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PREPARATION AND CHARACTERIZATION OF CONDUCTIVE PAPER VIA IN-SITU POLYMERIZATION OF PYRROLE

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Electrically conductive paper was prepared via in-situ chemical oxidative polymerization of pyrrole by using ferric chloride as an oxidant and *p*-toluenesulfonic acid (PTSA) as a dopant. The deposition of polypyrrole (PPy) on the fiber surface was verified by ATR-FTIR and SEM analyses. Pyrrole concentration had a significant effect on the surface resistivity of conductive paper, especially when the pyrrole concentration was less than 1.8 $g \cdot L^{-1}$. The conductivity of the PPy-coated paper could be controlled by adjusting pyrrole concentration. The threshold concentration of pyrrole was 1.2 $g \cdot L^{-1}$ when the molar ratio of dopant to pyrrole was 2:1. Very little polymerization reaction in solution occurred when pyrrole concentration was less than 2.5 $g \cdot L^{-1}$. The pyrrole concentration should reach a higher value to prepare a relatively stable conductive paper with lower resistivity. The XPS results showed that the amount of the PPy coating increased, while the doping level first decreased then increased with the increase of pyrrole concentration. The SEM-EDXA results showed that there was no difference in the amount of PPy coated between the outer surface and the internal wall, but the doping level of the outer surface was higher than that of the internal wall.

INTRODUCTION

Electrically conductive polymer-paper composite materials have potential use in new functional papers and packaging applications, including anti-static and electromagnetic shielding papers, electrical resistive heating papers, novel wall coverings, papers with electrochromic and redox properties, anti-bacterial papers, and new functional packaging materials (Johnston et al. 2005).

Various paths could be adopted to prepare such paper. It could be prepared by polymerizing conductive polymers directly onto the paper sheet, both in gas and liquid phase (Chen and Qian 2008; Johnston et al. 2005), or inkjet printing conducting polymer dispersion, or application of oxidant solution followed by vapor phase polymerization of conducting polymer to the paper matrix (Winther-Jensen et al. 2007). It also could be prepared in two steps: the preparation of electrically conductive composite fibers and then the manufacture of the conductive paper by using the fibers from the first step. Researchers at Louisiana Tech University had developed a simple technique to fabricate an electrically conductive paper by applying a layer-by-layer nanoassembly coating directly onto wood microfibers during the papermaking process (Agarwal et al. 2006).

In recent years, conductive paper produced by in-situ chemical polymerization of pyrrole and aniline in aqueous electrolytes has aroused a great interest because of simplicity, cost effectiveness, and environmental friendliness (Johnston et al. 2006; Huang et al. 2006; Beneventil 2006; Kim et al. 2006; Chen and Qian 2007). The in-situ chemical polymerization process is a process in which a monomer such as aniline or pyrrole is polymerized in the presence of pulp fibers.

Here, electrically conductive cellulose/polypyrrole (PPy) composite fibers were prepared via in-situ chemical oxidative polymerization of pyrrole by using ferric chloride as an oxidant and *p*-toluenesulfonic acid (PTSA) as a dopant. The deposition of PPy on the fiber surface was verified by attenuated total reflectance Fourier transform infra-red spectrometry (ATR-FTIR) and scanning electron microscopy (SEM). The threshold concentration of pyrrole and the adsorption efficiency of PPy were investigated, the doping level of PPy was measured by X-ray photoelectron spectroscopy (XPS), and the topochemistry of the composite fibers was analyzed by energy dispersive X-ray analysis imaging (SEM-EDXA).

EXPERIMENTAL

Materials

Bleached kraft softwood pulp imported from Canada was obtained from Mudanjiang Hengfeng Paper Co., Ltd. Pyrrole (CP) was purchased from Shanghai Kefeng Chemical Reagent Co., Ltd., and was distilled and refrigerated before use. Ferric chloride hexahydrate (AR) and *p*-toluenesulfonic acid (PTSA, AR) were purchased from Tianjin Kermel Chemical Reagent Development Center, and were used as received.

Preparation of Composite Fibers and Conductive Paper

2 g of pulp fibers (based on oven-dried basis), water, and ferric chloride were put in a flask with mechanical stirring for several minutes, and then PTSA solution was added to the system (the pulp consistency was 1 %) and the flask was kept in an ice bath. Subsequently the desired amount of pyrrole was injected into this solution to start the polymerization. The molar ratio of monomer (pyrrole) : oxidant ($FeCl_3$) : dopant (PTSA) was kept at 1:2:2. After 2 h, this reaction was stopped, the treated mixture was diluted, and then the fibers were washed and filtered (Chen and Qian 2007).

The resulting fibers were made into paper sheets by using the conventional papermaking facilities. Those paper sheets were pressed at 0.4MPa for 5mins and dried at 105°C after formation, and kept in an atmospheric environment.

Measurement of the Amount of PPy

The amount of PPy coated on composite fibers, A (%), was measured by a weight method, and was calculated as follows,

$$A\ (\%) = \{\ (W_2 - W_1)/W_1\ \} \times 100 \tag{1}$$

where W_1 and W_2 are the oven-dry weight of fibers before and after treatment, respectively.

The value of A (%) mainly reflects the amount of PPy generated from surface polymerization. In order to determine the amount of PPy generated from bulk polymerization, A' (%), we collected and washed the all solid products from the reaction system and measured their oven-dry weight, named as W_2'. During operation, all of the reaction products were filtered on a Buchner funnel, and the filtrate was recycled twice to recover the fines. Thus, A' (%) can be calculated by the following equation:

$$A' (\%) = \{ (W_2' - W_1)/W_1 \} \times 100 \tag{2}$$

Therefore, the amount of the free PPy generated in solution can be represented by ΔA, the difference between A' and A.

Resistivity Testing

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

$$R\text{s} = R/(2.5 \times 1.2) \tag{3}$$

where Rs is the surface resistivity ($\Omega \cdot cm^{-2}$), and R is the resistance (Ω). The spacing of the electrodes was 2.5 cm, and electrode width was 1.2 cm.

Environment Stability Evaluation

The environmental stability of the electrical performance of conductive paper was characterized by the relative resistivity change, ΔRs/Rs$_0$ (%), which was calculated using the following equation,

$$\Delta R\text{s}/R\text{s}_0 (\%) = \{ (R\text{s} - R\text{s}_0)/R\text{s}_0 \} \times 100 \tag{4}$$

where, Rs is the surface resistivity ($\Omega \cdot cm^{-2}$) after storing in the air at room temperature for a period of time (15 days in this research), and Rs$_0$ is the initial value of the surface resistivity ($\Omega \cdot cm^{-2}$).

ATR-FTIR, XPS, SEM and SEM-EDXA Analysis

ATR-FTIR (attenuated total reflection-Fourier transform infrared) spectra in the range 600–4000 cm^{-1} were recorded on a FT-IR spectrometer equipped with an InspectIR microscope (Magna-IR 560 E.S.P, Nicolet Corp.). The crystal used in the ATR cell was Si. The resolution was 4 cm^{-1} and 40 scans were averaged.

X-ray photoelectron spectroscopic (XPS) data were obtained using a Thermo Fisher Scientific's K-Alpha X-ray photoelectron spectrometer (XPS) system. An Al $K\alpha$ 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.

SEM observation was performed using a FEI Quanta-200 environment scanning electronic microscope. The specimens were treated by spray-gold before the observation and analysis.

SEM-EDXA analyses were also carried out using a FEI Quanta-200 environment scanning electronic microscope, but the specimens were not coated with gold.

RESULTS AND DISCUSSION

Deposition of PPy on the Fiber Surface

ATR-FTIR studies were performed to reveal the deposition of PPy on the composite fiber surface. In the ATR-FTIR spectrum of composite fibers, the characteristic bands of PPy, the pyrrole ring fundamental vibration at 1550 cm^{-1} and C–N stretching vibration in the ring at 1456 cm^{-1}, were observed. These peaks confirmed the presence of PPy.
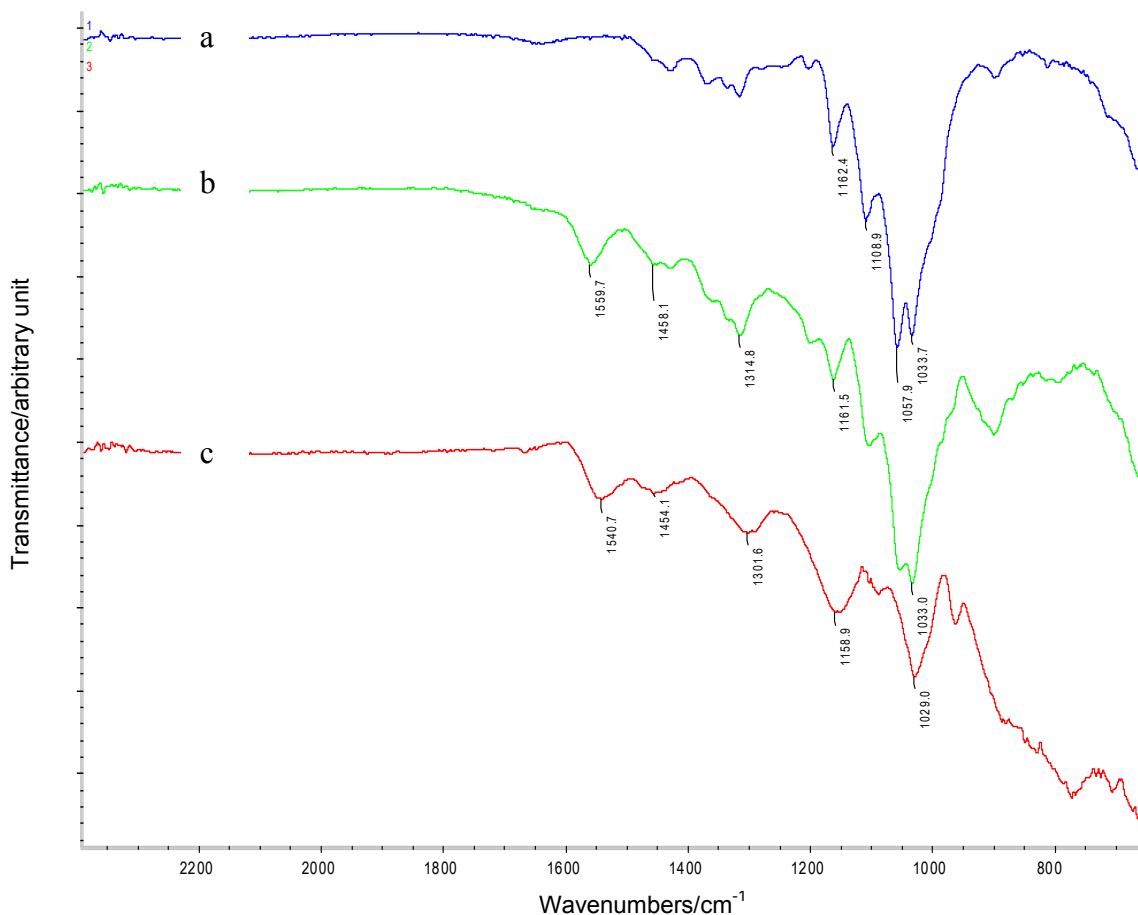
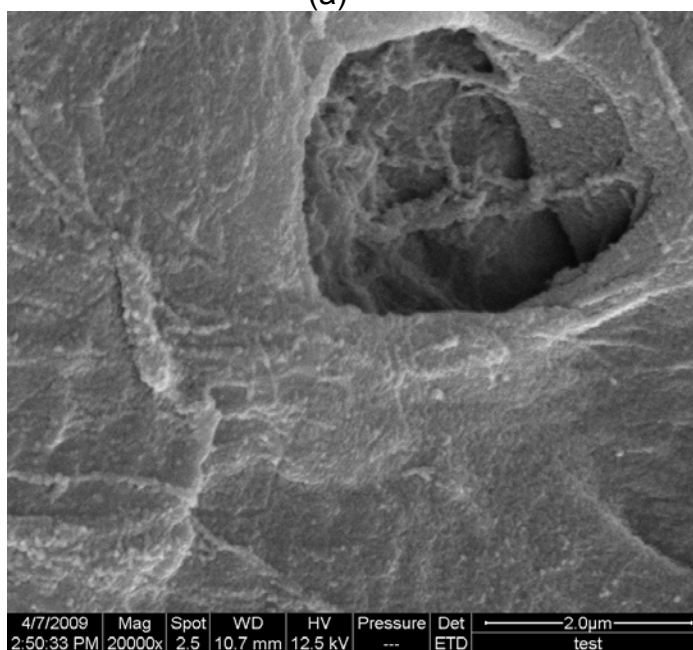**Fig. 1.** ATR-FTIR spectra of untreated pulp fibers (a), PPy-coated pulp fibers prepared at 1.5 g·L^{-1} of pyrrole (b), and 5.0 g·L^{-1} of pyrrole (c)

As shown in Fig. 2, the differences between the untreated fibers and the composite fibers were obvious; polymer clusters appeared and fully encapsulated the surfaces of the treated fibers. The SEM picture of the composite fibers prepared at 1.5 $g \cdot L^{-1}$ showed that the PPy consisted of spheres ca. 100 nm in size, and those spheres were distributed on the outside surface. The spheres of PPy prepared at higher pyrrole concentration were larger than those at lower pyrrole concentration. The existence of PPy in the internal wall of pulp fibers was also confirmed by SEM-EDXA analysis.
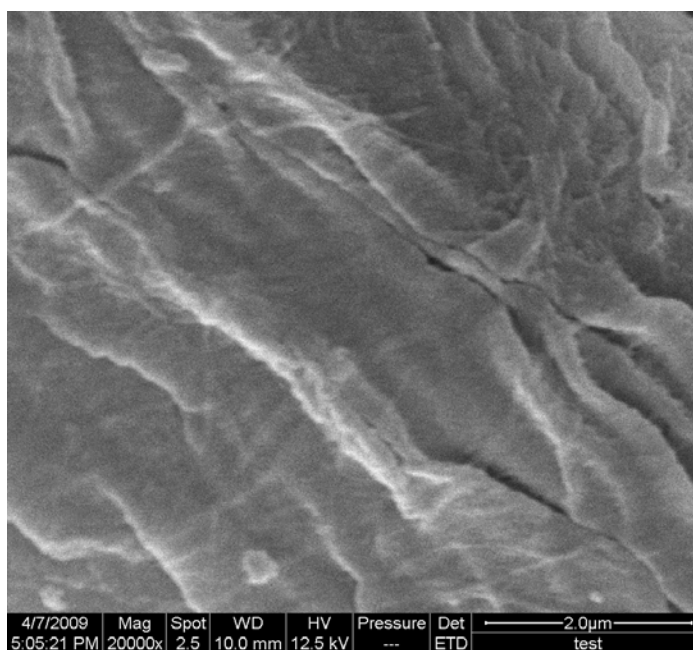
(a)

(b)
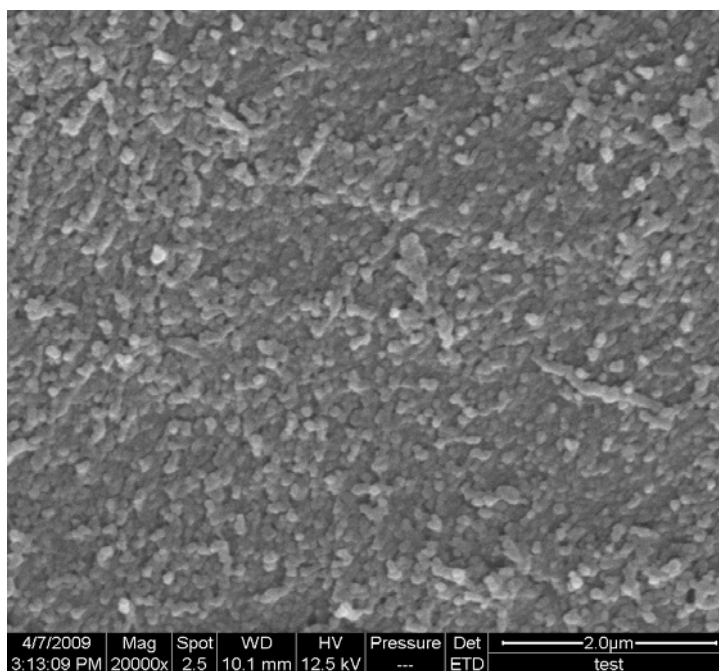
(c)

Fig. 2. SEM pictures of untreated pulp fibers (a), PPy-coated pulp fibers prepared at 1.5 g·L^{-1} of pyrrole (b), and 5.0 g·L^{-1} of pyrrole (c)

Threshold Concentration of Pyrrole and Adsorption Efficiency of PPy

As shown in Table 1 and Fig. 3, the surface resistivity of conductive paper decreased with increasing pyrrole concentration and the rate of decrease of surface resistivity at lower reactant concentrations ($\leq$1.8 g·L^{-1}) was faster than that at higher concentrations. There were 3 critical transition points, 1.2 g·L^{-1}, 1.8 g·L^{-1}, and 3.0 g·L^{-1}. At very low reactant concentrations, there was no detectable electrical conductivity until a threshold concentration of about 1.2 g·L^{-1} was reached, after which a sudden rise in conductivity was observed. The surface resistivity decreased from 156 to 3 kΩ·cm^{-2}, about two orders of magnitude, with a small increase in the pyrrole concentration. It continued to decrease with further increase in the pyrrole concentration with about one order of magnitude decrease in the range of 2.0 to 3.0 g·L^{-1}.

The percolation theory can be used to explain the above results. This theory describes the phenomenon of current conduction in composite materials. It allows evaluation of the magnitude of conductivity in relation to the content of a conductive component, related to the mass of the entire composite (Navarro-Laboulais et al. 1998). According to the percolation theory creation of the conducting paths resulting from direct contact between PPy molecules in a non-conductive pulp fiber leads to a significant drop of resistivity. This phenomenon was evident when the pyrrole concentration exceeded 1.2 g·L^{-1}. In turn, at higher pyrrole concentration (over 3.0 g·L^{-1}) additional PPy did not lead to a further significant drop in resistivity.

Table 1. Effect of Pyrrole Concentration on the Electrical Performance of Conductive Paper

Pyrrole concentration $(g \cdot L^{-1})$	pH	A (%)	A' (%)	ΔA (%)	Rs_0 $(k\Omega \cdot cm^{-2})$	$\Delta Rs/Rs_0$ (%)
0	5.47	0.32	1.03	0.71	out of range	–
0.5	1.89	1.66	2.7	1.04	out of range	–
1.0	1.56	3.54	4.95	1.41	out of range	–
1.1	–	–	–	–	out of range	–
1.15	–	–	–	–	out of range	–
1.2	1.57	6.25	7.72	1.47	155.67	224
1.3	–	–	–	–	123.03	69.9
1.5	1.37	8.25	9.97	1.72	59.53	48.7
1.6	–	–	–	–	36.56	46.8
1.8	1.46	9.78	11.51	1.73	3.41	38.4
2.0	1.29	19.74	21.39	1.65	2.99	52.4
2.5	1.23	–	–	–	0.96	50.8
3.0	1.28	24.77	29.30	4.53	0.27	50.7
3.5	1.24	31.38	35.43	4.05	0.11	57.4
4.0	1.19	36.95	42.82	5.87	0.06	48.4
5.0	1.12	53.85	62.38	8.53	0.02	29.8
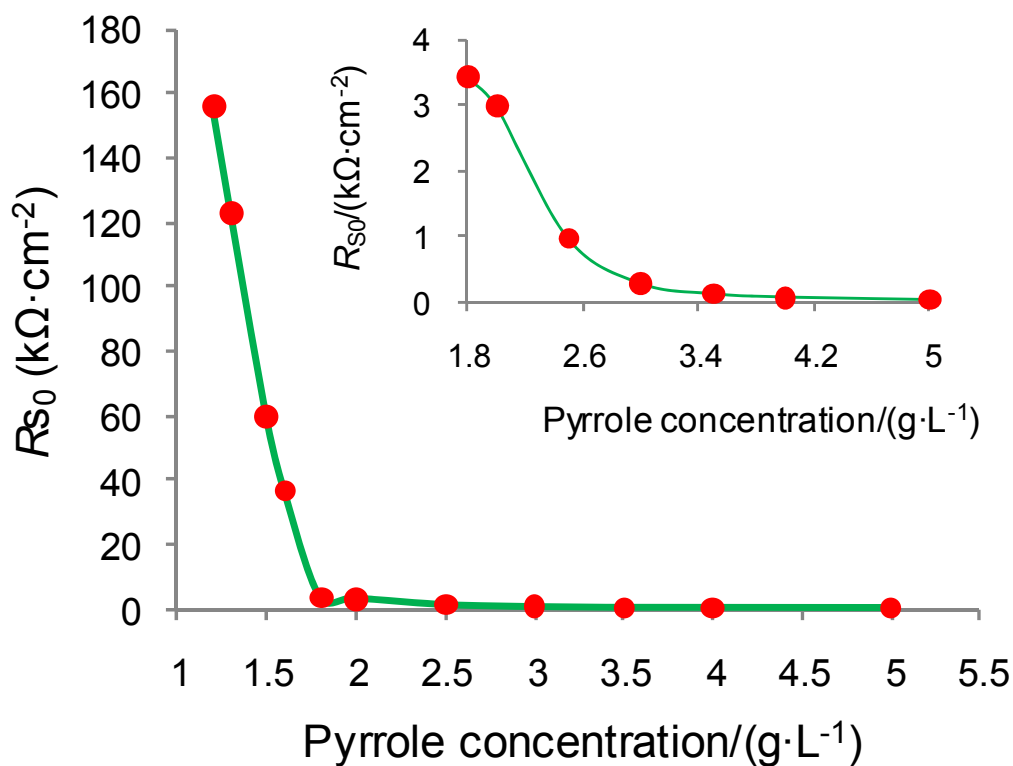
Fig. 3. Effect of pyrrole concentration on resistivity of composite paper

Two competitive processes occur simultaneously in the reaction: polymerization in the substrate and in the solution (Lin et al. 2004). It was observed that the color of pulp fibers changed from white to bright green and finally to black, indicating an increase of the polymer deposition during the reaction (Malinauskas 2001). At very low monomer concentrations (<1.2 $g·L^{-1}$), bulk polymerization was not observed. However, higher concentration of pyrrole ($\geq$3.0 $g·L^{-1}$) led to polymers forming in the reaction solution and on the walls of the reaction vessel (Fig. 4). The coating process was attributed to a physical adsorption mechanism. It is reasonable to assume that a larger quantity of polymer is adsorbed on the outer surface and internal wall of the pulp fibers compared to the quantity polymerized in solution due to the larger surface area and porous structure of the pulp fiber substrate. In addition, pulp fibers are negatively charged, while polypyrrole is positively charged. So it is reasonable that the positive-charged polypyrrole molecules generated in the reaction solution should be easily adsorbed on the negative-charged pulp fiber surface. At a given reaction temperature, reaction and transport rates of reactants in the solution were determined by the reactant concentrations. Higher reaction rate led to an excess of oligomers that could not be effectively transported in fibers, resulting in formation and accumulation of polymer particles in the solution.
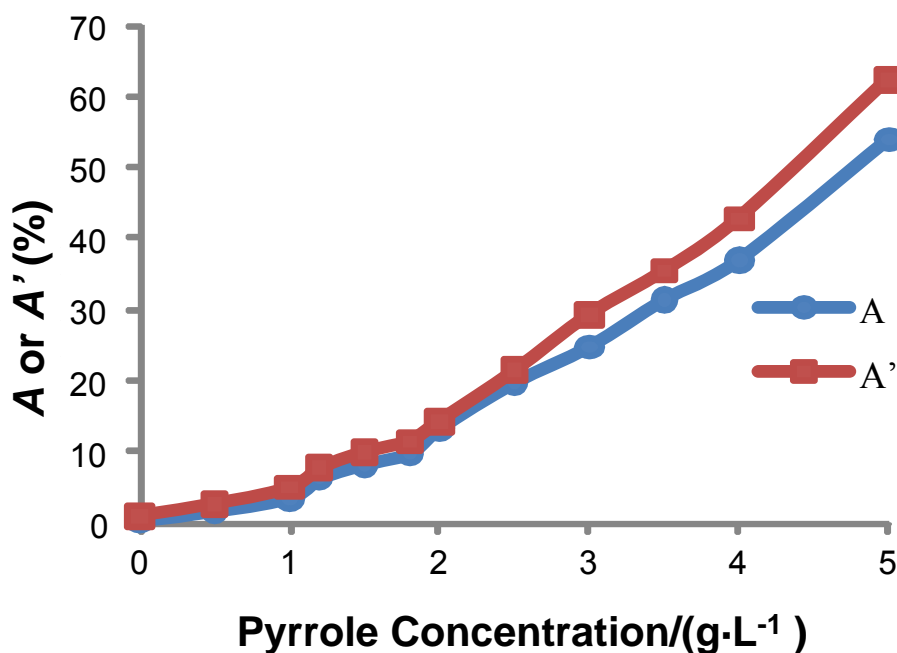

Fig. 4. Relationship between PPy amount (*A*, *A'*) and pyrrole concentration

Environmental Stability

In general, the conductive PPy-coated materials is less stable in air due to their reactivity with a variety of atmospheric chemicals, especially oxygen (Wu et al. 2005). Because of the low oxidation potential of PPy conducting polymers, the redox reactions of PPys are more sensitive to the oxygen than those polymers that are more difficult to oxidize (Ansari 2006).

The environmental stability of conductive paper was investigated by observing $\Delta R_s/R_{s_0}$. A smaller value of $\Delta R_s/R_{s_0}$ was taken as evidence of better environmental stability. As shown in Table 1, the value of $\Delta R_s/R_{s_0}$ of the PPy-coated samples dramatically decreased with increasing concentration of pyrrole when the concentration of pyrrole was less than 1.8 $g \cdot L^{-1}$. This result indicated that the reactant concentration should reach a higher value to prepare relatively stable conductive paper. Compared with high reactant concentrations, the PPy-coated conductive papers prepared at relatively low reactant concentrations exhibited low environmental stability. This is attributed to the porosity of cellulosic materials and the thin and discontinuous PPy coatings, which promote the penetration of oxygen. The values basically remained at around 50% when the concentration of pyrrole was more than 1.8 $g \cdot L^{-1}$. The values of $\Delta R_s/R_{s_0}$ at high pyrrole concentrations slightly increased, which was related to the partial aggregation of large PPy particles and the uniformity of coatings. This was also verified by SEM images (Fig. 2).

Doping Level of PPy

X-ray photoelectron spectroscopy, XPS, was used for the characterization of electrically conducting polymeric materials. As shown in Fig. 5, the N content almost linearly increased with the increase of the pyrrole concentration. The value of sulfur-to-nitrogen atomic ratio (S/N ratio) first decreased then increased with the increase of pyrrole concentration, and reached the minimum value at 3.0 $g \cdot L^{-1}$ pyrrole concentration (Fig. 6).
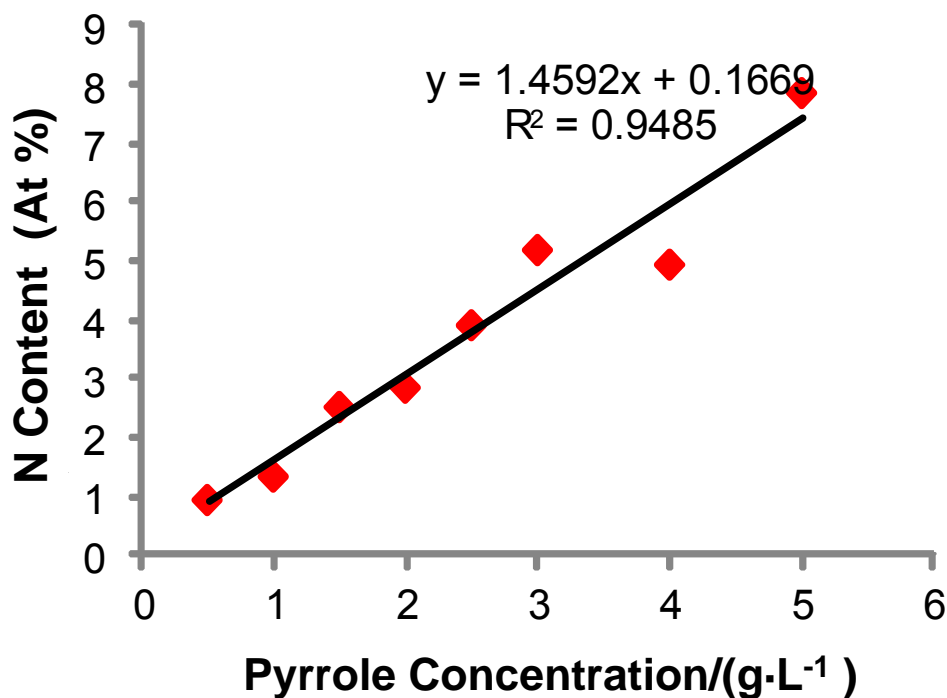

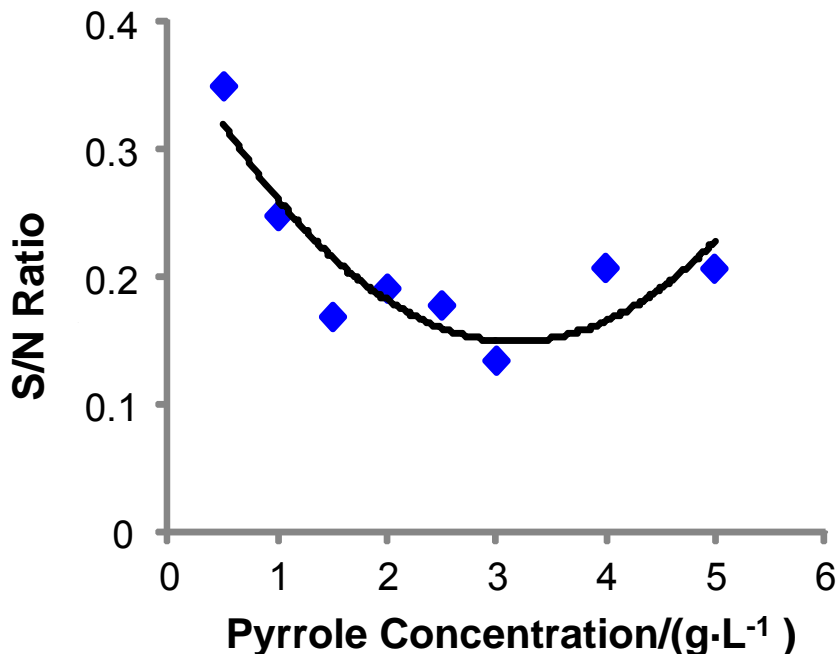**Fig. 5.** Relationship between N content and pyrrole concentration

Fig. 6. Relationship between S/N ratio and pyrrole concentration

Since sulfur is present only in the sulfonic group of the dopant, and nitrogen is found only 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. Consequently, N content is an indicator of the amount of PPy, while S/N ratio is an indicator of the doping level of PPy. The XPS results showed that the amount of PPy coated increased, while the doping level first decreased then increased with the increase of pyrrole concentration. When the pyrrole concentration increased, more PPy particles were formed and deposited on the surface of the fibers, which might hinder the further penetration of PTSA. However, if the pyrrole concentration was greater than 3.0 g·L^{-1}, then the amount of PTSA added into this system became larger correspondingly, and more PTSA molecules were mainly accumulated in the solution; these molecules in solution had more chances to contact with the PPy on the outer surface of the fibers, and they could be easily incorporated into the chains of PPy.

Topochemistry of the Composite Fibers

SEM-EDXA was used to study the topochemistry of the composite fibers. When calculating the N content and the doping level in internal walls, we prepared the transversal cross-section slices of PPy coated pulp fibers, and selected internal walls for SEM-EDXA analysis. As shown in Fig. 7, the N content increased with increasing pyrrole concentration, and no difference was found between the outer surface and the internal wall. The values of S/N ratio based on the outer surface were higher than those based on the internal wall (Fig. 8). As mentioned above, these results imply that PPy on the outer surface had a higher doping level than that in internal wall. The results of this study revealed that pyrrole (or its oligomers) was first adsorbed to the pulp fibers,

followed by the oxidative polymerization of pyrrole in pulp fibers. The rate of doping reaction was slower than that of the oxidation reaction. It was easy for oxidant (ferric chloride) to penetrate the porous structure into the internal wall of fibers at the beginning of the reaction, while it became difficult for dopant (PTSA), because the resulting PPy had deposited in the fibers and hindered the further penetration of PTSA. Therefore, more dopant was incorporated into the PPy on the outer surface.
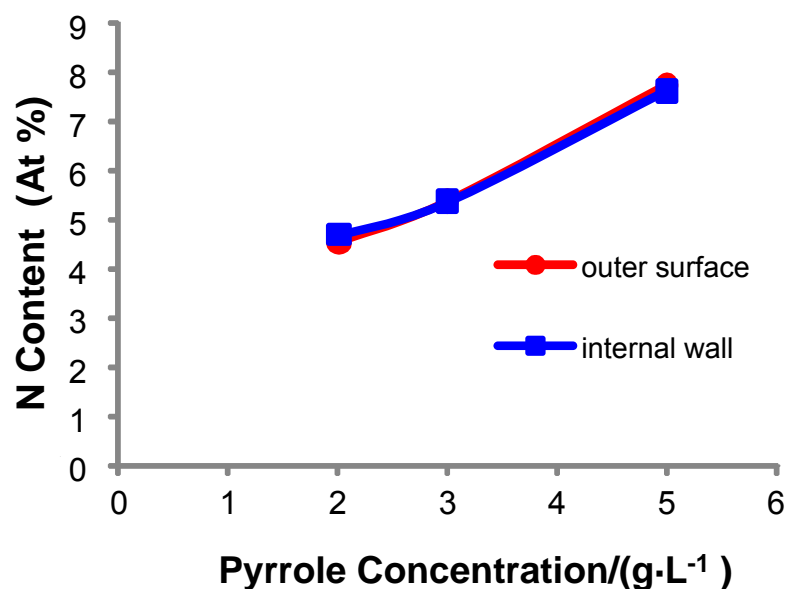

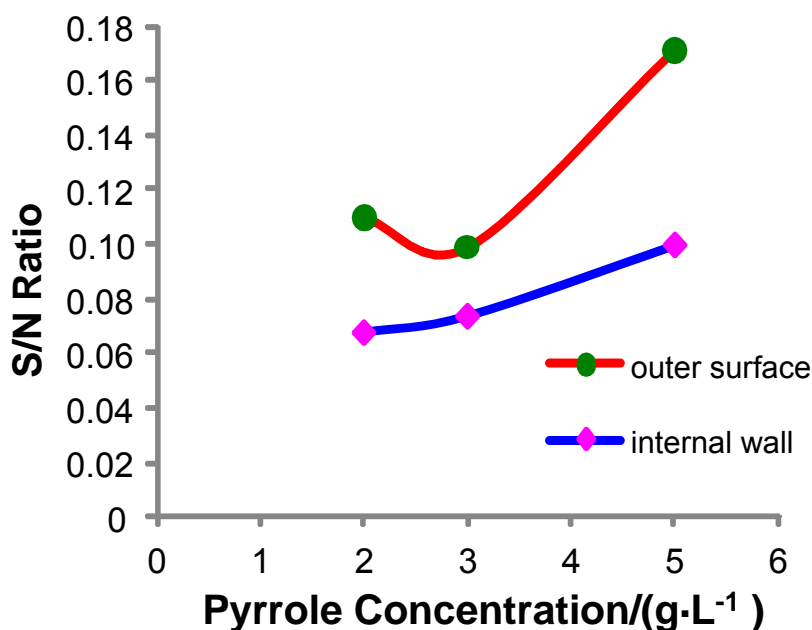**Fig. 7.** Relationship between N content and Pyrrole concentration

Fig. 8. Relationship between S/N ratio and Pyrrole concentration

CONCLUSIONS

1. The concentration of pyrrole used during the preparation had a significant effect on the surface resistivity of cellulose/PPy composite paper. The threshold of pyrrole concentration was 1.2 g·L^{-1}.
2. The adsorption efficiency of PPy was high, and very little polymerization reaction in solution occurred when the pyrrole concentration was less than 2.5 g·L^{-1}.
3. The pyrrole concentration should reach a higher value (more than 1.8 g·L^{-1}) to prepare relatively stable conductive paper with lower resistivity.
4. The XPS results showed that the amount of the PPy coated on the fibers increased, while the doping level first decreased then increased, with the increase of pyrrole concentration.
5. The SEM-EDXA results showed that there was no difference in the amount of PPy coated between the outer surface and the internal wall, and the values of S/N ratio based on the outer surface were higher than those based on the internal wall.

ACKNOWLEDGMENTS

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