90} \leq 4.5 \mu m$  was obtained from Albemarle Corporation, Germany. Graphite, Silvershine, was obtained from Skaland Graphite As, Norway; and  $TiO_2$  master batch, Plastwite 7038,  $TiO_2 : PE$  (polyethylene) = 50 : 50, was acquired from Cabot Clariant, Finland.

**Table 1.** Formulations of the Shell Layers of the Composites

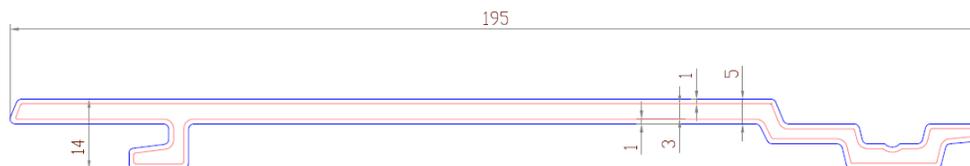
Composite number	Filler (%)					PC (%)	PP (%)	MAPP (%)	Lubricant (%)	Pigment (%)**
	ATH	Melamine	ZB	Graphite	$TiO_2$					
1 Reference						50	43	3	3	1
2	10					40	43	3	3	1
3		10				40	43	3	3	1
4			10			40	43	3	3	1
5				10		40	43	3	3	1
6					10*	40	43	3	3	1

\* - master batch ( $TiO_2 : PE = 50 : 50$ ); PE-polyethylene; \*\* Rematin

## Methods

### *Preparation of the composites*

Six different composite materials having the same core material and differences in the shell layer were produced. The core layer was produced from a blend with the percentage ratio of WF (wood flour) : PP : MAPP : UV-stab: lubricant : pigment : talc = 63 : 20 : 5 : 1 : 1.5 : 1.5 : 8. The materials and formulations used in the shell are listed in Table 1. A co-extrusion system, the Weber CE 7.2 counter-rotation conical twin-screw extruder, was used to produce the core layer. A fiberEX extruder was used to produce the shell layer. The processing temperatures in both extruders were between 174 and 202 °C. The schematic co-extrusion profile is shown in Fig. 1.



**Fig. 1.** Schematic of the co-extrusion profile

### *Composite characterization*

The tensile properties of the composites were measured in accordance with the standard EN ISO 527-1 in a Zwick/Roell Z020 testing machine. The un-notched impact strength was measured with a Zwick 5102 model impact tester in accordance with ISO 179. Water absorption (WA) and thickness swelling (TS) were determined according to EN 317. The moisture uptake was measured according to the ISO 3130 standard. All the physical and mechanical tests were carried out with 20 replicates for each type of WPC.

The flammability of the samples was studied with a horizontal burning test using a cone calorimeter (Fire Testing Technology, UK), according to ISO 5660-1. The sample size was  $100 \times 100 \times 5 \text{ mm}^3$ . The sides of the samples unexposed to flame were wrapped in aluminum foil. The samples, placed into a retainer frame, were positioned horizontally under the cone heater; the distance between the cone heater and the sample was 25 mm. All samples were tested under irradiation of  $50 \text{ kW/m}^2$ ; the exhaust system flow rate was 24 L/s. Three replicates for each type of WPC were tested.

#### Microstructure analysis

The microstructure of the composites was studied using a Jeol JSM-5800 LV scanning electron microscope (SEM) at an accelerated voltage of 15 kV. Prior to the analysis, the fracture surfaces were covered with a layer of gold using a sputter coater.

## RESULTS AND DISCUSSION

### Fire Test

Currently, the cone calorimeter technique is widely applied for testing the flammability of composites. The name cone calorimeter comes from the geometric parameter of the radiant heater. The standard (ISO 5660-1) of the cone calorimeter heat release calculation is based on oxygen consumption theory, in that most fuels generate approximately 13.1 kJ of energy per one g of oxygen consumed. Thus, the heat released from the material can be estimated by monitoring the amount of oxygen decrease during burning. The heat release rate (HRR) of fire is usually estimated as a function of time, and the peak of HRR (pHRR) is the prime parameter that describes the fire intensity and material properties. Simultaneously, parameters such as ignition time (IT), total heat release (THR), mass loss rate (MLR), effective heat of combustion (EHOc), and carbon oxide release can be evaluated.

The HRR curve profiles of the studied WPCs as a function of time are shown in Fig. 2. Each profile represents the average HRR results for a set of three samples. The curves have almost identical shapes and can be described according to a commonly accepted scenario. The initial peak starts to rise sharply due to combustion of the volatiles released by the material. Soon after this sharp rise, the HRR curve declines due to surface char layer formation. The formation of the char layer slows the material decomposition of the underlayer. The second HRR peak can be caused by char crack and burning out of the whole sample or the thermal feedback effect of the sample support materials (Schartel *et al.* 2003; Borysiak *et al.* 2006).

**Table 2.** Fire Test Results

WPC/type of FR filler	IT (s)	pHRR ( $\text{kW/m}^2$ )	THR ( $\text{MJ/m}^2$ )	MLR ( $\text{g/s}\cdot\text{m}^2$ )	EHOc ( $\text{MJ/kg}$ )	CO ( $\text{kg/kg}$ )
1 Reference	$28 \pm 1.4$	$395 \pm 21$	$162 \pm 5.4$	$5.3 \pm 0.07$	$27.3 \pm 0.7$	$0.036^*$
2 ATH	$29.7 \pm 1.5$	$336 \pm 5.5$	$152 \pm 1.7$	$5.1 \pm 0.1$	$27.9 \pm 0.5$	0.035
3 Melamine	$29.7 \pm 0.6$	$310 \pm 3.5$	$160 \pm 5.3$	$5.1 \pm 0.08$	$27.6 \pm 0.9$	0.033
4 ZB	$28.7 \pm 1.5$	$325 \pm 8.0$	$155 \pm 2.7$	$4.8 \pm 0.05$	$27.1 \pm 0.6$	0.063
5 Graphite	$43.7 \pm 1.2$	$343 \pm 3.0$	$162 \pm 3.1$	$4.7 \pm 0.04$	$28.7 \pm 0.6$	0.049
6 $\text{TiO}_2$	$29.3 \pm 1.0$	$362 \pm 6.8$	$154 \pm 3.5$	$5.1 \pm 0.3$	$27.4 \pm 0.5$	0.037

\* standard deviation for mean was  $< 1\%$

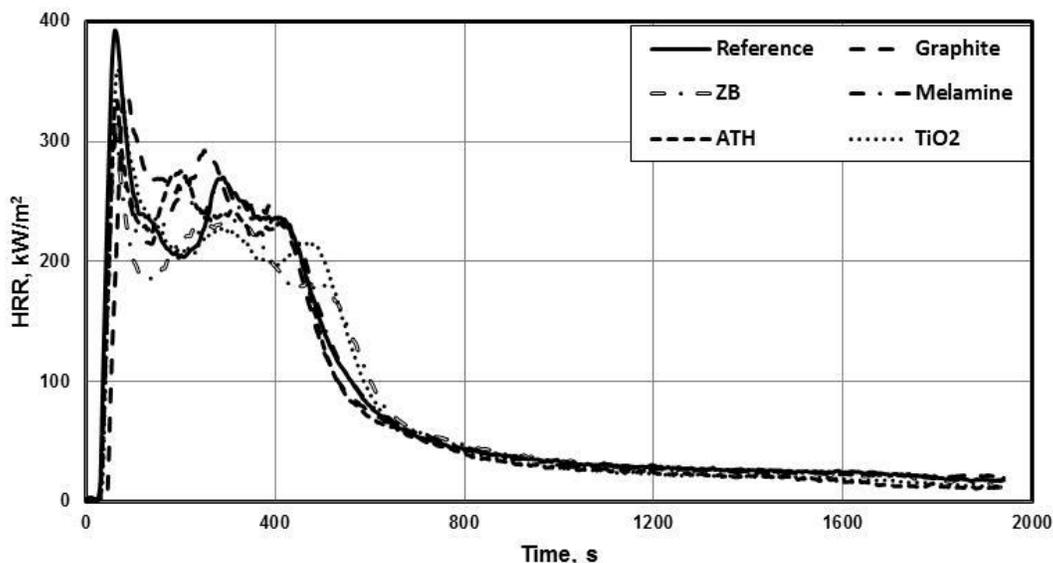


Fig. 2. Heat release rate curves for WPCs

The effect of the fire retardants on the fire scenario of the WPCs is summarized in Table 2. The results show that the conventional FRs, ATH, ZB, and melamine, had an impact on the initial peak of the HRR, decreasing it by 15%, 18%, and 22%, respectively. Melamine had a slightly higher impact on the pHRR than the other FRs did. However, the total heat release did not change much compared to the reference and was also slightly higher than for ATH- and ZB-WPCs. The IT was prolonged with the addition of FRs, but the changes in the case of ZB were insignificant. The mass loss rate decreased with the addition of all three FRs, and ZB showed the greatest impact. In another study, it was reported that ZB had a positive effect on the mass residue in PP-based composites (Suppakarn *et al.* 2009). The EHOc did not change after the FR loading. The ATH and melamine-loaded composites had the same CO release as the reference, whereas ZB increased the CO production significantly. It is suggested that residual ZB promotes the oxidation of residual organic matter to carbon monoxide.

The decrease of the pHRR with the incorporation of ATH, ZB, and melamine phosphate has been previously observed by other researchers in conventional PE-based WPCs (Stark *et al.* 2010). Stark *et al.* loaded 10 wt.% of FR into conventional WPC and detected peak of heat release rate decrease between 11% and 35%. In the present work, the presence of 10 wt.% in the shell layer resulted in the HRR decreasing between 15% and 22%, a finding that is comparable to that of Stark *et al.* Thus, it seems that the presence of FR in the surface layer might play a predominant role with respect to the effects of the material modification on flammability. It was also reported that the fire retardant, *e.g.*, expandable graphite, distributed in outer layer of strandboard reduced flame spread; and the best efficiency of coating were observed when graphite layer was concentrated on or just below the surface of board (Krassowski *et al.* 2012).

Nanometric particles were found to be effective in flame retardation of the studied composites. It can be seen in Fig. 2 and Table 2 that the incorporation of graphite resulted in a decrease of the initial peak, and the time of the peak moved from 60 s (reference and other studied composites) to 80 s (graphite). The reason for this is the longer time for ignition (44 s) compared to the reference (28 s). The peak HRR of the sample with graphite was reduced by 13% compared to the reference. The mass loss rate was the

lowest among the studied composites. However, the total heat release was not changed. The EHOc increased slightly after the graphite loading. The CO production increased with the presence graphite. The increased CO release was probably due to the thermal oxidation of graphite to carbon oxides (Hahn 2005). However, in another study, it was reported that expandable graphite reduced toxic gas release during the burning of a PP/flax composite (Schartel *et al.* 2003).

**Table 3.** Simulated FIGRA Index and Predicted SBI Classification of WPCs on the Basis of Cone Calorimeter Results

WPC/Type of FR filler	FIGRA (W/s)	Euro class
1 Reference	802 ± 63	E (FIGRA > 750 W/s)
2 ATH	633 ± 12	D (250 W/s > FIGRA > 750 W/s)
3 Melamine	586 ± 29	D (250 W/s > FIGRA > 750 W/s)
4 ZB	587 ± 46	D (250 W/s > FIGRA > 750 W/s)
5 Graphite	500 ± 10	D (250 W/s > FIGRA > 750 W/s)
6 TiO <sub>2</sub>	648 ± 17	D (250 W/s > FIGRA > 750 W/s)

FIGRA – fire growth rate

TiO<sub>2</sub> was found to reduce the pHRR by about 8%, and the THR was decreased slightly as well. Improvement of the thermal stability of the WPCs with clay/TiO<sub>2</sub> has been reported by Deka and Maji (2011). They concluded that the high thermal diffusivity of TiO<sub>2</sub> nanoparticles provided a better dispersion of heat inside the composite, which in turn could delay the burning of the surface and suppress the release of combustible volatiles throughout the composite. The MLR slowed down insignificantly, and the EHOc and CO production per mass loss did not change with the oxide presence. It should be noted that the amount of TiO<sub>2</sub> was twice as small as the amount of other fillers used because TiO<sub>2</sub> was used as a master batch.

To estimate the improvement of the fire performance of the composites, cone calorimeter results were estimated with the European fire classification system. The European fire classification of materials, which is usually applied for building materials, is based on the SBI (single burning item) test. The data from the cone calorimetry (ISO 5660-1) were analyzed by tools incorporated into the cone calorimeter for simulating the SBI (ISO 13823) test. The fire Euroclass ranks of the WPCs, based on the simulated results, are shown in Table 3. The FR fillers improved the fire classification of the composites from class E (reference) to class D.

### Mechanical Properties

The influence of the fillers on the mechanical properties of the WPC is shown in Table 4. It can be seen that the tensile strength of the WPC increased after the filler loading. The addition of ATH, melamine, and ZB improved the tensile strength by 23%, 13%, and 26%, respectively; the addition of graphite and TiO<sub>2</sub> improved the tensile strength by 37% and 20%, respectively. However, the tensile modulus of the composites decreased slightly for all filler types, except for graphite. The addition of ATH, melamine, and ZB decreased the modulus by 8%, 13%, and 7%, respectively; the addition of graphite slightly improved the modulus, by 5%; and the addition of TiO<sub>2</sub> decreased the modulus by 3%, *i.e.*, insignificantly. A decreased modulus for a sisal/PP composite loaded with ZB was also observed by Suppakarn and Jarukujorn (2009). The decreased modulus can be related to the mechanical properties of the fillers. For example,

graphite, having a Young's modulus of 1 TPa (Ajayan 1999), does not deteriorate the composite modulus, and even improves it slightly, because the stiffness of graphite is much higher than that of PC, *i.e.*, 40 GPa (Kalia *et al.* 2009). Also, the stiffness of TiO<sub>2</sub> is 230 to 288 GPa (<http://www.azom.com>), which is higher than that of PC. On the other hand, melamine, having a Young's modulus of 9 GPa (Gindl and Gupta 2002), which is lower than that of cellulose fibers, resulted in a decreased WPC modulus. No information about the stiffness of the other used FRs was found.

**Table 4.** Mechanical and Physical Properties of the Composites

WPC/Type of filler	Tensile strength (MPa)	Tensile modulus (GPa)	Impact strength (kJ/m <sup>2</sup> )	Moisture content (%)
1 Reference	10.2 ± 1.8	5.2 ± 0.6	3.1 ± 0.3	1.13 ± 0.05
2 ATH	12.5 ± 1.6	4.7 ± 0.4	3.0 ± 0.3	1.15 ± 0.04
3 Melamine	11.6 ± 0.6	4.5 ± 0.3	4.0 ± 0.2	1.0 ± 0.07
4 ZB	12.9 ± 1.0	4.8 ± 0.3	3.3 ± 0.3	1.3 ± 0.05
5 Graphite	14.2 ± 2.0	5.4 ± 0.7	3.7 ± 0.4	1.1 ± 0.08
6 TiO <sub>2</sub>	12.3 ± 1.6	5.0 ± 0.6	3.3 ± 0.4	1.2 ± 0.06

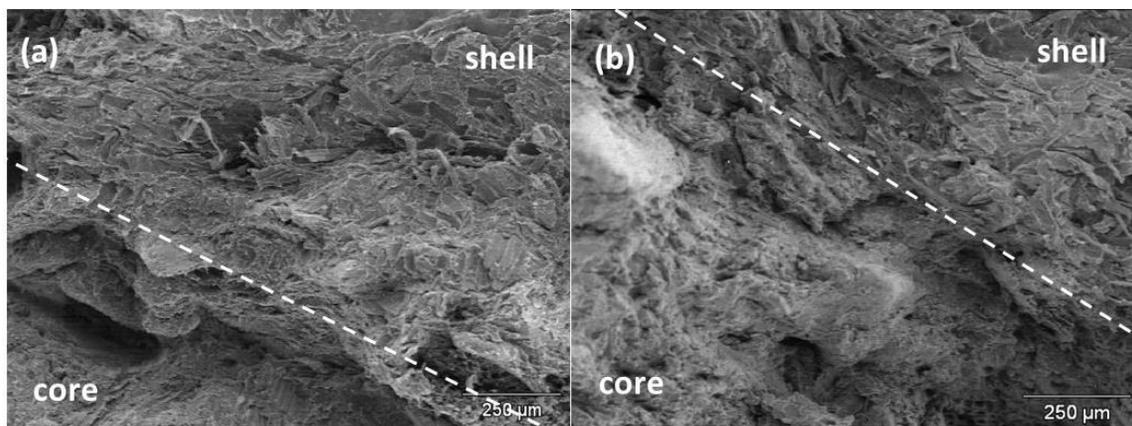
The effect of the fillers on the impact strength of the composite is also shown in Table 4. According to the results, the incorporation of melamine and ZB increased the impact strength by 29% and 7%, respectively; the impact strength of ATH-WPC was independent of the filler loading. Graphite and TiO<sub>2</sub> showed an improvement of 19% and 7%, respectively. A positive influence of ZB on the impact strength of a sisal/PP composite was observed by Suppakarn and Jarukujorn (2009). The significant improvement of the impact strength after the melamine loading may be associated with the interaction of melamine with cellulosic fibers and PP. The polar amine groups of melamine can interact with the hydrophilic moieties of cellulose. On the other hand, melamine is an aromatic compound due to *s-triazine* aromatic ring in its structure. The aromatic ring makes this molecule hydrophobic (Bansal *et al.* 2010) and hence capable of interacting with the hydrophobic PP-matrix through hydrophobic interactions. Such affinity for both phases can improve the interfacial interaction and thereby enhance the mechanical properties of the composite. It has also been reported that melamine can diffuse into the amorphous region of cellulose fibrils and form covalent bonds with cellulose (Gindl and Gupta 2002). Thus, melamine can fill pores and crosslink cell wall polymers, which may improve the performance of the composite.

The influence of the shell layer, *e.g.*, neat polymer or reinforced with different fillers, on the mechanical properties of the co-extruded WPC is reported in the literature. Yao and Wu (2010) report that shell-coated HDPE-based WPC exhibited improved flexural and impact strengths, as well as improved dimensional stability; however, modulus decreased compared to an unshelled composite. Jin and Matuana (2008) report that pure polyvinyl chloride (PVC)-coated WPC showed improved flexural strength but a decreased modulus compared to conventional WPC. A further reinforcement cap layer with wood flour (5 to 27%) resulted in improved strength; stiffness was reduced significantly at a low wood content and showed similar value to uncoated WPC at the highest wood content. Later, Jin and Matuana (2010) report that reinforcing the PVC outer layer with carbon nanotubes resulted in improved strength and modulus. They also describe that increasing temperature of the processing had a positive influence on the composite properties due to a decrease of the fusion time of the PVC that resulted in

enhanced wood particle encapsulation by the matrix in the core, as well as in core/cap interlayer interaction improvement. Kim *et al.* (2013) studied the properties of co-extruded composites with a weak and strong core as well as influence of the composition of fillers (*e.g.*, CaCO<sub>3</sub> and wood fibers) on the overall properties of the composite. It was shown that flexural strength of the WPC with weak core increased by about 40% with the precipitated calcium carbonate loadings (6 to 18%); flexural strength of the strong-core composite decreased with the mineral loading. Flexural modulus decreased with the CaCO<sub>3</sub> incorporation for both, strong- and weak-core WPCs; however, impact strength increased for the strong and weak core system on the 119% and 150%, respectively. Incorporation of wood fibers into shell layer has insignificant influence on the flexural strength and modulus of the co-extruded WPC; impact strength monotonically decreased with the WF incorporation (0 to 25%). Huang *et al.* (2013) improved the impact strength of HDPE-based WPC by coating it with a HDPE-based shell layer; further incorporation of talc (5 to 55%) improved the strength to a larger extent. They also report that the flexural properties of the pure polymer coated composite decreased, but slightly increased at a high loading of talc. The thermal expansion of the shelled composite decreased compared to conventional WPC. Turku *et al.* (2014) report that microfibrillated cellulose (MFC) loaded into shell layer of the PP-based WPC improved tensile strength by 22 to 35% depending on the MFC kind; tensile modulus was improved by 4 to 5%, *i.e.*, insignificantly; impact strength was independent on the MFC loading.

### Composite Morphology

The morphology of the composites was observed with SEM, and micrographs of the reference and melamine-WPC are shown in Fig. 3. The structures of the shell and core layers are different, but no borders or cracks can be observed between the two phases. On the basis of the SEM micrograph, it can be assumed that bonding between the layers is quite good. The melamine particles in the shell layer are not visible at this magnification. The PC fibers that can be observed in the shell are well distinguished. However, no visible changes in the morphologies of the reference and melamine-loaded shell layers can be observed. The cavities in the core layer are a result of pulled-out WF, which suggests weak interfacial interaction in the core. The other composites had similar morphologies, which is why their SEM micrographs are not shown here.



**Fig. 3.** SEM micrographs of the reference (a) and the composite with melamine in the shell layer (b)

## Water Absorption and Thickness Swelling

The water absorption and thickness swelling of the WPCs are displayed in Fig. 4. The presence of ZB resulted in an increased WA parameter. ZB is known as a highly hydrophilic compound (Gwon *et al.* 2012) that enhances water absorption significantly. On the other hand, the thickness swelling of the ZB-containing composite was comparable with the reference and only slightly higher than for the other composites. Gwon *et al.* (2011) associated the high water absorption of a ZB-containing composite with the high hygroscopicity of ZB and its cubic crystal structure, which was the reason for void formation in the composite body during manufacturing. Thus, a composite having empty space can take up more water without dramatic dimensional changes. The ATH-loaded WPC had the lowest water absorption and thickness swelling, probably due to the narrow particle size distribution of ATH, which results in a better dispersion property throughout the composite and hence a lower void formation probability. TiO<sub>2</sub> had lower water absorption and thickness swelling compared to the reference due to the slightly higher hydrophobic polymer content in this WPC. The less hydrophilic nature of melamine (see above) and graphite (Herwig and Trouw 1992) resulted in a lowered water ingress compared to the reference.

The influence of the shell layer on the co-extruded WPC wettability has been reported in the literature. Stark and Matuana (2007) report that WPC coating with a polymer layer improved the moisture resistance and durability of the composite compared to an uncoated one. Turku *et al.* (2014) report that MFC loading into shell layer did not influence on the water absorption of the co-extruded WPC; however, thickness swelling increased. Kim *et al.* (2013) showed that the shell layer decreased wettability of the WPC; however, WA and TS parameters were independent of the CaCO<sub>3</sub> loaded amount (6 to 18%). They also showed that wettability increased with the WF loading into shell layer.

Moisture uptake is the water uptake characteristic under unsaturated humidity conditions. The moisture content values of WPCs are given in Table 4. Obviously, the less hydrophilic nature of melamine and graphite resulted in the lowest moisture content of the melamine- and graphite-loaded composites compared to the other WPCs. The highly hydrophilic ZB resulted in the highest moisture content.

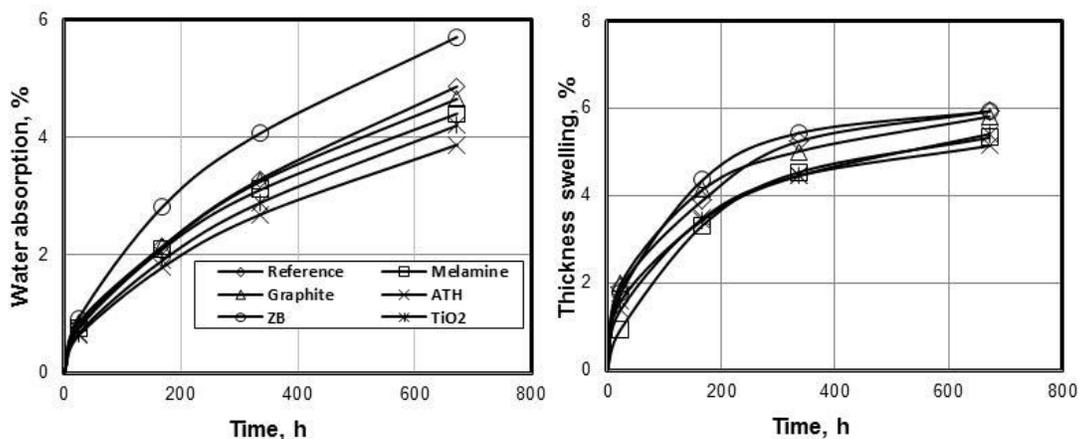


Fig. 4. Water absorption and thickness swelling

## CONCLUSIONS

1. The incorporation of ATH resulted in an increased ignition time (IT) and decreased peak of heat release rate (pHRR) as well as total heat release (THR) for the test duration, showing minimal value among the studied polypropylene-wood composites; the mass loss rate (MLR) slowed and the effective heat of combustion (EHOC) and CO release did not change. The tensile strength increased with ATH loading, but the tensile modulus decreased; the impact strength was independent of the ATH loading. The water absorption (WA) and thickness swelling (TS) values were the lowest among the studied composites.
2. ZB loading did not change the IT; the pHRR and THR decreased; the MLR was reduced; and the EHOC was independent of the ZB loading; however, the CO release increased and was maximal in this study. The tensile and impact strengths increased slightly after the ZB loading, and the tensile modulus decreased. The ZB-WPC showed the maximal WA value, and the TS was similar to that of the reference.
3. Melamine loading resulted in a delayed IT and decreased the pHRR and THR so that the HRR peak was minimal among the studied composites; the MLR decreased, but very insignificantly; the EHOC did not change; and the CO decreased slightly. Melamine improved the tensile and impact strengths so that the impact strength was maximal among the studied WPCs; the tensile modulus, however, decreased. The WA and TS decreased after melamine loading.
4. Graphite loading showed the most significant IT decrease, as well as a delayed and decreased pHRR and THR for the test duration; the MLR also decreased, showing a minimal value in this study; however, the EHOC and CO release increased compared to the reference. The mechanical properties of the composite improved, and the wettability decreased.
5. The presence of TiO<sub>2</sub> resulted in an increased IT and decreased both the pHRR and THR; the MLR slowed; the EHOC and CO release did not change. The tensile and impact strengths increased slightly, and the modulus decreased. TiO<sub>2</sub> also decreased the wettability of the WPC.
6. The European fire class of the composites was predicted with cone calorimeter test simulating tools. It was found that incorporation of all five fillers reduced the flammability, so that the Euro class was changed from E (for the reference) to D.

## ACKNOWLEDGMENTS

This study was supported by a grant (number A32028) from the Southern Finland ERDF program.

## REFERENCES CITED

Ajayan, P. M. (1999). "Nanotubes from carbon," *Chem. Rev.* 99(7), 1787-1799.

- Bansal, K. K., Kakde, D., Gupta, U., and Jain, N. K. (2010). "Development and characterization of triazine based dendrimers for delivery of antitumor agent," *J. Nanosci. Nanotechnol.* 10(12), 8395-8404.
- Beyer, G. (2001). "Flame retardant properties of EVA-nanocomposites and improvements by combination of nanofillers with aluminium trihydrate," *Fire Mater.* 25(5), 193-197.
- Borysiak, S., Paukszta, D., and Helwig, M. (2006). "Flammability of wood-polypropylene composites," *Polym. Degrad. Stab.* 91(12), 3339-3343.
- Bourbigot, S., Le Bras, M., Leeuwendal, R., Shen, K. K., and Schubert, D. (1999). "Recent advances in the use of zinc borates in flame retardancy of EVA," *Polym. Degrad. Stab.* 64(3), 419-425.
- Deka, B. K., and Maji, T. K. (2011). "Effect of TiO<sub>2</sub> and nanoclay on the properties of wood polymer nanocomposites," *Composites: Part A.* 42(12), 2117-2125.
- García, M., Hidalgo, J., Garmendia, I., and García-Jaca, J. (2009). "Wood-plastic composites with better fire retardancy and durability performance," *Composites: Part A.* 40(11), 1772-1776.
- Gindl, W., and Gupta, H. S. (2002). "Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation," *Composites: Part A.* 33(8), 1141-1145.
- Gwon, J. G., Lee, S. Y., Chun, S. Y., Doh, G. H., and Kim, J. H. (2012). "Physical and mechanical properties of wood-plastic composites hybridized with inorganic fillers," *J. Compos. Mater.* 46(3), 301-309.
- Hahn, J. R. (2005). "Kinetic study of graphite oxidation along two lattice directions," *Carbon.* 43(7), 1506-1511.
- Herwig, H. W., and Trouw, F. R. (1992). "Ethanol on graphite: The influence of hydrogen bonding on surface melting," *Physical Rev. Letters.* 69(1), 89-93.
- Huang, R., Xiong, W., Xu, X., and Wu, Q. (2012). "Thermal expansion behavior of co-extruded wood-plastic composites with glass-fiber reinforced shells," *BioResources* 7(4), 5514-5526.
- Huang, R., Kim, B. J., Lee, S., Yang Z., and Wu, Q. (2013). "Co-extruded wood-plastic composites with talc-filled shell: morphology, mechanical, and thermal expansion performance," *BioResources* 8(2), 2283-2299.
- Jin, S., and Matuana, L. M. (2008). "Coextruded PVC/wood-flour composites with WPC cap layers," *J. Vinyl. Add. Technol.* 14(4), 197-203.
- Jin, S., and Matuana, L. M. (2010). "Wood/plastic composites co-extruded with multi-walled carbon nanotube-filled rigid poly(vinyl chloride) cap layer," *Polym. Inter.* 59(5), 648-657.
- Kalia, S., Kaith, B. S., and Kaur, I. (2009). "Pretreatments of natural fibers and their application as reinforcing material in polymer composites – A review," *Polym. Eng. Sci.* 49(7), 1253-1272.
- Kim, B. J., Yao, F., Wang, Q., and Wu, Q. (2013). "Mechanical and physical properties of core-shell structured wood plastic composites: Effect of shells with hybrid mineral and wood filler," *Composites: Part B.* 45(1), 1040-1048.
- Klyosov, A. K. (2007). *Wood-plastic Composites*, Wiley-Interscience, New Jersey.
- Krassowski, D. W., Hutching, D. A., and Qureshi, S. P. (2012). "Expandable graphite flake as an additive for a new flame retardant resin," GrafTech International Ltd.
- Lowden, L. A., and Hull, T. R. (2013). "Flammability behavior of wood and review of the methods of its reduction," *Fire Sci. Rev.* 2, 2-19.

- Naumann, A., Seefeldt, H., Stephan, I., Braun, U., and Knoll, M. (2012). "Material resistance of flame retarded wood-plastic composites against fire and fungal decay," *Polym. Degrad. Stab.* 97(7), 1189-1196.
- Ning, Y., and Guo, S. (2000). "Flame retardant and smoke-suppressant properties of zinc borate and aluminum trihydrate-filled rigid PVC," *J. Appl. Polym. Sci.* 77(14), 3119-3127.
- Rakotomalala, M., Wagner, S., and Döring, M. (2010). "Recent developments in halogen free flame retardants for epoxy resins for electrical and electronic applications," *Materials.* 3(8), 4300-4327.
- Sain, M., Park, S. H., Suhara, F., and Law, S. (2004). "Flame retardant and mechanical properties of natural fibre-PP composites containing magnesium hydroxide," *Polym. Degrad. Stab.* 83(2), 363-367.
- Schartel, B., Braun, U., Schwarz, U., and Reinemann, S. (2003). "Fire retardancy of polypropylene/flax blends," *Polymer.* 44(20), 6241-6250.
- Seefeldt, H., Braun, U., and Wagner, M. H. (2012). "Residue stabilization in the fire retardancy of wood-plastic composites: Combination of ammonium polyphosphate, expandable graphite, and red phosphorus," *Macromol. Chem. Phys.* 213(22), 2370-2377.
- Stark, N. M., and Matuana, L. M. (2007). "Coating WPCs using co-extrusion to improve durability," Conference proceedings: *Coating Wood and Wood Composites: Designing for Durability*, Seattle, WA.
- Stark, N. M., White, R. H., Mueller, S. A., and Osswald, T. A. (2010). "Evaluation of various fire retardants for use in wood flour-polyethylene composites," *Polym. Degrad. Stab.* 95(9), 1903-1910.
- Suppakarn, N., and Jarukumjorn, K. (2009). "Mechanical properties and flammability of sisal/PP composites: Effect of flame retardant type and content," *Composites: Part B.* 40(7), 613-618.
- Turku, I., and Kärki, T. (2014). "Research progress in wood-plastic nanocomposites: A review," *J. Thermopl. Comp. Mater.* 27(2), 180-204.
- Turku, I., Hämäläinen, K., and Kärki, T. (2014). "Co-extrusion of wood flour/PP composites with PP-based cup layer reinforced with macro- and micro-sized cellulosic fibres," *Adv. Mater. Res.* 834-836, 203-210.
- Yao, F., and Wu, Q. (2010). "Co-extruded polyethylene and wood-flour composite: Effect of shell thickness, wood loading, and core quality," *J. Appl. Polym. Sci.* 118(6), 3594-3601.

Article submitted: October 28, 2013; Peer review completed: December 22, 2013;  
Revised version received and accepted: January 16, 2014; Published: January 30, 2014.