

Synergistic Flame Retardant Effects of Different Zeolites on Intumescent Fire Retardant Coating for Wood

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To investigate the fire-retardant properties of intumescent fire-retardant coatings of wood modified by different zeolites, tests were conducted by a cone calorimeter with poplar samples whose surfaces were covered by an intumescent fire-retardant coating modified by 3A, 4A, 5A, 13X zeolites, respectively. Results indicated that the ignition time (TTI) of the intumescent fire-retardant coating modified by 3A zeolite was prolonged 120 s, while the total smoke production (TSP) increased 60.1% as compared with the untreated group. The intumescent fire-retardant coating modified by the 13X zeolite had a smaller smoke production rate (SPR) and was the last to reach the peak-SPR. Its TSP remained in a very low state until 410 s and decreased 25%. Thus, 3A zeolite and 13X zeolite were of complementarily synergistic effects on improving the fire-retardant properties of an intumescent fire-retardant coating for wood. This paper suggested the alternative types of zeolites for flame-retardant coatings.

Keywords: Wood; Zeolite; Intumescent flame-retardant coatings; Fire-retardant properties; Cone calorimeter

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INTRODUCTION

Wood is a type of biomass material that is widely used in furniture and interior decoration. It has a naturally beautiful pattern, a strong weight ratio, and easy workability; however, it is inflammable. Fire may cause great casualties, especially due to breathing difficulties. According to a survey, in China there were 180 thousand fires per year with 1698 deaths, 1426 injured, and 1 billion 626 million RMB direct property loss from 2003 to 2012 (Fu 2014). The risk in fire caused by wood mainly has two aspects. One is the release of heat, which is the main enabling factor for flame propagation. The other is abundant toxic smoke produced during the burning process, which is the main cause of casualties (Du and Huang 2009; Martinka *et al.* 2012).

In recent years, wood flame-retardant treatments have attracted the interest and attention of researchers all over the world (Rhys 1980; Xing and Li 2014). Intumescent flame-retardant coatings have a wide application in construction, interior decoration, and other industries.

There are no differences between the visual and tactile aspects of intumescent flame-retardant coatings and ordinary coatings, but in the case of a fire, the coating film of the intumescent flame-retardant will melt when heated and create a foam. The spongy

carbon layer of the intumescent coating has a dozen times the original thickness, which may play a role in resistance to burning. Melamine modified urea formaldehyde resin (MUF) is a commonly used coating resin with strong water resistance, abrasion resistance, good size stability, and relatively low free formaldehyde (Chen *et al.* 2010). Ammonium polyphosphate (APP) can be used as an acid source for the modification of the base material. The flame-retardant coatings added with APP are effective, environmentally friendly, tactile, and are low cost. However, this leads to the problem of poor stability of the coating and bad water resistance, which means that the flame-retardant effect is reduced (Gu *et al.* 2007; Yuan *et al.* 2010; Pan *et al.* 2012).

A zeolite is a type of cubic crystal aluminosilicate compound having strong adsorption capability and catalytic performance. It also has a large surface area, high hydrothermal stability, and rich pore structure. Zeolites can reduce the number of amorphous carbons and prevent the formation of large areas of a fragile carbon layer when added to an intumescent flame-retardant system (Wang and Zeng 2007; Guo 2012). Thus, a zeolite will overcome the negative effects caused by APP, improve the strength of the carbon layer, and improve flame-retardant properties. Hence, there has been an increasing research focus on introducing zeolite into the intumescent flame-retardant systems to improve the flame-retardant properties.

A synergistic effect was observed between 3A zeolite and APP on reducing the heat release rate (HRR) and mean CO yield of poplar plywood (Wang *et al.* 2015). Studying how the synergistic effect of 4A zeolite performed next to APP and the pentaerythritol (PER) intumescent flame retardant, it was concluded that 4A zeolite is beneficial to improve the flame-retardant properties (Wei and Wang 2003). With the addition of 1.00% or 3.00% 4A zeolite, HRR peak, the total heat release (THR), and the mass loss rate (MLR) of the coated wood decreased (Zhang *et al.* 2015). When combined with APP, 5A zeolite not only achieved a high efficient flame retardant, but it also reduced the release of smoke gas (Chen *et al.* 2014). The results indicated that compositing the 13X zeolite and APP for the flame-retardant and smoke-suppression treatment of wood would improve the thermal stability of the carbon layer and flame-retardant, and achieve remarkable smoke-suppression characteristics (Xia *et al.* 2014).

A literature review revealed that the addition of different zeolites could improve the flame-retardant properties of intumescent flame-retardant systems in different ways (Wei and Wang 2003; Xia *et al.* 2008; Bao *et al.* 2011). However, research on the selection and proportion of zeolites was not found in searching the literature. Moreover, the previous studies mainly focused on the effect of a zeolite on fire-retardant properties. The main contribution and novelty of this paper is to study the influence of different zeolites on fire-retardant properties of intumescent fire-retardant coating for wood using the control variable method and to put forward the possibility of synergistic effect between zeolites by comprehensive comparative analysis. In this experiment, the intumescent flame-retardant coatings used poplar as the experimental material, MUF resin as the base material, and APP as the carbon catalyst and dehydrator. The CONE method was used to explore the influence of different zeolites and their ratio on the flame-retardant properties with intumescent fire-retardant coatings modified by 3A, 4A, 5A, and 13X zeolites.

EXPERIMENTAL

Materials

Melamine, urea, and 37% formaldehyde solution was purchased from Beijing Lanyi Chemical Products Co. Ltd. (Beijing, China). Ammonium polyphosphate (Average degree of polymerization is 30, and pH 4.5-6.5) was purchased from Beijing Jintongletai Chemical Products Co. Ltd. (Beijing, China). The 3A zeolite (potassium type zeolite and Bulk density ≥ 0.65 g/mL), 4A zeolite (sodium type zeolite and bulk density ≥ 0.65 g/mL), 5A zeolite (calcium type zeolite and bulk density ≥ 0.65 g/mL), and 13X zeolite (sodium type zeolite and Bulk density ≥ 0.65 g/mL) were purchased from Shanghai Jiuzhou Chemical Co., Ltd. (Shanghai, China).

Samples preparation and treatment of samples

The MUF resins were prepared according to the method of Ma *et al.* (2013) and Tohmura *et al.* (2001). Thus, 37% formaldehyde (F), urea (U), and melamine (M) with an initial M/U/F molar ratio of 4.5/1.0/1.0 were added to a flask. The mixture pH was adjusted to 7.0 to 7.5 with a 1 mol/L NaOH solution while stirring. The mixture was heated to 85 °C in a water bath for 30 min and kept at the same temperature for another 45 min to 60 min. The degree of condensation was measured by a turbidity point method every 5 min; one drop of resin was dispersed in 100 mL of water. When the solution was turbid and not dissolved, the reaction was stopped. The pH was adjusted again to 8.5 to 9.0 by adding 1 mol/L NaOH solution. The resin was allowed to cool to 60 °C. The additional urea and melamine were then added to the mixture and the resin was allowed to mature at 60 °C for 1 h. After the mixture was cooled to room temperature, the melamine modified urea-formaldehyde resin has been prepared successfully. Melamine modified urea-formaldehyde resins, APP, and zeolites were mixed and stirred equably according to the proportion and content shown in Table 1 and the coating was finally prepared.

Table 1. Preparation Conditions of Intumescent Flame-retardant Coatings Modified by Different Zeolites

Samples	Melamine Modified Urea-formaldehyde Resin (%)	APP (%)	3A zeolite (%)	4A zeolite (%)	5A zeolite (%)	13X zeolite (%)
Untreated	0	0				
M	100	0				
MA	100	50				
MA-3A	100	50	1			
MA-4A	100	50		1		
MA-5A	100	50			1	
MA-13X	100	50				1

Samples of poplar board (*Populus bonatii* Levli) with 10-mm thickness were cut to a size of 100 mm \times 100 mm. Each sample was brush coated on one of the 100 mm \times 100 mm surfaces and the coating prepared according to the above mixture ratio at the glue spread amount of 400 g/m². As shown in Table 1, 11 sets of samples were made and are represented by the corresponding group codes listed in the results and discussion section.

Methods

Fire retardancy test

A cone calorimeter is a type of measuring device for polymer material combustion (Fire Testing Technology Ltd., East Grinstead, UK) based on oxygen consumption. A CONE (short for cone calorimeter) is barely influenced by the type of fuel or whether it has a complete combustion. The combustion environment is extremely similar to a real environment. A variety of fire related parameters can be measured to characterize combustion properties (Xu *et al.* 2005). The fire retardancy test was conducted according to the ISO 5660-1 (2002) standard, using CONE whose model number is FTT0007 D. To prevent the samples from warping and expanding, they were horizontally-placed under the protection of stainless steel screens. All the tests were conducted at an irradiance level of 50 kW/m². The experimental data was collected by the special software of the cone calorimeter.

RESULTS AND DISCUSSION

In this study, characteristics of each sample were investigated, from the ignition time, heat release property, smoking status, fire performance index (FPI), and residual mass, to explore the effect of different zeolites and their ratio on the performance of the intumescent flame-retardant system.

Ignition Time

The ignition time (TTI) is the time needed to continue the ignition for the material surface to produce a burning flame. The higher the TTI values, the more difficult the material is to ignite (Xu *et al.* 2005). As shown in Table 2, the TTI of all samples were ranked as MA-3A > MA-5A > MA > MA-13X > MA-4A > M > Untreated. Compared with M (sample treated with Melamine) and the untreated sample, the TTI of MA (sample treated with Melamine and APP) was prolonged by 120 s, and it was clear that the addition of APP contributed to prolonging the ignition time.

Table 2. Combustion Parameters of the Different Zeolite Modified Intumescent Flame Retardant Coating by CONE Test

Samples Parameter	MA-3A	MA-4A	MA-5A	MA-13X	MA	M	Untreated
Mass (%)	18.57	17.35	17.44	21.74	15.40	6.75	8.57
Ignition time (TTI) (s)	279	123	171	127	138	20	15
Peak of heat release rate (pk-HRR) (kW·m ⁻²)	274.67	246.79	179.16	223.14	212.38	277.43	251.34
Effective heat of combustion (EHC) (MJ·kg ⁻¹)	50.61	73.00	63.60	68.50	58.31	62.93	79.08
Fire Performance index (FPI)	1.02	0.49	0.95	0.57	0.65	0.07	0.06

The results suggested that the intumescent fire-retardant coating modified by A-type zeolite had a better advantage in prolonging the ignition time than that modified by

the X-type zeolite. Moreover, TTI was extended to 279 s and 171 s by the addition of the 3A and 5A zeolite, respectively, which would mean more precious time for personnel evacuation and fire suppression.

Heat Release Property

The heat release rate (HRR) refers to the sum of the heat release from ignition to the end of the flame combustion under the preset incident heat flux. The HRR and peak HRR are important parameters to evaluate the risk of materials being exposed to fire (Xu *et al.* 2005). With an increased HRR, the thermal degradation rate became faster, more volatile combustible gases were generated, and the flame spread was faster. This led to a riskier situation during a fire. As shown in Fig. 1, two exothermic peaks appeared in the combustion process of each sample, except for the samples modified by the 3A zeolite.

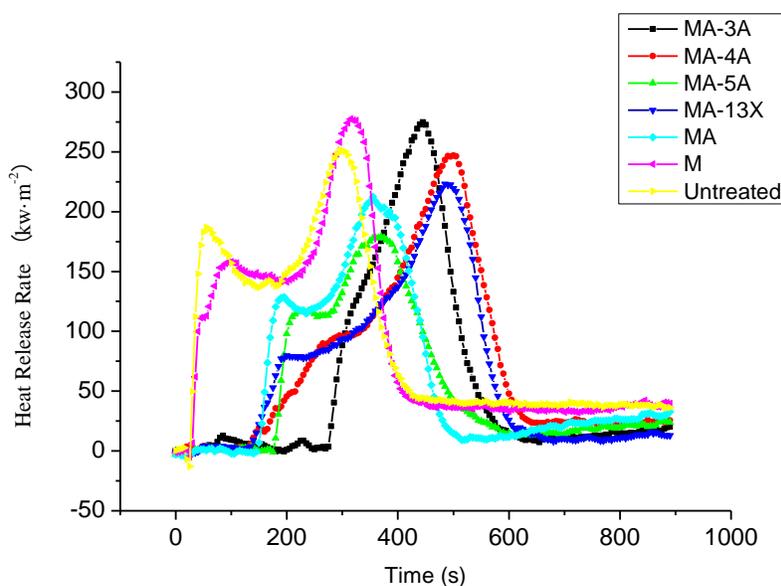


Fig. 1. HRR curves of intumescent flame-retardant coatings modified by different zeolites

When coupled with the wood combustion, wood decomposition produces a large amount of combustible gas. Combustion gives rise to flames and releases a large quantity of heat that forms the first exothermic peak. When wood burns, the surface forms a charcoal layer which separated the base material from the combustible gas. With the increase of temperature, the carbon layer is destroyed, and the combustible gas continues to release and produce a violent combustion, and the second exothermic peaks are formed. The peak HRR values of all samples were ranked as $M > MA-3A > Untreated > MA-4A > MA-13X > MA > MA-5A$. Although the peak HRR figure was $274.67 \text{ kW}\cdot\text{m}^{-2}$, it increased slightly when compared with the untreated group. The MA-3A-2 had only a single peak and prolonged nearly 260 s before the rapid increase of HRR. Heat release occurs later, which prolongs the time of a strong fire arriving and it is more favorable for personnel evacuation and rescue during a fire (Xu *et al.* 2005). As a result, the effect of the 3A zeolite on the inhibition of the fast pyrolysis and release of small molecular organic volatiles was remarkable.

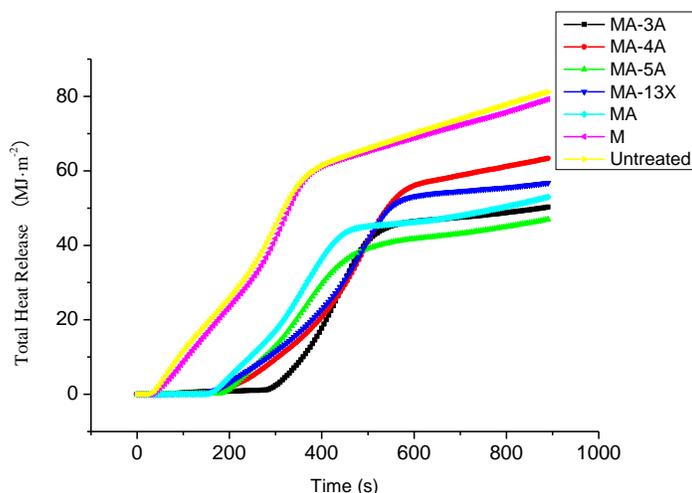


Fig. 2. THR curves of intumescent flame-retardant coatings modified by different zeolites

The total heat release (THR) is the heat release per unit area from ignition to the end of the flame combustion. The THR curve in Fig. 2 shows that the overall trend of each sample appeared to be consistent, and clearly proved the dominance of 3A zeolite in delaying the time of reaching the exothermic peak. The lowest THR was with MA-5A, which meant the 5A zeolite had a noticeable effect on reducing the total heat release.

The effective heat of combustion (EHC) refers to the ratio of heat release and mass loss at a certain time that reflects the degree of combustion with the degree of combustible volatile gas in the gas phase flame. Results in Table 2 indicated the EHC were ranked as Untreated > MA-4A > MA-13X > MA-5A > M > MA > MA-3A. The EHC of the sample added by APP showed a slight decline, however, after the addition of zeolite, the EHC of the samples treated with both APP and zeolite slightly improved. Compared with the untreated poplar, MA-3A was the only group whose EHC was remarkably decreased by 36%. The aperture of 3A zeolite was the smallest among all the zeolites selected in the experiment. Its adsorption ability was weaker than other zeolites, but 3A zeolite had the ability to reduce the heat release during the flaming period of combustion. Although the aperture of 3A zeolite was small, it was able to adsorb more molecule combustible gas produced by the pyrolysis of wood, decrease the quantity of heat released by the combustion, and reduce the effective heat of combustion.

Smoking Status

More than 80% of fire-related deaths are caused by smoke (Gou 2014). The smoke production rate (SPR) and total smoke production (TSP) are also important parameters in evaluating fire risk. The SPR is the ratio of a specific extinction area and mass loss rate indicating the smoke release per unit time. The TSP indicates the total smoke release of samples in the process of combustion or thermal cracking.

Figure 3 leads to the conclusion that MA was the only group that delayed the release rate of CO, keeping the rate very low within 450 s of the initiation of the fire. However, the release of CO₂ and CO increased compared to the untreated group. The flame retardant mechanism of APP had the characteristics of isolating oxygen and blocking free radical chain combustion reactions. This caused an increase of smoke production in a later period and more poisonous gases represented by CO were generated (Chen *et al.* 2014). Therefore,

it is necessary to employ a zeolite that can adsorb toxic gas to reduce toxicity. The CO and CO₂ production rates were greatly reduced after the addition of 13X zeolite.

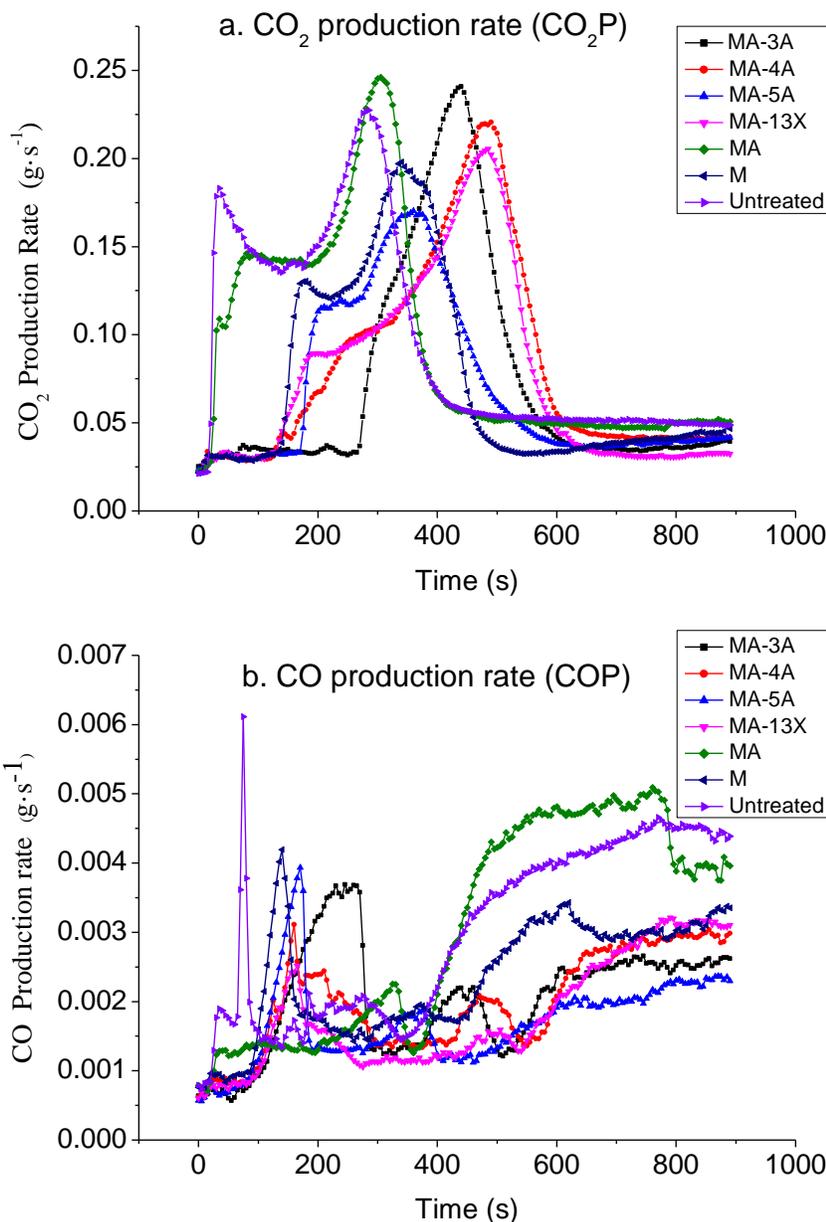


Fig. 3. The (a) CO₂P and (b) COP curves of intumescent flame-retardant coatings modified by different zeolites

The SPR and TSP curves (Figs. 4 and 5) suggested that the intumescent fire-retardant coating modified by X-type zeolite showed more of an advantage in smoke

suppression than the modification by A-type zeolite. The results clearly illustrated the dominance of MA-13X in smoke suppression.

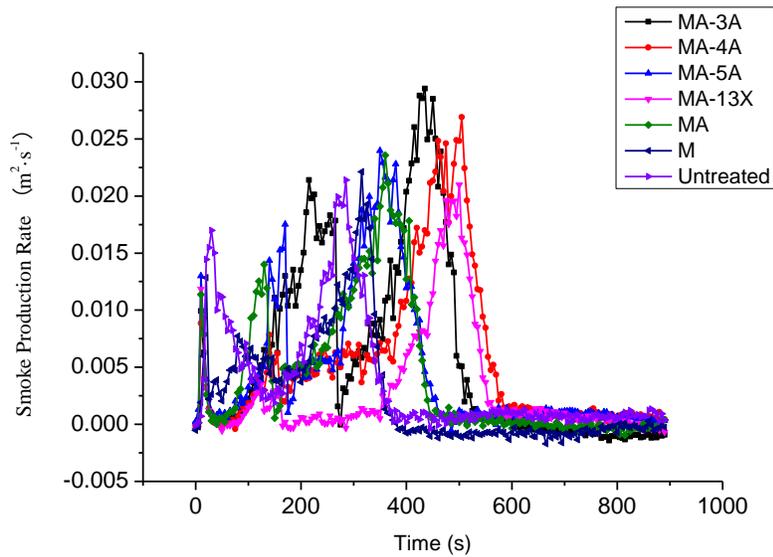


Fig. 4. The SPR curves of intumescent flame-retardant coatings modified by different zeolites

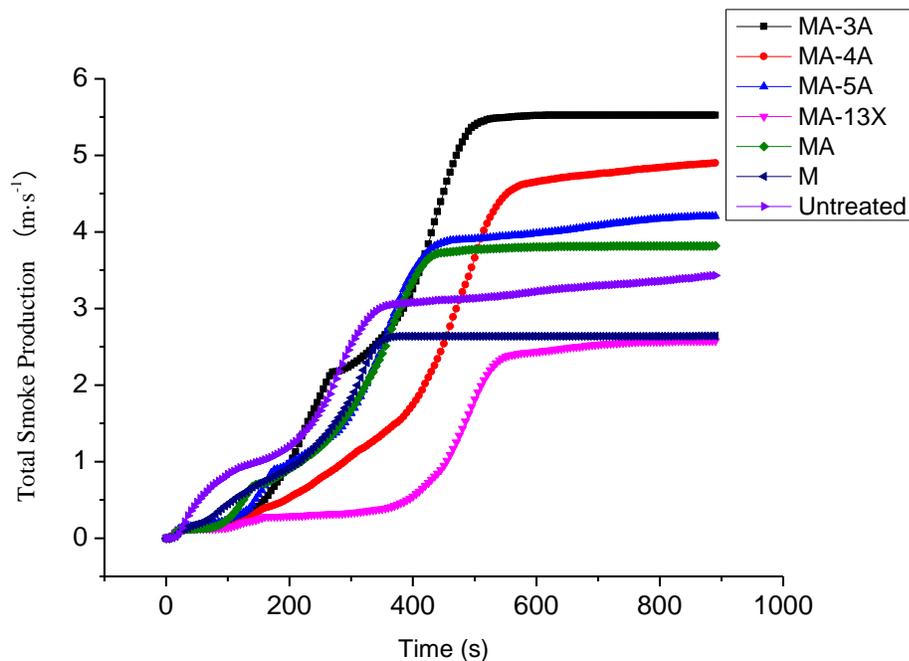


Fig. 5. The TSP curves of intumescent flame-retardant coatings modified by different zeolites

The release rate was relatively small and the last to reach the peak. The total smoke production remained at a very low level at 410 s that dropped 25.0%. The group MA-3A again showed the effect of delaying the time of reaching the peak of CO and CO₂ release rate. The generation of smoke in the former 120 s of combustion was very little; however, its total smoke production was the highest in all samples, which it increased 60.1% compared to the untreated group.

Fire Performance Index

The fire performance index (FPI) is the ratio of the ignition time and the heat release rate peak. The higher the FPI value means there is a smaller risk of fire (Wang *et al.* 2010). According to Table 2, the FPI values were ranked as MA-3A > MA-5A > MA > MA-13X > MA-4A > Untreated. The FPI increased from 0.06 to 0.65 as APP was added and it can be inferred that APP promoted the dehydration of wood into charcoal and improved the comprehensive fire-retardant properties of wood. The FPI also decreased slightly in most cases of adding zeolites. However, the FPI value increased to 1.02 and 0.95 when 3A and 5A zeolite were added, respectively. It was apparent from Table 2 that 3A and 5A zeolites performed better in the flame retardant effect on the combustion properties. The properties of comprehensive FPI, TTI, EHC, and THR of 3A zeolite were the best; however, the intumescent fire-retardant coating modified by 3A zeolite produced the most smoke.

Residual Mass

According to Table 2, the residual mass fraction of Untreated sample was 8.57% and the addition of APP increased the mass fraction to 15.40% (MA). The residual mass fraction of samples treated with intumescent fire-retardant coating modified by zeolites were further improved. Moreover, 13X and 3A zeolites improved the mass fraction by 2.54 and 2.17 times compared with the untreated. Results in Table 3 showed that the addition of zeolites could decrease the mass loss rate (MLR) to some extent especially in the initial 300s after the ignition time. The possible reason was that the coating film of the intumescent flame-retardant melted when heated and formed an expanded carbon layer which could delay the burning for some time so that the small fire could be put out in time and win more time in large fire accident for personnel to escape and reduce casualties. It can also be seen in Fig. 6 that the char residue of MA-3A (Fig. 6c) and MA-13X (Fig. 6d) were thicker and stronger than the untreated (Fig. 6a) and MA (Fig. 6b).

Table 3. Mass Loss Rate of the Different Zeolite Modified Intumescent Flame-retardant Coating at Different Time

Samples	Mass Loss Rate (g/s)					
	60s	120s	180s	240s	300s	360s
Untreated	0.116	0.107	0.107	0.110	0.116	0.107
M	0.094	0.101	0.100	0.101	0.112	0.106
MA	0.095	0.091	0.097	0.103	0.098	0.084
MA-3A	0.085	0.107	0.122	0.111	0.092	0.077
MA-4A	0.043	0.052	0.059	0.067	0.074	0.085
MA-5A	0.085	0.084	0.093	0.095	0.086	0.075
MA-13X	0.055	0.061	0.064	0.070	0.076	0.086

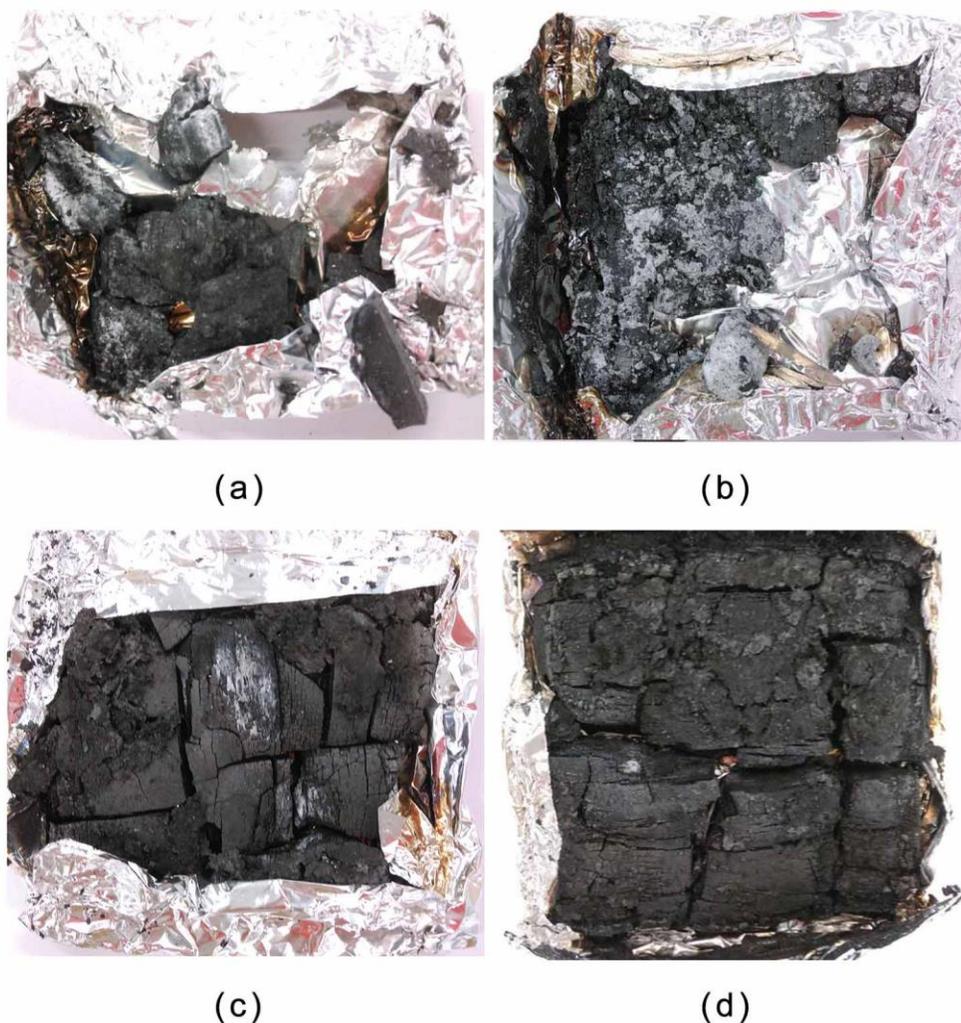


Fig. 6 Photos of residues of different samples (a) Untreated; (b) MA; (c) MA-3A; (d) MA-13X.

Synergistic Flame-retardant Mechanism of A-type and X-type Zeolites

The structure of the material, such as the silicon (aluminum) oxygen skeleton structure type of different zeolites, can determine different performances. A-type zeolite is a cubic tetrahedral structure further bridged by a sodalite cage that is oxygen-bridged by a single four-membered ring and six-membered ring. An X-type zeolite is arranged according to the pattern of a diamond crystal in which each carbon atom is replaced by a β cage and its cubic eight surface structure formed by six oxygen bridges to connect adjacent β cages. An X-type zeolite has a high affinity for CO_2 molecules and strong adsorption capacity (Li 2007; Xin 2009; Shang 2014). Experimental results indicated that the SPR of MA-13X was relatively small and was the last to reach the peak. The total smoke production was the smallest and dropped by 25.0% compared to the untreated sample. Then X-type zeolite showed more of an advantage in smoke suppression than A-type zeolite.

A large amount of heat was generated after the wood was ignited, the reaction was aggravated, and a large number of decomposition products, such as acetic acid, methanol, wood tar, methane, CO, CO_2 , and other gases were also generated when the temperature reached 275 °C (Ragland *et al.* 1991). Currently, a zeolite with a strong adsorption capacity

and rich pore structure will achieve the flame-retardant function through adsorbing these decomposition products. The framework of a zeolite has a certain flexibility and can adsorb some molecules slightly larger than its micro-pore diameter. However, the adsorption capacity and adsorption rate of zeolite will decrease noticeably when adsorbing larger molecules rather than smaller ones. The aperture of 3A zeolite is small, which made it possible to adsorb more molecule combustible gas produced by the pyrolysis of wood and decrease the quantity of heat released by the combustion of combustible gas. It was to some extent effective in reducing the effective heat of combustion. The EHC of MA-3A substantially decreased 36%. Therefore, 3A zeolite had a good effect on reducing the effective combustion heat. With increased temperature of combustion, zeolite may degrade and form SiO_4 and Al_2O_3 , which influences the chemical composition and structure of the carbonaceous layer by restraining the formation of the flammable compound and enhances the cross-linking in the condensed phase. The carbon barrier prevents further decomposition of the samples as a stronger insulation layer (Wang *et al.* 2014).

Though the fire-retardant mechanisms were different, 3A zeolite and 13X zeolite exhibited complementarily synergistic effects for improving the fire-retardant properties of an intumescent fire-retardant coating for wood. Whether the compound of different zeolites can improve the flame-retardant property of intumescent fire-retardant coatings calls for further experimental research.

CONCLUSIONS

1. The use of APP improved the fire-retardant properties by prolonging the ignition time and decreasing the HRR and THR values, but the release of CO_2 and CO increased.
2. The FPI and comprehensive properties of 3A zeolite were optimum; 3A zeolite further enhanced the fire-retardant properties compared with APP.
3. The group MA-3A was the only one for which one exothermic peak appeared in the combustion process and the value of EHC remarkably decreased 36%.
4. An X-type zeolite had a high affinity for CO_2 molecules and strong adsorption capacity compared to the A-type zeolite.
5. The 13X zeolite performed with an excellent advantage in smoke suppression. The release rate was relatively small, and it was the last to reach the peak. The total smoke production remained at a very low level at 410 s that dropped 25.0%.

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