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Flame retardancy of polyaniline-deposited paper composites prepared via in situ polymerization

Xianna Wu, Xueren Qian*, Xianhui An

Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin, Heilongjiang Province 150040, China

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ABSTRACT

Polyaniline-deposited paper composites doped with three inorganic acids were prepared via in situ polymerization, and their flame-retardant properties were investigated. Both the conductivity and flame retardancy of the composite increased with the increase of the amount of the polyaniline deposited. The doping acid played a very key role in both the conductivity and flame retardancy of the composite. The comprehensive properties of the composite could be improved when codoped with an equimolar mixture of H_3PO_4 and H_2SO_4 or H_3PO_4 and HCl. The decay of the flame retardancy of the composite in atmosphere was due to the dedoping of the polyaniline deposited on cellulose fibers.

1. Introduction

Conducting polymers such as polyaniline and polypyrrole have been deposited onto cellulose fibers to prepare conductive paper via the in situ chemical polymerization (Ding, Qian, Shen, & An, 2010; Ding, Qian, Yu, & An, 2010; Li, Qian, Chen, Ding, & An, 2010; Li, Qian, Wang, & An, 2010; Song, Qian, Wang, & Xie, 2006; Song, Qian, & Wang, 2006). The finding that conducting polymers are flame retardant agents is relatively recent and not yet widely studied and documented (Varesanol, Toninl, Ferrero, & Stringhetta, 2008). Plenty of researches have been carried out on the electrical conductivity property of conductive paper, but there are less reports on the study of the flame retardancy.

As one of conducting polymer materials, polyaniline has showed broad prospect of applications in various fields such as diode, electrochromism, sensor, secondary battery and electromagnetic shielding (Feng, Nuli, & Yang, 2007; McGovern, Spinks, & Wallace, 2005; Paligová et al., 2003; Xing et al., 2006; Zhang, Tao, Wei, Gong, & Wu, 2007). It has been reported that the polyaniline deposited on organic fibers has a flame retardant property (Bhat, Seshhadri, & Radhakrishnan, 2004). Cellulose fibers deposited with polyaniline yielded hollow carbonaceous microtubes after burning (Stejskal, Trchová, & Sapurina, 2005). There were also researches on the flame-retardation effect of polyaniline coating deposited on cotton (Bhat et al., 2004) and polyester fabrics (Salgaonkar & Jayaram, 2004). However, there are seldom reports about the flame retardancy of conductive paper composite deposited with conducting polymers such as polyaniline and polypyrrole.

In our previous studies, the possibility of several inorganic acids (e.g., sulfuric acid, hydrochloric acid, and nitric acid) and organic acids (*p*-toluene sulfonic acid, sulfosalicylic acid, and monochloroacetic acid) as the dopant in the preparation of polyaniline-deposited cellulose fiber composites was examined (Qian, Song, & Wang, 2006; Song, Qian, Wang, & Xie, 2006; Song, Qian, & Wang, 2006). Generally, inorganic acids are cheaper than organic acids. In addition, phosphoric acid is a good flame retardant. Therefore, three inorganic acids (i.e., sulfuric acid, hydrochloric acid, and phosphoric acid) were chosen to investigate the flame retardancy of polyaniline-deposited paper composite considering both its manufacturing cost and performance requirements.

In the present study, electro-conducting paper composites were prepared via the in situ polymerization of aniline in the presence of cellulose fibers in different doping acid solutions, and the flame-retardant property and conductivity of the resulting paper composites were investigated. The dedoping and redoping experiments were carried out to determine the role of the doping acid on polyaniline backbone in the flame retardancy of the composite.

2. Experimental

2.1. Materials

Bleached softwood kraft pulp imported from Canada was obtained from Mudanjiang Hengfeng Co., Ltd., and was beaten by

* Corresponding author at: No. 26, Hexing Road, Xiangfang District, Harbin City, Heilongjiang Province 150040, China. Tel.: +86 451 82192081; fax: +86 451 82192081.
E-mail address: qianxueren@yahoo.com.cn (X. Qian).

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Valley beater to a degree of 30° SR. Aniline monomer was purchased from Tianjin Tianli Chemical Reagents Co., Ltd., and was distilled under reduced pressure before use. Ammonium persulfate used as the oxidant was purchased from Tianjin Yongda Chemical Reagents Development Center, sulfuric acid (98%), hydrochloric acid (37%) and phosphoric acid (85%) were purchased from Beijing Yili Fine Chemicals Co., Ltd., and ammonia (25%) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. All the solutions were prepared from distilled water.

2.2. Preparation of electro-conducting fibers and handsheet

6.67 g of pulp fibers (oven-dry weight) were placed in a three-neck flask in an ice bath with a certain amount of aniline monomer, and then acid solution was poured into the flask in a certain concentration to keep pulp consistency at 1%. After stirring for 40 min, ammonium persulfate solution was dropwise added into the reaction system slowly to start the polymerization reaction. The mass ratio of aniline monomer to ammonium persulfate was 4:3. The reaction was conducted with continuous stirring for 105 min (Song, Qian, Wang, & Xie, 2006; Song, Qian, & Wang, 2006). The resulting modified fibers were washed with tap water several times and then a handsheet with a grammage of over 210 g/m^2 was made on a ZCX-200 handsheet former. The handsheet was pressed at 800 kPa for 2 min and dried at 105 °C for 10 min (5 min each side). The handsheet was conditioned at 23 °C and 50% relative humidity for 24 h before testing.

2.3. Dedoping and redoping

2.3.1. Dedoping

The composite fibers prepared according to the procedure described in Section 2.2 were treated with 0.6 mol/L ammonia solution at room temperature for 1 h.

2.3.2. Redoping

The dedoped composite fibers were treated with 0.6 mol/L acid solution at room temperature for 1 h.

2.4. Measurement of conductivity

Both the square resistance and bulk resistivity of the handsheets were measured by a four-point probe resistance tester and expressed as $R_{\square}$ (kΩ), ρ (kΩ cm), respectively. Since the bulk resistivity is related with the dimension of handsheet, the thickness (T) and basis weight (W) were measured beforehand.

The conductivity expressed as k was the inverse of the bulk resistivity, which expressed in SI unit of Siemens per meter (S/m), and was calculated as follows:

$$k = \frac{1}{10\rho} \quad (1)$$

2.5. Calculation of polyaniline deposition

The amount of polyaniline deposited on cellulose fibers was expressed as A (%), which was determined according to the following equation:

$$A = \frac{W - W_0}{W_0} \times 100\% \quad (2)$$

where, W_0 and W are the basis weight of the handsheets made from the cellulose fibers before and after polyaniline deposition, respectively, g/m^2.

2.6. Measurement of oxygen index

The flame retardancy of paper was determined in terms of the oxygen index (OI) which measured on a JF-3 Oxygen Index Meter made in China. The paper sample was cut into strips (120 mm × 15 mm), and then the strip was placed in the combustor where a mixture of oxygen and nitrogen flows upwards. The volume content of the oxygen was adjusted to keep the lowest oxygen concentration which just supported sustained burning. Oxygen index was expressed in volume percentage. Generally, an oxygen index of more than 25% is considered to be satisfactory for flame retardancy in paper and paperboard (Chen, Qian, & An, 2012).

2.7. SEM, XPS and TG analysis

Scanning electron microscopy (SEM) observations were carried out using an FEI Quanta-200 environment scanning electronic microscope. The sample surfaces were coated with gold before observations.

X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5700 ESCA System with an Al Kα X-ray source (1486.6 eV). The pass energies for the wide and narrow scans were 187.85 and 29.35 eV, respectively.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 6 Thermogravimetric Analyzer. The samples were heated from 40 °C to 700 °C at a heating rate of 10 °C/min and under a nitrogen flow rate of 20 mL/min.

3. Results and discussion

3.1. Characterization of burning products

The paper samples made from both unmodified and modified pulp fibers were ignited, and the burning process and the morphological changes of burning products were observed. It was found that the paper sample made from unmodified pulp fibers was burned very rapidly, and the amount of the residues was very little (only 0.004%). On the contrary, the paper sample made from modified pulp fibers was burned very slowly, and the amount of the residues was relatively higher (26.8%) and still held its original paper shape. The SEM images of polyaniline-deposited paper before and after burning are shown in Fig. 1. It can be observed that the polyaniline-deposited paper still retained its original fibrilar morphology after burning. XPS analysis was conducted to probe the change in elemental composition of polyaniline-deposited paper before and after burning. The phosphorus and sulfur contents were zero, the carbon content was significantly increased (from 70.49% to 86.69%), and the oxygen content was markedly decreased (from 22.18% to 5.14%) in the residue after burning, which indicated that cellulose was converted into char by acid catalysis. It is well-known that a noticeable difference between char and cellulose is the content of carbon and oxygen.

3.2. Effect of polyaniline

The mass ratio of fiber/aniline was changed during the preparation of polyaniline-deposited cellulose fibers to investigate the effect of polyaniline deposition on the conductivity and flame retardancy of the paper composite. As seen in Table 1, the amount of polyaniline deposited on cellulose fibers increased with increasing the dosage of aniline, and thereby both the conductivity and OI value of the paper composite increased. The conductivity and OI value of the paper composite were approximately invariant after the mass ratio of fibers/aniline was over 1:2, which indicated that the excess amount of polyaniline deposited on cellulose fibers was no contribution to the conductivity and flame retardancy. It could