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Preparation and characterization of microencapsulated ammonium polyphosphate with UMF and its application in WPCs

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HIGHLIGHTS

- Four different UMF/APP mass ratios were conducted to prepare MCU-APP.
- The water resistance and flame retardancy of APP were improved by microencapsulation.
- The MCU-APP/WPCs presented better flame retardancy than the APP/WPC.
- The MCU-APP/WPCs performed better physio-mechanical properties than the APP/WPC.

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ABSTRACT

Ammonium polyphosphate (APP) is an effective and common flame retardant for wood–plastic composites (WPCs), but its high water leaching rate and poor dispersibility will negatively affect the water resistance and mechanical properties of WPCs. In this research, urea–melamine–formaldehyde resin was used as clothing to microencapsulate APP via polymerization *in situ*. The products were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, thermogravimetric analysis and water solubility test. After modification by the microencapsulated APP, the flammability and physio-mechanical properties of WPCs were measured. The results showed that the WPC used microencapsulated APP as flame retardant performed better flame retardancy and better physio-mechanical properties compared with the WPC mixed with unmodified APP.

1. Introduction

Wood–plastic composites (WPCs) are potential material to be applied in furniture and building industries and have attracted both researchers and manufacturers with excellent machinability and recyclability, less use of petroleum-based resource, low cost of wood-flour and natural-organic fillers [1–3]. However, the primary limitation is poor flame retardancy, decided by the two main components (wood-flour (fibre) and plastics). Many efforts have been devoted to modification of WPCs using flame retardants (FRs) [3–9].

Among the FRs for wood and plastics, intumescent FRs (IFRs) have aroused great attention in recent years, because they are more environmentally friendly than the traditional halogen-containing FRs. The conventional IFR system contains three active components: an acid source (e.g. APP, etc.), a carbonization agent (e.g. pentaerythritol (PER), dipentaerythritol (DPER), polyurethane (PU), etc.), and a blowing agent (e.g. melamine (MEL), urea, etc.) [10–12]. APP as an important ingredient in halogen-free IFR does not produce toxic gases after thermal decomposition or combustion. Moreover, compared with other halogen-free FRs, APP has higher phosphorus content, less loading and smoke, and less damage to the properties of polymer matrix [13]. However, the APP IFR system is not durable due to its moisture sensitivity and low compatibility with organic materials. To deal with these problems, APP used as FR needs modification, and microencapsulation is a feasible and effective method.

Various thermosetting resins, such as PU [14–16], epoxy [17,18], melamine formaldehyde (MF) [19–21], urea formaldehyde [22], urea-MF [23], polyvinyl alcohol-MF [24] resins can be used to encapsulate APP. The microencapsulated APP (MCAPP) has been extensively used as FR in polypropylene (PP) [17,19,22–26], PU [18,27], ethylene-vinyl acetate (EVA) [20], and styrene–ethylene butylene–styrene (SEBS) [21], but the flammability of WPCs, which use MCAPP as FR has rarely been reported.

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The objective of our research was to prepare microencapsulated ammonium polyphosphate with urea–melamine–formaldehyde resin (MCU-APP) and investigate the effect of MCU-APP on the properties of wood-flour/polypropylene (WF/PP) composites. MCU-APP was prepared via polymerization *in situ* and characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and water solubility test. The use of MCU-APP or APP as FR in the WPCs was evaluated by limiting oxygen index (LOI), cone calorimeter, and measurement of physical properties (e.g. water absorption (WA), thickness swelling (TS)) and mechanical properties (e.g. modulus of rupture (MOR), modulus of elasticity (MOE), tensile strength, elongation at break and impact strength). The results from the WPCs containing MCU-APP and unmodified APP were compared.

2. Experimental

2.1. Materials

PP with a melt flow index (MFI) of 1.5 g/10 min was purchased from Beijing Yanshan Petrochemical Co., Ltd., China. Wood-flour of poplar (*Populus tomentasa* Carr.) with particle size larger than 100 mesh was kindly provided by Gaocheng Xingda Wood Flour Company, Hebei, China. APP with an average polymerization $n > 1000$ was produced by Shenzhen Jingcai Chemical Co., Ltd., China. Urea, MEL and formaldehyde were chemical reagents purchased from Zhongyuan Chemical Co., Ltd., Henan, China.

2.2. Sample preparation

2.2.1. Preparation of the UMF prepolymer

Urea, MEL and 37% formaldehyde solution were put into a three-neck bottle and mixed under stirring. First, the mixture was adjusted to pH 8.5–9.0 with 20% NaOH solution, then heated to about 75 °C and kept for 10 min. Second, 20 g of urea was added to the mixture, heated to about 80 °C, and kept at pH 7.5 at constant temperature for 20 min. Finally, 40 g of urea (with a final mole ratio of 1:1) was added to the mixture, cooled to about 60 °C, and kept at constant temperature for 30 min to obtain UMF prepolymer.

2.2.2. Preparation of MCU-APP

The mixture of APP (50 g) and ethanol (100 ml) was first stirred at 1000 rpm and room temperature for 10 min. Then with addition of the UMF prepolymer (with APP/UMF mass ratio = 7:1, 5:1, 2:1), the mixture was adjusted to pH 4–5 with 20% acetic acid. The resulting mixture was heated at 80 °C under stirring (300 rpm) for 3 h. After cooling to room temperature, the product was filtered, washed with distilled water, and dried at 105 °C. Finally, the MCU-APP powder was obtained.

2.2.3. Preparation of WPCs

The WF was oven-dried at 105 °C for at least 24 h until the weight was constant. Then PP, WF and MCU-APP (or APP) (45 wt%, 30 wt%, 25 wt%, respectively) were mixed in a high-speed mixer (2900 rpm) for 4 min, followed by melt-blending in a twin-screw co-rotating extruder. The corresponding temperatures of the extruder from hopper to diezones were controlled at 165, 170, 175, 180 and 175 °C, respectively. The extruded strands were cooled to room temperature and were subsequently pelletized. Then these pellets were dried again at 105 °C for 2 h. The WPC was produced in a hot presser by compressing at about 180 °C under 4 MPa for 6 min. After that, the WPC was cold-pressed under 4 MPa and room temperature for another 6 min. The control of WPC (PP = 60 wt%, WF = 40 wt%) without FR was prepared similarly. The dimension of all the WPCs was $270 \times 270 \times 3$ mm^3 with target density of 1.0 g/cm^3.

2.3. Characterizations of MCU-APP

Powder samples were mixed with KBr powder, and each mixture was pressed into a tablet. The FTIR spectra were recorded using a Nicolet 6700 spectrophotometer (Thermo Scientific, USA).

The XPS spectra were recorded with a Thermofisher K-Alpha XPS analyzer (Thermo Scientific, USA) employing a monochromated Al Kα excitation radiation ($h\nu$ = 1486.6 eV).

The SEM micrographs were recorded by a Hitachi S-3400 SEM analyzer (Philips, Japan) with an acceleration voltage of 15 kV. The particles were sprinkled onto a double-sided tape and sputter-coated with gold layer.

All TGA tests were carried out by a Q50 TGA analyzer (TA Instruments, USA) at a linear heating rate of 20 °C/min under pure nitrogen. The temperature ranged from ambient to 700 °C. The weight of all samples was kept within 5–8 mg in an open platinum pan.

APP and MCU-APP samples (each 5 g) were encased with filter paper, then packaged with cotton cloth and tied by cotton thread tightly. After that, each kind of parcels (marked W_1) was put in 400 ml of distilled water at the test temperatures (25, 50 and 80 °C) and kept for 72 h, respectively. Then each of them was taken out and dried to constant weight at 105 °C (marked W_2). The solubility of APP or MCU-APP at 100 ml distilled water can be calculated as $(W_1 - W_2)/4$.

2.4. Fire performance tests

The LOIs of the WPCs before and after hot water treatment (50 °C, 24 h) were measured using a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) with the sheets ($100 \times 6.5 \times 3$ mm) according to ASTM D2863-77. Eight replicate specimens were tested for each group.

The combustion tests were performed with a cone calorimeter (Stanton Redcroft, UK) in accordance with ISO 5660 standard procedures. Each specimen ($100 \times 100 \times 3$ mm) was wrapped in aluminum foil and exposed horizontally to 35 kW/m^2 external heat flux. Three replicate specimens were tested for each group.

2.5. Physical property tests

The WA and TS tests were carried out according to Chinese standard GB/T 17657-1999 [28]. The test specimens (each $50 \times 50 \times 3$ mm) were entirely immersed into distilled water at 20 ± 2 °C for 8 days. Then the WA values were calculated based on the weight percent gains after 6, 24 and 48 h and thereafter at 48 h intervals by removing excess water on the surface. TSs were calculated based on the mid-span thickness changes after 24 h. Four replicate specimens of each group were tested and the standard deviations (SDs) were calculated.

2.6. Mechanical property tests

The flexural tests were conducted in accordance with Chinese standard GB/T 9341-2000 [29], which involves a three-point bending test at a crosshead speed of 1 mm/min. Five replicate specimens ($60 \times 25 \times 3$ mm) of each group were tested and SDs were calculated. The tested flexural properties included MOR and MOE.

The tensile tests were carried out according to Chinese standard GB/T 1040-92 [30] at a testing speed of 2 mm/min. Five replicate dumbbell samples of each group were tested and SDs were calculated. The tested tensile properties included tensile strength and elongation at break.

Unnotched Izod impact tests were performed in accordance with Chinese standard GB/T 1843-1996 [31]. Six replicate unnotched specimens of each group were tested to calculate the izod impact strength.

3. Results and discussion

3.1. Characterizations of MCU-APP

The FTIR spectra of APP and MCU-APP (APP:UMF = 2:1) are shown in Fig. 1. The typical absorption peaks of APP include

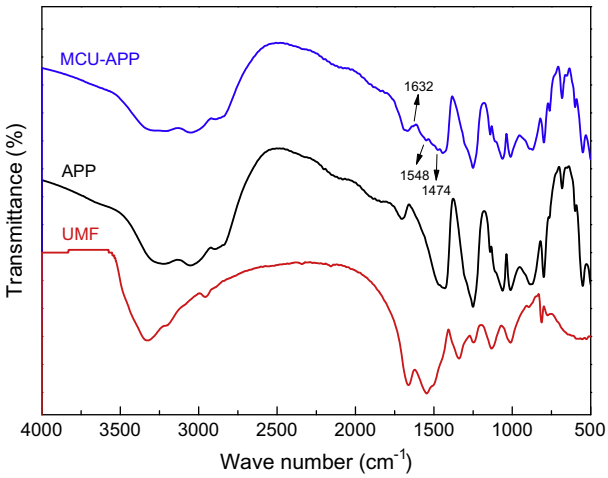

Fig. 1. FTIR spectra of APP and MCU-APP.