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Synthesis and characterisation of nanocellulose-based polyaniline conducting films

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ABSTRACT

In this paper, a relatively new concept of using nanocellulose as matrix material in a composite system has been explored. The functionality of the composite has been enhanced by using polyaniline (PANI) as a functional component. These tunable electrically conducting biocomposites have potential applications in anti-static, electromagnetic interference shielding, sensors, electrodes, and storage devices. Nanocellulose was extracted by hydrolysing bleached flax yarn with sulphuric acid (60 wt.%) at 55 °C for 1 h under vigorous stirring. Thin composite films of nanocellulose with PANI inclusions at different loadings were manufactured using in situ polymerisation where aniline-HCl was polymerised with ammonium peroxydisulfate (APS) as oxidant in aqueous nanocellulose suspension. Thin composite films showed improved combination of flexibility and conductivity. These films could be bent by 180° without breaking. The dependence of electrical conductivity on the concentration of polyaniline (0, 10, 20, 30 wt.%), was investigated. It was found that the conductivity of a film increased significantly with the increase in PANI content from 10% to 30%. The conductivity of the nanocomposite containing 30 wt.% reached 1.9×10^{-2} S/cm, which shows promise in the application of paper-based sensors, flexible electrode and conducting adhesives. The composite film showed improved thermal stability above 300 °C by 15% less weight loss at 500 °C compared to pure nanocellulose films. The morphologies, microstructures, thermal stability properties of the nanocomposite films were also investigated.

1. Introduction

There is a growing interest in developing bio-based products derived from renewable sources and innovative processing technologies that can reduce the dependence on fossil fuels and encourage movement towards a sustainable material basis [1,2]. Cellulose is the most abundant natural bioresource in the world, and the annual biomass production is about 1 trillion tons [3]. Cellulose fibres have been widely used due to their sustainability and good mechanical properties. Nanocellulose fibrils has recently gained attention from researchers and industry because it has high tensile modulus (138 GPa), which is higher than that of the S-glass (86–90 GPa) and comparable to Kevlar (131 GPa), rendering them good reinforcement for natural and synthetic polymer matrices [4–6]. Cellulose nanowhiskers, with size ranging from a few to tens of nanometres in one dimension, have some unique properties, including renewable resource, excellent mechanical properties, high specific surface area, biodegradability, and biocompatibility [7]. Moreover, cellulose, rich in hydroxyl group, has good affinity with a variety of polymers, including conducting polymers [8–11]. Cellulose nanowhiskers can be prepared from a variety of sources, such as wood pulp, plant fibres (e.g. hemp, sisal, flax, ramie, jute, algae) [12], microbial (Acetobacter Xylinum)[13], sea creatures (tunicate) [14], fruits (banana and grape skin) [15], and even agricultural products (e.g. cornhusk, wheat straw) [16], which makes them more attractive and applicable. There are mainly three methods for producing nanocellulose, namely, chemical acid hydrolysis, chemical treatment in combination with mechanical refining and enzymatic method.

Polyaniline, as one of intrinsically conducting polymers, is a very promising material because of its ease of synthesis, low cost monomer, tunable properties, and high environmental stability. It has potential applications in anti-static and electromagnetic interference shielding, sensors, electrodes, and batteries fields. However, it is very difficult to produce the neat polyaniline films because of its infusibility, poor mechanical properties, and poor solubility in all available solvents except doping with a suitable dopant or modifying the monomer [17]. Cellulose has been recognised as good matrix/substrate for biodegradable batteries,

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sensors, and actuators [11,18,19]. The polymer composites containing polyaniline are mostly investigated for blending with commercial polymers in order to obtain improved processability and fairly good mechanical properties together with good conductivity for practical applications [20–22]. However, the electrical conductivity of the composite was not improved effectively; especially the composites became more brittle due to addition of polyaniline. Cellulose fibres have been used to reinforce brittle conducting polymers, such us polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTP) for energy storage applications [23]. Cellulose and PPy all polymer composite battery with high reported charge capacities and charging rates [11]. Recently, Polyaniline-based aqueous suspensions containing polyaniline (PANi) contents ranging between 5 and 80 wt.% have been successfully developed, the composite films showed high mechanical strength of 178 MPa, and a percolation threshold of electrical conductivity of 4.57 vol.% of PANi content [24]. Compared with PPy and PTP, PANI has relatively high theoretical specific capacity [23]. Combining cellulose nanowhiskers and polyaniline is promising for developing green functional polymer nanocomposites. Recently, polyaniline modified and cellulose nanowhisker reinforced smart composites have been reported [25].

In this research, nanocellulose was used as the matrix and polyaniline was added as conducting component to produce the nanocellulose-based flexible and electrically conducting composite films. Aqueous nanocellulose suspension has good film formability because of strong hydrogen bond between the whiskers, which facilitates the film forming ability of the composites. The combination of nanocellulose and polyaniline gives good conductivity and excellent mechanical properties to the nanocomposites. The composites, combining good mechanical properties of cellulose nanowhiskers and conductivity of polyaniline, have great potential in anti-corrosion coatings, conducting adhesives, anti-static and electromagnetic interference shielding materials, biodegradable smart sensors/actuators, and batteries.

2. Materials and testing methods

2.1. Materials

Bleached flax yarns were purchased from Jayashree Textiles, Kolkata, India. Sulphuric acid with concentration of 95–97%, was supplied by Merck KGaA, Darmstadt, Germany. Sodium hydroxide was purchased from Ajax Finechem Pty Ltd., Taren Point, Australia. Aniline hydrochloride and Ammonium persulfate (APS) were bought from Sigma–Aldrich, Inc., St. Louis, USA. The chemicals were used as received without further purification.

2.2. Preparation of cellulose nanowhiskers

Cellulose nanowhiskers were prepared by acid hydrolysis, following a procedure reported earlier [5]. The oven dried flax yarns were hydrolysed in sulphuric acid solution (60 wt.%) at 55 °C for 1 h. Then the suspension was centrifuged and diluted with D. I. water, which was followed by neutralisation with NaOH solution (10 wt.%) to remove free acid. The suspension was freeze-dried prior to being redispersed in D. I. water.

2.3. Preparation of nanocellulose/polyaniline composite films

0.2 g aniline HCl powder and 0.44 g APS were dissolved in distilled water. Aniline HCl solution was added into cellulose nanowhiskers aqueous suspension (0.5 wt%) followed by dropwise addition of APS. The weight ratio of aniline HCl monomer and nanocellulose is 1:9, 2:8, and 3:7. The mixture was kept stirred for 24 h at room temperature and then was diluted and washed with D. I. water under centrifugation until the supernatant was clear. The mixture was cast directly onto petri dishes. The composite film was peeled off after water fully evaporated at room temperature.

2.4. Testing methods

The morphology of the nanocomposites was studied using field emission scanning electron microscopy (FE-SEM, FEI XL30s) with an accelerating voltage of 5 kV. Fourier transform infrared – attenuated total reflectance (FTIR, ATR-FTIR, Nicolet 8700, USA) spectroscopy was used to analyse the chemical structures of the specimens. All spectra were collected with 4 cm^{-1} wave number resolution after 64 continuous scans at a wavelength range of 4000–600 cm^{-1}. UV–Vis absorption analysis was recorded with UV–Vis scanning spectrophotometer (UV-2101 PC, Shimadzu, Japan) on PANI solution by using N, N-dimethylformamide (DMF) as solvent. Thermal stability analysis was carried out with thermogravimetric analysis (TGA, Q5000, USA). Samples were heated in open platinum pan from room temperature to 600 °C, under a nitrogen atmosphere in order to avoid thermoxidative degradation due to oxygen, at a heating rate of 10 °C/min. A four-probe conductivity apparatus (Keithley 6517, USA) was used for electrical conductivity test. Storage modulus was tested on dynamic thermal mechanical analysis (DMTA, Q800, USA) at a heating rate of 3 °C/min. The dynamic storage was determined at a constant frequency of 1 Hz as a function of temperature from 20 to 150 °C.

3. Results and discussions

3.1. Morphology

Flexible nanocellulose-based polyaniline electrically conductive films are obtained by the in situ polymerisation of aniline HCl onto cellulose nanowhiskers. The composite has very good film formability by easily casting the resulted aqueous mixtures onto petri dish, which is not the case for pure polyaniline powder. This method is also environment friendly without any chemical solvent being involved. The resulting composite film appears in dark green colour and has high flexibility so that it can be bent by 180° without breaking, Fig. 1.

Fig. 2 shows the typical morphology of nanocellulose film and nanocellulose/PANI composite films. The nanocellulose film is composed of randomly oriented cellulose nanowhiskers with diameters varying from a few to around 20 nm. The composites have the similar morphology; however, the surface is rougher and the diameters of the whiskers are larger with an increase in PANI content due to the polymerisation of polyaniline on the whisker surface. The whiskers are well bonded with each other, which indicate the existence of strong hydrogen bonding in spite of surface coating of PANI powder. No detectable polyaniline precipitation is observed from the top surface of the films with 10 and 20 wt.% PANI, indicating that tiny polyaniline has been preferably polymerised on the surfaces of cellulose nanowhiskers. Individual cellulose nanowhiskers could not be distinguished and aggregates of PANI powder can be seen on the surface of the composite film with 30 wt.% PANI.

Fracture surfaces of pure nanocellulose and nanocellulose/PANI composite films are shown in Fig. 3. Nanocellulose film shows layered structure due to the strong hydrogen bonding among the whiskers. The composite film shows a similar layered structure (contributing to good flexibility) and white dots are clearly seen at the fractured ends of the whiskers, indicating good bonding between cellulose nanowhiskers and PANI powder.