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Conductivity decay of cellulose–polypyrrole conductive paper composite prepared by in situ polymerization method

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ABSTRACT

Cellulose–polypyrrole (PPy) conductive paper composite was prepared using an in situ chemical polymerization process, and its conductivity stability was investigated. When the PPy-coated pulp fibers were dipped in an alkaline solution or the paper composite was exposed to an alkaline environment, the conductivity stability became poor. Contrarily, if the PPy-coated pulp fibers were dipped in an acidic solution or the paper composite was exposed to an acidic environment, the conductivity stability would be improved. The conductivity decay occurred when the paper composite was stored in air atmosphere at ambient temperature. The rate of conductivity decay also depended on temperature and atmosphere. The conductivity decay in air occurred quicker than that in nitrogen, especially at elevated temperature. The PPy-coated pulp fibers and the paper composite were characterized by TGA, XPS, SEM and SEM-EDX analyses to elucidate the mechanism of conductivity decay of the paper composite.

1. Introduction

Electrically conductive paper composite would be very useful in various fields, including the manufacture of antistatic material, electromagnetic interference (EMI) shielding material, sensing elements, heating elements, and packing of electronic components and equipment, etc. (Jang & Ryu, 2006).

In recent years, conductive paper composite produced by in situ chemical polymerization of pyrrole and aniline in a pulp fiber system has aroused a great interest (Beneventi, Alila, Boufi, Chaussy, & Nortier, 2006; Chen & Qian, 2007; Ding, Qian, Shen, & An, 2010; Huang, Kang, & Ni, 2006; Johnston, Kelly, Moraes, Borrmann, & Flynn, 2006; Kim, Deshpande, Yun, & Li, 2006; Song, Qian, Wang, & Xie, 2006; Song, Qian, & Wang, 2006). The in situ polymerization process is a process that the monomer such as aniline and pyrrole is polymerized in the presence of pulp fibers and deposited onto the surface of the pulp fibers.

The conductivity stability is one of important properties of conductive paper composite. In our previous studies, we found that the conductivity stability of cellulose–polyaniline (PAn) conductive paper composite depended on the type of dopants used (Song, Qian, & Wang, 2006). *p*-Toluenesulfonic acid and sulfosalicylic acid in organic acids and sulfuric acid in inorganic acids were excellent dopants. In fact, the conductivity stability of the cellulose–PAn conductive paper composite doped with *p*-toluenesulfonic acid was very good. The surface resistivity remained almost unchanged after storing in air environment for 1 month. The increase in the surface resistivity was not beyond 15% even after storing in air environment for 5 months. However, the conductivity stability of cellulose–polypyrrole (PPy) conductive paper composite was much poorer as compared to that of cellulose–PAn conductive paper composite (Chen & Qian, 2007; Ding et al., 2010).

In general, the conductive PPy composites are less stable in air due to their reactivity with a variety of atmospheric chemicals, especially oxygen (Wu, Zhou, Too, & Wallace, 2005). Because of the low oxidation potential of PPy, the redox reaction of PPy is more sensitive to the oxygen than those polymers that are more difficult to oxidize (Ansari, 2006). Our recent studies showed that the conductivity stability of cellulose–PPy conductive paper composite in the atmospheric environment depended on the preparation conditions, especially pyrrole concentration, oxidant charge and reaction time (Chen & Qian, 2007; Ding et al., 2010). In addition, the use and recycling of this paper composite may involve various chemicals (including acids, alkalines and oxidants, etc.) as well as elevated temperatures. Therefore, for successful industrial application of the paper composite in future, its conductivity stability is one of the key properties that should be considered first.

In this work, the conductivity decay of cellulose–PPy conductive paper composite was investigated by observing the changes of surface resistivities with storage time under different treatment or storage conditions. The PPy-coated pulp fibers and the paper composite were characterized by TGA, XPS, SEM and SEM-EDX analyses to elucidate the mechanism of conductivity decay of the paper composite.

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2. Experimental

2.1. Materials

Pyrrole was chemical grade and was freshly distilled before use. All the other chemicals were of analytical grade and used without further purification.

The pulp used in this research was softwood bleached sulfite pulp (NBSP) and was obtained from Yanbian Shiyan Bailu Paper Co., Ltd. (Jilin Province, China).

2.2. Preparation of cellulose–PPy conductive paper composite

Ferric chloride solution and *p*-toluenesulfonic acid (PTSA) solution were added separately to the pulp suspension containing 2 g (oven-dry basis) of pulp. Then a given amount of pyrrole monomer was injected with a liquid injector. The mixture was stirred at ice bath temperature for 2 h. The resulting PPy-coated pulp fibers were repeatedly washed with tap water in a filter bag to remove any free PPy. Unless otherwise indicated, the preparation conditions of cellulose–PPy conductive fiber composite are as follows: pulp consistency 1%, pyrrole concentration $5\,\mathrm{g\,L^{-1}}$, ferric chloride/pyrrole molar ratio 2:1, and PTSA/pyrrole molar ratio 2:1. For comparison, pure PPy powder was also prepared following the above procedure but without adding pulp fibers.

Next, the pulp fibers were made into a handsheet with a basis weight of $80\,\mathrm{g\,m^{-2}}$ on a ZCX-200 handsheet former. Finally, the handsheet was dried at 110 °C on a plate dryer for 3 min.

2.3. Measurement of surface resistivity

The resistance (*R*) of conductive paper was recorded with a YD2511A intelligent low resistance meter. The surface resistivity was calculated as follows,

$$R_s = \frac{R}{2.0 \times 0.8}$$

where R_s is the surface resistivity ($\Omega\,\mathrm{cm^{-2}}$) and *R* is the resistance (Ω). The spacing of the electrodes was 2.0 cm and electrode width was 0.8 cm.

2.4. TGA, XPS, SEM and SEM-EDX analysis

TGA curves were obtained on a Perkin Elmer-Pyris6 thermo gravimetric analyzer under a dry nitrogen atmosphere operating at a heating rate of $15\,^{\circ}\mathrm{C\,min^{-1}}$.

XPS spectra were obtained using a Thermo Fisher Scientific's K-Alpha X-ray photoelectron spectrometer (XPS) system. An Al Kα 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.

Scanning electron microscopy (SEM) observation was performed using an FEI Quanta-200 environmental scanning electronic microscope. The fiber samples were mounted on specimen stubs with double-sided adhesive tape, and coated with gold prior to SEM observation. SEM-EDX analyses were also carried out with the same instrument, but the paper samples were not coated with gold.

3. Results and discussion

3.1. Conductivity decay of the paper composite

3.1.1. Effect of chemical treatment

In this section, the PPy-coated pulp fibers were treated with NaOH solution, HCl solution, and H_2O_2 solution separately, the treated pulp fibers were then made into handsheets for conductivity decay tests. As shown in Fig. 1, by a treatment of PPy-coated pulp fibers with 3% NaOH solution for 30 min, a significant decrease in conductivity with storage time in air was observed. However, by a treatment of PPy-coated pulp fibers with 3% HCl solution for 30 min, the conductivity almost kept stable with storage time in air. This was because that the PPy on pulp fibers was changed to PPy (A^-) when dipped in an acidic solution and changed to PPy (OH^-) when dipped in an alkaline solution (Ansari, 2006). The surface resistivity slightly increased with storage time in air when the PPy-coated pulp fibers were treated with 3% H_2O_2 solution for 30 min, which is attributed to the oxidation of PPy by this oxidative compound. We also investigated the effect of time of treatment with 3% H_2O_2 solution on the conductivity of cellulose–PPy conductive paper composite. The result showed that the surface resistivity increased with increasing treatment time, but the extent of the increase declined when the treatment time was more than 30 min.

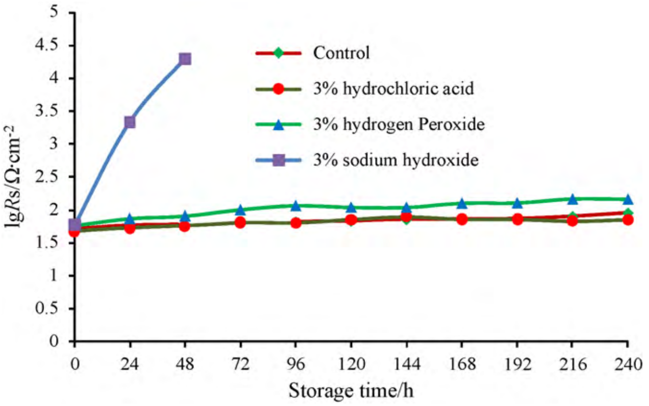

Fig. 1. Effect of chemical treatment on the conductivity decay.

3.1.2. Effect of temperature and atmosphere

As seen in Fig. 2, the paper composite stored in air at ambient temperature (25 °C) was electrically unstable. The conductivity stability decreased with increasing the storage temperature. The surface resistivity of the paper composite stored in air at 100 °C for 1 week increased by around four orders of magnitude. In addition, the conductivity stability of the paper composite stored in nitrogen was better than that stored in air, especially at elevated temperature. The above results showed that the conductivity stability of the paper composite was related to the oxidation of PPy. Temperature played an important role in determining product stability, increasing the temperature accelerated the oxidation of PPy.

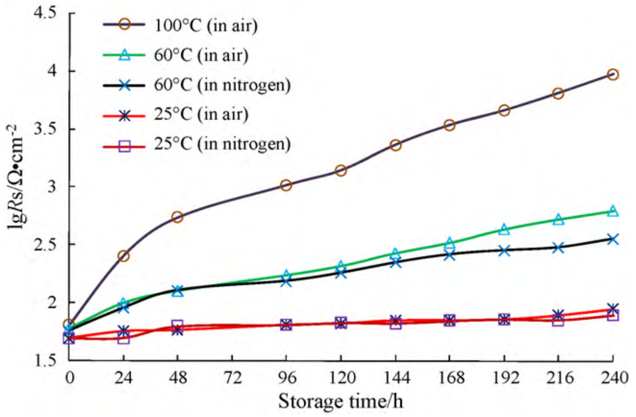

Fig. 2. Effect of temperature and atmosphere on the conductivity decay.

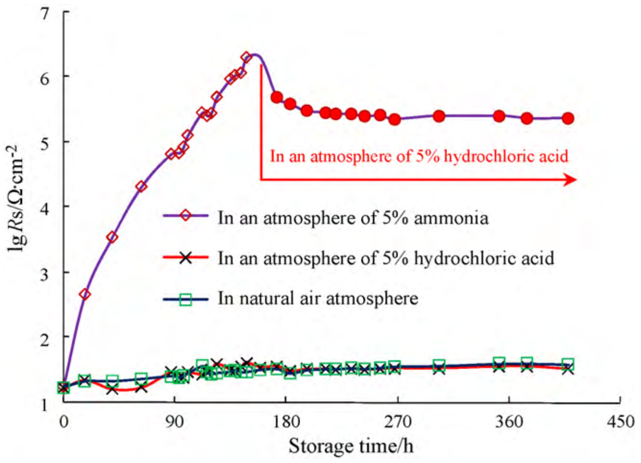

Fig. 3. Effect of environmental pH on the conductivity decay at ambient temperature.

The heat treatment itself also markedly affected the conductivity stability besides oxidation, because the conductivity decay of the paper composite stored in nitrogen at 60 °C was still very high. Exposure of conducting polymers to elevated temperatures was known to induce changes in the molecular structure. The changes might be related to the interaction between the charged polymer backbone and the counterion, or the thermal stability of the counterion and the charged polymer itself. At elevated temperatures, structural changes such as cross-linking or chemical interactions between counterion and polymer that led to block charge carriers paths or shorten conjugated system would result in a decrease in electrical conductivity (Ansari, 2006). However, it was noted that the paper drying operation had not have adverse impact on the electrical conductivity and stability of the paper composite due to a short drying time (Chen & Qian, 2007).

3.1.3. *Effect of environmental pH*

As seen from Fig. 3, the conductive stabilities of the paper composites exposed to acidic and natural environments at ambient temperature were good, and in fact the acidic environment improved the conductive stability. However, the surface resistivity of the paper composite exposed to an alkaline environment sharply rised up, and the value increased by five orders of magnitude in about 1 week. This was because when the PPy on the paper composite was exposed to NH_3 (electron-donating gas), a redox reaction occurred and its effective number of charge carriers (polarons or bipolarons) decreased, thus reducing its conductivity. Interestingly, the surface resistivity of the paper composite (more than 2 MΩ cm^{-2}) was found to decrease by one order of magnitude when removed from the alkaline environment and then placed it into the acidic environment. We thought this might be due to the stabilization of charge carriers. The above research results showed that the paper composite has a great potential as an ammonia gas sensor.

3.2. *Characterization of the composite*

3.2.1. *TGA analysis*

The TGA curve of PPy-coated pulp fibers is shown in Fig. 4. For comparison, the TGA curves of uncoated pulp fibers and pure PPy are also shown in Fig. 4. As seen in Fig. 4, the three samples all showed main weight losses in two stages. For uncoated pulp fibers (a), the first stage of weight loss was range of 330 °C and 400 °C and showed about 80% loss in weight. The second stage of weight loss started at 400 °C and continued up to 650 °C during which there was a 20% of weight loss. For pure PPy powder (b), the first stage range was between 250 °C and 430 °C and showed about a 20% loss in weight. The second stage of weight loss started at 430 °C and continued up to 770 °C during which there was nearly a 80% of weight loss. For PPy-coated pulp fibers (c), the first stage of weight loss was range of 250 °C and 350 °C and showed about 60% loss in weight, and the second stage started at 350 °C and continued to up 770 °C during which there only was a 17% of weight loss. From the above analysis we can clearly see that the thermal stability of cellulose was greatly affected by incorporating PPy. The incorporated PPy lowered the starting thermal degradation of cellulose, but promoted the formation of char. Recently, Varesano, Tonin, Ferrero, and Stringhetta (2008) presented that the high thermal stability of char produced in the PPy–PET interface protected the PET fibers from heat and fire. Of specific importance was that the weight losses of pure PPy and PPy-coated pulp fibers at a temperature in the range from 50 °C to 150 °C were higher than that of uncoated pulp fibers, which might be related to the thermal stability of the counterions in PPy besides water evaporation. This could partly interpret the conductivity decay of the paper composite at elevated temperatures in nitrogen atmosphere. The above explanation needs to be confirmed by further studies. Differential scanning calorimetry (DSC) and cyclic voltammetry (CV) analysis might be useful to reveal the interaction of PPy with counterions and other materials.

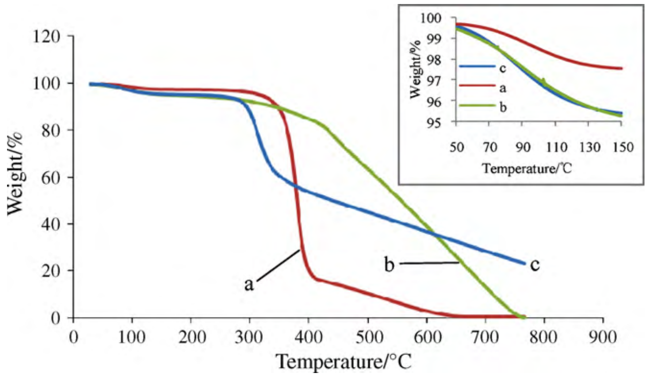

Fig. 4. TGA curves of (a) uncoated pulp fibers, (b) pure PPy and (c) PPy-coated pulp fibers.

3.2.2. *XPS analysis*

Pure PPy (a) and cellulose–PPy paper composite (b) were analyzed by XPS, and the results of XPS quantitative analysis are shown in Table 1. The existence of S and Cl in pure PPy indicated that the PPy was doped by PTSA and ferric chloride. The C/N ratio of pure PPy (5.86) was higher than the theoretical C/N ratio of pure undoped PPy (4). Clearly some of the excess carbon could be attributed to PPy doping with PTSA ($C_7H_8O_3S$). In addition, the O/S ratio of pure PPy (3.17) was consistent with the theoretical O/S ratio of PTSA (3), which revealed the oxygen in pure PPy came from PTSA. Since sulfur is only present in the sulfonic group of the dopant and nitrogen is only found in the PPy backbone, the ratio of these elements is an approximation of the doping level and represents the number of positive charges induced per pyrrole ring. The value of S/N in pure PPy was 0.27, which was in agreement with the common ratios measured in PPy films (0.25–0.33) (Sonmez, Schottland, Zong, & Reynolds, 2001).

Compared with pure PPy, the content of oxygen in cellulose–PPy paper composite significantly increased. The C/N ratio increased to about 11, and the O/S ratio increased to 55.5 (far more than 3), which were mainly contributed by cellulose. Moreover, the paper composite gave the lower doping level (8%) when compared to pure PPy, which indicated pulp fibers might interfere with PPy doping with PTSA. The intensity of the Cl 2p peak at 201 eV indicated the doping efficiency.

Table 1
Results of XPS quantitative analysis of pure PPy and cellulose–PPy paper composite.

Sample	C 1s/%	N 1s/%	O 1s/%	S 2p/%	Cl 2p/%	O/C	O/S	C/N	S/N
Pure PPy	72.92	12.44	10.81	3.41	0.42	0.15	3.17	5.86	0.27
Cellulose–PPy paper composite	66.09	6.05	26.65	0.48	0.74	0.40	55.52	10.92	0.08

Table 2
Surface resistivity and stoichiometric components of nitrogen in the cellulose–PPy paper composites freshly prepared and aged in air for 30 days (or exposed to NH_3 for 24 h).

Sample	Preparation conditions	$R_s/(\Omega\,cm^{-2})$	C/%	N/%	S/N	O/N	N1/N	N2/N	N3/N
1	5 g L^{-1} Py, $FeCl_3$/Py 2:1, freshly prepared	54.35	67.63	6.03	0.101	4.26	0.082	0.684	0.234
2	5 g L^{-1} Py, $FeCl_3$/Py 2:1, aged in air	89.78	69.44	5.29	0.149	4.60	0.144	0.665	0.191
3	5 g L^{-1} Py, $FeCl_3$/Py 2:1, exposed to NH_3	851.1	62.94	9.00	0.088	3.02	0.236	0.626	0.138
4	1.5 g L^{-1} Py, $FeCl_3$/Py 2:1, freshly prepared	2115	61.77	2.46	0.073	14.46	0.143	0.689	0.168
5	1.5 g L^{-1} Py, $FeCl_3$/Py 2:1, aged in air	7994	65.20	2.15	0.084	15.10	0.191	0.637	0.172
6	5 g L^{-1} Py, $FeCl_3$/Py 1:1, freshly prepared	170.5	63.71	3.72	0.113	8.64	0.130	0.696	0.175
7	5 g L^{-1} Py, $FeCl_3$/Py 1:1, aged in air	398.2	67.01	4.41	0.109	6.37	0.192	0.704	0.104

In order to interpret the conductivity decay of the paper composite stored in air, the XPS spectra of N 1s were deconvoluted into separate peaks using the Gaussian–Lorentzian method. The N 1s XPS spectrum of the paper composite could be decomposed into three components at 398.9 eV (N1), 400.2 eV (N2) and 401.8 eV (N3), respectively. The N1 and N2 components can be assigned to C=N species and N–H species respectively, and the N3 component can be assigned to $C–N^+$ species and $C=N^+$ species (Malitesta, Losito, Sabbatini, & Zambonin, 1995; Suzer, Birer, Sevil, & Guven, 1998).

The results from Table 2 clearly showed that the atomic O/N and N1/N ratios increased for the samples aged in air for 30 days, which were evidence of the oxidation of the PPy layer. The most important factor in decay of conductivity in air atmosphere was attributed to the chemical reaction of O_2 with double bonds in conjugated system (Ansari, 2006). In addition, the paper composite prepared at 1.5 g L^{-1} pyrrole showed the poorer stability in comparison with that prepared at 5 g L^{-1} pyrrole. This was because the incomplete encapsulation of the cellulose fibers by the PPy particles allowed more oxygen to penetrate the composite. Moreover, the carbon and nitrogen content of the aged paper composite prepared with 1:1 molar ratio of $FeCl_3$/pyrrole were higher than those of the freshly prepared paper composite, whereas the oxygen content and the O/N atomic ratio were lower. This was because the PPy oligomers generated in the event of insufficient ferric chloride were further oxidized by oxygen in air to form the polymers that could not escape from the tested sample at high vacuum.

The N 1s XPS spectrum of the cellulose–PPy paper composite exposed to NH_3 for 24 h was also deconvoluted, and the results are also listed in Table 2. Compared with the unexposed sample (Sample 1), the N1/N ratio of the sample exposed to NH_3 (Sample 3) markedly increased (from 0.082 to 0.236) but the N3/N ratio decreased, which was likely attributed to the formation of the deprotonated pyrrolyl nitrogen or the imine-like structure (Wang et al., 2009). In this study, $FeCl_3$ was used as an oxidant and PTSA was used as a dopant. The protonated form of PPy ($PPyH^+$) is susceptible to the redox reaction when it interacts with the reduction gas. When such cellulose–PPy paper composite was exposed to ammonia, the nitrogen atom of the ammonia molecules established a coordinate bonding with the free atomic orbital of the dopant proton (H^+). This led to the deprotonation of PPy nitrogen atom, favoring the disappearance of charge carriers that increased the surface resistivity (Kharat et al., 2007). This can be shown by following reversible reaction.

$$PPyH^+ + NH_3 \leftrightarrow PPy + NH_4{}^+$$

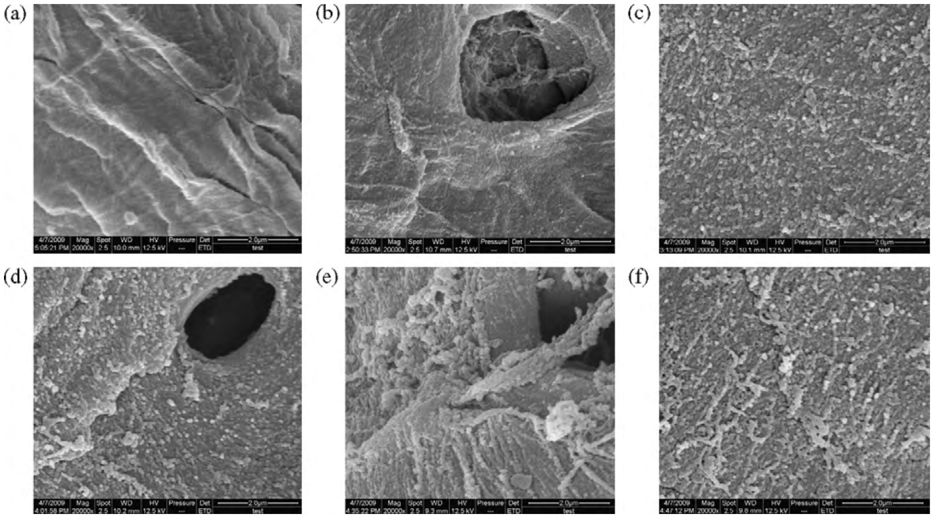

Fig. 5. SEM images of (a) uncoated pulp fibers, (b) PPy-coated pulp fibers prepared at 1.5 g L^{-1} of pyrrole, (c) PPy-coated pulp fibers prepared at 5 g L^{-1} of pyrrole, (d) paper made from PPy-coated pulp fibers prepared at 5 g L^{-1} of pyrrole, (e) PPy-coated pulp fibers prepared at 5 g L^{-1} of pyrrole, aged in a forced air oven at 100 °C for 12 h, and (f) PPy-coated pulp fibers prepared at 5 g L^{-1} of pyrrole, aged in a vacuum oven at 100 °C for 12 h.

Table 3
SEM-EDX results of PPy-coated papers prepared at various conditions.

Preparation conditions	C/%	O/%	N/%	S/%	Cl/%	S/N
1.5 g L^{-1} Py, freshly prepared	63.52	31.12	5.00	0.25	0.05	0.050
2.0 g L^{-1} Py, freshly prepared	64.56	28.90	6.13	0.33	0.05	0.054
3.0 g L^{-1} Py, freshly prepared	65.45	27.11	6.66	0.49	0.19	0.074
5.0 g L^{-1} Py, freshly prepared	67.08	22.64	9.28	0.83	0.11	0.089
5.0 g L^{-1} Py, aged in a forced air oven at 100 °C for 12 h	67.77	23.41	7.79	0.78	0.14	0.100
5.0 g L^{-1} Py, aged in a vacuum oven at 100 °C for 12 h	67.55	22.91	8.56	0.80	0.14	0.093

It was especially noted that the nitrogen content of the sample exposed to NH_3 (Sample 3) was much higher than that of the unexposed sample (Sample 1). In this study, the high vacuum (1.0×10^{-8} Pa) was used for XPS analysis. Therefore, the physically absorbed NH_3 should be removed from the tested sample. The higher nitrogen content revealed the incomplete reversibility of the redox reaction.

3.2.3. SEM and SEM-EDX analysis

Surface morphological properties of the PPy-coated pulp fibers (or paper) were investigated by scanning electron microscopy (SEM). A smooth surface morphology was obtained for uncoated pulp fibers as illustrated by Fig. 5a, whereas rough-coated polymer particles were observed on the PPy-coated pulp fibers and paper surfaces (Figs. 5b–d). The size of PPy particles prepared at 5 g L^{-1} of pyrrole was around 50–100 nm. The surface morphology of the paper was very similar to that of the PPy-coated pulp fibers, indicating that the paper drying operation had no impact on the surface morphology. This was agreement with the surface resistivity results reported previously (Chen & Qian, 2007). For the PPy-coated pulp fibers aged in air at 100 °C for 12 h (the corresponding surface resistivity value increased 771%), the PPy particles seemed to get larger (Fig. 5e), most likely due to thermal oxidation. However, for the PPy-coated pulp fibers aged in vacuum at 100 °C for 12 h (the corresponding surface resistivity value only increased 65%), the PPy particles were believed to show no obvious change (Fig. 5f). Since the rate determining degradation mechanism involved the diffusion or reaction of oxygen, the conductivity loss in an oxygen-free atmosphere would proceed by a slower, non oxygen-dependent process (Kuhn, Child, & Kimbrell, 1995).

The SEM-EDX results of cellulose–PPy paper composites prepared at various conditions are showed in Table 3. The atomic percent contents of carbon, nitrogen and sulfur almost linearly increased but the atomic percent content of oxygen almost linearly decreased with the increase of pyrrole concentration, indicating the linear increase in the amount of PPy coated. This result implied that SEM-EDX can be used as an alternative to XPS for estimating the amount of PPy coated and the doping level. Compared with the paper composite freshly prepared and aged in vacuum at 100 °C for 12 h, the paper composite aged in air at 100 °C for 12 h gave a little higher oxygen content. This was the evidence of the oxidation of PPy.

4. Conclusions

When the PPy-coated pulp fibers were dipped in an alkaline solution or the paper composite was exposed to an alkaline environment, the conductivity stability became poor. Contrarily, if the PPy-coated pulp fibers were dipped in an acidic solution or the paper composite was exposed to an acidic environment, the conductivity stability would be improved. The conductivity decay occurred when the paper composite was stored in air atmosphere at ambient temperature. The rate of conductivity decay also depended on temperature and atmosphere. The conductivity decay in air occurred quicker than that in nitrogen, especially at elevated temperature. TGA analysis indicated that the incorporated PPy promoted the formation of char during the thermal degradation of the composite. The thermal behavior at a temperature in the range from 50 °C to 150 °C could partly interpret the conductivity decay of the paper composite at elevated temperatures in nitrogen atmosphere. XPS and SEM-EDX results confirmed the occurrence of PPy oxidation during aging in air. XPS results also revealed the reasons why the conductivity stabilities became poor when exposed to ammonia or prepared with insufficient pyrrole and ferric chloride. SEM observation showed that the PPy particles seemed to get larger for the PPy-coated pulp fibers aged in air at 100 °C, likely due to thermal oxidation.

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