Conductive paper through LbL multilayering with conductive polymer: dominant factors to increase electrical conductivity

Jegon Lee · Jaeho Ryu · Hye Jung Youn

Abstract A conductive paper was made of cellulose fibers with a multilayer of polyethyleneimine (PEI) and poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) and the factors to increase the conductivity of the paper were investigated. The adsorption amount and the structure of PEI and PEDOT:PSS multilayer was changed by controlling salt concentration and the number of layers, and inter-contact degree of fibers was controlled by calendering. The adsorption behavior of the polyelectrolytes onto cellulose was evaluated using a quartz crystal microbalance with dissipation monitoring, and the adsorption amount was quantitatively analyzed through Kjeldahl nitrogen analysis and an Inductively Coupled Plasma Optical Emission Spectrometer. The conductivity of the resultant paper was in the range of 10^{-5}–10^{-4} S/cm without loss of paper strength. The conductivity of the paper increased when the multilayer was formed at low salt concentration and the conductive paper was calendered. It appeared that electron transfer by increased contact between PEDOT:PSS improved the conductivity of the paper.

J. Lee · J. Ryu · H. J. Youn (✉)
Department of Forest Sciences, College of Agriculture and Life Sciences, Seoul National University, 1, Gwanak-ro, Gwanak-gu, Seoul 151-921, Korea
e-mail: page94@snu.ac.kr

H. J. Youn
Research Institute for Agriculture and Life Sciences, 1, Gwanak-ro, Gwanak-gu, Seoul 151-921, Korea

Introduction

Cellulose has been widely used in scientific and industrial fields with many advantages such as good mechanical and physical properties, low-cost, renewable and environmental-friendly material. Cellulose also is one of the lightest materials of the known substrate materials. For these reasons, interest in the use of cellulosic materials in electronic devices has increased. Cellulosic materials have been mainly used as dielectrics for capacitors (Pushparaj et al. 2007) and substrates for transistors (Fortunato et al. 2008) and RFID-tags (Unander and Nilsson 2009), but their use in electronics has been limited due to non-conductive characteristic. Cellulosic materials can be used in electronics such as ID-tags or disposable batteries or various indicators, however, provided that appropriate electrical property is given (Martins et al. 2011). In addition, the porous, bulk cellulosic materials like paper can expand their utilization in electronic devices with properties unlike dense materials such as metal or conductive film.

To develop the electrical conductivity of cellulosic materials, various techniques have been incorporated. Cellulose-based conductive films have been

manufactured by blending conductive polymer with cellulose materials (Mičušík et al. 2006; Ebrahim et al. 2007; Jung et al. 2008; Hu et al. 2011) or polymerizing conductive monomer on cellulose (Nyström et al. 2010; Russler et al. 2011). Layer-by-Layer (LbL) multilayering can be used to develop conductivity in cellulosic materials. LbL multilayering is a simple technique to adsorb materials on a substrate (Decher and Hong 1991). LbL multilayering can control the surface properties of the substrate by adsorbing materials according to various interaction mechanisms such as electrostatic interaction and hydrophobic interaction. LbL multilayering can also modify electrochemical properties of bulk materials as well. This technique has been incorporated into paper science to increase paper strength (Wågberg et al. 2002; Zheng et al. 2006; Ryu et al. 2011) and control wettability of fibers (Lingström et al. 2006, 2007) since 2002. Electrical conductivity of paper also is greatly improved through LbL multilayering of conductive materials on fibers. It was reported that poly(3,4-ethylenedioxythiophene):poly(sodium 4-styrenesulfonate) (PEDOT:PSS) (Agarwal et al. 2006; Wistrand et al. 2007), carbon nanotube (Agarwal et al. 2009), or indium tin oxide nanoparticles (Peng et al. 2008) are adsorbed on fibers and then conductive papers are made of treated fibers. According to previous researches, the degree of the conductivity was dependant on various factors such as the type of conductive materials and cationic polyelectrolyte, adsorption amount, and contact degree (Agarwal et al. 2006, 2009; Wistrand et al. 2007; Peng et al. 2008). However, there has not been reported to determine what is the dominant factor to develop and improve cellulose paper conductivity with conductive polymer.

In this study, contact degree and adsorption amount of PEDOT:PSS were considered as factors to increase conductivity of paper made of fibers treated by polyethyleneimine (PEI)/PEDOT:PSS multilayering. Control of intra-contact of PEDOT:PSS on a fiber was investigated by changing the multilayer structure on fibers through controlling salt concentration in LbL multilayering (Lundin et al. 2011; Ramos et al. 2011). We also examined the effect of PEDOT:PSS inter-contacts between treated fibers through sheet densification by calendering. The adsorption amount of PEDOT:PSS was controlled by the number of layers and salt concentration. We expected to find a key factor to develop and improve paper conductivity.

Experimental

Materials

Unbeaten Eucalyptus bleached kraft pulp fibers were used. Anionic poly(3,4-ethylenedioxythiophene):poly(sodium 4-styrenesulfonate) (PEDOT:PSS, ratio of PSS/PEDOT 2.5, Orgacon ICP, AGFA) as conductive polymer and cationic polyethyleneimine (PEI, Mw 25,000 g/mol, Sigma Aldrich) were used for LbL multilayering onto pulp fibers. Sodium chloride, 1 N hydrochloric acid (HCl) solution, and 1 N sodium hydroxide (NaOH) solution were used for adjusting salt concentration and pH. Also, analytical grade hydrochloric acid solution (37 wt%), nitric acid (HNO$_3$) solution (70 wt%), and hydrogen peroxide (H$_2$O$_2$) solution (31 wt%) purchased from OCI company Ltd (Korea) were used.

LbL multilayering on fibers and handsheet forming

The pulp was disintegrated using a laboratory Valley beater. The dissolved and colloidal materials in the pulp suspension were removed using a vibration screen (Sweco Co.) equipped with 400 mesh wire. The fiber suspension was diluted to 0.5 wt% with deionized water. Salt concentration of fiber suspension was controlled by adjusting the conductivity of the fiber suspension to 300, 600, or 1,200 μS/cm using NaCl solution. These levels of the conductivity correspond to NaCl 2.5, 5.0, or 10.0 mM. The pH was adjusted at 8.0 ± 0.5 for odd layers, and at 4.0 ± 0.5 for even layers using 1 N HCl and NaOH to increase the adsorption amount of polyelectrolyte. Addition ratio of PEI and PEDOT:PSS was 0.5 and 0.6 wt% based on oven-dried fibers, respectively. The cationic polyelectrolyte PEI was adsorbed onto the pulp fibers at pH 8.0 ± 0.5 for 20 min. After adsorption, the pulp suspension was washed twice each for 5 min with deionized water to remove any unadsorbed PEI. This created one layer of polyelectrolyte on fibers. Subsequently, the pulp suspension (0.5 wt%) of which the pH and conductivity were adjusted by the method mentioned above, was treated with PEDOT:PSS at pH 4.0 ± 0.5 for 20 min and was then washed again. The LbL multilayering process progressed in the same manner until the target layer number was reached. After washing at each layer, the streaming zeta-potential of the treated fiber was

measured with System Zeta Potential (SZP 04, Mütek, Germany). Handsheets of 100 g/m^2 were prepared with the treated fibers using a handsheet former.

Evaluation of adsorption behavior of PEI and PEDOT:PSS on a cellulose film by QCM-D

Adsorption behavior of the PEI and PEDOT:PSS during the LbL multilayering process was evaluated by Quartz Crystal Microbalance with dissipation monitoring (QCM-D, Q-Sense E4, Biolin, Sweden). A cellulose film which was prepared by hydrolyzing trimethylsilyl cellulose (TMSC) film was used as a substrate. TMSC solution was spin-coated onto a silicon-coated QCM sensor (QSX 303, Biolin, Sweden) using a spin coater (YS 100MD, Yooil Eng. Co., Korea). The TMSC film was hydrolyzed by exposing the film to 2 M HCl acid vapor for 4 min and was then dried at 80 °C for 30 min (Kontturi et al. 2003). The changes in frequency and dissipation were monitored by the QCM-D when the PEI and PEDOT:PSS were alternately adsorbed on the cellulose coated QCM sensor (resonance frequency 25 MHz). The concentrations of PEI and PEDOT:PSS solutions were 100 mg/L, respectively. During the adsorption process, the salt concentration of the solutions was adjusted to be 2.5, 5.0, and 10.0 mM NaCl. The pH of the solutions was adjusted to 8.0 ± 0.5 in the PEI solution and 4.0 ± 0.5 in the PEDOT:PSS solution using 0.1 N NaOH and HCl. LbL multilayering was conducted up to 10 layers and each layer treatment consisted of adsorption of 20 min and a washing stage of 10 min.

Evaluation of PEI and PEDOT: PSS contents of handsheets

The PEI content in the handsheets was quantitatively analyzed by Kjeldahl nitrogen analysis (Liu et al. 2001). The handsheets made of treated fibers were disintegrated in sulfuric acid with a catalyst. The fiber suspension was heated to transfer the nitrogen compound of PEI to an ammonia complex. After the heated suspension was distilled with alkali to separate sulfuric acid, nitrogen content in the final suspensions was detected by a Kjeldahl Protein/Nitrogen Analyzer (Kjeltec Auto 1035/1038 System, Tecator AB, Sweden). The amount of PEI in the handsheets was calculated using the PEI-nitrogen calibration curve which was obtained by varying PEI concentration. The PEDOT:PSS contents in the handsheets were quantified by sulfur content analysis using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, ICP-730 ES, Varian, Australia) (Okamoto et al. 2004; Wennrich et al. 1995). The handsheet specimens (about 0.5 g) were added in mixture of HNO$_3$ 8 mL, HCl 1 mL, and H$_2$O$_2$ 1 mL. The mixed suspension was digested using a microwave (Multiwave 3000, Anton-paar, Austria) for 70 min. The sulfur content in PEDOT:PSS was also determined at different PEDOT:PSS concentrations as described above. The detected sulfur ratio in PEDOT:PSS was 21.8 %. The PEDOT:PSS contents in the handsheets were calculated with the obtained PEDOT:PSS-sulfur ratio.

Densification of paper

The handsheets were calendered with a laboratory soft nip calender (Dong Won Roll, Korea) for densification of the handsheets. The handsheets were passed once at linear pressure of 50–400 kg$_f$/cm with the top side of the handsheet facing the hard roll. The temperature of the calender roll was 40 °C and the operating speed was 10 cm/min. The density of the calendered handsheets was evaluated. The surface image of the calendered handsheets was measured with an optical microscope (Video microscope system, ICS 305B, Alphasystec, Korea).

Evaluation of mechanical properties and conductivity of paper

The strength and conductivity of the handsheet were evaluated. The paper strength was presented as a tensile index in accordance with the TAPPI test method T494. The surface images of the handsheets were observed by a Field Emission Scanning Electron Microscope (FE-SEM, SUPRA 55VP, Sweden) and an optical microscope. The conductivity of handsheets was evaluated by a 4-point probe type surface resistance meter (RS8-1, probe pin spacing 1.00 mm, current range 10^{-2}–10^2 mA, BEGA Technologies, Korea). Surface resistance (ohm/sq) was measured at room temperature and 30 ± 5 % RH, and converted to the conductivity of the handsheet according to Eq. (1).

$$A = (B \times t)^{-1} \tag{1}$$

where A was conductivity (S/cm), B was surface resistance (ohm/sq), and t was the thickness (cm) of the handsheets. When the thickness of a handsheet was

less than the distance between probe tips, the inverse of resistivity which is the product of surface resistance and thickness is expressed as the conductivity of the handsheet.

Results and discussion

Characterization of polyelectrolyte adsorption on cellulose surface

To develop electrical properties of cellulose fibers and paper, LbL multilayering was performed on fibers with cationic PEI and anionic PEDOT:PSS. The zeta-potential of treated fibers was measured to confirm whether the polyelectrolytes were adsorbed or not. Figure 1 shows the zeta-potential of treated fibers with number of layers at different salt concentrations. Untreated fibers had negative potential. The zeta potential was changed to positive after adsorption of cationic PEI on fibers. This indicates the formation of one layer. After anionic PEDOT:PSS was adsorbed on 1 layer fibers, the positive potential of the fibers changed to negative potential. The zeta-potential of treated fibers was changed alternately with repetitive treatment of polyelecetrolytes, which was dependent on polyelectrolyte in the outermost layer of fiber. It was confirmed that LbL multilayering of PEI and PEDOT:PSS was effectively accomplished when the PEI and PEDOT:PSS were adsorbed on fibers at different salt concentrations. However, the zeta-potential of fibers at the same layer number was only slightly different with salt concentration condition. It appears that the number of free functional groups at the outermost layer was similar, even though adsorption amount of polyelectrolytes increased with increasing salt concentration.

The adsorption behavior of the PEI and PEDOT:PSS was investigated to find the relationship between adsorption of conductive polymer and paper conductivity. In this study, quantitative analysis of adsorption weight was conducted by element analysis and frequency changes (Δf) measurement using a quartz crystal microbalance with dissipation (QCM-D), and the structure of a multilayer was evaluated by dissipation changes (ΔD) measurement using QCM-D.

Figure 2 presents the adsorption amount of the PEI and PEDOT:PSS with the layer number, which is the
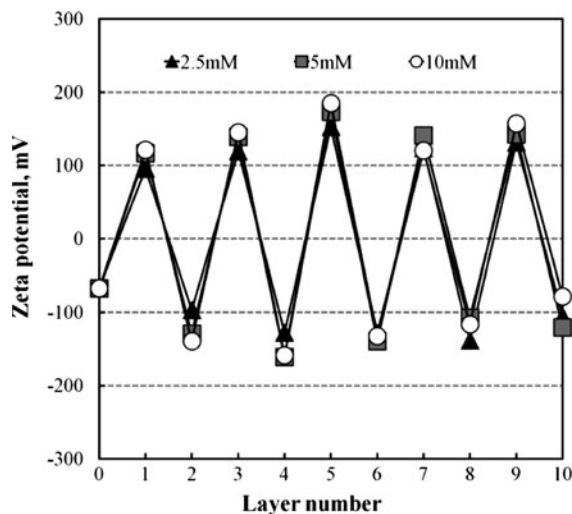

Fig. 1 Zeta potential of fibers with the number of layers depending on salt concentration of 2.5 mM (*triangle*), 5 mM (*square*), and 10 mM (*circle*)

total cumulative adsorption amount of each polymer until corresponding number of layering. The adsorbed amounts of PEI and PEDOT:PSS were obtained from nitrogen content using Kjeldahl method and sulfur content using ICP-OES in the prepared paper sheets. In Fig. 2, the adsorption weight of PEI and PEDOT:PSS increased with repeated treatment of PEI and PEDOT:PSS in a relatively linear relationship. It indicates the build-up of multilayers on fibers through LbL multilayering treatment. As the salt concentration increased, more PEI and PEDOT:PSS were adsorbed. This phenomenon became more prominent as the number of layers increased. It could contribute to increase adsorption amount of the polyelectrolyte on fibers because the screening effect by the added salt reduces electrostatic repulsion over the range of salt concentration in this experiment (Enarsson and Wågberg 2008).

Polymer adsorption was confirmed by the images of the fiber surface in Fig. 3. Microfibrils are seen at the fiber surface in Fig. 3a. On the other hand, the microfibrils are hidden by polyelectrolytes of 4 layer (Fig. 3b) and 10 layer (Fig. 3c) because the multilayer of polymer covered the bare surface of the fiber.

Figure 4 shows frequency change (Δf) (a) and dissipation change (ΔD) (b) in monitoring with QCM-D, when the PEI and PEDOT:PSS were adsorbed on the cellulose model film. The Δf is related to the adsorbed mass per unit area, Δm. The ΔD indicates a
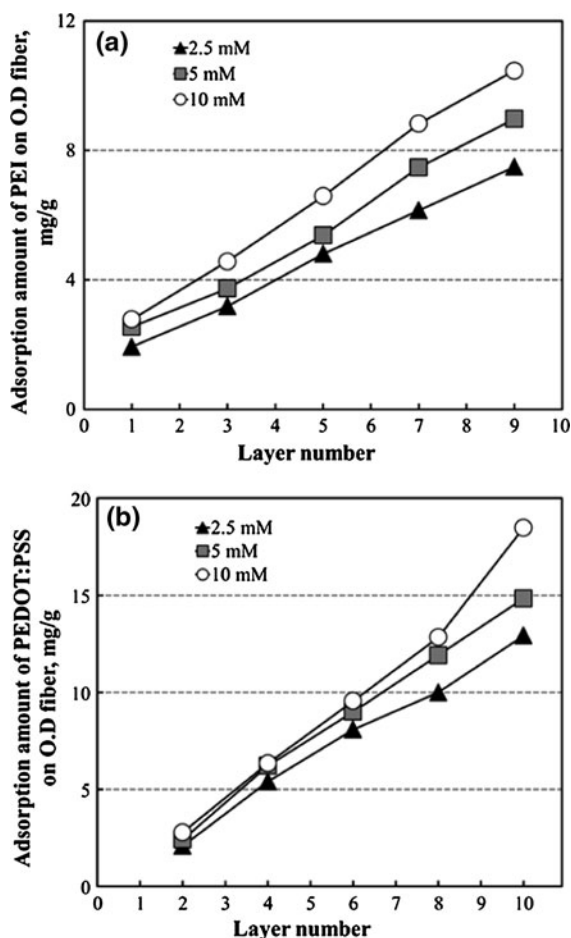
Fig. 2 Cumulative adsorption amount of PEI (**a**) and PEDOT:PSS (**b**) on fibers with the number of layers

Fig. 3 FE-SEM images of handsheet made of untreated fibers (**a**) and treated fibers with 4 layer (**b**) and 10 layer (**c**) at 10 mM NaCl. The scalebar represents 200 nm

change in the viscoelastic property of the adsorbed layer. Each layer step includes adsorption of 20 min and washing time of 10 min. In Fig. 4a, the Δf decreased with an increase in the layer number. It indicated the PEI and PEDOT:PSS were adsorbed on the cellulose film at each layer step, similar to the result of adsorption amount in Fig. 2. The even layer where the PEDOT:PSS was adsorbed showed a lower Δf than the odd layer where the PEI was adsorbed. This means the adsorbed amount of PEDOT:PSS was larger than that of the PEI. Also, the Δf decreased with increasing salt concentration up to NaCl 10 mM during the same layer step. This indicates the PEI and PEDOT:PSS were adsorbed more at higher salt concentrations due to screening effects.

Figure 4b describes the changes in dissipation (ΔD) during the adsorption of the PEI and PEDOT:PSS on
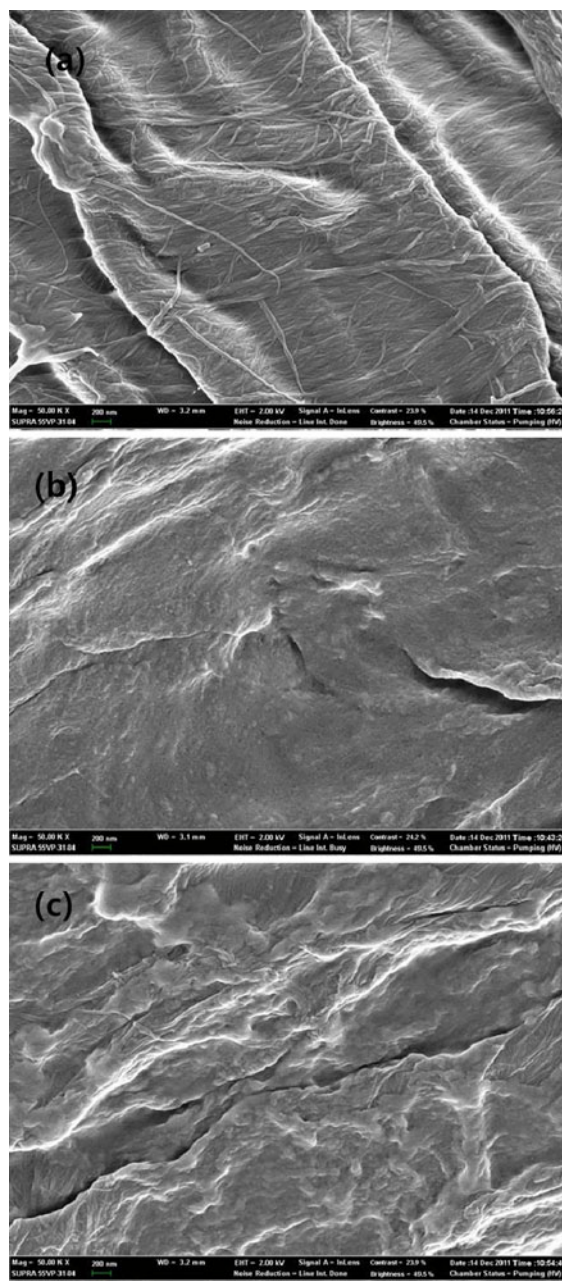
the cellulose film. The ΔD was related to the adsorbed layer structure. The increased ΔD indicates a bulkier structure of the multilayer, but the decreased ΔD indicates more rigid structure (Höök et al. 1998). When the PEDOT:PSS was adsorbed, ΔD increased, suggesting that the adsorbed layer was loose and bulky.

Fig. 4 QCM-D monitoring of the LbL multilayering of PEI and PEDOT:PSS on cellulose film. Change in frequency (**a**) and change in dissipation (**b**) during adsorption of PEI and PEDOT:PSS at different salt concentrations
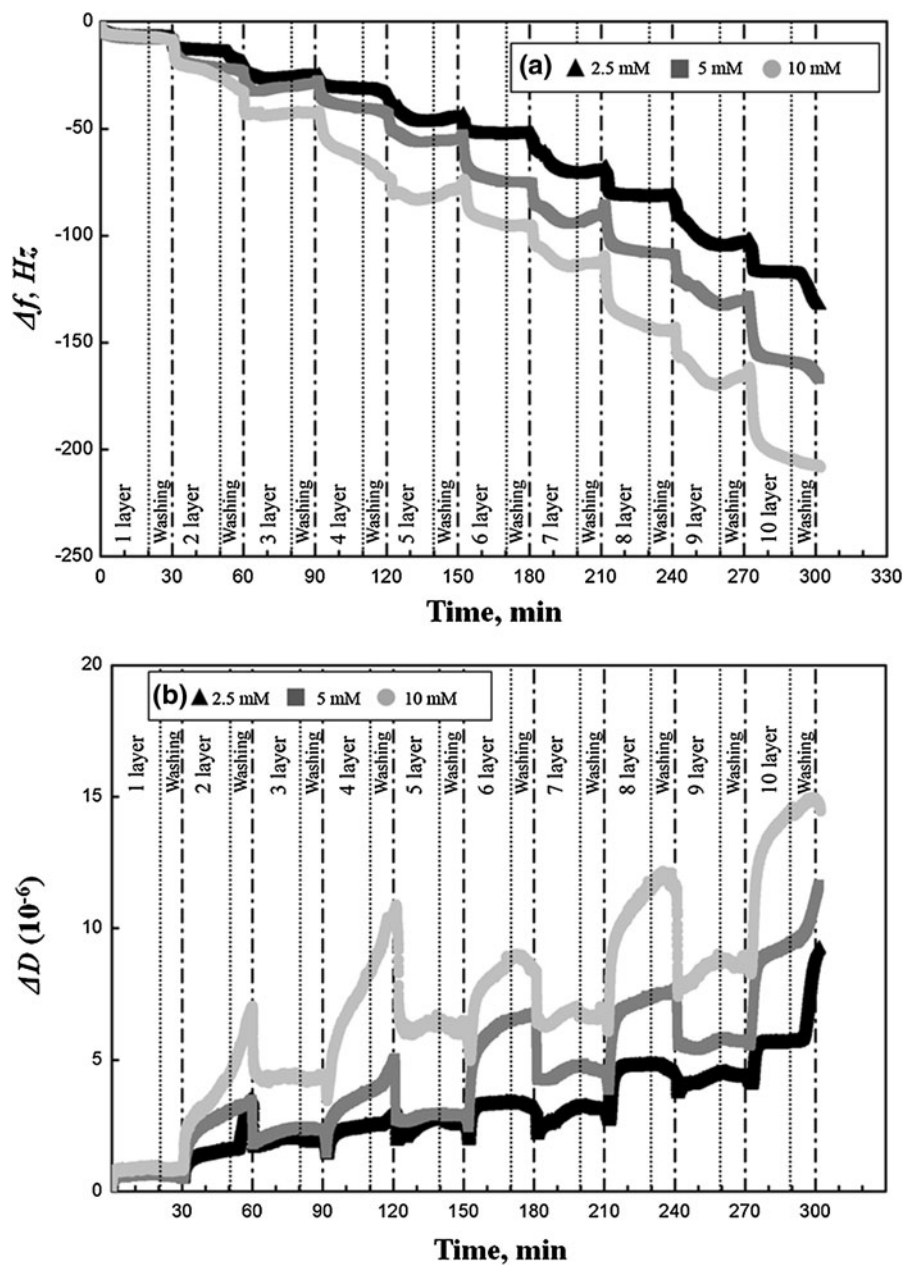
ΔD decreased when the PEI was adsorbed on the PEDOT:PSS layer. The decrease in ΔD has two possible explanations. One is a detachment of polymer formed in a previous layer, and the other is formation of a layer with rigid structure. Our result is most likely due to the formation of a rigid and compact layer because of the decrease in Δf despite of a decrease in ΔD. According to Notley et al. ΔD and Δf decreased

when the PAA was adsorbed in the multilayer of PAH/PAA because the PAA was likely to penetrate into the multilayer and then take up some fraction of the pore while the multilayer was built (Notley et al. 2005). The mobility of the PEDOT:PSS was lower than that of the PEI because the PEDOT:PSS behaves similar to particulate (Lang et al. 2009). When the PEI was adsorbed, it is likely that the PEI with higher mobility
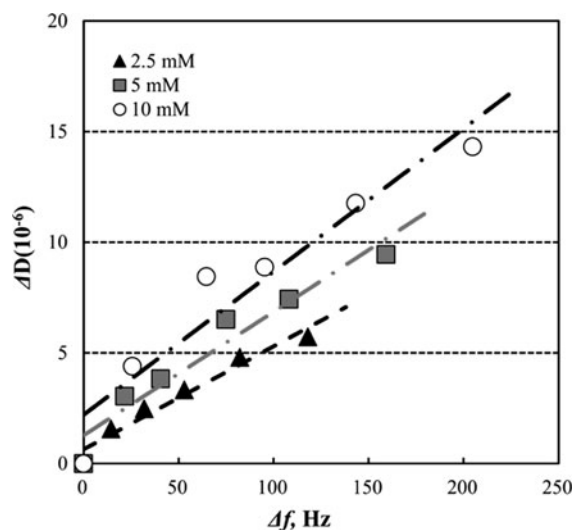
Fig. 5 Relationship of Δf and ΔD at different salt concentrations

Fig. 6 Conductivity of handsheet made of PEI/PEDOT:PSS LbL multilayered fibers with the number of layers depending on salt concentration of 2.5 mM (*triangle*), 5 mM (*square*), and 10 mM (*circle*)

penetrated into the former PEDOT:PSS layer and the multilayer structure became rigid and compact. This pattern was shown at every bilayer.

The result of the increase in ΔD and the decrease in Δf at even layers with the increase in salt concentration was notable. While ΔD showed a big change, the adsorbed amount (Δf) was large at a high salt concentration. The effect of salt concentration on a multilayer structure was observed at the same change in Δf. Figure 5 shows the relationship between Δf and ΔD at even layers, which is linear. The slope of the regression line in Fig. 5 was related to the change in ΔD at the unit change of the adsorption amount of polyelectrolytes. In other words, a higher slope means a bulkier multilayer structure. When the PEDOT:PSS was adsorbed at high salt concentration, the formed multilayer was bulkier and looser compared to the low salt concentration condition. This bulky multilayer greatly affected the subsequent adsorbed PEI, which more penetrated into the multilayer (Notley et al. 2005).

Effect of salt concentration on the conductivity of paper

The conductivity of handsheets made of fibers treated by LbL multilayering with PEI and PEDOT:PSS was evaluated. Figure 6 shows the conductivity of the handsheets with the number of layers at different salt concentrations. The adsorbed PEDOT:PSS at the 2
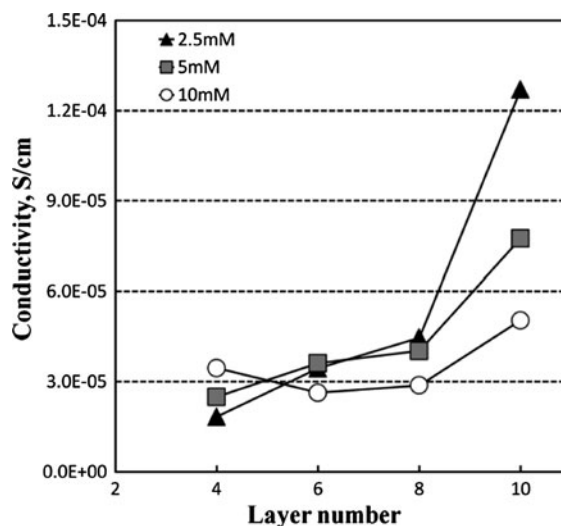
layer was too small to measure the conductivity of a paper. The conductivity of 4 layer handsheets was about 10^{-5} S/cm. The conductivity of paper was typically about 10^{-14} S/cm depending on moisture content and temperature (Murphy 1960a, b). The conductivity of "conductive" paper improved significantly, by a factor of up to 10^9. The conductivity was insignificantly increased until 8 layers were formed but sharply increased at 10 layers.

Both adsorption amount of PEDOT:PSS and structure of the multilayer were considered to affect development and improvement of the conductivity. A certain amount of PEDOT:PSS (4 layer in the experiment) was needed to develop the conductivity. However, the adsorption amount of the PEDOT:PSS did not affect the conductivity above a certain adsorption amount as shown in the 6 and 8 layer papers. Rather, the conductivity was improved at low salt concentration that resulted in the low adsorption amount. It is likely to be due to the multilayer structure of the adsorbed PEDOT:PSS and the obstruction of the PEI. The structure of multilayer at different salt concentrations would be proposed as Fig. 7 based on the results of QCM-D measurement and conductivity. The PEI described as branched polymer, and the PEDOT:PSS as linear polymer with PEDOT particulate. At low salt concentration condition (ex) 2.5 mM NaCl), the compact multilayer is formed because the
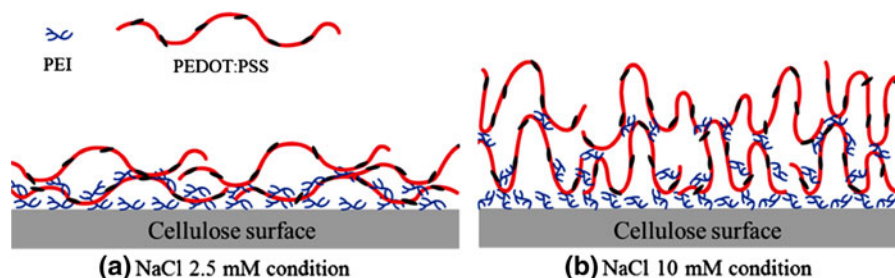
Fig. 7 Proposed multilayer structure which was formed at low salt concentration (**a**) and high salt concentration (**b**)

Table 1 The conductivity of cellulose-based conductive composites

|	Base substrate	Preparation	Conductivity, S/cm	References
Conductive paper	Cellulose fiber (unbeaten)	PEDOT:PSS multilayer	$10^{-5}–10^{-4}$	Our result
	Cellulose fiber (beaten)	PEDOT:PSS multilayer	Max. 0.25	Agarwal et al. (2006)
	Carboxymethylated cellulose fiber	PEDOT:PSS multilayer	$10^{-9}–10^{-7}$	Wistrand et al. (2007)
	Cellulose fiber (unbeaten)	ITO multilayer	$10^{-13}–10^{-6}$	Peng et al. (2008)
Conductive fiber	Cellulose fiber (beaten)	PEDOT:PSS multilayer	Max. 10	Agarwal et al. (2006)
	Cellulose fiber (beaten)	SWCNT multilayer	Max. 20	Agarwal et al. (2009)
Conductive film	Cellulose triacetate	Blending with PANi	$10^{-16}–10^{-4}$	Ebrahim et al. (2007)
	Bacterial cellulose membrane	Adsorption ofMWCNT	$10^{-5}–10^{-2}$	Jung et al. (2008)
	Dissolved cellulose	Blending with PANi	$10^{-7}–10^{-4}$	Russler et al. (2011)
	Pure microfiber	Polymerization of PPy	Max. 6×10^{-4}	Mičušík et al. (2006)
	Microfibrillated cellulose	Polymerization of PPy	Max. 1.5	Nyström et al. (2010)
	Bacterial cellulose membrane	Polymerization of PANi	$10^{-4}–10^{-2}$	Hu et al. (2011)
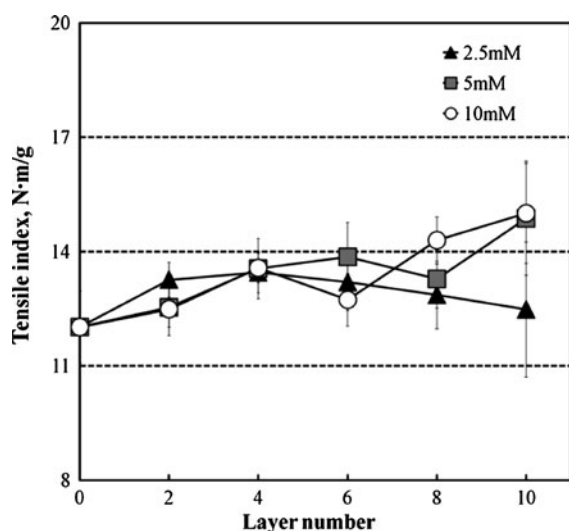
Fig. 8 Tensile index of handsheet made of PEI/PEDOT:PSS LbL multilayered fibers with the number of layers depending on salt concentrations. Error bars represent one standard deviation

PEI and the PEDOT:PSS are rigidly adsorbed on cellulose (Fig. 7a). On the other hand, the PEDOT:PSS layer is more loosely formed and the loop and tails are more extended away from the surface at high salt concentration because of screening effect (Fig. 7b). This makes the PEI molecule more interpenetrate into the PEDOT:PSS layer. Therefore, the PEDOT:PSS is hard to get close and can be easily isolated by the PEI at high salt concentration compared to low salt concentration condition. These result in the interruption of the electron transfer between PEDOT:PSS.

The conductivity levels of cellulose-based conductive composites reported in previous studies and that in this study are listed in Table 1. The conductive composites were categorized into conductive fiber, paper, and film. The conductivity differed depending on the types of base substrate and conductive polymer and depending on the preparation method. For the conductive film, the polymerization method (Nyström et al. 2010; Hu et al. 2011) was more effective when
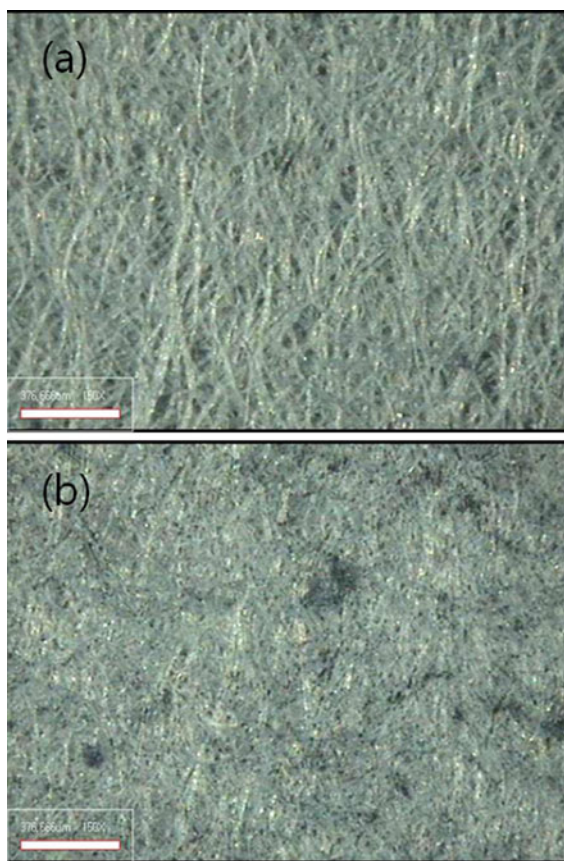
Fig. 9 Microscopic images of a surface of handsheet made of PEI/PEDOT:PSS LbL multilayered fibers with 10 layer at 10 mM salt concentration before (**a**) and after (**b**) calendering at 400 kg$_f$/cm. The scalebar represents about 376.7 μm

Fig. 10 Conductivity of handsheet made of PEI/PEDOT:PSS LbL multilayered fibers with 4 layer (**a**) and 10 layer (**b**) as a function of linear pressure when calendering

developing the conductivity compared to the blending or adsorbing method (Ebrahim et al. 2007; Jung et al. 2008; Russler et al. 2011). It appeared that a greater electrical pathway was produced by the polymerization method owing to the homogeneous structure. According to the references, the paper conductivity was lower than the fiber conductivity. Because a paper sheet has numerous pores and because the fibers are randomly oriented, especially in the case of a handsheet, the resistance to electron transfer undeniably increases. For the conductive paper prepared by PEDOT:PSS multilayering, the result of Agarwal et al. (2006) is higher compared to the results published by Wistrand et al. (2007) and compared to our result. Agarwal et al. (2006) used beaten fibers as a base substrate. The surface area of the fibers was greatly increased by the beating process due to internal and external fibrillation, and the resulting paper
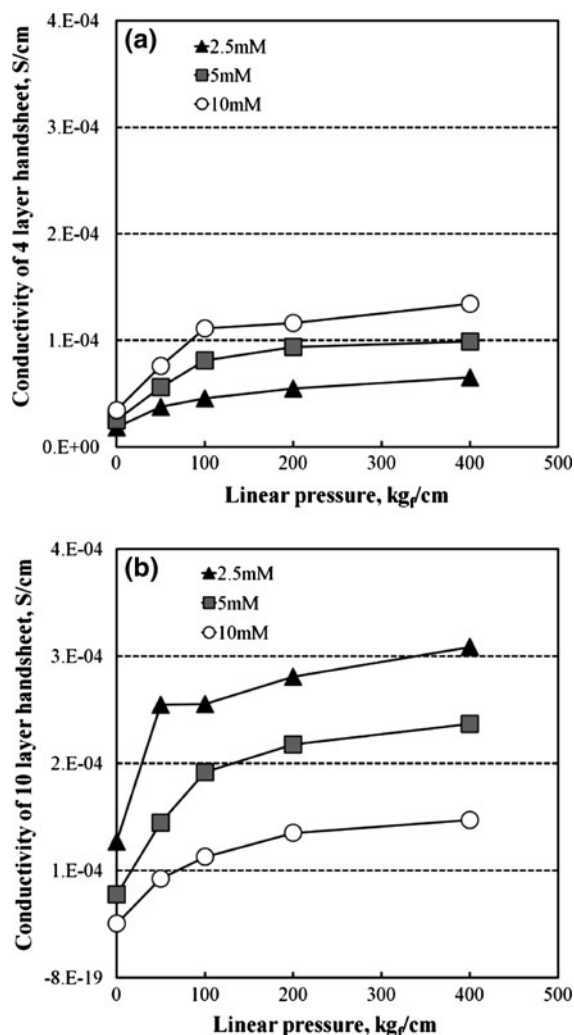
became dense due to the increased fiber bonding. Accordingly, the adsorption of the conductive polymer and the electrical contact can be increased. The difference in the conductivity between our study and the work of Wistrand et al. (2007) may have been caused by the type of cationic polyelectrolyte used. The PEI may have formed a denser multilayer with the PEDOT:PSS than that formed by the PAH such that contact of the PEDOT:PSS was greater in the PEI and PEDOT:PSS multilayer. Consequently, the conductivity of conductive paper can be further improved by creating a homogeneous structure and increasing the degree of fiber contact through a beating treatment.

When hydrophobic materials are adsorbed on fibers, the paper strength becomes weak because of interrupted hydrogen bonding between fibers. Since PEDOT is a hydrophobic material, we were concerned about loss of paper strength. Nevertheless, the strength of the paper increased compared to that of the control (Fig. 8). The tensile index of 10 layer paper increased by about 25 % at 5 and 10 mM salt concentrations. Although the hydrophobic PEDOT:PSS interrupted hydrogen bonds between fibers, LbL multilayering treatment can overcome it by creating new hydrogen bonds with the PEI and increasing conformability of fibers (Wågberg et al. 2002). Consequently, conductive paper can be prepared without loss of strength.

Effect of densification on conductivity of paper

The increase in fiber contact was considered to improve the conductivity of the conductive paper. It was unclear whether an increasing degree of contact between the treated fibers enables the PEDOT:PSS of the outermost layer on the fibers to have more contact. The degree of contact between fibers in a paper can be controlled through densification such as refining of fibers, increasing fine content, wet pressing, and calendering. In the present work, the densification of paper was performed by calendering, which is a process of pressing with a dry sheet at controlled temperature and pressure. Density of uncalendered paper was about 0.5 g/cm^3. The density of calendered paper ranged from 0.8 to 1.1 g/cm^3 with increasing linear pressure. There were more pores in the uncalendered paper sheet than in the calendered paper sheet. This is supported by the surface images of paper sheets. The surface images of the uncalendered and calendered sheets are shown in Fig. 9. The uncalendered sheet had numerous pores between fibers (Fig. 9a), while there were few pores between fibers at the surface of the calendered sheets (Fig. 9b). This means the fibers had more contact with each other in the case of the calendered paper sheet. Figure 10 shows the conductivity of the paper with calendering. The conductivity of both 4 layer and 10 layer paper increased with the increase in linear pressure up to 100 kg$_f$/cm and reached a plateau after 100 kg$_f$/cm. It is likely that the increase in inter-contacts of the PEDOT:PSS between fibers by calendering greatly improved electron transfer through the fibers, resulting

in the improvement in conductivity of paper. This improved the conductivity of the calendered paper. In addition, the conductivity of the calendered 4 layer paper was similar to the conductivity of the uncalendered 10 layer paper, even though the 4 layer paper had less PEDOT:PSS than the 10 layer paper. This suggests that the increased degree of contact between PEDOT:PSS was more important to increase the conductivity of the paper than the increased adsorption of PEDOT:PSS.

The conductive paper in this study did not have sufficient conductivity as a conductive material for practical applications. However, further improvement of the conductivity would be possible with an LbL process in a controlled salt concentration and densification of the paper by, for instance, beating the fibers, adding fines, and calendering.

Conclusions

The conductive paper was prepared with fibers treated by LbL multilayering of the PEI and PEDOT:PSS. Successive adsorption of the PEI and PEDOT:PSS was confirmed by changes in zeta-potential of the treated fibers and FE-SEM images of the papers. The conductivity of the paper ranged from 10^{-5} to 10^{-4} S/cm and increased up to 10^{10} times compared to typical cellulose paper. Furthermore, the conductive paper had no loss of strength.

The multilayer structure was changed by controlling the salt concentration during LbL multilayering and the paper was densified by calendering to improve the conductivity of the paper. The increased adsorption of the PEDOT:PSS did not improve the conductivity of the paper above a certain amount, which is the amount of PEDOT:PSS needed for conductivity. Paper conductivity improved with increased electrical contact by forming a compact structure in the multilayer at low salt concentration and densifying the paper by calendering. A compact multilayer affects the intra-contact between the PEDOT:PSS in the multilayer, and densification enables more inter-contact between the PEDOT:PSS at the outside of the multilayer. Consequently, the increased contact between PEDOT:PSS was the main factor improving the electrical conductivity of the paper. It would be helpful to produce conductive fibers and paper with better conductivity.

References

Agarwal M, Lvov Y, Varahramyan K (2006) Conductive wood microfibres for smart paper through layer-by-layer nanocoating. Nanotechnology 17(21):5319–5325. doi:10.1088/0957-4484/17/21/006

Agarwal M, Xing Q, Shim BS, Kotov N, Varahramyan K, Lvov Y (2009) Conductive paper from lignocellulose wood microfibers coated with a nanocomposite of carbon nanotubes and conductive polymers. Nanotechnology 20(21):215602. doi:10.1088/0957-4484/20/21/215602 (Artn 215602)

Decher G, Hong JD (1991) Buildup of ultrathin multilayer films by a self-assembly process.1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces. Makromol Chem Macromol Symp 46:321–327

Ebrahim SM, Kashyout AB, Soliman MM (2007) Electrical and structural properties of polyaniline/cellulose triacetate blend films. J Polym Res 14(5):423–429. doi:10.1007/s10965-007-9125-7

Enarsson LE, Wågberg L (2008) Adsorption kinetics of cationic polyelectrolytes studied with stagnation point adsorption reflectometry and quartz crystal microgravimetry. Langmuir 24(14):7329–7337. doi:10.1021/La800198e

Fortunato E, Correia N, Barquinha P, Pereira L, Goncalves G, Martins R (2008) High-performance flexible hybrid field-effect transistors based on cellulose fiber paper. IEEE Electron Device Lett 29(9):988–990. doi:10.1109/Led.2008.2001549

Höök F, Rodahl M, Brzezinski P, Kasemo B (1998) Energy dissipation kinetics for protein and antibody-antigen adsorption under shear oscillation on a quartz crystal microbalance. Langmuir 14(4):729–734

Hu WL, Chen SY, Yang ZH, Liu LT, Wang HP (2011) Flexible electrically conductive nanocomposite membrane based on bacterial cellulose and polyaniline. J Phys Chem B 115(26):8453–8457. doi:10.1021/Jp204422v

Jung R, Kim HS, Kim Y, Kwon SM, Lee HS, In HJ (2008) Electrically conductive transparent papers using multiwalled carbon nanotubes. J Polym Sci Pol Phys 46(12):1235–1242. doi:10.1002/Polb.21457

Kontturi E, Thune PC, Niemantsverdriet JW (2003) Novel method for preparing cellulose model surfaces by spin coating. Polymer 44(13):3621–3625. doi:10.1016/S0032-3861(03)00283-0

Lang U, Muller E, Naujoks N, Dual J (2009) Microscopical Investigations of PEDOT:PSS thin films. Adv Funct Mater 19(8):1215–1220. doi:10.1002/adfm.200801258

Lingström R, Wågberg L, Larsson PT (2006) Formation of polyelectrolyte multilayers on fibres: influence on wettability and fibre/fibre interaction. J Colloid Interf Sci 296(2):396–408. doi:10.1016/j.jcis.2005.09.017

Lingström R, Notley SM, Wågberg L (2007) Wettability changes in the formation of polymeric multilayers on cellulose fibres and their influence on wet adhesion. J Colloid Interf Sci 314(1):1–9. doi:10.1016/j.jcis.2007.04.046

Liu XD, Nishi N, Tokura S, Sakairi N (2001) Chitosan coated cotton fiber: preparation and physical properties. Carbohydr Polym 44(3):233–238

Lundin M, Solaqa F, Thormann E, Macakova L, Blomberg E (2011) Layer-by-layer assemblies of chitosan and heparin: effect of solution ionic strength and pH. Langmuir 27(12):7537–7548. doi:10.1021/La200441u

Martins R, Ferreira I, Fortunato E (2011) Electronics with and on paper. Phys Status Solid R 5(9):332–335. doi:10.1002/pssr.201105247

Mičušík M, Omastová M, Prokeš J, Krupa I (2006) Mechanical and electrical properties of composites based on thermoplastic matrices and conductive cellulose fibers. J Appl Polym Sci 101(1):133–142. doi:10.1002/App.23041

Murphy EJ (1960a) The dependence of the conductivity of cellulose, silk and wool on their water content. J Phys Chem Solids 16(1–2):115–122

Murphy EJ (1960b) The temperature dependence of the conductivity of dry cellulose. J Phys Chem Solids 15(1–2):66–71

Notley SM, Eriksson M, Wågberg L (2005) Visco-elastic and adhesive properties of adsorbed polyelectrolyte multilayers determined in situ with QCM-D and AFM measurements. J Colloid Interf Sci 292(1):29–37. doi:10.1016/j.jcis.2005.05.057

Nyström G, Mihranyan A, Razaq A, Lindström T, Nyholm L, Stromme M (2010) A nanocellulose polypyrrole composite based on microfibrillated cellulose from wood. J Phys Chem B 114(12):4178–4182. doi:10.1021/Jp911272m

Okamoto Y, Kanda K, Kishiwada S, Fujiwara T (2004) Determination of phosphorous and sulfur in environmental samples by electrothermal vaporization inductively coupled plasma atomic emission spectrometry. Appl Spectrosc 58(1):105–110

Peng CQ, Thio YS, Gerhardt RA (2008) Conductive paper fabricated by layer-by-layer assembly of polyelectrolytes and ITO nanoparticles. Nanotechnology 19(50):505603. doi:10.1088/0957-4484/19/50/505603 (Artn 505603)

Pushparaj VL, Shaijumon MM, Kumar A, Murugesan S, Ci L, Vajtai R, Linhardt RJ, Nalamasu O, Ajayan PM (2007) Flexible energy storage devices based on nanocomposite paper. Proc Natl Acad Sci USA 104(34):13574–13577

Ramos JJI, Llarena I, Moya SE (2011) Unusual collapse of highly hydrated polyelectrolyte multilayers with the ionic strength. J Polym Sci Pol Chem 49(11):2346–2352. doi:10.1002/Pola.24662

Russler A, Sakakibara K, Rosenau T (2011) Cellulose as matrix component of conducting films. Cellulose 18(4):937–944. doi:10.1007/s10570-011-9555-6

Ryu J, Youn HJ, Chin SM, Lee S (2011) Effect of pH and conductivity in weak polyelectrolytes multilayering on paper properties. Nord Pulp Pap Res J 26(4):410–414

Unander T, Nilsson HE (2009) Characterization of printed moisture sensors in packaging surveillance applications. IEEE Sens J 9(8):922–928. doi:10.1109/Jsen.2009.2024866

Wågberg L, Forsberg S, Johansson A, Juntti P (2002) Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I: modification of paper strength. J Pulp Pap Sci 28(7):222–228

Wennrich R, Mroczek A, Dittrich K, Werner G (1995) Determination of nonmetals using ICP-AES-techniques. Fresenius J Anal Chem 352(5):461–469

Wistrand I, Lingström R, Wågberg L (2007) Preparation of electrically conducting cellulose fibres utilizing polyelectrolyte multilayers of poly(3,4-ethylenedioxythiophene): poly(styrene sulphonate) and poly(allyl amine). Eur Polym J 43(10):4075–4091. doi:10.1016/j.eurpolymj.2007.03.053

Zheng ZG, McDonald J, Khillan R, Su Y, Shutava T, Grozdits G, Lvov YM (2006) Layer-by-layer nanocoating of lignocellulose fibers for enhanced paper properties. J Nanosci Nanotechnol 6(3):624–632. doi:10.1166/Jnn.2006.081