

XPS CHARACTERIZATION AND PERCOLATION BEHAVIOR OF POLYANILINE-COATED CONDUCTIVE PAPER

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Polyaniline (PAn)-coated conductive paper was prepared by in-situ polymerization of aniline and a two-step process. XPS results confirmed that the bond between PAn and cellulose existed in the form of hydrogen bonding. The mild treatment did not result in the oxidation and degradation of cellulose. Decreased bonding strength of conductive paper was attributed to the coverage of hydroxyl groups on pulp fibers by PAn. For the PAn-coated paper about one in every three nitrogen atoms was doped with *p*-toluenesulfonic acid (PTSA). The quinoid imine nitrogens of the PAn molecular chain were preferentially doped. Pulp fibers seemed to be favorable for the doping of PAn with PTSA. The surface resistivity sharply decreased at least two orders of magnitude with a very small increase in the amount of PAn coated (from 3.6% to 4.2%). A continuous conductive network was formed and the surface resistivity was lowest when the amount of PAn coated reached 30.1%. The upper and lower threshold values were around 4% and 30%, respectively. SEM study showed that the shape of the PAn coated on pulp fibers was spherical with a diameter from 100 to 200 nm.

Keywords: Conductive paper; Polyaniline; In-situ polymerization; XPS; Conductive percolation

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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).

In recent years, conductive paper produced by in-situ chemical polymerization of pyrrole and aniline in aqueous electrolytes has aroused a great deal of interest because of simplicity, cost effectiveness, and environmental friendliness (Johnston et al. 2006; Huang et al. 2006; Beneventil et al. 2006; Kim et al. 2006; Chen and Qian 2007; Kelly et al. 2007; Ding et al. 2010). The in-situ chemical polymerization process is a process in which the monomer such as aniline and pyrrole is polymerized in the presence of pulp fibers and deposits onto the surface of the pulp fibers.

Very recently, by polymerizing polypyrrole (PPy) on large specific surface area *Cladophora* cellulose, some researchers obtained a flexible, moldable paper material with exceptionally high ion sorption capacity (Mihrianyan et al. 2008; Razaq et al. 2009; Gelin et al. 2009; Nyström et al. 2009; Strømme et al. 2009). This novel material had been

characterized, and the feasibility of its use in various industrial applications including the electrochemically controlled ion-exchange membranes for separation of biologically active substances (e.g. oligonucleotides, DNA, batteries and supercapacitors, etc.) had also been investigated. However, there are relatively few studies on polyaniline (PAn)/cellulose conductive paper composite.

The conductivity of PAn-coated conductive paper mainly depends on two factors besides the amount of PAn coated on pulp fibers: the extent of PAn oxidation and the extent of PAn doping. In fact, the oxidative polymerization of aniline and the PAn doping occur simultaneously during the adsorption and polymerization of PAn. However, the extent of PAn doping is not optimum when the extent of PAn oxidation is optimum. Therefore, secondary doping is needed. Our research results showed that the surface resistivities of the conductive papers without secondary doping were $1240 \Omega \cdot \text{cm}^{-2}$ and $840 \Omega \cdot \text{cm}^{-2}$, whereas those of the conductive papers with secondary doping were $108 \Omega \cdot \text{cm}^{-2}$ and $95 \Omega \cdot \text{cm}^{-2}$ when ammonium persulfate was used as oxidant and sulphuric acid and paratoluenesulfonic acid were used as dopant, respectively. Thus we could see that secondary doping is very important to increasing the conductivity of PAn-coated paper. Based on the above analyses, we presented a two-step process to prepare PAn-coated conductive pulp fibers, i.e., oxidative polymerization (Step 1) and secondary doping (Step 2) (Song et al. 2006a,b).

In our previous studies, we optimized the preparation conditions of PAn-coated conductive pulp fibers (Song et al. 2006a,b). From these investigations, we obtained optimized PAn-coated conductive pulp fibers by using the following conditions: oxidative polymerization (Step 1): 5°C , 105 minutes, 3:4 of ammonium persulfate/aniline mass ratio, and $0.6 \text{ mol} \cdot \text{L}^{-1}$ of doping acid concentration; and secondary doping (Step 2): room temperature and 5 hours.

However, much remains to be done. For example, we do not as yet know the conductive percolation threshold of PAn-coated paper. The conductive percolation threshold is very important parameter for characterizing the novel composite since it determines the concentration of conductive particles at which the dramatic change in conductivity occurs. In addition, little work has been done to characterize the PAn/pulp fiber composite, and this characterization could be very helpful for understanding the structure-property relationship in the novel composite.

Here, we focused on the conductive percolation behavior of PAn-coated paper. Also, we characterized the PAn-coated paper with X-ray photoelectron spectroscopy (XPS), and observed the morphology of the obtained PAn-coated pulp fibers by means of scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Aniline was of analytical 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 study was bleached softwood kraft pulp (BSKP) imported from Canada and obtained from Mudanjiang Hengfeng Paper Co., Ltd. (Heilongjiang

Province, China). The pulp was soaked with water and was beaten to 47 °SR in a Valley Hollander beater before use.

Preparation of PAn-coated Pulp Fibers and Paper

The two-step process presented in our previous study was used to prepare PAn-coated conductive pulp fibers.

Step 1: Two grams of pulp fibers (oven dried basis) and a given amount of aniline monomers were put in a 500 mL of three-neck flask, then a given volume of *p*-toluenesulfonic acid (PTSA) solution ($0.6 \text{ mol}\cdot\text{L}^{-1}$) was added to the system (the pulp consistency was 0.5 %). The suspension was dispersed with effective stirring for 40 minutes for allowing aniline to be adsorbed by the individual pulp fibers. A given amount of ammonium persulfate (APS) solution was dripped slowly to polymerize the aniline monomers at 5 °C for 105 min. The aniline concentration was $7.5 \text{ g}\cdot\text{L}^{-1}$, except where indicated otherwise. The mass ratio of ammonium persulfate to aniline was 3:4. Subsequently, the suspension was removed from the reactor, filtered on a Buchner funnel, and washed two or three times with acetone to remove any free aniline, and next washed with distilled water.

Step 2: The composite fibers obtained were doped with the same concentration of PTSA solution at room temperature for 5 hours. Then, the composite fibers doped were washed thoroughly with distilled water to neutral pH.

A handsheet with a target basis weight of $80 \text{ g}\cdot\text{m}^{-2}$ was formed in a sheet former (ZCX-200, made in China). These handsheets were pressed at 0.4 MPa for 5 min and dried at 105 °C for 4 min.

Measurement of the Amount of PAn

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

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

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

There were not large amounts of fines, dissolved, and colloidal substances generated during the preparation of PAn-coated conductive fibers. Thus, the quantity *A* can be used to represent the amount of PAn coated on pulp fibers.

Measurement of Surface Resistivity

The surface resistivity (R_s) of conductive paper was measured by a diagonal method according to the schematic diagram shown in Fig. 1, and referencing to the General Specification for Chinese Military Electromagnetic Shielding Coating (GJB2604-1996). Two square graphite electrodes ($8\times 8 \text{ mm}^2$) separated by 2 cm were placed on the paper sample with a diameter of 200 mm. The resistance was recorded with a YD2511A intelligent low resistance meter. During measuring, a given pressure was impressed on electrode in order to ensure the pressure between electrode and paper sample more than 0.2 MPa to eliminate the contact resistance.

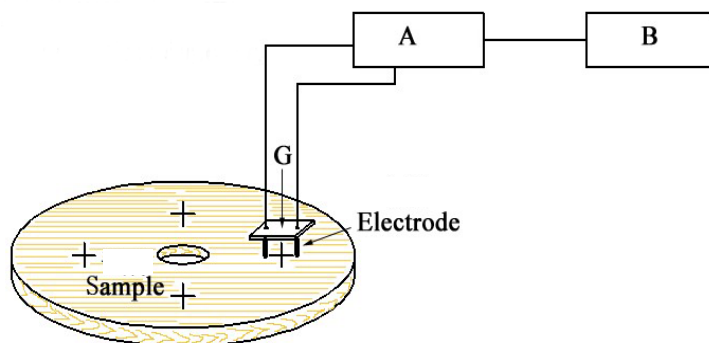


Fig. 1. Schematic diagram of measuring the surface resistivity of conductive paper. Note that A is an intelligent low resistance measuring meter, and B is a computer

The surface resistivity was calculated by the following equation,

$$R_s = R/(2.0 \times 0.8) \quad (2)$$

where R_s is the surface resistivity ($\Omega \cdot \text{cm}^{-2}$), and R is the resistance (Ω). Electrode interval is 2.0 cm, and electrode width is 0.8 cm.

Measurement of Paper Strength

Tensile strength (100 mm span) was measured with a ZLD-300 electronic tensile tester, and zero- and short-span tensile strengths were measured with a Pulmac Z-span 1000 troubleshooter under the standard test conditions (23 °C and 50% relative humidity).

The bonding contribution to tensile strength was determined using the simplified Page Equation (Page 1969) such that

$$1/T = 1/Z + 1/B \quad (3)$$

where T is tensile index, Z is zero-span tensile index, and B is the bonding contribution to tensile strength; all properties have units $\text{N} \cdot \text{m} \cdot \text{g}^{-1}$.

XPS and SEM Analysis

XPS spectra were obtained using a PHI5700 X-ray photoelectron spectrometer (XPS) system. PAN powder was affixed to the sample platform with double-sided adhesive tape, and the surface was flattened; whereas paper samples were cut into small pieces (10 mm × 10 mm) and then fixed on the sample platform. An Al $K\alpha$ X-ray source was used. The vacuum in the analyzing chamber was 4 to 5×10^{-7} 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. The O1s peak at 533.2 eV was used as an internal standard to correct the peak positions. Data fitting was carried out by a least square routine supplied by the instrument manufacturer, using mixed Gaussian-Lorentzian peaks.

Pulp fibers were observed and analyzed by using an FEI Quanta-200 environmental scanning electronic microscope (SEM). The specimens were evenly fixed on the sample platform, and then coated with gold. Finally SEM observations were conducted at different magnifications.

RESULTS AND DISCUSSION

XPS Characterization of PAn-coated Paper

From the data in Table 1, it can be seen that the O/C ratio of PAn-coated conductive paper (Sample B) decreased, which was attributable to the deposition of PAn. There were no nitrogen (N) and sulfur (S) in Sample A and Sample C at all, whereas there were nitrogen and sulfur in Sample B and Sample D; their S/N ratios were 0.27 and 0.18 respectively.

Table 1. XPS Results of Paper Samples

Sample *	C1s (%)	O1s (%)	N1s (%)	S2p (%)	O/C ratio	S/N ratio
A	59.25	40.75	0	0	0.69	0
B	68.64	25.08	4.95	1.33	0.36	0.27
C	62.55	37.45	0	0	0.60	0
D	69.33	15.52	12.82	2.33	0.22	0.18

* Sample A, the handsheet made from the chemically untreated pulp fibers (i.e., the control); Sample B, the handsheet made from the chemically treated pulp fibers (i.e., 30.12% PAn-coated pulp fibers) basing on the above mentioned experimental procedure of preparing conductive paper; Sample C, the handsheet made from chemically treated pulp fibers following the procedure of preparing sample B but without adding aniline monomers; and Sample D (i.e., pure PAn), prepared following the procedure of preparing sample B but without adding pulp fibers. The following Figs. 2 through 4 are the same as given here, with no more explanation.

In this research, the O1s peak at 533.2 eV was used as an internal standard to correct the peak positions. We found that the peak positions of Samples A and C shifted 7.32eV and 6.87eV to the high binding energy side respectively, which was due to the charging effect of insulating materials. The peak positions of Samples B and D did not shift and did not need to be corrected. This fact indicated that the pure PAn and the PAn-coated paper possessed better conductivity. In fact, the O1s peaks of Samples A and C were very symmetric, although they were deconvoluted into two curves. It was noted that the oxygen XPS spectra for the PAn-coated paper (Sample B) and pure PAn (Sample D) had a distinct change when compared to the same spectra for Samples A and B. In the XPS O1s spectra of Samples B and D, the new component at around 535 eV corresponded to S–O bond, which was strong evidence for PAn doping with PTSA (Fig. 2). Of specific importance was the appearance of a shoulder at around 531.5 eV associated directly with C–OH bonding to N in the O1s spectrum for the PAn-coated conductive paper (Sample B). Previous studies had suggested that the bond between PAn and cellulose substrates existed in the form of hydrogen bonding (Johnston et al. 2005; Kelly et al. 2007). Our XPS results supported this hypothesis as well. Compared to Sample A, the oxygen content of Sample C did not increase, and there was no obvious

difference in the O1s and C1s spectra (Fig. 2). So we could infer that the pulp fibers did not become oxidized by APS.

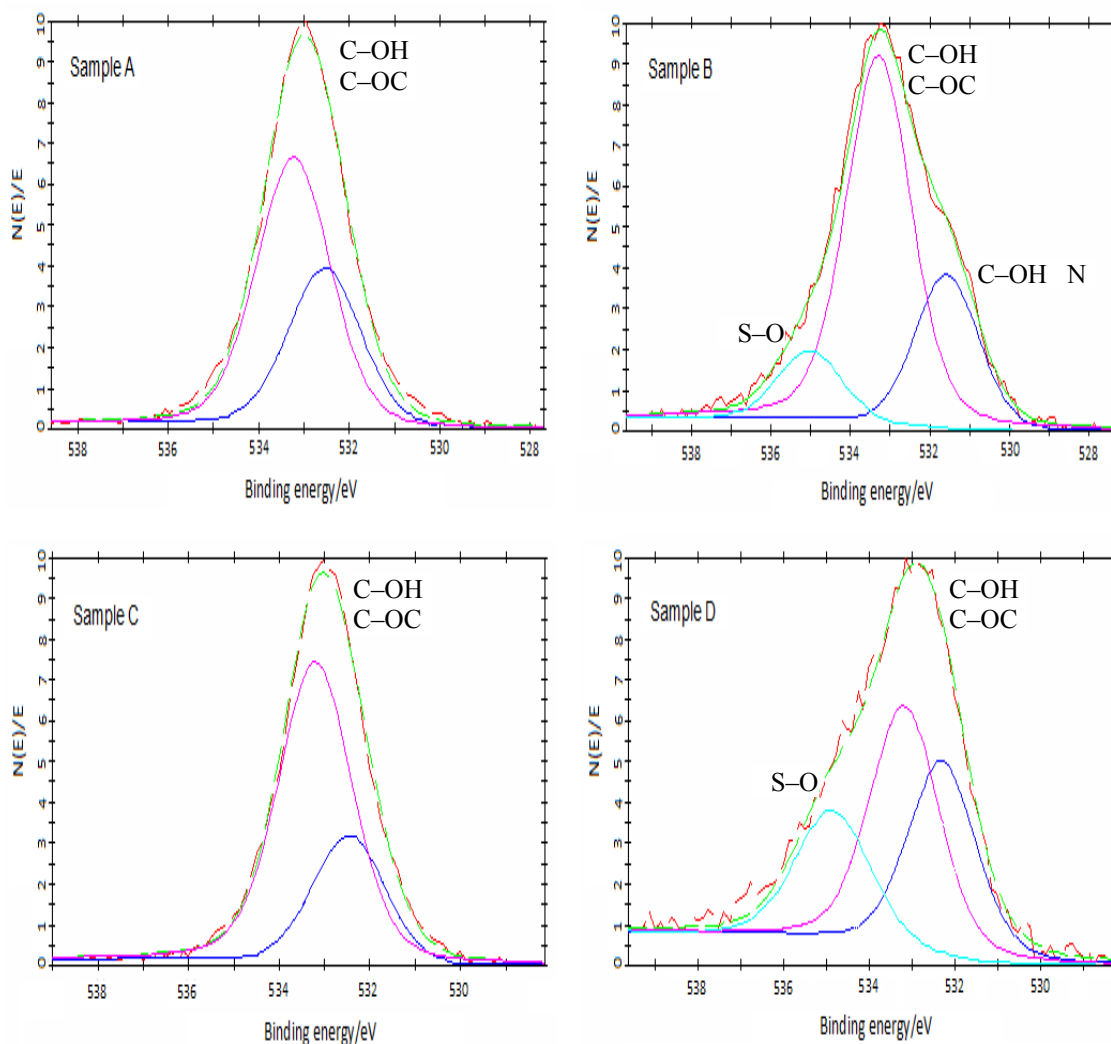


Fig. 2. XPS O1s spectra

Three main components were obtained in the C1s peak of Samples A and C (Fig. 3). The first component at 284.8 eV corresponded to C–C or C–H bonds. The second contribution at 286.6 eV was assigned to C–O bonds. The third line at 288.2 eV was attributed to C=O bonds. However, the XPS C1s spectrum of PAN-coated paper (Sample B) could be deconvoluted into four distinct curves. The second contribution at 286.6 eV decreased greatly, indicating that a large number of hydroxyl groups in cellulose chains were covered by PAN. The new fourth component at 289.6 eV was assigned to C–N bonds, which was the strong evidence of PAN coating. It was noted that, compared to Sample B, the C1s peak position of Sample D shifted about 1 eV to the high binding energy side.

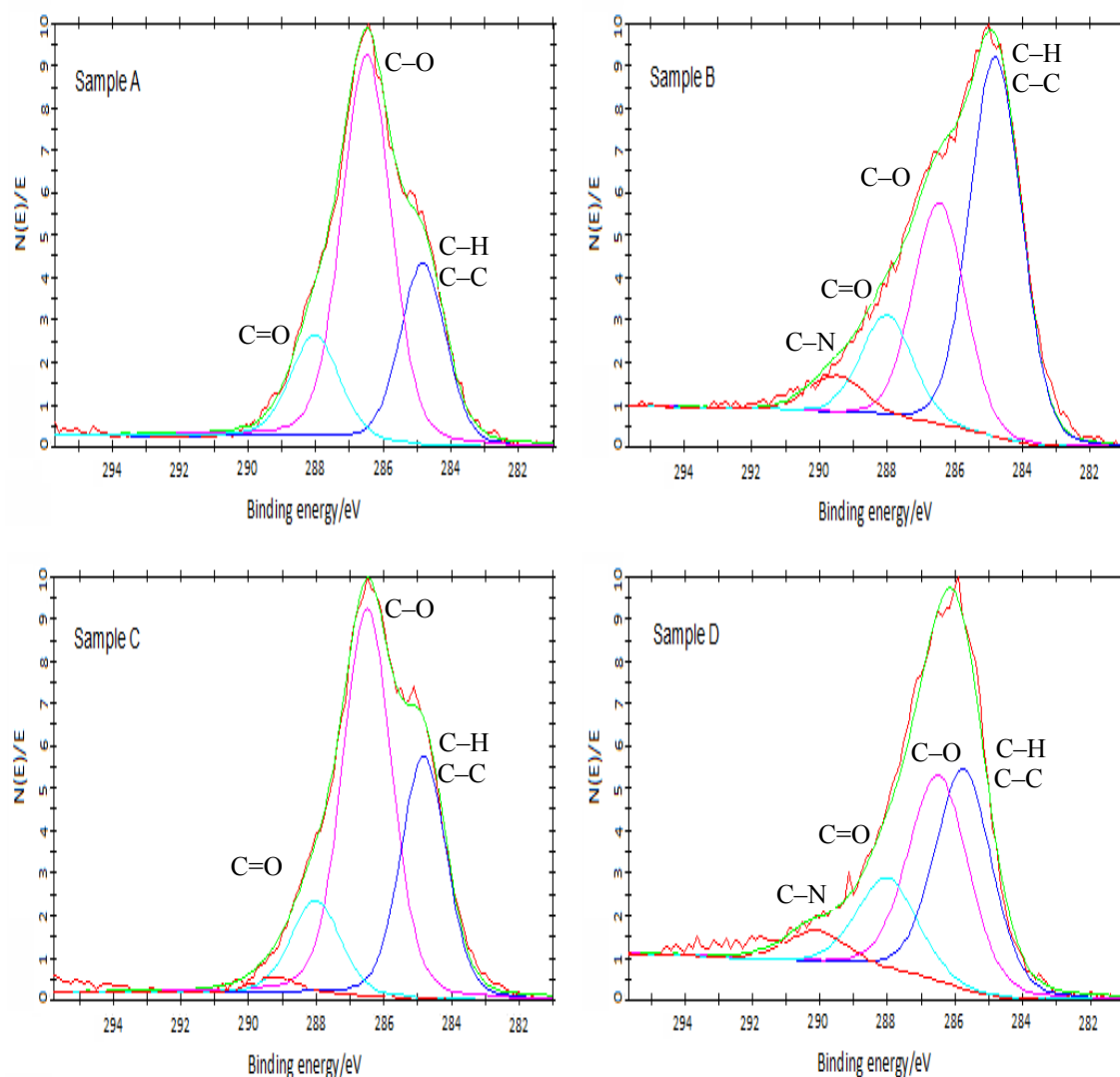


Fig. 3. XPS C1s spectra

As shown in Fig. 4, the XPS N1s spectrum of PAN-coated paper (Sample B) could be deconvoluted into three distinct curves, which were related to the benzenoid amine ($-NH$) (peak at 399.7 eV) and to two positively charged nitrogen atoms, the protonated imine ($-N^+=$) and the protonated amine ($-N^+-$), (peaks at 401.25 eV and 402.5 eV), respectively. These two N^+ species were related to the existence of different protonation environments, which led to formation of a polaron (at lower eV) and a bipolaron (at higher eV) (Han et al. 2002). The quinoid imine ($-N=$) at around 397.5 eV presenting in undoped PAN disappeared, which indicated that the quinoid imines were preferentially protonated by PTSA. The ratio of the protonated nitrogen (N^+ , the sum of $-N^+=$ and $-N^+-$) to total nitrogen (N^+/N) represented doping level (Kang et al. 1998; Molina et al. 2009), and the value was 0.35, which was accordance to the S/N ratio discussed earlier.

This indicated that about one in every three monomer units of PAN in the cellulose/PAN composite was doped with PTSA.

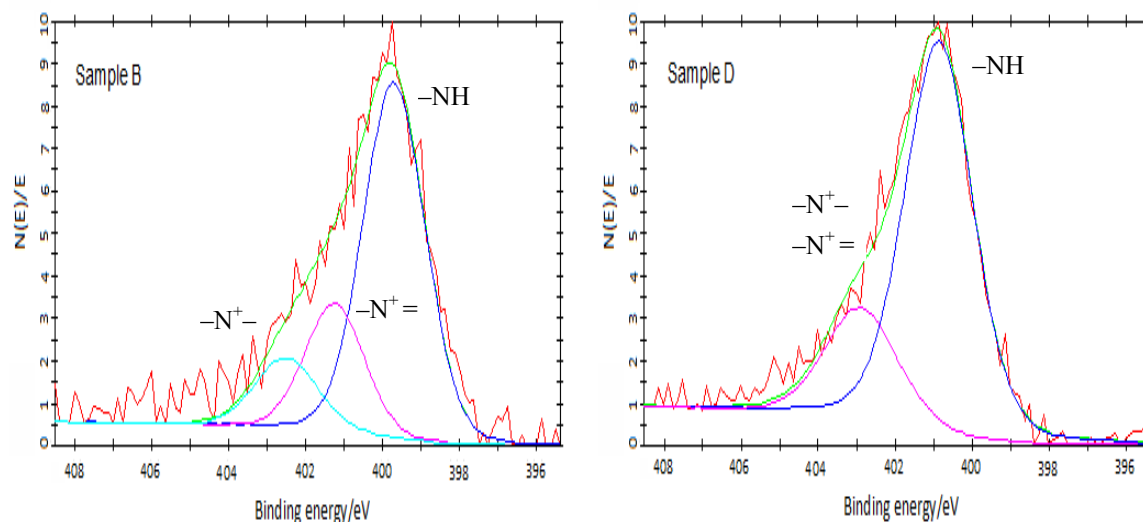


Fig. 4. XPS N1s spectra

On the other hand, the pure PAN (Sample D) showed a different behavior, as observed in Fig. 4. The XPS N1s spectrum of the pure PAN could only be deconvoluted into two distinct curves, which were related to the benzenoid amine (peak at around 401 eV) and to one positively charged nitrogen atom (peak at around 403 eV), respectively. Simultaneously, the N1s peak position shifted about 1 eV to the high binding energy side. The doping level of pure PAN calculated by N^+/N ratio was 0.23, which was in good agreement with the literature (Zhu et al. 2007). This meant that about one in every four monomer units of PAN was doped with PTSA. Compared to the PAN coated on pulp fibers, the pure PAN possessed lower doping level. Therefore, it could be assumed that the pulp fibers promoted the dispersion of the PAN particles generated and prevented their aggregation in the reaction system, which was favorable for the doping of PAN with PTSA. Moreover, the higher doping level of the PAN in the cellulose/PAN composite might be attributed to the interaction of cellulose with PAN chains. As pointed out earlier in this article, it was easy to form hydrogen bonding between the $-OH$ of cellulose and the $-NH$ of PAN.

Mechanical Properties of PAN-coated Paper

The tensile indexes of different paper samples are given in Table 2. The zero-span tensile index of Samples A and C were $82.11 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ and $83.21 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ respectively, and the tensile index of Samples A and C were $54.5 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ and $42.6 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$, respectively. There was only 1.9% mass loss during mild chemical treatment for Sample C. These results indicated that the mild chemical treatment did not result in the severe damage of pulp fibers, which was in agreement with the XPS results in Fig. 2. The slightly low tensile strength of Sample C was probably because the chemical deactivation of pulp fiber surface resulted in a decrease of the bonding contribution to tensile strength.

However, the tensile index and zero-span tensile index of Sample B were $22.6 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ and $81.18 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$, respectively. Therefore, the bonding contribution to the tensile strength of conductive paper was low due to the coverage of hydroxyl groups on pulp fibers by PAn. In addition, the resulting fibers gave rise to a paper with low flexibility and high fragility due to the encapsulation of fibers with PAn. The strength properties of conductive paper need to be improved. The blended papermaking process might be able to solve this problem.

Table 2. Tensile Indexes of Paper Samples

Sample	Tensile index ($\text{N}\cdot\text{m}\cdot\text{g}^{-1}$)				Bonding contribution ($\text{N}\cdot\text{m}\cdot\text{g}^{-1}$)
	0 mm span	0.2 mm span	0.6 mm span	100 mm span	
A	82.11	49.56	28.11	54.5	162.05
B	81.18	46.13	23.41	22.6	31.32
C	83.21	50.22	27.11	42.6	87.29

Conductive Percolation of PAn-coated Paper

The data for aniline concentration, amount of PAn coated (*A*), and surface resistivity (R_{s0}) are shown in Table 3. The amount of PAn coated on pulp fibers increased linearly when aniline concentration was from 0.75 to $7.5 \text{ g}\cdot\text{L}^{-1}$, but kept constant beyond $10 \text{ g}\cdot\text{L}^{-1}$ because the saturation adsorption was reached (Fig. 5). Therefore, the adsorption of PAn onto pulp fibers belongs to the classical Langmuir type. It was noted that at 0.5% pulp consistency and $5 \text{ g}\cdot\text{L}^{-1}$ aniline concentration, the dosage of aniline to pulp was 100% , but the amount of PAn on fibers was only 19.16% . We speculated that this was due to both a lower conversion rate of aniline to PAn and a lower retention rate of PAn on fibers. The lower conversion rate resulted from the very low pulp consistency and the barrier effect of fibers. The medium and high consistency at mill conditions can improve the conversion rate. The lower retention rate resulted from the adsorption equilibrium of PAn onto pulp fibers.

Table 3. Aniline Concentration, Amount of PAn Coated (*A*), and Surface Resistivity (R_{s0})

Aniline concentration ($\text{g}\cdot\text{L}^{-1}$)	<i>A</i> (%)	R_{s0} ($\Omega\cdot\text{cm}^{-2}$)
0.75	3.60	$> 5\times 10^5$
1.25	4.20	1445.4
2.5	9.09	912.0
3.75	14.80	660.7
5.0	19.16	407.4
6.25	25.10	218.8
7.5	30.12	95.0
8.75	32.62	107.0
10.0	35.18	115.0
11.25	35.64	123.0
12.5	36.06	125.9
13.75	36.07	125.9

At very low PAn content ($\leq 3.6\%$), there was no detectable electrical conductivity. However, the surface resistivity sharply decreased from more than 5×10^5 to $1445 \Omega \cdot \text{cm}^{-2}$, at least two orders of magnitude, with a very small increase in the amount of PAn coated (from 3.6% to 4.2%). It continued to decrease with further increase in the amount of PAn coated with about one order of magnitude decrease in the range of 4.2% to 30.1% (Fig. 6). The surface resistivity was lowest, and its value was $95 \Omega \cdot \text{cm}^{-2}$ when the amount of PAn coated reached 30.1%. Beyond this point, the surface resistivity no longer decreased but slightly increased.

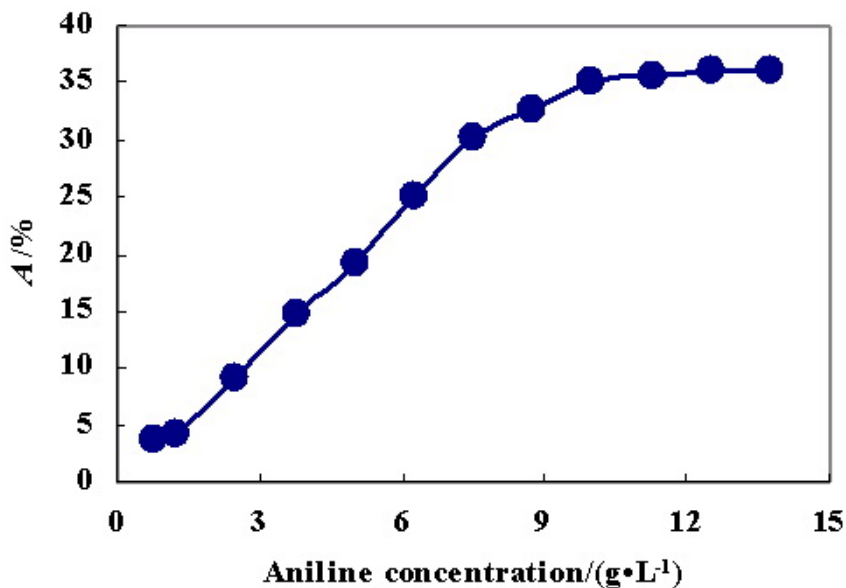


Fig. 5. Relation between amount of PAn coated (A) and aniline concentration

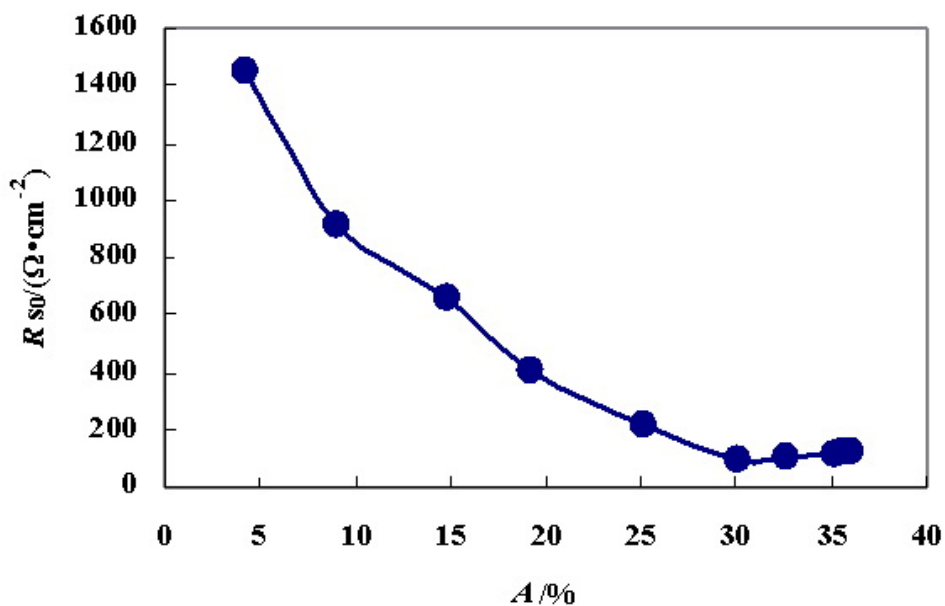


Fig. 6. Relation between surface resistivity (R_{s0}) and amount of PAn coated (A)

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 PAN molecules in a non-conductive pulp fiber leads to a significant drop of resistivity. This phenomenon was evident when the amount of PAN coated increased from 3.6% to 4.2%. In turn, at higher PAN content (over 30.1%) additional PAN did not lead to a further significant drop in resistivity. According to the above experimental results, the upper and lower threshold values were around 4% and 30%, respectively.

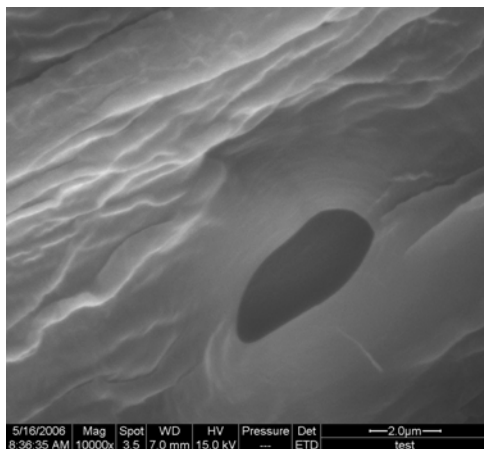
Morphology of PAN-coated Pulp Fibers

The pulp fibers observed in this study included untreated (Fig. 7a) and PAN-coated fibers (Figs. 7b-f). The shape of the PAN coated on pulp fibers was spherical with a diameter from 100 to 200 nm. The spheres of PAN prepared at higher aniline concentration were larger than those at lower aniline concentration. We could observe from Fig. 7b that the PAN on the pulp fiber surface were scarce, they did not mutually contact each other, and were not be able to form conductive network in the composite. This is in agreement with the fact the resistance of conductive paper surpassed the highest measurable value of the instrument.

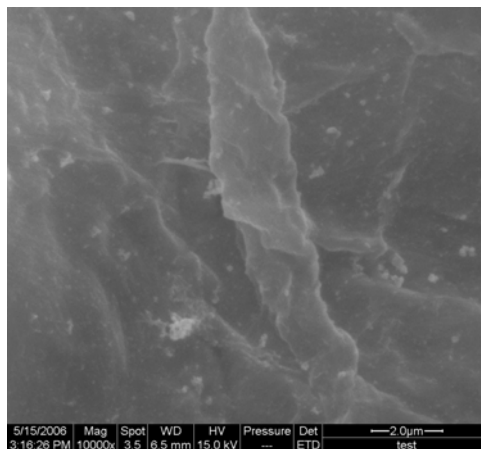
From Fig. 7c we could observe that a conductive network was formed on the pulp fiber surface, although it was not continuous when the amount of PAN coated reached 9.1%. From Figs. 7c-e, we found that the conductive network became more and more continuous with increasing amounts of PAN coated. This was advantageous for reducing surface resistivity. The pulp fiber surface was fully encapsulated by PAN particles, and the surface resistivity was lowest when the amount of PAN coated reached 30.1%. However, a large extent of PAN particle aggregation phenomena on pulp fiber surface occurred when the amount of PAN coated was excessive and reached 35.2% (Fig. 7f), so the surface resistivity instead slightly increased.

As shown in Fig. 8, the pits of 9.1% PAN coated pulp fibers were not plugged, while those of 30.1% PAN coated pulp fibers were plugged with PAN. In addition, a large number of PAN particles at pulp fiber lumen entrances were observed when the amount of PAN coated reached 30.1%, although there was no PAN within the lumen.

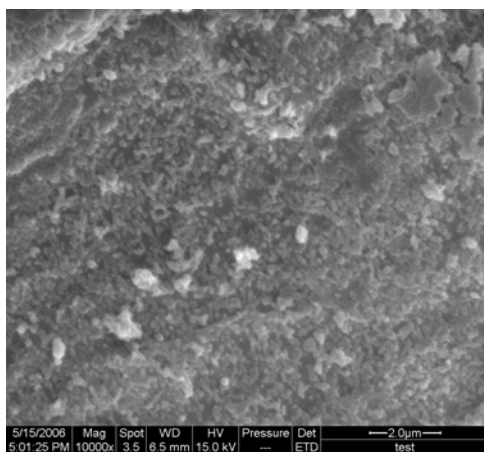
The above results can explain why the amount of PAN coated remained constant when aniline concentration was beyond 10 g·L⁻¹. The excess PAN particles were only formed in solution, because all transport channels were plugged with PAN, and the saturation adsorption of PAN on pulp fibers had been reached.



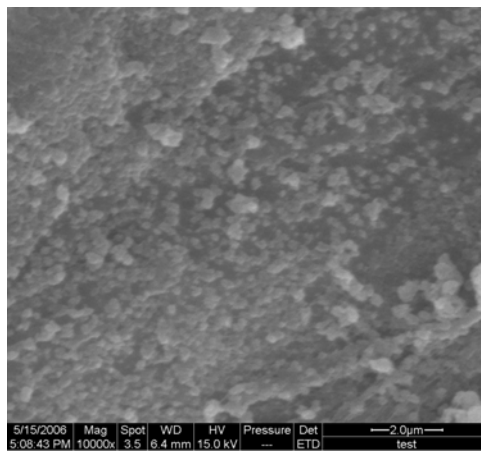
a. untreated fibers



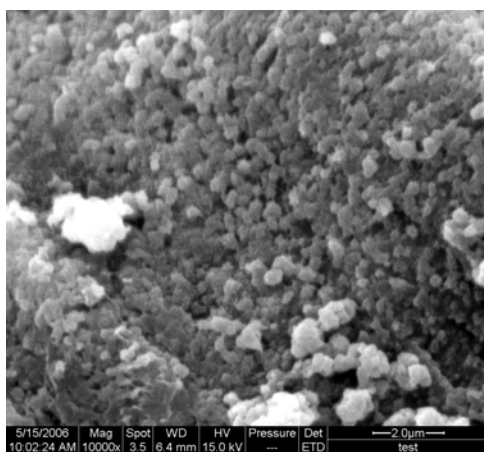
b. 3.6 % PAn coated fibers



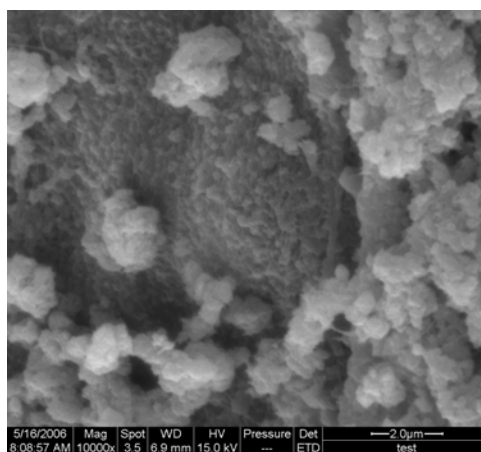
c. 9.1 % PAn coated fibers



d. 19.6 % PAn coated fibers

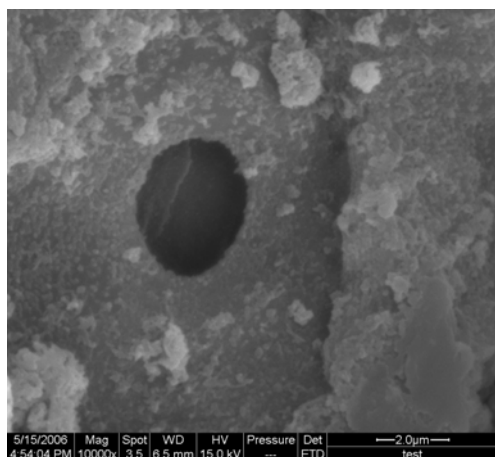


e. 30.1 % PAn coated fibers

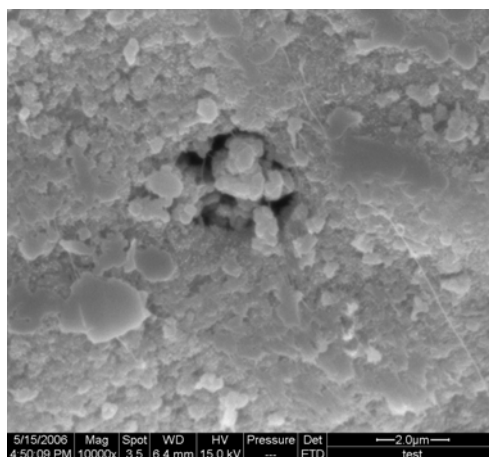


f. 35.2 % PAn-coated fibers

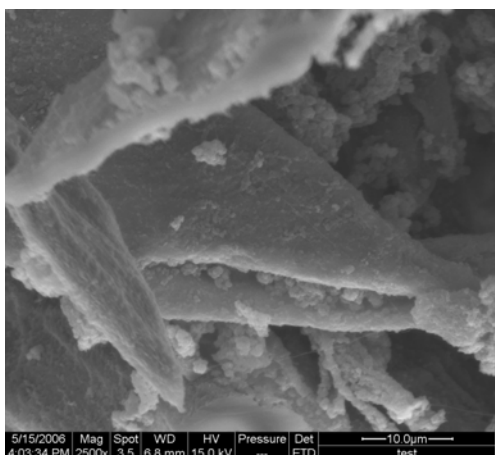
Fig. 7. SEM images of PAN-coated pulp fiber surfaces



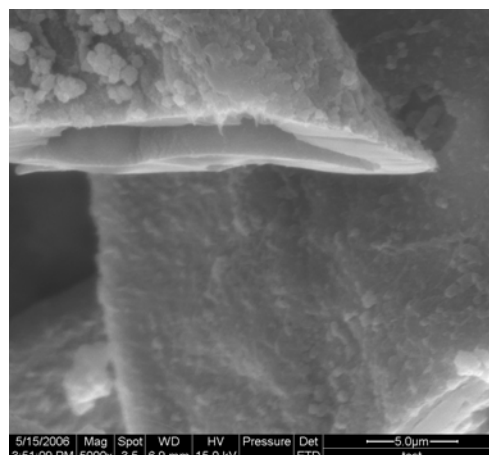
a. 9.1 % PAN coated fibers, the pit was not plugged with PAN



b. 30.1 % PAN coated fibers, the pit was plugged with PAN



c. 30.1 % PAN coated fibers, there were PAN at fiber lumen entrance



d. 30.1 % PAN coated and cut fibers, there was no PAN within the lumen

Fig. 8. SEM images of PAN coated pulp fiber pits and lumens

CONCLUSIONS

In this study, PAN-coated conductive paper was characterized by XPS, and its percolation behavior was investigated by combining with SEM observation. From the results of this study, we could draw the following conclusions:

1. The bond between PAN and cellulose existed in the form of hydrogen bonding. The mild treatment did not result in the oxidation and degradation of cellulose. The lower bonding strength of conductive paper was due to the coverage of hydroxyl groups on pulp fibers by PAN.

2. For the PAN-coated paper about one in every three nitrogen atoms was doped with PTSA. The quinoid imine nitrogens of the PAN molecular chain were preferentially doped. Pulp fibers seemed to be favorable for the doping of PAN with PTSA.
3. The amount of PAN coated remained constant beyond $10 \text{ g}\cdot\text{L}^{-1}$ of aniline concentration because all transport channels were plugged with PAN and the saturation adsorption of PAN had been reached. At very low PAN content ($\leq 3.6\%$), there was no detectable electrical conductivity. The surface resistivity sharply decreased at least two orders of magnitude with a very small increase in the amount of PAN coated.
4. A continuous conductive network was formed and the surface resistivity was lowest when the amount of PAN coated reached 30.1%. Beyond this point, the surface resistivity no longer decreased but slightly increased due to a large extent of PAN particle aggregation. The upper and lower threshold values were around 4% and 30% respectively.

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