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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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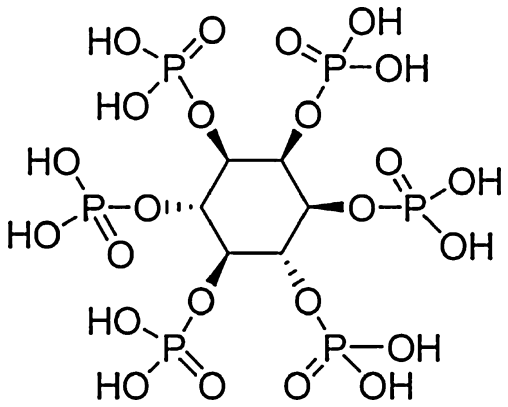

Fig. 1. Structure of phytic acid (PA).

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.

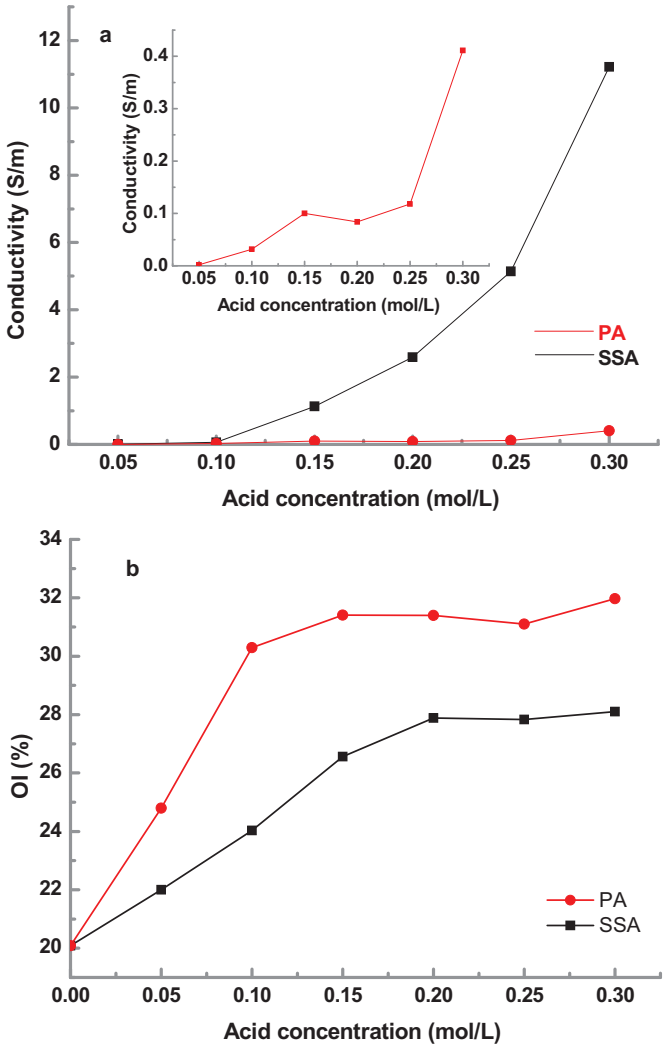

Fig. 2. Effect of doping acid concentration on conductivity (a) and OI (b) of PANI-deposited paper prepared at room temperature (20 °C) for 105 min.

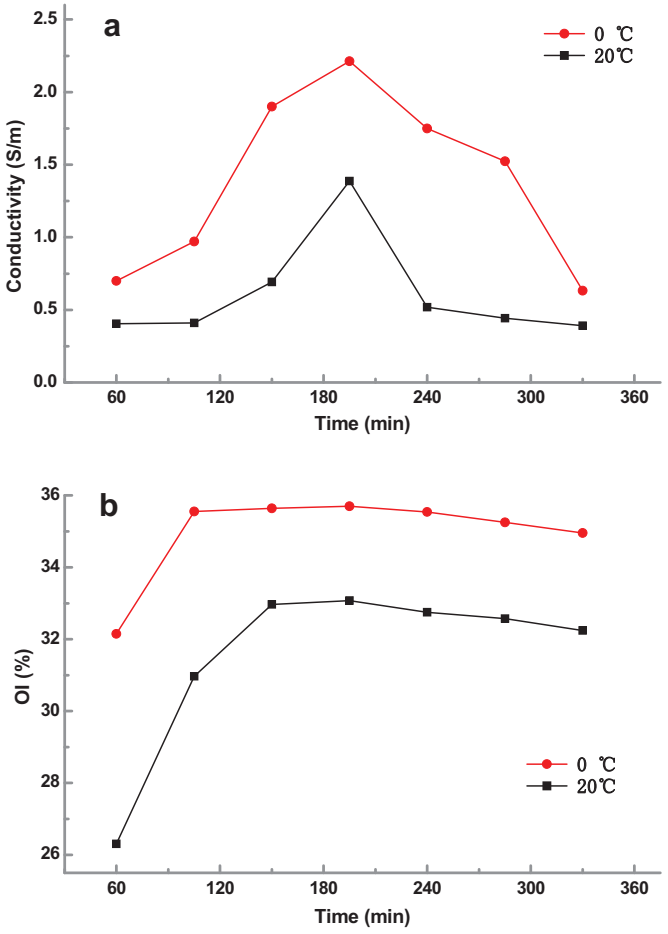

Fig. 3. Effect of time and temperature on conductivity (a) and OI (b) of PANI-deposited paper (all samples were prepared in 0.3 mol/L phytic acid).

3. Results and discussion

3.1. Effect of doping acid concentration

The effect of doping acid concentration on the electrical conductivity and flame retardancy of PANI-deposited paper prepared at room temperature (20 °C) for 105 min is shown in Fig. 2. The electrical conductivity of the paper composite sample increased with increasing the concentration of doping acid, and sulfosalicylic acid (SSA) performed much better than phytic acid (PA). Amongst those adopted doping acid concentrations, the highest conductivity was obtained at 0.3 mol/L for both SSA and PA. It could be speculated that the electrical conductivity of the paper composite sample had a close relationship with the species and concentration of doping acid and higher doping acid concentration got paper composite with higher conductivity. The OI value of the paper sample made from undeposited pulp fibers (i.e., the control sample) was 20.09%. The OI value of the paper composite sample prepared without doping acid (i.e., the concentration doping acid was 0 mol/L) was around 20.10%, which was nearly the same as that of the control sample. The OI value of the paper composite sample increased with the increasing concentration of doping acid. And PA outperformed SSA as doping acid in improving the flame retardancy of the paper composite. The OI of PA doped paper composite reached 31.41% (local maximum) at concentration of 0.15 mol/L and that of SSA doped sample reached 27.88% (local maximum) at concentration of 0.2 mol/L. Nevertheless no obvious variations of OI value were observed as further increasing the concentrations of doping acid. So considering conductivity concurrently, the suitable concentration of PA would be at the range of 0.15–0.3 mol/L.

3.2. Effect of temperature and time

As shown in Fig. 3, reaction temperature and time also significantly affected conductivity and OI value (doping acid: PA, aniline concentration: 15 g/L). Paper composite prepared at lower temperature (0 °C) outperformed the sample prepared at higher temperature (20 °C) in conductivity and flame retardancy. That is because polymerization of aniline is an exothermic reaction (Bavane, Shirsat, & Mahajan, 2010; Li, Huang, & Kaner, 2009; Šeděnková, Trchová, Blinova, & Stejskal, 2006); lower temperature can facilitate the polymerization and produce more PANI. Larger amount of PANI can contribute to better performance in both conductivity and flame retardancy (Wu et al., 2013).

Reaction time is another important factor. Conductivity increased and then decreased with the increase of time. The probable cause was that a certain period of time was required for the polymerization of aniline. When the reaction time was not long enough, the degree of polymerization and doping level of PANI were low. As a consequence, the small molecular weight and short conjugation chain of the polymerized aniline were resulted. The conductivity and OI value were lower accordingly. The OI value

increased obviously until the reaction time approached 105 min at 0 °C and 150 min at 20 °C. And the conductivity reached the highest when the reaction time was 195 min at both temperatures. The OI value only dropped slightly if the reaction time was prolonged. The conductivity decreased with a longer reaction time perhaps due to undesired reactions like formation of aniline oligemers, pH decrease of the medium and deprotonation of PANI (Brožová, Holler, Kovářová, Stejskal, & Trchová, 2008; Stejskal and Trchová, 2012; Stejskal, Sapurina, & Trchová, 2010).

3.3. SEM, TG and XPS characterization

Unlike the smooth surface of the control sample (Fig. 4a), PANI depositing was observed from the PA doped composite fiber (Fig. 4c). These observations indicated the PANI (30.38%, based on oven-dried fibers) was successfully deposited on the fiber surface. Compared with the PANI on the SSA doped composite fiber (33.69%, based on oven-dried fibers, Fig. 4b), PANI particles on the PA doped composite fiber had larger size and slightly lower amount. XPS results from our previous study confirmed that the bond between PANI and cellulose existed in the form of hydrogen bonding (Li et al., 2010a,b), which deposition was irreversible. Protonic acid is doped in PANI through ion pairs. The binding is reversible, and easy to be dedoped in humid air or alkaline solution.

It can be observed from Fig. 5 that the thermogravimetric curves of the paper samples doped with the acids had the same trend, but they were markedly different from that of the control sample. The weight loss of the paper sample doped with PA was the lowest. Both of the composite samples had a total weight loss of 54–58% when the temperature reached 600 °C but the control lost notably 90%. The peak temperatures of maximum decomposition for PA and SSA doped composites were 240 °C and 285 °C, respectively, much lower than that of the control (350 °C). These curves showed the maximum decomposition temperatures of the doped composites were decreased greatly. The PANI coating deposited on cellulose fibers may produce a barrier to oxygen diffusion into the burning material, thus reduce its combustion (Stejskal et al., 2005).

As for the PA doped PANI paper, a series of degradation reactions of PA (insitol hexaphosphate) occurred at around 300 °C. PA was hydrolyzed into inositol and orthophosphoric acid (H_3PO_4) (Jiang et al., 2012). It has already well known that H_3PO_4 has effective flame retardance. So a better flame retardance (namely higher OI value) of PA doped PANI paper may be due to the synergetic effect of PANI coating and H_3PO_4.

Like the previous observation (Wu et al., 2013), the paper sample made from PANI-deposited pulp fibers doped by PA was burned very slowly, and the amount of the residues was much higher and still held its original paper shape. It can be observed through SEM that the PANI-deposited paper doped by PA still retained its original fibrilar morphology after burning (SEM images not shown here). XPS analysis showed the phosphorus content was decreased from 2.83% to 0.88%, the carbon content was significantly increased (from 54.44% to 93.71%), and the oxygen content was markedly decreased (from 34.88% to 4.30%) in the residue after burning, which indicated that cellulose was converted into char.

As shown in Fig. 6, the XPS N1s spectrum of PANI-deposited paper doped by PA could be deconvoluted into three distinct curves, which were related to the benzenoid amine (—NH) (peak at 399.7 eV), the protonated imine (—N^+=) (peak at 400.8 eV) and the quinoid imine (—N=) at around 398.0 eV, respectively, quite different from that of PANI-deposited paper doped by SSA (Mao et al., 2014). The very small amount of protonated amine (—N^+—) at higher binding energy indicated that a small formation of bipolaron. The existence of quinoid imine (—N=) indicated that the quinoid imines were not fully protonated by PA, which was agreement with the small amount of phosphorus in the composite paper and the low conductivity of the composite paper.

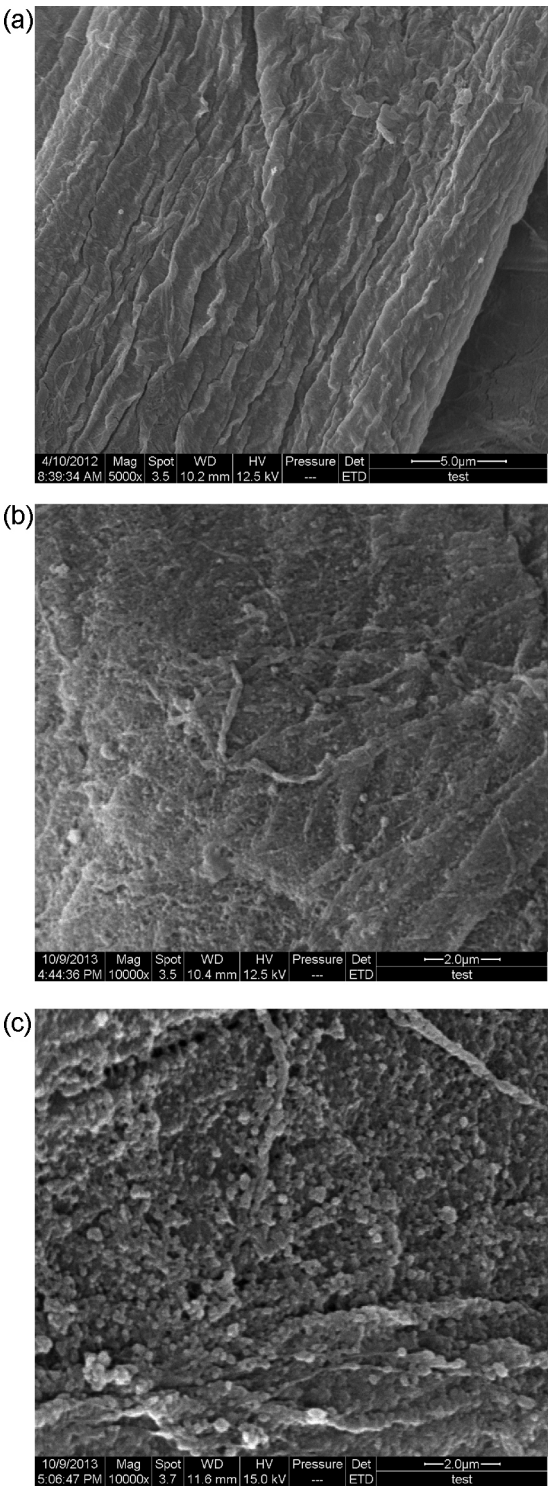

Fig. 4. SEM images of control paper sample (a), PANI-deposited paper samples doped with SSA (b) and PA (c) (all samples were prepared in 0.3 mol/L acid solution at ice bath temperature (0 °C) for 105 min).

3.4. Co-doping effect of SSA with PA

As discussion above, PA doping was able to improve the flame retardancy of the paper composite effectively. SSA doping was proved to benefit for the conductivity of the paper composite.

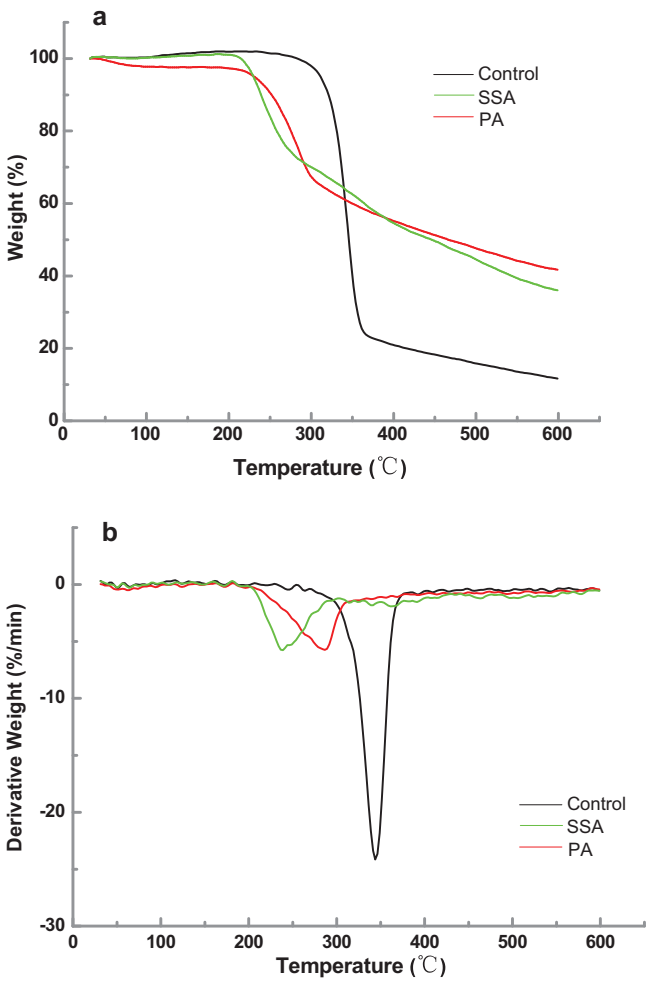

Fig. 5. TGA (a) and DTG (b) curves of PANI-deposited paper samples doped with different doping acids (all samples were prepared in 0.3 mol/L acid solution at ice bath temperature (0 °C) for 105 min).

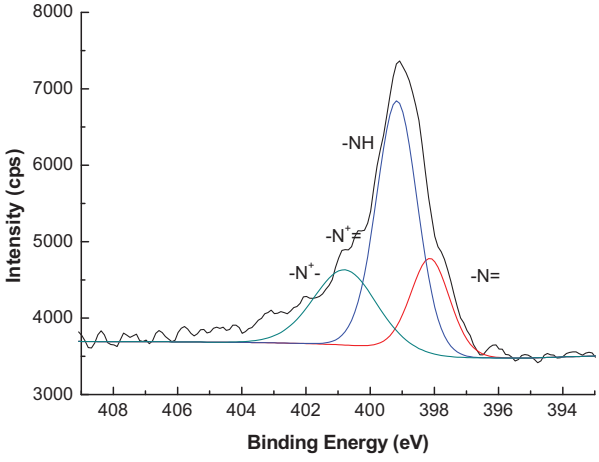

Fig. 6. XPS N1s spectrum of PANI-deposited paper sample doped with 0.3 mol/L PA at ice bath temperature (0 °C) for 105 min.

Co-doping of SSA with PA might offer an opportunity to obtain both higher conductivity and higher flame retardancy.

Conductivity and OI value of paper composite prepared using SSA and PA as codopants are shown in Fig. 7. The co-doping effect was quite apparent: Co-doping of SSA with PA could significantly enhance conductivity. The conductivity of co-doping samples was

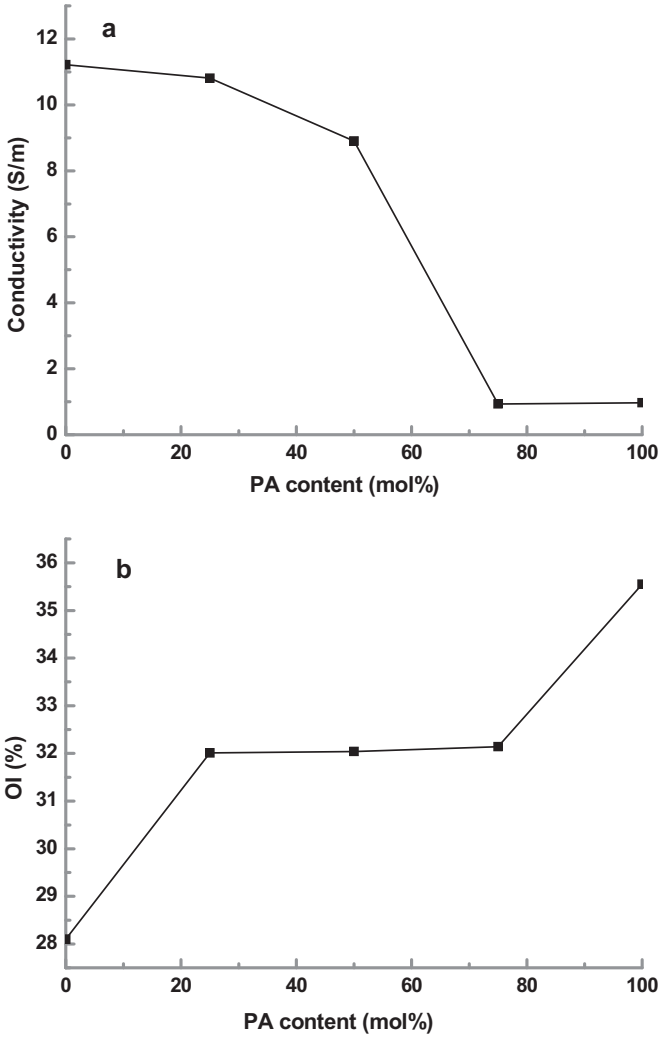

Fig. 7. Conductivity (a) and OI (b) of paper samples co-doped with a mixture of SSA and PA (all samples were prepared at total acid concentration of 0.3 mol/L at ice bath temperature (0 °C) for 105 min).

increased nearly by 10 times compared with 100% PA doped composite. OI value of the co-doping samples was still kept above 30%, and higher than that of SSA doped sample. When the molar fraction of PA was 25%, both of the conductivity and the flame retardancy were maintained at higher levels. Even higher fraction of PA led to much loss of conductivity.

3.5. Environmental stability

Environmental stability for the paper composite is particularly important for the applications, like package. So the conductivity and OI values of paper samples stored in atmospheric environment were measured every 15 days to investigate the environmental stability. As shown in Fig. 8, the conductivity decreased sharply within the first 30 days, especially the first 15 days. It remained basically stable after 30 days. The decay of conductivity probably stemmed from reactivity with atmosphere, especially oxygen. PANI, like other reactive and conducting organic materials, suffers from its poor environmental stability in air because of the chemical reaction of oxygen with the highly conjugated system of PANI. In contrast to most conducting polymers which are less stable in atmospheric environment, PANI is very stable (Ansari & Keivani, 2006). However, the PANI deposited on cellulose fibers is less stable in atmospheric environment compared with pure PANI film,

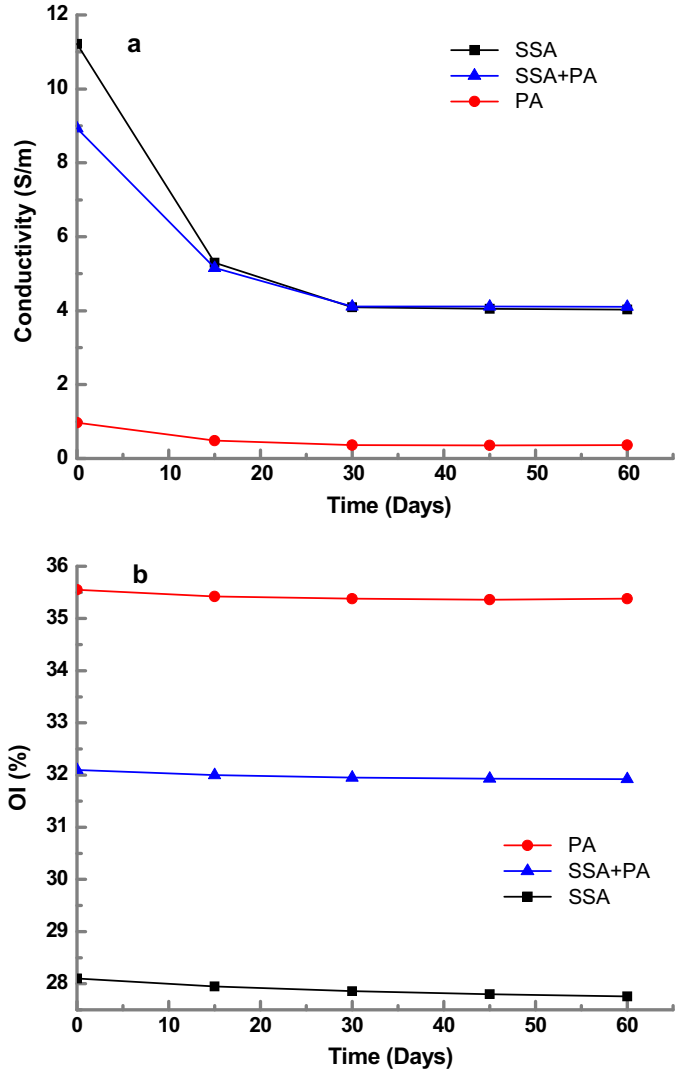

Fig. 8. Conductivity (a) and OI (b) of paper samples within 60 days of storage time (all samples were prepared at total acid concentration of 0.3 mol/L at ice bath temperature for 105 min, and the molar ratio of PA to SSA for the co-doped sample was 1:3).

because paper is a porous material, which results in the penetration of more oxygen. However, unlike the decay of conductivity, OI values decreased quite slightly within the investigation period.

4. Conclusions

PA was an excellent doping acid in improving flame retardancy of PANI-deposited paper composite. The outstanding flame retardancy of PA-doped paper composite was caused by the synergetic effect of PANI coating and H_3PO_4. The conductivity of PA-doped paper composite was poor due to the low doping level. Lower temperature was favorable to obtain PANI-deposited paper composite with both higher conductivity and better flame retardancy. Both higher flame retardancy and higher conductivity of PANI-deposited paper composite were obtained by co-doping of SSA with PA. The PANI-deposited paper composites possessed good flame retardancy stability in the atmospheric environment.

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