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Evaluation of intumescent fire retardants and synergistic agents for use in wood flour/recycled polypropylene composites

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HIGHLIGHTS

- Low cost WPC was prepared with recycled PP nonwoven and wood flour.
- Fire retardant synergistic agents enhanced the fire retarded performance of WPC.
- The mechanical property was increased by adding fire retardant synergistic agent.
- The synergy between IFR and ZB or MnO_2 was greater than that of MMT or SnO_2.
- 5 wt% of ZB or MnO_2, MMT and SnO_2 addition made WPC with a V0 rating.

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ABSTRACT

The effects of fire retardant synergistic agents zinc borate (ZB), montmorillonite (MMT), manganese dioxide (MnO_2) and stannic oxide (SnO_2) on the mechanical properties, thermal degradation and flame retardant performance of wood flour–recycled polypropylene composites (WPC) comprised of intumescent flame retardants (IFR) were studied. The species were characterized by thermogravimetric analysis (TGA), limiting oxygen index (LOI), UL-94 tests, and cone calorimeter measurements. The results showed that the synergistic effect between IFR and ZB or MnO_2 was greater than that of MMT or SnO_2. The addition of 5 wt% of ZB or MnO_2, MMT and SnO_2 created fire retardant WPC with a V0 rating, exhibiting excellent fire retardancy.

1. Introduction

Wood plastic composites (WPC) are promising and sustainable green materials with excellent mechanical performance, specific functionality and the combined properties of wood and plastics. These materials can be widely applied in residential construction, and the decking and furniture industry [1–4]. Generally, wood fiber is used as the reinforcing material, while plastics, such as polyethylene (PE) [3,5], polypropylene (PP) [6–10], polyvinyl chloride (PVC) [11], polylactic acid (PLA) [12,13] and polystyrene (PS) [14] are used as the matrices. Among these plastics, PP, PE and PVC are the most widely used in WPC fabrication [2].

In recent years, decreasing forest area, rising white pollution and diminishing petroleum resources have become of increasing concern. Fortunately, WPCs have proven to be an ideal substitute for wood and plastics. Moreover, many researchers have found that the wood materials used in WPCs can be replaced by a wide variety of other cellulose-based materials, such as wheat and cereal straw, flax straw, corn, sunflower and pepper stalks, kiwi prunings, peanut hulls, corn piths, and grass clippings [15–21]. However, the cellulose-based reinforcing materials and plastic matrices are highly flammable, and thus it is important that fire retardant WPCs are researched and developed.

Due to growing environmental issues, the application of halogenated flame retardants is gradually becoming restricted [22,23]. Intumescent flame retardants (IFR), comprised of ammonium polyphosphate (APP), pentaerythritol (PER), or melamine (MEL) are suitable fire retardants for WPCs [22,24–26]. Garcia et al. [2] concluded that the addition of ammonium polyphosphate or aluminium hydroxide led to an auto-extinguishing effect of wood-high density polyethylene composite. Wang et al. [11] found that organomodified montmorillonite improved the mechanical properties, flame retardancy and smoke suppression of wood flour–polyvinyl chloride composites. Baysal et al. [14] found that

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boric acid and borax mixture improved the fire resistance of WPC to some extent. Suppakarn et al. [4] studied the effect of magnesium hydroxide and zinc borate on the mechanics and flammability of sisal–PP composite, and concluded that the addition of magnesium hydroxide and zinc borate enhanced the flame retardancy of sisal/PP composites without sacrificing their mechanical properties. Naumann et al. [10] found that the fire resistance of expandable graphite was better than two different ammonium polyphosphates and nitrogen containing fire retardant. Ayrilmis et al. [27] researched the effect of boron and phosphate compounds on fire performance, and concluded that the phosphate compound exhibited better fire retardancy than the boron compound. Kim et al. [9] revealed that ammonium polyphosphate and silica had a synergistic effect, and were effective flame retardants for wood–fiber/PP composites, although the mechanical properties of the composites decreased with their addition. Stark et al. [3] studied the effect of different fire retardants on flame performance of wood–polyethylene composites, with magnesium hydroxide and ammonium polyphosphate showing the most improved composite fire retardancy whereas decabromodiphenyl oxide and synergistic antimony trioxide and zinc borate exhibiting the poorest.

Zinc borate (ZB) is a flame retardant and smoke suppressant [3,27–29], and plays a role in fire retardancy during the vapor phase, condensed phase and dehydration in the presence of hydrogen chloride [30]. Further, it can contribute to the enhanced formation of a glassy char at the surface of the polymer substrate condensed phase to protect the polymer from the combustion zone [31], and can catalyze char formation in intumescent systems [32]. Montmorillonite (MMT) can enhance both mechanical properties and fire retardancy [11,33–35]. Manganese dioxide (MnO_2) can react with intumescent fire retardant [36], and has synergy with intumescent fire retardants to enhance the fire retardancy of materials [37,38]. Stannic oxide (SnO_2) is an effective fire retardant and smoke suppressant for natural or synthetic polymers, which can reduce the toxicity of degradation products [39,40] and may react with char residue to increase char stability [41].

In this work, the synergistic effect of IFR and fire retardant synergistic agents on improving fire retardant efficiency was researched. The aim of this study was to investigate the synergistic effect of ZB, MMT, MnO_2 and SnO_2 with IFR, i.e. ammonium polyphosphate (APP), dipentaerythritol (DPER) and melamine (MEL) on the mechanical properties and flame retardant performance of WPCs. The fire performances of WPCs were characterized by TGA, LOI, UL-94 and cone calorimeter tests.

2. Experimental

2.1. Materials

Recycled polypropylene melt blown nonwoven was acquired from Tianjin Polytechnic University (Tianjin, China). It was processed in a 30 mm parallel co-rotating twin-screw extruder with a length to diameter (L/D) ratio of 30:1 for melting and was extruded and cut into pellets with a melt flow index (MFI) of 850 g/min. Wood flour (200 meshes) from pine species was obtained by the Ren Jia Decoration Company (Tianjin, China), and the wood flour was dried in an oven at 110 °C for 24 h to a moisture content of 0–1 wt% based on oven-dry weight of the wood, and was then stored in a sealed polyethylene bag. Ammonium polyphosphate (APP), dipentaerythritol (DPER) and melamine (MEL) were obtained from the Shandong Shian Chemical Co., Ltd. (Shandong, China), Jinan Yinhe Chemical Co., Ltd. (Jinan, China) and Suzhou Dongyang Co., Ltd. (Suzhou, China), respectively. The MMT, MnO_2, ZB, and SnO_2 were all supplied by the Nanjing Duodian Chemical Co., Ltd. (Nanjing, China). All chemical reagents were used as received.

2.2. Sample preparation

The technological preparation of WPC samples was as follows. Firstly, well-dried wood flour and recycled PP pellets with or without fire retardants were premixed by a high-speed mixer (Suzhou New Chicheng Machinery Co., Ltd., SRL-Z300/600) for 10 min. Secondly, the mixed raw materials were processed in a 30 mm parallel co-rotating twin-screw extruder (BRABENDER, TSE 25) with a length to diameter (L/D) ratio of 30:1 at the temperature range of 170–195 °C for melting and were extruded and pelletized to composite granules. Thirdly, the composite granules were pressed on a molding machine at a pressure of 20 MPa and temperature of 200 °C for 30 min to form sheets of desired thickness.

2.3. Characterization

Tensile strength and flexural strength of all samples were determined by a computer controlled mechanical instrument (INSTRON, Instron 3369) according to previous research [42], and Izod pendulum impact resistance was performed by an Izod impact instrument (Dongguan Lixian Instrument Scientific Co., HZ-1702C) [43].

The LOI values of all samples ($150 \times 10 \times 5$ mm^3 in size) were tested on a limited oxygen index instrument (Stanton Redcroft Tarlin Scientific Co. Ltd., FTA) at room temperature according to ASTM D 2863 [44]. The UL-94 test was performed according to ASTM D 3801 [45].

Cone calorimeter tests were carried out using a cone calorimeter (Fire Testing Technology Ltd., FTT) following the procedure defined in ASTM E 906 [46] with the sample size of 100 mm × 100 mm × 3 mm. The cone data obtained were reproducible to within ±10% with heat flux of 35 kW/m^2. The equipment was similar to that used in oxygen consumption cone calorimetry.

Thermal behaviors were examined using a thermogravimetric analyzer (TGA) (NETZSCH, STA 409PC). In each case, the specimens were heated from room temperature to 800 °C at a heating rate of 20 °C/min under nitrogen flow.

3. Results and discussion

3.1. Mechanical properties

The compositions of the WPCs with or without fire retardants are shown in Table 1, with sample WF-25 consisting of wood flour and PP the control specimen. The other samples all contained intumescent fire retardant and samples of WF-ZB, WF-MMT, WF-MD and WF-TD had synergistic fire retardants of ZB, MMT, MnO_2 and SnO_2, respectively. The mechanical properties of all specimens are correspondingly listed in Table 2.

As shown in Table 2, the mechanical properties of the WPCs changed significantly with the addition of intumescent fire retardants and fire retardant synergistic agents. For example, in contrast to the control sample WF-25, the tensile strength, flexural strength and Izod impact strength of WF-IFR increased by 72.4%, 120% and 17.6%, respectively. Compared with WF-IFR, with the addition of flame retardant synergistic agent, i.e. ZB, MMT, MnO_2 and SnO_2, flexural strength was slightly reduced and tensile strength and Izod impact increased obviously. However, the tensile strength and flexural strength among WF-ZB, WF-MMT, WF-MD and WF-TD changed only a little, while Izod impact strength was improved greatly, especially for WF-ZB and WF-MD with 28.3% and 41.7% improvement, respectively, compared with WF-IFR. This may be because the flame retardant synergistic agents compatibilized WPC to some extent and, as a result, the mechanical properties were enhanced accordingly. Taking WF-MMT as an example, MMT is a 2:1 layered clay mineral crystalline with a central

Table 1
Formulations of WPCs.

Code	Composition based on mass fraction (%)								
	PP	WF	APP	DPER	MEL	ZB	MMT	MD	TD
WF-25	75	25							
WF-IFR	57	18	15	5	5				
WF-ZB	57	18	12	4	4	5			
WF-MMT	57	18	12	4	4		5		
WF-MD	57	18	12	4	4			5	
WF-TD	57	18	12	4	4				5

PP-polypropylene, WF-wood flour, APP-ammonium polyphosphate, DPER-dipentaerythritol, MEL-melamine, ZB-zinc borate, MMT-montmorillonite, MD-manganese dioxide, TD-stannic oxide.