



# Synthesis and characterization of polyaniline/tosylcellulose stearate composites as promising semiconducting materials



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## ARTICLE INFO

### Keywords:

Tosylcellulose stearate  
Polyaniline  
Composite  
Thermal stability  
Electrical conductivity

## ABSTRACT

Tosylcellulose stearate (TCSt) as a thermoplastic polymer has been prepared starting from microcrystalline cellulose (MCC) which was converted into a more reactive and solvent soluble tosylcellulose (TC) with degree of substitution = 0.45 under homogenous conditions. Then, tosylcellulose underwent esterification reaction through its reaction with stearic anhydride in DMF/DCM to afford tosylcellulose stearate. FT-IR, <sup>13</sup>C NMR, and elemental analyses confirmed the chemical structure of both tosylcellulose and tosylcellulose stearate. TCSt fibers were used as matrix for polyaniline (PANI) which had been prepared via in situ oxidative polymerization of aniline hydrochloride using hydrochloric acid as dopant and ammonium persulfate as an oxidizing agent. PANI/TCSt composites with loading ratios of 75:25, 50:50, and 25:75 wt/wt were fabricated. The thermal stability, degree of crystallinity, and surface morphology of the prepared composites were characterized. The presence of PANI improved the thermal stability of the PANI/TCSt composites with (50:50 wt:wt). The electrical conductivity for PANI/TCSt composites was measured by Broadband Dielectric Spectrometer, and the conductivity values of PANI/TCSt composite prepared at weight ratio 75:25 wt% was coincided with those of PANI alone. Increasing the temperature from -40 to +50 °C increased the conductivity of the composites by about two orders of magnitudes for all investigated samples. The films prepared from TCSt and PANI/TCSt composite (50:50 wt:wt) displayed improved mechanical properties when compared with the films prepared from cellulose acetate (CA) and CA/PANI composite (50:50 wt:wt).

## 1. Introduction

Recently, there is a growing interest in the development of new electrically conductive materials based on natural fibers to be employed in different biomedical and industrial fields. Intrinsically conductive polymers (ICPs) are a group of conductive materials that have the chemical structure and mechanical characteristics of polymers and the electronic properties of metals and their electrical conductivity arises from their conjugated electronic structure [1]. ICPs are intensively used in the manufacturing of organic electronic devices e.g. diodes transistors, ion exchange membranes, and electronic switches [2]. Polyaniline (PANI), polypyrrole (PPY), poly(3,4-ethylenedioxythiophene) (PEDOT), and polyacetylene are the most extensively used ICPs. The conductivity of polyaniline depends on its degree of oxidation [3], where the fully reduced structures is known as leucoemeraldine base (LEB), the fully oxidized structure is known as pernigraniline base (PNB), and the half oxidized/half reduced structure is known as emeraldine state (EB). The protonated or doped EB form is highly

conducting, while LEB and PNB are generally insulators. In addition to the electrical and semiconducting features of PANIs, they retain characteristic tunable properties, optical activity, and thermochemical stability. Also they can be prepared with high yield at a low production cost [4]. These advantages enabled their use in numerous technological applications such as electric rechargeable batteries, supercapacitors, electrochromic, electromagnetic, corrosion preventing materials, biosensors, and tissue engineering [5–11]. However, the rigidity which is attributed to the polymer conjugated electronic system besides the poor mechanical properties because of their relatively low molecular weight limit its tendency for molding into electrodes or casting into films [12].

Several approaches have been employed to improve the processibility of PANI including the electrostatic deposition, graft copolymerization, and direct in situ oxidative polymerization of PANI on the surface of different substrates [13–15]. Thermoplastic polymers, metal oxides, graphene oxide, carbon nanotubes, paper sheets, and natural fibers were the most investigated materials for the reinforcement of PANI [15–20]. Furthermore, the biodegradability and the good film-

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forming ability of chitosan, bacterial cellulose, cellulose nanofibers (CNF), and cellulose esters (CEs) make them ideal matrices for the fabrication of PANI composite films [20–23]. Generally in the films represented PANI as conducting filler, the mechanical properties and flexibility of conducting PANI composite films depends on the amount and the nature of the matrix used. While, the degree of conductivity of the composite films depends on the amount of PANI incorporated into the film, PANI polymerization technique, and the type of dopant used [23–25].

In this work, tosylcellulose stearate (TCSt) was prepared under homogenous conditions and used as a thermoplastic matrix for PANI. We intended from this work to investigate the impact of deposition of PANI onto the surface of TCSt fibers by studying the thermal stability, morphology, electrical properties and the tensile strength of PANI/TCSt new composites prepared at different weight ratios. As well as optimize the proper ratio between PANI and TCSt which can be used to fabricate new conducting films that combine the features of thermoplasticity of TCSt fibers and the electrical conductivity of PANI. To the best of our knowledge, this is the first report about the use of tosylcellulose stearate as a matrix component for PANI.

## 2. Materials and methods

### 2.1. Materials

Microcrystalline cellulose (MCC) with average particle size of 20  $\mu\text{m}$ , triethylamine (TEA), anhydrous lithium chloride (LiCl), stearic anhydride (SA), *p*-toluenesulfonyl chloride, and aniline hydrochloride were purchased from Sigma–Aldrich. Cellulose acetate (CA) from Fluka BioChemika  $M_r \sim 29000$ , degree of substitution: 40% acetyl groups, Ammonium persulfate (APS) was obtained from S.D. Fine Chem. Ltd. Dimethyl acetamide (DMA), ethanol, and hydrochloric acid were purchased from Thermo Fisher Scientific.

### 2.2. Methods

#### 2.2.1. Preparation of tosylcellulose (TC)

TC was prepared according to the method described by Rahn et al. [26] and Liu et al. [27], where 5.0 g (30.8 mmol of anhydroglucose unit) of MCC was dried in oven at 70 °C for 72 h. The oven dried MCC was suspended in 120 mL of DMA and heated under reflux at 160 °C with stirring for 2 h. The suspension was allowed to cool to 100 °C, then 10 g of anhydrous LiCl (235.9 mmol) dissolved in 25 mL of DMA were added with stirring and the temperature was allowed to cool down to the RT. The stirring of MCC solution was continued for 12 h or till the complete dissolution of MCC affording a slight yellowish viscous solution. This was followed by addition of 15 mL of TEA (107.62 mmol) diluted in 10 mL of DMA under stirring at room temperature for additional 30 min. After cooling the solution to 3–8 °C, a solution of *p*-toluenesulfonyl chloride 35.3 g (183.6 mmol) in 25 mL of DMA was added drop wise over 30–45 min. The stirring was continued for another 24 h and the temperature was kept at 3–8 °C. The reaction mixture was poured slowly into 1L of ice-cold water and the precipitate was filtered off, washed with about 3L of distilled water. The crude tosylcellulose product was suspended in 250 mL of boiling acetone, re-precipitated in 1 L of distilled water, and filtered off. Finally, TC was washed with 500 mL of ethanol, dried at 50 °C in oven for 48 h.

#### 2.2.2. Preparation of tosylcellulose stearate (TCSt)

TCSt was prepared by esterification of tosylcellulose using stearic anhydride according to the method described by Heinze et al. [28]. Stearic anhydride (5 g, 9 mmol) was dissolved in 50 mL of anhydrous dichloromethane and 253  $\mu\text{L}$  of TEA (1.81 mmol) was added as based catalyst to the stearic anhydride solution and mixed by vortex for 60 s (solution A). TC (2 g, 6.36 mmol) was dissolved in 10 mL of DMF (solution B). Solution A was added drop wise to solution B with stirring,

the reaction mixture was heated under reflux at 80 °C for 12 h. The product was precipitated by addition of 400 mL of ethanol. The precipitate was filtered off followed by Soxhlet extraction for 24 h with 500 mL of methanol. The solid product was washed with cold ethanol and vacuum dried at 35 °C for 48 h.

#### 2.2.3. Preparation of PANI/TCSt composite

PANI/TCSt composites at different weight ratios were prepared according to the procedures described by Liu et al. [21]. Where 0.75 g of TCSt was dispersed in 20 mL of distilled water and homogenized by homogenizer for 15 min at 20000 rpm (solution A). A different amount of aniline hydrochloride monomer (0.25, 0.75 and 2.25 g) was dissolved in 2 mL of ethanol to prepared solution B. Then, the two solutions were mixed and stirred for 5 min. Then HCl solution (37%) was added in the ratio of 1:1 v/wt of aniline hydrochloride into the reaction mixture, and magnetically stirred for 10 min. To start the polymerization reaction, a certain amount of ammonium persulfate (2.1:1 wt/wt of aniline hydrochloride) was dissolved in 1 mL of distilled water and added dropwise to the mixture with stirring at room temperature. The stirring was continued for 24 h and the resulted composites were washed with 50% ethanol in water for several times to remove the un-polymerized aniline, then the composites were oven dried under vacuum at 50 °C till dryness.

#### 2.2.4. Preparation of TCSt and CA films

For the preparation of TCSt or CA films, 0.5 g of TCSt or CA powder were dissolved in 10 mL of using a  $\text{CHCl}_3/\text{DMF}$  (8:2) mixture or acetone/glacial acetic acid (3:2) by heating the mixture at 70 °C with stirring till complete dissolution of the sample. The solution was filtered and poured onto a flat glass plate of 10 cm diameter and the solvent evaporated in air at the room temperature for 48 h. Finally, the films were peeled off from the glass plates by addition of water [24].

#### 2.2.5. Preparation of PANI/TCSt composite film

A strip of TCSt films weighting 0.5 g was immersed in 20 mL of distilled water, then a solution of aniline hydrochloride 0.5 g dissolved in 2 mL ethanol was added. This was followed by addition of an aqueous solution of HCl (37%) (1:1 mL/wt of aniline hydrochloride), and the mixture was magnetically stirred for 10 min. Then ammonium persulfate (2.1:1 wt/wt of aniline hydrochloride) was dissolved in 1 mL of distilled water and added drop wise to the mixture with stirring at room temperature. The stirring was continued for 24 h and the resulted composite film was washed with 50% ethanol in water for several times till the filtrate become colorless. Then the composite film was vacuum dried at 50 °C till dryness [25].

#### 2.2.6. Fourier transfer infrared spectroscopy (FTIR)

The FTIR spectra of MCC, TC, TCSt, PANI, and PANI/TCSt composite were recorded with Nicolet Impact-400 FT-IR spectrophotometer in the range of 400–4000  $\text{cm}^{-1}$ .

#### 2.2.7. $^{13}\text{C}$ NMR spectroscopy

The  $^{13}\text{C}$  NMR analysis for TC and TCSt samples were determined by JEOL JXA-840A 500 MHz spectrometer at 25 °C using  $\text{DMSO}-d_6$  as solvent. The chemical shifts ( $\delta$ ) were expressed as part per million (ppm) against TMS as internal reference.

#### 2.2.8. X-Ray diffraction (XRD)

The XRD patterns of MCC, TCSt, PANI, and PANI/TCSt composites were investigated on a Diano X-ray diffractometer using  $\text{CoK}\alpha$  radiation source energized at 45 kV and a Philips X-ray diffractometer (PW 1930 generator, PW 1820 goniometer) with  $\text{CuK}$  radiation source ( $\lambda = 0.15418$  nm), at a diffraction angle range of  $2\theta$  from 10° to 80° in reflection mode.

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