

Electroconductive Paper Prepared by Coating with Blends of Poly(3,4-ethylenedioxythiophene)/Poly(4-styrenesulfonate) and Organic Solvents

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Received 13 October 2009; accepted 5 February 2010

DOI 10.1002/app.32250

Published online 12 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Electroconductive papers were produced by coating commercial base papers with blends of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT:PSS) and organic solvents. The bulk conductivities of the coated papers were measured using a four-probe technique. One-sided and two-sided coating gave comparable conductivity levels. The presence of sorbitol and isopropanol in the PEDOT:PSS blends did not enhance the bulk conductivity of the coated paper, and with increasing concentrations of these solvents, the conductivity decreased due to dilution of the conducting component. Samples coated with PEDOT:PSS blends containing *N*-methylpyrrolidone (NMP) or dimethyl sulfoxide (DMSO) exhibited a higher conductivity than those coated with pure PEDOT:PSS because of their plasticizing effect and conformational changes of PEDOT molecules

indicated by the red shift and disappearance of the shoulder peak at about 1442 cm^{-1} in the Raman spectra of the coated samples. EDS imaging showed that PEDOT:PSS is distributed throughout the thickness direction of the paper. Contact angle measurements were made to monitor the hydrophilicity of the paper surface and total sulfur analysis was used to determine the amount of PEDOT:PSS deposited onto the paper. The tensile strength of all the paper samples increased slightly after treatment. Thus, it is demonstrated that enhanced bulk conductivity in the order of 10^{-3} S/cm can be achieved by using organic conductive materials and surface treatment techniques. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3524–3532, 2010

Key words: coatings; conducting polymer; Raman spectroscopy; PEDOT:PSS; fiber

INTRODUCTION

There is a growing interest in the development of conducting papers because of possible new applications. Many applications, such as interactive wallpapers, sensors, and other electronic devices have been proposed and are starting to gain entries into the market. The realization of electronic paper will open the way to robust, light-weight, low power-consuming matrix displays that can be manufactured on thin flexible carriers and will complement cellulose-based paper as a medium for information distribution.¹ Paper as a renewable source is becoming an alternative substrate for flexible electronics. The abundance of wood-based paper and its cost-effective production are among the many advantages of paper over plastic substrates and the porosity of paper offers an added versatility over plastic films.

Conducting polymers have been deposited on the surface of coated papers, and commercial products are available in the market, for example, Orgacon by Agfa.² This is produced through screen, gravure, flexographic, inkjet printing, and even through the spin coating of conducting polymer. Various substrates are being used including polycarbonate, polyethylene, paper, or thin film polyester laminates. The conducting polymer used is poly(3,4-ethylenedioxythiophene):poly(4-styrene sulfonate) (PEDOT:PSS) because it is water-soluble, environmentally stable, and exhibits relatively high conductivity.^{2,3} This product has demonstrated color-switching characteristics for displays and is being used in studies on flexible paper electronic device propagation.^{1,4} However, these coated papers exhibit only surface conductivity and not bulk conductivity. Recent attempts at making bulk-conductive paper have been reported using layer-by-layer coating of conducting polymer onto wood fibers,^{5–8} *in situ* polymerization,⁹ and the treatment of pulp fibers with metallized polyester¹⁰ and silver-plated carbon fibers¹¹ before forming hand-sheets. Papers published several decades ago had reported a surface-conductive paper with a surface resistivity of $30\ \Omega/\text{sq}$ using 72% graphite,¹² and a variety of patents have described conductive papers using chemical impregnations, such as poly(diallyldimethyl-

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Contract grant sponsors: National Graduate School of Materials Science (Sweden), Karlstad University Faculty (Sweden).

ammonium chloride),¹³ which is mainly used for anti-static applications.

This article describes the use of a conventional coating technique as a way to deposit a conducting polymer onto the fiber network. Coating formulations for paper traditionally have a high solids content containing pigment and other additives. However, blends of PEDOT:PSS and organic solvents that contain very low solids have been applied directly onto the paper surface in this study. The goal has been to produce a bulk-conductive paper for use as a substrate for electronics devices and to determine the effect of organic solvents and calendering on the bulk conductivity of the coated samples.

EXPERIMENTAL

Materials

Baytron[®] P from H.C. Starck GmbH, Germany was used. This conducting polymer is known as poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate) (PEDOT:PSS) with a particle size of about 80 nm, a solids content of 1.3% (w/w), a PEDOT to PSS ratio of 1 : 2.5, and a film conductivity of about 1 S/cm.^{3,14} It is composed of water-insoluble conducting PEDOT molecules surrounded by PSS molecules (see Fig. 1). Analytical grades of sorbitol, dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and isopropanol were added to the polymer dispersion as conductivity enhancers. Commercial bleached base papers taken before chemical impregnation (150 g/m²) were provided by Munksjö Paper, Sweden. This type of base paper is normally used for electrical insulation. The thicknesses of the base and coated papers were measured using the STFI Thickness Tester M201 (Sweden). The tensile strength of the paper samples was performed using Instron 441 (USA), according to ISO 1924-2.

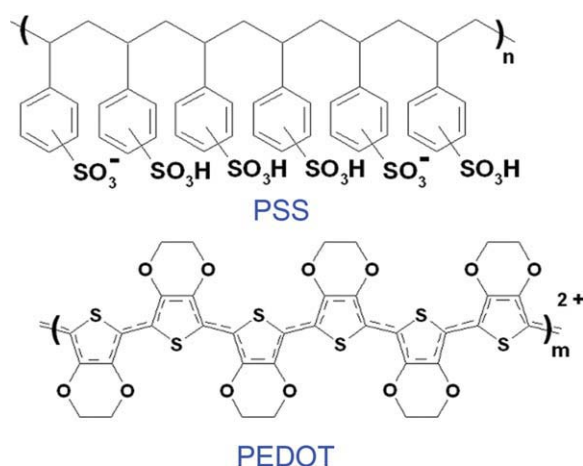


Figure 1 Chemical structure of PEDOT:PSS (Baytron[®] P). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Surface treatment

The base paper was placed on top of a blotter and coated using an RK Laboratory Control Coater (UK) with different blends of PEDOT:PSS. A rod with a wire diameter of 0.08 mm was used to ensure deep deposition of PEDOT:PSS blends into the paper. Coating was applied to both sides of the paper unless otherwise specified. The coated paper sample and the blotter were dried for 5 min at about 110°C using the STFI Infrared (IR) dryer (Sweden). Dried samples were stored at a temperature of 23°C and a relative humidity (RH) of 50%. The papers were calendered at different pressures (12, 50, and 100 bar) using DT Lab Calender Machine (Turku, Finland) at 23°C and 50% RH. The nip loads were 21, 87, and 174 kN/m. At least five samples were subjected to each treatment.

Total sulfur analysis

The amount of PEDOT:PSS deposited on the paper samples was determined using Schöniger Burning, according to SCAN-CM5799. Samples were burned in an oxygen atmosphere inside the heavy-walled Schöniger flask containing water and hydrogen peroxide producing sulfate. The signal was analyzed using ion chromatography at StoraEnso Research, Karlstad, Sweden.

Electrical conductivity measurement

All the samples were preconditioned in a climate chamber (CTS, Sweden) at 23°C and 28% RH for 48 h before measurement of the conductivity. The bulk conductivity of the base paper (reference) was measured using a Broadband Dielectric Spectrometer (Novocontrol GmbH, Germany) inside the clean laboratory at a temperature of 21 ± 1°C and a RH of 45 ± 5%. The four-probe technique was used to measure the conductivity of the coated paper samples according to ASTM D4496-04¹⁵ inside the climate room at 23°C and 50% RH. This standard measurement was used for moderately conductive sheets. The instrument was calibrated using a sheet of known resistance. The coated paper samples were cut to 10 × 15 cm and placed in the measurement chamber. The outer two current electrodes were connected to one multimeter (Keithley 2000, USA), whereas the inner two potential electrodes were connected to another multimeter (Keithley 2000, USA). A bias of 200 V was applied to the sample. The voltage and current across the sample were read after 30 s. The bulk conductivity, σ_{DC} (S/cm) is calculated using the equation

$$\sigma_{DC} = \frac{c}{t} \left(\frac{I}{V} \right) \quad (1)$$

where c is the ratio of the distance between potential electrodes to the width of the paper, t is the thickness of the paper (cm), I is the current that passes through the sample (A), and V is the voltage across the potential electrodes (V). There were at least five samples per treatment with similar conductivities.

Raman spectroscopy

Raman spectroscopy was performed using a Raman-Station™ 400 Dispersive Raman Spectroscopy (Perkin Elmer, USA). A piece of the coated paper was cut to dimensions of 5×5 cm and put on the sample holder. An excitation wavelength of 785 nm and 25% laser power were used to prevent destruction of sample.

Scanning electron microscopy and energy-dispersive spectrometry

A cross section was prepared by vertically mounting a paper strip into the sample holder, pouring epoxy resin into the mold and allowing it to dry. The resin was removed by sequential grinding until the cross section of the sample was exposed. The sample was then coated with carbon before SEM. The SEM images were obtained from a JSM-6460 (JEOL, Japan) field emission scanning electron microscope operated at an accelerating voltage of 20 kV. Samples were examined with a secondary detector at two magnifications: $350\times$ and $750\times$. The same field of view was then scanned using an energy-dispersive X-ray spectrometer to acquire a set of X-ray maps for S, O, and C using 1 ms point acquisition for approximately one million counts.

Contact angle measurement

Contact angles were measured on both sides of the paper using a FTÅ 200 instrument (Portsmouth, VA). Deionized water was used as liquid. The droplet size was about 10 μL . All the measurements were carried at 23°C and 50% RH. The angle obtained was the apparent contact angle as a function of time. No correction was made for any absorption effect.

RESULTS AND DISCUSSION

Bulk conductivity

Figure 2 shows the bulk conductivity of the paper samples coated with PEDOT:PSS and various organic solvents measured according to ASTM 4496-04. After one-sided coating with PEDOT:PSS, the bulk conductivity of the paper was significantly increased from 1×10^{-12} S/cm to about 1.5×10^{-3} S/cm. This implies that the surface treatment of base paper with a PEDOT:PSS dispersion achieves

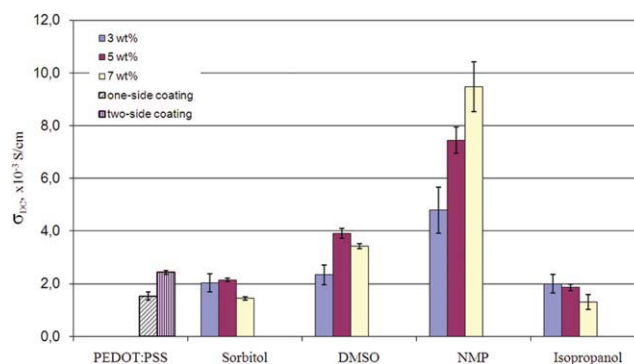


Figure 2 Bulk conductivity of paper coated with various blends of PEDOT:PSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

a much higher conductivity than treatment of pulp fibers before forming, as reported by some studies.⁵⁻⁸ Coating the paper on both sides leads to a further small increase in the bulk conductivity. This increase is small because only a few PEDOT networks are added in the bulk of the paper when both sides of the paper are coated instead of only one side.

Figure 3(a) shows that after one-sided coating, the PEDOT:PSS penetrates to the other side of the paper but that there are still some unfilled portions. After coating the other side [see Fig. 3(b)], the remaining few vacancies are filled up.

The amount of PEDOT:PSS deposited in the fiber network was determined indirectly by assessing the total sulfur content of the coated paper samples. PEDOT:PSS molecules contain sulfur whereas the base paper exhibits no detectable amount of sulfur. Other additives contained no sulfur except for the blend containing DMSO. Table I shows the total sulfur amount in the paper samples coated with various blends of PEDOT:PSS and organic solvents. The different amounts of sulfur observed in the one-sided and two-sided coated papers with pure PEDOT:PSS confirm that the slightly higher conductivity of the two-side coating is due to a greater amount PEDOT:PSS deposited in the network. The coated paper sample containing NMP or isopropanol showed almost the same amount of sulfur even when the concentration of NMP or isopropanol was increased from 3 wt % to 7 wt %.

The total sulfur content of the PEDOT:PSS-DMSO coated samples can be used to estimate the residual amounts of solvent in the coated paper. Assuming that the average sulfur content attributed to the PEDOT:PSS is 2.3 g/kg of paper, the estimated residual amount of DMSO (solvent) is between 4.87 and 13.89 g/kg. The lower sulfur content in the case of the 7 wt % DMSO is due to the lower deposition of conducting polymer blends upon rod coating. An increase in the amount of DMSO (at 7%) may

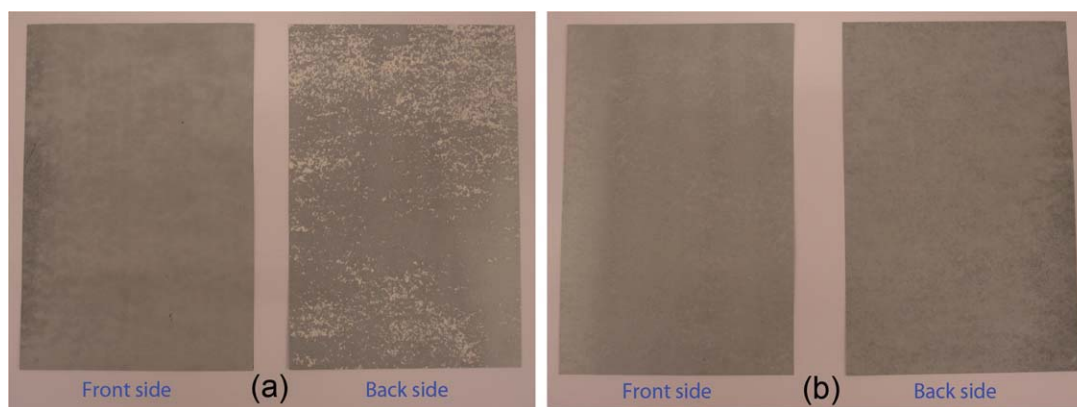


Figure 3 Paper samples coated with pure PEDOT:PSS dispersion: (a) one-sided coating, and (b) two-sided coating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decrease the penetration rate of PEDOT:PSS-DMSO blends into the paper.

In Figure 2, the paper coated with a blend containing NMP exhibits the highest conductivity followed by the blend with DMSO. As the concentration of NMP in the bulk liquid increased, the conductivity of the coated paper also increased but blends with DMSO exhibited a maximum value at 5 wt % DMSO in the bulk. On the other hand, the addition of sorbitol or isopropanol showed no enhancement of the conductivity and increasing their amounts decreased the conductivity. The mechanism of how organic solvents affect the conductivity of a PEDOT:PSS film has been debated by researchers in the field of organic electronics. To the authors' knowledge, there are four reported mechanisms of bulk conductivity enhancement; a plasticizing effect,^{16,17} a screening effect,^{18,19} the possible washing out of PSS-ions,²⁰ and a conformational change.^{21,22} The plasticizing effect suggests that secondary dopants such as high boiling polyalcohols

serve as plasticizers, which facilitate the reorientation of the PEDOT:PSS chains at high temperature to form better connections of conducting PEDOT chains.^{16,17} The screening effect suggests that there is a reduction in Coulombic interaction between positively charged PEDOT and negatively charged PSS dopant by residual polar solvents with high dielectric constants.^{18,19} PSS-chains could possibly be washed out from the surface of the PEDOT:PSS film during the film-forming process so that a thin film of high PEDOT concentration is formed on the surface of the film.²⁰ Lastly, the PEDOT molecule may undergo chemical structure transformation from a benzoid to a quinoid resonant structure which has a higher charge-carrier mobility.^{21,22} Organic solvents with two or more polar groups may induce a conformational change. The driving force for this conformational change is the formation of a hydrogen bond of one polar group to a sulfonate or sulfonic acid group, whereas another polar group is very close to the PEDOT chain, which leads to an interaction between the dipole of this polar group and the dipole moment or the positive charge on the PEDOT. The increase in the charge-carrier mobility due to the interaction of the secondary dopant and PEDOT:PSS should be a reason for an enhanced conductivity regardless of the mechanism of polymer-organic solvent interaction.^{21,22} However, how these two species interact, especially in a heterogeneous system, is still unclear.

The determination of the conduction and conductivity enhancement mechanism of PEDOT:PSS deposited in the fiber networks is rather challenging. Figure 4 shows cross section EDS images of the PEDOT:PSS-coated paper sample at two magnifications: 350 \times and 700 \times . The blue color, which is highly visible at 750 \times magnification is due to the sulfur signal, which can be attributed to PEDOT:PSS [Fig. 4(b)] as the base paper contains no traceable

TABLE I
Total Sulfur Content of Paper Samples Coated with Various PEDOT:PSS Blends

Paper Samples	Sulfur content (g/kg) ^a		
	3 wt %	5 wt %	7 wt %
PEDOT:PSS-DMSO	4.3	8.0	6.4
PEDOT:PSS-NMP	2.0	2.0	2.2
PEDOT:PSS-isopropanol	2.2	2.1	2.0 ^b
		One-sided coating	Two-sided coating
PEDOT:PSS		2.1	2.5

^a Results are given as dry substance.

^b Results have high spread, highest 2.7 and lowest 1.4 for four replicates. All the rest have a spread of less than 6% from the mean value.

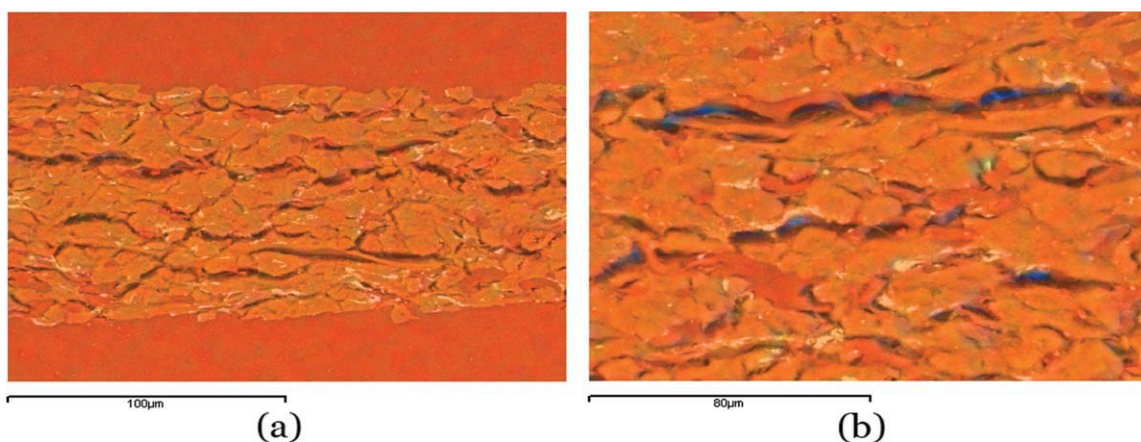


Figure 4 EDS map of the cross section of paper sample coated on both sides with PEDOT:PSS (dark red = epoxy resin, light orange = fiber, white = TiO_2 , blue = PEDOT:PSS): (a) at $350\times$ magnification, and (b) at $750\times$ magnification taken at the middle of the cross section. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

amount of sulfur. The PEDOT:PSS molecules are distributed throughout the thickness of the paper and not just on the surface, as Figure 4(b) is the image taken at the middle of the cross section. However, the conduction and conductivity enhancement mechanisms are yet to be explained.

In this study, the conductivity enhancement is probably because of the better connectivity of PEDOT grains along the fiber networks as a result of the plasticizing effect of the organic solvents. The organic solvents that enhanced the conductivity are those that are known to act as plasticizers. Both DMSO and NMP have high solvating power and are normally used as paint strippers to remove paint.^{23,24} The coated sample containing NMP exhibits the highest conductivity (see Fig. 2). NMP is known for its high solvent power, which when it is used in coating, yields a greater homogeneity and higher coverage of coating on the surface after curing at high temperature.²⁵ This may imply that NMP facilitates the better connectivity of PEDOT molecules along the fiber network and that this leads to an increase in bulk conductivity of the paper.

Chemical transformation of the PEDOT molecules may also occur as a result of the interaction between PEDOT:PSS and the organic solvents, that is, NMP and DMSO, transforming the benzoid to a quinoid structure. Coil and linear or expanded coil conformations are possible for PEDOT chains.^{21,26} Figure 5 shows the dominant PEDOT peak in the Raman spectrum between 1300 and 1500 cm^{-1} , which is assigned to the $\text{C}_\alpha=\text{C}_\beta$ symmetric stretching of the five-member thiophene ring on the PEDOT chains.^{26,27} There is an observed red shift of this Raman peak in the presence of organic solvents, such as NMP and DMSO from 1422 to 1414 cm^{-1} and the shoulder at about 1442 cm^{-1} disappears, which indicates the transformation of benzoid to

quinoid resonant structures.^{21,26} Both benzoid and quinoid structures are present in the pure PEDOT:PSS. In the presence of organic solvents, such as NMP or DMSO, the quinoid structure dominates, which implies a conformational transformation of the PEDOT chains from a coil to a linear or an expanded coil conformation along the fiber networks. The linear or expanded coil conformations have higher charge-carrier mobility and this phenomenon has also been observed in PEDOT:PSS film with ethylene glycol as a conductivity enhancer.²²

The screening effect is the least probable mechanism in this system because the dielectric constants of the solvents do not correlate with the observed conductivity. NMP has a lower dielectric constant

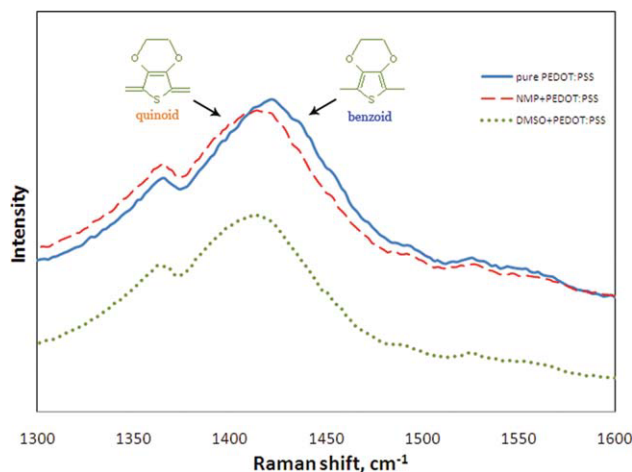


Figure 5 Dominant Raman spectra of paper samples coated with NMP/PEDOT:PSS, DMSO/PEDOT:PSS, and pure PEDOT:PSS at an excitation wavelength of 785 nm . Both NMP and DMSO have 7% (w/w) concentration. (Inset: benzoid and quinoid resonant structures).²¹ [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

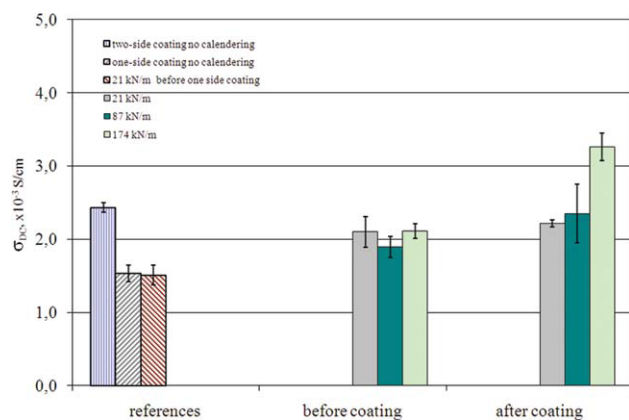


Figure 6 Bulk conductivity of paper calendered before and after coating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

than DMSO and sorbitol,^{24,28} but the paper with added NMP exhibits the highest conductivity. Furthermore, charge screening by organic solvents on the electrostatic interaction between PEDOT and PSS may not be significant due to the presence of charged functional groups within the nonhomogeneous cellulosic network. Washing out of PSS⁻ chains may happen with or without the solvent because of the presence of space charges and permanent polar groups in the network that may interact with PSS. A number of theoretical studies dealing with the behavior of hydroxyl groups in cellulose in the presence of plasticizer or water have been reported,^{29–31} but no mechanism for the interaction of cellulosic material and conducting polymer has been proposed. In the present study, a plasticizing effect and a conformational change of the PEDOT chains are the most probable mechanisms for the conductivity enhancement by NMP and DMSO on coated paper, which sorbitol and isopropanol do not exhibit.

Another factor that may affect the conductivity of coated paper is calendering. In paper production,

the purpose of calendering is to modify the surface characteristics, that is, gloss, smoothness, density, brightness, and opacity.³² Earlier investigations have claimed that calendering improves the conductivity of paper.¹² In Figure 6, only the coated paper that was subjected to a line load of 174 kN/m exhibited enhanced conductivity, whereas the others showed a conductivity comparable to that of the uncalendered samples. Applying a certain pressure in the rolling nip reduces the paper thickness considerably, thereby decreasing the distance between the PEDOT chains within the paper network. Subjecting the coated paper to calendering loads of 21 and 87 kN/m did not however lead to any significant increase in the conductivity. It is possible that the coated paper recovers to its original thickness after calendering or that the collapsed fibers hinder the pathways for electron transfer. All the one-sided coatings (no calendering or calendering before coating) exhibited similar behavior regarding the conductivity. Calendering the paper before coating does not have any significant effect because the paper returns to its original thickness upon coating. A PEDOT:PSS dispersion consists mostly of water,^{3,14} which disrupts the fiber bonds. In Figure 7, it appears that calendering the paper before the one-sided coating reduces the PEDOT:PSS penetration as indicated by the color variation on the rear-side image. However, the measured bulk conductivities for the two samples were similar. This implies that the distribution of PEDOT molecules in the bulk fiber network rather than on the surface determines the conductivity of the coated paper.

Contact angle measurement

The wetting and hydrophobicity of the paper surfaces after different treatments was investigated by measuring the contact angle of water on the surface. In principle, a liquid wets a surface only if its surface tension is lower than that of the substrate.

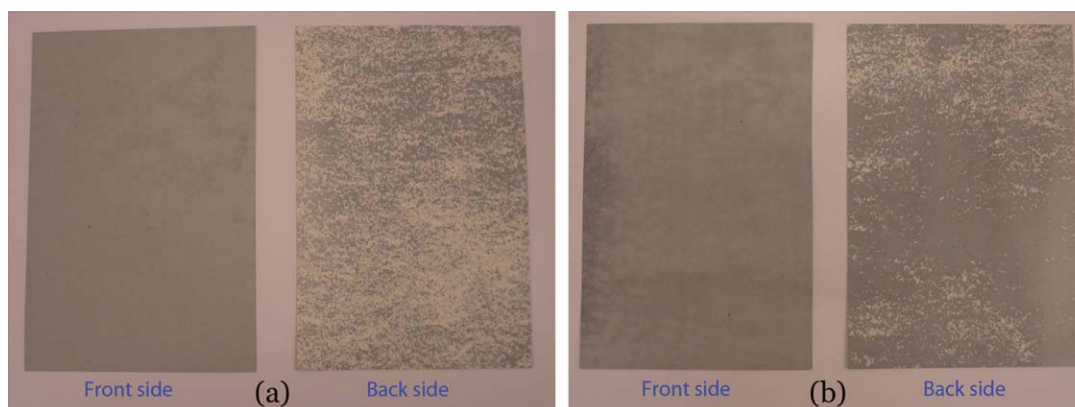


Figure 7 Front and rear-side images of paper samples (a) calendered and one-side coated, and (b) one-side coated without calendering. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

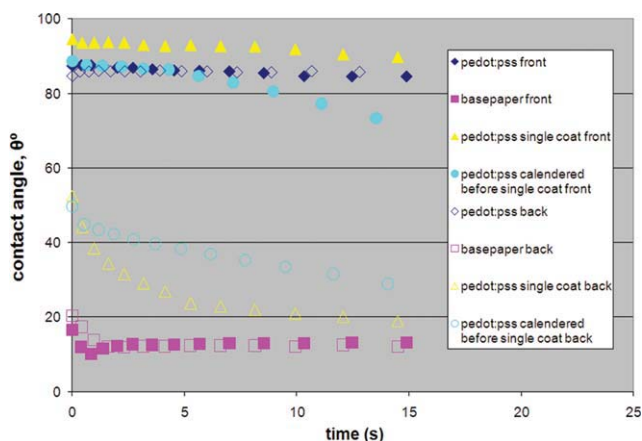


Figure 8 Apparent contact angle of water as a function of time on uncoated and PEDOT:PSS-coated paper samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8 shows the apparent contact angle as a function of time for both sides of all the paper samples. Both sides of the base paper exhibited hydrophilicity and the water was easily absorbed.

The samples coated with pure PEDOT:PSS on both sides exhibited hydrophobicity on both sides, whereas single-side coated samples exhibited hydrophobicity only on the coated side (front). This hydrophobicity was not stable since the contact angle decreased with time. A pure PEDOT:PSS coating thus converts the hydrophilic surface to a hydrophobic surface. Previous studies of water contact angles on PEDOT:PSS film deposited on an indium tin oxide (ITO) substrate reported a decrease in the contact angle from 85° (ITO surface) to 20° (PEDOT:PSS film).³³ In the present investigation, the opposite trend was observed, that is, the contact angle increased from $\sim 10^\circ$ to $\sim 90^\circ$, as shown in Figure 8.

As the paper is a rough and porous material, contact angle data are sometimes difficult to interpret. Both surface roughness and hydrophobicity affect the contact angle. An increase in the hydrophobicity of the surface leads to an increase in the contact angle of water on the coated sample. The present results may be due to an increase in the ratio of PEDOT to PSS on the surface of the paper rendering the surface more hydrophobic, as PEDOT molecules do not bind with water. This implies that PSS preferentially stays closer to the cellulosic fibers, whereas PEDOT stays on the outermost surface. A hydrophobic surface can be created by converting the outermost layer, such as a polyelectrolyte, into uncharged molecules.³⁴ In this respect, the contact angle of the coated paper samples agrees with the earlier suggestion that there is an increase in water-insoluble PEDOT on the outermost surface of the paper, as indicated by the X-ray photoelectron spectroscopy analysis on PEDOT:PSS-coated paper.³⁵ Micro-roughness and macro-roughness may also affect the contact angle measurements but this has not been quantified in this study. Calendering the base paper before coating neither had significant effect on the contact angle of water nor did the presence of organic solvents on the coating affect the apparent contact angle, except in the case of the sample containing NMP (see Fig. 9). The sample that contained 7 wt % NMP exhibited a contact angle, which decreased with time and this sample exhibited the highest conductivity (Fig. 2). As the fiber network is porous, coating with NMP may render better coverage of the fibers with PEDOT:PSS along the bulk structure and not merely on the surface of the paper. A slight spreading and absorption were observed on this sample [Fig. 9(b)] whereas the sample coated with pure PEDOT:PSS exhibited no spreading or

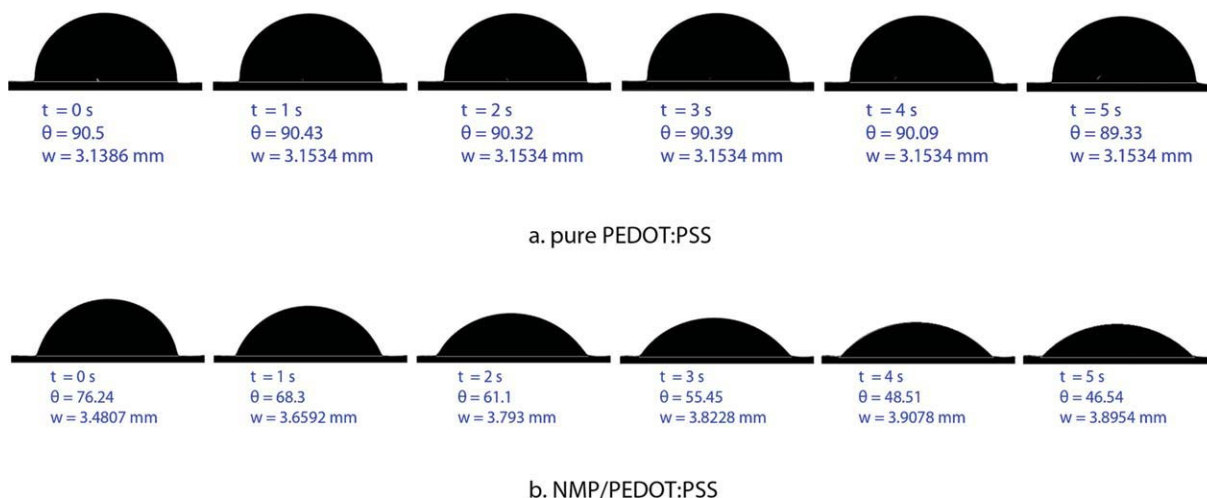


Figure 9 Apparent contact angles as a function of time for water on paper samples coated with (a) pure PEDOT:PSS, and (b) PEDOT:PSS and 7 wt % NMP [t = time (s), Θ = contact angle ($^\circ$), w = base diameter (mm)]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Machine Direction (MD) Tensile Strengths of All Paper samples

Paper Samples ^a	Tensile Strength (kN/m) ^c		
	3 wt %	5 wt %	7 wt %
Organic solvent blends			
PEDOT:PSS-sorbitol	9.0 ± 0.2	8.5 ± 0.2	8.9 ± 0.1
PEDOT:PSS-DMSO	8.9 ± 0.2	8.6 ± 0.3	8.4 ± 0.3
PEDOT:PSS-NMP	8.7 ± 0.2	8.4 ± 0.2	8.2 ± 0.2
PEDOT:PSS-isopropanol	9.0 ± 0.2	9.0 ± 0.3	8.3 ± 0.2
Calendering line load ^b	21 kN/m	87 kN/m	174 kN/m
Before coating	9.0 ± 0.2	9.3 ± 0.2	9.1 ± 0.2
After coating	9.2 ± 0.2	9.2 ± 0.2	9.2 ± 0.2
	One-sided coating		Two-sided coating
PEDOT:PSS	9.2 ± 0.2		9.0 ± 0.2
Base paper	8.0 ± 0.1		

^a All samples are coated on both sides except those described.

^b Pure PEDOT:PSS coating formulation.

^c Errors are calculated from standard error based on the number of samples prescribed by ISO 1924-02.

absorption at all [Fig. 9(a)]. The apparent contact angles on paper samples that were calendered either before or after coating were similar to those on the uncalendered coated samples.

Tensile strength

Table II shows the tensile strength values for all the paper samples. All the coated samples exhibited a higher MD (machine direction) tensile strength than the reference base paper. The tensile strength of paper usually decreases when the paper is wetted and redried because of a disruption of interfiber bonds. However, all the papers coated with PEDOT:PSS blends exhibited a slightly higher tensile strength. Some studies have reported a slight increase in tensile strength after treatment with a conductive polymer,⁵⁻⁷ whereas others have reported a decrease in tensile strength.^{9,11,12} In the present study, it is possible that the PEDOT:PSS acts as an adhesive between fibers, increasing the fiber-fiber bonds. PEDOT:PSS molecules may also form a supporting network that leads to an increase in strength. Although the presence of the residual amount of solvents may decrease the fiber-fiber bonds, it is not significantly observed in this study. It appears that the deposition of conducting polymer blends does not in itself significantly alter the paper strength.

CONCLUSIONS

Coating of PEDOT:PSS dispersion on base paper was an effective way of producing electroconductive paper with a conductivity of the order of 10^{-3} S/cm.

One-sided coating gave a high bulk conductivity. The effect of organic solvents on the bulk conductivity was investigated. Sorbitol and isopropanol did not enhance the conductivity. The blend containing NMP exhibited the highest conductivity enhancement followed by the blend containing DMSO. Four mechanisms of conduction enhancement have previously been proposed, including a screening effect, a plasticizing effect, a possible washing out of PSS^- , and a conformational change of PEDOT in the fiber network. Among these mechanisms, the plasticizing effects of NMP and DMSO and the conformational change of PEDOT molecules are the most probable mechanisms for conductivity enhancement in the present case. Calendering the paper had no significant effect on the conductivity except in the case of the coated sample subjected to 174 kN/m line load. Contact angles were measured to monitor the change in hydrophobicity of the coated paper samples. The tensile strength of all the coated samples was slightly higher than that of the base paper, and the presence of organic solvents in the PEDOT:PSS dispersion did not significantly affect the tensile strength. A conventional coating technique offers a practical approach to producing conductive paper by deposition of conducting material onto the paper without altering the strength of the paper.

The authors thank Peter Lilja (StoraEnso Research, Karlstad Sweden) for the total sulfur analysis, Hans-Olof Larsson (Munksjö Paper Ltd, Sweden) for supplying the base paper, Payman Tehrani (Linköping University, Sweden) for help with the impedance spectroscopy, Siv Skoglund of Korsnäs Frövi (Sweden) for help with the SEM/EDS analysis, Artur Bartkowiak (West Pomeranian University of Technology,

Poland) for allowing the first-named author to perform Raman spectroscopy in his laboratory, and Anthony Bristow for linguistic help and valuable comments.

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