Fire Performance of Plywood Treated with Ammonium Polyphosphate and 4A Zeolite

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Plywood samples treated with ammonium polyphosphate (APP) and 4A zeolite were prepared to investigate the effect of zeolite on wood's burning behavior using a cone calorimeter under a heat flux of 35 kW/m^2. Results showed that APP decreased the heat release rate (HRR), total heat release (THR), and mass loss rate (MLR) of treated plywood. However, APP significantly increased the total smoke release (TSR) and carbon monoxide (CO) yield. The addition of 4A zeolite reduced the HRR, peak HRR, and THR of the plywood treated with only APP. The second HRR peak in a typical plywood curve diminished with the addition of as little as 2% 4A zeolite. The average specific extinction area (ASEA) and CO yield decreased significantly with the presence of zeolite in the APP. The ignition time did not change significantly and the TSR increased when zeolite was present. Thus, a suitable amount of 4A zeolite works synergistically with APP in promoting flame retardancy in flame retardant plywood.

Keywords: Plywood; Ammonium polyphosphate (APP); 4A zeolite; Cone calorimeter

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INTRODUCTION

With increasing income levels, wood is becoming more and more widely used in furniture, buildings, and for indoor decoration, as it is an environmentally friendly, renewable raw material. The main components of wood are cellulose, hemicellulose, and lignin, each of which can catch fire easily and burn vigorously (Mahr *et al.* 2012). To protect it from fire and to minimize the losses caused by fires, wood is usually treated with a flame retardant (LeVan and Winandy 1990). Fire retardant systems used on wood and plywood generally contain phosphorus, nitrogen, halogens, and boron (Troitzsch 1998).

Phosphorus-containing compounds such as ammonium phosphate (APP), melamine-phosphoric acid, and other phosphoric amines are notably effective flame retardants for use in wood and plywood (LeVan and Winandy 1990; Li *et al.* 2006). It is well known that phosphates promote dehydration reactions within wood and increase the char residue in the process of wood burning (Gao *et al.* 2006; Ma *et al.* 2013). APP is a stable, non-volatile compound with high contents of phosphorus and nitrogen, which makes it suitable for use as a flame retardant. Recently, many researchers have attempted to enhance the efficiency of flame retardants and to inhibit the smoke production of wood as it burns (Li *et al.* 2006; Morgan and Gilman 2013). Some reports have indicated that, when used as a synergistic agent with intumescent flame retardant components, 4A zeolite can effectively enhance the strength and stability of char layer, promote reactions, and decrease smoke and flames generated (Bourbigot *et al.* 1996; Zestos *et al.* 2009). However, there are few reports regarding zeolite use in the flame retardant treatment of plywood (Wang *et al.* 2012).

In this study, the fire performance of plywood treated with flame retardant was evaluated using a cone calorimeter. 4A zeolite was used in conjunction with a common flame retardant, ammonium polyphosphate (APP), as a synergistic agent for the wood veneer. The flammability parameters, including heat release rate (HRR), total heat release (THR), effective heat of combustion (EHC), smoke production rate (SPR), average specific extinction area (ASEA), and carbon monoxide (CO) yield were recorded to evaluate the burning behavior of the plywood. The intent of this study was to determine the flame retardancy of APP-treated plywood and whether or not 4A zeolite provides an appreciable increase in the flame retardancy of APP-treated plywood.

EXPERIMENTAL

Materials and Methods

Commercially manufactured, 1.5-mm-thick, rotary-cut poplar (*Populus* sp.) wood veneers were purchased from Hebei province, China. Veneers were immersed into aqueous solutions of flame retardant ammonium polyphosphate (APP) of concentrations of 5, 10, 15, and 20 wt. %. 4A zeolite powder was purchased from Shanghai Jiuzhou Co., China. It was added to the 20% APP solution at levels of 0, 2, and 4% based on the mass of the APP. The treated veneers were dried to 7% moisture content in an oven at 80 °C before the plywood samples were manufactured. The urea formaldehyde (UF) resin was provided by a local plant. Ammonium chloride (NH_4Cl) was added as a hardener to UF resin at a level of 1% based on the oven-dry weight of the resin. The UF resin mixture was applied to the veneers at a coating weight of 280 g/m^2 using a glue brush. The mixture contains UF resin, wheat flour, and 15% of NH_4Cl solution. The ratio of UF/wheat flour/NH4Cl was 100:15:10. The veneers were weighed before and after spreading to determine the exact amount of adhesive applied. The 3-layer plywood was assembled immediately after the veneers were spread with adhesive and hot pressed into panels with dimensions of 400 mm by 400 mm by 4.5 mm using a pressure of 1.0 MPa at 110 °C for 5 min in a laboratory-scale hydraulic hot press (Zhengzhou Xinhe Co., China). The characteristics of the prepared plywood are listed in Table 1.

Table 1. Identification of the Prepared Plywood

Sample code	Control	APP5	APP10	APP15	APP20	APPZ2	APPZ4
APP (%)	-	5	10	15	20	20	20
4A Zeolite (%)	-	0	0	0	0	2	4

Cone Calorimeter Tests

The fire retardancy test was conducted according to the standard of the International Organization for Standardization ISO5660-1 using a cone calorimeter. The 100 mm by 100 mm by 9 mm plywood specimens were tested in a horizontal orientation with the conical, radiant, electric heater located above the specimens. The unexposed surfaces of the test specimens were wrapped in aluminum foil, and the specimens were placed on a piece of low density refractory fiber blanket within the holder. The external heat flux was 35 kW/m^2 and the retainer frame for the test specimens was used with the wire grid. The electric spark igniter was inserted above the test specimens until sustained ignition of the test specimens was observed, at which point the elapsed time was recorded. The cutoff time for sustained ignition was 10 s. For the duration of the test, the heat release rate (HRR), total heat release (THR), and peak HRR due to combustion were determined using the oxygen consumption method. In addition, the mass loss of the specimens was recorded during the test. The effective heat of combustion (heat release per unit mass lost) was calculated from the heat release and mass loss data. The average specific extinction area (ASEA), smoke production rate (SPR), and carbon monoxide (CO) yield were also recorded. Each specimen was tested three times. The results were reported based on the average of the three experiments' data.

RESULTS AND DISCUSSION

Effect of APP Concentration on Fire Retardancy

The heat release rate (HRR) was the main parameter measured by the cone calorimeter. HRR curves for untreated and APP-treated plywood are shown in Fig. 1. The shape of the untreated, control plywood's curve was typical for wood and wood products (Ayrilmis *et al.* 2007). The curve initially increased toward a first peak, then dropped to steady-state, then increased again to a second peak. The first peak in the HRR curve represents the conditions at and shortly after ignition (Grexa *et al.* 1999). The steady-state region indicates the formation of a char layer on the plywood surface. The formed char layer acts as a barrier for inhibiting heat transfer into the plywood and the process of burning is slowed. The heat in the cone calorimeter is transferred to the plywood predominantly from one side. The plywood burns gradually through its thickness. The second peak represents the rear edge effects. The last part of the curve corresponds to the glowing combustion of the char residue when volatiles had been already burnt out.

The APP-treated plywood samples displayed different curves (Fig. 1). The HRR corresponds to the size of the fire (Quintiere 1993). Compared to those of the control sample, the values of the first and second HRR peaks were reduced in the APP-treated samples.

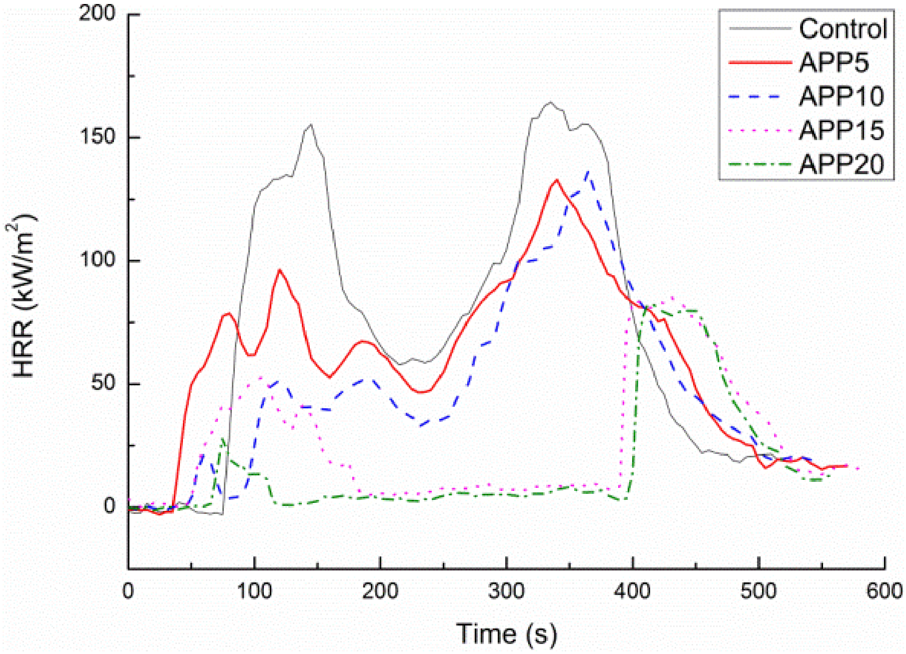

Fig. 1. Heat release rate of plywood samples treated with APP

The untreated, control plywood curves had a peak HRR of about 164.5 kW/m^2, while the peak HRR of plywood treated with 5, 10, 15, and 20% APP were 133.0, 136.7, 85.9, and 82.8 kW/m^2, respectively (Table 2). The decrease in peak HRR was not significant for the 5 and 10% APP-treated plywood samples, whereas the peak HRR values of the 15 and 20% APP-treated samples decreased dramatically. Also worthy of note is that the time at which the second HRR peak occurred was delayed (Fig. 1). The peak HRR decreased by 47.8 and 49.7% for the 15 and 20% APP-treated plywood samples, respectively. From Fig. 1, it is also clear that more than one peak occurred and there was a shift (before a drop to semi-steady-state) in the curves of plywood treated with 5 and 10% APP. The first HRR peak for the 20% APP-treated samples (28.5 kW/m^2) was much lower than that of 15% APP-treated ones (52.5 kW/m^2). The curves become an almost horizontal line between the first and second peaks. It is well-known that APP often degrades into polyphosphoric acid, which catalyzes the dehydration and carbonization of plywood. This leads to the formation of a char layer at lower temperatures (Li *et al.* 2006).

The total heat release (THR) for plywood treated with 5 to 20% APP is presented in Fig. 2. THR represents flame spread and is recognized as an important parameter representing the total available energy within a material. For the 5% APP-treated plywood sample, there was no significant change in THR compared to that of the untreated, control plywood. The flame spreads of APP-treated plywood samples decreased with the increase of the concentration of APP. The THR of 15, and 20% APP treated plywood samples in the first 400 s was below 5 MJ/m^2, compared to about 35 MJ/m^2 in the control sample. This suggests that the heat release of the plywood is suppressed by high concentrations of APP.

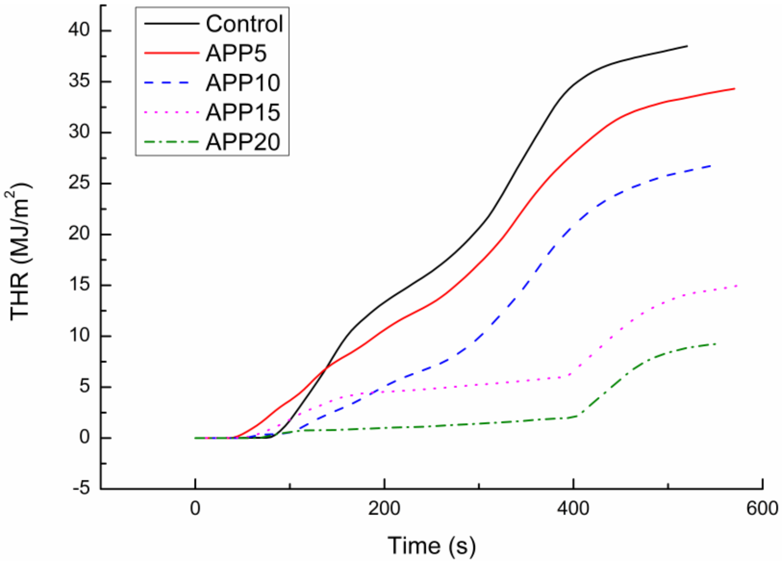

Fig. 2. Total heat release for the plywood samples treated with APP

The average and peak mass loss rates for plywood treated with APP are listed in Table 2. The mean and peak mass loss rates decreased significantly with only 5% added APP. No further decrease in the mass loss rate was observed with increasing concentration of APP.

Time to ignition is the time from the beginning of combustion to the start of sustained burning (Craft *et al.* 2008). It indicates the fire resistance performance of the material being tested. The longer it takes for a material to ignite, the more resistant the material is to burning. For plywood samples treated with APP, the time to ignition was shorter than for the untreated control sample (Table 2). This was due to the presence of APP within the treated veneers. It is proposed that APP promotes the degradation processes of wood and lowers its degradation temperature. The ignition time is related to the external irradiance in the cone test. The higher the irradiance value, the shorter the ignition time.

Table 2. Burning Behavior of APP Flame Retardant Treated Plywood

Parameter	Control	APP5	APP10	APP15	APP20
Time to ignition (s)	78	34	50	47	62
Time to flameout (s)	446	495	497	172	108
Peak heat release rate (kW/m^2)	164.5	133.0	136.7	85.9	82.8
Mean mass loss rate (g/s)	0.15	0.05	0.06	0.06	0.02
Peak mass loss rate (g/s)	4.0	0.2	0.3	0.6	0.6
Peak EHC (MJ/kg)	36.2	75.6	28.9	20.6	14.2
Total smoke release (m^2/m^2)	41.6	23.9	31.2	209.7	255.9
Carbon monoxide yield (kg/kg)	0.007	0.03	0.03	0.04	0.09

The effective heat of combustion (EHC) measured in the cone calorimeter corresponds mostly to the flame burning condition and thus to the combustion of volatiles from within the material (Grexa and Lübke 2001). It is calculated by dividing the THR by the mass loss within a specified time. The EHC and peak EHC values of the plywood samples treated with APP are presented in Fig. 3 and Table 2. For 5% APP-treated plywood samples, the EHC curve was higher than that of the untreated, control samples.

The peak EHC values for the 10, 15, and 20% APP-treated samples were lower; values were 28.9, 20.6, and 14.2 MJ/kg, respectively.

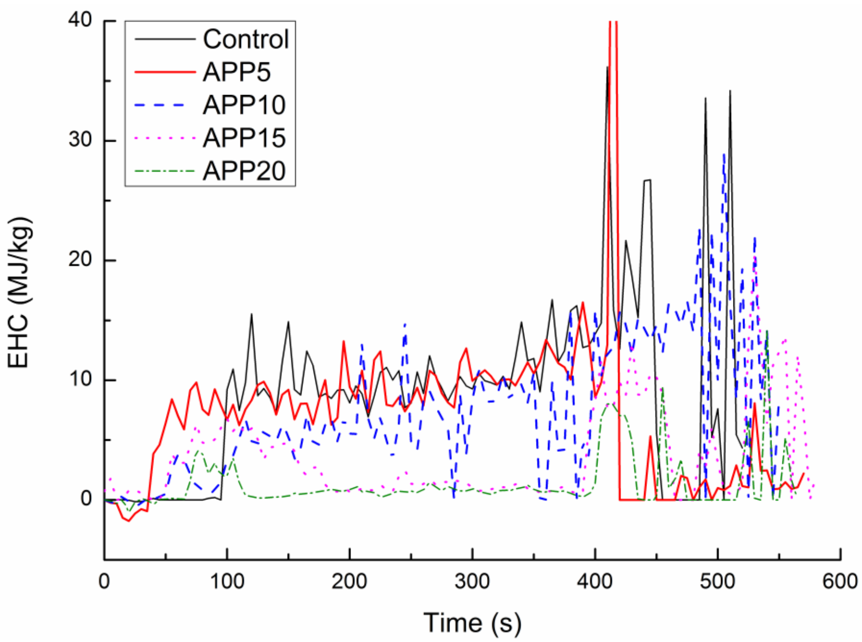

Fig. 3. The effective heat of combustion curves of plywood treated with APP

In addition to the heat release rate, smoke and toxic gas formation play a critical role in the burning behavior of wood (Grexa and Lübke 2001). Smoke reduces visibility and thus reduces the chance for one to escape from a fire. Toxic gases can cause the death of victims trapped in a fire.

Figure 4 shows the smoke production rate (SPR) as a function of time. The total smoke release (TSR) values during the test are listed in Table 2. In plywood samples, smoke formed at the beginning of burning and continued until shortly prior to the end of burning. The effects of 5 and 10% APP-treatments were relatively small. However, for samples treated with 15 and 20% APP, the TSR increased by 404.1 and 515.1%, respectively, due to the gaseous ammonia released *via* the degradation of APP (Eickner and Schaffer 1967).

One of the most toxic gases released from burning wood is carbon monoxide (CO). The average yields of carbon monoxide for plywood treated with APP are listed in Table 2. For the APP-treated plywood, the CO yield was much greater than that of the untreated, control plywood. It is suggested that when heated, APP degraded and released much inflammable gases leading to the incomplete combustion of wood (Annakutty and Kishore 1988; Wu *et al.* 2002). Therefore, much more CO was formed.

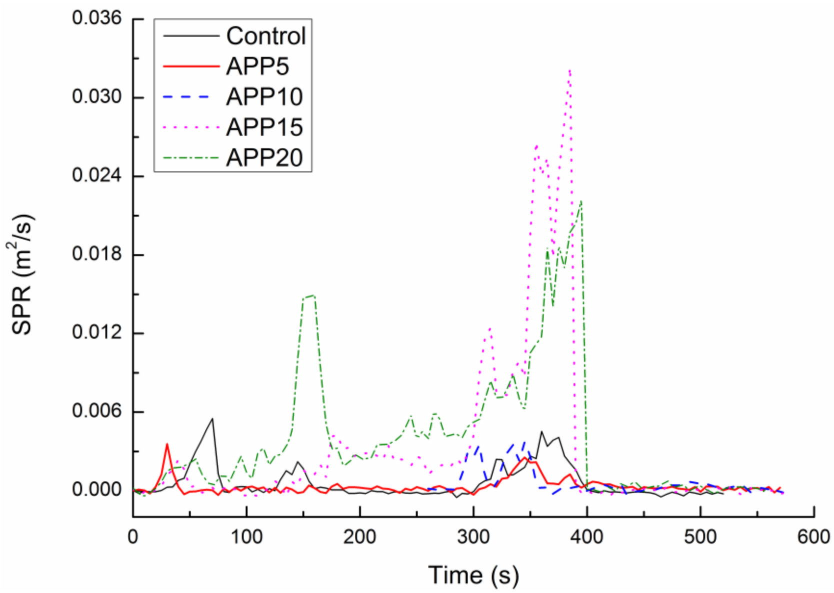

Fig. 4. The smoke production rate of plywood samples treated with APP

Effect of 4A Zeolite on Flame Retardancy

The effects of 4A zeolite on the flame retardancy of plywood samples are shown in Figs. 5 through 7 and Table 3. The HRR and THR curves of the samples are presented in Figs. 5 and 6. The typical HRR peaks apparent for the APP-treated samples were not found in the HRR curves of APP- and zeolite-treated plywood. According to the cone test, the first HRR peak corresponds to the short flame combustion process when the plywood sample ignites. The second HRR peak shows when there appears to be a higher flame combustion process. The second HRR peak for APP 20 was higher than the first HRR peak. With the addition of zeolite into APP solution, the second HRR peak vanished completely. This means that zeolite can inhibit the higher flame combustion process. Compared to the 20% APP-treated samples, the first peak HRR values of the samples with 2 and 4% added 4A zeolite were decreased remarkably from 82.8 to 17.7 and 11.5 kW/m^2, respectively. This suggests that by adding 4A zeolite to plywood, the strength of the char layer was increased. This restricts heat from entering the cone calorimeter and deters material from undergoing further degradation (Feng *et al.* 2013).

The THR of control increased rapidly from the ignition time until the flame combustion finished. Then the THR increased very slowly after the second HRR peak. The THR mainly provides by the flame combustion of plywood. The THR values of samples with the addition of 2 and 4% of zeolite were 3.74 and 2.45 MJ/ m^2, respectively, which were much lower than that of APP 20. This demonstrated that zeolite and APP can effectively inhibit the flame combustion of plywood.

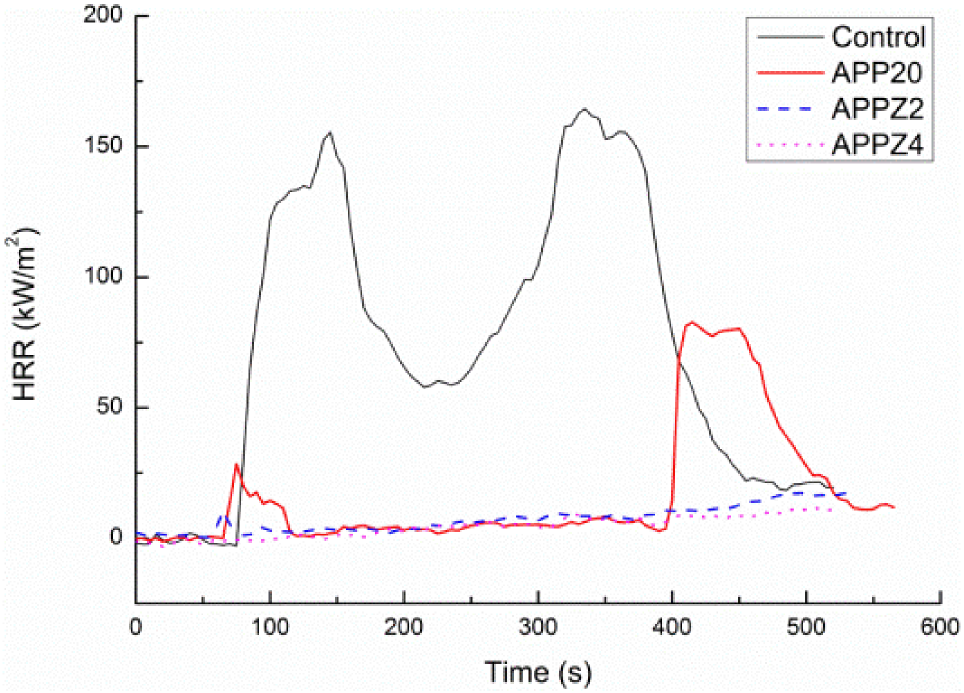

Fig. 5. Heat release rates of plywood treated with APP and 4A zeolite

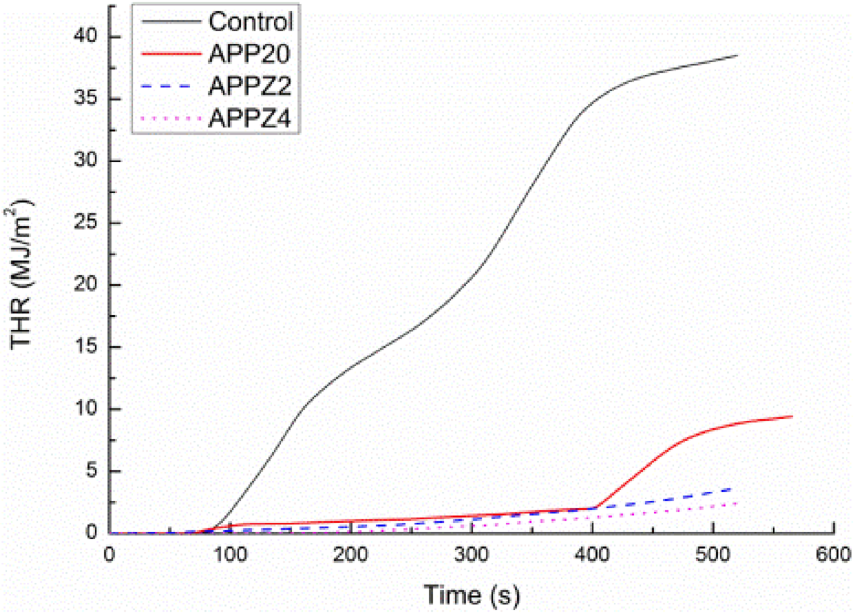

Fig. 6. Total heat release rates of plywood treated with APP and 4A zeolite

The average specific extinction area (ASEA) is a measurement of the amount of visible smoke generated (Table 3). Higher numbers reflect more visible smoke generation. The addition of zeolite at a 2% level caused a dramatic reduction in the ASEA compared to that of the 20% APP-treated sample.

Table 3. Burning Behavior of Plywood Samples Treated with APP and Zeolite

Parameter	Control	APP20	APPZ2	APPZ4
Ignition times (s)	78	62	62	58
Time to flameout (s)	446	108	103	88
Peak heat release rate (kW/m^2)	164.5	82.8	17.7	11.5
Average Specific extinction area (m^2/kg)	3.4	214.5	101.7	104.7
Total smoke release (m^2/m^2)	41.6	255.9	321.3	308.4
Carbon monoxide yield (kg/kg)	0.007	0.09	0.04	0.05

The SPR curves and the TSR values of the samples with 2 and 4% added 4A zeolite were much higher than those of the 20% APP-treated (255.9 m^2/m^2), increasing to 321.3 and 308.4 m^2/m^2, respectively. This is likely due to the catalytic properties of zeolite accelerating the degradation of APP (Wang and Chen 2008). However, by incorporating 2% zeolite into the APP solution, the CO yield was decreased significantly, from 0.09 kg/kg to 0.04 kg/kg. These results show that the addition of 4A zeolite inhibits the production of CO in the presence of APP.

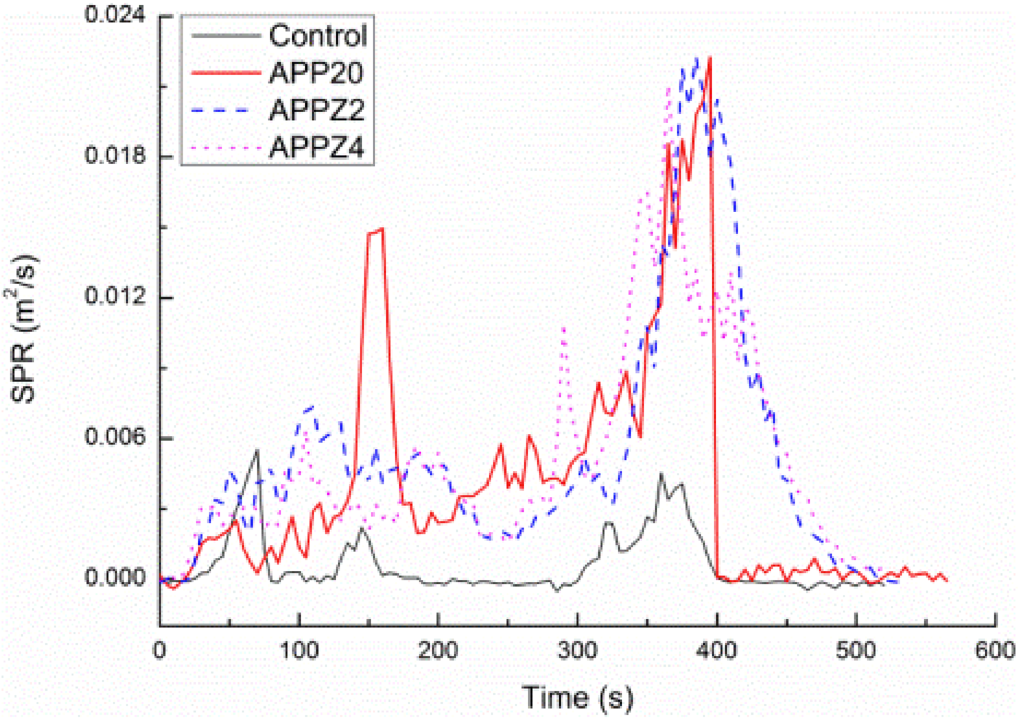

Fig. 7. Smoke production rates of plywood samples treated with APP and zeolite

Flame Retardant Mechanism of 4A zeolite and APP

Regarding these results, one may explain why the addition of 4A zeolite into APP solution had better fire-retardant properties. When wood materials treated with APP are exposed to heat, APP starts to decompose into polymeric phosphoric acid and ammonia.

The polyphosphoric acid reacts with hydroxyl groups in wood and catalyzes the formation of carbon foam on the surface of the plywood samples. Zeolite contains Lewis acid sites. It is proposed that Lewis acid offered by 4A zeolite enhanced the acid catalysis and induced the plywood samples to form more char residue. Furthermore, zeolites are aluminosilicates characterized by a three-dimensional framework of AlO_4 and SiO_4 tetrahedra (Smith 1976; Wei *et al*. 2005). 4A zeolite may degrade and form SiO_2 and Al_2O_3 at higher temperature, which influences the chemical composition and structure of carbonaceous layer by restraining the formation of flammable compound and enhancing the cross-linking in the condensed phase. The carbon barrier prevents further decomposition of the plywood samples better as a stronger insulation layer.

CONCLUSIONS

1. APP improved the fire retardancy of the plywood samples by reducing the mass loss rate and decreasing the HRR and THR values at 15 and 20% APP concentrations. However, treatment with APP increased the TSR and CO yield significantly.
2. The HRR, peak HRR, and THR of the plywood were reduced dramatically by the addition of just 2% 4A zeolite to the APP solution. The second peak, typical to the HRR curve of normal plywood, disappeared when the wood veneers were treated with APP and zeolite together.
3. The ASEA and CO yield decreased significantly with the addition of zeolite to the APP solution.
4. The ignition did not change significantly with the addition of 20 % of APP or 4A zeolite.
5. The TSR increased in the presence of APP and the zeolite.
6. Thus, a suitable amount of 4A zeolite functions synergistically with APP to enhance flame retardancy of plywood.

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