Evaluating the Effectiveness of Complex Fire-Retardants on the Fire Properties of Ultra-low Density Fiberboard (ULDF)

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The preparation conditions of complex fire-retardant (FR) agents containing boron compounds (BF, X_1), nitrogen-phosphorus compounds (NPF, X_2), silicon compounds (SF, X_3), and halogen compounds (HF, X_4) for ultra-low density fiberboard (ULDF) were optimized using a response surface methodology. The effects and interactions of X_1, X_2, X_3, and X_4 on the fire properties of ULDF were investigated. An optimum char yield of 61.4% was obtained when the complex fire-retardant agents contained 33.9% boron, 27.2% nitrogen-phosphorus, 15.0% silicon, and 28.6% halogen. Compared with control fiberboard (CF), the heat release rate (HRR) profiles of all fiberboards with FRs were reduced. The peak HRR reduction in BF and NPF was more pronounced than for SF and HF at this stage. And the mixed fiberboard (MF) had the lowest pkHRR of 75.02 kW m^{-2}. In total heat release (THR) profiles, all fiberboards with FRs were lower than the CF. Unlike the HRR profiles, HF had the lowest THR profile of 15.33 MJ m^{-2}. Additionally, Si compounds showed greater effectiveness in preventing ULDF mass loss than BF, NPF, and HF. MF showed the highest residual mass (40.94%). Furthermore, the synergistic effect between four FR agents showed more significant results in ULDFs.

Keywords: Ultra-low density fiberboard; Fire-retardant; Char yield; Optimization; Response surface methodology

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INTRODUCTION

Wood-based composites are combustible materials, and their applications are always limited by their inflammability. To mitigate this disadvantage, fire-retardant treatments that modify or impede burning in the condensed and/or gaseous phases are used. Depending on the specific fire retardant and environment, the fire retardancy of wood-based composites involves a complex series of simultaneous chemical and physical reactions (Hornsby 2001; Genovese and Shanks 2008). There are several ways in which the combustion process can be slowed by fire-retardant treatment. A protective layer with low thermal conductivity can be formed that reduces heat transfer from the heat source, or the substrate is cooled by the degradation reactions of the additive. Furthermore, the fuel in the solid and gaseous phases can be diluted in order to decrease the ignition limit of the gas mixture. Two chemical reactions interfere with the combustion process in the condensed and gas phases (Gao *et al*. 2005; Bourbigot and Duquesne 2007; Hagen *et al*. 2009; Schartel 2010). Some fire retardants have one or more ways of improving the fire properties of composites. For example, silicon (Si) compounds dilute the combustible organic gases in the flame zone by initiating the vapor phase, and they also form a barrier to heat and mass transfer (Ebdon *et al*. 1996). The fire properties of wood-based composites have been improved by many types of fire retardant additives including halogens (Lewin 2005), silicon (Genovese and Shanks 2008; Niu *et al*. 2014; Chen *et al*. 2015a,c), boron (Baysal *et al*. 2007a, b), and phosphorous (Gao *et al*. 2003; Gao *et al*. 2005; Branca and Blasi 2007; Schartel *et al*. 2010). Fire retardants generally are not used alone; they are usually used with other additives in polymeric materials to obtain a synergistic effect (Durin-France *et al*. 2000; Hagen *et al*. 2009). Wang and Li (2004) improved the fire properties of wood by using complex fire retardants containing guanylurea phosphate, boric acid, and other additives. These materials accelerate the formation of wood char, despite forming a protective layer and diluting the fuel in the combustion process.

Ultra-low density fiberboards (ULDFs) are manufactured by liquid frothing (Xie *et al.* 2004). Although they have many excellent properties including ultra-low density (ranging from 10 to 90 kg m^{-3}), low thermal conductivity, good sound absorption, *etc.* (Chen *et al.* 2015d; Xie *et al.* 2004, 2011; Niu *et al.* 2014), their application is restricted by their inflammability (Xie *et al.* 2011; Niu *et al.* 2014). To overcome this disadvantage, halogen-containing fire retardants (Liu *et al.* 2014) and Si or aluminum compounds (Niu *et al.* 2014; Chen *et al.* 2015c) have been added. Liu (2013) showed that the fire-resistant properties of ULDF were further improved when chlorinated paraffin and Si-Al compounds were combined, indicating synergy between these compounds. The goal of this paper was mainly to clarify the synergistic effect in complex fire-retardant agents containing boron, nitrogen-phosphorus compounds, Si, and halogens. Their preparation conditions were optimized by a standard response surface methodology (RSM) design called central composite design (CCD). The fire performance of the fiberboard was measured using cone calorimetry. The results of char yield, combustion behavior, and mass loss of ULDFs were all considered.

EXPERIMENTAL

Materials

Kraft pulp (KP, spruce-pine-fir; Tembec Inc., Québec, Canada) was utilized as a raw material to manufacture ULDF. The additives used are presented in Table 1.

Table 1. Detailed Information and Parameters for Additives

Additives		Additive amount	Manufacturer
Category	Main Composition		
Boron Compounds	Boracic Acid and Borax	See in Table 2	Deer Boron Industry Chemical Co., Ltd. (Zhengzhou, China)
Nitrogen-Phosphorus Compounds	Diammonium Hydrogen Phosphate		Suzhou High-energy Chemical Technology Co., Ltd. (Suzhou, China)
Si Compounds	Sodium Silicate		Tianjin Fuchen Chemical Reagents Factory (Tianjin, China)
Halogen Compounds	Chlorinated Paraffin		Changzhou Fengshuo Chemical Co., Ltd. (Changzhou, China)
Sodium Dodecylbenzene Sulfonate (10% concentration, forming agent)		80 mL	Jiangsu Qingting Washing Products Co., Ltd. (Yancheng, China)
Polyacrylamide resin		20 mL	Prepared by the authors
Alkyl Ketene Dimer (AKD, water-proofing agent)		50 mL	Suzhou Tianma Chemicals Co., Ltd. (Suzhou, China)

Methods

Preparation of ultra-low density fiberboard

Ultra-low density fiberboards (200 mm × 200 mm × 50 mm) consisted of 55 g dry pulp fiber, with a target bulk density of 50 to 90 kg·m^{-3}. They were manufactured separately using various parameters in a demonstration line (Fig. 1). The parameters for manufacturing fiberboards are presented in Table 1. The composition of each complex fire-retardant is shown in Table 2. Their respective masses were based on fire-retardant content *versus* dry fiber mass. The nomenclature of the corresponding fiberboards were BF (fiberboard with boron compounds), NPF (fiberboard with nitrogen-phosphorus compounds), SF (fiberboard with Si compounds), and HF (fiberboard with halogen compounds).

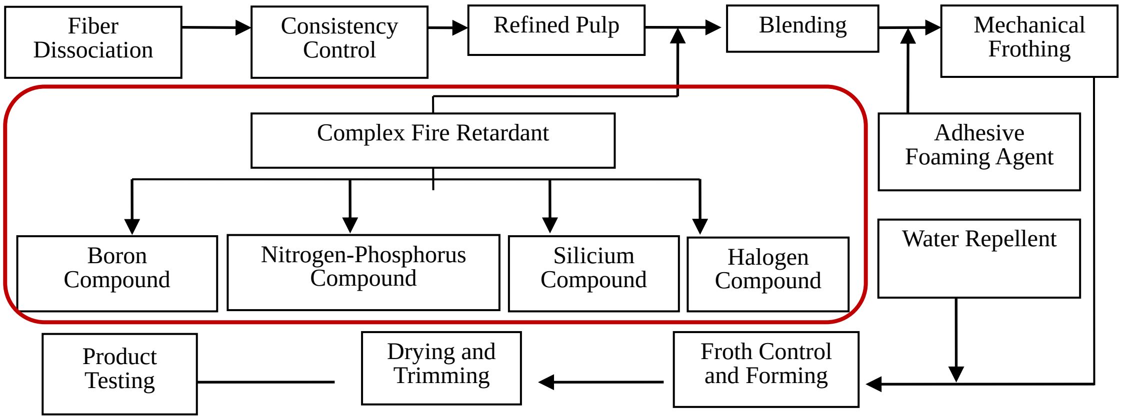


Fig. 1. The ULDF preparation process

Char yield of ultra-low density fiberboard

The char yield of ULDF was obtained using a controlled electric resistance furnace at high temperatures (model KDF-S70G, Denken Co., Jingdu, Japan). When the temperature of the furnace reached 400 °C, 1.000 g of fiberboard encased in aluminum foil was heated in a furnace under a nitrogen atmosphere. After 30 min of heating, the fiberboards were cooled at room temperature in a closed container. The char yield of ULDF was tested when the temperature of the residue fell below 40 °C.

Experimental design

The boron compounds (X_1), nitrogen-phosphorus compounds (X_2), Si compounds (X_3), and halogen compounds (X_4) were chosen as the variables, and char yield (Y) was their function. A standard RSM design CCD was applied to study the effects of X_1, X_2, X_3, and X_4 on Y. Design-Expert software (Trial Version 8.0.6, Stat-Ease, Minneapolis, USA) was used to analyze data and build the models. The selection range of each variable is shown in Table 2.

Table 2. Levels of Parameter Variables used in RSM Design

	Levels				
Coded-Variables (Xi)	−2	−1	0	1	2
Boron Compounds (X_1, %)	15	20	25	30	35
Nitrogen-Phosphorus Compounds (X_2, %)	15	20	25	30	35
Silicium Compounds (X_3, %)	15	20	25	30	35
Halogen Compounds (X_4, %)	15	20	25	30	35

Testing of fire properties by cone calorimeter method

Fire properties of the ULDFs were evaluated using a cone calorimeter (model FTT2000, FTT Co., East Grinstead, UK), which has been adopted by the International Organization for Standardization (ISO 5660 2002) to evaluate the parameters of heat release rate (HRR), total heat released (THR), and mass loss rate (MLR). The size of the fiberboards was 100 × 100 × 30 mm ($L \times W \times H$). They were encased in aluminum foil, except for the heating surface, and mounted in a stainless steel holder with a grid placed on top of the fiberboard. The tests were performed at a heat flux level of 50 kW m^{-2}.

Table 3. Central Composite Design and Response to the Char Yield of ULDF

Run No.	Coded Levels of Compounds				Char Yield (%)	
	Boron (X_1, %)	Nitrogen-Phosphorus (X_2, %)	Silicium (X_3, %)	Halogen (X_4, %)	Experimental	Predicted
1	−1(20)	−1(20)	−1(20)	−1(20)	34.2	34.3
2	1(30)	−1	−1	−1	41.7	40.6
3	−1	1(30)	−1	−1	40.9	42.0
4	1	1	−1	−1	44.3	46.0
5	−1	−1	1(30)	−1	37.1	36.5
6	1	−1	1	−1	34.4	38.2
7	−1	1	1	−1	38.8	38.9
8	1	1	1	−1	39.7	38.4
9	−1	−1	−1	1(30)	43.0	44.5
10	1	−1	−1	1	49.5	49.9
11	−1	1	−1	1	51.7	48.4
12	1	1	−1	1	50.7	51.5
13	−1	−1	1	1	43.4	42.2
14	1	−1	1	1	43.8	42.9
15	−1	1	1	1	39.4	40.7
16	1	1	1	1	38.9	39.3
17	−2(15)	0(25)	0(25)	0(25)	40.7	41.5
18	2(35)	0	0	0	47.8	46.3
19	0(25)	−2(15)	0	0	37.1	36.4
20	0	2(35)	0	0	40.5	40.5
21	0	0	−2(15)	0	55.9	55.7
22	0	0	2(35)	0	46.1	45.6
23	0	0	0	−2(15)	31.5	30.0
24	0	0	0	2(35)	40.3	41.1
25	0	0	0	0	47.3	47.4
26	0	0	0	0	47.4	47.4
27	0	0	0	0	47.5	47.4
28	0	0	0	0	47.2	47.4
29	0	0	0	0	47.3	47.4
30	0	0	0	0	47.4	47.4

RESULTS AND DISCUSSION

Model Fitting

The design matrix and the results of RSM experiments for determining the effects of the four independent variables are shown in Table 3. The mathematical model representing the char yield of ULDF against the function of the independent variables was expressed as follows (Eq. 1),

$$Y= 47.35 + 1.20X_1 + 1.00X_2 – 2.50X_3 + 2.79X_4 – 0.56X_1X_2 – 1.14X_1X_3 – 0.23X_1X_4 – 1.32X_2X_3 – 0.96X_2X_4 – 1.14X_3X_4 – 0.86X_1^2 – 2.22X_2^2 + 0.83X_3^2 – 2.95X_4^2 \tag{1}$$

where Y is the char yield of ULDF and X_1, X_2, X_3, and X_4 are the coded variables for boron compounds, nitrogen-phosphorus compounds, silicium compounds, and halogen compounds, respectively.

The *p*-value of the model and the lack of fit value were less than 0.0001, which indicated that the model's fitness was high (Table 4; Brown and Brown 2012; Singh *et al.* 2013). The value of R^2 (0.9983) was in reasonable agreement with that of R_{adj}^2 (0.9930), which indicated a high degree of correlation between the observed values and the predicted values (Chen *et al.* 2012). Thus, the regression model accurately explained the true behavior of the system.

Table 4. Analysis of Variance for Regression Model for the Char Yield of ULDF

Source	Sum of Squares	Degrees of Freedom	Mean Square	*F*-Value	*p*-Value
Model	880.96	14	62.93	20.13	<0.0001
X_1	34.32	1	34.32	10.98	0.0047
X_2	24.20	1	24.20	7.74	0.0140
X_3	150.50	1	150.50	48.13	<0.0001
X_4	186.48	1	186.48	59.64	<0.0001
X_1X_2	4.95	1	4.95	1.58	0.2275
X_1X_3	20.93	1	20.93	6.69	0.0206
X_1X_4	0.86	1	0.86	0.27	0.6085
X_2X_3	27.83	1	27.83	8.90	0.0093
X_2X_4	14.63	1	14.63	4.68	0.0471
X_3X_4	20.93	1	20.93	6.69	0.0206
X_1^2	20.36	1	20.36	6.51	0.0221
X_2^2	135.66	1	135.66	43.39	<0.0001
X_3^2	18.72	1	18.72	5.99	0.0272
X_4^2	238.53	1	238.53	76.29	<0.0001
Residual	46.90	15	3.13		
Lack of Fit	46.85	10	4.68	425.87	<0.0001
Pure Error	0.06	5	0.01		
Correlation Total	927.86	29			

$p < 0.01$ highly significant; $0.01 < p < 0.05$ significant; $p > 0.05$ insignificant

As can be seen in Table 4, the *F*-value (20.13) and *p*-values (less than 0.0001) implied that this model was significant, and only a 0.01% chance could occur due to noise (Amini *et al.* 2008). X_1, X_3, X_4, X_2X_3, and two quadratic terms (X_2^2 and X_4^2) significantly affected the ULDF char yield. The variables X_2, X_1X_3, X_2X_3, X_2X_4, X_3X_4, X_1^2, and X_3^2 also significantly affected the ULDF char yield, whereas X_1X_2 and X_1X_4 had no significant effect. In order of decreasing effect on char yield, the independent variables were ranked as follows: halogen compounds (X_4) > silicium compounds (X_3) > boron compounds (X_1) > nitrogen-phosphorus compounds (X_2).

Analysis of Response Surface and Optimization

The relationship between the parameters and the response variable was plotted in a 3D representation of the response surface (Fig. 2).

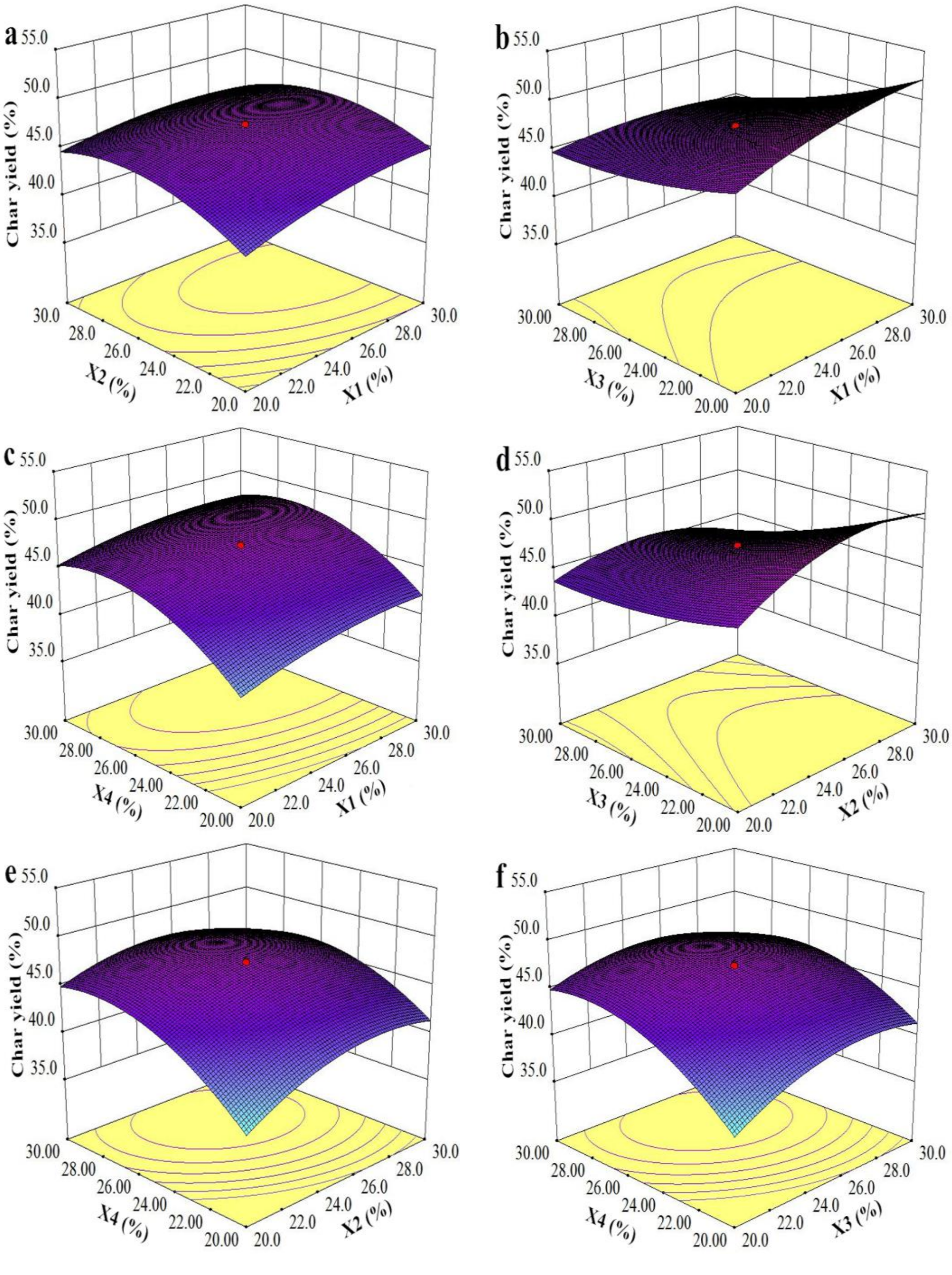
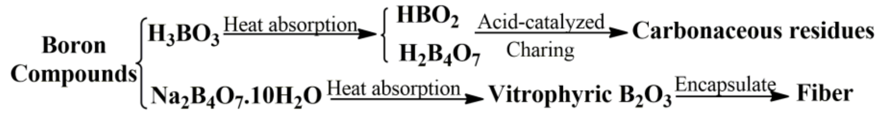
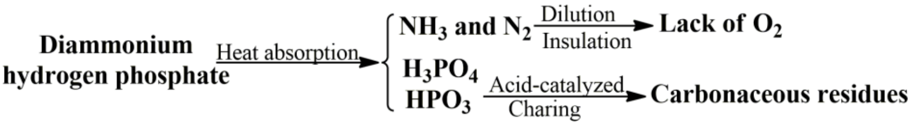


Fig. 2. Response surface plots for the maximum ULDF char yield of and various combinations of parameters. (a) X_1 and X_2; (b) X_1 and X_3; (c) X_1 and X_4; (d) X_2 and X_3; (e) X_2 and X_4; and (f) X_3 and X_4

As can be seen in Fig. 2a-c, the results were elliptical, indicating significant interactions between the independent variables and the char yield of ULDFs (Tang *et al*. 2011). Boron compounds thermally decompose, producing boron oxide and driving decomposition of the polymer toward carbonaceous residues. Nitrogen-phosphorus compounds act similarly; they increase dehydration reactions during thermal degradation to produce more char and less total volatiles (Hagen *et al*. 2009). Therefore, ULDF fire properties were improved more significantly when these compounds were combined. Their fire-retardant mechanisms are described in Eqs. 2 and 3:



(2)



(3)

Additionally, Si compounds generate polysilicic acid, which reacts with wood to form an inorganic film on its surface (Eq. 4). The inorganic film insulates wood against air during combustion (Unger *et al.* 2012; Chen *et al.* 2015c).

$$\equiv\text{Si - OH} + \text{HO - wood} \underset{hydrolysis\,/\,depolymerisation}{\overset{water\ condensation}{\rightleftharpoons}} \equiv\text{Si - O - Wood} + H_2O \qquad (4)$$

Halogen-based fire retardants act in the vapor phase by a radical mechanism that interrupts the exothermic processes and suppresses combustion. Halogen hydrides dilute combustible gas or prevent its exposure to the air, which delays pyrolysis. Boron compounds reduce or eliminate afterglow in halogen compounds (Lu and Hamerton 2002). Therefore, the fire properties of ULDF were improved when all of the fire retardants were added.

When the fixed content of Si was added, the char yield of ULDF was increased with the increasing content of nitrogen-phosphorus (Fig. 2d). Similar trends were observed for the nitrogen-phosphorus compounds, silicon compounds, and halogen compounds in (Figs. 2e, f). These results showed that nitrogen-phosphorus-, Si-, and halogen-based fire retardants improved ULDF fire properties alone but had different roles in achieving flame retardation. When added together, they produced a synergistic effect. Based on Eq. 1, the optimal fire-retardant for ULDFs contained 33.9% boracic acid and borax, 27.2% diammonium hydrogen phosphate, 15.0% sodium silicate, and 28.6% chlorinated paraffin. These conditions produced the optimal ULDF char yield (61.4%).

Fire Resistance of ULDFs

Combustion behavior

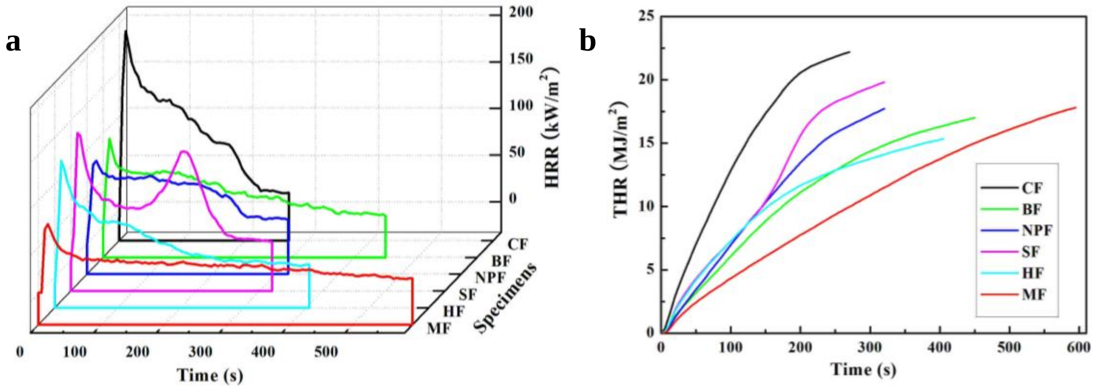


Fig. 3. HRR profiles (a) and THR profiles (b) of the control fiberboard (CF), boron-based fiberboard (BF), nitrogen-phosphorus-based fiberboard (NPF), silicium-based fiberboard (SF), halogen-based fiberboard (HF), and mixed fiberboard (MF)

The fire properties of ULDFs were evaluated using cone calorimetry with a heat flux of 50 kW m^{-2} (Fig. 3). The HRR curves demonstrated a two-peak profile, especially the SF curve, due to the thermo-oxidative decomposition of the char. Furthermore, Si compounds formed a barrier to heat and mass transfer that caused the further decomposition and cracking of the char towards the burned ends where the second peak occurred (Hagen *et al.* 2009; Shabir Mahr *et al.* 2012; Chen *et al.* 2015b). Compared with CF, the HRR profiles of BF, NPF, SF, HF, and MF were reduced. Also, the peak of HRR (pkHRR) of BF (94.91 kW m^{-2}), NPF (89.01 kW m^{-2}), SF (137.04 kW m^{-2}), HF (125.01 kW m^{-2}), and MF (75.02 kW m^{-2}) were lower than that of CF (192.01 kW m^{-2}) (Table 5). The degree of pkHRR reduction in BF and NPF was more pronounced than for SF and HF at this stage. The results indicated that the boron and nitrogen-phosphorus fire retardant-treated ULDFs were the most successful in reducing HRR, which could be attributed to changes in the condensing phase of char production (Hagen *et al*. 2009). Notably, the pkHRR of MF (75.02 kW m^{-2}) was the lowest of the six fiberboards studied; thus, the four agents in the complex fire retardant had a synergistic effect.

Table 5. Parameters and Peak HRR of the Fiberboards

Fiberboards	Fire Retardant	Additives (g)	AKD (mL)	pkHRR (kW·m^{-2})	THR (MJ·m^{-2})
CF	-	-	50	192.03	22.18
BF	Boron Compounds	50.0		94.91	16.98
NPF	Nitrogen-Phosphorus Compounds	50.0		89.01	17.71
SF	Silicium Compounds	50.0		137.04	19.81
HF	Halogen Compounds	50.0		125.01	15.33
MF	Complex Fire Retardant	57.6		75.02	17.81

As shown in Fig. 3b and Table 5, the THR profiles of the fiberboards with fire retardant treatment (16.98 MJ m^{-2}, 17.71 MJ m^{-2}, 19.81 MJ m^{-2}, 15.33 MJ m^{-2}, and 17.81 MJ m^{-2}) were lower than that of the CF (22.18 MJ m^{-2}).

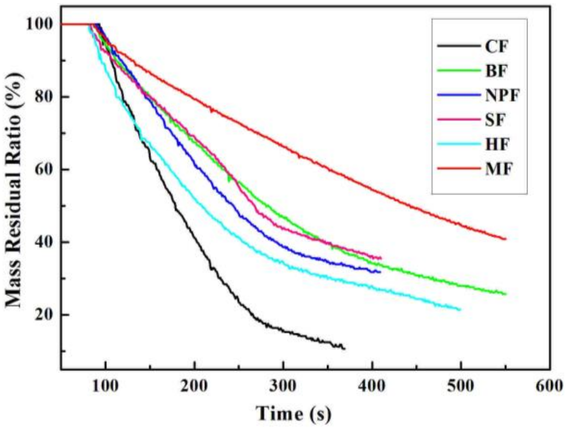


Fig. 4. Mass residual ratios of the control fiberboard (CF), boron-based fiberboard (BF), nitrogen-phosphorus-based fiberboard (NPF), silicium-based fiberboard (SF), halogen-based fiberboard (HF), and mixed fiberboard (MF)

All of the fire retardants played an important role, but there were different results in the THR profiles of the fiberboards. Unlike the HRR profiles, HF had the lowest THR profile (15.33 MJ m^{-2}), indicating that HF combusted least effectively and that the chlorinated paraffins were sufficient in counteracting the decrease in total heat release. This occurred because halogen-based fire retardants act in the vapor and condensed phases. They generate halogen hydride gas, which accelerates hemicellulose and cellulose dehydration into charcoal in low temperatures. The described processes can also generate a large amount of hydroxyl radicals, which interrupt the exothermic processes and suppress combustion (Lu *et al.* 2002; Liu 2013). These reactions are described in Eq. 5:

$$\begin{aligned}&HO\cdot + CO \rightarrow CO_2\uparrow + H\cdot\\&2H\cdot + O_2 \rightarrow 2HO\cdot\\&Cl\cdot + HR \rightarrow HCl + R\cdot\\&HCl + HO\cdot \rightarrow H_2O + Cl\cdot\end{aligned} \tag{5}$$

Mass loss vs. time

Percentage mass loss curves were calculated as a function of time (Fig. 4). Mass loss differences between the fiberboards were due to their HRR differences. CF showed the lowest residual mass of 10.69%. Among BF, NPF, SF, and HF, the residual mass of SF (35.49%) was higher by 9.78%, 3.68%, and 14.01% than BF, NPF, and HF, respectively. This result could be ascribed to the inorganic film, which acts as a barrier to fuel transport (Sacristán *et al.* 2010; Chen *et al.* 2015b). In contrast, chlorinated paraffins cannot form a barrier to slow or prevent the release of fuel to the flame front, which corresponded to its high value of HHR and low percentage mass loss (21.48%). MF showed the largest residual mass (40.94%), which was higher than that of CF by 30.25%. These results indicated that the boron compounds, nitrogen-phosphorus compounds, silicium compounds, and halogen compounds in complex fire retardants had a significant synergistic effect on improving the fire resistance of ULDFs.

CONCLUSIONS

1. The fire properties of ULDFs were effectively improved by treatment with complex fire retardants. The optimal complex fire retardant was predicted by response surface methodology, and an optimal char yield of 61.4% was obtained. The optimal complex fire retardant contained 33.9% boracic acid and borax, 27.2% diammonium hydrogen phosphate, 15.0% sodium silicate, and 28.6% chlorinated paraffin.
2. Compared with CF, the HRRs of BF, NPF, SF, HF, and MF were reduced. This result indicated that ULDF fire properties were effectively improved by all of four fire retardants. Additionally, the THR profiles of BF, NPF, SF, HF, and MF were lower than those of CF. Fiberboards with chlorinated paraffins showed a significant reduction in the amount of total heat released.
3. The overall mass loss was remarkably decreased in all fiberboards. Si compounds were the most effective in preventing ULDF mass loss. MF showed the highest residual mass (40.94%), which was 30.25% higher than CF. The four fire retardant agents showed synergistic effects in ULDFs.

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