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# Morphology and Dielectric Properties of Directly Collected and Polyaniline Coated Lignocelluloses Fibers

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## ABSTRACT

In era of modern technology, light-weight, flexible, low-cost and environmentally safe substrates/electrodes are highly feasible for application in disposable electronics and energy storage devices. This study presents morphological and dielectric characteristics of naked and polyaniline (PANI) coated lignocelluloses fibers, directly collected from self-growing plant, Typha Angustifolia. Impedance spectroscopy measurements performed in frequency range from 0.1 Hz to 10 MHz revealed increase of six orders magnitude in conductive properties of lignocelluloses fibers coated with polyaniline. Dielectric constant of polyaniline coated lignocelluloses fibers also increased by three to five orders magnitude and revealed weak frequency dependence. Presented morphological and dielectric investigations of directly collected and PANI coated lignocelluloses fibers will open possibilities to develop facile, low-cost, flexible and environment friendly paper substrates for energy storage and disposable electronic applications.

## 1. Introduction

Conducting polymers (CPs) have attracted the attention of researchers worldwide due to their unique electrochemical, optical, chemical and opto-electronic properties [1,2]. CPs are excessively investigated for a variety of applications in diverse technological fields e.g. biosensors [3,4], LEDs [5,6], molecular electronics [7], corrosion resistance [8], thin film transistors [9], ion-exchange membrane [10], artificial muscles [11], printed circuit boards [12], and energy storage devices[13–17]. Among all CPs, polyaniline (PANI) is advantageous due to ease in preparation, stability in air, relatively higher electrical conductivity and superior chemical/physical properties [18,19]. PANI also has distinct characteristics of controlling the electrical properties by reversibly charge transfer doping as well as by protonation, which is highly feasible for high-tech applications e.g. supercapacitors, chemical and biological sensors, actuators and microelectronic devices [20,21]. PANI has limited uses as flexible electrodes/substrates for high-tech applications due to rigid structure. However several flexible composites of PANI have been reported for versatile applications like in automobile industry, electronics, packaging and construction due to enhanced mechanical properties [22–24].

PANI is a suitable candidate for coating of natural fibers to meet the demands of modern disposable technology in terms of flexibility, electrically conductive, electro-active, light-weight, all organic constituents, low cost and environmentally safe characteristics. Several investigations have been reported for PANI/natural fibers composites for versatile applications [25–27]. Polyaniline coated coconut fibers have been reported for pressure sensitive applications [28]. Kenaf fibers (KF)/PANI exhibits excellent conductive and morphological characteristics as a result of in situ PANI coating, which is feasible as suitable green conductive filler for insulating composite matrix [29]. Among natural fibers, directly collected lignocelluloses fibers are highly feasible due to abundance, ease in process, light-weight and flexibility characteristics.

Insulating to conducting polymers are widely used as dielectric materials due to ease of processing and flexibility of tailoring in electronic properties [30]. PANI/Carbon nanotube(CNT) composites showed modification of dielectric properties and reduced loss tangent [31] whereas Polyaniline/carbon black composite was reported as dielectric material to apply as corrosion resistant coating and microwave absorption [32]. Relatively high dielectric constant of~ 3000 was observed for PANI/epoxy composite prepared via in situ polymerization [33].

Dielectric constant of natural fibers and conducting polymers has a

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huge significance in disposable electronics and energy storage devices [34–40]. Literature survey reveals the tuning of dielectric properties by combination of different materials in composite formation [19]. Since both low (for packing/capsulation) to high dielectric (for capacitor & memory elements) materials are feasible in disposable electronics[1]. Environmentally safe, flexible, light-weight and low cost substrates/electrodes coated with conducting polymers are also suitable candidates for above mentioned high-tech applications. In this wok, morphology and dielectric properties of directly collected and PANI coated lignocelluloses fibers are investigated for the development of suitable substrate/electrode for disposable electronics and energy storage applications.

## 2. Experimental

### 2.1. Chemicals and reagents

Raw lignocelluloses fibers were directly collected from the stem of self-growing Typha Angustifolia plant [41]. Collected fibers were dried in air under sunlight for four days for removal of moisture. Aniline, ammoniumpersulphate (APS), sodium hypochlorite (NaOCl), hydrochloric acid (HCl) and sulfuric acid ($H_2SO_4$) were used as supplied by Merck.

### 2.2. Synthesis of paper sheets

### 2.2.1. Preparation of lignocelluloses sheet [41]

1.5 g of dried (as described above) raw lignocelluloses fibers were dispersed in 200 mL of 20% sodium hypochlorite (NaOCl) solution at temperature of 50 °C (4 h) for bleaching. The bleached fibers were filtered on Buchner funnel (90 mm-d) and pressed overnight to achieve surface smoothness of sheet. The yield of fibers was approximately 70% after bleaching process in comparison of dry weights.

### 2.2.2. Preparation of lignocelluloses/PANI Composite Sheet [41]

0.5 g of bleached lignocelluloses fibers (as describe above) were dispersed in 50 mL of distilled water for 30 min. l.3 g of APS and 0.5 mL aniline were dissolved in 50 mL and 68 mL of 1 M HCl solutions, respectively. Lignocelluloses fiber and Aniline solutions were stirred for 10 min at room temperature. Subsequently APS solution was added drop wise. The reaction was allowed to continue for 20 h in water ice bath for oxidative polymerization. The homogenous solution of PANI coated lignocelluloses fibers were filtered on Buchner funnel and converted into sheet by pressing overnight in air.

### 2.3. Characterization

### 2.3.1. Scanning Electron Microscopy (SEM)

Structural morphology and microscopic information were obtained by using FESEM (Quanta FEG-480) having E-SEM (environmental SEM) mode. The samples were mounted on aluminum stubs using double-sided adhesive black carbon tape.

### 2.3.2. Impedance Measurements

The ac electrical properties in a wide frequency range (0.1 Hz – 10 MHz) were measured at room temperature using Alpha N Impedance analyzer (Novocontrol, Germany). The contacts were made on opposite sides of sheet using silver paste, and cured under a tungsten lamp for 3 h. Leads were carefully checked to ensure the absence of any irrelevant resistive or capacitive coupling in measured frequency range.

## 3. Results and Discussion

Figure 1 shows Scanning Electron Microscopy (SEM) images of lignocelluloses fibers before and after coating with conducting layer of PANI. Figure 1(a) displays the fibril morphology of lignocelluloses fibers which confirm that fibers are randomly oriented and interlocked with each other to reinforce the mechanical strength, particularly favorable for use as a bulk paper sheet in high-tech applications. The inset image of figure 1(a) reveals sheet like structure of lignocelluloses fibrils directly collected from self-growing plant, Typha Angustifolia. Figure 1(b) displays the cauliflower like morphology of lignocelluloses fibers coated with PANI. Inset image in figure 2(b) reveals the compact black paper sheet like morphology and confirm that lignocelluloses fibers retained the structure even after coating with PANI. It can conclude from Figure 1 that presented paper sheets were flexible, environmental friendly and can be cut in any shape with the help of a scissor. Thermal, structural, conductive and electroactive characteristics of lignocelluloses fibril and lignocelluloses/PANI sheets are already presented [41].

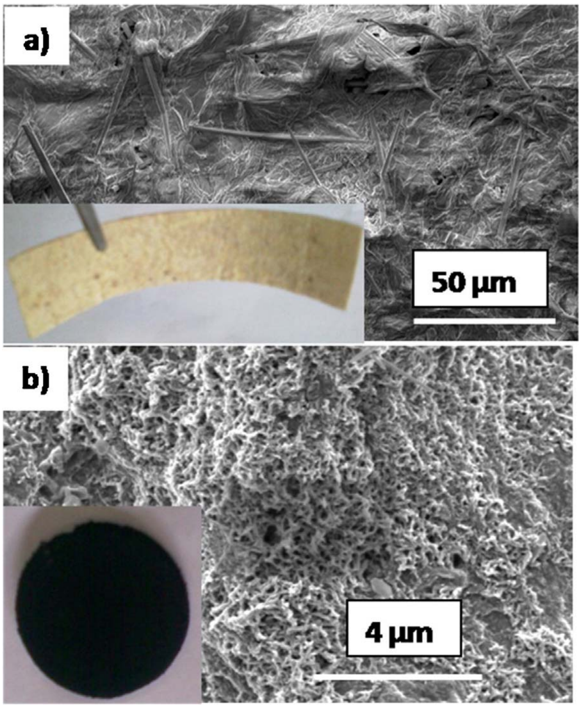

**Figure 1.** Scanning Electron Microscopy (SEM) images of a) lignocelluloses fibril b) lignocelluloses/PANI sheets. Inset images shows the bulk structure of) lignocelluloses fibril and lignocelluloses/PANI sheets, respectively.

Figure 2 (a,b & c) show impedance plane plots Z/vs. $Z^{//}$as a parametric functions of frequency from data collected at room temperature for natural lignocelluloses(LC), bleached LC and PANI coated LC fibrils sheets. The solid symbols represent the experimental data and joining lines are guide to eye whereas arrows show directions of increase in frequency. Generally, curve appeared as straight lines along real and imaginary axes in linear complex plane plots of impedance which is characteristic of a conduction process with purely resistive (R) and capacitive (C) behavior, respectively. However, when both behaviors (R and C) are present in parallel, the response is a semicircular arc [42]. The systems under investigation consist of different micro-structural heterogeneities such as lignin, hemicelluloses, and celluloses therefore impedance plane plots consists of more than one semicircular arcs. This might be due to the different mean relaxation frequencies ($f_{ri} = 1/2\pi R_i C_i$) of charge carriers at different micro-structural heterogeneities. Here $R_i$ and $C_i$ are the resistance and capacitance of ith heterogeneity, respectively. Generally the component with larger resistance also possesses larger capacitance and hence the larger RC product. The component with larger RC product will offer the larger resistance and the mobility of the charge carriers will be low across the component. Owing to low mobility, carrier can follow the variations in applied ac electric field and relax up to relatively low frequencies. The diameter of ith