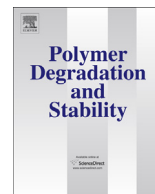




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Preparation of a novel biobased flame retardant containing phosphorus and nitrogen and its performance on the flame retardancy and thermal stability of poly(vinyl alcohol)

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ABSTRACT

A novel biodegradable type flame retardants (PCA) based on phosphorylated cellulose derivatives was synthesized by the reaction of phosphorylated cellulose with ammonium hydroxide at room temperature. The chemical structure of PCA was characterized by Fourier transformed infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). A series of poly(vinyl alcohol) (PVA) composites with various PCA contents were prepared by the method of casting evaporation. The incorporation of PCA could effectively improve the flame retardancy of PVA matrix. When the PCA content reached 15 wt%, the PVA/PCA composite met the UL-94 V-0 classification and got the LOI value of 30.0. Thermal and combustion properties of PVA composites were investigated by TGA and MCC. The char yield of PVA composites with 15% PCA at 700 °C in air was as high as 19.71%. Moreover, the MCC result indicated that the incorporation of PCA could decrease effectively the value of peak heat release rate and total heat release of the PVA composites. The mechanical property of PVA/PCA composites was also investigated. The result showed that PVA/PCA exhibited excellent thermal properties and flame retardancy.

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1. Introduction

Cellulose is the world's most abundant, natural, renewable, inexpensive and biodegradable polymer. Polysaccharides, like cellulose, are the polymer group with the longest and widest medical applications experience due to their unique properties: nontoxicity, water solubility or high swelling ability by simple chemical modification, stability to temperature and pH variations. Cellulose and its derivatives are wide applications of polymers in therapy [1,2] and used as a wound dressing and have been proposed for bone regeneration [3,4].

Cellulose is a linear syndiotactic homopolymer composed of D-anhydroglucopyranose units (AGU), which are linked together by β-(1→4)-glucosidic bonds. Each of the AGU-s possesses hydroxy groups in C-2, C-3 and C-6 positions, capable of undergoing the

typical reactions of primary and secondary alcohols. The structure of plentiful polyhydroxy makes cellulose acts as a carbon resource. Phosphorylated cellulose derivatives can be mentioned where the phosphorus can be covalently attached to the cellulose chain via a reaction of hydroxy groups to give phosphate groups Cell-O-P(O)(OH)₂, phosphate groups Cell-O-P(OH)₂, or phosphonic acid groups Cell-P(O)(OH)₂ [5]. The flame retardancy of phosphorylated cellulose derivatives is ascribable to dehydrating the polysaccharide molecules and promoting the consequent char formation during heating. Therefore, phosphorylated cellulose is not only carbonate resource but also acid agent and can offer excellent flame retardancy. Furthermore, in comparison with external flame-retardant additives, there is another advantage for the 'internal' phosphorylation, i.e., it causes no bleeding-out problem. Aoki [6] reported that as for the phosphorylated cellulose derivatives, the C6-O phosphorylation was found to noticeably prevent the phosphorylated cellulose derivatives from weight loss in the pyrolysis process under dynamic air, i.e., providing them with flame resistance functionality, whereas the C2-O and C3-O phosphorylation did not give rise to such an appreciable resistance effect. Some literature have reported that flame retardants containing both

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phosphorus and nitrogen compounds are more efficient flame retardants owing to the synergistic effect [7–9].

In some reported works, flame retardant modification of various biodegradable polymers and bio-composites was deeply studied by the using ammonium polyphosphate (APP) combining with some bio-based materials (lignin or starch) [10,11]. Casetta et al. studied the flammability properties of PLA/APP/PER, PLA/APP/starch, and PLA/APP/LIG. Compared to the PLA/APP/PER composite, materials containing lignin and starch showed lower LOI values but obtained V-0 ratings in vertical burning test. Because of their excellent mechanical properties, good chemical resistance, easy processability, biodegradability and water solubility properties, poly(vinyl alcohol) (PVA) have been widely used in home textiles, coating materials and industrial materials, etc. [12–14]. However, widespread applications are limited owing to the disadvantage of its flammability. In our group previous works, phosphorylated chitosan that contain nitrogen and nickel has been used as flame retardant additives for PVA composites [15–17]. In this paper, a novel biodegradable type flame retardant based on phosphorylated cellulose derivatives was synthesized by the reaction of phosphorylated cellulose with ammonium hydroxide at room temperature. The incorporation of PCA could improve effectively the flame retardancy of PVA matrix. When the PCA content reached 15 wt%, the PVA/PCA composites could meet the UL-94 V-0 classification and got the LOI value of 30.0. Thermal and combustion properties of PVA composites were investigated by TGA and MCC. The mechanical property of PVA/PCA composites was also investigated by DMTA. All results indicated that the novel flame retardant can improve the thermal stability and flame retardancy of PVA matrix.

2. Experimental part

2.1. Materials

Poly(vinyl alcohol) (PVA) with the degree of polymerization of 1788 ± 50 and the degree of saponification of 98%, was purchased from Aldrich Chemical Corp. Microcrystalline cellulose (Avicel PH101) delivered as a dry powder with $20 \mu\text{m}$ average particle size, was used and purchased from ShangHai Gaoli Chemical Company. Ethanol, phosphorous acid and ammonia solution were received from Changzheng Chemical Reagent Corp. The water used in this experiment was distilled.

2.2. Synthesis of PCA

Phosphorylated cellulose (PC) could be synthesized by the reaction of microcrystalline cellulose with phosphorous acid in molten urea [18–20]. In a 250 ml three-necked flask equipped with a nitrogen inlet, a condenser and a stirrer, 12.48 g (0.208 mol) urea was added, heated at 140°C and flushed with nitrogen atmosphere. 2 g (0.012 mol) microcrystalline cellulose and 10.28 g (0.125 mol) phosphorous acid were added alternatively portionwise to the molten urea. The reaction was allowed to proceed at 150°C for 5 h. After that, the reacted mixture was dissolved in water, then precipitated with ethanol. The process was repeated several times until the supernatant become clarified. And then the phosphorylated cellulose was dried in vacuum oven at 65°C for 12 h in presence of phosphorus pentoxide. Phosphorylated cellulose (PC) was a white and water-soluble powder.

In a 250 ml, three-necked flask equipped with a nitrogen inlet, a condenser and a stirrer, phosphorylated cellulose was added. And then 60 ml water was introduced. The mixture was stirred at room temperature until the solution was obtained. Then 16 g ammonia water was added to the above solution. The reaction was continued for 0.5 h. The product was washed with ethanol for three times and

then dried at vacuum oven at 65°C for 24 h in the presence of phosphorus pentoxide. The final product was a white, water-soluble powder. The synthetic route is shown in Scheme 1.

2.3. Preparation of PVA/PCA composites

PVA was dissolved in deionized water at 90°C in a three-neck flask with mechanical stirring. After an aqueous solution (0.08 g/ml) was formed, PCA was added to the above solution, stirring slowly for 6 h. At last, the blend was cast into glass plates and dried at 40°C for 2 days to form flat membranes. Then membranes were peeled off and further heated at 80°C for another 2 days to remove residual water. As a result, the thickness of obtained membranes was $0.5 \pm 0.1 \text{ mm}$.

2.4. Characterization

FTIR spectra were recorded on a Nicolet MAGNA-IR 750 FTIR spectrometer. KBr ground in a mortar with a pestle and enough solid sample was ground with KBr to make a 1 wt.% mixture for making KBr pellets. The mixture was pressed into a tablet, which was then placed in a ventilated oven. The transition mode was used, and the wavelength range was set from 4000 to 500 cm^{-1} .

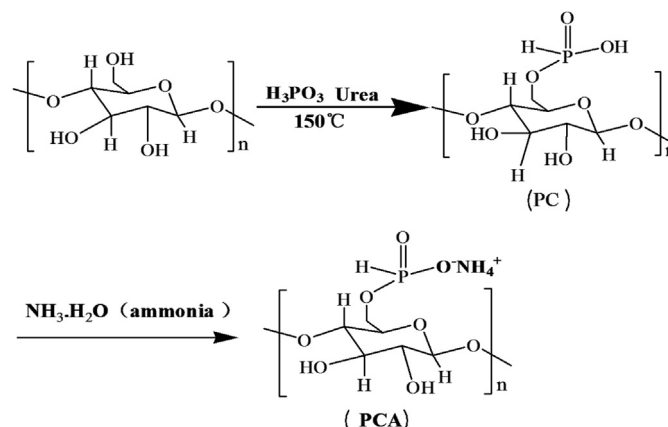
The X-ray photoelectron spectroscopy measurement was carried out using an ESCALAB MK II (VG Co., Ltd., England) spectrometer with Al K α excitation radiation ($h\nu = 1253.6 \text{ eV}$) in ultrahigh vacuum conditions.

Heat release rate (HRR) and total heat release (THR) were measured in a microscale combustion calorimeter (GOVMARK MCC-2). About 5 mg samples were heated at a heating rate of 1 K/s in a nitrogen stream flowing at $80 \text{ cm}^3/\text{min}$. The degradation products of the sample in nitrogen atmosphere were mixed with a $20 \text{ cm}^3/\text{min}$ stream of pure oxygen prior to entering a 900°C combustion furnace.

The vertical burning test was conducted by a CZF-II horizontal and vertical burning tester (Jiang Ning Analysis Instrument Company, China). The specimens used were $130 \times 13 \times 0.5 \text{ mm}^3$ according to ASTM D3801.

LOI was measured using an HC-2 oxygen index meter (Jiang Ning Analysis Instrument Company, China) on sheets $100 \times 6.5 \times 0.5 \text{ mm}^3$ according to the standard oxygen index test GB/T 2406-93.

The TGA of samples was examined on a TGA-Q5000 apparatus (TACompany, USA) from 50 to 700°C at a heating rate of $20^\circ\text{C}/\text{min}$. The weight of all samples was kept within 3–5 mg in an open Al pan.



Scheme 1. Synthesis route of PCA.

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