

PREPARATION AND CHARACTERIZATION OF CONDUCTIVE PAPER VIA IN SITU POLYMERIZATION OF 3,4-ETHYLENEDIOXYTHIOPHENE

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Conductive paper was prepared via in situ chemical oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) in pulp suspension by using iron(III) *p*-toluenesulfonate ($\text{Fe}(\text{OTs})_3$) as both an oxidant and a dopant source. The deposition of poly(3,4-ethylenedioxythiophene) (PEDOT) on the pulp fiber surface was verified and characterized by ATR-FTIR and SEM analyses. The factors affecting the conductivity of the PEDOT-coated paper were investigated, and the preparation conditions of the conductive paper with a low resistivity and excellent environmental stability was obtained. The optimum reaction temperature and time were 60 °C and 4 h, respectively. The molar ratio of EDOT to $\text{Fe}(\text{OTs})_3$ of 1:1 was optimal when considering both cost and performance factors. The conductivity of the PEDOT-coated paper could be controlled by adjusting EDOT concentration. The threshold concentration of EDOT was about $3 \text{ g}\cdot\text{L}^{-1}$, and a volume resistivity as low as $5.9\times 10^3 \Omega\cdot\text{cm}$ could be achieved, which reached the conductivity range of an electrical conductor. The environmental stability of the PEDOT-coated conductive paper was very good due to the much higher oxidation potential of PEDOT.

Keywords: Conductive Paper; Poly(3,4-ethylenedioxythiophene); In Situ Polymerization; Iron *p*-Toluenesulfonate

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INTRODUCTION

Electrically conductive paper composite (ECPC) is potentially 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 (Jang et al. 2006). Various methods may be used to prepare electrically conductive (EC) paper. It may be prepared by directly polymerizing conducting polymers (polyaniline and polypyrrole) onto the paper sheet, both in liquid and gas phase (Johnston et al. 2005; Chen et al. 2008; Qian et al. 2010a), by inkjet-printing conducting polymer dispersion, or by application of oxidant solution followed by vapor-phase polymerization of the conducting polymer to the paper matrix (Winther-Jensen et al. 2007).

Because of the simplicity of design and preparation, cost effectiveness, and environmental friendliness, EC paper produced by in situ chemical polymerization of pyrrole and aniline in aqueous electrolytes has received much attention (Johnston et al.

2006; Huang et al. 2006; Kim et al. 2006; Chen and Qian 2007; Ding et al. 2010a; Li et al. 2010a, b; Qian et al. 2010b). In situ chemical polymerization is a process by which a monomer such as aniline or pyrrole is polymerized in the presence of wood pulp fibers. However, there are still some disadvantages of the polyaniline- and polypyrrole-coated conductive papers, such as low conductivity, poor environmental stability, and low strength properties.

Poly(3,4-ethylenedioxythiophene) (PEDOT) has been one of the most successful conducting polymers because of its advantageous properties, including excellent transparency in the visible range, high conductivity, and good environmental stability. Typical applications of PEDOT include antistatic coating, electrically switchable windows, and hole injection layers in organic light emitting diodes (Kim et al. 2009).

Researchers at Louisiana Tech University developed a simple technique to fabricate EC paper by applying a layer-by-layer nanoassembly coating directly to wood microfibers during the paper-making process (Agarwal et al. 2006). They used an aqueous dispersion of the anionic polyelectrolyte poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and either poly(allylamine hydrochloride) (PAH) or poly(ethyleneimine) (PEI) cationic polyelectrolytes for layer-by-layer assembly. By creating organized multilayers of these polyelectrolytes on a surface of wood microfibers, they produced a nanocoating that enabled the microfibers to exhibit moderate electrical conductivity, which could be increased by increasing the number of conductive polymer layers in the coating. Subsequently, they used these fibers for the production of handsheets that displayed measurable electrical conductivity. Montibon (2009) described investigations of interactions between a conducting polymer blend consisting of PEDOT:PSS and cellulosic materials and the adsorption behavior of PEDOT:PSS at various pH levels and salt concentrations. The bulk of EC paper may be made electronically conductive by deposition of the conductive coating material to the base paper either before or after the forming process. Montibon chose the latter process.

In the present study, electrically conductive cellulose/PEDOT composite fibers were prepared via in situ chemical oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) by using iron(III) *p*-toluenesulfonate ($\text{Fe}(\text{OTs})_3$) as both an oxidant and a dopant source prior to forming the paper sheet. The factors affecting the conductivity of the composite paper were investigated.

EXPERIMENTAL

Materials

Bleached softwood kraft pulp from Canada was obtained from Mudanjiang Hengfeng Paper Co., Ltd. Chemical-grade EDOT was purchased from Shanghai Bayee Biotech Co., Ltd. $\text{Fe}(\text{OTs})_3$ (analytical grade) was purchased from Shanghai Chunyuan Phytochemistry Co. Ltd. All chemicals were used without further purification.

Preparation of PEDOT-Cellulose Composite Fibers and Conductive Paper

A certain amount of $\text{Fe}(\text{OTs})_3$ solution was added into a pulp suspension containing 2 g (oven-dry basis) of pulp fibers under magnetic stirring, and then the flask

containing the above mixture was placed in an electro-thermostatic water bath. Subsequently, the desired amount of EDOT was injected into this system with a liquid injector to initiate the polymerization reaction. This reaction was stopped after a desired time, the treated mixture was diluted, and then the fibers were washed and filtered. A handsheet with a target basis weight of $80 \text{ g} \cdot \text{m}^{-2}$ was formed in a sheet former (ZCX-200, China). The handsheet was pressed at 400 kPa of compression force for 5 min, dried at $110 \text{ }^\circ\text{C}$ for 6 min, and kept in an atmospheric environment for resistivity testing.

Resistivity Testing and Environment Stability Evaluation

A RTS-8 four-point probe meter produced by Guangzhou Ximei Electric Co., Ltd. was used to measure the resistivity of the conductive paper. The initial values of the surface resistivity (ρ_{S0}) and volume resistivity (ρ_{V0}) were measured after the paper sample was preconditioned in air at room temperature for 24 h.

The values of relative resistivity change, $\Delta\rho_S/\rho_{S0}$ (%) and $\Delta\rho_V/\rho_{V0}$ (%), were taken as indicators of the environmental stability of the electrical performance of the ECPC, and the calculation equations were as follows,

$$\Delta\rho_S/\rho_{S0} (\%) = \{(\rho_S/\rho_{S0})/\rho_{S0}\} \times 100 \quad (1)$$

$$\Delta\rho_V/\rho_{V0} (\%) = \{(\rho_V/\rho_{V0})/\rho_{V0}\} \times 100 \quad (2)$$

where, ρ_S and ρ_V are the surface resistivity (Ω/\square) and volume resistivity ($\Omega \cdot \text{cm}$) after storing in air at room temperature for one month, respectively.

Measurement of the Amount of PEDOT Coated

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

$$A (\%) = \{(W_2 - W_1)/W_1\} \times 100 \quad (3)$$

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

There were no large amounts of fine, dissolved, and colloidal substances generated during the preparation of PEDOT-coated conductive fibers. Thus, the quantity A was used to represent the amount of PEDOT coated on pulp fibers.

Measurement of Paper Strength

Tensile strength (100 mm span) was measured with a ZLD-300 electronic tensile tester, and the zero-span tensile strength was measured with a Pulmac Z-span 1000 troubleshooter under the standard test conditions ($23 \pm 1 \text{ }^\circ\text{C}$ and $50 \pm 2\%$ relative humidity).

ATR-FTIR and SEM Analysis

ATR-FTIR (attenuated total reflection-Fourier transform infrared) spectra in the range $600\text{--}4000 \text{ cm}^{-1}$ were recorded on a FT-IR spectrometer equipped with an Inspect

IR microscope (Magna-IR 560 E.S.P, Nicolet Corp.). The crystal used in the ATR cell was composed of silicon. The resolution was 4 cm^{-1} and 40 scans were averaged.

SEM observation was performed using an FEI Quanta-200 environment scanning electronic microscope. The samples were coated with gold before observation.

RESULTS AND DISCUSSION

Observation and Characterization

After the polymerization reaction was started by adding EDOT, the fiber color changed from pale yellow (the color of $\text{Fe}(\text{OTs})_3$ solution) to light blue (a few minutes later) and then dark blue or grey several hours later. The longer the reaction time or higher the reaction temperature, the deeper blue the change in fiber color. In addition, the higher the EDOT (or $\text{Fe}(\text{OTs})_3$) concentration, the deeper change in fiber color. For example, the color of PEDOT-coated pulp fibers was dark blue when the EDOT concentration was less than $5\text{ g}\cdot\text{L}^{-1}$, but grey when the EDOT concentration was more than $5\text{ g}\cdot\text{L}^{-1}$. The color dependency on time, temperature, and concentration of the reactants may be related to the redox state of PEDOT. Changes in optical properties and electrical conductivity occur in association with different redox states of PEDOT:PSS (Chen et al. 2002).

PEDOT-coated pulp fibers behave similarly to conventional wood pulp fibers and may be made into paper sheets by using the same papermaking facilities as conventional pulps. The formed PEDOT-coated paper is electrically conductivity. A volume resistivity as low as $5.9\times 10^3\ \Omega\cdot\text{cm}$ was achieved with an EDOT concentration of $3\text{ g}\cdot\text{L}^{-1}$, well within the conductivity range of an electrostatic conductor. By contrast, the volume resistivity of conventional paper is usually 10^{12} to $10^{16}\ \Omega\cdot\text{cm}$ (Huang et al. 2006). We noted that unlike the polyaniline- and polypyrrole-coated conductive papers that have lower strength properties, the PEDOT-coated paper has good tensile strength.

ATR-FTIR studies were performed to examine the deposition of PEDOT on the composite fiber surface. The ATR-FTIR spectrum of untreated pulp fibers indicated peak absorbances at 1429 cm^{-1} , 1371 cm^{-1} , and 897 cm^{-1} attributed to in-plane C–H bond-stretching in CH_2 , characteristic of cellulose (Fig. 1). The spectrum of PEDOT-coated pulp fibers, prepared at $3\text{ g}\cdot\text{L}^{-1}$ of EDOT, was very similar to untreated pulp fibers due to the relatively low amount of PEDOT on the cellulose fiber surface. However, in the ATR-FTIR spectrum of composite fibers prepared at $8\text{ g}\cdot\text{L}^{-1}$ of EDOT, the characteristic bands of PEDOT, the C–O–C bond-stretching absorbance, at 1052 cm^{-1} and the C=C and C–C in the thiophene ring bond-stretching absorbance, at 1518 cm^{-1} and 1317 cm^{-1} , were observed, confirming the presence of PEDOT. Absorbance peaks at 1202 cm^{-1} and 980 cm^{-1} correspond to S=O bond-stretching in the molecule of $\text{Fe}(\text{OTs})_3$. This result indicated clearly that $\text{Fe}(\text{OTs})_3$ had been successfully doped into the resulting PEDOT polymer matrix (Han et al. 2006a).

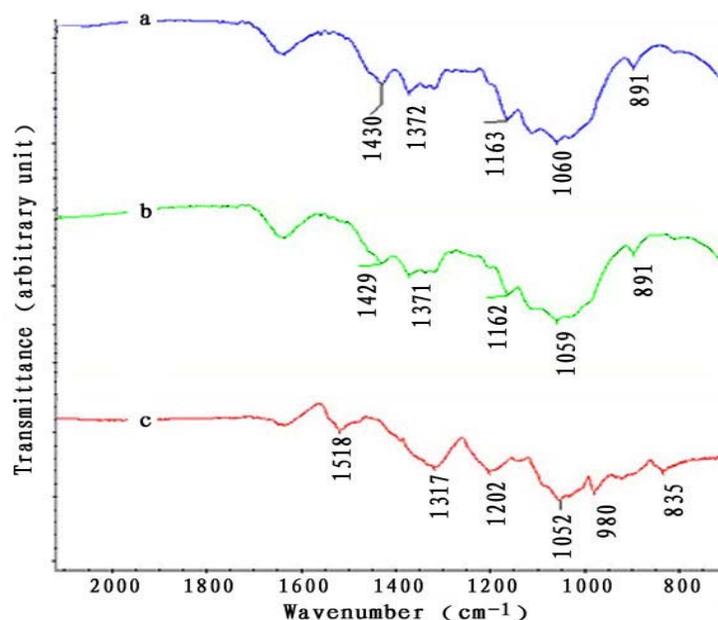
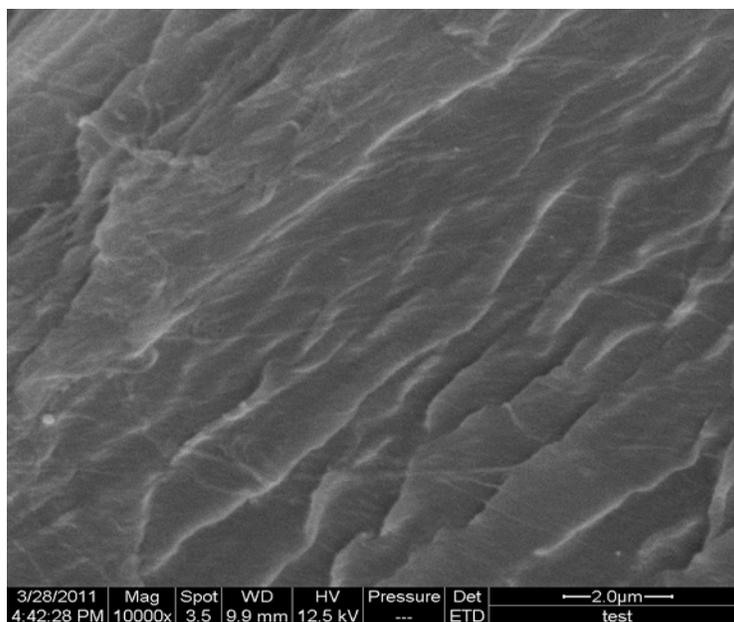
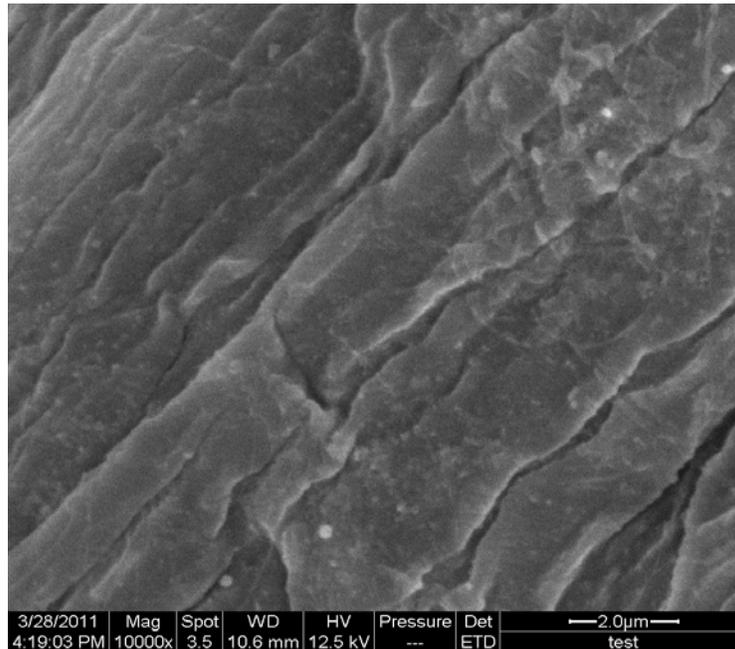


Fig. 1. ATR-FTIR spectra of untreated pulp fibers (a), PEDOT-coated pulp fibers prepared at $3 \text{ g}\cdot\text{L}^{-1}$ of EDOT (b), and $8 \text{ g}\cdot\text{L}^{-1}$ of EDOT (c)

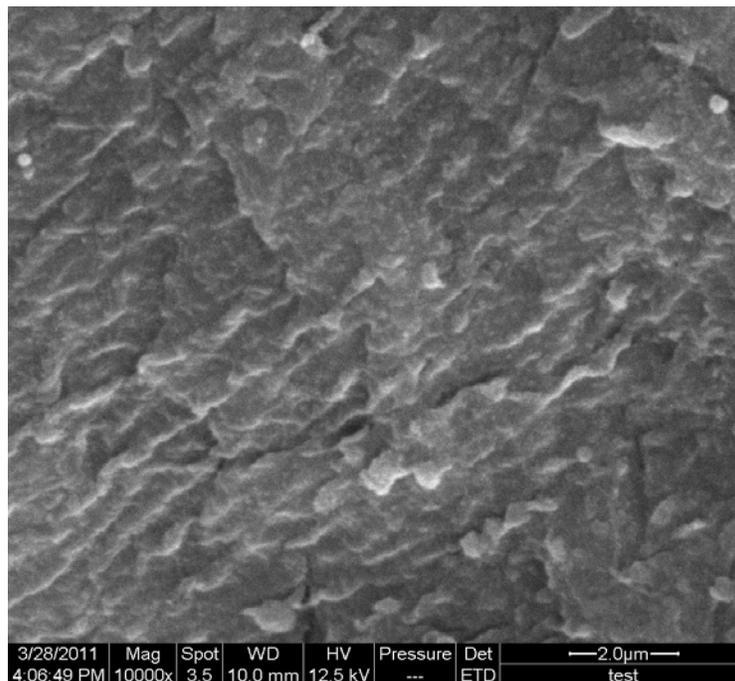
The differences between the untreated fibers and the composite fibers were distinct (Fig. 2). The surface of the untreated fibers was very smooth and had no PEDOT particles. However, the PEDOT particles could be seen on the surface of the composite fibers prepared at an EDOT concentration of $3 \text{ g}\cdot\text{L}^{-1}$, and the surface of the treated fibers was fully coated with polymer clusters when the EDOT concentration was $8 \text{ g}\cdot\text{L}^{-1}$. The SEM results are in accordance with naked-eye observations, conductivity measurements and FTIR analysis.



(a)



(b)



(c)

Fig. 2. SEM pictures of untreated pulp fibers (a), PEDOT-coated pulp fibers prepared at $3 \text{ g}\cdot\text{L}^{-1}$ of EDOT (b), and $8 \text{ g}\cdot\text{L}^{-1}$ of EDOT(c)

Effect of Reaction Temperature

Reaction temperature had significant effects on surface resistivity (Fig. 3) and volume resistivity (Fig. 4) responses of PEDOT-coated EC paper, prepared at an EDOT concentration of $8 \text{ g}\cdot\text{L}^{-1}$ and reaction time of 4 h, with iron (III) *p*-toluenesulfonate ($\text{Fe}(\text{OTs})_3$) (molar ratio of EDOT/ $\text{Fe}(\text{OTs})_3 = 1:1$) used as both an oxidant and a dopant. Based on these results, we concluded that the reaction temperature had a significant effect on the surface resistivity and volume resistivity of PEDOT-coated EC paper. Obviously, the conductivity was very poor at 40°C . With increasing reaction temperature, the surface resistivity and volume resistivity of conductive paper gradually decreased and reached the lowest value at 60°C .

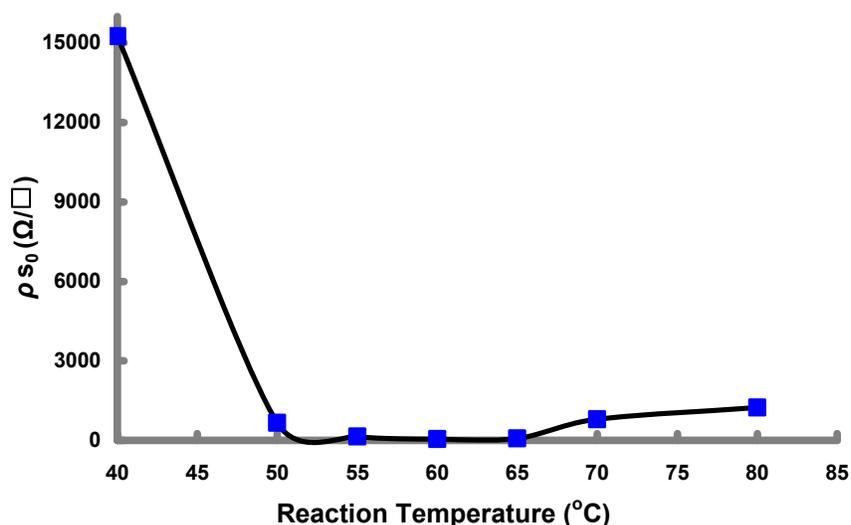


Fig. 3. Effect of reaction temperature on surface resistivity (ρ_{s0})

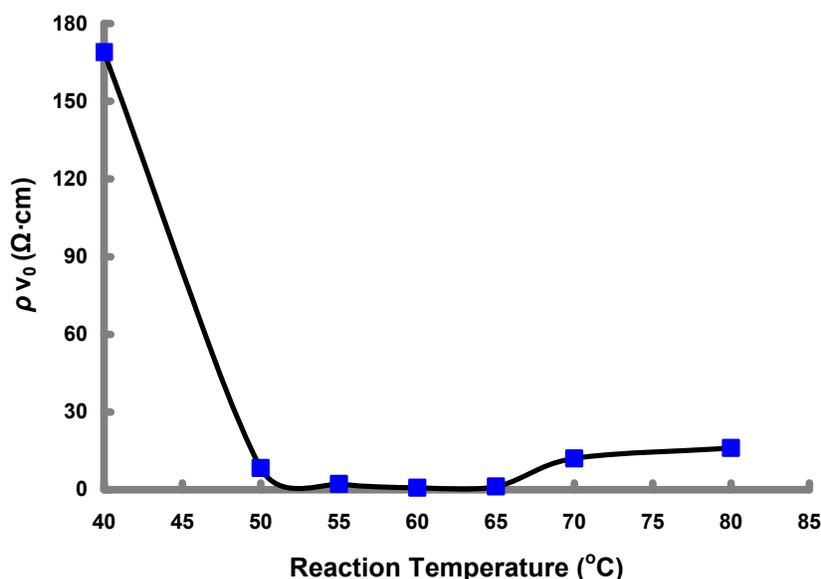


Fig. 4. Effect of reaction temperature on volume resistivity (ρ_{v0})

With further increases in reaction temperature, the surface resistivity and volume resistivity tended to increase, rather than decrease. The oxidation potential of the monomer EDOT is about 1.1 V, which is higher than those of pyrrole (0.65V) and aniline (0.7V). So the oxidation polymerization of EDOT is difficult compared to pyrrole and aniline, and higher temperature and longer time are needed. When the temperature was low (40 °C), a relatively slow polymerization reaction of EDOT would happen. However, too high temperature (>70 °C) might lead to a decrease in the conductivity, because a part of the resultant polymer might be over-oxidized.

Effect of Reaction Time

Reaction time at an EDOT concentration of 8 g·L⁻¹ and reaction temperature of 60°C also significantly affected surface resistivity (Fig. 5) and volume resistivity (Fig. 6) of the conductive paper.

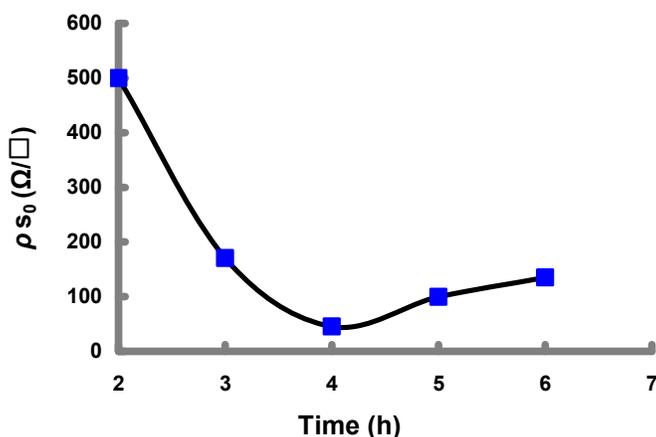


Fig. 5. Effect of reaction time on surface resistivity (ρ_{s0})

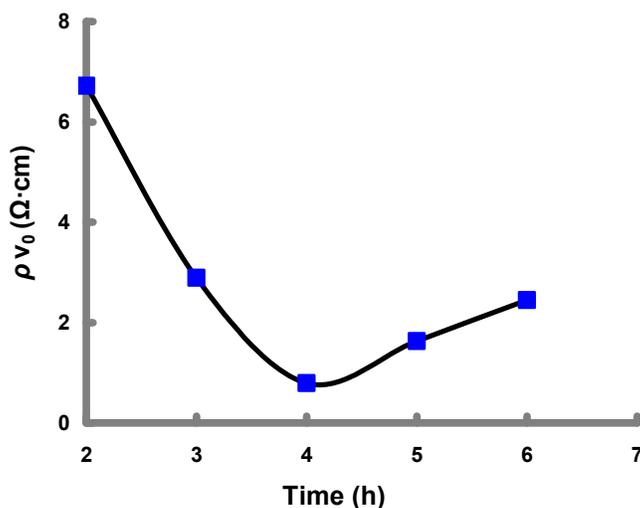


Fig. 6. Effect of reaction time on volume resistivity (ρ_{v0})

The probable cause of the reaction-time effect was a required period of time to achieve the permeation of $\text{Fe}(\text{OTs})_3$ and the polymerization of EDOT. When the reaction time was not long enough, the polymerization degree and doping level of PEDOT were low. As a result, the molecular weight of PEDOT was small, and the conjugation chain was short; thus the resistivity was high. Surface resistivity and volume resistivity were lowest when the reaction time was 4 h. With the optimum reaction time of 4 h, the in situ generated PEDOT particles were uniformly adsorbed onto the fiber surface, resulting in a conductive paper with the highest obtainable conductivity. The resistivity increased slightly with additional reaction time perhaps due to the formation of PEDOT particle clusters (aggregates).

Effect of Molar Ratio of EDOT/ $\text{Fe}(\text{OTs})_3$

Molar ratio of EDOT to $\text{Fe}(\text{OTs})_3$ had a significant effect on PEDOT yield. When the ratio was 1:0.5, insufficient oxidant was available to oxidize all of the EDOT monomers, resulting in lower PEDOT yield (Table 1). Therefore, the surface resistivity and volume resistivity of the conductive paper were at a relatively higher level of 739.5 Ω/\square and 10.17 $\Omega\cdot\text{cm}$, respectively. When the molar ratio of EDOT to $\text{Fe}(\text{OTs})_3$ was 1:1, the surface resistivity and volume resistivity were 43.0 Ω/\square and 0.66 $\Omega\cdot\text{cm}$, respectively, or more than one order of magnitude lower than for the conductive paper prepared with an EDOT/ $\text{Fe}(\text{OTs})_3$ molar ratio of 1:0.5. With additional increases in the $\text{Fe}(\text{OTs})_3$ concentration, the resistivity of resulting conductive paper continued to decrease slowly. The choice of the molar ratio of EDOT to $\text{Fe}(\text{OTs})_3$ mainly depends on the desired conductivity of the conductive paper. The molar ratio of EDOT to $\text{Fe}(\text{OTs})_3$ of 1:1 was optimal when considering both cost and performance factors.

Table 1. Effect of Molar Ratio on Surface Resistivity (ρ_{S0}) and Volume Resistivity (ρ_{V0})

Molar Ratio of EDOT/ $\text{Fe}(\text{OTs})_3$	ρ_{S0} (Ω/\square)	ρ_{V0} ($\Omega\cdot\text{cm}$)
1:0.5	739.5	10.17
1:1	43.0	0.66
1:2	11.72	0.22

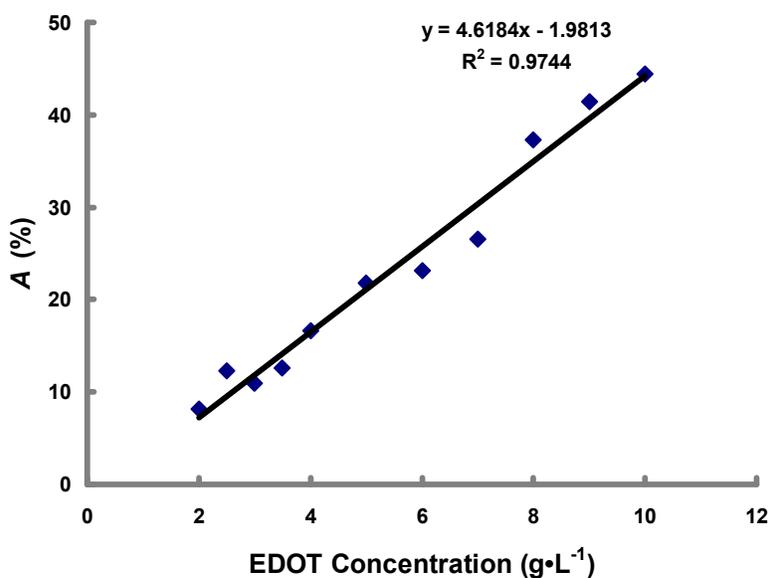
Threshold Concentration of EDOT

There was no detectable electrical conductivity of papers prepared at very low EDOT concentration $\leq 2.5\text{g}\cdot\text{L}^{-1}$ (Table 2). Conductivity was not detected until a EDOT-concentration threshold of about $3.0\text{g}\cdot\text{L}^{-1}$ was reached, corresponding to a PEDOT concentration of about 10%. Beyond this threshold concentration, the surface resistivity and volume resistivity of PEDOT-coated conductive paper both decreased with increasing EDOT concentration. For example, surface resistivity decreased from 450384 to 2463 Ω/\square , and volume resistivity decreased from 5855 to 34 $\Omega\cdot\text{cm}$ with a relatively small increase in EDOT concentration (from 3.0 to 5.0 $\text{g}\cdot\text{L}^{-1}$), a decrease of about two orders of magnitude. In the range of 5.0 to 8.0 $\text{g}\cdot\text{L}^{-1}$, surface and volume resistivity continued to decrease by two orders of magnitude with further increase in the EDOT concentration.

Table 2. Effect of EDOT Concentration on PEDOT Deposition and Electrical Performance of Paper

EDOT Concentration (g·L ⁻¹)	A (%)	ρ_{s0} (Ω/\square)	$\Delta\rho_s/\rho_{s0}$ (%)	ρ_{v0} ($\Omega\cdot\text{cm}$)	$\Delta\rho_v/\rho_{v0}$ (%)
2.0	8.15	out of range	—	out of range	—
2.5	12.29	out of range	—	out of range	—
3.0	10.95	450384	5.6	5855	11.7
3.5	12.61	110070	-4.9	1482	-8.4
4.0	16.61	22566	-7.6	276.3	-4.1
5.0	21.83	2463	8.2	34.0	4.6
6.0	23.11	482.3	7.3	6.57	10.3
7.0	26.59	437.0	5.1	6.26	7.9
8.0	37.30	43.0	4.8	0.66	8.3
9.0	41.46	27.9	4.9	0.49	6.7
10.0	44.41	17.5	13.1	0.33	5.5

The amount of PEDOT coated on pulp fibers increased almost linearly with the increase of the concentration of EDOT (Fig. 7). The surface resistivity and volume resistivity of PEDOT-coated conductive paper decreased nonlinearly with increasing PEDOT amount. Increasing the amount of PEDOT coated on pulp fibers, gradually improved the conductivity of the PEDOT-coated conductive paper. However, additional deposition of PEDOT (>37.30%) did not significantly improve the conductivity of the paper.

**Fig. 7.** Relationship between PEDOT amount (A) and EDOT concentration

Environmental Stability

Environmental stability of the conducting polymer coated on cellulose fibers is related to its reactivity to atmospheric chemicals, especially oxygen. In our previous study we found that polypyrrole-coated paper had lower environmental stability than polyaniline-coated paper (Ding et al. 2010b). This was likely due to the low oxidation potential of polypyrrole relative to polyaniline. The redox potential of polypyrrole is about -0.3 V (Ohnishi et al. 2004), significantly lower than polyaniline ($0.2-0.8$ V) (Ram et al. 1994). Therefore, polypyrrole is more sensitive to oxygen than polyaniline. In the current study, the environmental stability of PEDOT-coated conductive paper was investigated by observing $\Delta\rho_S/\rho_{S0}$ and $\Delta\rho_V/\rho_{V0}$. The maximum values of $\Delta\rho_S/\rho_{S0}$ and $\Delta\rho_V/\rho_{V0}$ were 13.1% and 11.7%, respectively (Table 2), providing strong evidence for good environmental stability. The environmental stability of PEDOT-coated conductive paper is attributable to the relatively high oxidation potential of PEDOT compared with most other conducting polymers, even though the oxidation potential range of PEDOT is very wide (Han et al. 2006b). PEDOT is very stable in the doped state but not in the neutral form due to its very low oxidation potential (Szkurlat et al. 2003).

Tensile Strength

The tensile index values of different paper samples are presented in Table 3. The zero-span tensile index values of Samples A, B, and C were 148.8, 132.5, and 112.8 $\text{N}\cdot\text{m}\cdot\text{g}^{-1}$, respectively. The tensile index values were 39.7, 44.6, and 34.5 $\text{N}\cdot\text{m}\cdot\text{g}^{-1}$, respectively. In addition, the bonding contribution values of Samples A, B and C were 54.1, 69.2, and 49.7 $\text{N}\cdot\text{m}\cdot\text{g}^{-1}$, respectively. These data indicate that the deposition of a small amount of PEDOT did not lead to any decrease in paper tensile strength. The slight increase in paper tensile strength might be attributed to the contribution of hydrogen bonding between the sulfonate groups of PEDOT-OTs. Tensile strength decreased slightly when a large amount of PEDOT was deposited on the fiber surface, likely due to hydrolysis of the cellulose fibers in acidic medium. The pH values at the beginning and end of the experiment were determined. The beginning and ending pH values at $3\text{ g}\cdot\text{L}^{-1}$ of EDOT were 2.75 and 2.29, respectively. The pH values at $8\text{ g}\cdot\text{L}^{-1}$ of EDOT were 2.45 and 2.13, respectively.

Table 3. Tensile Index Values of Paper Samples

Sample *	Tensile Index ($\text{N}\cdot\text{m}\cdot\text{g}^{-1}$)		Bonding Contribution ** ($\text{N}\cdot\text{m}\cdot\text{g}^{-1}$)
	100 mm Span	0 mm Span	
A	39.7	148.8	54.1
B	44.6	132.5	69.2
C	34.5	112.8	49.7

* Sample A: the handsheet made from the untreated pulp fibers; Sample B: the handsheet made from PEDOT-coated fibers at $3\text{ g}\cdot\text{L}^{-1}$ of EDOT; Sample C: the handsheet made from PEDOT-coated fibers at $8\text{ g}\cdot\text{L}^{-1}$ of EDOT.
 ** Calculated using the simplified Page Equation (Page 1969).

CONCLUSIONS

1. The deposition of PEDOT onto the pulp fiber surface was verified by ATR-FTIR and SEM analysis.
2. The optimum reaction temperature and time for deposition of the electroconductive material were found to be 60 °C and 4 h, respectively. The molar ratio of EDOT to Fe(OTs)₃ of 1:1 was considered optimal based on both cost and performance factors.
3. The amount of PEDOT coated on pulp fibers increased almost linearly with increasing EDOT concentration. The conductivity of the PEDOT-coated paper could be controlled by adjusting EDOT concentration. The threshold concentration of EDOT was about 3 g·L⁻¹. Volume resistivity as low as 5.9×10³ Ω·cm could be achieved with an EDOT concentration of 3 g·L⁻¹, within the conductivity range of an electrical conductor.
4. The environmental stability of the PEDOT-coated conductive paper was very good due to the much higher oxidation potential of PEDOT compared with most other conducting polymers. The tensile strength of PEDOT-coated conductive paper also was satisfactory for most common applications.

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