



## Synergistic effect of synthetic zeolites on flame-retardant wood-flour/polypropylene composites



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### HIGHLIGHTS

- Different loadings of synthetic 4A or 13X zeolites were used to prepare WPCs.
- The zeolites had effects on both gas and solid phase flame-retardancy mechanism.
- WPC/APP/zeolites performed better flame retardancy than WPC/APP.
- WPC/APP/zeolites presented better mechanical properties than WPC/APP.

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### ABSTRACT

Flame-retardant wood-plastic composites (WPCs) consisting of ammonium polyphosphate (APP) as flame retardant and four different concentrations (2, 4, 6, and 8 wt%) of synthetic zeolites (type 4A and 13X) as synergistic agent were prepared. The results of thermogravimetry analysis showed that the inclusion of synthetic zeolites catalyzed the thermal degradation of WPCs. Both limiting oxygen index and cone calorimetry tests were used to evaluate the flame performance of WPCs, and the results proved that the addition of 4A or 13X zeolites had synergistic effect on the flame retardancy of WPCs. The residues of burned WPCs after cone calorimetry tests were characterized by scanning electron microscopy, energy dispersive spectroscopy, and Fourier transform infrared spectroscopy. All above data in series were integrated to speculate the synergistic mechanism. Moreover, all the measured mechanical tests proved that the incorporation of zeolites increased flexural properties and impact strength, and decreased tensile properties of WPCs.

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### 1. Introduction

Now-a-days, wood-plastic composites (WPCs) have emerged as a new generation of construction engineering materials for different indoor and outdoor usage, such as decking for terrace and balconies, landscaping timbers, fencing, furniture and automobile products etc. [1–3]. They have attracted both researchers and manufacturers with excellent performance, including low cost, high dimensional stability during lifetime, high relative strength and stiffness [4]. However, the high flammability of WPCs limits their application in various fields. Therefore, improvement of the flame retardancy of WPCs is increasingly important and many efforts have been devoted to it.

The most expeditious method to impart flame retardancy of WPCs is the incorporation of flame retardants (FRs) during the compounding process [5–10]. Ammonium polyphosphate (APP) is

one of the most effective and widely used environmental-friendly FRs for the flame-retardancy modification of WPCs [6–9]. However, the significant disadvantage of APP is that it enhances the flame retardancy of WPCs with obviously deteriorating the mechanical properties, because of the poor compatibility between APP and WPC matrix. In our previous researches, we have used thermosetting resins to microencapsulate APP to overcome this problem [5]. Although nanoclay [11], carbon nanotube [12], and nano-SiO<sub>2</sub> [13] have been reported by other researchers as synergistic agent to modify the flammability, the synergistic mechanism was not clear enough. Therefore, further research needs to be done to improve both the flame-retardant and mechanical performance of WPCs and also investigate the synergistic mechanism.

Zeolites are hydrated crystalline aluminosilicates with microporous nanostructures and pore sizes ranging from about 3–15 Å. The structure of zeolites consists of 3-dimensional frameworks made up by SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. They possess permanent negative charges in their structural framework, which has the capability of adsorbing or rejecting molecules, thus they are widely used in

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catalysis, separation, adsorption and ion-exchange [14–18]. Furthermore, zeolites have also been used to reinforce nanocomposites [19–21] or as synergistic agents to improve the flame retardancy or thermal stability of polymers [22–25] due to their high mechanical strength, good thermal and chemical stability, but there is little reports about effect of zeolites on the properties of WPCs.

In this research, the goal was to investigate the effect of synthetic zeolites (type 4A and 13X) on WPCs using APP as flame retardant. Thermal degradation behavior of WPC/APP and WPC/APP/zeolites were investigated by thermogravimetry analysis (TGA). The synergistic effects of synthetic zeolites on the flame retardancy of WPCs were evaluated by limiting oxygen index (LOI) and cone calorimetry tests. To further investigate the synergistic mechanism of synthetic zeolites, the residues of WPCs after burning were studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Fourier transform infrared spectroscopy (FTIR). Moreover, the effects of the zeolites on the mechanical properties of WPCs have also been highlighted in the present study.

## 2. Experimental methods

### 2.1. Materials

The materials were all made in China, including flour of poplar (*Populus tomentosa* Carr., particle size between 60–80 mesh sieve), Gaocheng Xingda Wood Flour Company, Hebei. Polypropylene (PP, K8303, melt-flow rate 1.5 g/10 min) and maleic anhydride-grafted PP (MAPP, melt-flow rate 120 g/10 min), Beijing Yanshan Petrochemical Co. Ltd. APP (average polymerization degree  $n > 1000$ ), Shenzhen Jingcai Chemical Co. Ltd. 4A zeolites (Si/Al = 1, compensation cation: Na) and 13X zeolites (Si/Al = 1.5, compensation cation: Na) (chemical reagents), Shanghai Jiuzhou Chemical Co. Ltd.

### 2.2. Preparation of WPCs

First, the wood-flour was oven-dried at 105 °C until the weight stabilized, which took about 24 h. Then, MAPP, APP, and synthetic zeolites (type 4A or 13X) were added into PP and wood-flour (PP/wood-flour = 6:4) with constant weight percentage (Table 1), each group of the raw materials was mixed in a high-speed mixer at a mixing speed of 2900 rpm for 4 min before being melt-blended in a co-rotating twin-screw extruder (KESUN KS-20, Kunshan, China) to produce composite pellets. The corresponding temperatures in the extruder barrel were 165/170/175/180/175 °C from hopper to die zones, and the screw speed was 167 rpm. Then the extrudates were cut into small particles about 5 mm, and then dried again at 105 °C for 3 h before being taken out for hand matting. A hot press (SYSTEM-II, China Academy of Forestry, Beijing, China) was used to produce the composites by compressing the mat at 180 °C with a pressure of 4 MPa for 6 min. After hot pressing, the formed mat was cooled down at 4 MPa for another 6 min at room temperature in a cold press. The control WPC without APP or zeolites was prepared similarly. The dimension of the composites was  $270 \times 270 \times 3$  mm<sup>3</sup> with a target density of 1.0 g/cm<sup>3</sup>.

### 2.3. FTIR

The surface structure of zeolites, WPCs and the residues for WPCs at the end of cone calorimetry tests were examined by a Nicolet 6700 spectrophotometer

**Table 1**  
Formulations of WPCs.

WPC type	Composition based on weight (%)			
	MAPP	APP	4A	13X
Control	8			
WPC/APP	8	25		
WPC/APP/4A	8	25	2	
	8	25	4	
	8	25	6	
	8	25	8	
	8	25		
WPC/APP/13X	8	25		2
	8	25		4
	8	25		6
	8	25		8
	8	25		

(Thermo Scientific, USA) used in the attenuated total reflection mode. Before tests, all samples were grounded into powders. Each spectrum was collected at a resolution of 4 cm<sup>-1</sup> and a scan rate of 32 over the range of 4000–650 cm<sup>-1</sup>.

### 2.4. TGA

To investigate the effect of synthetic zeolites on the thermal decomposition behavior of WPCs, TGA analysis was conducted. All TGA tests were carried out by a Q50 TGA analyzer (TA Instruments, USA) at a linear heating rate of 10 °C/min under pure nitrogen. The temperature ranged from ambient to 700 °C. Before test, each sample was grounded into powders and kept within 5–8 mg in an open platinum pan.

### 2.5. Fire performance experiments

#### 2.5.1. LOI

LOIs of all the WPCs were measured using a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) with the sheets ( $135 \times 6.5 \times 3$  mm<sup>3</sup>) according to ASTM D2863-77. Fifteen replicates were tested for each group.

#### 2.5.2. Cone calorimetry

The combustion experiments were carried out with a cone calorimeter (Stanton Redcroft, UK) in accordance with ISO 5660 procedures. Each specimen ( $100 \times 100 \times 3$  mm<sup>3</sup>) was wrapped in aluminum foil and exposed horizontally to 50 kW/m<sup>2</sup> external heat flux. Three replicates were tested for each group.

### 2.6. SEM-EDS

The morphologies of residues for WPCs at the end of cone calorimetry tests and the fracture surfaces of impact tested WPCs were investigated by a Hitachi S-3400 SEM analyzer (Philips, Japan) with an acceleration voltage of 5 kV. EDS spectra showed the quantified surface elemental compositions of the residues.

### 2.7. Mechanical property experiments

#### 2.7.1. Flexural properties

Flexural properties including modulus of rupture (MOR) and modulus of elasticity (MOE) were measured as Chinese standard GB/T 9341-2000, which involves a three-point bending test at a crosshead speed of 1 mm/min. Six replicates ( $60 \times 25 \times 3$  mm<sup>3</sup>) of each group were tested and standard deviations (SDs) were calculated.

#### 2.7.2. Tensile properties

Tensile properties including tensile strength and elongation at break were measured according to Chinese standard GB/T 1040-1992 at a testing speed of 2 mm/min. Six dumbbell replicates of each group were tested and SDs were calculated.

#### 2.7.3. Impact strength

Unnotched izod impact tests were performed in accordance with Chinese standard GB/T 1843-1996. Six unnotched replicates ( $80 \times 10 \times 3$  mm<sup>3</sup>) of each group were tested to calculate the izod impact strength.

## 3. Results and discussion

### 3.1. FTIR analysis

Before FTIR tests, all the synthetic zeolites were dried under vacuum at 80 °C for 24 h. Fig. 1a shows the FTIR spectra of 4A and 13X zeolites. Generally, the absorption bands at 3600–3300 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> could be attributed to the –OH stretching and deformation of zeolites, respectively [26]. The intensive absorption band at around 960 cm<sup>-1</sup> could be assigned to the Si–O and Al–O asymmetric stretching belonging to the SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra [27]. The bands observed at about 750 and 665 cm<sup>-1</sup> were due to the Si–O symmetric stretching and oscillations of chains of aluminosilicate oxygen tetrahedrals, respectively [26,27].

The FTIR spectra of control WPC, WPC/APP and WPC/APP/zeolites are shown in Fig. 1b. A broad absorption band in the region of 3600–3100 cm<sup>-1</sup> could be assigned to the –OH groups in control WPC. The intensity of this band slightly decreased with the addition of 4A or 13X zeolites. This may due to the hydrogen-bonding or ionic interactions between WPC and zeolites [25]. The spectrum of control WPC in the region of 3000–1000 cm<sup>-1</sup> could be

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