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Conductive Nanocomposites Based on Cellulose Nanofibrils Coated with Polyaniline-DBSA Via *In Situ* Polymerization

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Summary: Cellulose nanofibrils (CNF) were extracted by acid hydrolysis from cotton microfibrils and nanocomposites with polyaniline doped with dodecyl benzenesulphonic acid (PANI-DBSA) were obtained by *in situ* polymerization of aniline onto CNF. The ratios between DBSA to aniline and aniline to oxidant were varied *in situ* and the nanocomposites characterized by four probe DC electrical conductivity, ultraviolet-visible-near infrared (UV-Vis - NIR) and Fourier-transform infrared (FTIR) spectroscopies and X-ray diffraction (XRD). FTIR and UV-Vis/NIR characterization confirmed the polymerization of PANI onto CNF surfaces. Electrical conductivity of about 10^{-1} S/cm was achieved for the composites; conductivity was mostly independent of DBSA/aniline (between 2 and 4) and aniline/oxidant (between 1 and 5) molar ratios. X-ray patterns of the samples showed crystalline peaks characteristic of cellulose I for CNF samples, and a mixture of both characteristic peaks of PANI and CNF for the nanocomposites. Field emission scanning electron microscopy (FESEM) characterization corroborated the abovementioned results showing that PANI coated the surface of the nanofibrils.

Keywords: cellulose nanofibrils; nanocomposite; polyaniline

Introduction

Among the intrinsically conductivity polymers (ICP), polyaniline (PANI) is the most studied and commercially used due to its good electrical conductivity, thermal stability, ease of synthesis and low production cost.[1] Owing to its good electrical conductivity, PANI can be used in applications such as electromagnetic shielding (EMI), rechargeable batteries, conductive adhesives and coatings, sensors, electrical and electrochemical devices.[2,3] However, poor infusibility and low solubility in organic solvents as well as poor mechanical properties limit the number of applications for PANI.[3,4] Solubility and infusibility, however, can be improved by using organic acids such as dodecylbenzene sulfonic acid (DBSA) and p-toluenesulphonic acid (PTSA) as dopants, while mechanical properties can be improved by mixing PANI with a polymeric host matrix, forming a composite.[4,5] There are many polymeric materials that can be used as supports for PANI. Among them, elastomers, plastics and cellulose have proved to be effective in blending with PANI.[6–8]

Cellulose is among the most abundant material in nature; its structure is composed of β-D-glucopyranose repeating units linked by (1–4)-glycosidic bonds and features low cost, high crystallinity and good mechanical properties.[9–12] Cellulose

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microfibers consist of ordered regions, nanocristals commonly referred to as whiskers, nanowhiskers or nanofibrils, linked by amorphous cellulose chains.[13] These nanocristals can be extracted by acid hydrolysis. When strong sulfuric acid is used, negatively charged sulfate groups are introduced[14] and consequently (due to the electrostatic effect) very stable aqueous suspensions are obtained. Cellulose nanofibrils have attracted attention as reinforcing agents in polymer nanocomposites[16,17] due to their high crystallinity, high elastic modulus[15] and greater strength than glass fibers (70 GPa). Naturally conductive nanofibrils have promise as polymer reinforcing agents because it is possible to combine reinforcement and conductivity with low electrical percolation threshold yet maintain the individual properties of the nanofibrils. The technical literature describes the preparation of cellulose-microfibrils coated with conducting polymers.[18–20] However, very few papers deal with cellulose nanofibrils (CNF) coated with polyaniline.[8,21]

In this work, cellulose nanofibrils coated with PANI were obtained by *in situ* polymerization of aniline in CNF suspension, using dodecylbenzenesulfonic acid (DBSA) and ammonium persulfate, respectively, as dopant and oxidant. DBSA can also act as a surfactant increasing the stability of CNF/PANI-DBSA suspensions - an important factor in polymer matrix dispersion. The nanocomposites produced were characterized by FTIR, XRD, FESEM, UV-Vis-NIR and four probe DC electrical conductivity.

Experimental Part

Materials

Analytical grade aniline was purchased from Sigma-Aldrich, distilled under vacuum and stored in a refrigerator before polymerizing. Ammonium peroxydisulfate (APS), dodecylbenzene sulfonic acid (DBSA) and sulfuric acid were purchased from Sigma-Aldrich and used as received. Cotton fibers with particle size of 50 μm (Sigmacell Cellulose type 50) were purchased from Sigma-Aldrich. Nanofibrils were dialyzed in Spectra/Por Dialysis Membranes with the following characteristics: membrane tube, MWCO: 12 to 14.000, 75 mm flat width, vol/length = 18mL/cm, length = 15mm.

Extraction of Cellulose Nanofibrils

Cellulose nanofibrils were extracted by acid hydrolysis according to the procedure described by Medeiros *et al.*[22] Briefly, microcrystalline cotton cellulose microfibers were immersed in a sulfuric acid solution (64%w/v) at 45°C using a ratio of microcrystalline cellulose to acid solution of 1:7.1 gmL^{-1}. The mixture was stirred vigorously for 60 minutes and then quenched in cold water (5 mass equivalents). The resulting dispersion was centrifuged at 10,000 rpm for 10 min at 10°C to separate nanofibrils from the acidic solution containing hydrolyzed amorphous cellulose chains. The centrifuged cake containing cellulose nanofibrils was dispersed in water and centrifuged again. This operation was performed three times and the final nanofibril content was dispersed in 250 mL deionized water followed by dialysis against water until reaching a constant pH.

Nanocomposite Preparation

Conductive cellulose nanofibrils were prepared by *in situ* polymerization of PANI onto nanofibril surfaces. A typical reaction consisted of mixing 16.6 mL of aqueous dispersion of CNF (4.3 g/100 mL) and 0.3 mL of aniline in 100 mL of deionized water. This mixture was left under constant stirring for two hours at a temperature of 5°C. DBSA was added to the CNF/aniline suspension and the mixture kept at constant stirring for one hour at 5°C. Finally, a defined amount of oxidant (APS), dissolved in deionized water, was added to the CNF/aniline/DBSA suspension in order to initiate the polymerization. After 12 hours, CNF/PANI-DBSA was separated from the reaction media by centrifugation. To eliminate reaction by-products CNF/PANI-DBSA was re-dispersed in water and centrifuged again. This procedure was repeated 3 times and the final content was either re-dispersed in water in the desirable concentration (e.g., for characterization) or kept at high concentration. Using this method, two sets of samples with varying amounts of (i) DBSA and (ii) oxidant with respect to aniline were obtained (see Table 1). Films of ~200 μm in thickness were obtained by casting concentrated CNF/PANI-DBSA composites onto microscope glass slides (75 × 25 × 1.2mm) which were allowed to dry in a conventional oven at 60°C for 12 h and then used in electrical and XRD measurements.

Characterization

The DC electrical conductivity of CNF/PANI-DBSA films was obtained by the four probe method using a voltage-current source (Model 236 Source measure unit – Keithley co. Ltd.).

FTIR analysis were carried out on samples prepared with potassium bromide (KBr) in form of pellets (dried for 1 hour at 100°C) using a Nexus 670 spectrophotometer (Nicolet Instrument Corporation). Spectra were recorded in the range of 4,000 to 650 cm^{-1} at 4 cm^{-1} resolution and 128 scans for each sample.

X-ray diffraction patterns were obtained by using XDR-6000 diffractometer (Shimadzu) using Cu Kα radiation (wavelength~1.5418 Å). Scans were carried out from $2\theta = 10$ to 60° at a scan rate of 1 deg/min.

UV-Vis-NIR absorption spectra of aqueous CNF/PANI-DBSA dispersions were obtained using a Cary 50 spectrophotometer (Varian). Spectra were recorded from 300 to 1100 nm.

The morphology of CNF and CNF/PANI-DBSA was accessed by Supra 35 field emission scanning electron microscope FESEM (Zeiss). 5 μL of CNF aqueous suspension (4.3 g/100 mL) was diluted in 1mL of isopropyl alcohol and 3 μL of the resultant suspension was cast onto silicon substrates, dried in dynamic vacuum for 1h at room temperature, and coated with carbon by sputtering prior to FESEM analysis.

Results and Discussion

The *in situ* polymerization of aniline was performed in the presence of cellulose nanofibrils dispersed in water. No precipitation or formation of PANI aggregates was visually observed. The CNF/PANI-DBSA concentrates had very good dispersion and stability in water, attributed to the surfactant action of DBSA. DBSA is an organic acid well-known for its surfactant effect and, similarly to HCl and camphorsulfonic acid (CSA), can be used as a dopant to PANI.

The electrical conductivities of CNF/PANI-DBSA obtained with different synthesis conditions are shown in Table 1. Electrical conductivities as high as 10^{-1} S/cm were obtained for CNF/PANI-DBSA films, which is one order of magnitude lower than PANI-DBSA obtained in the same conditions of sample C1-2. Keeping the aniline/oxidant molar ratio at 4 and varying the DBSA/aniline molar ratio from 2-4 did not significantly change the electrical conductivity. For DBSA/aniline ratio equal or lower than 1 the conductivity was so low (sample C1-1) that it was impossible to measure by the four probe method. Under this condition aniline polymerization did not occur. This fact was confirmed by the absence of the polaron band around

Table 1.
Values of the molar ratios used in the preparation of samples and their DC conductivities.

Samples	C1-1	C1-2	C1-3	C1-4	C2-1	C2-3	C2-4
Molar ratio Aniline/oxidant	4	4	4	4	5	2	1
Molar ratio DBSA/Aniline	1	2	3	4	2	2	2
Conductivity – 1×10^{-1} (S/cm)	–	2.1 ± 0.5	2.2 ± 0.5	1.5 ± 0.6	1.8 ± 0.7	3.0 ± 0.5	1.5 ± 0.6

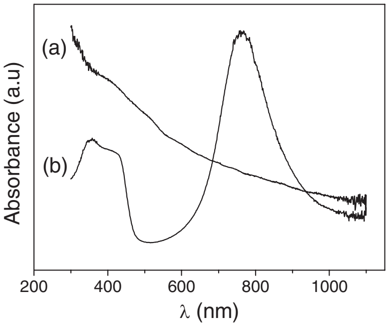

Figure 1.
UV-Vis spectra of the PANI-CNF nanocomposites. (a) C1-1 and (b) C1-2 sample.

800 nm and 420 nm in the UV-Vis-NIR spectrum, shown in Figure 1 for sample C1-1. This result is attributed to the reactive alkaline medium forming oligomers instead of long PANI molecules.[23] These bands can be seen in the spectrum of sample C1-2, characteristic of the emeraldine salt form of PANI[5,8] that is responsible for the high conductivity in PANI-CNF composites. Similar spectra were obtained for other samples (results not shown here).

Figure 2 illustrates the FTIR absorbance spectra of the CNF/PANI-DBSA nanocomposite (C1-2), CNF and PANI-DBSA and the major spectral assignments are summarized in Table 2. The broad peak between 3320 and 3570 cm^{-1} of the CNF spectrum is attributed to O–H stretching of hydrogen bonded hydroxyl groups (OH), and the peak at 2896 cm^{-1} to aliphatic saturated C–H stretching.[11,12] The peaks at 1064 cm^{-1} and 898 cm^{-1} are attributed to the C-O stretching and C-H rocking vibrations of cellulose.[12] The peak at 1164 cm^{-1} is assigned to C-O-C symmetric stretching of cellulose.[12] For PANI-DBSA, the peak at 669 cm^{-1} is attributed to the stretching deformation of the aromatic ring, and at 830 cm^{-1} is assigned to the out-of-plane bending vibration of the C-H band of the *p*-disubstitued benzene ring.[20,23] The peaks at 1540 and 1465 cm^{-1} correspond to the stretching vibration of the quinoid and benzenoids rings.[20,23] The peak at 1297 cm^{-1} is assigned to the C-N stretching vibration of secondary amine of PANI backbone.[5] In the FTIR spectrum of CNF/PANI-DBSA, the presence of characteristic peaks of both CNF and PANI-DBSA were found (Figure 2). The ratio between the absorption peaks at ~ 1540 cm^{-1} (quinoid ring stretching – Q) and ~1465 cm^{-1} (benzenoid ring stretching – B) was used to compare the doping efficiency between the composite and PANI-DBSA. The Q/B for doped PANI-DBSA is 0.69 and for CNF/PANI-DBSA is 0.81, which indicates a higher level of doping in PANI-DBSA. This result is in concordance with electrical conductivity

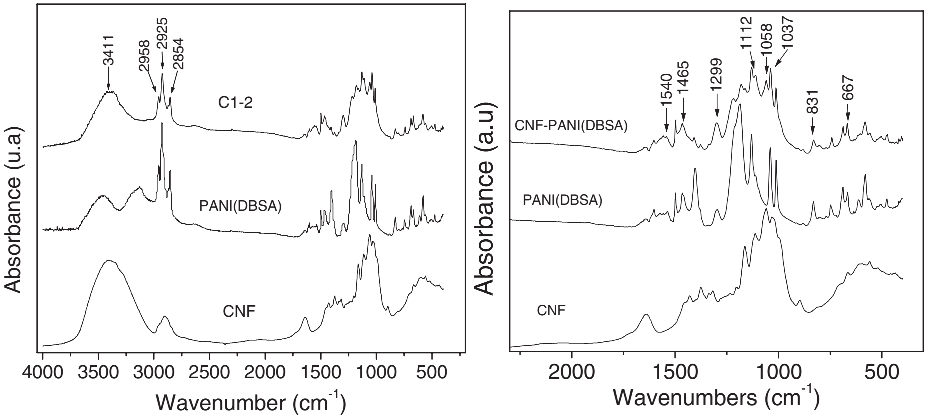

Figure 2.
FTIR spectra of samples: CNF, PANI-DBSA and CNF/PANI-DBSA Nanocomposite (C1-2).

Table 2.
Assignments of the main peaks in the FTIR spectra of CNF-PANI, PANI-DBSA and CNF samples.

Peak assignment	Wavenumber (cm^{-1})		
	CNF-PANI	PANI-DBSA	CNF
N-H out of plane bending [2]	503	503	
C-C bending [24]	580	580	
S = O stretching [2]	667	667	
C-C bending [24]	688	688	
Aromatic C-H out of plane bending [2]	830	830	
S = O stretching [2]	1012	1012	
S = O stretching [2]	1037	1039	
C-O stretching [12]	1060		1060
Glucose ring stretching [12]	1112		1112
Symmetric SO_2 stretching [2]	1130	1132	
C-O-C asymmetric stretching [12]	1162		1162
C-H bending [2]	1180	1184	
C-N stretching of secondary amine [2]	1297	1297	
C-H deformation [12]	1376		1376
N-B-N ring Stretching [24]	1465	1465	
Quinoid (Q) and benzenoid (B) ring stretching [2]	1498	1498	
N-Q-N Stretching [24]	1540	1540	
B and Q ring stretching [2]	1600	1600	
O-H deformation due to H_2O [12]	1637		1637
Symmetric CH_2 stretching [2]	2854	2854	
Aromatic C-H stretching [2]	2925	2925	
C-H stretching [2]	2958	2958	
O-H stretching of H_2O [12]	3411		3405

measurements of the CNF/PANI-DBSA that showed an order of magnitude lower than PANI-DBSA.

X-ray diffraction (XRD) patterns of CNF, CNF/PANI nanocomposite (C1-2) and PANI-DBSA are presented in Figure 3. Three peaks at 15° (d∼5.9 Å), 16.7° (d∼5.3 Å) and 22.7° (d∼3.9 Å) were observed for CNF and are characteristic of crystalline cellulose type I.[11] The PANI-DBSA diffractogram shows two sharp peaks at $2\theta = 21.1°$ (d∼4.2 Å) and 24.9° (d∼3.6 Å) and one small peak at $2\theta = 26.7°$ (d∼3.3 Å) – all attributed PANI-DBSA crystallinity.[25] The XRD patterns of the PANI/CNF composites also presented characteristic peaks related to both components. The peak at $2\theta = 22.7°$ of CNF was maintained in the same position, indicating that CNF structure was unmodified as expected. Nevertheless, the region between $2\theta = 10$ and 30° in the CNF/PANI-DBSA composite is slightly different from that of the individual components. For example, the peak at 21.1° shifts towards lower 2θ values (20.54°) and new peaks appear between $2\theta = 13$ and 20°. This result indicates that the PANI grown on cellulose surface is more crystalline and compact. The surface of acid hydrolyzed cellulose has sulfate group that can interfere in the PANI growth.

Morphological characterization of PANI-coated and uncoated cellulose nanofibrils by FESEM are shown in Figure 4. The FESEM micrograph in Figure 4(a) shows nanofibrils with average diameters in the range of 30–50 nm and length around

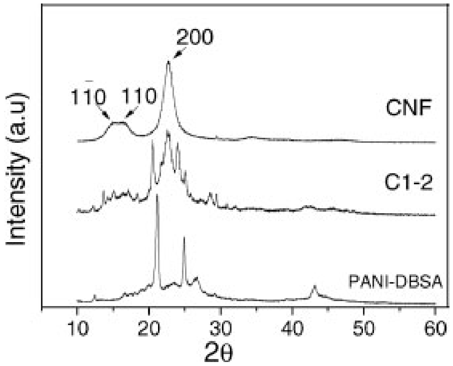

Figure 3.
X-ray diffraction patterns of samples CNF, CNF/PANI-DBSA nanocomposites (C1-2) and PANI.

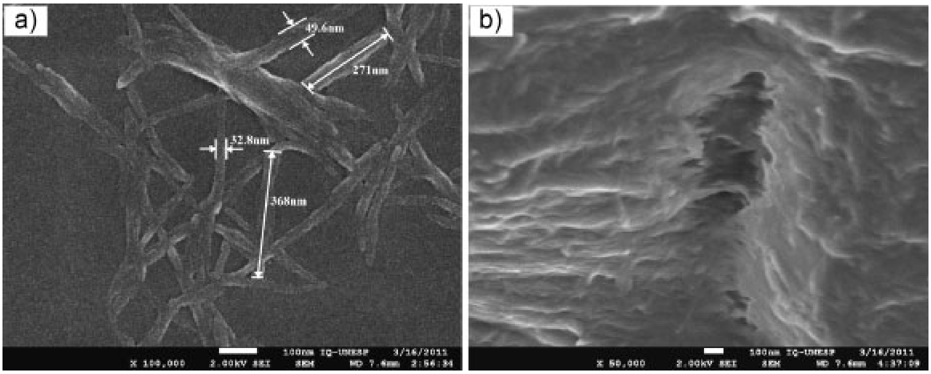

Figure 4.
FEG-SEM images of (a) CNF and (b) CNF/PANI-DBSA nanocomposite.

250–400 nm. The low roughness surface of the cellulose nanofibrils shown in Figure 4(b) indicates that PANI-DBSA are formed on CNF surface during *in situ* polymerization as expected (Figure 4b), thus forming a PANI–based nanocomposite that has a potential to be used as electrical conductive reinforcements to polymers.

Conclusion

Electrically conductive composites of cellulose nanofibrils coated with polyaniline (CNF/PANI-DBSA) were successfully prepared by *in situ* polymerization of aniline in the presence of nanofibrils. The optimum DBSA/aniline and aniline/oxidant molar ratios to produce CNF/PANI-DBSA composites with improved conductivity were 4 and 2, respectively. Conductivity as high as 10^{-1} S/cm were obtained. Besides doping PANI, the organic acid (DBSA) also plays a role as surfactant increasing the stability of CNF/PANI-DBSA suspensions.

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