Application of Polyaniline/Clay Combination to Cellulosic Paper as an Approach to Conductivity Development

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A polyaniline/clay combination was prepared *via*: 1) mixing polyaniline dispersion with clay; or 2) *in situ* polymerization of aniline in the presence of clay. To deliver electrical conductivity to cellulosic paper, the polyaniline/clay composition was applied to the paper surface by Meyer rod coating. The conductive paper was analyzed by Scanning Electron microscopy (SEM) and Fourier Transmission Infrared spectroscopy (FT-IR). For comparison purposes, conductive paper was also prepared by *in situ* polymerization of aniline in the presence of cellulosic fibers. The *in-situ* formed polyaniline was deposited on the fiber surface, and the polyaniline-deposited cellulosic fibers were made into paper sheets. It was found that at the same aniline content, paper surface coating with polyaniline/clay composition gave a much higher conductivity in comparison with the use of polyaniline-deposited cellulosic fibers for paper sheet formation.

Keywords: Polyaniline; Clay; Coating; Conductive paper; Conductivity; Cellulosic fibers

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INTRODUCTION

Conducting polymers such as polyaniline and polypyrrole have been the subject of considerable interest due to their unique electrical conductivity and numerous potential applications, including electromagnetic interference shielding (Taka 1991; Trivedi and Dhawan 1992), electronic and optical devices (Duek *et al.* 1992; Nishino *et al.* 1995), energy storage devices (Trinidad *et al.* 1991), rechargeable batteries (Kanatzidis *et al.* 1989; Kaneko and Nakamura 1985; Katz *et al.* 2010), catalysts (Palaniappan *et al.* 2004; Zhao *et al.* 2008), and light emitting diodes (Gustafsson *et al.* 1992). High electrical conductivity can be achieved by using an appropriate dopant (MacDiarmid 2001). Polyaniline is one of the most interesting conducting polymers due to its low cost and easy availability of raw materials, easy synthesis, good environmental stability, and controllable electrical conductivity and redox properties (Cao *et al.* 1989; Focke *et al.* 1987; Kingsborough and Swager 1998).

Cellulosic fibers are naturally abundant, renewable, sustainable, and fully recyclable materials. They can be manufactured at a low cost (Paakko *et al.* 2008; Richardson *et al.* 2006), and are ideal carriers for conductive polymers (Ding *et al.* 2010a,b; Huang *et al.* 2005, 2006; Li *et al.* 2010a,b; Qian *et al.* 2010) and functional chemicals; for example, they are used in the production of testing strips for heavy metals such as Cr(VI) in water samples (Kong and Ni 2009a,b).

Recently, there have been many publications related to *in situ* polymerization of pyrrole and aniline in the presence of cellulosic fibers, so that the conductive paper can be formed by the conventional papermaking process (Ding *et al.* 2010a,b; Huang *et al.* 2005; 2006; Li *et al.* 2010a,b; Qian *et al.* 2010). *In situ* polymerization of monomers in the presence of cellulosic filter paper can be another approach to the preparation of conductive paper (Johnston *et al*. 2005; Dutta *et al.* 2005). Nystrom *et al.* (2009) reported the formation of polypyrrole-based paper batteries using an ultrasonication method. Very recently, Sasso *et al.* (2011) prepared a highly conducting PPy/nanofibrillated film using birchwood xylan as an additive. Agarwal *et al.* (2006) prepared a poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonate)-polyethyleneimine based conductive paper composite by nano-coating. Kelly *et al.* (2007) prepared wool-fiber-based conductive composite by *in situ* polymerization. Li *et al.* (2010) and Qian *et al.* (2010) reported the formation of a conductive paper composite by a two-step process: *in situ* polymerization followed by a re-doping method.

For conductive polymers, such as polyaniline, the use of dopant is critical in inducing electro-conductivity, inorganic acids, such as hydrochloric acid, can be good dopants (Huang *et al.* 1986; Qian *et al.* 2010). Other dopants include organic sulfonic acids, dicarboxylic acids, and polymeric acids (Ghadimi *et al*. 2002). Polyaniline exists in different reversible oxidation states, which can be affected by the pH. Under high pH, de-protonization of the doped polyaniline occurs, and the doped polyaniline emeraldine salt, which is electro-conductive and green in color, will be converted into polyaniline emeraldine base, which is an insulator and blue in color (Huang *et al*. 1986).

An earlier study (Kang and Ni 2008) reported the application of the coating technology to impart electro-conductivity to cellulosic paper. The conductive clay was prepared by in-situ polymerization of pyrrole in the presence of clay, and then the polypyrrole-deposited clay was surface coated onto paper, using conventional paper coating technology. In the present work, polyaniline/clay composition was prepared *via in situ* polymerization of aniline in the presence of clay, or mixing of polyaniline dispersion with clay. The polyaniline/clay composition was applied to the paper surface by Meyer rod coating, and the conductive paper was prepared. It was proposed that the clay would act as a carrier for the conducting polymer, and the deposited polyaniline would be responsible for paper conductivity development. The conductive paper composite was characterized by SEM observations and FT-IR analyses. For comparison purposes, conductive paper was also prepared from polyaniline-deposited fibers prepared by *in situ* polymerization of aniline in the presence of cellulosic fibers.

MATERIALS AND METHODS

Materials

Mixed hardwood (birch/maple/aspen) bleached kraft pulp, and unbleached sulfite pulps were obtained from a pulp mill in Eastern Canada. Aniline (98%, Aldrich) was freshly distilled under reduced pressure and stored at 4 °C prior to use. All other chemicals, including dodecylbenzenesulfonic acid sodium salt (Aldrich), poly(4-styrene sulfonic acid) (Aldrich, 18 wt% solution, M_w = 10,192), ammonium persulfate (Aldrich), poly(4-styrene sulfonic acid-co-maleic acid) sodium salt (Aldrich, 25 wt% solution, M_w = 10,436), polyacrylic acid (Aldrich, M_w = 4,000,000), polyacrylic acid-co-maleic acid (Aldrich, M_w = 3,000), maleic acid, oxalic acid, malonic acid, and hydrochloride solution

(37%), were used as received. Clay (about 2 micro mean particle size) powder, supplied by an Eastern Canadian mill, was used as the carrier for polyaniline.

Preparation of Polyaniline Dispersion

For the preparation of polyaniline dispersion, the procedures described by Ngamna *et al.* (2007) were followed. Six grams of dodecylbenzenesulfonic acid sodium salt (acidified with concentrated hydrochloride solution to a pH of 1) was dissolved in 50 mL of deionized water and stirred at room temperature for 10 min. Acidified dodecylbenzenesulfonic solution was divided into two parts (2 × 25 mL): 2.4 g of ammonium persulfate was dissolved in 25 mL of the dodecylbenzenesulfonic solution, and 1 g of aniline was added to the remaining dodecylbenzenesulfonic solution (25 mL). The mixture was stirred for 10 min at 23 °C. Then, the solution containing ammonium persulfate was added drop-wise, followed by further stirring for 3 h. Upon the completion of the polymerization reaction, the mixture was purified by centrifugation. The obtained polyaniline particles were washed with deionized water four times and used in the subsequent studies.

Preparation of Polyaniline-Hydrochloride

Concentrated hydrogen chloride solution (8.8 mL) was added into a flask containing 1 g of aniline and stirred for 10 min, followed by drop-wise addition to 2.8 g of ammonium persulfate. The mixture was stirred at room temperature for 3 h. The resultant green reaction mixture was filtered and washed with 1 L of deionized water and dried under vacuum.

Preparation of Polyaniline/Clay Composition by Simple Mixing of Polyaniline Dispersion with Clay

The polyaniline/clay composition was prepared by mixing polyaniline dispersion with clay (10 to 50 wt% of the polyaniline dispersion with respect to clay). Then, the mixture was treated in a homogenizer for 15 min, so that a uniform composition was prepared. The resultant green-colored composition was used for paper surface treatment by the Meyer rod coating method.

Preparation of Polyaniline/Clay Composition by *In Situ* Polymerization of Aniline in the Presence of Clay

For the preparation of polyaniline/clay composition by *in situ* polymerization of aniline in the presence of clay, the above experimental procedures (preparation of polyaniline dispersion) were slightly modified. The concentration of reactants, the reaction condition, and the purification process were kept constant while using 20 wt% of aniline with respect to the total weight of clay used in the polymerization reaction. After the addition of clay into the reaction mixture, the batch was mixed in a homogenizer for 15 min to make a uniform composition prior to the drop-wise addition of the ammonium-persulphate-containing solution. The resultant green polyaniline/clay composition was used for coating on the surface of cellulosic paper.

Preparation of Polyaniline-Deposited Cellulosic Fibers by *In situ* Polymerization of Aniline in the Presence of Cellulosic Fibers

Polyaniline-deposited cellulosic fibers were prepared using cellulose fibers, 6 to 15 wt% of aniline (with respect to the oven-dry weight of the cellulose fibers), ammonium persulfate (1.15 mol ratio to aniline), and either one of the following acids: hydrochloric acid (100 mol ratio to aniline), dicarboxylic acid (1.5 mol ratio to aniline), and polymeric acid (1:1 wt % to aniline). The representative procedures were as follows: air-dried cellulosic fibers equivalent to 10 g oven-dry mass were dispersed in deionized water and then loaded into a plastic bag; 1.69 g of ammonium persulfate was added, and the mixture was hand-kneaded for 5 min. Subsequently, 5.28 mL of 37% concentrated hydrogen chloride solution was added, and the mixture was hand-kneaded for another 5 min. Finally, 0.6 g of aniline was added, and more hand-kneading was conducted for 15 min. The total quantity of water used in the reaction was 90 mL, and the final consistency of the cellulosic fiber was 10%. Upon the completion of the polymerization reaction, the resultant green cellulosic fibers were washed with 2 L of deionized water.

Conductive paper sheets with a basis weight of 100 $g.m^{-2}$ were formed with the prepared polyaniline-deposited cellulosic fibers on a sheet former using tap or deionized water. These paper sheets were pressed at 50 psi for 7 min and dried at 23 °C and 50% RH for 24 h.

Paper Surface Treatment by Meyer Rod Coating

The polyaniline/clay composition or polyaniline dispersion was coated on the paper sample using the Meyer rod coating set-up. The Meyer rod coating apparatus consists of a stainless steel wire-rod (rolling type) and a smooth flat glass pad. The paper sample was held down on the drawdown glass pad using adhesive tape. Then, the conductive polyaniline dispersion was poured on top of the adhesive tape, and the Meyer rod pulled across the surface of the paper sample. A portion of the solution flowed through the grooves in the wire-wound rod and formed a thin conductive film on the paper surface. The coating amount (Q_c) was calculated as grams per square meter of the paper surface by the following equation,

$$Q_c = (W_2 - W_1)/A \tag{1}$$

where W_2 is the weight of the paper after coating (g), W_1 is the weight of the paper before coating (g), and A is the coating area of the paper.

Surface Electrical Resistance and Conductivity Measurements

The resultant conductive paper was cut into strips (15 mm width). The electrical resistance of the paper strips was measured by using a Keithley digital multimeter (Model 2750) (using the two-probe method. The distance between the probes was 11 cm). Two samples were prepared under each condition, and the resistivity was measured 3 times at different spots on the surface, the average of these 6 results was reported. The surface electrical resistivity (ρ) and conductivity (σ) were calculated according to the following equations,

$$\rho = R*d/L \tag{2}$$

$$\sigma = 1/\rho \tag{3}$$

where R is the electrical resistance reading of a conductive paper strip from the multi-meter, d is the width of the paper strip, and L is the distance between the two probes, which was fixed at 11 cm.

SEM and FT-IR Analyses

The SEM images were obtained by using a JEOL JSM-6400 Scanning Electron Microscope operated at an accelerating voltage of 15 kV. The samples were prepared by placing dry material onto conductive carbon tape, which was then carbon-coated by evaporative coating, and subsequently gold-coated by sputter coating.

The samples for FT-IR analysis were prepared as pellets using KBr as the supporting material. FTIR spectra in the range 400 to 4000 cm^{-1} were recorded using a Nicolet 6700 FT-IR Spectrometer (Thermo Fisher Scientific Inc.).

RESULTS AND DICUSSION

Preparation of Conductive Paper

Aniline was polymerized on the surface of cellulosic fibers by *in situ* polymerization, and the process conditions including the aniline dosage, dopant type, and fiber type on the surface resistance of the conductive paper composite were studied. The effect of water pH (during the paper sheet formation process) on electrical resistivity was also investigated, so as to simulate the acidic papermaking (a typical pH of 4.5) or near-neutral paper making (a typical pH of 6.5) processes.

The aniline dosage was varied from 6 to 15 wt% (with respect to dry cellulose fibers), while one of the acids from hydrochloride, dicarboxylic acids, or polymeric acids, was used as the dopant. The resultant conductive paper from the laboratory paper sheet formation using tap water (around pH 8) showed the minimum conductivity, *i.e.*, the resistance was higher than the testing limit of 120 mega ohms, equivalent to 16,000 kΩ/sq surface resistivity (or 0.06 µS/sq surface conductivity) for 110 x 15 mm paper strips. The explanation for this is that the pH and the presence of ions in the tap water caused the de-protonization of polyaniline, thus resulting in the loss of conductivity (Okamoto *et al.* 2001).

As shown in Table 1, when deionized water (around pH 5) was used during the lab paper sheet formation process, the conductivity of the conductive paper ranged from 1.2 to 14.3 µS/sq (Table 1, Trials #1 to #4) by increasing the polyaniline dosage from 6 to 10, 12 and 15 wt% (hydrochloric acid as the dopant). However, the conductive paper prepared with dicarboxylic acids (oxalic, malonic, and maleic acids) and polymeric acids (poly(4-styrene sulfonic acid), poly(4-styrene sulfonic acid-co-maleic acid) sodium salt, polyacrylic acid) as the dopant did not yield measurable conductivity, even when deionized water was used during the paper sheet formation process. These results indicate that a strong acid, such as hydrochloric acid, would be needed to dope the formed polyaniline. Earlier studies related to the polyaniline-based conductive paper composites showed a good conductivity, but aniline with a much higher dosage was used in the *in situ* polymerization (about 150%, based on cellulose fibers) (Li *et al.* 2010; Qian *et al.* 2010) .

Table 1 further showed that the sulfite pulp led to a higher conductivity than the kraft pulp, under otherwise the same conditions (Trial #6 vs. Trial #4). This may be explained by the fact that the sulfite pulp fibers contain some lignosulfonic acid (about 3 to 4%), which may act as co-dopant and/or acid source (Huang *et al.* 2006). This is particularly true when tap water (around pH 8) instead of deionized water (around pH 5) was used for paper sheet formation (Trial #7 vs. Trial #5).

To examine the effect of the water pH during the paper sheet formation process on the conductivity of the resultant paper, the pH of the deionized water was adjusted to 4.5 (using diluted hydrochloric acid), or to 6.3 (using a diluted sodium hydroxide solution). The results are summarized in Table 2. It can be seen that the conductivity of the resultant paper decreased substantially when the water pH was increased from 4.5 to 6.3. At high pH, *i.e.*, 6.3, dedoping, *i.e.*, loss of hydrochloric acid, occurred, and it would be responsible for the decreased conductivity. The effect of water pH was much more pronounced at a low aniline content. These results indicate that the water pH played a critical role in the conductivity development.

Table 1. Effect of Pulp Type and Aniline Dosage during *In situ* Polymerization Process on the Conductivity of Conductive Paper

Trial #	Type of pulp fibers	Water pH during the paper sheet formation process	Aniline dosage, (%)	Surface conductivity, (µS/sq)
1	Kraft	Deionized	6	1.2
2	Kraft	Deionized	10	5.0
3	Kraft	Deionized	12	10.0
4	Kraft	Deionized	15	14.3
5	Kraft	Tap water	15	<0.1
6	Sulfite	Deionized	15	100
7	Sulfite	Tap water	15	1.7

Table 2. Effect of pH during Paper Sheet Formation on the Conductivity of Conductive Paper

Trial #	Aniline dosage, (%)	Water pH during the paper sheet formation process	Surface conductivity, (µS/sq)
8	10	4.5	5.0
9	10	6.3	0.2
10	15	4.5	9.1
11	15	6.3	5.0

Table 3. Effect of the Amount of Polyaniline Dispersion (prepared by the direct mixing method) on Conductivity of the Conductive Coated Paper

Trial #	Amount of polyaniline dispersion (%)	Surface conductivity, (µS/sq)
12	10	0.2
13	20	1.1
14	30	1.7
15	50	2.0

It has been shown that conductive clay can be prepared by a similar method to that of conductive fibers, and the resultant conductive clay can be used to make conductive paper either by wet-end addition or surface coating (Ni and Kang 2008). In this study, a polyaniline/clay combination (prepared by the direct mixing method) was used to coat the surface of commercial paper sheets. The polyaniline/clay combination was coated on the paper surface to make the conductive paper composite. With 6.5 to 9.6 g/m^2 coating on the paper surface, the coated paper composites showed a conductivity of

0.2 to 2.0 µS/sq, depending on the amount of polyaniline dispersion. As shown in Table 3, when the amount of polyaniline dispersion in the coating formulation increased from 10 to 20%, the paper conductivity increased significantly. If the basis weight of the base paper is 100 g/m^2, at an average coating coverage of 8 g/m^2 with a 20% polyaniline dispersion to clay ratio, the overall polyaniline content would be merely 1.2% (based on the total mass of the coated paper), and the conductivity of the paper would be about 1.1 µS/sq, which is similar to that for the conductive paper prepared by *in situ* polymerization of aniline in the presence of cellulosic fibers at 6% aniline (Table 1). Therefore, it can be concluded that compared with the *in situ* polymerization method, the coating method can produce conductive paper with a similar conductivity at a much lower aniline content, or higher conductivity at a similar aniline content.

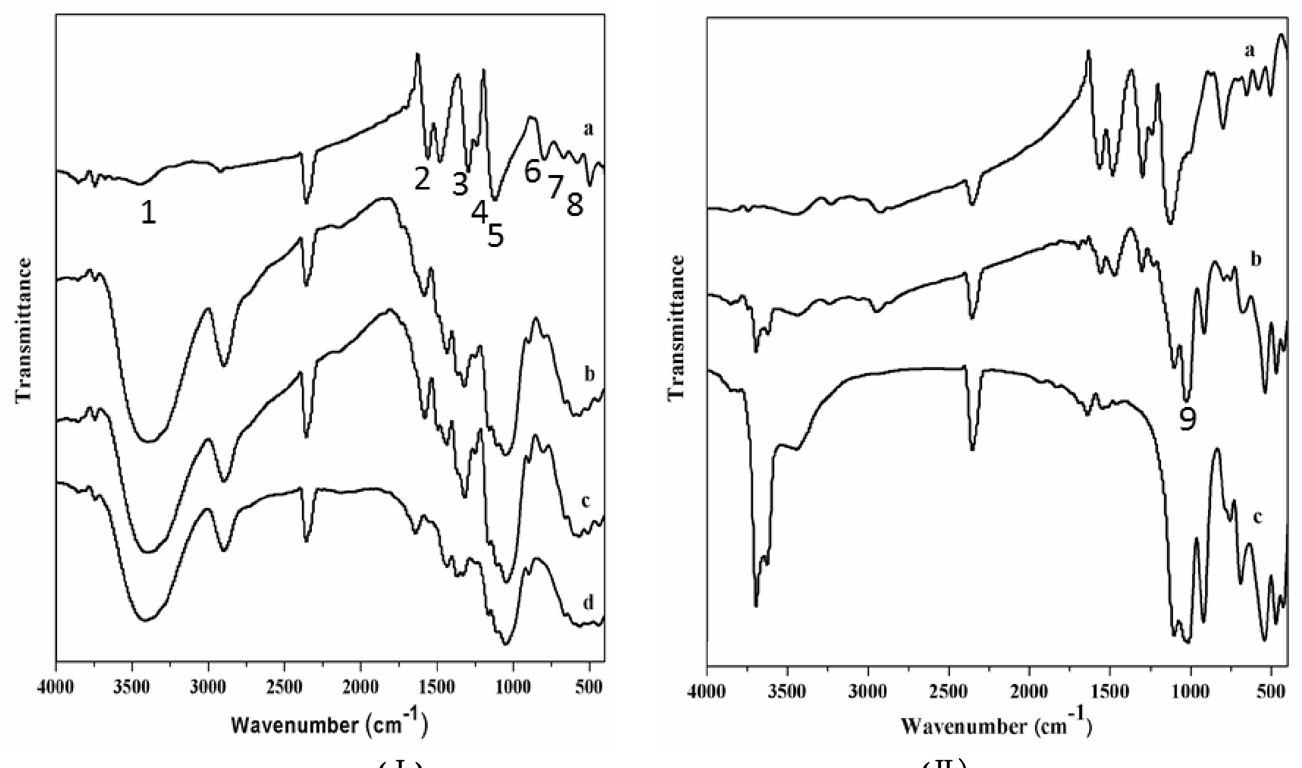
The polyaniline/clay composition was also prepared by the *in situ* polymerization method using 20% of aniline (on the basis of clay). The polyaniline/clay composition was then applied to the paper surface. With a 6.5 to 9.6 g/m^2 coating amount, the conductivity was about 0.1 µS/sq, which was lower than that of the paper prepared using the polyaniline/clay composition (results from the direct mixing method) (Table 3). This is probably due to the low retention of polyaniline on the clay particles in the case of *in situ* polymerization. It has been reported that the retention of polyaniline on cellulosic fibers was only about 20% of the aniline added during the *in situ* polymerization process (Li *et al.* 2010; Qian *et al.* 2010). Dodecylbenzene sulfonic acid sodium salt was also replaced with poly(4-styrene sulfonic acid), poly(4-styrene sulfonic acid-co-maleic acid) sodium salt, or polyacrylic acid-co-maleic acid as the dopant, and it was found that none of the above dopants were as good as dodecylbenzene sulfonic acid sodium salt in terms of the conductivity of the paper.

Structure and Morphology Analyses

The FT-IR spectra of cellulosic fibers, polyaniline-hydrochloride, and the resultant conductive paper are shown in Fig. 1(I). The vibrational bands observed for polyaniline-hydrochloride (Fig. 1a(I)) can be explained on the basis of the normal modes of aniline and benzene (a broad band (1) from 3420 to 3480 cm^{-1} assigned to N−H stretching vibration). The bands (2) at 1565 and 1490 cm^{-1} are due to C=C stretching vibrations of quinoid ring and benzenoid ring, respectively. The band (3) at 1300 cm^{-1} is assigned to C−N stretching vibration of secondary aromatic amine, while the band (4) at 1250 cm^{-1} is related to C-H in-plane bending vibration of 1,4-disubstituted benzene ring. For polyaniline, a strong band (5) appeared at 1140 cm^{-1}, which may be assigned to the vibration mode of protonated quinoid or benzenoid units of polyaniline-hydrochloride. The peak (6) at 800 cm^{-1} is attributed to C−H out-of-plane vibrations of 1,4-disubstituted benzene ring. A band (7) at 690 cm^{-1} is assigned to ring C−C bending vibration, while the band (8) at 590 cm^{-1} is due to ring-in-plane-deformation (Palaniappan *et al.* 2005; Kang *et al.* 1998). The spectra for the conductive paper prepared from the kraft pulp fibers (Fig. 1c) and from the unbleached sulfite pulp fibers (Fig. 1b(I)) were similar to that for the kraft pulp fibers (Fig. 1d(I)). The bands observed in the 3420 and 2900 cm^{-1} region are assigned to O−H stretching and C−H stretching, respectively (Du *et al*. 2013). The occurrence at 1645 is due to absorbed water and oxygen-containing group. The appearance of low intensity band at 1438 and 1115 cm^{-1} can be related to C−H deformation, while the band at 1259 cm^{-1} is related to C−O stretching vibration due to cellulose oxidation (Kline *et al*. 2010). The bands at 1372, 1167, 1054, and 898 cm^{-1}, are typical for those in cellulose and hemicelluloses (Yuan *et al*. 2013). The polyaniline peaks did not show up in the FT-IR spectra for these samples due to the small polyaniline content.

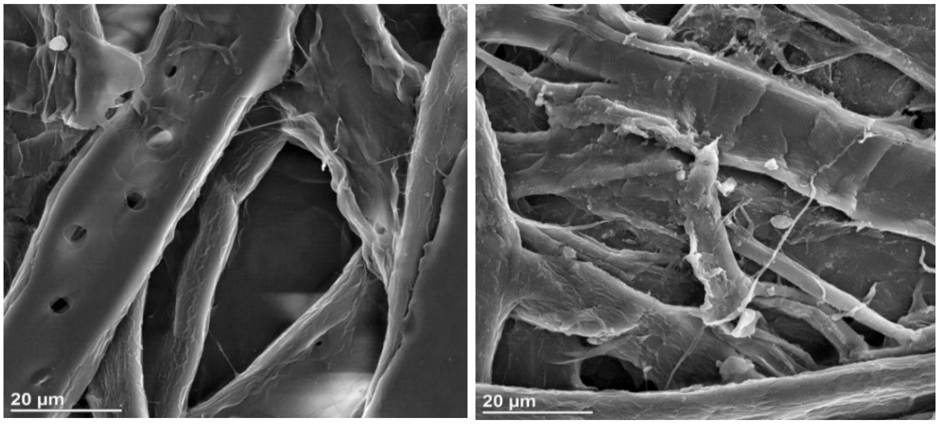
The FT-IR spectra of the conductive paper prepared by paper coating with polyaniline dispersion (polyaniline-dodecylbenzene sulfonic acid sodium salt), polyaniline-deposited clay, and clay are shown in Fig. 1(II). The characteristic peaks of polyaniline dispersion at 3460, 2950, 1570, 1490, 1300, 1250, 1140, and 810 cm^{-1} were found in the FTIR spectrum for the paper sample coated with polyaniline dispersion (Fig. 1a(II)), which are similar to those for polyaniline-hydrochloride in Fig. 1(a). However, a specific peak (9) at 1020 cm^{-1} was found for the paper sample coated with polyaniline dispersion due to $NH^{+\cdots}SO_3^-$ interaction between the polyaniline chain and dodecylbenzene sulfonic acid sodium salt (Babazadeh 2007). The spectrum of the polyaniline-deposited clay in Fig. 1b(II) showed the general peaks of polyaniline-dodecylbenzene sulfonic acid sodium salt, as well as the clay peaks at 1670, 1010, 926, 796, 700, and 428 cm^{-1} (Fig. 1c(II)) (Saikia *et al.* 2003).

The SEM observations were conducted to observe the surface morphologies of the conductive paper (Figs. 2 and 3). As shown in Fig. 2(a), the unbleached sulfite pulp fibers had a relatively smooth surface before the *in situ* polymerization of aniline, while in Fig. 2(b), the pulp fibers after the *in situ* polymerization treatment had a rough surface, which was due to the deposition of agglomerated polyaniline particles on the fiber surface.



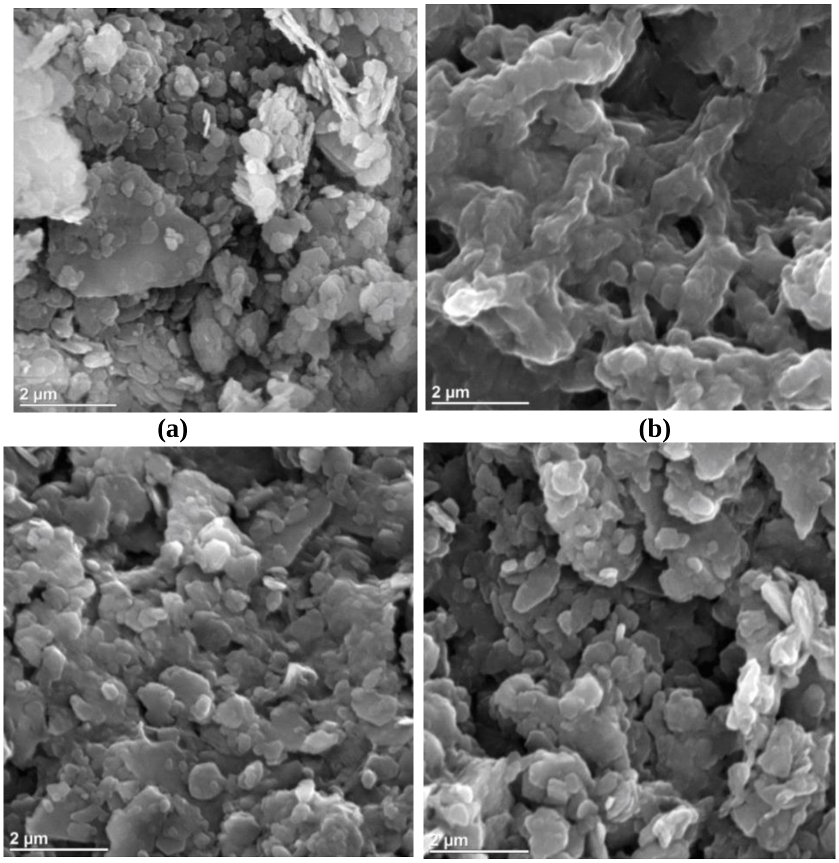
(I) (II)

Fig. 1. FT-IR spectra of various samples: Fig. 1(I). Spectra of: (a) polyaniline-hydrochloride, (b) conductive paper prepared with unbleached sulfite pulp fibers at 15% aniline, (c) conductive paper prepared with kraft pulp fibers at 15% aniline, and (d) kraft pulp fibers; Fig. 1(II) Spectra of: (a) paper coated with polyaniline-dodecylbenzene sulfonic acid sodium salt, (b) Paper coated with polyaniline-deposited clay; (c) paper coated with clay



(a) (b)

Fig. 2. SEM pictures of unbleached sulfite pulp fibers before (a) and after (b) *in-situ* polymerization treatment



(a) (b)

(c) (d)

Fig. 3. SEM pictures of paper surface coated with: a) clay; b) polyaniline dispersion; c) polyaniline/clay composition prepared using the mixing method; d) polyaniline/clay composition prepared using the *in situ* polymerization method

In Fig. 3, the SEM pictures show the flake-like structure of clay particles (Fig. 3a), and the polyaniline dispersion that is fused to form clusters (Fig. 3b). The conductive clay prepared by the mixing method shows that polyaniline and clay are very much physically separated (Fig. 3c), while for the sample prepared by in-situ polymerization in the presence of clay, polyaniline particles are on the clay surface."

CONCLUSIONS

1. Conductive paper was prepared by Meyer rod coating of cellulosic paper with polyaniline/clay composition prepared *via*: 1) mixing polyaniline dispersion with clay, or 2) *in* s*itu* polymerization of aniline in the presence of clay.
2. SEM and FT-IR analyses showed that polyaniline and clay were deposited on the surface of the cellulosic paper.
3. Conductive paper was also prepared by *in situ* polymerization of aniline in presence of cellulosic fibers. However, the conductivity of the resultant paper composite was affected significantly by the pH of the water used for paper sheet formation. An interesting finding is that at the same aniline content, paper coating with polyaniline led to a much higher paper conductivity, in comparison to the use of polyaniline-engineered fibers for the preparation of conductive paper.

REFERENCES CITED

Agarwal, M., Lvov, Y., and Varahramyan, K. (2006). "Conductive wood microfibers for smart paper through layer-by-layer nanocoating," *Nanotechnology* 17(21), 5319-5325.

Babazadeh, M. (2007). "A direct one-pot method for synthesis of polyaniline doped with dodecyl benzene sulphonic acid in aqueous medium and study of tis thermal properties," *Iran. Polym. J.* 16(6), 389-396.

Cao, Y., Andreatta, A., Heeger, A. J., and Smith, P. (1989). "Influence of chemical polymerization conditions on the properties of polyaniline," *Polymer* 30(12), 2305-2311.

Ding, C., Qian, X., Shen, J., and An, X. (2010a). "Preparation and characterization of conductive paper *via in situ* polymerization of pyrrole," *BioResources* 5(1), 303-315.

Ding, C., Qian, X., Yu, G., and An, X. (2010b). "Dopant effect and characterization of polypyrrole-cellulose composites prepared by *in situ* polymerization process," *Cellulose* 17 (6), 1067-1077.

Du, Y., Wu, T., Yan, N., Kortschot, M. T., and Farnood, R. (2013). "Pulp fiber-reinforced thermoset polymer composites: Effects of the pulp fibers and polymer," *Composites: Part B* 48, 10-17.

Duek, E. A. R., De Paoli, M. A., and Mastragostino, M. (1992). "An electrochromic device based on polyaniline and Prussian blue," *Adv. Mater.* 4(4), 287-291.

Dutta, D., Sarma, T. K., Chowdhury, D., and Chattopadhyay, A. (2005). "A polyaniline-containing filter paper that acts as a sensor, acid, base, and endpoint indicator and also filters acids and bases," *J. Colloid Interf. Sci.* 283(1), 153-159.

Focke, W. W., Wnek, G.E., and Wei, Y. (1987). "Influence of oxidation state, pH and counterion on the conductivity of polyaniline," *J. Phys. Chem. A* 91(22), 5813-5818.

Ghadimi, F., Safa, K. D., Massoumi, B., and Entezami, A. A. (2002). "Polyaniline doped with sulphosalicylic, salicylic and citric acid in solution and solid-state," *Iran. Polym. J.* 11(3), 159-166.

Gustafsson, G., Cao, Y., Treacy, G. M., Klavetter, F., Colaneri, N., and Heeger, A. J. (1992). "Flexible light-emitting diodes made from soluble conducting polymers," *Nature* 357(6378), 477-479.

Huang, B., Kang, G., and Ni, Y. (2005). "Electrically conductive fiber composites prepared from polypyrrole-engineered pulp fibers," *Can. J. Chem. Eng.* 83(5), 896-903.

Huang, B., Kang, G. J., and Ni, Y. (2006). "Preparation of conductive paper by *in situ* polymerization of pyrrole in a pulp fibre system," *Pulp Paper Canada* 107(2), 38-42.

Huang, W. S., Humphrey, B. D., and MacDiarmid, A. G. (1986). "Polyaniline, a novel conducting polymer (Morphology and chemistry of its oxidation and reduction in aqueous electrolytes)," *J. Chem. Soc., Faraday Trans.*, 82, 2385-2400.

Johnston, J. H., Moraes, J., and Borrmann, T. (2005). "Conducting polymers on paper fibres," *Synthetic Met.* 153(1-3), 65-68.

Kanatzidis, M. G., Wu, C. G., Marcy, H. O., and Kannewurf, C. R. (1989). "Conductive-polymer bronzes. Intercalated polyaniline in vanadium oxide xerogels," *J. Am. Chem. Soc.* 111(11), 4139-4141.

Kaneko, M., and Nakamura, H. (1985). "Photoresponse of a liquid junction polyaniline film," *J. Chem. Soc., Chem. Commun.* (6), 346-347.

Kang, E. T., Neoh, K. G., and Tan, K. L. (1998). "Polyaniline: A polymer with many interesting intrinsic redox states," *Prog. Polym. Sci.* 23(2), 277-324.

Kang, G, and Ni, Y. (2008). "Further optimization of polypyrrole-pulp composite for the production of conductive paper," *In: Proceedings of 2nd International Papermaking and Environment Conference*, Tianjin, China.

Katz, H. E., Searson, P. C., and Poehler, T. O. (2010). "Batteries and charge storage devices based on electronically conducting polymers," *J. Mater. Res.* 25(8), 1561-1574.

Kelly, F. M., Johnston, J. H., Borrmann, T., and Richardson, M. J. (2007). "Functionalised hybrid materials of conducting polymers with individual fibres of cellulose," *Eur. J. Inorg. Chem.* (35), 5571-5577.

Kingsborough, R. P., and Swager, T. M. (1998). "Electroactivity enhancement by redox matching in cobalt salen-based conducting polymers," *Adv. Mater.* 10(14), 1100.

Kline, L. M., Hayes, D. G., Womac, A. R., and Labbe, N. (2010). "Simplified determination of lignin content in hard and soft woods via UV-spectrophotometric analysis of biomass dissolved in ionic liquids," *BioResources* 5(3), 1366-1383.

Kong, F., and Ni, Y. (2009a). "Determination of Cr(VI) concentration in diluted samples based on the paper test strip method," *Water Sci. Technol.* 60(12), 3083-3089.

Kong, F., and Ni, Y. (2009b). "Development of cellulosic paper-based test strips for Cr(VI) determination," *BioResources* 4(3), 1088-1097.

Li, J., Qian, X., Wang, L., and An, X. (2010a). "XPS characterization and percolation behavior of polyaniline-coated conductive paper," *BioResources* 5(2), 712-726.

Li, J., Qian, X., Chen, J., Ding, C., and An, X. (2010b). "Conductivity decay of cellulose-polypyrrole conductive paper composite prepared by in situ polymerization method," *Carbohydr. Polym.* 82(2), 504-509.

MacDiarmid, A. G. (2001). "Synthetic metals: A novel role for organic polymers," *Synthetic Met.* 125(1), 11-22.

Ngamna, O., Morrin, A., Killard, A. J., Moulton, S. E., Smyth, M. R., and Wallace, G. G. (2007). "Inkjet printable polyaniline nanoformulations," *Langmuir* 23(16), 8569-8574.

Nishino, H., Yu, G., Heeger, A. J., Chen, T. A., and Rieke, R. D. (1995). "Electroluminescence from blend films of poly(3-hexylthiophene) and poly(N-vinylcarbazole)," *Synthetic Met.* 68(3), 243-247.

Nystrom, G., Razaq, A., Strømme, M., Nyholm, L., and Mihranyan, A. (2009). "Ultrafast all-polymer paper-based batteries," *Nano Lett.* 9(10), 3635-3639.

Okamoto, M., Morita, S., Kim, Y. H., Kotaka, T., and Tateyama, H. (2001). "Dispersed structure change of smectic clay/poly (methyl methacrylate) nanocomposites by copolymerization with polar comonomers," *Polymer* 42(3), 1201-1206.

Paakko, M., Vapaavuori, J., Silvennoinen, R., Kosonen, H., Ankerfors, M., Lindstrom, T., Berglund, L. A., and Ikkala, O. (2008). "Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically porous templates for functionalities," *Soft Matter* 4(12), 2492–2499.

Palaniappan, S., Saravanan, C., Amarnath, C. A., and Rao, V. J. (2004). "Polyaniline salts and complexes as catalyst in bisindole synthesis," *Catal. Lett.* 97(1-2), 77-81.

Palaniappan, S., Saravanan, C., and Rao, V. J. (2005). "Synthesis of polyaniline-bismoclite composite and its function as recoverable and reusable catalyst," *J. Mol. Catal. A-Chem.* 229(1-2), 221-226.

Qian, X., Shen, J., Yu, G., and An, X. (2010). "Influence of pulp fiber substrate on conductivity of polyaniline-coated conductive paper prepared by *in situ* polymerization," *BioResources* 5(2), 899-907.

Richardson, M. J., Johnston, J. H., and Borrmann, T. (2006). "Electronic properties of intrinsically conducting polymer-cellulose based composites," *Curr. Appl. Phys.* 6(3), 462-465.

Saikia, N. J., Bharali, D. J., Sengupta, P., Bordoloi, D., Goswamee, R. L., Saikia, P. C., Borthakur, P. C. (2003). "Characterization, beneficiation and utilization of a kaolinite clay from Assam, India," *Appl. Clay Sci.* 24(1-2), 93-103.

Sasso, C., Bruyant, N., Beneventi, D., Faure-Vincent, J., Zeno, E., Petit-Conil, M., Chaussy, D., and Belgacem, M. N. (2011). "Polypyrrole (PPy) chemical synthesis with xylan in aqueous medium and production of highly conducting, PPy/nanofibrillated cellulose films and coatings," *Cellulose* 18(6), 1455-1467.

Taka, T. (1991). "EMI shielding measurements on poly(3-octyl thiophene) blends," *Synthetic Met.* 41(3), 1177-1180.

Trinidad, F., Montemayor, M. C., and Fatas, E. (1991). "Performance study of Zn/$ZnCl_2$, NH4Cl/polyaniline/carbon battery," *J. Electrochem. Soc.* 138(11), 3186-3189.

Trivedi, D. C., and Dhawan, S. K. (1992). "Grafting of electronically conducting polyaniline on insulating surfaces," *J. Mater. Chem.* 2(10), 1091-1096.

Yuan, L., Wan, J., Ma, Y., Wang, Y., Huang, M., and Chen, Y. (2013). "The content of different hydrogen bond models and crystal structure of eucalyptus fibers during beating," *BioResources* 8(1), 717-734.

Zhao, H., Li, L., Yang, J., Zhang, Y., and Li, H. (2008). "Synthesis and characterization of bimetallic Pt-Fe/polypyrrole carbon catalyst as DMFC anode catalyst," *Electrochem. Comm.* 10(6), 876-879.

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