Fire Performance of Ultra-Low Density Fiberboard (ULDF) with Complex Fire-Retardants

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To clarify how the fire performance of ultra-low density fiberboard (ULDF) can be improved by complex fire-retardants, the limiting oxygen index (LOI) and microstructure of ULDFs with different additive amounts of complex fire-retardants was analyzed. The char yield, chemical bonding, and thermostability of ULDFs treated by different temperatures were also tested. Results showed that the LOI values and compactness of ULDFs were increased with increased amounts of fire-retardants. Three steps of char yield curves in control fiberboard (CF) and mixed fiberboard (MF) were apparent. The preliminary degradation in lignin and cellulose of CF occurred at 300 °C. The cellulose had completely decomposed at 400 °C, but in the case of MF, the lignin and cellulose were not completely decomposed at 400 °C. It was shown that there are different ways to improve the fire resistance of ULDF using boron, nitrogen-phosphorus, silica, and halogen-based fire-retardants. The fiberboard with silicium compounds had the lowest mass loss in three stages and total mass loss. Compared with CF, MF had a lower mass loss. Furthermore, the exothermic peak for MF at around 400.0 °C was decreased, indicating that the fire resistance of ULDF was improved by the complex fire-retardants.

Keywords: Char yield; Chemical bonding; Fire-retardant; Thermostability; Ultra-low density fiberboard

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INTRODUCTION

Ultra-low density fiberboard (ULDF), a combustible material, is made from plant fibers. It has many excellent properties, and it can serve as a substitute for petroleum-based polymers (Xie *et al.* 2004, 2008a,b, 2011; Chen *et al.* 2015c, 2016a). As a wood-based material, the inflammability of ULDF limits its applications. Therefore, many efforts have to be taken to improve the fire resistance of fiberboards.

To improve the fire resistance of wood-based composites, modifying or impeding the burning pathway by chemical agents is a good method. Combustion is impeded by fire retardant treatment in the condensed and/or gaseous phases (Hornsby 2001; Genovese and Shanks 2008). For example, forming a protective layer with a low thermal conductivity covering the composites can reduce the heat transfer from the heat source. Cooling down the substrate and diluting the fuel in the solid and gaseous phases delays combustion (Gao *et al.* 2005; Bourbigot and Duquesne 2007; Hagen *et al.* 2009; Schartel 2010).

Many fire-retardants have been used to treat wood-based composites, such as phosphorus, nitrogen, boron, silica-based compounds, halogen type fire retardants, titanium oxide, and their combinations (Saka and Ueno 1997; Lewin 2005; Baysal *et al.* 2007a,b; Branca and Blasi 2007; Genovese and Shanks 2008; Hagen *et al.* 2009; Sacristán *et al.* 2010; Schartel 2010; Fu *et al.* 2011; Mahr *et al.* 2012; Unger *et al.* 2012;

Xie and Liu 2012; Niu *et al.* 2014; Chen *et al.* 2015a). They can be used alone, together, or in association with other additives (Durin-France *et al.* 2000). For example, Wang and Li (2004) reported that the fire properties of wood were improved by the use of complex fire-retardants with guanylurea phosphate and boric acid. Moreover, there is more than one way in which fire-retardants improve the fire resistance of composites. Complex fire-retardants accelerate char-forming in wood, form a protective layer, and dilute the fuel. Ebdon *et al.* (1996) showed that silica compounds dilute the combustible organic gases and form a barrier to heat and mass transfer.

Previous studies have shown that the fire resistance of ULDF is better improved by complex fire-retardants than a one-component fire-retardant (Chen *et al.* 2016a). The optimal preparation conditions of complex fire-retardant agents were obtained in Chen *et al.* (2016a). There is a synergistic effect in complex fire-retardants containing boron, nitrogen-phosphorus, silica, and halogen compounds. The goal of this study was to clarify how the fire performance of ULDF can be improved by the complex fire-retardants and their additive amount. In this study, the limiting oxygen index (LOI) and microstructure of ULDFs as a function of the additive amount of complex fire-retardants were tested. The char yield, chemical bonding, and thermostability of the ULDFs treated by different temperatures were examined also.

EXPERIMENTAL

Materials

Kraft pulp (KP, *spruce-pine-fir*; Tembec Inc., Québec, Canada) was utilized as a raw material to manufacture ULDF. Sodium dodecylbenzene sulfonate, as a foaming agent, was purchased from Jiangsu Qingting Washing Products Co., Ltd. (Yancheng, China). Alkyl ketene dimmer (AKD) was purchased from Suzhou Tianma Chemicals Co., Ltd. (Suzhou, China). The boric acid and borax were purchased from Zhengzhou Deer Boron Industry Chemical Co., Ltd. (Zhengzhou, China). The diammonium hydrogen phosphate was purchased from Suzhou High-energy Chemical Technology Co., Ltd. (Suzhou, China). Sodium silicate was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Chlorinated paraffin was purchased from Changzhou Fengshuo Chemical Co., Ltd. (Changzhou, China).

Preparation of Ultra-Low Density Fiberboard

Ultra-low density fiberboards (200 mm × 200 mm × 50 mm) were made of 50.0 g dry kraft fiber, with a target bulk density of 50 to 90 $kg\cdot m^{-3}$. They were manufactured separately in a demonstration line as described in Fig. 1. The polyacrylamide resin, AKD, fire-retardants, and foaming agent (10 wt%) were added during different manufacturing stages in all specimens.

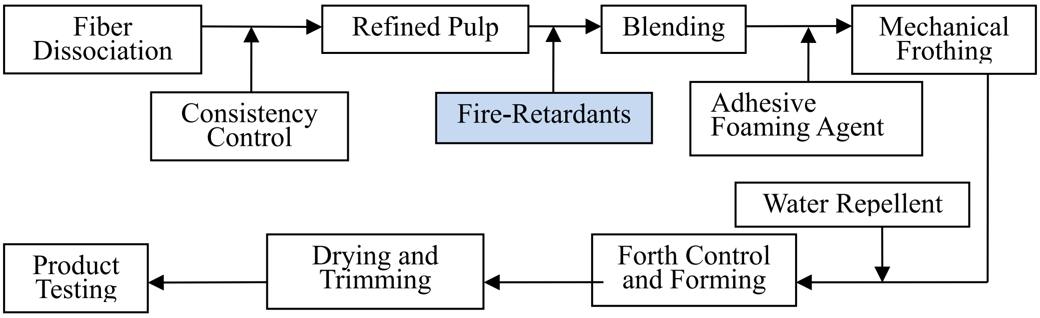

Fig. 1. The preparation process of ultra-low density fiberboards

In this study, the related nomenclature used for the corresponding fiberboards were CF (control fiberboard, fiberboard without fire-retardant), BF (fiberboard with boron compounds), NPF (fiberboard with nitrogen-phosphorus compounds), SF (fiberboard with silicium compounds), HF (fiberboard with halogen compounds), and MF (mixed fiberboard, fiberboard with 100% complex fire-retardant), respectively. Here, the additive amount of complex fire-retardants was based on dry fiber mass. The detailed parameters for fiberboards are presented in Table 1.

Table 1. Parameters for Fiberboards

NO.	Boron Compounds	Nitrogen-Phosphorus Compounds	Silicium Compounds	Halogen Compounds	Polyacrylamide resin	AKD	Foaming Agent
CF	-				20 mL	50 mL	80 mL
BF	80 g	-	-	-			
NPF	-	80 g	-	-			
SF	-	-	80 g	-			
HF	-	-	-	80 g			
MF	50 g Complex Fire-retardants*						

*Complex fire-retardants consisted of 34.0% boron compounds (boracic acid and borax), 27.0% nitrogen-phosphorus compounds (diammonium hydrogen phosphate), 15% silicium compounds (potassium silicate), and 29.0% halogen compounds (chlorinated paraffin) (Chen *et al.* 2016a). The mass of each composition was based on fire retardant contents.

Limiting Oxygen Index (LOI) of Ultra-Low Density Fiberboard

LOI was measured using a limiting oxygen index instrument (Jiang Ning county analysis instrument factory, Jiangning, China) according to GB/T2 406.2-2009 (2009). The size of the samples was 150 × 10 × 10 mm^3 ($L \times W \times H$). All samples were placed in a sample holder covered by vertical glass column, and the gas flow (oxygen and nitrogen) was adjusted until the atmosphere in the glass was stabilized and uniform in order to meet the test criteria. Each sample was ignited with a flame and burned downward on the top surface of samples. The minimum oxygen concentrations supporting combustion for all samples were recorded as a percentage. The results reported are the average of 15 replications.

Char Yield of Ultra-Low Density Fiberboard

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

Characterization

The micromorphology of ULDFs was characterized by scanning electron microscopy (SEM, Philips XL-30 TMP, Amsterdam, Netherlands) at an acceleration voltage of 10 kV. The surfaces of the specimens were coated with gold by an electro-deposition method to confer electrical conduction and reduce specimen charging before recording the SEM micrographs.

Fourier transform infrared (FTIR) analysis was performed by a Nicolet 380 FTIR spectrometer (Thermo Electron Scientific, Madison, WI, USA), employing the KBr pellet method, taking 32 scans for each sample with a resolution of 4 cm^{-1}, ranging from 4000 cm^{-1} to 400 cm^{-1}.

The thermal curves of thermogravimetric analysis (TGA) were obtained using a thermogravimetric analyzer (NETZSCH STA 449F3, Selby, Germany). The temperature range was from 30 °C to 600 °C with a heating rate of 10 °C min^{-1} under air atmosphere.

RESULTS AND DISCUSSION

Effect of the Additive Amount of Complex Fire-Retardants on the LOI and Micromorphology of Ultra-Low Density Fiberboards

The range of LOI as a function of the additive amount of complex fire-retardants (0%, 20%, 40%, 60%, 80%, 100%, 120%, and 140%) is presented in Fig. 2. The microstructures of ultra-low density fiberboards with different contents of complex fire-retardants (0%, 40%, 100%, and 140%) are presented in Fig. 3.

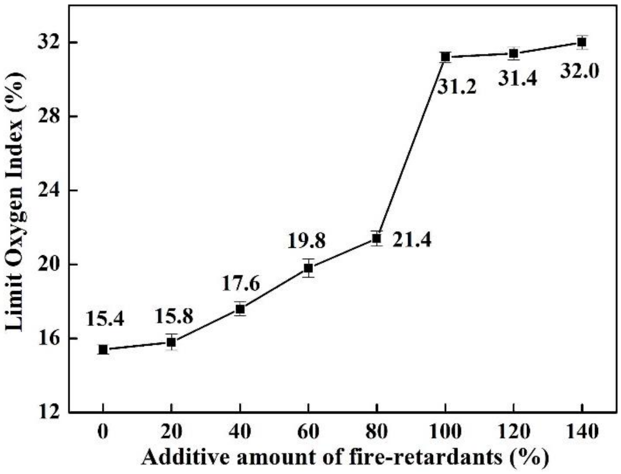

Fig. 2. Effect of the additive amount of fire-retardants on the limiting oxygen index of ultra-low density fiberboards

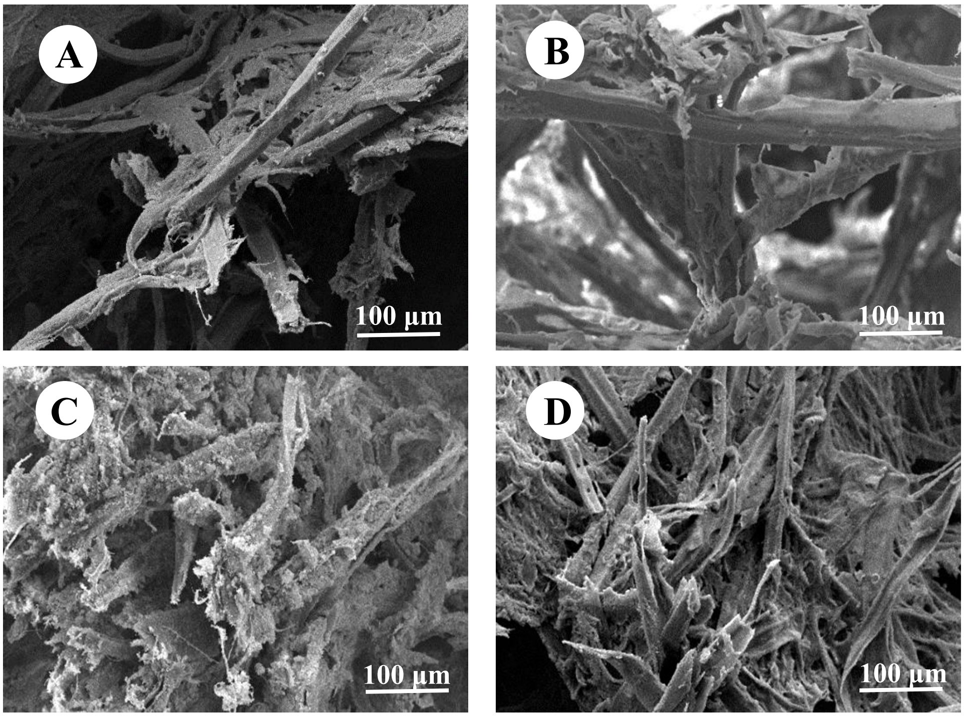

Fig. 3. SEM images of ultra-low density fiberboards with different contents of fire-retardants: (A) 0%, (B) 40%, (C) 100%, and (D) 140%

As shown in Fig. 2, the LOI values of ULDFs increased with an increase in the additive amount of fire-retardants. The LOI value of fiberboard with 100% fire-retardants was 31.2%, which increased by 102.60% compared with the fiberboard without fire-retardant. When the contents of fire-retardants were more than 100%, the changes in LOI values of ULDFs were not obvious. This is because the internal structure of ULDF with porosity is affected by the increasing additive amount of fire-retardants. Fire-retardants fill in fiberboards, which increases their compactness. As presented in Fig. 3A, there was a relatively smooth surface and large pores. Compared with control fiberboard, the fire-retardants deposited on the fiber surfaces are found in the fiberboard with 40% fire-retardants (Fig. 3B). When the additive amount of fire-retardants was more than 100%, almost all fiber surfaces were covered (Figs. 3C and D). This result indicated that fire-retardants covering the fiber surfaces are important to improve the fire resistance of ULDFs. However, the porosity of fiberboard with 140% fire-retardants was decreased, but its LOI value was just 0.8% higher than fiberboard with 100% fire-retardants. Taking practical conditions into consideration, there findings imply that the optimal additive amount of complex fire-retardants for improving the fire resistance of ULDFs was 100% (based on dry fiber mass).

Effect of Temperature on the Char Yield of Ultra-Low Density Fiberboards

The char yield of control fiberboard and mixed fiberboard treated by different temperatures (50, 100, 150, 180, 200, 230, 250, 280, 300, 350, 400, 450, and 500 °C) is presented in Fig. 4. There were three thermal decomposition steps. The first stage (below 250 °C) was assigned to the drying and pre-decomposition processing. Its mass loss was caused by the evaporation of imbibed water from the fibers, indicating that the native fiber is a non-hydrophobic composite (Vîlcu *et al.* 1985). The second rapid char yield loss around 250 to 400 °C was accompanied by the combustion and decomposition of cellulose, hemicellulose, and lignin. During the last stage (more than 400 °C), the char yield loss was not obvious, which was assigned to the calcining processing of charcoal. There were not any obvious differences between control fiberboard and mixed fiberboard in the first stage, but when the temperature was greater than 250 °C, the char yield of MF was remarkably increased. For example, the char yield of MF at 350 °C and 500 °C increased by 78.31% and 112.78%, respectively, compared with CF. These results indicated that the fire resistance of fiberboards is improved by complex fire-retardants, which improve the protection properties of the residues (Chen *et al.* 2015b, 2016a).

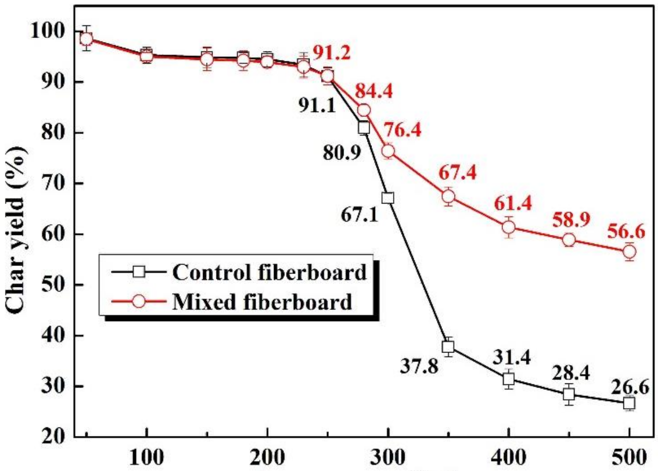

Fig. 4. Char yield of control fiberboard and mixed fiberboard treated by different temperatures

Chemical Bonding in Combustion Residues of Ultra-low Density Fiberboards

FTIR profiles of control fiberboard and mixed fiberboard treated by different temperatures (room temperature, 200, 300, 400, and 500 °C) are presented in Fig. 5. As shown in Fig. 5A, the infrared spectra of control fiberboard at room temperature exhibited the -OH peaks at around 3414 cm^{-1}, which reflected the presence of intramolecular and intermolecular hydroxyls groups, respectively (Alemdar and Sain 2008). The characteristic peaks at around 2920, 1458, and 1382 cm^{-1} are attributed to C-H bending of CH_2 groups, C-H bending of CH_3 groups, and CH_2 stretch, respectively. The characteristic peaks of lignin show the peaks at 1735, 1650, 1598, 1504, 1244, and 1160 cm^{-1}. The peaks at around 1112, 1056, 896, and 612 cm^{-1} correspond to the characteristic peaks of cellulose. For control fiberboard, the peak at 3414 cm^{-1} was gradually weakened with an increase in temperature, reflecting the evaporation of imbibed water during heating. When the fiberboards were treated at 300 °C, the characteristic peaks of lignin and cellulose were obviously weakened, indicating the preliminary degradation in lignin and cellulose. This result agreed with the char yield analysis. Starting at 400 °C, the characteristic peaks of cellulose disappeared, but the characteristic peaks of lignin remained. So the peak at 1056 cm^{-1} corresponds to the characteristic peaks of cellulose, which weakened and even disappeared with the increasing of temperature. This result indicated that the cellulose had completely decomposed but lignin remained. Interestingly, the peaks at around 3413 and 1106 cm^{-1} were observed again when the fiber composites were treated at 500 °C. This is because the fibers decomposed to form the charcoal with porosity and strong absorbability.

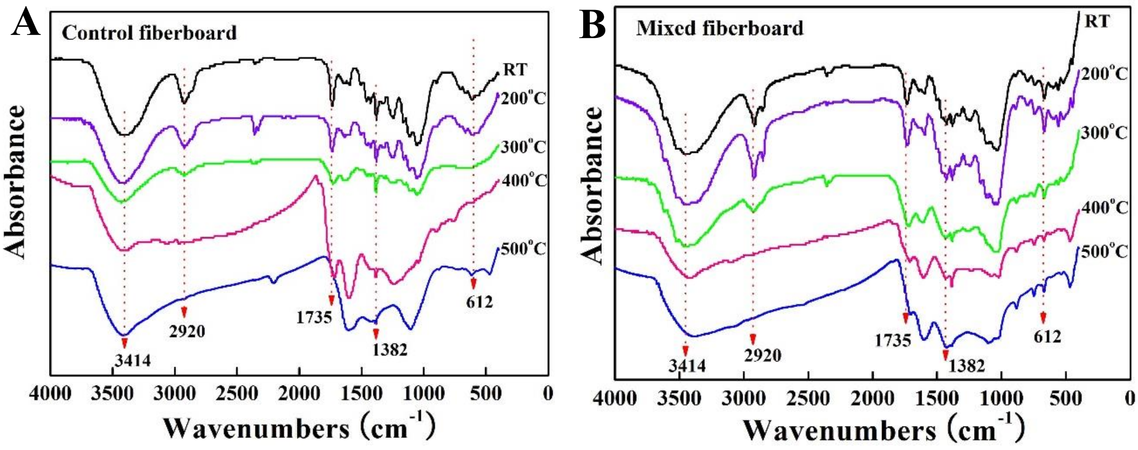

Fig. 5. FTIR profiles (A) control fiberboard and (B) mixed fiberboard treated at different temperatures

Compared with the CF at room temperature, the FTIR spectrum of MF shows most of the characteristic peaks of the CF (Fig. 5B). When the MF was treated at 400 °C, the peaks at 1735, 1382, 896, and 612 cm^{-1} were present, indicating that the lignin and cellulose were not completely decomposed (Cai *et al.* 2016). This result means the thermostability of ULDF is improved by the complex fire-retardants.

Thermogravimetric Analysis of Ultra-Low Density Fiberboards

To evaluate the thermostability of the ULDFs, the mass loss and differential scanning calorimetry (DSC) curves of CF, BF, NPF, SF, HF, and MF are presented in Figs. 6 and 7. As shown in Fig. 6 and Table 1, there were three distinct stages of mass loss in all specimens. The slight mass loss that occurred below 110 °C is caused by evaporation of imbibed water from the specimens (Vîlcu *et al.* 1985; Xiao *et al.* 2002; Yang *et al.* 2002). The second rapid mass loss stage around 110 to 400 °C is mainly attributed to the pyrogenic decomposition of cellulose and hemicellulose. The last stage (400 to 600 °C) of slight mass loss in fiberboards is accompanied by the calcination of charcoal (Chen *et al.* 1993; Zeriouh and Belkbir 1995; Shen and Kawi 1999; Chen *et al.* 2005; Chiranjeevi *et al.* 2006; Unuabonah *et al.* 2013). These results are in agreement with char yield and FTIR analysis. In Table 1, the mass loss of fiberboards was decreased after treatment by fire-retardants. In particular, the fiberboard with silicium compounds had the lowest mass loss in three stages and total mass loss.

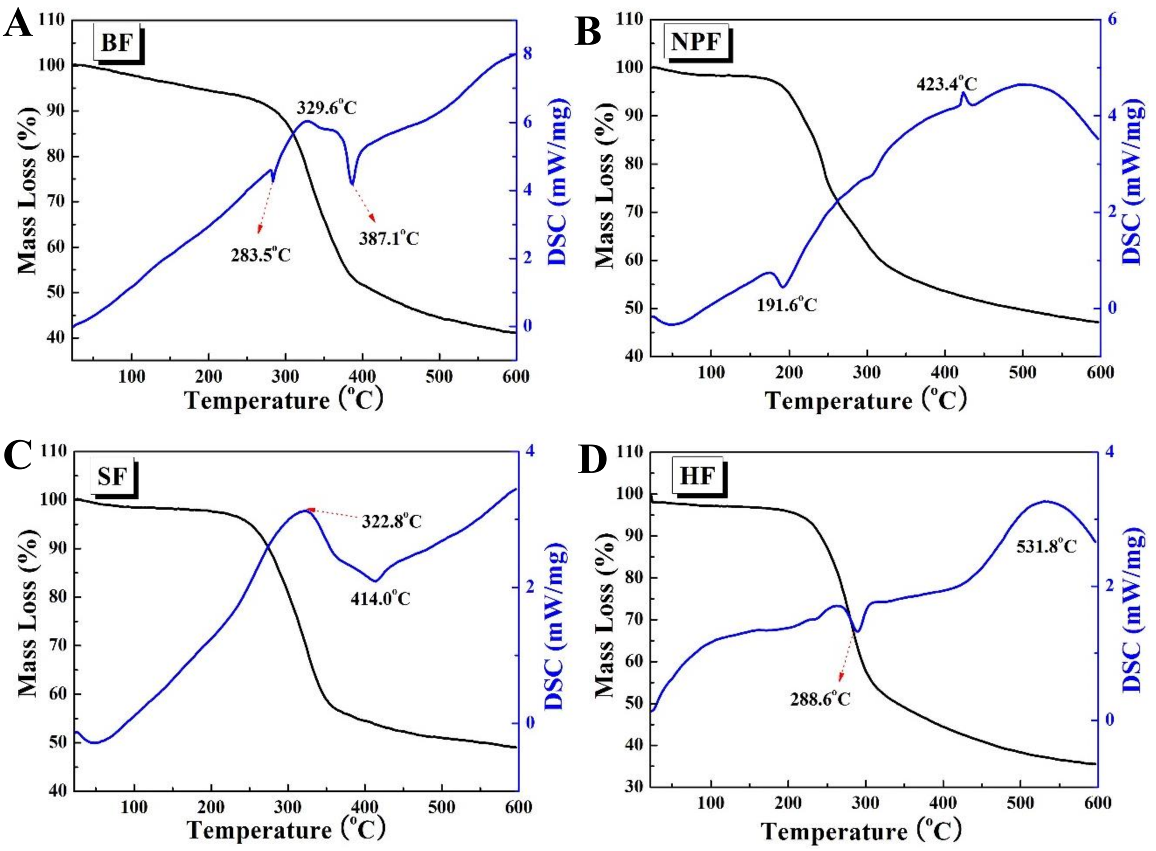

Fig. 6. TG and DSC curves of (A) boron-based fiberboard (BF), (B) nitrogen-phosphorus-based fiberboard (NPF), (C) silicate-based fiberboard (SF), and (D) halogen-based fiberboard (HF)

Table 1. Parameters and Mass Loss of the Fiberboards Obtained from the TG Curves

No.	Fire Retardant		Mass Loss (%)			
	Composition	Additives (g)	First	Second	Third	Total
			30 to 110 °C	110 to 400 °C	400 to 600 °C	
CF	-	-	5.7	86.7	2.7	95.1
BF	Boron Compounds	80.0	2.5	45.8	10.6	58.9
NPF	Nitrogen-Phosphorus Compounds	80.0	1.6	44.8	6.5	52.9
SF	Silicium Compounds	80.0	1.6	43.9	5.4	50.9
HF	Halogen Compounds	80.0	2.8	52.8	8.8	64.4
MF	Complex Fire-Retardant	50.0	5.0	67.0	12.4	84.4

For boron-based fiberboard, there were two endothermic peaks and one exothermic peak (Fig. 6A). The endothermic peak around 283.5 °C is caused by the thermal decomposition of boric acid (H_3BO_3). When the boric acid is heated, it can be changed into metaboric acid (HBO_2), pyroboric acid ($H_2B_4O_7$), and diboron trioxide (B_2O_3) (Eq. 1). The endothermic peak around 387.1 °C is attributed to the effects of refrigeration and heat absorption by water of crystallization obtained from sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$). The exothermic peak at 329.6 °C is caused by the combustion of combustible volatiles during the pyrogenic decomposition of cellulose and hemicellulose. Boron oxide is produced from boron compounds. It improves the thermostability of cellulose; the exothermic peak is smooth without deflagration (Chen *at al.* 2016a).

$$H_3BO_3 \xrightarrow[-H_2O]{105^{\circ}C} HBO_2 \xrightarrow{160^{\circ}C} H_2B_4O_7 \xrightarrow{260^{\circ}C} B_2O_3 \qquad (1)$$

As presented in Fig. 6B and Eq. 2, the endothermic peak around 191.6 °C is caused by the endothermic reactions in metaphosphoric acid (HPO_3) and noncombustible gas (NH_3) obtained from diammonium hydrogen phosphate [$(NH_4)_2HPO_4$]. The crystalline region is broken and releases combustible volatiles around 423.4 °C, where an exothermic peak is formed. The heat release is decreased when the temperature reached more than 500 °C. This is because HPO_3 can be decomposed into water and sticky phosphorus pentoxide (P_2O_5), which restrains the flameless calcination of charcoal (Hagen *et al.* 2009).

$$(NH_4)_2HPO_4 \xrightarrow[\text{Temperature}]{\text{Low}} \left\{\begin{array}{l} NH_3 \\ H_3PO_4 \longrightarrow HPO_3 \end{array}\right. \xrightarrow{\text{Around } 500^{\circ}C} \left\{\begin{array}{l} N_2 \\ H_2O \\ P_2O_5 \end{array}\right. \qquad (2)$$

Potassium silicate ($K_2O \cdot nSiO_2 \cdot nH_2O$) generates polysilicic acid at around 400 °C, which reacts with wood to form an inorganic film on its surface by the covalent bonds of Si-O-C and Si-C. The inorganic film insulates wood against air during combustion (Unger *et al.* 2012; Chen *et al.* 2015b). Potassium carbonate (K_2CO_3), a component of Si compounds, releases noncombustible gas (CO_2) at 400 °C. Therefore, there is an endothermic peak at around 414.0 °C (Fig. 6C).

Halogen-based fire retardants (chlorinated paraffins) act in the vapor and condensed phases. The condensed phase mainly depends on the generation of hydrogen chloride gas (HCl), which accelerates hemicellulose and cellulose dehydration into charcoal in low temperatures. The vapor phase follows the principle of free radical chain reaction. The large number of hydroxyl radicals ($HO\cdot$) can react with CO to form the CO_2 gas and hydrogen radical ($H\cdot$), which reacts with oxygen to form hydroxyl radicals (Chen *et al.* 2015b, 2016a). The described processes interrupt the exothermic processes and suppress combustion. Additionally, the generation of HCl captures the hydroxyl radicals to form the water, which absorbs heat during evaporation (Lu and Hamerton 2002; Liu 2013). An endothermic peak appears at around 288.6 °C.

As shown in Fig. 7, the total mass loss of CF and MF were 95.1% and 84.4, respectively. The mass losses of CF and MF in the first stage were 5.7% and 5.0%, respectively, indicating the fiberboards with fire-retardants are more hydrophobic than control fiberboard (Chen *et al.* 2016b). The mass loss of MF in the second stage was decreased by 19.7% compared with CF. This result indicated that the decomposition of cellulose and hemicellulose were restrained by complex fire-retardants. The mass loss of MF in the third stage was 9.7% higher than the CF, indicating that the complex fire-retardants prompted the decomposition of polymer toward carbonaceous residues. Additionally, the exothermic peak around 400.0 °C was obviously decreased, indicating the deflagration process in fiberboards was restrained by complex fire-retardants, which produce a synergistic effect between different compositions (Chen *et al.* 2016a). In sum, the thermostability of the ULDFs was improved by complex fire-retardants.

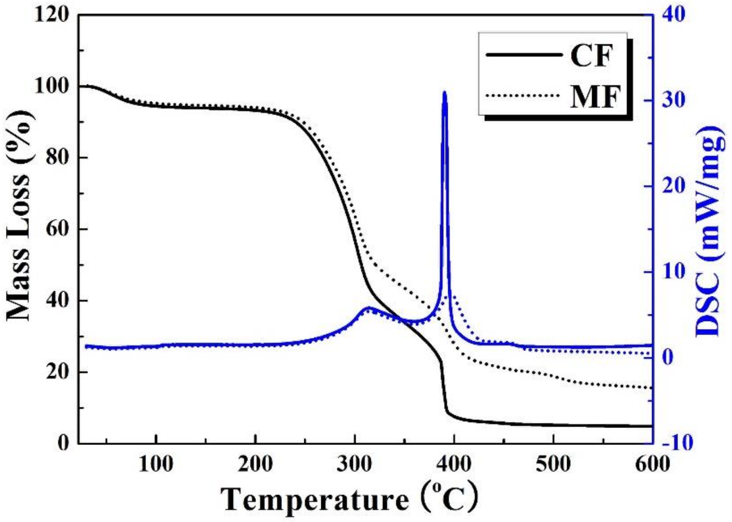

Fig. 7. TG and DSC curves of control fiberboard (CF, fiberboard without fire-retardant) and mixed fiberboard (MF, fiberboard with 100% complex fire-retardant)

CONCLUSIONS

1. The LOI values and compactness of ULDFs were increased with the increase in amount of fire-retardants. The LOI value of fiberboard with 100% fire-retardants increased by 102.60% compared with fiberboard without fire-retardant.
2. Three-step char yield curves were apparent in CF and MF. When the temperature was more than 250 °C, the char yield of MF was improved. The char yield of MF at 350 °C and 500 °C increased by 78.31% and 112.78%, respectively, compared with CF.
3. For control fiberboard, the preliminary degradation in lignin and cellulose occurred at 300 °C. When the temperature was greater than 400 °C, the cellulose had completely decomposed, but lignin still existed. In MF, the lignin and cellulose were not completely decomposed at 400 °C, indicating the thermostability of ULDF was improved by the complex fire-retardants.
4. The mass losses of fiberboards were decreased after treatment with fire-retardants. The fiberboard with silicium compounds had the lowest mass loss in three stages and total mass loss. Compared with CF, MF had a lower mass loss, and its exothermic peak around 400.0 °C was decreased.

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