Effect of Si-Al Compounds on Fire Properties of Ultra-low Density Fiberboard

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An ultra-low density fiberboard was made of plant fiber using a liquid frothing approach. The inflammability of the plant fiber limited its application as a candidate for building insulation materials and packaging buffering materials. Si-Al compounds were introduced into the foaming system because of the high temperature resistance of Si and Al compounds. The results from energy-dispersive spectroscopy suggested that the Si and Al relatively evenly covered the surface of the fibers, and their weight ratios in the material increased as a function of the amount of Si-Al compounds. The increasing weight ratios of Si and Al affected the fire properties of the material, reducing the released amount of heat, smoke, and off-gases such as CO and CO_2, as well as decreasing the mass loss percentage, shown through the use of a Cone Calorimeter. It follows that Si-Al compounds have an evident collaborative effect on the halogen fire retardant. The system can effectively restrain the fire hazard intensity and the yields of solid and gas volatiles.

INTRODUCTION

A plant fiber-based ultra-low density fiberboard made by a liquid frothing approach is a new product different from the traditional fiberboard (Xie *et al*. 2003, 2008a,b). It uses plant fiber as a matrix and several additives as the reinforcement. No common adhesives, such as phenol-formaldehyde resin (PF) and urea-formaldehyde resin (UF), or heat pressing techniques are used in its preparation process, which is good for health issues and energy conservation.

The product has some very good physical properties. For example, it has an ultra-low bulk density ranging from 10 to 90 kg/m^3 (Xie *et al*. 2012); a lower thermal conductivity of 0.035 W/mK than those of more popular building insulation materials such as rock wool (0.036 W/mK), NBT Pavadentro (0.042 W/mK), and Gutex (0.037 W/mK) (Xie *et al*. 2011); and a higher sound absorption coefficient of 0.67 than those of foam (0.55) and acoustic plaster (0.56) (Cox and D'Antonio 2009). It can be used as a candidate for building insulation materials or package buffering materials. It has a better biodegradability behavior than popular insulation materials in the market because the plant fiber is used as the matrix.

But a big problem is that the material has to be treated with fire retardants before its utilization. If no retardant treatment is employed, the fiber-based material will be highly flammable and burn up quickly, which is very dangerous for a building material.

However, a single type of fire retardant generally does not impart satisfactory fire retardation properties to the material; other fire retardants are still needed to support it. Liu (2013) paid attention to the synergistic effect of several types of fire retardants; the results showed that a mixed retardant has a better effect on the fire properties of the material; halogen compound chlorinated paraffin can decrease total heat release and smoke release; and silicon compounds (silica as a main component) have a positive synergistic effect on other fire retardants. Besides silicon compounds, aluminum compounds also play an active role in resisting combustion. The process in which aluminum compounds react with water and generate alumina can absorb a lot of combustion heat, thus decreasing a fire hazard's intensity. So in this study, chlorinated paraffin was used as a fire retardant, and a mixture water solution of Si and Al compounds was used to incorporate chlorinated paraffin to resist combustion.

The employment of Si-Al compounds is of great significance for the physical and mechanical properties of fiber-based materials. Silicon compounds can react with water and carbon dioxide in sequence to generate silicic acid by hydrolysis, polysilicic acid by self-condensation, and silicon oxide by dehydration reaction, and the final silicon oxide can form a fused inorganic glassy film on the surface of wood to insulate wood against air during combustion. This glassy film can significantly improve the fire resistance of wood (Liu 2010). Alumina compounds can be used as a binder of fire resistant material with higher purity (Yang and Troczynski 1999). The introduction of alumina compounds could also improve heat resistance of composite film (Lu *et al*. 2008) because of its high temperature resistances. Besides its prominent effect on fire properties, Si-Al compounds could also significantly improve mechanical properties of the fiber-based materials (Lin *et al*. 2013; Xie *et al*. 2011; 2012).

Much attention has been paid to the manufacturing process and properties of the composites with inorganic substances as the matrix and plant fiber as the filler; however, few researchers have focused on the fire resistance of plant fiber-based materials. So using Si-Al compounds to enhance fire properties of fiber-based ultra-low density material is a very novel thought in the field of inorganic-organic combination, and little literature about fire properties of ultra-low density fiberboards with Si-Al compounds has been reported. Besides, because of the electrostatic effect of the Si-Al compounds clusters for absorption (Yang and Troczynski 1999), Si-Al compounds can adsorb poisonous suspended particles (such as printing ink and lead remaining in the newspaper and cardboard), and thus there is less pollution of the water resource in the process of filtering water. Therefore, this also provides us an additional benefit in industrial production.

For the fire resistance mechanism of solid wood, there are four types of theories: such as covering, gas, heat, and chemical theory (Li 2003; Wang 2000). That is, a fire retardant can insulate wood against air by a covering function, or help to release nonflammable protective gases, or absorb heat released on the surface of the material, or catalyze wood to be carbonized. The combustion of the ultra-low density fiberboard is very similar to that of wood; it is also a degradation process of lignin, cellulose, and hemicellulose. A big difference from wood is that the ultra-low density material has a network structure built by fibers. Thus the combustion of fibers is continuous at a low temperature and occurs in a flash at a high temperature. Through mechanically mixing the fibers and the additives together before frothing, Si-Al compounds accompanied by chlorinated paraffin can possibly wrap or cover the surface of fibers to effectively prevent the fibers from continuous combustion. The degradation products from Si and Al

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components can possibly absorb the heat released on the surface of the material, or the degradation products are some non-flammable gases to restrain heat and smoke release during combustion, thus lowering the fire and smoke intensity. The goal of the research presented here is to clarify the distribution of Si-Al compounds in the material, the interactions among the amount of Si-Al compounds, and the distribution and fire properties of ultra-low density fiberboards from different raw materials. Compared with previous research from Liu (2013) on several fire retardants and fire resistant mechanisms, the goal of this paper is mainly to emphasize the interaction between Si-Al compounds and four types of plant fibers, and the effect of the interaction on fire properties of the material.

EXPERIMENTAL

Materials

Kraft pulp (KP, spruce-pine-fir from Canada), mechanical pulp (MP, *Pinus massoniana* from Fuzhou in China), cardboard (CB, collected in China), and newspaper (NP, collected in China) were utilized as raw materials to manufacture an ultra-low density fiberboard. The fiber morphology of each type of raw material was measured using a MorFi Compact device. The results are listed in Table 1.

Table 1. Fiber Morphology of Employed Four Types of Raw Materials

Raw Materials	Number of Fibers (million/g)	Fiber Morphology	
		Fiber Length (µm)	Fiber Width (µm)
Kraft Pulp (KP)	14.322	728 (200-2340)	29.3 (5-60)
Mechanical Pulp (MP)	5.651	908 (200-3520)	29.7 (5-60)
Cardboard (CB)	17.858	1091 (200-5310)	23.7 (5-60)
Newspaper (NP)	10.668	1047 (200-5310)	23.5 (5-60)
Values in the parentheses are the range of the data.			

For the four types of raw materials, the differences in fiber length and width were opposite, *i.e.*, KP and MP had relatively smaller fiber lengths and larger fiber widths, in contrast to CB and NP. This was probably beneficial for the fibrillation extent and the interaction between fibers and the additives such as Si-Al compounds.

Methods
Preparation of the ultra-low density fiberboard

The length and width of the dissociated four types of fibers were detected by Fiber & Shive Analyser (Techpap Company, France).

Four types of raw materials with different fiber morphology were dispersed into fine fibers using a fiberizer. Water and Si-Al compounds, as a mixture solvent, were transferred into an open foaming tank attached to a pulp disintegrator (AB Lorentzen & wetter, Sweden), mixing fibers together to adjust fiber concentration to 3.7-5%wt. Preparation process of the specimens was the same as Xie *et al*. (2011). In this study, Si-Al compounds were prepared as a mixture of an aqueous solution of sodium silicate with 0.82% concentration and aluminum sulfate with 1.08% concentration. Its pH value was about 3.8. After foaming, the pH value of the solution was controlled to be 6 to 7 for KP and MP by adding sodium silicate solution of 33%wt, and 4.8 to 5.4 for CB and NP by

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adding hydrofluoric acid of 10%wt. The adjustment of pH value was very important to get a desired foaming height.

The amount of Si-Al compounds was set as two levels, 500 mL and 900 mL, to compare the fire property changes of the specimens. The amount of other additives was equal. For each specimen being suitable for the mould of 200×200×60 mm (*L*×*W*×*H*), total volume of water and Si-Al compounds solution was 1000 mL; the amount of absolute dry fiber, adhesive, AKD, chlorinated paraffin, and foaming agent (10%wt) was 40-50 g, 30 mL, 50 mL, 46 g, and 50 mL, respectively. KP and MP had the same experimental conditions, as did CB and NP.

Distribution of Si-Al compounds in the ultra-low density fiberboard

A scanning electron microscope (SEM, Jeol JSM-6460, Japan) with an energy dispersive spectroscopy (EDS, INCA Energy EDS for X-ray analysis, Oxford Instruments) was used to localize and measure the weight ratios of silicon and aluminum in the fiberboard. The specimens were made by cutting a thin cross-sectional area. Their surfaces were unpolished and uncoated. The mapping was performed on an area displaying the additive and the matrix using an acceleration voltage of 25 kV, a current of 7 nA and a working distance of 10 mm. Detectable elements were registered during the mapping.

Testing of bulk density and fire properties

Bulk density of the specimen was measured using the same method as Xie *et al.* (2011). The result was the average for three times replication.

A cone calorimeter (FTT Co., England) is considered to be the most significant bench scale instrument for the testing of fire properties of a new product, adopted by the International Organization for Standardization (ISO 5660-1/2002) to evaluate the parameters of time to ignition, time to flameout, heat release, mass loss, smoke release, and off-gases release as a function of time. The size of the specimens was 100×100×30 mm (*L*×*W*×*H*). The specimens were covered by aluminum foil except for the heating surface, and then 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. The heat flow direction was vertical to the heating surface of the specimen and went down. The temperature on the surface of the specimen reached 780 $^{\circ}$C, close to the temperature of an actual fire hazard.

RESULTS AND DISCUSSION

Distribution of Si-Al Compounds in the Ultra-low Density Fiberboard

Figure 1 indicates SEM and EDS profiles of eight fiberboards from four types of raw materials: KP, MP, CB, and NP. The left frames show the micro morphology from SEM in a certain region of the specimen. The middle indicates the elemental distribution images or mappings from EDS of Si (red) and Al (green) on the surface of the specimen. And the right frames give the EDS spectra of different elements in the fiberboard.
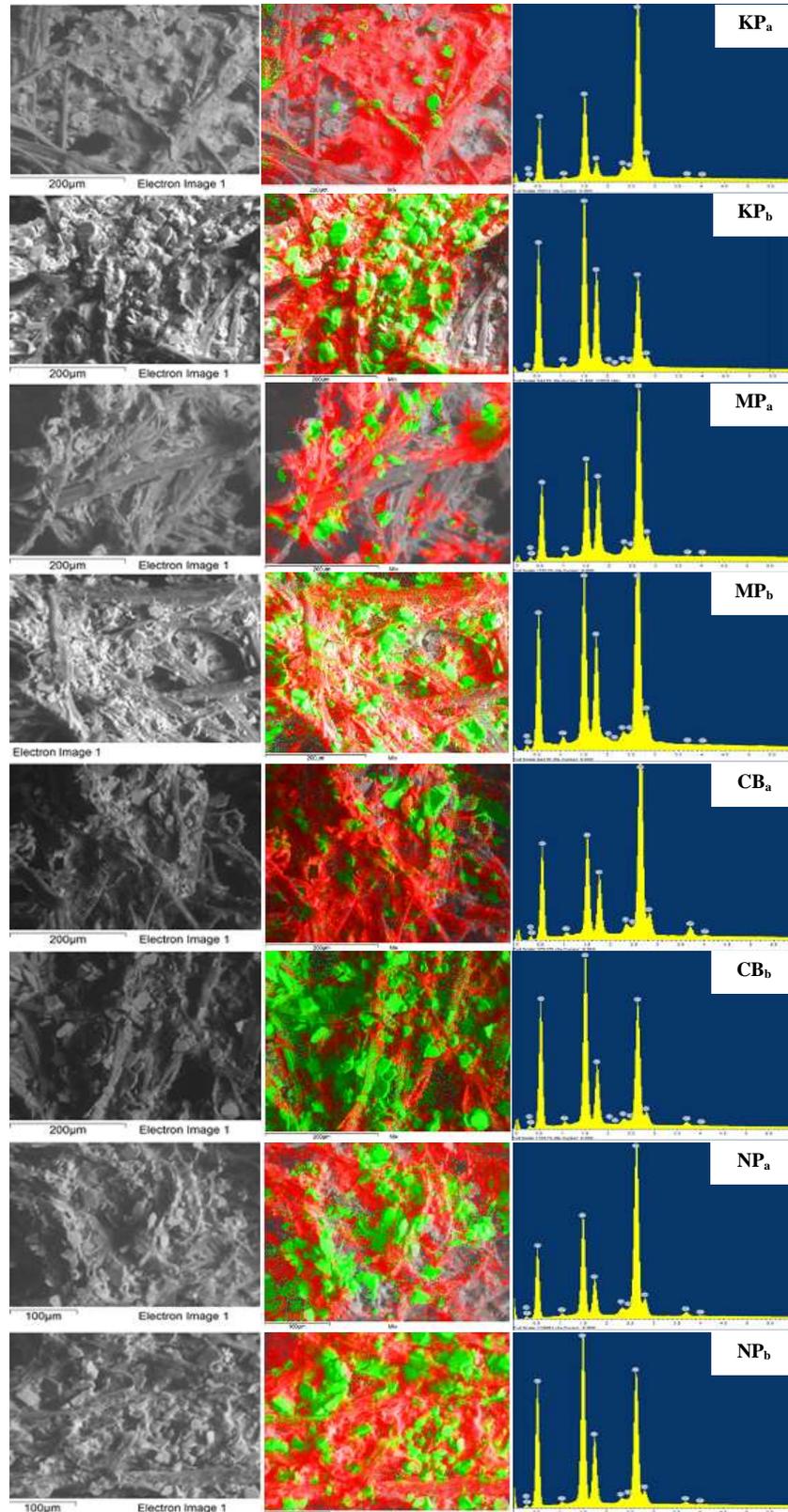
Fig. 1. Micromorphology (left), element mappings (middle, Si-red, Al-green) and elemental weight ratios (right) at a certain region of the fiberboards at the levels of Si-Al compounds of 500 mL (with label a) and 900 mL (with label b). KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.

Ultra-low density fiberboard made by using a liquid frothing technique has more interconnected holes in the network comprised of fibers. When the previously mentioned additives were introduced into the foaming system, they would dispersedly fill into these void spaces, thus improving the densification extent of the material, as is seen in the left column of Fig. 1. Chemical bonds from the interaction between plant fibers and additives can possibly be detected by some modern analyzers; however, the interaction appeared to be a physical connection under the conditions of mechanical stirring at about 30 ^{o}C. In other words, the additives primarily wrapped outside of fibers or covered the surface of fibers, insulating them against air and moisture. And for the different raw materials, it was different in the interaction strength, *e.g.*, compared with the fiberboards KP_a and MP_a, less naked fibers (seen from SEM), and more Si and Al elements (apparent in the mappings) could be seen in CB_a and NP_a. This was possibly because the surface of fibers from CB_a and NP_a had some suspension particles that could be adsorbed by Si-Al compounds. This was also one of the reasons why there were some differences in fire resistance and other properties of the fiberboard.

If other conditions were the same and only the amount of Si-Al compounds was regarded as a single variable in this foaming system, the differences in the interaction between Si-Al compounds and fibers would still be remarkable. This can be seen from the middle and right images of the Fig. 1. For the fiberboards from the same raw material, the distribution density and peak height of the two kinds of elements Si (red) and Al (green) were consistently proportional to Si-Al compounds charged, even if the rough surface of the specimen had more or less effect on the mappings in Fig. 1. A Si-Al compounds solution of 500 mL was obviously not enough to completely wrap the naked fibers, while Si-Al compounds solution of 900 mL was better for every type of raw material. From the mappings, it was found that the distributions of the two elements on the surface of the fiberboards were relatively dispersive and even, which was good for Si-Al compounds to play an important role of insulation. If the mappings were not enough to illustrate relative amount of Si and Al elements, the right spectrums in Fig. 1 and following Table 2 could further tell us the differences of the two elements in the amount as a function of Si-Al compounds. Table 2 shows the weight ratios of different elements in the fiberboards.

Table 2. Weight Ratios of Different Elements Distributed on the Surface of the Specimens

Specimens	Weight Ratios (%)			
	O	Al	Si	Cl
KP_a	50.32 (0.29)	9.22 (0.06)	1.77 (0.03)	23.32 (0.14)
KP_b	57.70 (0.17)	15.13 (0.06)	9.88 (0.05)	9.91 (0.05)
MP_a	50.18 (0.16)	9.33 (0.04)	7.77 (0.03)	19.12 (0.07)
MP_b	53.96 (0.17)	11.24 (0.04)	7.23 (0.04)	18.38 (0.07)
CB_a	53.50 (0.15)	8.60 (0.03)	5.38 (0.02)	20.27 (0.06)
CB_b	58.17 (0.12)	14.90 (0.04)	6.07 (0.03)	12.65 (0.04)
NP_a	52.43 (0.19)	11.04 (0.05)	4.33 (0.03)	22.16 (0.09)
NP_b	57.57 (0.15)	14.95 (0.05)	6.75 (0.03)	13.52 (0.05)
a and b stands for Si-Al compounds amount of 500 and 900 mL, respectively. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively. The values in the parentheses are the errors of weight ratios.				

Spectra from EDS can show almost all of the elements in fiberboards, apart from hydrogen. Four higher peaks as we seen in order from left to right, representing the proportions by weight of O, Al, Si, and Cl. The weight percentages from the four elements constituted almost 90% of the total weight, and their variations were more remarkable than those of other elements. When Si-Al compounds increased, the peaks of O, Al, and Si ascended and the peak of Cl descended. This could further prove that the increase of Si-Al compounds indeed resulted in more Si and Al elements being retained in the fiberboards. The increase of O was coincident with the two elements Si and Al, which probably suggested that Si and Al were present in the fiberboard in the form of oxides.

And yet, the extent of variation was different on account of different characteristics of the raw materials themselves. The fiberboards from KP were the most prominent in this variation. This larger leap in number probably can be attributed to fiber properties of KP itself. KP has smaller fiber length, thus it has a better chance to interact with the Si-Al compounds. When the viscosity of the solution rose due to the addition of Si-Al compounds, the retention ratio of Si-Al compounds in the material would improve during water filtering. As mentioned in the preparation of the ultra-low density fiberboard, KP and MP had the same experimental conditions, but, unlike those in KP, weight ratios of Al and Si in MP had less variation, especially for the weight ratio of Si that slightly decreased with the addition of Si-Al compounds. When the amount of Si-Al compounds reached 900 mL, weight ratios of Si and Al in CB and NP both increased to nearly equal levels. This suggested that the physical interactions between Si-Al compounds and the two fibers from CB and NP were possibly the same at the Si-Al compounds addition level of 900 mL.

Fire Resistance of the Fiberboards

Bulk density, time to ignition and time to flameout

Table 3 shows bulk density, time to ignition, and time to flameout of the fiberboards made of the raw material KP, MP, CB, and NP at the levels of 500 mL and 900 mL Si-Al compounds.

Table 3. Bulk Density, Time to Ignition, and Time to Flameout of the Specimens

Specimens	KP_a	KP_b	MP_a	MP_b	CB_a	CB_b	NP_a	NP_b
Bulk Density (kg/m^3)	47.76 ($\pm$3.10)	64.11 ($\pm$2.93)	48.83 ($\pm$4.29)	64.94 ($\pm$3.07)	60.57 ($\pm$4.06)	50.09 ($\pm$2.49)	55.67 ($\pm$0.87)	53.83 ($\pm$1.29)
Time to Ignition (s)	1	2	1	2	1	1	2	2
Time to Flameout (s)	250	342	275	385	333	90	295	395
a and b stands for Si-Al Si-Al compounds of 500 and 900 mL, respectively. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively. The values in the parentheses are standard deviations of bulk density.								

The fiberboards had a very low bulk density of 47 to 65 kg/m^3, in contrast with conventional LDF with the typical density of 160 to 550 kg/m^3. The bulk density of the specimen was in between those of Styrofoam LB (30 kg/m^3) (Xie *et al*. 2011) and rock wool (78 kg/m^3) (Kawasaki *et al*. 1998). Si-Al compounds could be regarded as a filler and enter into the open holes connected by fibers. More Si-Al compounds should be helpful to increase the density of the specimen in theory. The densities of the fiberboards

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from KP and MP increased when Si-Al compounds were raised from 500 mL to 900 mL, but decreased for CB and NP. The reason for the difference was not only relative to the addition amount of Si-Al compounds, but also probably because different reagents were used in the process of pH value adjustment of mixture solution. Sodium silicate solution was added only to adjust the pH value of KP and MP mixture solution; moreover, the amount of sodium silicate solution was corresponding to the increase of Si-Al compounds. On the contrary, because the solutions of NP and CB have stronger alkalinity than those of KP and MP, it was not easy for NP and CB to achieve the desired foaming height by adding sodium silicate solution, unless an acid compound like hydrofluoric acid was used to build a stronger acid environment. Acid catalyst can accelerate hydrolysis and condensation reaction of Si-Al compounds, and more hydrofluoric acid is helpful to form a lightweight Si-Al gel (He *et al*. 2011). The lightweight gel distributes in the fiberboard, and finally is bound to result in a lower density specimen.

The time to ignition can be defined as the time to existence of flaming on or over the surface of the specimen for periods of over 10 s (ISO 5660). It is a very important parameter to evaluate the ignitability of the material. The time to ignition of all the fiberboards was within the range of 1 to 2 s. Tsantaridis (2003) studied the relationship between time to ignition and heat flux, and suggested that the time to ignition is an inverse function of heat flux. The higher the heat flux, the shorter the time to ignition was. Judged by the results of Tsantaridis (2003), the heat flux of 50 kW/m^2 was high for the fiberboards in this study, as shown by the short time to ignition. Besides, the ignitability of the fiberboards was also dependent of their ultra-low densities. Harada (2001) studied the time to ignition of solid wood with the higher density. The results indicated that time to ignition for 10 mm thick Japan cedar and 10 mm thick Japanese beech was 8 s and 16 s, respectively.

Here, increasing Si-Al compounds did not play an important role in time to ignition. For KP and MP, time to ignition was delayed by only one second; For CB and NP, the time to ignition was completely equal. On the other hand, Si-Al compounds had more effect on a combustion time (from ignition to flameout). The combustion times for the fiberboards from KP, MP, and NP were extended with the increase of Si-Al compounds.

Heat release

The heat release rate (HRR) is the single most important of the parameters affecting fire hazards, as measured by oxygen consumption calorimetry (Babrauskas and Richard 1992). It is a heat release value from the fiberboards with the same surface area (100×100 mm^2) at a certain time under the same heat flux. Higher HRR means more heat gathered on the surface of the specimen. When the heat gathers together and reaches the fire point of the material, the flashover will happen, especially for the ultra-low density fiberboard. So some work should be done to decrease the HRR and the HRR peak. Figure 2 shows HRR profiles from the four types of raw materials as a function of time. Table 4 displays the peaks of HRR and the time to the peaks of HRR after ignition for the different specimens.

Two peaks can be seen in the HRR profiles for all the fiberboards. The first sharp one comes exactly at 10 s after ignition, and it is important for the evaluation of the fire intensity. The second peak appears around 200 s to 250 s when the surface of the specimen starts to break up and oxygen reaches the interior, and it is relative to the thickness of the specimen (Tsantaridis 2003). If the specimen is sufficiently thick, its

second HRR peak will eventually reach a steady value and be inconspicuous. Mikkola (1990) and Moghtaderi (1996) also reported similar results for 38 mm thick spruce and 42 mm thick pacific maple.
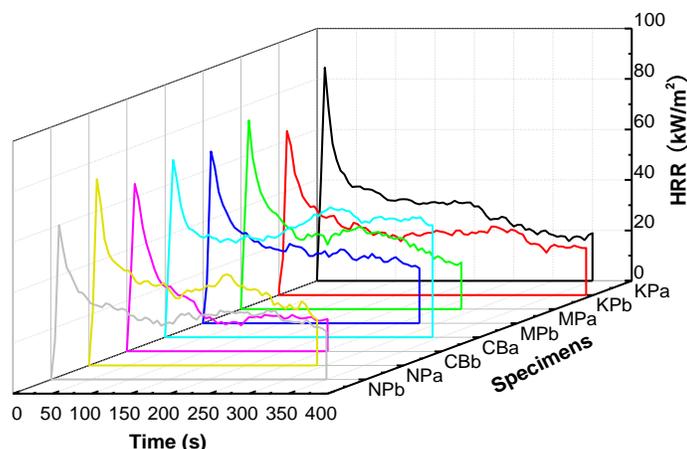
Fig. 2. HRR profiles of the specimens with 30 mm thickness from four types of raw materials at the levels of 500 mL (with label a) and 900 mL (with label b) Si-Al compounds at 50 kW/m^2. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.

Table 4. Peaks of HRR (pkHRR) and Time to the Peaks for the Different Specimens

Specimens	KP$_a$	KP$_b$	MP$_a$	MP$_b$	CB$_a$	CB$_b$	NP$_a$	NP$_b$
PkHRR(kW/m^2)	84.52	64.94	74.75	68.13	70.31	66.41	73.87	61.14
Time to Peak (s)	10	10	10	10	10	10	10	10
a and b stands for Si-Al compounds of 500 and 900 mL, respectively. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.								

All the first peaks with label b were lower than those with label a, the same results as shown in Table 4. In other words, the HRR maxima for the four types of raw materials distinctly decreased when the amount of Si-Al compounds shifted from 500 mL to 900 mL. The lower the pkHRR, the less likely it was that flame was self-propagated on the material in the absence of an external flame or ignition source. It was also less likely that the material caused nearby objects to ignite. Furthermore, not only the peaks, but also the HRR curves in total time were lower, as can be seen in Fig. 2. As suggested, that higher total weight ratio from Si and Al could effectively lower the HRR, in accordance with the result of Gilman (1999). Gilman (1999) studied the flammability and thermal stability of the nanocomposite made from polymer and layered-silicate (clay), and indicated a 80% reduction in the pkHRR for the nanocomposite with only a mass fraction of 4% clay (a Si-Al compound). Especially for the KP-based specimen, the difference of pkHRR was the most obvious. For example, the pkHRR of KP$_b$ was 64.94 kW/m^2 and nearly 20 kW/m^2 smaller than that of KP$_a$. This result was in accordance with the element analysis results from EDS, as shown in Fig. 1.

All the pkHRRs, with no exception even for KP$_a$ with the maximum peak, were lower than those of insulation wood fiberboard (100 kW/m^2) with 13 mm thickness and 260 kg/m^3 density at 50 kW/m^2 (Östman and Tsantaridis 1995). The lower pkHRRs are advantageous for the ultra-low density fiberboards to be building insulation materials. In

addition to the total weight ratios of Si and Al, the ultra-low density of the fiberboards is also responsible for the result. In general, a lower density induces a lower HRR. Simultaneously, Tsantaridis (2003) demonstrated that HRR was an increasing function of the density. On the other hand, the time to pkHRR was the same for all the fiberboards. It meant that the fiberboards would simultaneously reach the maximum of the energy release and the fire would also simultaneously grow after ignition, no matter what the raw material was.

Total heat release (THR) represents the total heat release from the specimen in the total time. It is basically the area under the heat release curve in Fig. 2. Like the HRR, it is also regarded as an important parameter when evaluating the fire properties of building materials. Figure 3 shows THR profiles of the fiberboards from the four types of raw materials as a function of time at 50 kW/m^2.
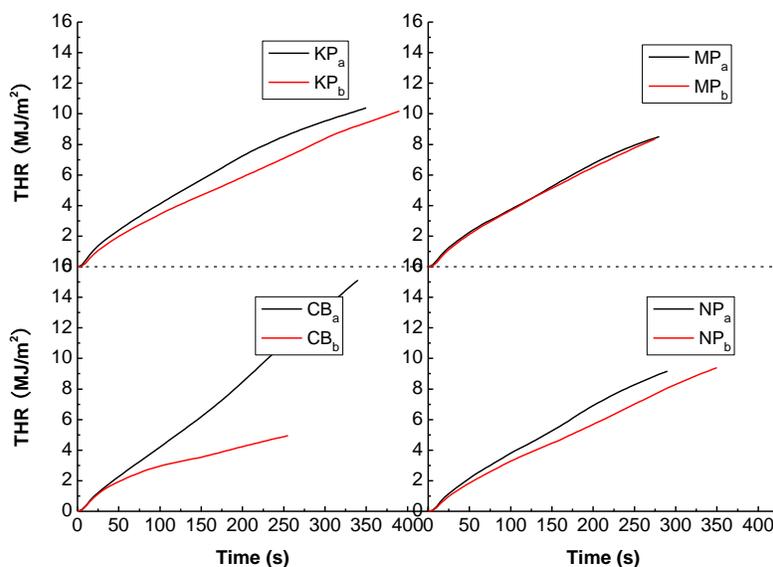
Fig. 3. THR profiles of the specimens with 30 mm thickness from the four types of raw materials at the levels of 500 mL (with label a) and 900 mL (with label b) Si-Al compounds at 50 kW/m^2. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.

The THRs for all the fiberboards increased almost linearly with time. The THR profiles for 900 mL Si-Al compounds were lower than those for 500 mL Si-Al compounds in the same time, possibly because of heat-trapping action of aluminum compounds and incomplete combustion of wrapped fibers by Si-Al compounds. Increasing Si-Al compounds indeed decreased heat release during the material burning. The effect was evident on the THR for the raw material CB. The specimen from CB had a maximum THR at the level of 500 mL Si-Al compounds, and a minimum THR at the level of 900 mL Si-Al compounds. The time was also obviously shorter due to the increase of Si-Al compounds. For every two fiberboards from KP, MP, and NP, the THRs were almost equal because time was prolonged with the increase of Si-Al compounds. Apart from the weight ratio of main elements in the fiberboards, chemical components of raw materials themselves also probably played a dominant role in the variation of THR.

Mass loss

Combustion is inevitably accompanied by mass loss. Mass residual ratio, as a parameter of mass loss, is usually used to estimate the flammability or the combustion extent of the material. Figure 4 represents the mass residual ratios of the fiberboards from the four types of raw materials during combustion.
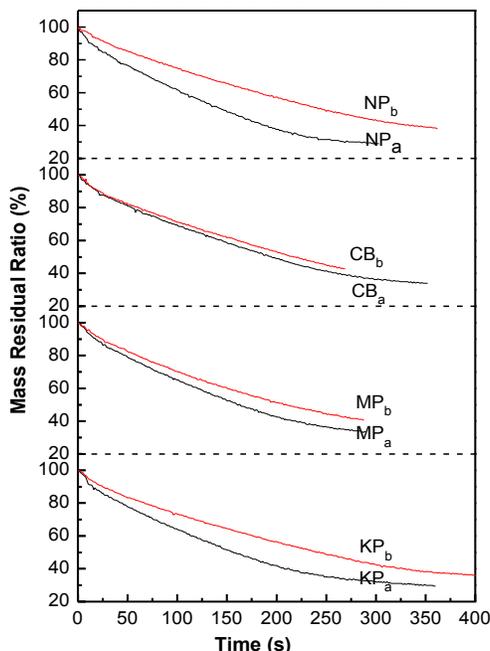
Fig. 4. Mass residual ratios of the specimens with 30 mm thickness from the four types of raw materials at the levels of 500 mL (with label a) and 900 mL (with label b) Si-Al compounds at 50 kW/m^2. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.

Mass loss differences between the two fiberboards with 500 mL and 900 mL Si-Al compounds were subjected to their THR differences. This was also the reason why the profiles about the mass residual ratios in Fig. 4 were similar to THR profiles in Fig. 3. If the THR from pyrolysis and glowing reaction of char was lower, the residual ratio of carbonaceous matrix and Si-Al inorganic matrix would be higher. For example, CB$_b$ had the lowest THR and the highest mass residual ratio (around 43%). The mass loss percentage ranged from about 66 to 72% for the fiberboards of 500 mL Si-Al compounds, and from about 57 to 65% for the fiberboards of 900 mL Si-Al compounds. In other words, the mass residual ratios of the fiberboards having the same raw material increased 6 to 10% with the increase of Si-Al compounds. The property differences among raw materials had a minor effect on the mass loss during combustion.

Smoke release

In fire hazards, people usually die from suffocation resulting from smoke, rather than being burned by high heat. So it is more important to study the smoke release in the process of combustion of the building materials. The total smoke release (TSR) profiles of the fiberboards from different raw materials are shown in Fig. 5.

There was a sharp increase for the TSR of all the fiberboards at the beginning of combustion. When oxygen was insufficient, plenty of volatile matters with lower molecular weight contributed to the smoke due to incomplete combustion. After 150 s,

one more big climb appeared in the TSR profiles of the fiberboards with label a. More smoke was possibly derived from burning residue and ash. For the fiberboards with label b, the second upward jumps of TSR were not apparent. The amount of smoke did not increase, because more Si and Al were distributed on the surface of the fibers and decreased the flammability of the fiberboards.
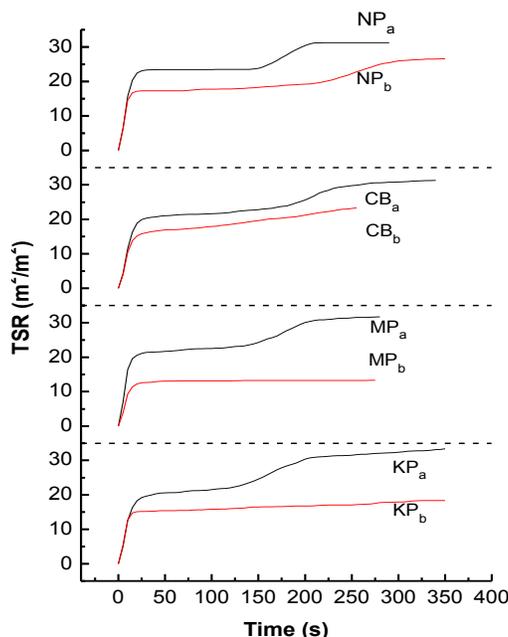
Fig. 5. TSR profiles of the specimens with 30 mm thickness from the four types of raw materials at the levels of 500 mL (with label a) and 900 mL (with label b) Si-Al compounds at 50 kW/m^2. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.

Si-Al compounds had a significant smoke suppression function. The TSRs of the fiberboards with label b were lower than those with label a. Of the four types of raw materials, TSR variation of MP was the most significant. The TSR of MP$_a$ was almost 2.5 times higher than that of MP$_b$. However, more Si-Al compounds had smaller influence on TSRs of CB and NP. This seemed to be less relevant between the TSR and the HRR shown in Fig. 2, which was different from the result of Mouritz *et al*. (2006). Mouritz *et al*. (2006) studied the relationship between heat release rate and smoke release, and pointed out that the smoke release of all the composites (*i.e.*, non-combustible fibers such as glass and carbon; combustible fibers such as aramid and extended-chain polyethylene) showed a general linear increase with heat release rate. The disagreement about the result was possibly caused by the ultra-low density of the fiberboard.

Off-gases (CO and CO$_2$) release
The ultra-low density fiberboard can be decomposed, at which point it releases a mixture of gases including CO, CO$_2$, and other low molecular weight gases such as Cl$_2$, HCl, H$_2$S, and SO$_2$ during combustion. The type and the mass of the gas can change, but CO and CO$_2$ always remain after all the composites' combustion, and their yields are higher than those of other off-gases (Koo *et al*. 2000). CO is a major safety concern because it is lethal at a relatively low concentration, with human death occurring within

one hour at a concentration of about 1500 ppm (Mouritz *et al.* 2006). It is a product of the incomplete combustion of the flammable volatiles at the middle stage of combustion and sprays free carbon particles due to the surface cracks of the fiberboards at the later glowing combustion stage (Liu 2013). It can be used to evaluate the incomplete combustion extent and the toxicity of the materials. The concentrations (left) and the yields (right) of CO of all the fiberboards are shown in Fig. 6.
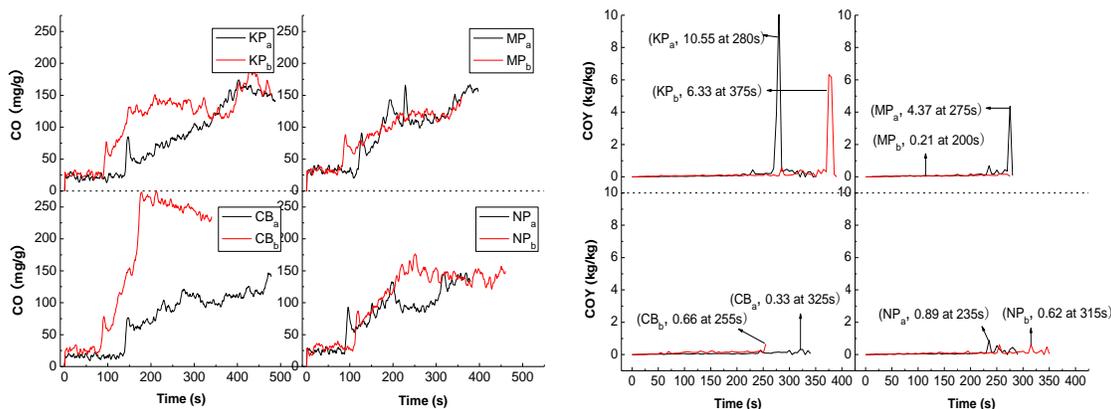
Fig. 6. CO concentration (left) and CO yield (COY, right) profiles of the specimens with 30 mm thickness from the four types of raw materials at the levels of 500 mL (with label a) and 900 mL (with label b) Si-Al compounds at 50 kW/m^2. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.

The CO concentration refers to a mass ratio of CO in volatiles. CO concentration profiles were fluctuant and gradually increased as a function of time. The CO concentrations of all the fiberboards more or less increased after Si-Al compounds shifted from 500 mL to 900 mL. This was mainly because more Si and Al could insulate the fibers from outside oxygen and render the combustion of fibers incomplete. Liu (2013) also obtained the same results by comparing the CO concentrations of the materials before and after fire retardant treatment. The effects of Si-Al compounds on the two CO concentrations of different raw materials were similar to those on the THRs. For instance, CB_a and CB_b had the largest difference, and MP_a and MP_b had the smallest difference in the CO profiles, similar to their THR profiles.

CO yield (COY) represents the CO mass produced by burning per kg specimen. Except for effectively reducing the total smoke released amount, increasing weights of Si and Al decreased the CO yields, particularly for the KP- and MP-based fiberboards. For the CB- and NP-based fiberboards, incomplete combustion mainly gave rise to large amounts of smoke release. Their CO yields were very low, no matter what the Si and Al weight ratios were. Furthermore, the times to the peaks of CO yield was delayed due to the increase of Si and Al. This showed that people could have more time to escape from the fire before CO yield reach the maximum.

According to the CO concentrations and the CO yields, we found that the release of CO mainly appeared in the process of glowing combustion of char, similar to that of basswood combustion after being treated by fire retardants FRW and Dricon (Li 2003). The concentrations (left) and the yields (right) of CO_2 released during the fiberboards combustion are illustrated in Fig. 7.

The concentration of CO_2 is a mass ratio of CO_2 in the volatiles. CO_2 concentrations in flaming combustion were higher than those in glowing combustion,

which was opposite to the CO production process. That is, CO_2 mainly came from the complete combustion of carbon at the flaming combustion stage. With the increase of Si-Al compounds, CO_2 concentration in volatiles more or less decreased, and the time to the peak of CO_2 concentration was shorter (except for NP_b), probably because Si-Al compounds restrained flaming combustion of the material. CO_2 concentration can represent combustion intensity and it is also equal to the amount of heat released in combustion. CO_2 profiles of the fiberboards were very similar to the HRR profiles (in Fig. 2), which suggested that the heat release mainly came from the complete combustion of carbon in the early stage of combustion.
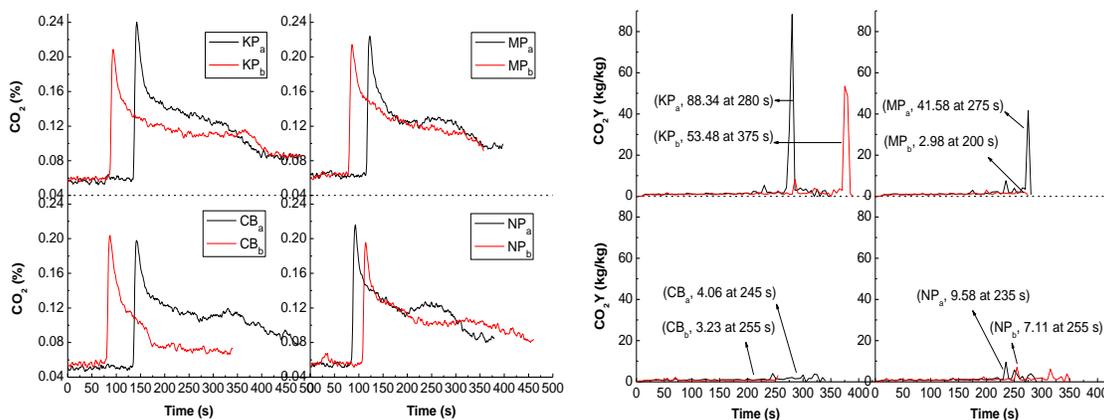
Fig. 7. CO_2 concentration (left) and the yield (CO_2Y, right) profiles of the specimens with 30 mm thickness from the four types of raw materials at the levels of 500 mL (with label a) and 900 mL (with label b) Si-Al compounds at 50 kW/m^2. KP, MP, CB, and NP stand for kraft pulp, mechanical pulp, cardboard, and newspaper, respectively.

CO_2 yield (CO_2Y) represents the CO_2 production as consumption of the specimen per unit mass. When the amount of Si-Al compounds was increased to 900 mL, CO_2 yields significantly decreased. This slow-down is good for people and animals staying in a place with bad air circulation, because more CO_2 can make people and animals suffocate when a fire event occurs. Furthermore, the time to the peak of CO_2 yield was also prolonged, as can be seen from the right of Fig. 7. The prolongation can give the victim more time to run away before CO_2 yield reaches its maximum.

CONCLUSIONS

1. Because of the increase of Si-Al compounds, more Si and Al were distributed on the surface of fibers and thus their weight ratios in the material increased, which significantly affected fire properties of the material during combustion.

2. The ultra-low density fiberboard with Si-Al compounds is apt to catch fire in the course of fire events. The time of ignition was in 1 to 2 s. But Si-Al compounds have an obvious restraint effect on fire intensity and the amounts of the volatiles. All the released amount of heat, smoke, and off-gases (CO and CO_2), as well as mass loss, were remarkably decreased as a function of the amount of Si-Al compounds.

3. Different reagents (*e.g.*, sodium silicate solution of 30%wt used for KP and MP, and hydrofluoric acid solution of 10% used for CB and NP) were used to adjust the pH values of the solutions mixing fibers and additives together, which definitely changed the formation mechanism of Si-Al compounds. So the densities of the fiberboards from KP and MP increased, while those from CB and NP decreased with the increase of Si-Al compounds.

4. Chlorinated paraffin has good fire properties for the plant fiber-based material, but because the weight ratios of Cl in all the fiberboards are high from Table 2 and this is bad for human health, it is reasonable to add lesser amounts of chlorinated paraffin during the preparation of the fiberboard or choose other fire retardants to substitute for it in the future.

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