Effect of Boron-Zinc-Aluminum-Silicium Compounds on the Fire Performance of Ultra-Low Density Fiberboards

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B-Zn-Si-Al compounds are modified Si-Al compounds made of sodium silicate, zinc sulfate, borax, and aluminum sulfate. They act as a fire retardant during the preparation of ultra-low density fiberboards (ULDFs). An orthogonal experiment was used to optimize the contents of the four compounds according to the limiting oxygen index. Fourier transform infrared spectroscopy was employed to preliminarily analyze the chemical structure of the compounds. Additionally, a cone calorimeter was used to assess the fire performance of the ULDFs. The results suggested that the optimized solution was made of 27.0 mL of sodium silicate solution, 27.0 mL of aluminum sulfate solution, 3.0 g of zinc sulfate, and 6.5 g of borax, resulting in an oxygen index of 29.5%. The bond Al-O-B was detected at 1397 and 796 cm^{-1}. The Si-O-Zn bonds were detected at 867 cm^{-1}. The heat release rate, total heat release, and total smoke release decreased and the mass residual ratio increased in the sample using the optimal conditions from the orthogonal array design. It was concluded that B-Zn-Si-Al compounds effectively protect fibers from fire.

Keywords: Ultra-low density; Optimization; Fire performance; B-Zn-Si-Al compounds; Cone calorimeter

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INTRODUCTION

Rising ecological and socio-economic awareness, overdependence on petroleum resources, and increasingly stringent environmental regulations have prompted many researchers to move towards fields that use so-called ‘green’ materials that cause less damage to the environment. This interest in eco-friendly materials has resulted in a rise in the use of natural fibers (Bismarck *et al.* 2005; Xie *et al.* 2011). Especially in recent years, natural fibers have been the preferred reinforcement or filler in polymer composites, rather than glass and carbon fiber, because of their low cost, sustainability, biodegradability, and light weight (Holbery and Houston 2006; Thomas *et al.* 2011; Kiziltas *et al.* 2014).

Ultra-low density fiberboard (ULDF), as an environmentally friendly material, has attracted a lot of attention in the fields of transportation and architecture (Xie *et al.* 2008a,b; Niu *et al.* 2014). In the conventional dry process, fiberboards are manufactured by applying heat and pressure to do two things: 1) consolidate the mat to a desired density and thickness and 2) cure the resin to provide bonding between the fibers (Youngquist 1999). However, ULDFs are processed using a liquid frothing method (Chen *et al.* 2015a) in which air is drawn into a reaction kettle by a high-speed stirrer, resulting in the formation of pulp froth. With the help of resin and bubbles, the fibers are cross-linked and form a reinforcing zone with arch shape. Si-Al compounds serve as adhesives that provide strength to support the arch shape of the fibers in case the arch structure collapses when the water is drained out and bubbles break up. In addition, the compounds also serve an excellent flocculant. The finished product has enhanced fire retardant qualities. ULDFs have many advantages, such as biodegradability, low density, high stiffness and strength, low thermal conductivity, and good sound absorption (Chen *et al.* 2014, 2015b). However, they are highly flammable. Because plant fibers have a low limiting oxygen index (LOI, only 19.6%), they can be easily ignited and subsequently burn rapidly. They therefore cannot be used without flame retardant processing. Many researchers (Xie *et al.* 2011; Chen *et al.* 2014; Niu *et al.* 2014) have used Si-Al compounds as modifiers to improve the flame-retardant and mechanical properties of ULDFs. There are a number of concerning properties of Si-Al compounds, such as larger partial size, lower initial strength, and inferior flocculation. As a result of these, the three-dimensional porous structure of the foaming material may collapse during the preparation of ULDFs, causing a massive loss of wood fibers and fines that are drained out with the water and leading to an increase in the white water concentration and deteriorating the fire performance.

In water treatment systems, attempts have been made to meet these challenges. One such attempt was by using a multinuclear assembly of metal ions (MAMI), such as Zn^{2+}, Fe^{3+}, and Mg^{2+} that could form linear inorganic polymers in aqueous solutions, which are long, rope-like chains of molecules. They are connected to each other and thus promote the formation of a three-dimensional network structure (Fan *et al.* 2006). Both the internal and external structures have considerable interfacial areas that could adsorb fine fibers and other smaller particles.

Meanwhile, the MAMI could neutralize the negatively charged wood fibers and fines in an aqueous system. Another attempt was made using borax, which can change the external features of Si-Al compounds in order to increase the crosslinking with each other and create a greater surface area. It also causes adsorption bridging action and sweep flocculation, because $B(OH)_3$, formed below pH 7.0, could react with Al-OH and Si-OH resulting in the formation of B-O-Al and Si-O-B bonds. These chemical bonds increase the molecular weight of the compound and favor absorption and bridge effects, as well as charge neutralization (Bian *et al.* 2012). Efforts should be made to achieve better flocculation during water treatment for the preparation of ULDFs. *Via* flocculation, more tiny fire-retardant particles could be absorbed and therefore remain in the fiberboards. Furthermore, Zn and B both contribute to fire-retardant properties.

Currently, there is no research in the literature concerning the modification of Si-Al compounds by adding Zn and B on ULDFs. The main objective of this study was to investigate the B-Zn-Si-Al compounds' capacity to improve the fire performance of ULDFs. An orthogonal array design was used to obtain the optimal preparation conditions for B-Zn-Si-Al compounds. FTIR was used to examine the chemical structure of B-Zn-Si-Al compounds, and a cone calorimeter was used to test the fire properties of ULDFs.

EXPERIMENTAL

Materials

Kraft pulp (KP, spruce-pine-fir; Tembec Inc., Quebec, Canada) was used to fabricate the ULDFs. Sodium silicate, aluminum sulfate, borax, and zinc sulfate were purchased from Tianjin Fuchen Chemical Reagents Factory (China) and were utilized in the preparation of Si-Al compounds and B-Zn-Si-Al compounds.

Methods

Preparation of B-Zn-Si-Al compound solution

The precursors of B-Zn-Si-Al compounds were prepared using a reaction vessel. First, zinc sulfate was added to an aluminum sulfate solution (20 wt%), which was kept in the vessel at 30 °C with a 1000 rpm rotation speed. Thirty minutes later, the Al-Zn solution was formed. Similarly, borax was added into a sodium silicate solution (33 wt%) to form the B-Si compounds. Then, the B-Si compounds were added into the Al-Zn solution to prepare the B-Zn-Si-Al compounds. The procedure used for the preparation is shown in Fig. 1.

Fig. 1. The preparation of B-Zn-Si-Al compounds

Manufacture of ultra-low density fiberboards

The ULDFs were manufactured using the same method described by Xie *et al.* (2011) with a target bulk density of 50 to 70 kg/m^3. Twenty mL of adhesive (25 wt% polyvinyl alcohol, 25 wt% gelatinized starch, and 0.25 wt% polyacrylamide), 40 mL of surfactant (20 wt% sodium dodecyl benzene sulfate), 50 mL of water repellent (alkyl ketene dimmer), and 10 g of flame-retarded synergistic agent (chlorinated paraffin) were added during mixing stages. The detailed process is shown in Fig. 2.

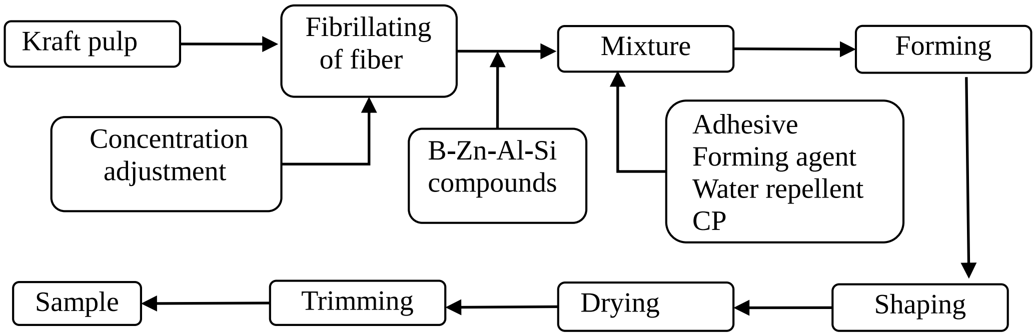


Fig. 2. The preparation of flame-retardant samples

Orthogonal array design statistical analysis

Orthogonal array design (OAD), or what is called Taguchi design, is considered to combine the advantages of a simplex optimization method and a factorial design. This method has been used widely in many industries since the 1980s. The beauty of it is that multiple factors can be considered in one experiment system. Moreover, it seeks nominal design points that are insensitive to variations in production and user environments to improve the yield in manufacturing and the reliability in performance of a product. Each factor for optimal conditions is designed in the experiment. The results of the OAD experiment can be statistically treated by two ways: variance analysis and range analysis. In variance analysis, the effects of different factors on response functions can be evaluated by significance (F ratio). In range analysis, the fluctuation range and tendency of response functions *versus* the levels of each factor can be seen from a line graph. From the results of variance analysis and range analysis, the factors that significantly affect the output responses can be found and optimal parameters for an analytical procedure can be obtained (Taguchi 1987).

Experimental design

An orthogonal experimental design was created to explore the preparation of B-Zn-Si-Al compounds and the significance of the factors. Sodium silicate solution (A, 33 wt%), aluminum sulfate solution (B, 20 wt%), borax (C), and zinc sulfate (D) were the four variables, while LOI was the function. The factors and levels were chosen by a preliminary experiment. The selection of variables is shown in Table 1.

Table 1. Factors and Levels for L_{16} (4^5) Orthogonal Array Design

Levels	Factors			
	A (mL)	B (mL)	C (g)	D (g)
1	23	23	2.0	6.0
2	25	25	2.5	6.5
3	27	27	3.0	7.0
4	29	29	3.5	7.5

Fourier transform infrared spectroscopy (FTIR)

FTIR (Nicolet 380 FTIR, Thermal Electron Instruments, USA) was used to test the functional groups of the samples using the KBr disk method and recorded by means of an average of 32 scans at a resolution of 4 cm^{-1} ranging from 4000 to 400 cm^{-1}.

Limiting oxygen index test (LOI)

LOI was chosen as the standard to measure the performance of ULDFs against fire. Measurements were performed using a limiting oxygen index instrument (Jiang Ning County Analysis Instrument Factory, China) according to GB/T 2406.2-2009 (2009). The dimensions of the test samples were 150 × 10 × 10 mm ($L \times W \times H$). All samples were placed in a sample holder covered by a vertical glass column, and the gas flow (oxygen and nitrogen) was adjusted until the atmosphere in the glass was stable and uniform in order to meet the test criteria. Each sample was ignited on the top surface with a flame and burned downward. Then, the minimum oxygen concentration that supported combustion was recorded as a percentage for all samples. The results were taken from an average of fifteen parallel experiments.

Fire properties test

A cone calorimeter (FTT Co., England) was used to test the fire properties of ULDFs, and ISO 5660-1 (2002) was used to evaluate the heat release (HRR), total heat release (THR), effective heat of combustion (EHC), mass residual ratio (MRR), specific extinction area (SEA), and total smoke release (TSR) against time. Test samples were cut to dimensions of 100 × 100 × 30 mm ($L \times W \times H$), wrapped in aluminum foil, and placed in a stainless-steel frame with an asbestos board in the bottom. The tests were performed at a heat flux level of 50 kW/m^2, which was capable of raising the temperature to 780 °C to simulate real fire conditions.

RESULTS AND DISCUSSION

Orthogonal Array Design and Results

The orthogonal array design of 16 experiments and the corresponding results of LOI are shown in Table 2.

Table 2. L_{16} (4^5) Orthogonal Array Design and Results

No.	*A*	*B*	*C*	*D*	LOI
1	1(23)	1(23)	1(2.0)	1(6.0)	23.1
2	1	2(25)	2(2.5)	2(6.5)	25.7
3	1	3(27)	3(3.0)	3(7.0)	26.5
4	1	4(29)	4(3.5)	4(7.5)	25.3
5	2(25)	1	2	3	26.8
6	2	2	1	4	26.4
7	2	3	4	1	25.8
8	2	4	3	2	28.8
9	3(27)	1	3	4	27.9
10	3	2	4	3	29.2
11	3	3	1	2	29.1
12	3	4	2	1	27.0
13	4	1	4	2	27.3
14	4(29)	2	3	1	27.5
15	4	3	2	4	28.0
16	4	4	1	3	26.9

Table 3. Range Analysis on Influence of Oxygen Index of ULDFs

		A	*B*	*C*	*D*
LOI (%)	K_1	25.150	26.275	26.375	25.850
	K_2	26.950	27.200	26.875	27.725
	K_3	28.300	27.350	27.675	27.350
	K_4	27.425	27.000	26.900	26.900
	R	3.150	1.075	1.300	1.875
	Rank	1	4	3	2
	Q^a	A_3	B_3	C_3	D_2

a: Optimal level

Range analysis

A range analysis on the influence of the oxygen index of ULDFs is presented in Table 3. The rank of range was *R*A > *R*D > *R*C > *R*B, so it could be inferred that the effects of the independent variables on the LOI of ULDFs were in the following order: addition of sodium silicate solution > addition of zinc sulfate > addition of borax > addition of aluminum sulfate solution. The Q value represented the optimal level of each factor from the highest value among K_1, K_2, K_3, and K_4. According to the Q value, the optimal conditions of B-Zn-Si-Al compounds for ULDFs were $A_3B_3C_3D_2$, *i.e.*, 27.0 mL of sodium silicate solution, 27.0 mL of aluminum sulfate solution, 3.0 g of borax, and 6.5 g of zinc sulfate.

Range tendency of LOI vs. single factor

The range tendency of LOI obtained as a function of each single factor is shown in Fig. 3, and a variance analysis on the influence of the oxygen index of ULDFs is shown in Table 4. As can be seen, A had a highly significant effect on the LOI, D had a significant effect, and C and B displayed no significant effect.

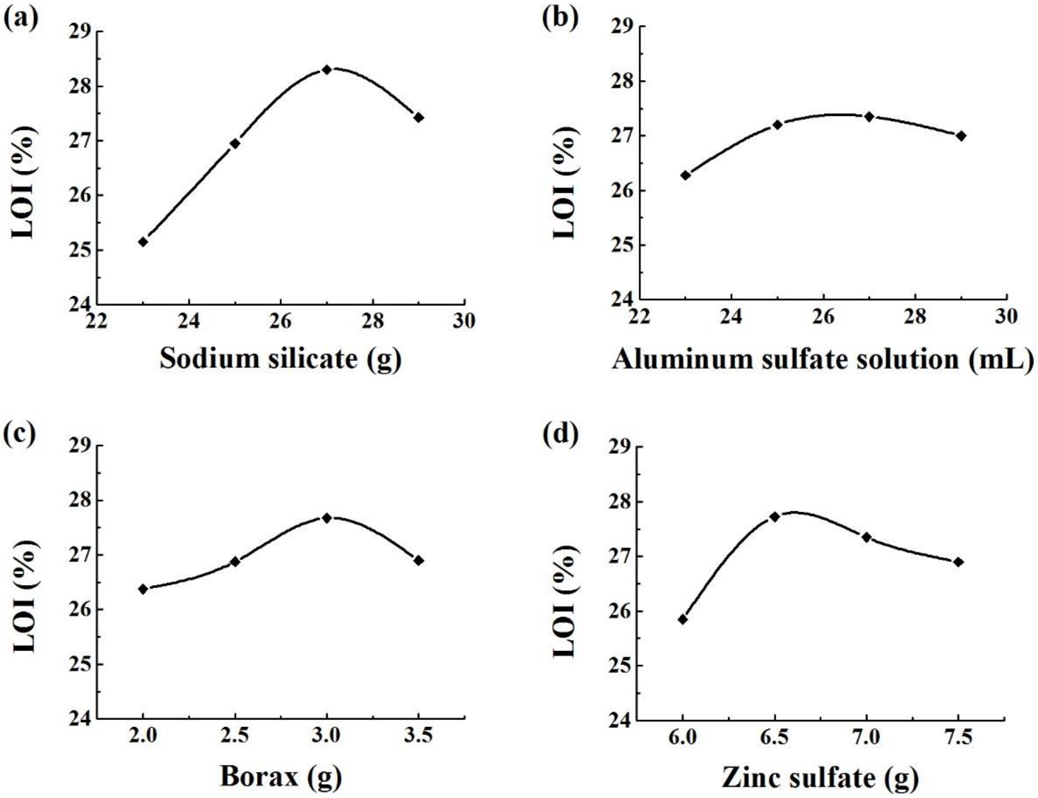


Fig. 3. Range tendency of LOI *vs.* single factor, (a) sodium silicate, (b) aluminum sulfate solution, (c) borax, (d) zinc sulfate

The addition of sodium silicate and zinc sulfate played an important role in the LOI of ULDFs, followed by borax, while the aluminum sulfate solution lagged behind. This is because the addition of sodium silicate, zinc sulfate, and aluminum sulfate could significantly change the pH values of the solution. Any pH values that were too high or too low would affect the morphology of fibers and the foaming system during the preparation of ULDFs. However, borax could increase the branches on the surface of compounds and therefore increase the contact for absorbing more fine fibers and fire retardant particles in the fiberboard. However, when more borax was added, the particle size of compounds became drastically larger, which led to agglomeration. The larger particles in turn led to the collapse of bubbles and the instability of the foam as a whole.

Table 4. Variance Analysis on the Influence of Oxygen Index of ULDFs

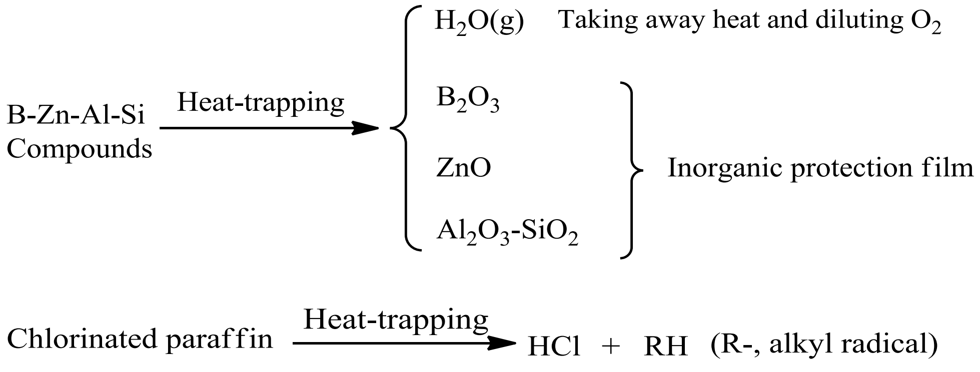
	Variance	Square of Deviance	DF[a]	F-value[b]	Significant
LOI/%	*A*	21.152	3	16.564	**
	B	2.722	3	2.132	
	C	3.457	3	2.707	
	D	7.892	3	6.180	*
	Se	1.28	3	1	

F0.1(3,3) = 5.39 F0.05(3,3) = 9.28 F0.01(3,3) = 29.50

a) degrees of freedom

b) F < 5.39 insignificant; 5.39 < F < 9.28 significant; 9.28 < F < 29.5 highly significant

In fire, B-Zn-Si-Al compounds and CP could absorb the heat from the environment and produce an inorganic protective film. The gases, coming from the decomposition of B-Zn-Al-Si compounds and chlorinated paraffin, could insulate the heat from fiber and reduce part of the heat from fire, as described in Eqs. (1). Additionally, in the gas phase, HCl and BCl_3 could substantially reduce hydroxyl radicals (HO·) and hydrogen radicals (H·), which could interrupt the chain reaction of combustion (Chen *et al.* 2016). This mechanism is described in Eqs. 2 and 3.



$$B_2O_3 + HCl \longrightarrow BCl_3 + H_2O \qquad (1)$$

HCl absorption mechanism of free radicals:

$$HCl + HO\cdot \rightarrow H_2O + Cl\cdot$$
$$RH + Cl\cdot \rightarrow R\cdot + HCl$$
$$RH + H\cdot \rightarrow H_2 + Cl_2 \qquad (2)$$

BCl_3 absorption mechanism of free radicals:

$$BCl_3 + 3HO\cdot \rightarrow H_3BO_3\cdot + 3Cl\cdot$$
$$RH + Cl\cdot \rightarrow R\cdot + HCl$$
$$2HCl + 2H\cdot \rightarrow Cl_2 + 2H_2 \qquad (3)$$

Verification of best test conditions

Based on the discussion above, the optimal conditions of B-Zn-Si-Al compounds for ULDFs were 27.0 mL of sodium silicate, 27.0 mL of aluminum sulfate solution, 3.0 g of borax, and 6.5 g of zinc sulfate ($A_3B_3C_3D_2$). Under these conditions, the optimal LOI of ULDF (29.5) was obtained, which was higher than any of the results in Table 2.

FTIR Analysis

FTIR profiles of Si-Al compounds and B-Zn-Si-Al compounds are shown in Fig. 4. In curve I, the peaks at 1628 and 1152 cm^{-1} are the Si-O characteristic peak and H-O-H bending vibration, respectively (Chen *et al.* 2002). The peaks near 1058 and 936 cm^{-1} are assumed to be Si-O-Al bending vibration, and 608 cm^{-1} is a mass gathering of the Al-OH bending vibration and moisture absorption peaks (Gao *et al.* 2000). Compared with curve I, the additional peak at 1445 cm^{-1} indicates a B-O bond. The peaks at 1397 and 796 cm^{-1} are for A1-O-B bond (Fang *et al.* 2010; Bian *et al.* 2012). The peak at 867 cm^{-1} might be attributed to the Si-O-Zn bending vibration, and the peak at 456 cm^{-1} is the cumulative effect of Zn-O bending vibration and moisture absorption vibration (Sun *et al.* 2014). The peaks at 867 and 456 cm^{-1} might be attributed to Si-O-Zn bending vibration and Zn-O bending vibration (Sun *et al.* 2014). Additionally, the peaks at 936 and 608 cm^{-1} became smoother, indicating that Si-O-Al and Al-OH bending vibrations were weakened. This is because the addition of boron could interact with Si, Al^{3+}, and hydrolysis products from Al^{3+}, which generated Al-O-B, Si-O-B, and Al-O-B. Little Al-OH remained in the compounds, and there was less of a chance to form Si-O-Al bonds. It could be concluded that the B-Zn-Al-Si compound was a complex compound resulting from reactions among the four ingredients, rather than being a simple mixture of raw materials.

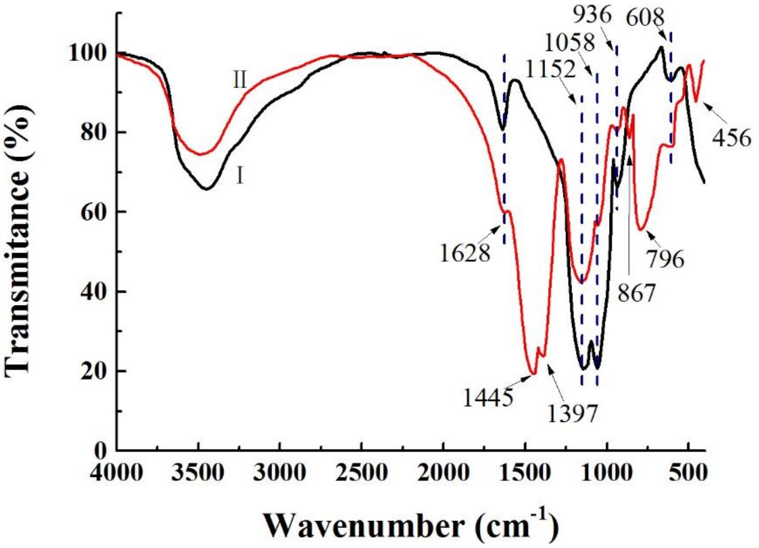


Fig. 4. FTIR profiles of I (Si-Al compounds) and II (B-Zn-Si-Al compounds)

Fire Performance of ULDFs

Heat release

To test the fire performance of B-Zn-Si-Al compounds on ULDFs, the optimal conditions from the orthogonal array design were used to prepare ULDFs. The Si-Al compounds were prepared using the same process parameters without B and Zn.

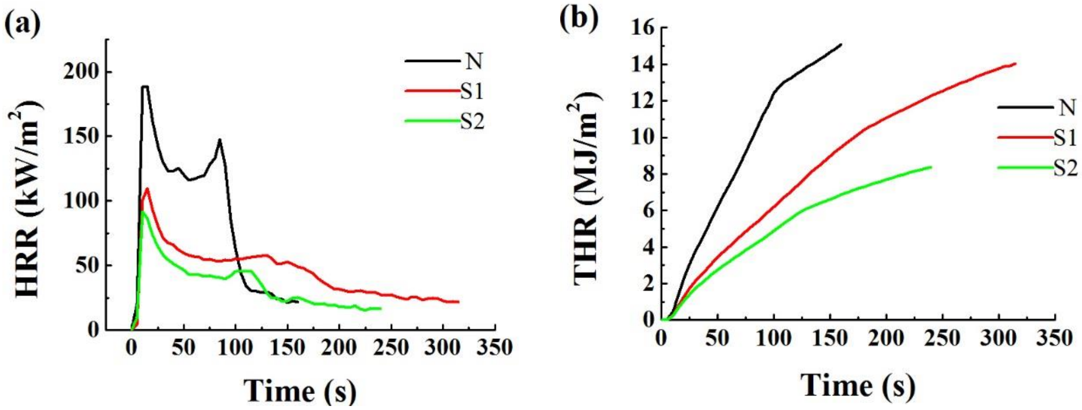


Fig. 5. (a) HRR curves and (b) THR curves of the control fiberboard (N), fiberboard with Al-Si compounds (S1), and fiberboard with B-Zn-Al-Si compounds (S2)

The heat release rate is one of the most important variables in characterizing the flammability of products. As more energy is produced during combustion, the heat release rate increases. This aggravates the flame, resulting in spreading because of a higher thermal degradation rate and more degradation products (Babrauskas and Peacock 1992).

As can be seen in Fig. 5(a), there were two peaks in the control sample, which were typical of burning wood. The appearance of the first peak was mostly due to the formation of the char layer, which decreased the amount of heat and emission of gas within the burning area (Xu *et al.* 2015). With the further combustion, the char layer, unfortunately, collapsed. The heat, coming out rom flame, could pierce though into the bottom of sample. As a result, more heat was released and the second peak appeared. Compared to N, the second peak in S1 and S2 appeared to be smaller after the addition of Si-Al and B-Zn-Si-Al compounds. It was concluded that adding the compounds could enhance the structure of the char layer and slow the rate of pyrolysis gases migrating from an exposed surface towards the heat source.

The total heat release, that is, the amount of heat liberated per unit time from equal surface areas exposed to a certain heat flux from a cone calorimeter, was the main parameter that reflected fire performance. The same tendency was found in the THR curves of each sample. The N curve presented a dramatic rise to the highest point at 15.06 MJ/m^2, while S1 and S2 curves rose more gently. This was because of the heat-trapping ability of Si-Al compounds and the protection coming from inorganic films covering the fibers (Chen *et al.* 2014; Niu *et al.* 2014). Consequently, the heat release of S1 and S2 was reduced to only 14.01 MJ/m^2 and 8.38 MJ/m^2, respectively. The THR of S2 was lower than the value reported by Niu *et al*. (2014), which was nearly 10 MJ/m^2 and around 14 MJ/m^2 reported in Chen *et al*. (2015). Additionally, when the crystal water in B-Zn-Si-Al compounds was evaporated into steam, heat around the burning material was taken in (see Eq. 4) (Zhu 2009). As a result, the THR profile of S2 was the lowest. When more heat was absorbed and the temperature dropped, it was less likely that the fire was fanned (Jian *et al.* 2006).

$$ZnO\cdot B_2O_3\cdot H_2O \rightarrow ZnO\cdot B_2O_3 + H_2O;\ \Delta H = +924\ J\cdot g^{-1} \qquad (4)$$

Mass loss and thermal degradation

The mass residual ratio is the percentage of residual mass at some time during burning. Great differences were seen in the MRR of control and treated samples. The control sample displayed a substantial downward trend of MRR in the first 50 s (Fig. 6 (a)), and only 0.01% remained at the end.

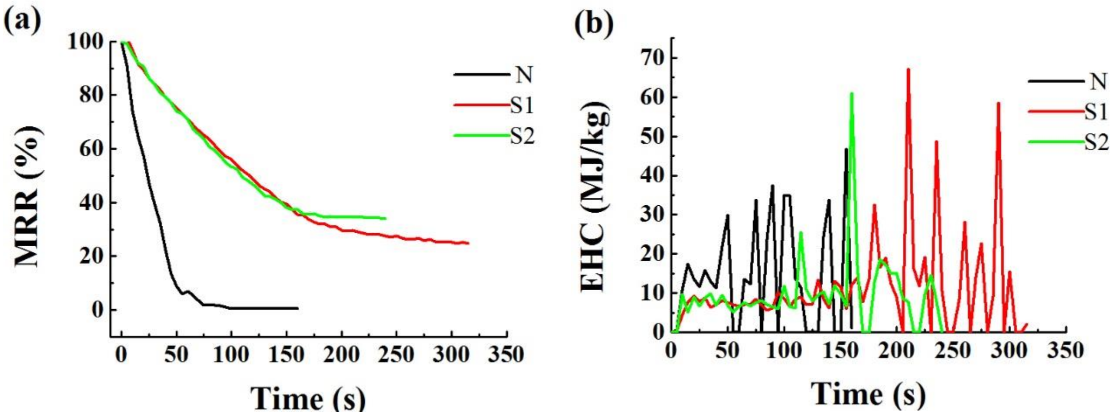


Fig. 6. (a) MRR curves and (b) EHC curves of the control fiberboard (N), fiberboard with Al-Si compounds (S1), and fiberboard with B-Zn-Al-Si compounds (S2)

The MRR values of S1 and S2 nearly completely overlapped each other in the first 150 s, then decreased at a smooth and constant rate before reaching a plateau as high as 24.67% and 34.01%, respectively. The reason may be explained by the THR figures above: in the treated samples, there was a lower rate of reaction for oxidation and pyrolytion of char and a higher mass residual ratio (Niu *et al.* 2014). However, $ZnCl_2$ and ZnOCl, formed from the reaction between B-Zn-Si-Al compounds and chlorinated paraffin as shown in Eq. 5, exhibited strong Lewis acidity. Those acids could help form a dense and solid carbonized layer which covered the fiber. This layer could not only protect the fiber from further oxidation and thermal decomposition, but also markedly promote to accelerate char formation in the solid phase (Wu *et al.* 2015).

$$ZnO + HCl \rightarrow ZnCl_2 + ZnOCl \qquad (5)$$

Effective heat of combustion is the ratio between HRR and MRR, which indicates the level of thermal degradation of material burning in the gas phase. As can be seen in Fig. 6(b), two different processes occurred: (1) pyrolysis, in which flammable vapors were emitted and burned during early heating in the gas phase, and (2) surface oxidation at later heating involving the glowing combustion of char (Babrauskas 2006). Both S1 and S2 had significantly reduced emissions of flammable vapors from pyrolysis, although in the second stage S1 presented aggregate fluctuations as a result of large-scale breakage of the fiber char layer. This did not occur with S2, suggesting that the structure of B-Zn-Si-Al compounds was superior to Si-Al compounds.

Smoke release

The specific extinction area is the ratio between the extinction area of flue gases and the mass loss of sample. It shows the release of smoke per kilogram of sample during combustion. As can be seen in Fig. 7(a), there were flaming combustion and thermal decomposition phases on the SEA curve. The demarcation point was at 60 seconds. In the first stage, the substance decomposed in heat and low-molecular-weight gas was generated from this process. These gases burn violently when lit by the electric arc of a cone calorimeter, sucking in large amounts of oxygen in a short span of time. As a result, a lot of smoke was produced because of the incomplete combustion of gases. As the combustion process continued, pyrolysis products and oxygen consumption decreased, so the oxygen concentration increased as normal. This allowed more efficient burning to occur, so the

SEA followed a downward trend. In the second stage, the char layer of fiber ruptured and poured out a large amount of smoke, which was made of ash and burned residues, and a series of peaks in SEA appeared (Liu *et al.* 2014).

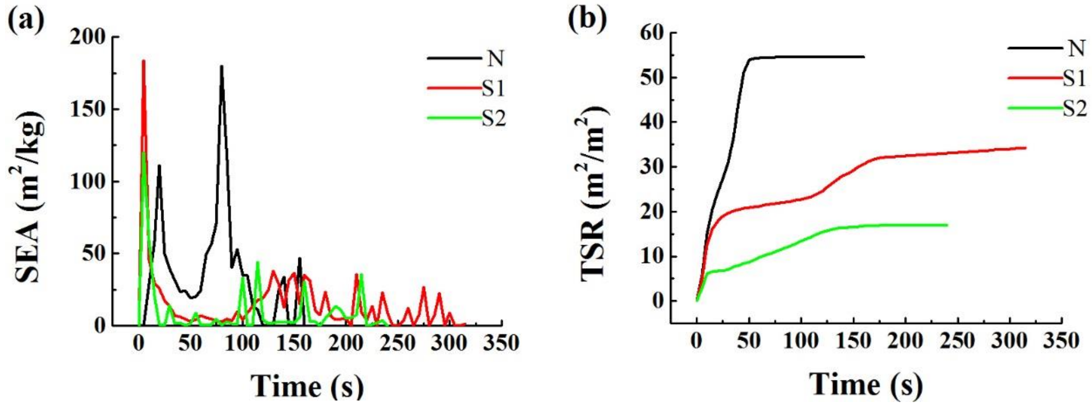


Fig. 7. (a) SEA curves and (b) TSR curves of the control fiberboard (N), fiberboard with Al-Si compounds (S1), and fiberboard with B-Zn-Al-Si compounds (S2)

On the basis of this study, it can be concluded that treated samples can decrease the amount of released smoke in two stages. The TSR of different samples is shown in Fig. 7(b); S2 was lower (16.93 $m^2 \cdot m^{-2}$) than N and S1, at 54.49 $m^2 \cdot m^{-2}$ and 34.27 $m^2 \cdot m^{-2}$, respectively. Additionally, the S2 curve had fewer SEA peaks than S1, suggesting that B-Zn-Si-Al compounds could provide better protection for the char layer against fire.

CONCLUSIONS

1. The optimal conditions of B-Zn-Al-Si compounds for ULDFs are 27.0 mL of sodium silicate solution, 27.0 mL of aluminum sulfate solution, 3.0 g of borax, and 6.5 g of zinc sulfate ($A_3B_3C_3D_2$). Under these conditions, the optimal LOI of ULDF was 29.5. There are covalent bonds among B-Zn-Al-Si compounds.
2. B-Zn-Si-Al compounds had better fire performance than Si-Al compounds, not only during the pyrolysis process where it suppressed the emission of flammable vapors, but also in the surface-oxidation reaction where it could consolidate the char layer, reduce heat release, and decrease the total smoke release.

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REFERENCES CITED

Babrauskas, V. (2006). "Effective heat of combustion for flaming combustion of conifers," *Canadian Journal of Forest Research* 36(3), 659-663. DOI: 10.1139/x05-253

Babrauskas, V., and Peacock, R. D. (1992). “Heat release rate: The single most important variable in fire hazard,” *Fire Safety Journal* 18(3), 255-272. DOI: 10.1016/0379-7112(92)90019-9

Bian, W., Liu, N. R., and Li, X. (2012). “Preparation of boron-containing polysilicate aluminium ferric and its disposal of oilfield produced water,” *Chemical Engineering (China)* 40(8), 14-18. DOI: 10.3969/j.issn.1005-9954.2012.08.004

Bismarck, A., Mishra, S., and Lampke, T. (2005). “Plant fibers as reinforcement for green composites,” in: *Natural Fibers, Biopolymers, and Biocomposites,* A. K. Mohanty, M. Misra, and L. T. Drzal (eds.), CRC Press, Boca Raton, FL, pp. 37-97. DOI: 10.1201/9780203508206.ch2

Chen, W. N., Zhong, H. P., Yang, J., Chen, Y. J., and Li, L. (2002). “Analysis of IR spectrum and crystal morphology of polyalumina-silica chloid (PASC) prepared by various method,” *Chemical Research and Application* 14(1), 73-75. DOI: 10.3969/j.issn.1004-1656.2002.01.022

Chen, T. J., Niu, M., Xie, Y. Q., Wu, Z. Z., Liu, X. Z., Cai, L. L., and Zhuang, B. L. (2014). “Modification of ultra-low density fiberboards by an inorganic film formed by Si-Al deposition and their mechanical properties,” *BioResources* 10(1), 538-547. DOI: 10.15376/biores.10.1.538-547

Chen, T. J., Niu, M., Wang, X. D., Wei, W., Liu, J. H., and Xie, Y. Q. (2015a). “Synthesis and characterization of poly-aluminum silicate sulphate (PASS) for ultra-low density fiberboard (ULDF),” *RSC Advances* 5(113), 93187-93193. DOI: 10.1039/C5RA13996A

Chen, T. J., Niu, M., Wu, Z. Z., Cai, L. L., and Xie, Y. Q. (2015b). “Fire performance of Si-Al ultra-low density fiberboards evaluated by cone calorimetry,” *BioResources* 10(2), 3254-3264. DOI: 10.15376/biores.10.2.3254-3264

Chen, T. J., Liu, J. H., Wu, Z. Z., Wang, W., Niu, M., Wang, X. A., and Xie, Y. Q. (2016). “Evaluating the effectiveness of complex fire-retardants on the fire properties of ultra-low density fiberboard (ULDF),” *BioResources* 11(1), 1796-1807. DOI: 10.15376/biores.11.1.1796-1807

Fan, W. Y., Qiu, X. H., Zhao, S. F., and Liu, Y. S. (2006). “Study on applied properties of polymerized silicate containing aluminum sulfate and zinc sulfate (PSAZS),” *Journal of Shenyang Institute of Chemical Technology* 20(1), 16-19. DOI: 10.3969/j.issn.2095-2198.2006.01.005

Fang, Y. M., Liu, Z. G., and Zhao, X. D. (2010). “Study on image and structure of flocculant ploysilicate-aluminum containing boron,” *Journal of Huangshi Institute of Technology* 26(5), 21-24. DOI: 10.3969/j.issn.1008-8245.2010.05.007

Gao, B. Y., Wang, Z. S., and Tang, H. X. (2000). “Study on the hydrolysis-polymerization process of aluminum and the interaction between hydrolyzed aluminum species and polysilicic acid in flocculant polyaluminum silicate chloride (PASC),” *ACTA Scientiae Circumstantiae* 20(2), 151-153. DOI: 10.3321/j.issn:0253-2468.2000.02.005

GB/T 2406.2-2009 (2009). “Plastics-Determination of burning behaviour by oxygen index-Part 2: Ambient-temperature test,” Standardization Administration of the People’s Republic of China, Beijing, China.

Holbery, J., and Houston, D. (2006). “Natural-fiber-reinforced polymer composites in automotive applications,” *JOM* 58(11), 80-86. DOI: 10.1007/s11837-006-0234-2

ISO 5660-1 (2002). “Fire tests – Reaction to fire- Heat release, smoke production and mass loss rate- Part 1: Heat release rate (cone calorimeter method),” International Organization for Standardization, Geneva, Switzerland.

Kiziltas, A., Nazari, B., Gardner, D. J., and Bousfield, D. W. (2014). “Polyamide 6–cellulose composites: Effect of cellulose composition on melt rheology and crystallization behavior,” *Polymer Engineering and Science* 54(4), 739-746. DOI: 10.1002/pen.23603

Liu, J. H., Xie, Y. Q., and Wei, Q. H. (2014). “Fire retardant properties of ultra-low density wood fiber-based foaming material by cone calorimeter,” *Journal of Northwest Forestry University* 29(1), 174-177. DOI: 10.3969/j.issn.1001-7461.2014.01.35

Niu, M., Hagman, O., Wang, X. A., Xie, Y. Q., Karlsson, O., and Cai, L. L. (2014). “Effect of Si-Al compounds on fire properties of ultra-low density fiberboard,” *BioResources* 9(2), 2415-2430. DOI: 10.15376/biores.9.2.2415-2430

Sun, Y., Zhao, B. X., Sun, Y. Y., Gao, M., and Wang, M. (2014). “A study on the preparation of boron-containing polysilicate aluminium zinc and its flocculation capacity,” *Environmental Chemistry* 33(7), 1214-1221. DOI: 10.7524/j.issn.0254-6108.2014.07.008

Taguchi, G. (1987). “System of experimental design: Engineering methods to optimize quality and minimize costs,” Kraus International Publications, White Plains, New York.

Thomas, S., Paul, S. A., Pothan, L. A., and Deepa, B. (2011). “Natural fibres: Structure, properties and applications,” in: *Cellulose Fibers: Bio- and Nano-Polymer Composites: Green Chemistry and Technology*, S. Kalia, B. S. Kaith, and I. Kaur (eds.), Springer-Verlag, Berlin, Germany, pp. 3-42.

Wu, Z. Z., Xie, Y. Q., Chen, T. J., and Cai, L. L. (2015). “Effects of synergistic flame retardancy of zinc borate and chloroparaffin on ultra-low density wood fiber-based material,” *Journal of Fujian Agriculture and Forestry University (Natural Science Edition)* 44(5), 436-441. DOI: 10.13323/j.cnki.j.fafu(nat.sci.).2015.05.017

Xie, Y. Q., Chen, Y., Wei, Q. H., and Zhang, D. Z. (2008a). “Study on forming a truss-like reticular structure made from nature fiber under the effect of liquid frothing,” *Journal of Fujian College of Forestry* 28(3), 299-303. DOI: 10.3969/j.issn.1001-389X.2008.03.003

Xie, Y. Q., Tong, Q. J., and Cheon, Y. (2008b). “Construction mechanism of reticular structure of plant fiber,” *Journal of Korea Furniture Society* 19(2), 106-110.

Xie, Y. Q., Tong, Q. J., Chen, Y., Liu, J. H., and Lin, M. (2011). “Manufacture and properties of ultra-low density fibreboard from wood fibre,” *BioResources* 6(4), 4055-4066. DOI: 10.15376/biores.6.4.4055-4066

Xu, Q. F., Chen, L. Z., Harries, K. A., Zhang, F. W., Liu, Q., and Feng, J. H. (2015). “Combustion and charring properties of five common constructional wood species from cone calorimeter tests,” *Construction and Building Materials* 96, 416-427. DOI: 10.3969/j.issn.1001-9456.2006.02.006

Youngquist, J. A. (1999). "Wood-based composites and panel products," *Wood Handbook - Wood as an Engineering Material*, USDA Forest Service, Forest Products Laboratory, Madison, WI.

Zhu, L. (2009). *Study on Synthesis of Zinc Borate and Surface Modification*, M.S. thesis, Jiangnan University, Wuxi, Jiangsu, China. DOI: 10.7666/d.y1583780

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