Effect of zinc borate and wood flour on thermal degradation and fire retardancy of Polyvinyl chloride (PVC) composites

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ABSTRACT

The thermal decomposition, fire retardancy and mechanical properties of wood-flour–polyvinyl chloride composites (WF–PVC) were investigated. Thermogravimetric analysis (TGA) tests showed that the addition of wood flour (WF) and zinc borate (ZB) significantly influenced the thermal degradation behavior of PVC and WF–PVC composite. WF reduced the initiation temperature ($T_{initial}$) for thermal degradation of PVC, while ZB scarcely affected the initial temperature of WF–PVC. WF retarded the thermal decomposition of PVC in the early stage while ZB increased the rapidest decomposition temperature and reduced the decomposition rate of WF–PVC. The mechanism of thermal decomposition of the composite was analyzed by Fourier transform infrared (FTIR) spectroscopy using the attenuated total reflectance (ATR) method. The decrease of C—H bonds and increase of C=C bonds indicated WF and ZB promote the crosslinking and charring reactions of PVC. According to the cone calorimetry (CONE) tests, WF had a positive effect on fire performance of PVC but had little effect on smoke suppression. In contrast, the incorporation of ZB had little effect on flame retardancy of WF–PVC but it was an effective smoke suppressant, decreasing the total smoke produced (TSP) by more than 50%. Mechanical results indicated that ZB had some negative effects on the strength properties of WF–PVC, however the modulus increased compared with the untreated composite.

1. Introduction

Wood thermoplastic composites (WPCs) are manufactured by dispersing wood fibers or wood flour (WF) into molten plastics to form composite materials by processing techniques such as extrusion, thermoforming, and compression or injection molding [1]. The advantages of using a wood component in thermoplastic composites is that the bio-based resource is non-abrasive, low cost, widely available, sustainable flexible and recyclable. Also, high filling levels are possible, and high specific properties and lower density per weight of raw material are conferred [2]. The most commonly used thermoplastics in manufacturing WPCs are polyethylene (PE) [3–6], polypropylene (PP) [7–9], polystyrene (PS) [10,11], and polyvinyl chloride (PVC) [12–15]. They are now being widely used in the auto industry, residential products, and many other applications with growing markets [16].

However, one of the critical drawbacks facing WPCs is their high flammability. As organic materials, plastics and wood-derived fillers are sensitive to flame. Thus, the improvement of the flame retardancy of composite materials has become important for

complying with the safety requirements of WPC products [17]. Many strategies have been used by researchers to improve the fire retardancy of these composites [18,19]. One strategy used to acquire fire retardancy is the incorporation of fire retardants (FRs) that can be added to the composites melt during processing and that come in many forms, although most are particles or powders. Halogenated compounds based on chlorine and bromine are effective flame retardants; however they are seldom used in WPCs due to the threat to the environment and human health. The most widely used additive-type FRs published on WPCs are phosphorus compounds, based mainly on ammonium polyphosphate (APP) [20]; metal hydroxides [8,21]; boron-based fire retardants [22,23]; nitrogen fire retardants, often compounded with phosphates to achieve a phosphorus–nitrogen synergism [24]; nanoparticle fire retardants, such as clays and layered silicates [25–27], expandable-graphite (EG) [7] and carbon nanotubes [13,28].

PVC-based composites, unlike the other thermoplastic-based composites, are called "natural" fire-resistant materials [29]. Because of its high level of combustion resistance as well as its low cost, demands for WF–PVC composites are increasing dramatically. They are typically used in building construction applications, such as window/door profiles, decking, railing and siding [12]. However, it is more and more recognized that WF–PVC is not a safe material because PVC can generate high levels of black

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Table 1
Characteristics of the zinc borate.

Ingredients	$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$
Appearance	White crystalline powder
B_2O (%)	45.0–48.0
ZnO (%)	37.0–40.0
Loss on ignition (%)	13.5–15.5
Water (%)	≤1.0
Fineness (325 mesh residue on screen) (%)	≤1.0

smoke and toxic gases (i.e., chlorine compounds, benzene, and other aromatic compounds) when it is forced to burn [30]. Additionally, the easy flammability of the high content of wood flour and other low-molecular-mass additives as well as the subsequent thermal degradation is also an important issue [15]. Therefore, wood-flour/poly(vinyl chloride) composites (WF–PVC) also often incorporate fire retardants to further decrease their flammability and smoke evolution. Even though a lot of work has been reported on the flammability of PVC providing in-depth information on developments around fire retardants and mineral fillers for PVC [30–36], very little work has been reported on the flammability of the composites [13,15].

Boron-containing fire retardants have been developed as cheaper, yet less toxic alternatives to such traditional fire retardants as antimony oxide [37]. As one of the most important borates, zinc borate (ZB) mainly used as a synergistic agent, was combined with other fire retardants to play its role through melting and coating the surface of material to prevent oxygen entry. Sain et al. [8] found that a partial replacement of magnesium hydroxide with zinc borate decreased oxygen index, improving fire performance of PP composites. It should be noted that ZB has a unique function of being both a fire retardant and a smoke suppressant of PVC [38]. Garba [39] also confirmed that zinc borate in the presence of hydrogen chloride (HCl) functioned effectively as a fire retardant for some tropical woods. It seems that ZB should be an effective fire retardant in WF–PVC. In our previous work, we have confirmed that wood flour has a positive effect on thermal and burning properties of PVC [40]. The objective of this study was to investigate the synergistic effect of the combination of ZB and wood flour on the fire retardancy, smoke suppression, and thermal degradation of WF–PVC. The effects of ZB on mechanical properties of WF–PVC were also investigated.

2. Experimental

2.1. Materials

PVC (type SG-5) with a number average molar mass of 1000 was supplied by Harbin Huaer Chemical Ltd. Co., Poplar wood flour (WF) (50–80 mesh size) used as filling material were purchased from a local timber market. Zinc borate used here was from Zibo Wuwei Industrial Ltd. Co, China, and its characteristics are listed in Table 1. Other additives such as dioctyl phthalate, calcium stearate (standard grade), chlorinated polyethylene (CPE), rare earth heat stabilizer (KB-7) were purchased from a local chemical supplier.

2.2. Sample preparation

100 parts PVC resin, 60 parts well dried wood flour, 12 parts other additives were dry-blended with and without ZB (represented by WF–PVC and WF–PVC–ZB, respectively) in a high-intensity mixer for 5 min. The ZB content in the WF–PVC–ZB matrix was fixed at 6 wt.% based on the total weight of materials. The dried mixture was incorporated into a twin-screw/single-screw extruder system. The temperature of the barrel was controlled by 9 sections, the twin screw extruder had 7 temperature zones, the single screw

extruder had 2 temperature zones. During the extrusion, the temperatures of the 9 processing zones were from 140 to 180 °C, and the die temperature was 165 °C. The twin screw extruder speed was 30 rpm and the single screw extruder was 8 rpm. Extrusion temperature was kept at less than 200 °C to avoid decomposition and degradation of wood and PVC.

In the last stage, the extruded composite was pressed in order to obtain samples for fire retardancy testing. The samples were prepared with the use of the following parameters: pressure 7 MPa, temperature 180 °C and cooling under pressure until solidified. The board specimens were cut into 100 mm × 100 mm × 4 mm samples for CONE tests.

2.3. Characterization

Thermogravimetric tests were performed using a Perkin-Elmer System Pro-6 thermogravimetric analysis (TGA) system. The dynamic measurements were carried out in a nitrogen atmosphere from room temperature to 800 °C at a heating rate of 10 °C/min. Residue of the pyrolyzed samples was saved for the FTIR test.

The structure of residue of the pyrolyzed samples obtained from the aforementioned TG tests was analyzed by FTIR (Nicolet 6700 FTIR spectrometer) using an ATR accessory. Spectra were measured at a resolution of 4 cm^{-1} and 32 scans.

The fire retardancy tests were conducted on a cone calorimeter (FTT Company, UK) in accordance with ISO 5660-1 (cone calorimeter) at a heat flux of 50 kW/m^2. All of the samples were laid on a horizontal sample holder, and the samples were protected with a stainless steel grid to prevent bending and expanding during heating.

Tensile and flexural properties were measured on a universal mechanical machine (Shenzhen Regear Instrument Cooperation, China). Tensile samples were tested according to ASTM D 638. The crosshead speed of 5 mm/min and gage length of 50 mm were used for the test. Flexural specimens were tested according to ASTM D790 in three point loading mode. The span length between two supporting nodes was 64 mm and the crosshead speed was 1.9 mm/min. At least five specimens were tested for each sample.

3. Results and discussion

3.1. Thermal decomposition by TGA

Thermogravimetric analysis results (curves of TG and DTG) of the WF–PVC composite system in pure nitrogen atmosphere are shown in Figs. 1 and 2, and the calculated typical data are listed in Table 2.

The primary constituents of the WF–PVC were first investigated. Fig. 1 shows thermal degradation behavior of WF–PVC composite and its components. In the case of wood flour, two peaks occur in the DTG curve. The first was assigned to the vaporization of water in the sample. It is a common feature observed for lignocellulosic materials [41,42]. The second stage with a high mass loss rate is attributed to the thermal decomposition of hemicellulose and cellulose [43]. From mass loss in the second peak shown in Table 2, the mass loss of WF is 67% which demonstrates the second stage corresponds to the main decomposition process. For PVC two peaks in DTG curve of PVC were assigned as HCl-elimination reaction taking place mainly in the first peak and thermal degradation of carbon chain of PVC that produces flammable volatiles in the second peak [44].

Similar to pure PVC, the WF–PVC underwent two-stage degradation; this indicates that WF–PVC composites act more like PVC. Curve WF–PVC* in Fig. 1 is the result calculated by adding curve WF and curve PVC based on their percentages in the composite.