INFLUENCE OF PULP FIBER SUBSTRATE ON CONDUCTIVITY OF POLYANILINE-COATED CONDUCTIVE PAPER PREPARED BY IN-SITU POLYMERIZATION

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The influences of pulp type, content of acidic groups (i.e., sulfonic and carboxylic groups) in CTMP, kappa number (i.e., residual lignin content) of unbleached kraft pulp, and beating degree of bleached kraft pulp on the conductivity of polyaniline (PAn)-coated conductive paper were investigated. The amounts of PAn coated on chemical pulps were higher than those coated on high yield pulps, and the surface resistivities of conductive papers prepared from chemical pulps were lower than those prepared from high yield pulps. As the substrates for the production of PAn-coated conductive paper, bleached chemical pulps were better than unbleached chemical pulps. The conductivity had a significant positive linear correlation with the amount of PAn coated. The amount of PAn coated increased with increasing content of sulfonic groups in CTMP or decreasing kappa number of unbleached kraft pulp. We hypothesized that this might be associated with the ionizability of acidic groups and the inhibiting effect of lignin on aniline polymerization. The beating degree of pulp seemed to have an insignificant effect on the conductivity of PAn-coated conductive paper. As a whole, the interpretations of the influence of the chemical composition are based on proposed ideas and need to be confirmed by future experimental work.

Keywords: Conductive paper; Polyaniline; Pulp fibers; In-situ polymerization

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INTRODUCTION

Conductive polymers have generated a great deal of interest because of their physical and chemical properties as well as their potential in industrially useful materials. However, one of the shortcomings of most electricity-conducting polymers is that they are often formed as intractable films that are difficult to process (Oh et al. 2002; Negi and Adhyapak 2002). To overcome this problem, aniline or pyrrole was polymerized into pulp fibers by an in-situ polymerization process in order to manufacture polyaniline (PAn)- or polypyrrole (PPy)-coated conductive paper (Huang et al. 2005; Johnston et al. 2006; Huang et al. 2006; Beneventil et al. 2006; Kim et al. 2006; Song et al. 2006a,b; Chen and Qian 2007; Kelly et al. 2007; Ding et al. 2010). The conductive paper is a kind of functional paper that can be widely used as antistatic packaging material, electromagnetic shielding material, new energy and electrochemical material, as a component of sensor and driven material, and other such applications.

The structure, morphology, and properties of the substrate influence and even determine, to a large degree, the final performance of composite materials. The structures, morphologies, components, and properties of the pulp fiber substrates which are used in PAn- or PPy-coated conductive paper production depend on plant fiber categories, pulping processes used, and the extent of pulping (delignification) and refining (beating), etc. The differences of pulp fiber substrates in structures, morphologies and properties will cause differences in the conductivity of PAn- or PPy-coated conductive paper.

The study results from Huang et al. (2006) indicated that PPy-coated BCTMP showed the highest paper conductivity among all the PPy-coated pulps. Since acid chlorite delignified BCTMP showed almost identical paper resistivity after the same in-situ polymerization treatment, the existence of sulfonated lignin in BCTMP, which could possibly act as self-dopant for the PPy, had negligible influence on paper conductivity. Kang and Ni (2008) also investigated the effect of fiber morphology on the conductivity of the PPy-coated conductive paper. The results showed that above a critical average fiber length of about 0.5 mm, pulp fibers with a lower average fiber length gave better conductivity. However, if pulp fibers are too short, their ability to form an effective fiber network could be hampered, consequently decreasing the conductivity. The presence of fines improved the conductivity, and the fiber curl had insignificant effect on the conductivity.

In the present work, we focused on the influence of pulp fiber substrate on the conductivity of PAn-coated conductive paper. Pulp type, content of acidic groups (i.e., sulfonic and carboxylic groups) in CTMP, kappa number (i.e., residual lignin content) of unbleached kraft pulp, and beating degree of bleached kraft pulp were considered as the main factors influencing the conductivity.

EXPERIMENTAL

Materials

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

The CTMPs with different contents of acidic groups were provided by Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology. The unbleached larch kraft pulps with different kappa numbers in the range 20–46 were prepared by varying the alkali charge (15%–21%), heating-up time (70–130 min), and retention time at the maximum temperature (20–60 min) in our lab. The bleached softwood kraft pulps with different beating degrees in the range 30–74 ^{o}SR were prepared by beating in a ZQS-PFI vertical refiner at 10% of pulp consistency for different times. Bleached softwood kraft pulp imported from Canada was obtained from Mudanjiang Hengfeng Paper Co., Ltd. The sources of the other pulps used in this study are given in Table 1.

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 (Song et al. 2006a,b; Li et al. 2010).

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 mol·L^{-1}) was added to the system (the pulp consistency was 0.5 %). The suspension was dispersed with effective stirring for 40 minutes to allow aniline to be absorbed by the individual pulp fibers. A given amount of ammonium persulfate (APS) solution was dripped slowly to polymerize the aniline monomers at 5 ^{o}C for 105 min. In all preparations the initial concentration of aniline was 7.5 g·L^{-1}, and 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 g·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 ^{o}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,

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

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

Measurement of Surface Resistivity

The resistance (*R*) of conductive paper was recorded with a YD2511A intelligent low resistance meter. The surface resistivity was calculated by the following equation,

$$R\text{s} = R/(2.0\times0.8) \qquad (2)$$

where *R*s is the surface resistivity (Ω·cm^{-2}), and *R* is the resistance (Ω). The electrode interval was 2.0 cm, and the electrode width was 0.8 cm.

A more detailed testing procedure was given elsewhere (Li et al. 2010).

RESULTS AND DISCUSSION

Influence of Pulp Type

Ten different pulps (five high yield pulps and five chemical pulps) were used to evaluate the influence of pulp type. Four of the ten pulps used were laboratory-prepared pulps, and the others were mill-produced pulps. As seen in Table 1, the amounts of PAn coated on chemical pulps were higher than those coated on high yield pulps, and the surface resistivities of conductive papers prepared from chemical pulps were lower than those prepared from high yield pulps. As the substrates for the production of PAn-coated conductive paper, bleached chemical pulps were better than unbleached chemical pulps. The amounts of PAn coated and the surface resistivities for sulfite pulps were not obviously different from those for kraft pulps. Since the amounts of PAn coated on CTMPs were higher than those coated on ECMPs (Extruder Chemi-Mechanical Pulps) and APMP, the conductivities of conductive papers prepared from CTMPs were higher than those of conductive papers prepared from ECMPs and APMP. In addition, we found that the surface resistivity had a significant linear correlation with the amount of PAn coated (see Fig. 1). The surface resistivity of conductive paper linearly decreased with the increase of the amount of PAn coated. This result possibly revealed that the conductivity of conductive paper seemed to only depend on the amount of PAn coated.

Table 1. Influence of Pulp Type

Pulp type	Pulp source	*A* (%)	*R*s ($\Omega\cdot cm^{-2}$)
Cotton stalk CTMP [a]	Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology	22.02	259.8
Triploid poplar CTMP [b]	Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology	21.64	298.0
Cotton stalk ECMP [c]	Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University	14.95	498.5
Wheatstraw ECMP [d]	Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University	14.50	501.6
Aspen APMP	Qiqihar Paper Co., Ltd. (Qiqihar, China)	17.84	424.6
Larch unbleached kraft pulp (UBKP)	Heilongjiang Sida Paper Co., Ltd. (Qiqihar, China)	25.40	226.0
Larch unbleached kraft pulp (UBKP)	Jiamusi Paper Group Co., Ltd. (Jiamusi, China)	24.50	249.7
Softwood bleached kraft pulp (BKP)	Imported from Canada, and obtained from Mudanjiang Hengfeng Paper Co., Ltd.	30.12	95.0
Pine unbleached sulfite pulp (UBSP)	Yanbian Shixian Bailu Paper Co., Ltd. (Tumen, China)	25.60	216.0
Pine bleached sulfite pulp (BSP)	Yanbian Shixian Bailu Paper Co., Ltd. (Tumen, China)	29.02	105.0

(a) 2.5 % NaOH, 3.0 % Na_2SO_3; (b) 2.0 % NaOH, 3.0 % Na_2SO_3; (c) presoaking with 2 $g\cdot L^{-1}$ NaOH for 5min, then refining by a twin-screw extruder with 12% NaOH for 90 min; and (d) presoaking with 3.95 $g\cdot L^{-1}$ NaOH for 10min, then refining by a twin-screw extruder.

We speculated that the dissimilarities in structures, components and properties of different types of pulp fibers might play a key role in determining the polymerization of aniline or the adsorption of PAn. Therefore, in the following study, we investigated the influence of content of acidic groups (i.e., sulfonic and carboxylic groups) in CTMP, kappa number of unbleached kraft pulp, and beating degree of bleached kraft pulp.

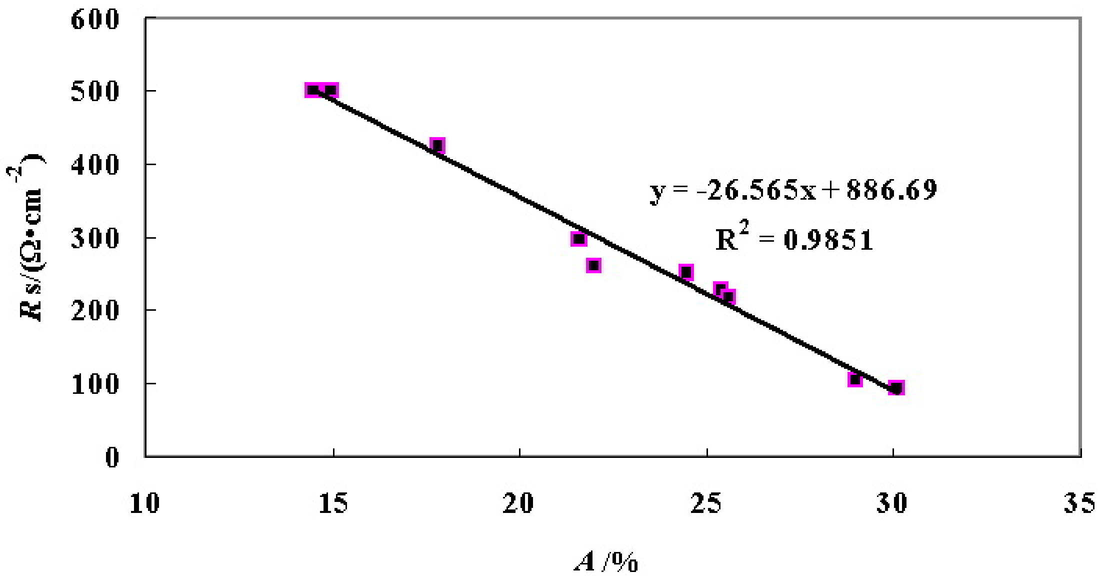

Fig. 1. Relation between surface resistivity (*R*s) and amount of PAn coated (*A*)

Influence of Content of Acidic Groups in CTMP

Conductive papers were prepared by using cotton stalk CTMPs and triploid poplar CTMPs with different contents of acidic groups as pulp fiber substrates, and the results are shown in Table 2. Through a detailed analysis of these data (especially from cotton stalk CTMP), we found that the amount of PAn coated and the surface resistivity had a good correlation with the content of sulfonic groups in CTMP, but a very weak or no clear correlation with the content of carboxylic groups and total acidic groups in CTMP. The amount of PAn coated increased with increasing content of sulfonic groups in CTMP, and thereby the surface resistivity of conductive paper decreased.

Table 2. Influence of Content of Acidic Groups in CTMP

Pulp type	Chemical treatment conditions		Acidic groups *			*A* (%)	*R*s ($\Omega \cdot cm^{-2}$)
	NaOH (%)	Na_2SO_3 (%)	Sulfonic group ($mmol \cdot kg^{-1}$)	Carboxylic group ($mmol \cdot kg^{-1}$)	Total ($mmol \cdot kg^{-1}$)		
Cotton stalk CTMP	2.5	2.0	64.5	107.4	171.9	18.81	326.8
		2.5	79.0	102.9	181.9	20.63	306.5
		3.0	102.9	110.5	213.4	22.02	259.8
		3.5	89.0	78.9	167.9	21.96	266.9
Triploid poplar CTMP	2.0	3.0	94.6	51.7	146.3	21.64	298.0
		4.0	107.5	67.0	174.5	23.42	241.7

* The amounts of sulfonic and carboxylic groups in CTMP were measured in accordance with the conductometric titration method proposed by Katz et al. (1984).

As we have known, the dissociation of acidic groups in pulp fibers depends on the pH of the system. To ionize the acidic groups in pulp fibers, the system pH should be 2 pH units higher than their p*K*a values. The sulfonic group is a strong acid (p*K*a<1), so it can be dissociated in any pH condition. However, carboxylic group is a weak acid (p*K*a = 4–5), so it can be fully dissociated only when the medium pH is above 6. According to the above analysis, the sulfonic groups in pulp fibers could be dissociated, while the carboxylic groups could not be dissociated under our experimental conditions (pH<2). This might mean that only the sulfonic groups in pulp fibers were negatively charged, and could promote the adsorption of the positively charged PAn. The carboxylic groups in pulp fibers might have no contribution to the adsorption of PAn due to their low ionizability in the acidic reaction medium. In addition, although the self-doping effect of sulfonic groups in CTMP fibers could not be excluded, it could be inferred from the strong dependence of the conductivity on the amount of PAn coated that this self-doping effect should be very weak. This could be explained from the high steric hindrance of the sulfonic groups in pulp fibers. The sufficient existence of PTSA with low steric hindrance made the PAn be preferentially doped with PTSA. The above interpretations are based on proposed but not proven ideas and need to be confirmed by experiments.

Influence of Kappa Number of Unbleached Kraft Pulp

As seen from the results shown in Table 3, the amount of PAn coated and the surface resistivity of conductive paper had a very close correlation with the kappa number of pulp. The amount of PAn on the fiber increased as the kappa number decreased from 45.8 to 19.7, thereby the surface resistivity of the paper decreased. This result might indicate that the residual lignin in pulp fibers greatly affected the polymerization of aniline or the adsorption of PAn. Generally, aniline polymerization proceeds via a cation-redical mechanism (Ding et al. 1999). The study based on model compounds indicated that phenolic hydroxyl groups could inhibit the polymerization of aniline, since they trapped aniline cation-radicals (Chen 2003). Lignin is a polymer having phenolic hydroxyl groups, so it is possible that lignin could inhibit the polymerization of aniline. This could also be used to explain why the amount of PAn coated was low and the surface resistivity was high when high yield pulp was used as the substrate.

On the other hand, the content of carboxyl groups and hexenuronic acid (HexA) in pulp fibers linearly decreased with decreasing kappa number during kraft pulping (Bhardwaj et al. 2006). The fact that the amount of PAn coated did not decrease but increased with decreasing kappa number also indirectly indicated that the carboxylic groups in pulp fibers might not affect the adsorption of PAn. In addition, pulp fiber porosity had been reported to increase with decreasing yields in both sulfite and kraft pulping processes (Wong et al. 1988), so the increase of the porosity of pulp fibers might have contributed to the increase of the amount of PAn coated. High inner porosity might promote the permeation of aniline and oligoaniline into fiber matrix. The above inferences need to be confirmed by future experimental work.

Table 3. Influence of Kappa Number of Unbleached Kraft Pulp

Exp. No.	1#	2#	3#	4#	5#	6#
Alkali charge (%, based on Na_2O)	15	17	18	19	20	21
Time from 120 °C to the maximum temp. (min)	70	90	100	110	120	130
Time at the maximum temp. (min)	20	30	45	50	55	60
Coarse pulp yield (%)	49.56	47.62	45.86	45.42	45.02	44.56
Screened pulp yield (%)	39.37	43.5	44.92	45.04	44.67	44.56
Kappa number of pulp	45.8	33.0	29.9	26.2	23.0	19.7
A (%)	16.05	21.02	25.02	25.68	26.02	26.86
*R*s ($\Omega \cdot cm^{-2}$)	359.9	271.5	232.5	216.8	200.3	186.0
Note: sulfidity 26% (based on Na_2O), the ratio of wood to liquor 1:3.5, raising temperature to 120 °C for 1 h, the maximum temp. 168 °C.						

Influence of Beating Degree of Bleached Kraft Pulp

As seen in Table 4, when the beating degree of pulp increased from 30 °SR to 74 °SR, the amount of PAn coated (*A*) and the surface resistivity (*R*s) of conductive paper varied in the range 30.1%–27.4% and 94.5–99.8 $\Omega \cdot cm^{-2}$, respectively. Thus, we tentatively concluded that the beating degree of bleached softwood kraft pulp had an insignificant effect on the surface resistivity of conductive paper, although higher beating degree (>47 °SR) led to slightly lower amount of PAn coated. The study results from Bhardwaj et al. (2007) showed that refining increased the surface charge, specific surface area and specific volume of pulp fibers, but did not change the total fiber charge. In principle, the high specific surface area of pulp should be favorable for the adsorption of PAn. A little lower amount of PAn coated at higher beating level (>47 °SR) might be associated with the loss of fines. Existing studies have shown that beating/refining can produce fines. If so, it would be very easy to understand why the conductivity nearly did not decrease. However, more extensive experiments need to be done to verify the above inference.

Table 4. Influence of Beating Degree of Bleached Kraft Pulp

Beating degree (°SR)	*A* (%)	*R*s ($\Omega \cdot cm^{-2}$)
30	30.09	97.9
40	30.18	96.0
47	30.11	94.8
64	28.30	97.4
74	27.40	99.8

CONCLUSIONS

1. The amounts of PAn coated on chemical pulps were higher than those coated on high yield pulps, and the surface resistivities of conductive papers prepared from chemical pulps were lower than those prepared from high yield pulps. As substrates for the

production of PAn-coated conductive paper, bleached chemical pulps were more suitable than unbleached chemical pulps.
2. The conductivity of conductive paper had a significant positive linear correlation with the amount of PAn coated, probably revealing that the conductivity seemed to only depend on the amount of PAn coated.
3. The amount of PAn coated increased with increasing content of sulfonic groups in CTMP or decreasing kappa number of unbleached kraft pulp, which might be associated with the ionizability of acidic groups and the inhibiting effect of lignin on aniline polymerization.
4. The beating degree of pulp seemed to have an insignificant effect on the conductivity of PAn-coated conductive paper, although higher beating degree (>47 ^{o}SR) led to a somewhat lower amount of PAn coated.

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