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Further improvement of flame retardancy of polyaniline-deposited paper composite through using phytic acid as dopant or co-dopant

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ABSTRACT

Polyaniline (PANI)-deposited electrically conductive and flame retardant paper composite was prepared using phytic acid (PA) as dopant or co-dopant. PA as doping acid greatly improved the flame retardancy of PANI-deposited paper composite whilst the conductivity was lower compared with using 5-sulfosalicylic acid (SSA) as doping acid. Lower temperature was favorable to obtain PANI-deposited paper composite with both higher conductivity and better flame retardancy. Conductivity of PANI-deposited paper composite increased with increase of doping acid concentration and the suitable PA concentration range was 0.15–0.3 mol/L depending on the requirement of conductivity and flame retardancy. The PANI-deposited paper composite was characterized by SEM, TGA and XPS. The outstanding flame retardancy of PA-doped paper composite was caused by the synergetic effect of PANI coating and H_3PO_4. Both higher flame retardancy and higher conductivity of PANI-deposited paper composite were obtained by co-doping of SSA with PA.

1. Introduction

In recent years, the research and development of conductive-polymer-deposited cellulose fiber composites were extensively concerned. Up to now, the involved conductive polymers mainly included polyaniline (PANI) (Camacho, Gerongay, & Macalinao, 2013; Goto, 2011; Gu & Huang, 2013; Janaki, Vijayaraghavan, Oh, Ramasamy, & Kamala-Kannan, 2013; Johnston, Moraes, & Borrmann, 2005; Li, Qian, Wang, & An, 2010a; Liu, Qian, Shen, Zhou, & An, 2012; Liu, Zhou, Qian, Shen, & An, 2013; Müller et al., 2012), polypyrrole (PPY) (Ding, Qian, Shen, & An, 2010a; Ding, Qian, Yu, & An, 2010b; Huang, Kang, & Ni, 2005; Huang, Kang, & Ni, 2006; Johnston et al., 2005; Li, Qian, Chen, Ding, & An, 2010b; Lei, Qian, Shen, & An, 2012; Lei, Qian, Shen, & An, 2013; Qian, Chen, & An, 2010; Wang et al., 2013), and poly(3,4-ethylenedioxythiophene) (PEDOT) (Chen, Qian, & An, 2011). Their applications were mainly focused in two areas: (1) antistatic package, electromagnetic shielding and sensor by utilizing their electrical conductivity; and (2) detoxication of chromium(VI) and textile effluent by utilizing their redox behavior.

Some studies found that conductive polymers are also good flame retardant agents. There were researches on the flame-retardation effect of PANI coating deposited on cotton (Bhat, Seshhadri, & Radhakrishnan, 2004) and polyester fabrics (Salgaonkar & Jayaram, 2004). It has also been reported that cellulose fibers deposited with PANI yielded hollow carbonaceous microtubes after burning (Stejskal, Trchová, & Sapurina, 2005). The carbonization of PANI composites was studied to obtain a novel nitrogen-containing carbon-like material in some recently published articles (Ciric-Marjanovic, Pasti, Gavrilov, Janošević, & Mentus, 2013; Morávková, Trchová, Exnerová, & Stejskal, 2012a; Morávková, Trchová, Tomšík, Čechvala, & Stejskal, 2012b; Morávková, Trchová, Tomšík, & Stejskal, 2013; Rozlívková, Trchová, Exnerová, & Stejskal, 2011; Stejskal, Trchová, Brodinová, & Sapurina, 2007; Trchová, Konyushenko, Stejskal, Kovářová, & Ćirić-Marjanović, 2009). These studies promoted us to investigate the feasibility of preparing the PANI-deposited cellulose fiber composite with both electrical conductivity and flame retardancy.

In our previous studies, PANI-deposited electrically conductive and flame retardant paper composite was prepared via the in situ polymerization of aniline in the presence of cellulose fibers. The research results proved that doping acid played a very key role in both the conductivity and flame retardancy of the paper composite. The used doping acids included both inorganic doping acids (sulfuric acid, hydrochloric acid and phosphoric acid) (Wu, Qian, & An, 2013) and organic doping acids (*p*-toluenesulfonic acid (PTSA) and sulfosalicylic acid (SSA)) (Mao, Wu, Qian, & An, 2014).

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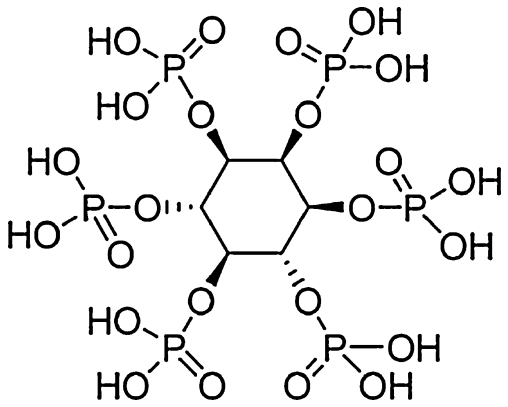

Fig. 1. Structure of phytic acid (PA).

Generally, organic acids showed great better doping effect than inorganic acids in both conductivity and flame retardancy. Among these acids, SSA was proved to be the best dopant. However, there is still room for further improvement regarding to the flame retardancy of PANI-deposited paper composite.

A recent research indicated that the thin films of cationic chitosan (CH) and anionic phytic acid (PA) deposited on cotton fabric via layer-by-layer (LbL) assembly were able to effectively reduce flammability (Laufer, Kirkland, Morgan, & Grunlan, 2012). PA is a major component of plant seeds, constituting 1–3% by weight of many cereals and oilseeds and typically accounting for 60–90% of the total phosphorus (Graf, 1984). As an environmentally friendly, biocompatible, nontoxic, inexpensive and easily obtained organic acid, PA is extensively applied in biosensor, nanomaterial, cation exchange resin, anticorrosion and other fields because of its special inositol hexaphosphate structure shown in Fig. 1 (Jiang, Qiao, & Hong, 2012). From a flame-retardant perspective, molecules with higher phosphorus content can deliver more active flame retardant atoms per molecule, and PA has remarkable 28 wt% phosphorus based upon molecular weight. This aroused our interest to use PA as dopant or co-dopant in an endeavor to further improve the flame retardancy of PANI-deposited paper composite.

In the present study, PANI-deposited electrically conductive and flame retardant paper composite was prepared through using PA as dopant or co-dopant to further improve the flame retardancy. The PANI-deposited paper composite was characterized by SEM, TGA and XPS. The major factors affecting conductivity and flame retardancy, including dopant concentration, reaction temperature and time were analyzed. Co-doping effect of SSA with PA was studied as well. In addition, the conductivity and flame retardancy stability of the PANI-deposited paper composites in the natural environment were investigated.

2. Experimental

2.1. Materials

Bleached softwood kraft pulp from Canada was obtained from Mudanjiang Hengfeng Co., Ltd., and was beaten by Valley beater to a degree of 30°SR. Aniline monomer was purchased from Tianjin Tianli Chemical Reagents Co., Ltd., and was distilled and refrigerated before use. Ammonium persulfate (APS) used as the oxidant was purchased from Tianjin Yongda Chemical Reagents Development Center. 5-Sulfosalicylic acid dihydrate (SSA) was of AR grade and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Phytic acid (PA) (70% aqueous solution) was of BR grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification and all the solutions were prepared with distilled water.

2.2. Preparation of fiber composite and paper

Four gram pulp fibers (oven-dry basis), doping acid solution and 6 g aniline were placed in a three-neck flask under stirring. After stirring for 40 min, APS solution was dropwise added into the reaction system slowly to start the polymerization reaction. The mass ratio of aniline monomer to APS was 4:3, and the pulp consistency was kept at 1% (Song, Qian, & Wang, 2006a; Song, Qian, Wang, & Xie, 2006b). After the reaction time completed, the mixture was diluted with water to stop the polymerization and then washed with water. A handsheet with a grammage of over 120 g/m^2 was made on a ZCX-200 handsheet former. The handsheet was pressed at 400 kPa for 5 min and dried at 105 °C for 6 min (3 min each side). The handsheet was kept in the atmospheric environment for 24 h before testing.

2.3. Measurement of conductivity

After conditioning in air at room temperature for 24 h, the square resistance and bulk resistivity of the handsheets were measured by a four-point probe resistance tester (Guangzhou Ximei Electric Co., Ltd.). The conductivity was the inverse of the bulk resistivity and expressed in SI unit of Siemens per meter (S/m).

2.4. Measurement of oxygen index (OI)

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 (Chen, Qian, & An, 2012; Wu et al., 2013; Mao et al., 2014).

2.5. Measurement of environmental stability

Paper samples from Section 2.2 were stored in atmospheric environment to investigate the environmental stability. Conductivity and flame retardancy of paper samples were measured once every 15 days.

2.6. SEM, TG and XPS analyses

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

Thermogravimetric analysis (TGA) was performed on TG 209 F3 Tarsus Thermogravimetric Analyzer from NETZSCH Tarsus. The samples were heated from 40 to 600 °C at a heating rate of 10 °C/min and under a nitrogen flow rate of 20 mL/min.

X-ray photoelectron spectroscopic (XPS) data were obtained using a Thermo Fisher Scientific's *K*-Alpha X-ray photoelectron spectrometer (XPS) system. An Al *K*α X-ray source was used. The vacuum in the analyzing chamber was 1.0×10^{-8} Pa during analysis. The analyzer was operated at 50 eV pass energy for survey spectra. Elemental atomic concentrations were calculated from the XPS peak areas.