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Synergistic Effect of 3A Zeolite on The Flame Retardant Properties of Poplar Plywood Treated with APP[1]

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ABSTRACT

To evaluate the influence of 3A zeolite on the flame retardant properties of poplar plywood. Ammonium polyphosphate (APP) and 3A zeolite were used as flame retardants to prepare plywood samples. The combustion properties, such as heat release rate (HRR), total heat release (THR), mean CO and CO_2 yield, smoke production rate (SPR), and total smoke production (TSP), were characterized by a cone calorimeter. A synergistic effect was observed between 3A zeolite and APP on reducing the HRR and mean CO yield. The probable flame retardation mechanism was proposed.

Keywords : plywood, poplar, ammonium polyphosphate, 3A zeolite, cone calorimeter

1. INTRODUCTION

Wood has been widely used in building industry for many centuries, but its flammability is a problem in many applications (Tomak *et al*. 2012; Mahr *et al*. 2012). Many commercial flame retardants for wood and wood composites contain phosphorus, nitrogen, and boron (Lebow *et al*. 1999). Zeolites are tectosilicates with a framework of SiO_4 and AlO_4 tetrahedra. Zeolites with intumescent flame retardants can enhance the flame retardant performance and action of polymers (Bourbigot *et al*. 1996; Demir *et al*. 2005; Xia *et al*. 2008; Nie *et al*. 2013).

There are three main ways of applying flame retardants to wood and wood composite products: by impregnation of wood with a flame retardant solution, incorporation of flame retardant into glues in the case of wood composites and surface coatings (LeVan 1984; Grexa *et al*. 1999; Qu *et al*. 2011). Incorporating flame retardant into glues can decrease the adhesive properties of wood composites (Hashim *et al*.

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2009). Surface coatings are susceptible to cracking which reduces flame retardant efficiency (Gao *et al*. 2006).

Impregnation distributes the flame retardant throughout the wood, which can be desirable (Son *et al*. 2012). Phosphorus containing chemicals are commonly used as flame retardants for wood (Sumi *et al*. 1971; LeVan *et al*. 1990; Marney *et al*. 2008; Gao *et al*. 2006). Phosphates like monoammonium phosphate, diammonium phosphate, and ammonium polyphosphate (APP) are recognized as strong flame retardants and have been used for wood for many years. Phosphates can promote the dehydration reactions of wood and increase the char residue in the combustion process (Browne 1958). However, they increase smoke and carbon monoxide (CO) emissions and decrease carbon dioxide (CO_2) concentrations (Liodakis *et al*. 2003). Zeolite has been added to fire retadants to adsorb gases and it has been shown that it can act synergistically to improve the flame retardancy of materials (Wu *et al*. 2012; Bourbigot *et al*. 1996). For example the heat release rate (HRR) and CO yield of treated plywood decreased significantly with the presence of 4A zeolite in APP (Wang *et al*. 2014). Hence, we hypothesize that the addition of 3A zeolite would have a beneficial effect on the flame retardant properties of poplar treated with ammonium polyphosphate.

The aim of this study was to analyze the effect of 3A zeolite on the combustion properties of plywood treated with APP. The flame retardant parameters, including heat release rate (HRR), total heat release (THR), yield of CO and CO_2, smoke production rate (SPR) and total smoke production (TSP) were evaluated using a cone calorimeter. Results showed that there was a synergistic effect between 3A zeolite and APP of treated poplar plywood, and we suggest a possible flame retardation mechanism to explain our findings.

2. MATERIALS and METHODS

2.1. Materials

Commercially manufactured, 1.5-mm-thick, rotary-cut poplar (*Populus sp.*) wood veneers were purchased from Hebei province, China. 3A zeolite powder was purchased from Shanghai Jiuzhou Co., China. The urea formaldehyde (UF) resin was provided by a local plant. Ammonium chloride (NH_4Cl) was provided by Lanyi Chemical Co., Beijing, China.

2.2. Manufacture of plywood samples

Veneers were immersed into 20 wt.% of flame retardant APP aqueous solutions with the addition of 3A zeolite at levels of 0, 2, and 4% based on the mass of the APP for 2 h. The treated veneers were dried to 7% moisture content in an oven at 80℃ before the plywood samples were manufactured. The UF resin mixture was applied to the veneers at a coating weight of 280 g/m^2 using a brush. The mixture contained UF resin, wheat flour, and 15% NH_4Cl solution. The ratio of UF/wheat flour/NH_4Cl was 100:15:10. The veneers were weighed before and after spreading to determine the exact amount of adhesive applied. Three-layer plywood was assembled immediately after adhesive was applied to the veneers and the assembly was 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℃ for 5 min in a laboratory-scale hydraulic hot press (Zhengzhou Xinhe Co., China). Untreated plywood was also prepared as a control.

2.3. Cone calorimeter

Cone calorimeter tests were performed according to the procedures indicated in the ISO 5660-1 standard using a FTT cone calorimeter (Fire Testing Technology Ltd., UK). The 100 mm × 100 mm plywood samples were measured in a horizontal orientation and irradiated with a heat flux of 35 kW/m^2. Each sample was tested three times. The results were calculated based on the average of three experimental data.

3. RESULTS and DISCUSSION

3.1. Heat release

Heat release rate (HRR) and total heat release (THR) are the most important parameters used to quantify the intensity of fires. Lower HRR and THR values indicate that flame retardants are more effective. Fig. 1 shows the HRR curves of untreated and treated plywood. As can be seen, the untreated plywood control burned rapidly after ignition and gave a sharp HRR peak (p-HRR_1) due to the production and combustion reaction of flammable gases. The second HRR peak (p-HRR_2) was produced by the flame burning when cracks appeared in the carbon residue. The two peak HRR values decreased remarkably for plywood treated with 20% APP (APP20). Untreated plywood showed p-HRR_1 and p-HRR_2 values of 155.43 and 164.46 kW/m^2, respectively, while comparable figures for plywood treated with APP were 28.45 and 80.22 kW/m^2, respectively (Table 1). Thus the two peak HRR values decreased by 81.7% and 51.2%. It is well known that ammonium polyphosphate can degrade and release polyphosphoric acid which catalyzes the dehydration and carbonization of wood, resulting in formation of less combustible products and more char. A greater retardant effect was measured for plywood treated with APP and 2 or 4% of 3A zeolite (3A2 and 3A4). The second typical peak for plywood was not detected for samples 3A2 and 3A4. The reason may be that when the APP and 3A zeolite were combined, the latter promoted the strength of intumescent char layer, which was strong enough to restrict heat from cone calorimeter penetrating into samples, hindering wood cracking and preventing further degradation.

The THR curves for plywood samples prepared are presented in Fig. 2. The slope of THR curve can be assumed to be representative of fire spread. It is obvious that the flame spread of treated plywood samples decreased

Table 1. Cone combustion parameters of plywood samples

Sample	p-HRR$_1$ (kW/m^2)	p-HRR$_2$ (kW/m^2)	THR (MJ/m^2)	TSP (m^2)	Mean COY (kg/kg)	Mean CO$_2$Y (kg/kg)
Control	155.43	164.46	38.47	0.2574	0.0071	0.4899
APP20	28.45	80.22	9.42	2.1967	0.0901	0.9786
3A2	50.43	-	9.14	2.3945	0.0492	0.2838
3A4	18.35	-	2.84	2.3131	0.0377	0.1905

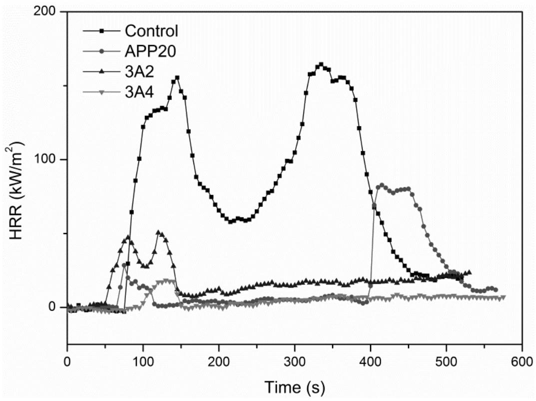

Fig. 1. Heat release rate curves of untreated and treated plywood samples.

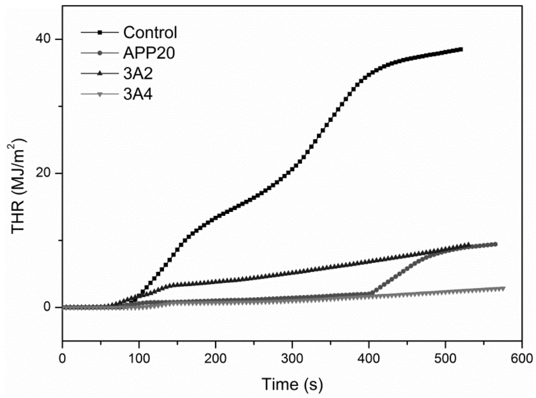

Fig. 2. Total heat release curves of untreated and treated plywood samples.

significantly. From Table 1, it can be seen that the THR for plywood treated with APP and 4% of 3A zeolite (3A4) was 2.84 MJ/m^2, a decrease of 69.9% compared to plywood treated with only APP. We suggest that there is a synergistic effect of flame retardancy between APP and 3A zeolite (Bourbigot *et al*. 1996).

3.2. Gas and smoke release

Gas production and smoke production in fires are important aspects of the fire safety of materials. The toxic gases can directly cause the death of occupants in a fire situation. The smoke reduces visibility and reduces the chances of escaping from a fire (Grexa *et al*. 1999).

The carbon monoxide production (COP) as a function of time is presented in Fig. 3. It can be seen that the COP for treated plywood samples are much higher than that of untreated plywood sample. The mean yield of carbon monoxide and carbon dioxide (CO_2) of the plywood are presented in Table 1. For plywood treated with APP (APP20) the mean CO yield was much higher than that of the untreated plywood controls. The CO2P for APP20 decreased dramatically compared to that of the control (Fig. 4). It is suggested that APP promotes the oxidation processes in favor of CO yield at the expense of CO_2. For plywood treated with APP

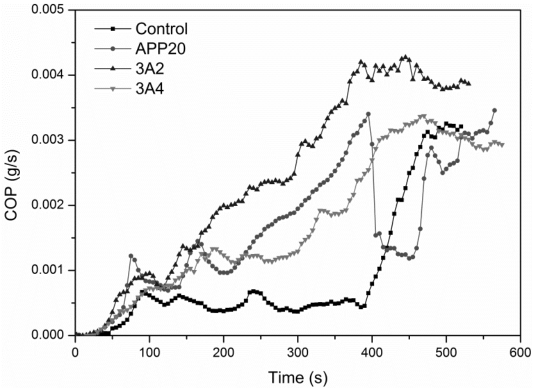

Fig. 3. Carbon monoxide production curves of untreated and treated plywood samples.

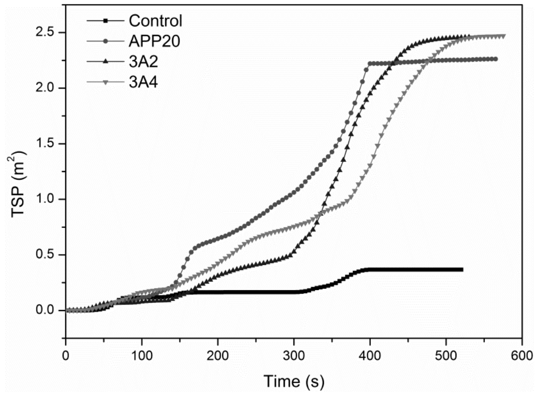

Fig. 5. Total smoke production curves of untreated and treated plywood samples.

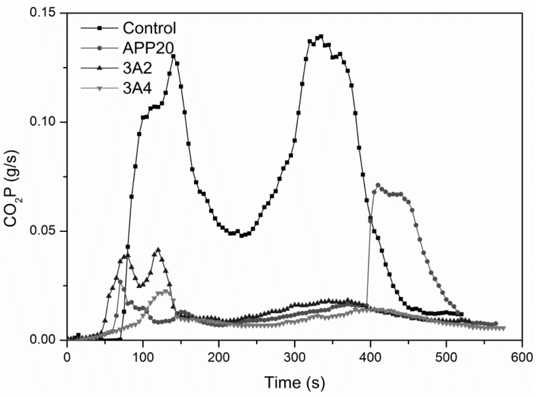

Fig. 4. Carbon dioxide production curves of untreated and treated plywood samples.

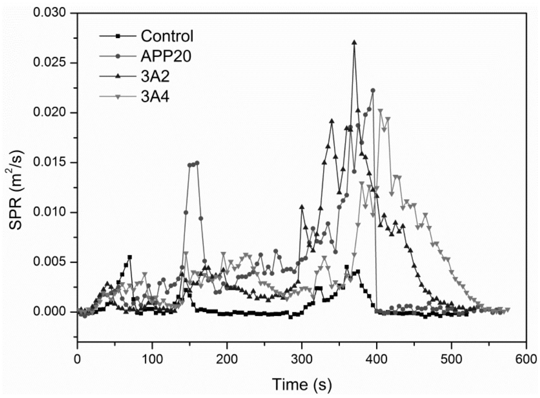

Fig. 6. Smoke production rate curves of untreated and treated plywood samples.

and 3A zeolite the mean CO yields were much lower than that for plywood treated with APP20 and even higher compared to that of untreated plywood. The mean CO_2 yields for samples 3A2 and 3A4 were much lower than that of the control and the sample treated with APP20. This observation is probably caused by the 3A zeolite and APP acting together to promote a stable char layer at the surface of the plywood. In addition the 3A zeolite may have the capacity to adsorb some gases.

Smoke production also plays an important part in fires, including TSP and SPR. Fig. 5 presents the TSP curves of the plywood. It is clear that the TSP curves of treated plywood samples were much higher than that of untreated plywood. The TSP increased from 0.2574 m^2 to 2.1967 m^2 for APP20 (Table 1). With the addition of 3A zeolite into APP solution, the TSP values were lower 400 s into the test and it then increased slightly compared to plywood treated with only APP.

Fig. 6 shows the SPR curves of plywood samples. For untreated plywood samples the first peak SPR value was 0.0055 m^2/s at 70 s. This is probably due to the burning of combustible gases. The first SPR peak was slightly smaller for plywood treated with flame retardant. However, the SPR for treated plywood samples was higher than that of untreated plywood.

As discussed above, 3A zeolite suppressed the heat, CO and CO_2 production of plywood treated with APP. Some research also reported that zeolites in APP or intumescent formulations of wood and polymers leads to a great improvement in their fire retardant performance (Bourbigot *et al*. 1996; Xia *et al*. 2013). APP has been used to treat wood in China. Thus, it is a way to use zeolite to reduce loadings of APP used to plywood.

4. CONCLUSION

Addition of 3A zeolite to APP could increase the flame retardant properties of poplar plywood. The application of ammonium polyphosphate (APP) decreased the peak heat release rate values and total heat released while it increased the mean carbon monoxide and total smoke production. A synergistic effect was observed between 3A zeolite and APP on heat release and mean carbon monoxide yield. It is proposed that 3A zeolite and APP can catalyze the dehydration and carbonization of plywood together which results in a stable char layer. In addition3A zeolite may adsorb the produced gases which leads to the decrease of CO and CO_2 yields. The results obtained in this paper indicate that 3A zeolite can be added as a synergistic agent in plywood treated with APP. This may reduce the loadings of APP used to treated plywood. The synergistic mechanism needs to be studied further.

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