Conductivity of Paper Containing Poly(3,4-ethylenedioxythiophene)/Poly(4-styrenesulfonate) and Multiwall Carbon Nanotubes

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ABSTRACT: Multiwall carbon nanotubes (MWCNT) were added to a dispersion of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate)–dimethyl sulfoxide (DMSO) at various dosage levels (0.1, 0.3, 0.5 wt %). The mixture was characterized in terms of its rheological behavior, and a difference was observed between ultrasonicated and nonultrasonicated mixtures. All the dispersions exhibited shear thinning behavior. Ultrasonication helped to minimize the aggregation of nanotubes in the dispersion. Coating the dispersions onto a commercial base paper on both sides turned the paper into a moderately conductive material with a bulk conductivity level of 10^{-3} S/cm. The proposed equivalent circuits of the coated papers which were derived from the Nyquist plot of the Impedance Spectroscopy data consist of a resistor connected in parallel to a capacitor. Likewise, the Bode plot showed the behavior of the complex impedance and phase angle of the coated paper as a function of frequency. The I-V characteristic and the bulk conductivity values of the paper samples are reported. Scanning Electron Microscopy (SEM)—Energy dispersive spectroscopy showed the deposition of the conducting polymer in the fiber network. The tensile indices of all coated papers were slightly higher than that of the base paper. Apart from altering the conductive properties of the paper, opening the way to new uses of the paper, the equivalent circuit behavior of the modified paper allows for the development of other functions, such as sensors or energy storage. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: E34–E40, 2012

Key words: PEDOT:PSS; MWCNT; electroconductive paper; fiber network

INTRODUCTION

The deposition of conductive materials in the fiber network gives the paper electrical functionality. Electronic structures can be constructed on paper surfaces that are useful in electronic devices, such as electrochromic displays, electroluminescence, thin-film transistor, solar devices, etc. Likewise, the conductive paper may also be used as a sensor and energy storage device. Nowadays, a variety of conducting materials have been deposited on flexible surfaces to achieve electronic properties, which include carbon nanotubes,[1–3] conductive particles,[4] ionic compounds,[5] and conducting polymers.[6–15] The challenge, of course, is to optimize the process and to use green technology to minimize the environmental impact.

Paper, as a flexible substrate, offers attractive properties, such as renewability and low cost of production. In our previous papers, we deposited poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) or PEDOT : SS onto the fiber network by means of rod coating and studied the conductivity of the coated paper.[7,8] PEDOT:PSS is used as conducting polymer because it is water-soluble, highly stable in the p-doped state, with a relatively high conductivity, and environmentally stable.[16–18] In this study, the aim is to investigate the effect of adding multiwall carbon nanotubes (MWCNT) into the PEDOT:PSS dispersion on the rheology of the dispersion, its influence on the bulk electrical conductivity and strength of the coated paper sheets. Carbon nanotubes have remarkable electrical and mechanical properties which are excellent for electrical conducting composites.[19] This study also investigates the effect of ultrasonication in reducing the aggregation of MWCNT in the dispersion. Bulk conductivity obtained by three electrical characterization techniques (impedance spectroscopy, I-V curves, and four probe technique) are presented here.

EXPERIMENTAL

Materials

The conducting polymer Clevios PH 1000 was purchased from Clevios Gmbh, Germany. This conducting polymer is poly(3,4-ethylenedioxythiophene)/

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poly(4-styrene sulfonate) (PEDOT:PSS) with a particle size of about 80 nm, a solids content of 1.3% (w/w), and a PEDOT to PSS ratio of 1 : 2.5. It is composed of water-insoluble conducting PEDOT molecules surrounded by PSS molecules. Analytical grade dimethyl sulfoxide (DMSO) was added to the polymer dispersion as a conductivity enhancer. The multiwall carbon nanotubes (MWCNT) were purchased from Sigma-Aldrich (Germany) and had >90% carbon basis, O.D. × I.D. × L 10–15 nm × 2–6 nm × 0.1–10 μm. Commercial base papers (100 g/m^2) were provided by Nordic Pulp and Paper, Sweden. The thicknesses of the base and coated papers were measured using the STFI Thickness Tester M201 (Sweden). The tensile index of the paper samples was determined using a Zwick Z050 Material Tester (Zwick GmbH, Germany) according to ISO 1924-3. The amount of PEDOT:PSS/DMSO/MWCNT deposited on the paper samples was determined by the weight difference of the coated and base paper at 23°C and 50% RH.

Preparation of the coating dispersion

Various amounts of MWCNTs were added onto PEDOT:PSS dispersions containing 5 wt % DMSO. The resulting dispersions were subjected to ultrasonication at 35 kHz (Bandelin Sonorex RK 100H, Sigma Aldrich GmbH, Germany) for 30 minutes, and then stirred for another 30 minutes. Two trials were made.

Viscosity measurement

The viscosity of the PEDOT:PSS/DMSO/MWCNT suspensions was measured using an MCR 300 Rheometer (Physica Messtechnik GmbH, Germany). An amount of 5 mL of the suspension was poured into the vessel (CC 17) and a ramp log profile of shear rates from 0.1 to 1000 s^{-1} was chosen. The measurement interval was 30 s and the temperature was maintained at 23°C.

Laboratory coating

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. The coated paper sample and the blotter were dried for 5 minutes at about 110°C using the STFI Infra-Red (IR) dryer (Innventia, Sweden). Dried samples were stored at a temperature of 23°C and 50% relative humidity (RH).

I-V characteristics

The paper samples were cut into 0.5 × 1.0 cm^2 strips. Conductive epoxy resin was deposited on the surface near the edges of the paper and allowed to dry overnight inside the climate room (23°C and 50% RH). This was done to facilitate better contact between the measuring electrodes and the surface of the paper. The I-V characteristic was measured using two point probes connected to the Keithley 2636A System Sourcemeter and the data was acquired using LabView. The voltage sweep was from −0.5 to 0.5 V in steps of 0.05 V. The corresponding current values were recorded for all the paper samples at room temperature. At least five measurements were made per sample.

Four-probe technique

The four-probe technique was used to measure the conductivity of the coated paper samples according to ASTM D4496-04 inside the climate room at 23°C and 50% RH. This 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 two outer current electrodes were connected to one multimeter (Keithley 2000), while the two inner potential electrodes were connected to another multimeter (Keithley 2000). 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). At least five samples were tested per treatment with similar conductivities.

Impedance spectroscopy

The impedance behavior of the base and coated paper was measured using a Broadband Dielectric Spectrometer (Novocontrol Gmbh, Germany) inside the clean laboratory at a temperature of 21 ± 1°C and a relative humidity of 45 ± 5 %. Circular samples were cut with a diameter 2.5 cm and sandwiched between two circular gold electrodes in the measurement cell. The set-up was tightened to ensure better contact between electrodes and the

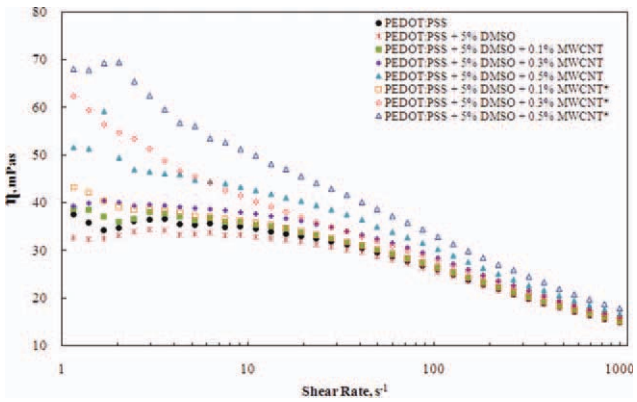

Figure 1 Viscosity as a function of shear rate for various dispersions of PEDOT:PSS. [Note: *: indicates ultrasonicated samples]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

paper sample. Bias voltages of 0.1, 1, 2 V were applied to the PEDOT:PSS-coated paper in the preliminary investigation. The impedance of the sample was measured from 0.1 to 10 MHz. For the subsequent measurements, a bias of 0.1 V was used. At least five measurements were made per sample.

Scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS)

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 with 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 750x magnification. 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.

RESULTS AND DISCUSSION

Rheological behavior

The rheological behavior of the different suspensions of PEDOT:PSS/DMSO and MWCNT dispersions is shown as a function of shear rate in Figure 1. All the samples exhibited a shear thinning behavior throughout the whole shear rate range. As the dosage of MWCNT increased, the viscosity of the suspension also increased. The samples exhibited higher viscosities in the lower shear rate region after ultrasonication, which implies that this treatment reduces the formation of aggregates. MWCNT tends to form aggregates in solution[20] which was observed as a problem when coating the dispersion onto the base paper. For a dispersion containing MWCNT, ultrasonication was therefore performed before laboratory coating.

Ultrasonic agitation is a physical method commonly used to separate agglomerates or bundles of MWCNT held together by Van der Waals forces.[20,21] The increase in viscosity of the suspension after ultrasonication suggests that a large amount of smaller MWCNT bundles or particles were present in the suspension. This was apparent in the suspension containing 0.5 wt % MWCNT. The increase in the number of smaller particles increased the particle-particle interaction and resulted in an increase in the resistance to flow. However, as the shear rate increased, this effect became less apparent suggesting that any particle-particle interactions were relatively weak and broken down at high shear rates. It is also possible to maintain the stability of the suspension of MWCNT by functionalizing the surface of the nanoparticles or by using surfactants that attach to the MWCNT.[20,22] In this study, however, ultrasonication was thought to be enough to disperse the MWCNT before coating the suspension onto the base paper.

Electrical characterizations

In this study, three electrical characterizations have been used: I-V curve, Four-probe technique, and impedance spectroscopy. The I-V curve simply shows the current behavior as the voltage is changed. This technique evaluates the material property (conductivity) simply by looking at the behavior of the curve. For Ohmic materials, the current is linearly dependent on the voltage. The greater the slope of the curve, the higher is the conductivity of the material. In Figure 2, the paper that exhibits the greatest slope is the sample containing 0.5 wt % MWCNT.

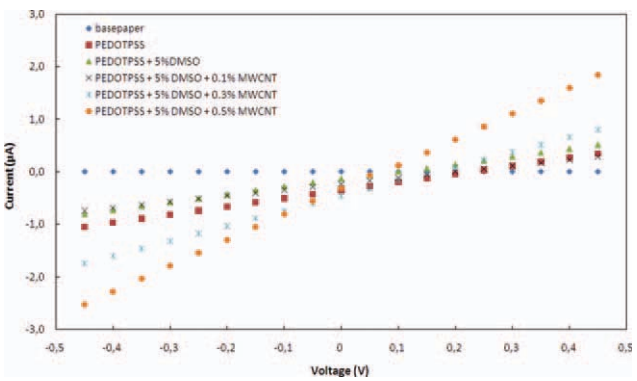

Figure 2 The I-V characteristics of the different paper samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Bulk Conductivities of Paper Samples Coated with Different Blends of PEDOT:PSS

Coated paper samples	Conductivity $\times 10^{-3}$ S/cm	Standard deviation
PEDOT:PSS	0.475	0.133
PEDOT:PSS + 5% DMSO	0.638	0.099
PEDOT:PSS + 5% DMSO + 0.1% MWCNT	0.500	0.021
PEDOT:PSS + 5% DMSO + 0.3% MWCNT	0.727	0.024
PEDOT:PSS + 5% DMSO + 0.5% MWCNT	1.133	0.081

The resistance decreased as the amount of MWCNT increased.

The four-probe technique calculates both the surface and bulk conductivities of the sheet. In previous papers, we used this technique as a way to evaluate the bulk conductivity of PEDOT:PSS-coated paper.[7,8] In this technique, a value of the bulk conductivity can be calculated from the current and voltage measurement and from the geometry of the set-up. In Table I, the addition of 5% DMSO and carbon nanotubes enhanced the conductivity of the coated paper. The coated paper containing 0.1 wt % MWCNT had a lower conductivity than the coated paper containing only PEDOT:PSS + 5 wt % DMSO. Increasing the dosage of MWCNT had a positive effect on the conductivity of the coated sheets.

Another technique that is often employed in characterizing conductive sheets is the Electrochemical Impedance Spectroscopy. It is a powerful technique for studying electrochemical systems and processes which is based on small perturbations of a electrochemical cell, e.g., applied voltage, with alternating signal of small magnitude that allows measurements at equilibrium or steady state.[23] From the impedance data, the imaginary part can be plotted versus the real part of the impedance. This plot is known as the Nyquist plot (Cole-Cole plot) or the complex plane and is shown in Figure 3. The inset graph shows the effect of the amplitude perturbation on the shape of the Nyquist plot. In this case, the higher amplitude perturbations (1.0 and 2.0 V) showed unsteady behavior. The amount of perturbation applied in the subsequent experiments was therefore 0.1 V. From the Nyquist plot, the network of electrical circuit elements known as equivalent circuits can be determined based on the shape of the plot. All the coated paper samples had equivalent circuits consisting of a contact resistance R_E in series with the capacitance C_{dl} connected in parallel to a resistor R_{CT} (see inset drawing). The values of R_E were between 110 and 150 Ω. The contact resistance values may be due to the roughness of the paper surface which affects the contact between the gold electrodes and the paper. This is minimized by applying an adequate compressive force to compress the paper.[24]

Among the coated paper samples, the sample containing 0.5 wt % MWCNT had the lowest bulk resistance, as can be seen from the distance of the line connecting the two x-intercept points, whereas the sample with pristine PEDOT:PSS had the highest bulk resistance. Figure 4 is the Bode diagram showing the logarithmic plot of the magnitude of the impedance and phase angle versus the logarithm of the frequency. This plot shows the behavior of the impedance throughout the frequency range which normally complements the Nyquist plot. It is apparent that the resistive behavior dominates for a wide range of frequency in the samples containing MWCNTs, while the capacitive behavior of samples containing pristine PEDOT:PSS starts to dominate at a frequency of 1000 Hz.

In all the electrical characterizations presented, increasing the amount of MWCNT added to the dispersion increased the conductivity of the coated paper. MWCNT has remarkable electronic properties that make it attractive for many applications.[19] The presence of DMSO also enhances the conductivity of

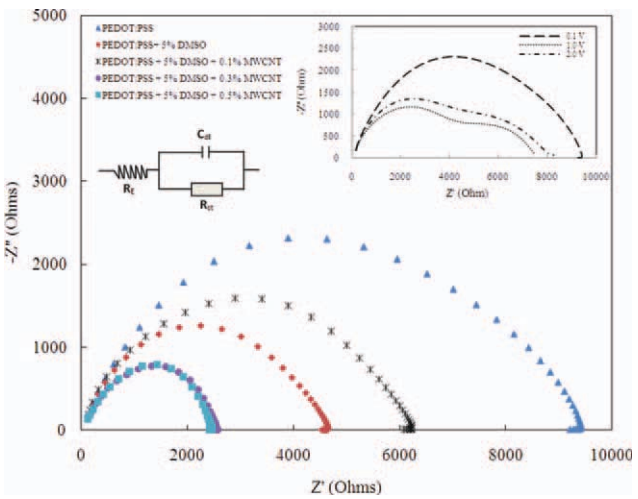

Figure 3 Nyquist representation of the impedance data of various coated papers at a perturbation voltage of 0.1 V [Insets: equivalent circuit drawing, and Nyquist plot of PEDOT:PSS-coated paper at different perturbation voltages]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

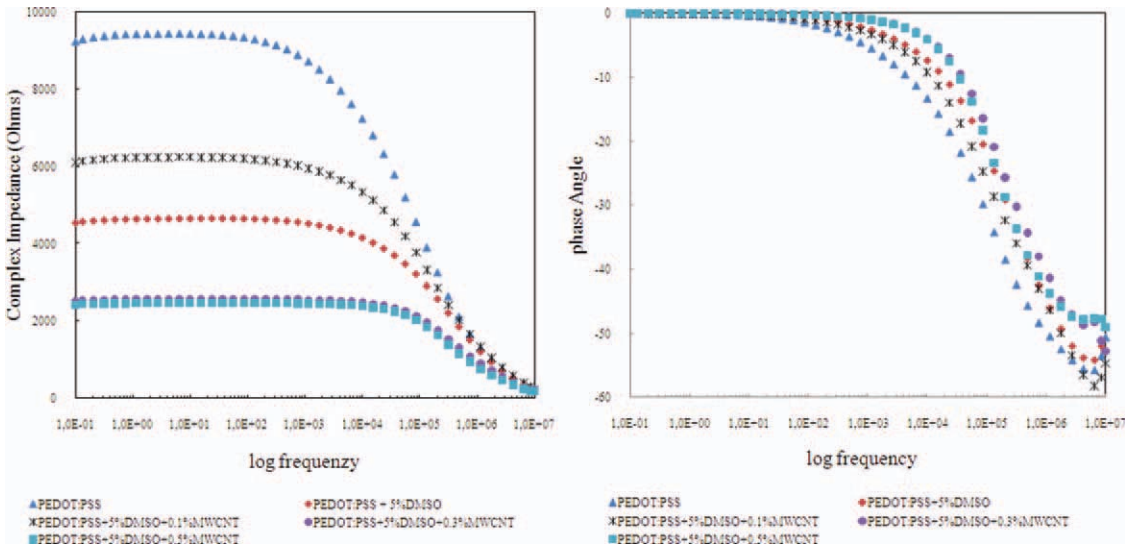

Figure 4 Bode plot showing the magnitude of the impedance and phase angle of all the coated paper samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the coated paper, where the mechanism of enhancement was discussed in our previous paper.[7,8]

SEM/EDS

Figure 5 shows the SEM/EDS maps of the cross section (left) and the surface (center) of the coated paper containing the PEDOT:PSS mixed with 5 wt % DMSO and with 0.1 wt % MWCNT. The conducting polymer was preferentially deposited on the fiber–fiber contact areas, similar to the results found in our previous studies where *N*-methylpyrrolidone (NMP) was added as conductivity enhancer.[7] This confirms that PEDOT:PSS is deposited onto the surface of the fiber. The lower sulfur intensity signal from the EDX analysis of the coated sample that

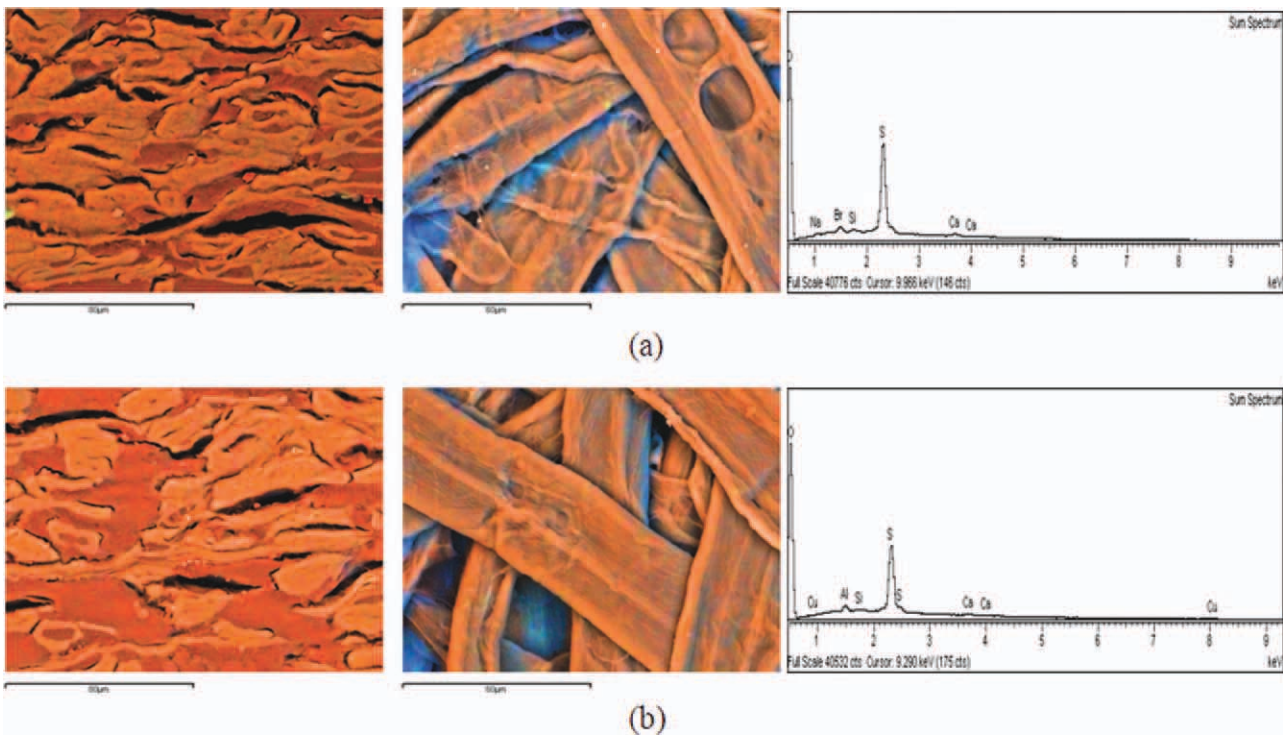

Figure 5 SEM/EDX images of the cross section (left), surface (center), and corresponding elemental EDX analysis of the coated paper containing (a) PEDOT:PSS blended with 5 wt% DMSO, and (b) PEDOT:PSS blended with 5 wt % DMSO and 0.1 wt % MWCNT [Note: the blue color is attributed to the sulfur signal from both PEDOT:PSS molecules and DMSO]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Tensile Index of Various Paper Samples

Paper sample	Tensile index kNm/kg
Base paper	62.88 ± 0.85
PEDOT:PSS	71.92 ± 0.23
PEDOT:PSS + 5%DMSO	69.47 ± 0.51
PEDOT:PSS + 5%DMSO + 0.1%MWCNT	66.44 ± 0.24
PEDOT:PSS + 5%DMSO + 0.3%MWCNT	69.87 ± 0.32
PEDOT:PSS + 5%DMSO + 0.5%MWCNT	73.12 ± 0.23

containing 0.1 wt % MWCNT [see Fig. 4(b), right] suggests that less conducting polymer is present on the surface of this paper sample than on the paper that contains PEDOT:PSS + 5 wt % DMSO. Despite this observation, the bulk conductivity of the PEDOT:PSS-coated paper was sufficiently high (see Table I).

Tensile index

Coating the commercial base paper with a dispersion of PEDOT:PSS having a low solids content wets the paper and may disrupt fiber–fiber bonds. This process is known to negatively affect the tensile strength of paper. The tensile strength is influenced by fiber strength, fiber length, and relative bonded area (RBA) according to the equation.[25]

$$\frac{1}{T} = \frac{9}{8Z} + \frac{3w_f}{\tau_b l_f RBA} \quad (2)$$

where Z is the zero span strength of paper (reflecting the fiber strength), RBA is the relative bonded area, w_f is the fiber width, l_f is the fiber length, and τ_b is the breaking stress of bonds (breaking force over area). The presence of PEDOT:PSS increases the paper strength as shown in Table II. This was observed in a previous paper where a different commercial base paper was used.[7] It is then inferred that PEDOT:PSS may positively affect the fiber strength and increase the RBA because it is deposited along the fiber lines and in fiber–fiber contact areas [see Fig. (5)]. It is suggested that PEDOT:PSS may form a support network increasing the tensile strength. The presence of DMSO, however, reduces this effect as is evident in the decrease in the tensile index. An increasing dosage of MWCNT improved the tensile index which could be due to a better effective load transfer from the fiber to the adsorbed MWCNTs, known as a reinforcement effect.[26]

CONCLUSIONS

The rheological behavior of the various PEDOT:PSS suspensions was investigated. All dispersions exhibited shear thinning behavior. It was found that ultrasonic agitation was useful in separating bundles of MWCNTs in the suspension. Three characterization techniques were used to describe the electrical behavior of the paper samples, which include I-V characterization, four-probe technique, and electrochemical impedance spectroscopy. All the techniques showed that the coated paper containing 0.5 wt % MWCNT had the highest conductivity. The SEM/EDX map confirmed that the PEDOT:PSS was preferentially deposited in the fiber-fiber contact regions. The tensile index of all the coated samples increased after treatment, which is a positive indication that the presence of PEDOT:PSS increased the tensile strength of the paper after drying. The increased dosage of MWCNT increased the tensile strength of the paper sheets.

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