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

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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

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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

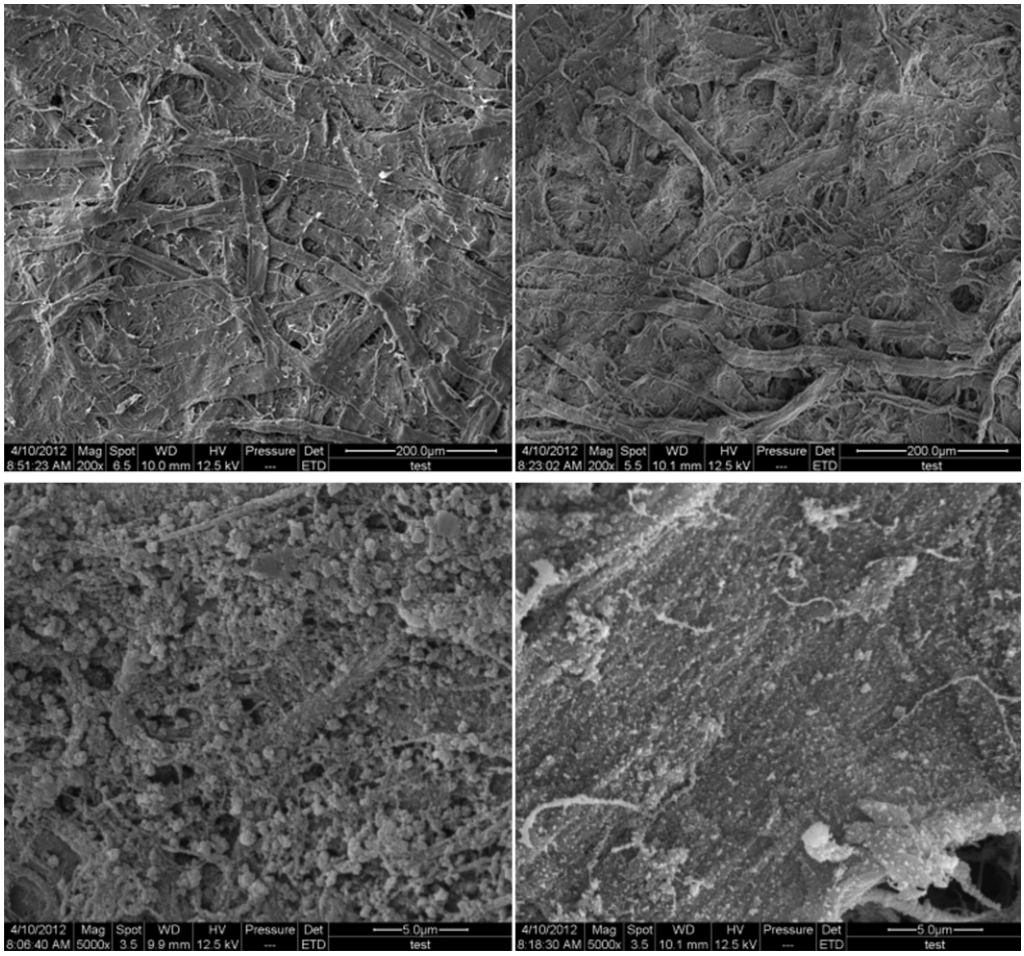

Fig. 1. SEM images of polyaniline-deposited paper before (left) and after (right) burning at lower (top) and larger (bottom) magnifications (sample was prepared in 1 mol/L phosphoric acid solution).

be speculated that both the conductivity and flame retardancy of the paper composite were attributed to the polyaniline deposited on cellulose fibers. However, whether the polyaniline itself or the doping acid incorporated into polyaniline backbone is contributed to the flame retardancy remains to be further discussed. Therefore, the dedoping and redoping experiments were designed to determine the effect of doping (see Section 3.3).

3.3. Effect of doping

The polyaniline/cellulose fibers doped with sulfuric acid, phosphoric acid and hydrochloric acid were dedoped and redoped to investigate the effect of doping on the conductivity and flame retardancy of the paper composite, and the results are shown in Table 2. The paper had no detectable conductivity, and the OI values all decreased and almost approached the blank value after dedoping. However, both the conductivity and flame retardancy of the paper composite were recovered to a certain degree after redoping. The conductivity change can be explained by the deprotonation of the polyaniline deposited onto cellulose fibers. The polyaniline in its non-protonated state is an electric insulator, it becomes an excellent semiconductor only after a protonic doping process which causes the delocalization of charges along the polymer backbone (Ayad, Amer, & Stejskal, 2009). On the other hand, the results in Table 2 verified that the flame retardancy of the paper composite had a close relationship with the incorporation of doping acid.

Thermogravimetric results of samples are shown in Fig. 2. The TGA and DTG curves of the dedoped sample were different from those of the doped and redoped samples, and the weight loss of the dedoped sample was higher than those of the other two samples. The TGA and DTG curves of the doped and redoped samples had the same trend, and both of them had a weight loss of 44–46% in the temperature range of 238–404 °C. The temperature at the maximum thermal decomposition rate was about 325 °C for the doped

Table 1
Effect of mass ratio of fibers/aniline on the properties of paper.[a]

Mass ratio of fibers/aniline	W (g/m^2)	T (mm)	A (%)	$R_{\square}$ (kΩ)	ρ (kΩ cm)	k (S/m)	OI (%)
1:0.25	224.82	0.39	4.81	Out of range	Out of range	–	20.31
1:0.5	234.21	0.40	9.19	Out of range	Out of range	–	21.61
1:1	258.09	0.46	20.32	3.717	0.164	0.619	26.54
1:1.5	282.56	0.53	31.73	2.068	0.112	0.894	28.81
1:2	297.26	0.54	38.58	1.360	0.0715	1.399	31.30
1:2.5	330.00	0.62	53.85	0.390	0.0965	1.336	31.90

[a] All samples were prepared in 1.0 mol/L phosphoric acid solution.

Table 2
Effect of doping on the properties of paper.

Sample[a]	W (g/m^2)	T (mm)	A (%)	$R_{\square}$ (kΩ)	ρ (kΩ cm)	k (S/m)	OI (%)
Blank	214.50	0.36	0	Out of range	Out of range	–	20.09
Doping							
H_3PO_4	284.92	0.52	32.83	2.585	0.140	0.712	28.60
H_2SO_4	284.94	0.51	32.84	1.744	0.0948	1.034	28.51
HCl	257.88	0.45	20.22	3.782	0.181	0.552	25.51
Doping–dedoping							
H_3PO_4	242.18	0.49	12.90	Out of range	Out of range	–	20.95
H_2SO_4	259.66	0.50	21.05	Out of range	Out of range	–	21.31
HCl	245.71	0.44	14.55	Out of range	Out of range	–	20.51
Doping–dedoping–redoping							
H_3PO_4	264.35	0.48	23.24	139.875	5.577	0.018	25.29
H_2SO_4	266.34	0.48	24.17	2.925	0.161	0.621	26.29
HCl	255.23	0.43	18.99	5.264	0.256	0.391	24.89

[a] All samples were prepared in 0.6 mol/L acid solution.

sample and was 370 °C for the dedoped sample, which indicated that the doping acid lowered the thermal decomposition temperature of cellulose. The TGA and DTG results confirmed that the flame retardancy of the composite was attributed to char formation catalyzed by the protonic acid doped on polyaniline backbone.

3.4. Effect of doping acid concentration

The effect of doping acid concentration on paper flame retardancy is discussed in this section in view of the importance of doping.

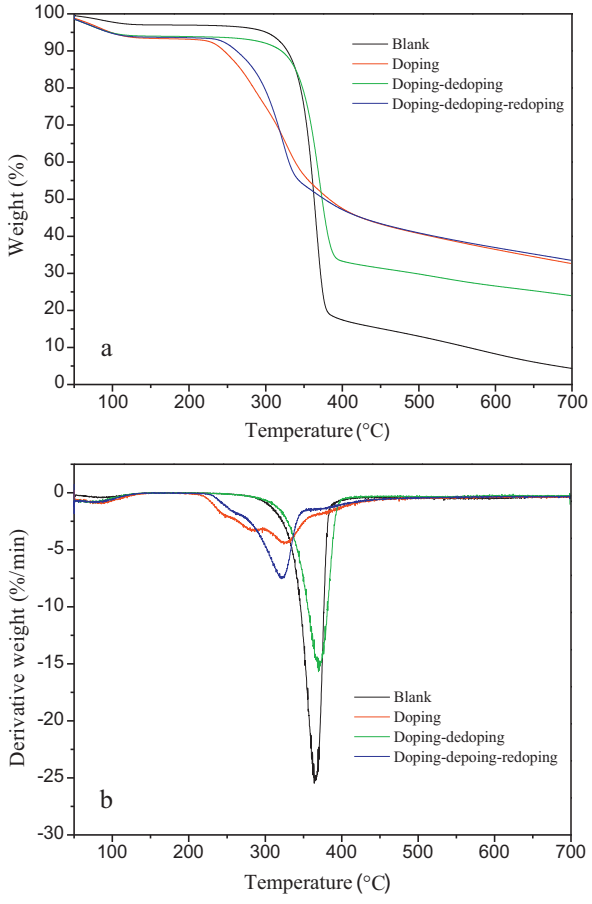

Fig. 2. TGA (a) and DTG (b) curves of paper samples made from original fibers (blank), polyaniline deposited fibers doped with phosphoric acid solution (doping), polyaniline deposited fibers doped with phosphoric acid solution then dedoped with ammonia solution (doping–dedoping), and polyaniline deposited fibers doped with phosphoric acid solution then dedoped with ammonia solution, finally redoped with phosphoric acid solution (doping–dedoping–redoping).

Fig. 3a shows that the conductivity of paper increased with increasing the concentration of doping acid, and sulfuric acid performed the best among the three doping acids. The highest conductivity value was obtained when the acid concentration was 1.0 mol/L for phosphoric acid and hydrochloric acid. Compared with Fig. 3b, small amounts of data points in Fig. 3a were missing because the bulk resistivity values of the samples prepared at less than 0.1 mol/L of doping acid concentration were beyond the range of the instrument used. It could be speculated that the conductivity of paper had a close relationship with the species and concentration of doping acid. The OI value of the paper made from unmodified pulp fibers (the blank paper sample) was 20.09%. Fig. 3b shows that the OI value of paper was around 20.0% at the acid concentration of 0.05 mol/L, which was nearly the same as that of the blank sample. The OI value increased with increasing the concentration of doping acid, and the highest value was obtained when the acid concentration was 0.6 mol/L. Phosphoric acid was the best doping acid among the three inorganic acids from the point view of flame retardancy.

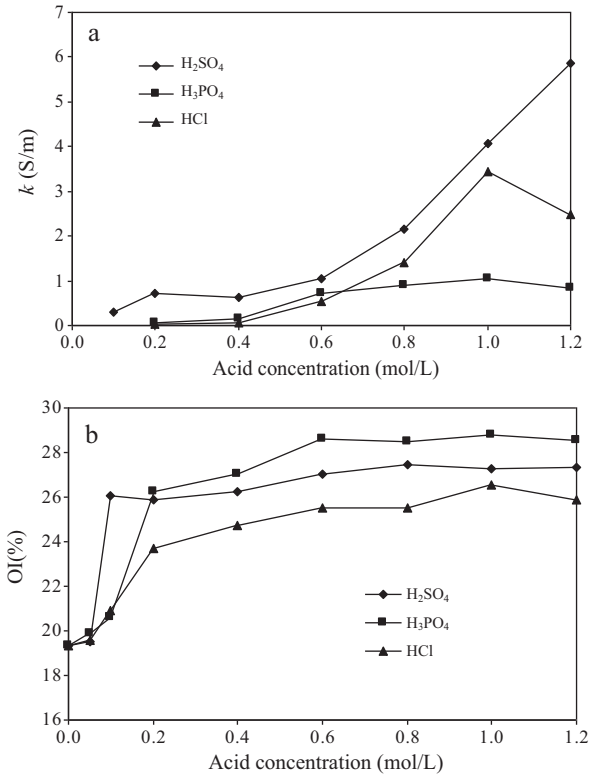

Fig. 3. Effect of doping acid concentration on conductivity (a) and OI (b) of paper.

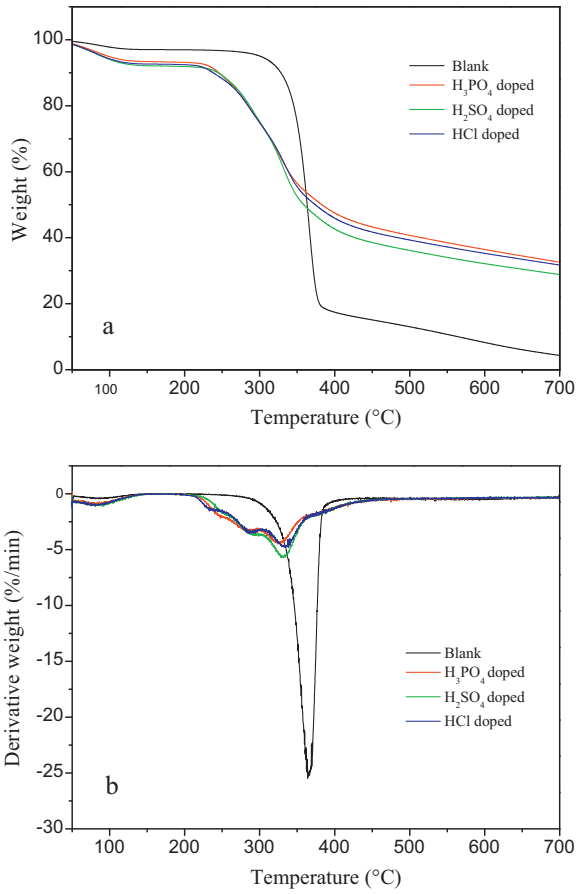

Fig. 4. TGA (a) and DTG (b) results of paper samples doped with different doping acids (all samples were prepared in 1 mol/L acid solution).

It can be observed from Fig. 4 that the thermogravimetric curves of the paper samples doped with three inorganic acids had the same trend, but they were markedly different from that of the blank sample. The weight loss of the paper sample doped with H_3PO_4 was the lowest among the three paper samples. All of them had a total weight loss of 67–72% when the temperature was 700 °C. The maximum decomposition peak temperatures for the three paper samples were all around 325 °C, lower than that of the blank (370 °C), indicating doping acid played an important role in the flame retardancy of conductive paper composite.

3.5. Effect of codoping

A previous study had indicated that the codoping of polyaniline with a mixture of two or more acids could improve both the doping level and conductivity of polyaniline (Shi & Shi, 2001). As the above discussed, H_2SO_4 and HCl were excellent doping acids for conductivity and H_3PO_4 was good doping acid for flame retandancy. The codoping with a mixture of H_3PO_4 and H_2SO_4 or H_3PO_4 and HCl was investigated to further improve the comprehensive properties of the paper composite. Fig. 5 shows that the codoping with a mixture of H_3PO_4 and H_2SO_4 or H_3PO_4 and HCl could improve both the conductivity and flame retandancy of the paper composite, and the codoping with a mixture of H_3PO_4 and H_2SO_4 was better than that with a mixture of H_3PO_4 and HCl. The comprehensive properties of the paper composite were excellent when the molar fraction of H_3PO_4 was 50% (i.e., equimolar mixture).

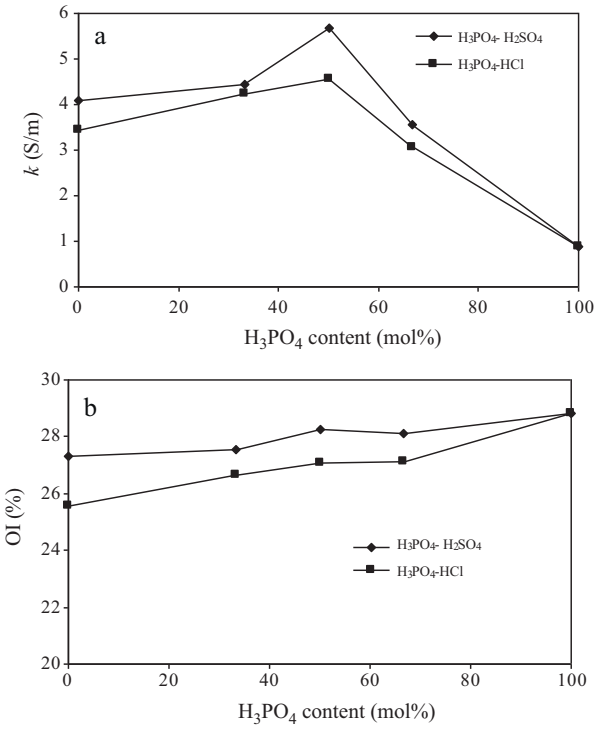

Fig. 5. Conductivity (a) and OI (b) of paper samples codoped with a mixture of H_3PO_4 and H_2SO_4 or H_3PO_4 and HCl (concentration was 1 mol/L for all acids).

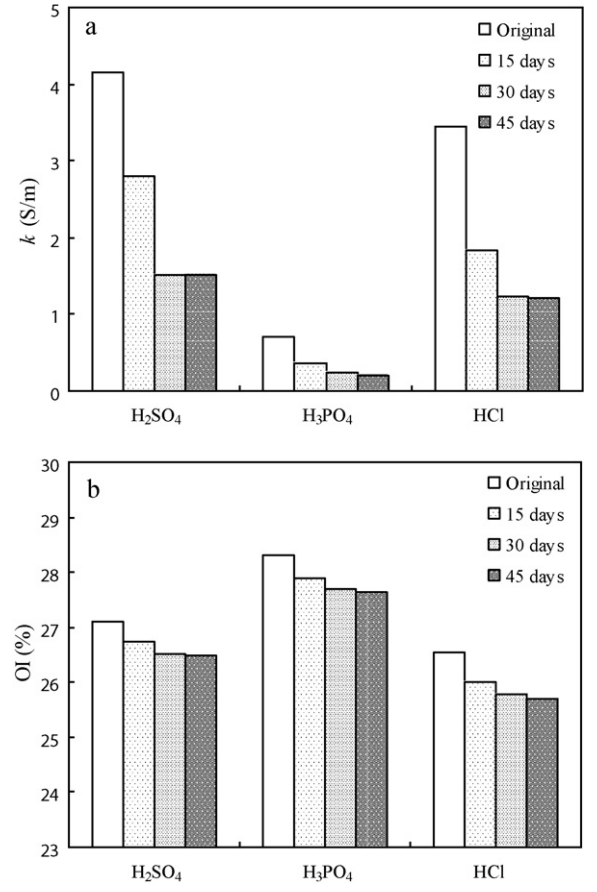

Fig. 6. Conductivity (a) and OI value (b) of conductive paper samples within 45 days of storage time.

3.6. Environmental stability of paper composite

Paper samples were stored in natural environment, and the conductivity and OI values were measured every 15 days to investigate the environmental stability of conductive paper samples. As shown in Fig. 6, the conductivity values decreased and the OI values slightly decreased within 30 days of storage time. However, both the conductivity and OI values of paper samples were basically unchangeable after 30 days. The decay of the flame retardancy of the composite in atmosphere was due to the dedoping of the polyaniline deposited on cellulose fibers.

4. Conclusions

The conductive paper composite made from polyaniline-deposited cellulose fibers possesses flame retardancy. Both the conductivity and flame retardancy of polyaniline-deposited conductive paper composite increased with the increase of the amount of the polyaniline deposited. Doping acid played an important role in imparting flame retardancy to the paper composite. The conductivity and flame retardancy of the paper composite had a close relationship with the doping acids used. Sulfuric acid and hydrochloric acid could impart excellent conductivity, and phosphoric acid could impart good flame retardancy to the paper composite. The comprehensive properties of the paper composite made from polyaniline-deposited cellulose fibers codoped with an equimolar mixture of H_3PO_4 and H_2SO_4 or H_3PO_4 and HCl could be improved. Both the conductivity and flame retardancy of the paper composite were basically stable after storing 30 days in natural environment.

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