Comparative Mechanical, Fire-Retarding, and Morphological Properties of High-Density Polyethylene/(Wood Flour) Composites with Different Flame Retardants

Jinlong Zhang,¹ Changtong Mei,² Runzhou Huang,² Xinwu Xu,² Sunyoung Lee,³ Birm-June Kim,⁴ Qinglin Wu^{1,2}

¹School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA

 2 College of Material Science and Engineering, Nanjing Forestry University Nanjing, 210037, China

³Department of Forest Products, Korea Forest Research Institute, Seoul 130-712, Republic of Korea

⁴Department of Forest Products and Biotechnology, Kookmin University, Seoul 136-702, Korea

Aluminum hydroxide, magnesium hydroxide, and 1,2-bis(pentabromophenyl) ethane were incorporated into highdensity polyethylene (HDPE) and wood flour composites, and their mechanical properties, morphology, and fireretardancy performance were characterized. The addition of flame retardants slightly reduced the modulus of elasticity and modulus of rupture of composites. Morphology characterization showed reduced interfacial adhesion among wood flour, HDPE, and flame retardants in the composites compared with control composites (HDPE and wood flour composites without the addition of flame retardants). The flame retardancy of composites was improved with the addition of the flame retardants, magnesium hydroxide and 1,2-bis(pentabromophenyl) ethane, especially 1,2-bis(pentabromophenyl) ethane, with a significant decrease in the heat release rate and total heat release. Char residue composition and morphology, analyzed by attenuated total reflectance, Fourier-transform infrared spectroscopy, and scanning electron microscopy, showed that the char layer was formed on the composite surface with the addition of flame retardants, which promoted the fire performance of composites. The composites with 10 wt% 1,2-bis(pentabromophenyl) ethane had good fire performance with a continuous and compact char layer on the composite surface. J. VINYL ADDIT. TECHNOL., 24:3-12, 2018. © 2015 Society of Plastics Engineers

INTRODUCTION

Wood-plastic composites (WPC), as an emerging class of environmentally friendly materials, have been developed and used in recent years. Wood fiber is widely

DOI 10.1002/vnl.21516

Published online in Wiley Online Library (wileyonlinelibrary.com). @ 2015 Society of Plastics Engineers

available and relatively less expensive, which helps lower overall composite costs and improves stiffness as well [1]. Plastics offer advantages of melt processing, water resistance, and biological resistance. WPC can be altered in shapes and sizes and have good dimensional stability during the service life [2]. Thus, WPC have gained popularity in several fields, especially interior panels for automobiles and deck boards for construction. However, one of the primary concerns for WPC, which limits its wider application, is its low fire resistance because plastics and wood as organic materials are sensitive to flame. Thus, it is crucial to enhance the fire performance of WPC to accommodate the fire requirements and regulations so as to expand the potential industrial application of WPC [3].

One strategy used to acquire fire resistance for WPC is the incorporation of fire retardants during processing, such as extrusion, compression, and injection molding. Much research has been focused on phosphorous compound flame retardants [1, 4-7]. Compared with that of control WPC, the intumescent char layer was formed with the addition of flame-retardant ammonium polyphosphate (APP), and thus a better fire performance was achieved [8]. In addition, APP also promoted esterification, dehydration, and char formation for WPC [9]. Phosphorus compounds are usually combined with other flame retardants to achieve synergistic effects. The synergism of expandable graphite and APP improved fire performance of WPC. The formation of graphite layers blocked the heat and gas transfer between the flame zone and matrix, thus retarding the smoke production of WPC and protecting the matrix from decomposition [10, 11]. However, phosphorous compound flame retardants release harmful gases on degradation due to their phosphorus element [12]. In addition, it is commonly used for polymers with

Correspondence to: Q. Wu; e-mail: wuqing@lsu.edu and C. Mei, e-mail: mei@njfu.edu.cn

TABLE 1. Structural formulas and characteristic properties of flame retardants used.

Properties of flame retardants	Aluminum hydroxide	Magnesium hydroxide	Ethane-1,2-bis (pentabromophenyl)	
Commercial name	Martinal ON-310	Magnifin H-5	SAYTEX 8010	
Structural formulas	Al(OH) ₃	$Mg(OH)_2$	$C_{14}H_4Br_{10}$	
Molecular weight	78.00	58.32	971.20	
Appearance	White powder	White powder	White powder	
Thermal stability (°C)	251	340	350	
Density (g/cm ³)	2.4	2.4	NA	
Particle size (µm)	18.0-26.0 (d ₉₀)	2.4-4.4 (d ₉₀)	Average 5.63	

relatively low melting points because they can easily suffer thermal degradation beyond 200°C, which deteriorates the composite fire-resistance performance [13].

Boron compounds also play an important role in fire retardancy of WPC. Zinc borate, as a potential filler, has been used to retard the thermal degradation of WPC because of its high thermal stability. Zinc borate helps form a glassy protection layer as a barrier to reduce the heat release rate (HRR) and thus slow the combustion of composites [3, 14]. In addition, the combination of boron compounds and APP shows synergistic effects for WPC in flame retardancy [15]. It promotes the reaction with hydroxyl groups of the cellulose and hemicellulose to enhance the formation of the char and also has a positive effect on smoke suppression of composites [16, 17]. However, most synergistic effects normally occur at high chemical loading levels. At these levels of addition, mechanical properties of composites decrease sharply owing to the poor compatibility between flame retardants and polymer matrix [18].

Metal hydroxides are the most commonly used flame retardants in the industry. The metal hydroxides endothermically decompose to release water when being heated, which retards the ignition by increasing decomposition temperature, reduces heating of the plastic substrate, and thereby slows thermal decomposition of the plastics [19–22]. In addition, metal hydroxides are environmentally friendly flame retardants and significantly decrease the emission of toxic gases, such as carbon monoxide, because the decomposed residue is nonflammable inorganic compounds. However, the drawback of the metal hydroxides is that high loadings of flame retardants are required to achieve good fire performance, which deteriorates composite mechanical properties [23]. Therefore, it is necessary to surface modify metal hydroxides with certain couple agents. Moreover, halogenated compound based on chlorine or bromine has also been used as effective flame retardants for WPC [21]. Halogened flame retardants work in the vapor phase to retard combustion and show highly effective flame retardancy for WPC [13, 24].

The objective of this work was to provide a comparative study on mechanical properties, morphology, and fire retardance of various compounds for use in WPC. The residual char after complete combustion was further studied by using (attenuated total reflection)/(Fourier-transform infrared) spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM) techniques to further understand the reaction of fire retardants in the composites.

MATERIALS AND METHODS

Materials

High-density polyethylene (HDPE; AD60-007) pellets with a density of 0.963 g/cm³, a melt flow index of 0.73 g/10 min (190°C, 2.16 kg), and a softening temperature of 127°C were purchased from ExxonMobile Chemical Co. (Houston, TX). Pine wood flour (WF; 40-mesh particle size) was obtained from American Wood Fiber Inc. (Schofield, WI). Maleic anhydride-grafted-polyethylene (MA-g-PE) as a compatibilizer (G2608) with a melt index of 8 g/10 min (190°C, 2.16 kg) and an acid number of 8 mg KOH/g was supplied by Eastman Chemical Co. (Kingsport, TN). Aluminum hydroxide (M-ON310), magnesium hydroxide (MAH-5), and 1,2-bis(pentabromophenyl) ethane (SA-8010) were supplied by Albemarle Co. (Baton Rouge, LA). The structural formulas and characteristic properties of the flame retardants are listed in Table 1. To promote the processing of composites and maintain good composite surface characteristics, a lubricant (TPW 306) from Struktol Co. (Stow, OH) was also used. This plasticizer is a mixture of fatty aliphatic carboxylic derivatives, and its appearance is off-white to light tan powder.

Compounding and Sample Extrusion

Before processing, WF was dried in a laboratory oven at 80°C for 24 h to reduce its moisture content, while HDPE, coupling agents, and lubricant materials (being kept in sealed bags) were used directly without further drying. The components were compounded by using a computer-controlled Leistritz Micro-27 co-rotating parallel twin-screw extruder (Leistritz Co., Allendale, NJ). The extruder has 11 heating zones with a screw length-todiameter ratio of 40:1. For compounding each target formulation, a mixture of HDPE and MA-g-PE pellets was fed upstream with a weight-in-loss pellet feeder, and a mixture of WF, lubricant, and fire-retardant additives was fed downstream by using a weight-in-loss powder feeder through a side-stuffer. The compounding conditions include a screw speed of 50 rpm and a temperature

TABLE 2. Formulations of HDPE/(wood composites) manufactured with different fire retardants.

Composition based on weight (%)							
Samples	HDPE	WF	MAPE	Lub	M-ON310	MAH-5	SA-8010
A0	40.0	50.0	4.0	6.0	_	_	_
B5	35.5	50.6	3.6	5.3	5.0	_	_
B10	31.6	50.5	3.2	4.7	10.0	_	_
C5	35.5	50.6	3.6	5.3		5.0	
C10	31.6	50.5	3.2	4.7		10.0	
D5	35.5	50.6	3.6	5.3			5.0
D10	31.6	50.5	3.2	4.7	—	_	10.0

profile of 155 (feeder), 160, 165, 170, 170, 170, 160, 155, 140, 140, and 155°C (die). The extrudate was continuously pelletized into granules with a BT 25 pelletizer (Scheer Bay Co., Bay City, MI). The pellets were kept in sealed bags based on actual formulations for further processing.

Composite samples were made with compound pellets by using the Leistritz extrusion machine and a profile die to produce 5-mm-thick \times 100-mm-wide test samples. The material was fed with the weight-in-loss pellet feeder upstream. The extrusion speed was 50 rpm and extruder temperature profile of 155 (feeder), 160, 165, 170, 170, 170, 160, 155, 155, 150, and 150°C (die). Designation and composition of composites with fire retardants are listed in Table 2.

Characterization

Composite Mechanical Property Analysis. The modulus of elasticity (MOE) and modulus of rupture (MOR) of composites with and without flame retardants were measured according to ASTM D790 standard using an INS-TRON 5582 Testing Machine (Instron Co., Grove City, PA). The conditions for the sample test were 23°C and 50% relative humidity. A three-point loading system was utilized with a crosshead speed of 2.3 mm/min. The span length was 127 mm with a sample width of 32 mm. For each formulation, five replicates were tested.

Composite Flammability Analysis. Fire performance was measured with a Stanton Redcroft (Fire Testing Technology Ltd., London, UK) cone calorimeter according to the ISO 5660-1 standard using 100 mm \times 100 mm test samples. For each test, a test sample was placed on the surface of a piece of aluminum foil inside a corundum crucible (100 mm length \times 100 mm width). Subsequently, the crucible was mounted horizontally on the loader and exposed to a heat radiation of 50 kW/m². This heat radiation corresponded to a temperature of 780°C on the upper surface of the test sample.

After the combustion test, the crucible with the sample was removed from the loader and cooled. The top sample surface morphology was taken with a digital camera, and composite residue was collected and stored in plastic bags for further analysis.

Combustion Residue Analysis. ATR/FTIR spectroscopy was used to characterize the residue powder of the composites with and without flame retardants. The spectra of composites were recorded by the FTIR spectrophotometer (Nicolet Nexus 670-FTIR; Thermo Electron Corp., Gormley, Canada). The ATR mode was used, and the scanning range of wavenumber was from 4,000 to 800 cm^{-1} .

Composite Morphology Analysis. The fractured sample surface and residual char after complete combustion for composites with and without flame retardants were examined with a Hitachi S4800 (Hitachi Ltd., Tokyo, Japan) scanning electron microscope at 20 kV. The fractured samples after the mechanical properties test were cut into appropriate dimensions and then fixed on the sample plate with conductive adhesive. For the residual powders, they were dispersed on the conductive adhesive. The fractured surfaces and residual powders were then coated with gold to improve the surface conductivity before observation.

RESULTS AND DISCUSSION

Mechanical Properties

MOE values for composites with and without flame retardants are summarized in Table 3. For composites with flame retardant MAH-5, the MOE value was basically the same as that of control composites without fire retardants. Composites containing flame retardants, aluminum hydroxide and 1,2-bis(pentabromophenyl) ethane, retained more than 90% of their original MOE values compared with that of control composites. This result is in agreement with the common trend of WF-reinforced plastics [4, 5]. This could be attributed to the decrease of compatibility among flame retardants, HDPE and WF.

MOR values of control composites and composites with the same amount of flame retardants, aluminum hydroxide and 1,2-bis(pentabromophenyl) ethane, are summarized in Table 3. Compared with control composites, the MOR values of composites were reduced after the addition of aluminum hydroxide, MAH-5 and 1,2bis(pentabromophenyl) ethane. Reduction of the

TABLE 3. MOE and MOR values of the control HDPE/(wood composites) and its composites with different types of flame retardants.

Samples	Flame retardants	MOE (GPa)	MOR (MPa)
A0	None	4.24 ± 0.12	34.45 ± 1.19
B5	M-ON310	3.94 ± 0.48	33.62 ± 3.50
C5	MAH-5	4.24 ± 0.11	31.67 ± 1.80
D5	SA-8010	4.10 ± 0.38	30.13 ± 0.72
B10	M-ON310	3.89 ± 0.42	32.25 ± 2.77
C10	MAH-5	4.30 ± 0.48	30.55 ± 1.55
D10	SA-8010	4.11 ± 0.31	30.21 ± 1.79

mechanical properties for WPC with the addition of flame retardants has been reported by researchers [14, 16]. The composites containing aluminum hydroxide had the highest MOR value, whereas the lowest MOR value was found for the composites containing 1,2-bis(pentabromophenyl) ethane. It was possible that interfacial bonding between WF and HDPE decreased after the addition of the flame retardants.

Comparative MOE values for composites with 5 and 10 wt% flame retardants in different types are shown in Table 3. The MOE value of composites containing 10 wt% aluminum hydroxide was lower than that of composites with 5 wt% aluminum hydroxide. This could be attributed to the poor interaction and compatibility among the flame retardants, WF and HDPE [25]. However, as the content of MAH-5 and 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%, the composite MOE values were not reduced.

The MOR values for the composites with different amounts of aluminum hydroxide, MAH-5, and 1,2-bis(pentabromophenyl) ethane are shown in Table 3. As the content of aluminum hydroxide and MAH-5 increased from 5 to 10 wt%, the MOR values of the composites were reduced, respectively. However, for composites containing 1,2-bis(pentabromophenyl) ethane, the MOR value remained about the same value as the content of 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%.

Composite Morphology

The investigation of surface morphology after mechanical properties testing for composites with different loadings of flame retardants is the basis to further study the fire performance. Compared with flame retardants, aluminum hydroxide and MAH-5, 1,2-bis(pentabromophenyl) ethane showed the best fire performance (see later discussion). Observation of the morphology variation of composites with the addition of 1,2-bis(pentabromophenyl) ethane is very important. Therefore, it is necessary to compare the surface morphology of composites without flame retardants and composites with 1,2-bis(pentabromophenyl) ethane.

The morphology of the fractured surface for control composites and composites with 1,2-bis(pentabromophenyl) ethane in the content of 5 and 10 wt% is shown in Fig. 1. It was seen that the control composites (a, b) showed a ductile fracture surface in some regions with excellent mechanical properties reflected in Table 3. The compatibilizer MA-g-PE promoted the dispersion of WF in the HDPE matrix and improved the interfacial adhesion between WF and HDPE, and the schematic illustration for the interaction is shown in Fig. 2. However, it was also shown that some apparent cavities existed due to wood fibers pulled out from the HDPE matrix. For composites with 5 wt% (c, d) and 10 wt% (e, f) 1,2-bis(pentabromophenyl) ethane, heterogeneous dispersion of WF and flame retardants in HDPE matrix were seen. Some apparent cavities were presented in the composites with 5 and 10 wt% 1,2-bis(pentabromophenyl) ethane, indicating that the surface adhesion among WF, HDPE, and flame retardants relatively decreased after the incorporation of flame retardants 1,2-bis(pentabromophenyl) ethane. For the composites with 5 wt% 1,2-bis(pentabromophenyl) ethane, the brittle fracture surface was observed, revealing that the WF and flame retardants had poor interfacial adhesion with HDPE matrix, which acted as stress concentrators of failure points of the composites [7]. This could lead to inferior mechanical properties. However, for composites with 10 wt% 1,2-bis(pentabromophenyl) ethane, the flame retardants and WF were embedded into the HDPE matrix and showed a relatively good interfacial adhesion with HDPE matrix compared with composites with 5 wt% 1,2-bis(pentabromophenyl) ethane. MA-g-PE promoted the formation of an ester bond between the anhydride carbonyl group of MA-g-PE and the hydroxyl group of WF. On esterification, the exposed PE chains diffused into the HDPE matrix and entangled with HDPE chains during extruder compounding. Therefore, the flame-retardant 1,2-bis(pentabromophenyl) ethane was relatively better dispersed in the entangled chains.

Composite Flammability

Cone calorimetry analysis produced test data on HRR, peak of heat release rate (pHRR), total heat release (THR), total smoke production (TSP), and mass loss (ML) [26, 27].

Flame Retardant Types on Fire Performance of the Composites. Figures 3a and 3b show the HRR and THR of control composites and composites with the same amount of aluminum hydroxide, MAH-5, and 1,2-bis(pentabromophenyl) ethane, respectively. The HRR curves of all samples indicated a significant increase after ignition until a peak value was reached and decreased gradually toward the end of combustion. Two HRR peaks were observed for all samples. The first peak as the consequence of ignition and the flame spread on the surface of samples [12] appeared between 60 and 75 s after ignition. The highest peak of 382.94 kW/m² at 75 s corresponded to the composites with aluminum hydroxide, and the lowest peak of 293.00 kW/m² at 70 s was related to the composites with MAH-5. The second peak occurred when the degradation for the surface of samples started, and oxygen entered the inner part of the samples to combust with high efficiency. Finally, a carbonaceous char was formed [12] and occurred in the range from 200 to 330 s. The highest peak of 405.78 kW/m² at 280 s was related to the composites with MAH-5, and the lowest peak of 257.73 kW/m² at 330 s was associated with the composites with 1,2-bis(pentabromophenyl) ethane. The HRR and THR for composites with MAH-5 and 1,2-bis(pentabromophenyl) ethane were reduced compared with that of composites without flame retardants. The best reduction in the THR was achieved by the composites with 1,2-bis(pentabromophenyl) ethane. Bromine radicals released from the 1,2-bis(pentabromophenyl) ethane scavenged the high-energy radicals in the combustion zone



FIG. 1. SEM micrographs of the fractured WPC sample surface: (a) A0, $\times 200$; (b) A0, $\times 2,000$; (c) D5, $\times 500$; (d) D5, $\times 2,000$; (e) D10, $\times 500$; and (f) D10, $\times 2,000$.

according to a vapor phase fire-retarding mechanism [24]. For flame-retardant MAH-5, the flame-retardant effect was based on cooling and dilution through endothermic decomposition and water release [28]. In addition, decomposed product of nonflammable magnesium oxide insulated the HDPE from heat and produced char that impeded the flow of potentially flammable gases to the flame [19]. However, for composites containing aluminum hydroxide, the reduction of the THR was not observed compared with that of control composites, which was in accordance with the HRR as well as pHRR of composites with aluminum hydroxide. It indicated that flame-retardant aluminum hydroxide did not show effective flame retardancy for composites. The thermal stability of aluminum hydroxide is around 251°C. It started to decom-

pose at 251°C, and then a higher proportion of aluminum hydroxide was decomposed in the early stage of combustion. However, very little water can be released from aluminum hydroxide during the higher temperatures above 300°C or even higher, which resulted in low efficiency of fire retardancy for the HDPE substrate.

Figure 3c shows the TSP curves vs. time for control composites and composites with the same amount of fire retardants, aluminum hydroxide, MAH-5, and 1,2-bis(pen-tabromophenyl) ethane, respectively. It was seen that control composites exhibited a relatively low TSP of 11.07 m². Although the incorporation of flame-retardant 1,2-bis(pen-tabromophenyl) ethane into composites showed high flame retardancy, the total amount of smoke emission was higher



FIG. 2. Schematic illustration of interaction among wood flour, HDPE, and flame retardants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

than that of control composites. The TSP increased for composites with aluminum hydroxide, which was attributed to the low efficiency in flame retardance and resulted in the combustion of HDPE to produce volatile gases after the overall decomposition of flame retardants [19]. However, the best reduction in the TSP was achieved with MAH-5 compared with the control composites. During MAH-5 degradation into magnesium oxide and water, it absorbed heat from the HDPE substrate and formed a protective layer for HDPE, which acted as a smoke suppresser [20].

The ML vs. time curves for the control composites and composites containing different fire retardants are shown in Fig. 3d. It can be seen that the highest ML was obtained by 85.76% with the control composites. For the composites containing flame retardants, the ML values were reduced compared with that of control composites. The fire retardants can be ranked for decrease in ML as follows: MAH-5 > 1,2-bis(pentabromophenyl) ethane > aluminum hydroxide. The best improvement in the reduction of ML was achieved with MAH-5 as the ML value was decreased by 8.43% compared with the control composites, indicating that the addition of MAH-5 decreased the thermal degradation of composites.

Flame-Retardant Levels on the Fire Performance of Composites. The HRR and THR curves for composites with 5 and 10 wt% of different flame retardants are shown in Fig. 4a, b. The partial substitution of WF with fire retardants resulted not only in a significant reduction of the first peak HRR but also in a dramatic decrease of the second peak HRR. The pHRR values for composites with 10 wt% aluminum hydroxide, MAH-5, and 1,2-bis(pentabromophenyl) ethane were lower than these for the composites with the content of 5 wt% as the pHRR values were decreased by 9.1, 29.8, and 7.8%, respectively. It indicated that an increase in the content of flame retardants had a positive effect in retarding flame. In addition, the content of flame retardants, aluminum hydroxide, MAH-5, and 1,2-bis(pentabromophenyl) ethane, increased from 5 to 10 wt%, and the THR as well as the HRR of composites was reduced as the THR values were decreased by 29.9, 16.1, and 18.8%, respectively. For the composites with aluminum hydroxide and MAH-5, the formation of dense char layers limited the diffusion of oxygen toward the HDPE substrate and protected it from burning. In addition, bromine radicals from the decomposition of 1,2-bis(pentabromophenyl) ethane were efficient to absorb the high-energy



FIG. 3. A comparison of combustion data for composites at 5% flame retardant loading level as a function of time. (a) Heat release rate, (b) total heat release, (c) total smoke production, and (d) mass loss. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

radicals from the combustion zone and thus reduced the prospect of continued burning [24].

TSP curves vs. time for composites with 5 and 10 wt% flame retardants are shown in Fig. 4c. With the content of flame-retardant 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%, a significant improvement of TSP was observed. For the composites with MAH-5, the TSP did not change much after the loading of flame retardants increased from 5 to 10 wt%. In the case of the composites with aluminum hydroxide, the increase in the content of flame retardants from 5 to 10 wt% led to the reduction of TSP. Flame-retardant aluminum hydroxide released water into a vapor phase and diluted the volatile components from HDPE degradation, and a dense layer of aluminum oxide as a barrier retarded the heat and gas transfer between flame zone and HDPE substrate, which reduced the release of smoke [19].

The ML for composites with 5 and 10 wt% flame retardants is shown in Fig. 4d. As the content of flame retardants, aluminum hydroxide and MAH-5, increased from 5 to 10 wt%, the ML of composites was reduced. The best reduction in the ML of flame retardants was achieved with MAH-5 among all the samples. The metal oxides acted as an insulating protective layer, protecting HDPE from the heat source and limiting the diffusion of gases into the combustion zone [20]. However, the ML for the composites with 1,2-bis(pentabromophenyl) ethane was increased by 11.03% as the loading of flame retardants increased from 5 to 10 wt%.

Char Residue Composition and Morphology

The FTIR spectra for the char residue of control composites and composites with different contents of flame retardants after complete combustion are shown in Fig. 5. For the control composites (a), peaks at 3,671 and 2,969 cm⁻¹ assigned to the O-H and C-H stretching vibration, respectively, and 1,007 cm⁻¹ related to the C-OH stretching and deformation vibration indicated the hydroxyl group in WF. The peaks at 1,736 and 1,440 cm^{-1} were C=O band stretching vibration and H-C-H band deformation vibration, respectively. Compared with that of control composites, for the composites with aluminum hydroxide and MAH-5 (b, c), the peak values at 3,671 and 1,007 cm⁻¹ associated with O-H and C-OH band decreased, and the band at $1,736 \text{ cm}^{-1}$ related to ester group increased, which demonstrated that the protective layer formed by the dehydration of WF protected the HDPE from combustion. The peaks of O-H and C-OH band for composites with 1,2-bis(pentabromophenyl) ethane (d) decreased significantly and even disappeared with respect to the H-C-H band. However, the peak assigned



FIG. 4. A comparison of combustion data for composites at 5 and 10% flame retardant levels as a function of time. (a) Heat release rate, (b) total heat release, (c) total smoke production, and (d) mass loss. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

to the C=O band was enhanced. It indicated that flameretardant 1,2-bis(pentabromophenyl) ethane promoted the hydroxyl group in the WF to hydrolyze and form a char layer, which retarded HDPE from further combustion.

Figure 6 shows the control composites and composites with 5 and 10 wt% 1,2-bis(pentabromophenyl) ethane after cone calorimeter test. It was clearly seen that the char residue was crisp for the control composites (a), and the surface layer was broken into small pieces. Moreover, the residue of the composites tended to aggregate together with many cracks and holes. For the residue of composites with 5 wt% 1,2-bis(pentabromophenyl) ethane (b), the residual char layer was continuous with some holes in the surface. However, the char layer was thin and broken into several big pieces. In contrast, the char of the composites with 10 wt% 1,2-bis(pentabromophenyl) ethane (c) was compact and continuous, which acted as an effective barrier for heat and mass transfer. It suggested that the cohesive and dense char surface blocked the release of internal combustible gases and thus protected the HDPE from combustion [10]. The barrier effect of the stable char structure could also reduce the HRR and THR, which corresponded to the heat release curves.

As shown in Fig. 7 for the SEM micrographs of the char residues after combustion, the char layer of control composites (a) was loose and rough with many large

holes, so the structure promoted heat transfer and gas diffusion. Thus, the composites burned rapidly. However, when 5 wt% 1,2-bis(pentabromophenyl) ethane was incorporated into composites (b), the porous and loose surface changed into a more compact one; the char layer



FIG. 5. ART-FTIR spectra of composites with and without flame retardants: (a) A0, (b) B5, (c) C5, and (d) D5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]



FIG. 6. Photographs of the char residues after cone calorimetery test for selected samples: (a) A0, (b) D5, and (c) D10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIG. 7. SEM micrographs of the char residues after cone calorimetery test: A0, ×2,000; (b) D5, ×2,000; (c) D10, ×2,000; and (d) D10, ×5,000.

exhibited a continuous structure with fewer cracks and holes. The dense char layer could decrease the transfer efficiency of heat and volatiles and thus provide a good barrier for HDPE. However, this char could not effectively prevent the sample from degradation. The char for composites with 5 wt% 1,2-bis(pentabromophenyl) ethane was brittle and easy to collapse, while the char surface of composites with 10 wt% 1,2-bis(pentabromophenyl) ethane (c, d) was compact, thick, and tight. This dense layer reduced the heat and oxygen diffusion into the burning substrate and thereby protected the HDPE from further combustion, which was in agreement with the low pHRR and THR data [29].

CONCLUSIONS

The WF and HDPE composites with different types of flame retardants (aluminum hydroxide, MAH-5, and 1,2-bis[pentabromophenyl]) ethane were prepared. After the addition of 5 wt% aluminum hydroxide, MAH-5, and 1,2-

bis(pentabromophenyl) ethane, the MOE and MOR values for composites retained more than 90% of their original values. As the content of aluminum hydroxide and MAH-5 increased from 5 to 10 wt%, the MOE and MOR values remained about the same. Morphology tests indicated that, compared with the brittle fracture surface for the composites with 5 wt% 1,2-bis(pentabromophenyl) ethane, composites with 10 wt% 1,2-bis(pentabromophenyl) ethane showed a good interfacial adhesion as the 1,2-bis(pentabromophenyl) ethane was better dispersed in the entangled chains of HDPE and esterificated WF with MA-g-PE through extruder compounding. Flammability testing by cone calorimeter showed that the HRR and THR were reduced for composites with MAH-5 and 1,2-bis(pentabromophenyl) ethane compared with that of control composites. The composites with 1,2-bis(pentabromophenyl) ethane exhibited the best fire resistance. The pHRR, THR, and HRR for composites significantly reduced after the aluminum hydroxide, MAH-5, and 1,2-bis(pentabromophenyl) ethane increased from 5 to 10 wt%. The best improvement in the reduction of ML and TSP was achieved with MAH-5 for all samples. ATR/FTIR analysis for the char residue indicated that flame retardants of 1,2bis(pentabromophenyl) ethane with the content of 10 wt% could effectively promote wood to char and show a better fire resistance for composites, reflected on the decrease in peak at 3671 cm^{-1} assigned to the stretching vibration of the O–H band and the increase in the peak at 1.736 cm^{-1} associated with C=O band stretching vibration. Morphology analysis of char residue demonstrated that flameretardant 1,2-bis(pentabromophenyl) ethane promoted the formation of continuous and compacted char layer on the composite surface, which acted as an efficient physical barrier to combustion of composites.

ACKNOWLEDGMENTS

The authors appreciate the financial support from the National State Bureau of Forestry 948 Plan of China (Grant No. 2014-4-49), the Natural Science Foundation of China (Grant No. 31300482), and the Korea Forest Research Institute through a research project to the LSU Ag Center.

REFERENCES

- 1. Y. Arao, S. Nakamura, Y. Tomita, K. Takakuwa, T. Umemura, and T. Tanaka, *Polym. Degrad. Stab.*, **100**, 79 (2014).
- 2. M. Nikolaeva and T. Kärki, Fire Mater., 37, 612 (2013).

- Y.Q. Fang, Q.W. Wang, C.G. Guo, Y.M. Song, and P.A. Cooper, J. Anal. Appl. Pyrolys., 100, 230 (2013).
- M.B. Abu Bakar, Z.A. Mohd Ishak, R. Mat Taib, H.D. Rozman, and S. Mohamad Jani, J. Appl. Polym. Sci., 116, 2714 (2010).
- 5. N. Aryilmis, J.T. Benthien, H. Thoemen, and R.H. White, J. Appl. Polym. Sci., **122**, 3201 (2011).
- J.Q. Zheng, B. Li, C.G. Guo, Q. Wu, and Y.F. Wang, J. Appl. Polym. Sci., 131, 40281 (2014).
- Z.X. Zhang, J. Zhang, B.X. Lu, Z.X. Xin, C.K. Kang, and J.K. Kim, *Compos. Part B – Appl. Sci.*, 43, 150 (2012).
- L. Zhou, C.G. Guo, and L.P. Li, J. Appl. Polym. Sci., 122, 849 (2011).
- 9. B. Li and J.M. He, Polym. Degrad. Stab., 83, 241 (2004).
- G. Bai, C.G. Guo, and L.P. Li, *Constr. Build. Mater.*, 50, 148 (2014).
- 11. H. Seefeldt, U. Braun, and M.H. Wagner, *Macromol. Chem. Phys.*, **213**, 2370 (2012).
- K. Lu, X.J. Cao, Q.S. Liang, H.T. Wang, X.W. Cui, and Y.J. Li, *Ind. Eng. Chem. Res.*, **53**, 8784 (2014).
- 13. A.B. Morgan and J.W. Gilman, Fire Mater., 37, 259 (2013).
- N. Ayrilmis, T. Akbulut, T. Dundar, R.H. White, F. Mengeloglu, U. Buyuksari, Z. Candan, and E. Avci, *Constr. Build. Mater.*, 33, 63 (2012).
- 15. N. Ayrilmis, *Bioresources*, 6, 3178 (2011).
- 16. N. Ayrilmis, Compos. Part B Appl. Sci., 44, 745 (2013).
- 17. R. Kurt, F. Mengeloglu, and H. Meric, *Eur. J. Wood Prod.*, **70**, 177 (2012).
- X.S. Wang, H.C. Pang, W.D. Chen, Y. Lin, L.S. Zong, and G.L. Ning. ACS Appl. Mater. Interfaces, 6, 7223 (2014).
- J.G. Gwon, S.Y. Lee, and J.H. Kim, J. Appl. Polym. Sci., 131, 40120 (2014).
- M. Sain, S.H. Park, F. Suhara, and S. Law, *Polym. Degrad.* Stab., 83, 363 (2004).
- N.M. Stark, R.H. White, S.A. Mueller, and T.A. Osswald, *Polym. Degrad. Stab.*, **95**, 1903 (2010).
- N. Ayrilmis, J.T. Benthien, H. Thoemen, and R.H. White, *Eur. J. Wood Prod.*, **70**, 215 (2012).
- 23. S. Chen, B.S. Sun, G.B. Huang, H.C. Guo, and S.Q. Wang, J. Vinyl Addit. Technol., 19, 285 (2013).
- 24. A. Dasari, Z.Z. Yu, G.P. Cai, and Y.W. Mai, *Prog. Polym. Sci.*, 38, 1357 (2013).
- 25. G.F. Wu and M. Xu, Bioresources, 9, 4173 (2014).
- H.B. Chen, Y.Z. Wang, and D.A. Schiraldi, ACS Appl. Mater. Interfaces, 6, 6790 (2014).
- 27. W.Z. Hu, J. Zhan, X. Wang, N.N. Hong, B. Wang, L. Song, A.A. Stec, T.R. Hull, J. Wang, and Y. Hu, *Ind. Eng. Chem. Res.*, **53**, 3073 (2014).
- 28. S.T. Bee, A. Hassan, C. Ratnam, T.T. Tee, and L.T. Sin, J. Vinyl Addit. Technol., 20, 91 (2014).
- 29. Z.P. Wu, Y.C. Hu, and W.G. Shu, J. Vinyl Addit. Technol., 15, 260 (2009).