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Preparation and characterization of conductive nanostructured particles based on polyaniline and cellulose nanofibers

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ABSTRACT

Conducting polyaniline (PANI) and cellulose coated PANI (PANI-NC) nanostructures with sizes of about 80–100 nm, doped with hydrochloric acid were synthesized by a sonochemical method. Both type of particles resulted electrically conductive (direct current conductivity of 0.059 and 0.075 S/cm for PANI and PANI-NC structures, respectively) and could be dispersed easily in water, leading to green colored suspensions that remain stable for more than 4 h. The morphology, crystallinity, electrical conductivity (σ) and thermal stability of the obtained PANI based structures were investigated and compared. Furthermore, UV–Vis spectroscopy and rheology of water suspensions were used to explain the measured properties. Although the concentration of cellulose fibers used to synthesize the PANI-NC structures was very low, important differences respect to the neat PANI fibers regarding the microstructure, electrical conductivity and suspension behavior were found.

1. Introduction

The controlled synthesis of nanometer-scale materials is a fascinating objective in modern material science. Recently, much attention has been paid to the synthesis of micro/nanostructured conducting polymers for their unique properties and promising potential applications in nanodevices [1–3]. Among the conducting nanostructured polymers, polyaniline (PANI) nanostructures have received much attention for their applications in novel optoelectronic devices, sensors and actuators, and conducting polymer composites [4–6] because of their low cost, ease of preparation, environmental stability, and reversible acid/base doping/dedoping characteristics [7]. PANI nanostructures, including nanowires, nanorods, nanotubes and nanofibers (NFs), have shown superior performance over other forms of the polymer [8]. Among their many advantages, the large interfacial area between PANI nanostructures and their surrounding [5] improves the dispersibility in the hosting matrices. Various strategies, including template synthesis, self-assembly, electrospinning, electrochemical methods, rapid mixing polymerization, sonochemical synthesis and interfacial polymerization have been developed for the synthesis of PANI nanofibers and nanotubes [9,10].

In recent years, it has been investigated the possibility of PANI coatings on fillers like clay, silica, silicates, carbon black, poly(methyl methacrylate) [11,12]. In particular, PANI was polymerized in the presence of $BaTiO_3$ nanoparticles to produce nanohybrid conductors [13], as well as SnO_2 nanoparticles to produce gas sensors [14], and Ag_2Te to produce core–shell nanoparticles [15]. Also, PANI-Ag hybrid has attracted considerable interest because of its potential in technological applications in the field of the electronic industry: transducers, actuators, sensors, batteries and biomaterials [16,17]. PANI has poor mechanical properties, but it is possible to improve and modify it through the incorporation of micro and nanosized particles. However, there are very few papers that report the utilization of PANI as the polymeric matrix and nano-/microsized fillers as reinforcement for improving mechanical properties [12]. Cellulose is one of the most abundant materials in nature; it can be extracted from different plants and it is naturally present as ordered and well-packed aggregates of nanofibrils. Cellulose nanofibrils possess several advantages such as low cost, low density, non-toxicity, renewable nature, biodegradability, capability of forming stable aqueous suspensions and remarkable mechanical properties that allows improving the mechanical performance of polymers at quite low fiber concentrations [6,18,19]. Thus, carrying out the polymerization of aniline in presence of nanocellulose fibers seems to be an obvious alternative to prepare conductive particles with improved mechanical properties. In fact, the existent literature demonstrates these hybrid particles present several benefits, as compared with neat PANI structures. Mattoso et al. [20] prepared polyaniline coated cellulose by in situ polymerization of aniline onto "never-dried" nano

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cellulose fibers and demonstrated that the resulting aqueous suspensions were much more stable than PANI ones and thus, shining films with interesting electrical conductivities were obtained. Casado et al. [6] found that PANI-NC fibers resulted more conductive than neat PANI ones and the same behavior was found for the resulting shape memory composite films. Li et al. [21] prepared PANI-coated conductive paper by in situ polymerization of aniline, indicating that the pulp fibers promoted the dispersion of the PANI particles generated, preventing their aggregation in the reaction system, which was favorable for the doping of PANI with *p*-toluenesulfonic acid. However, these research works were focused on the final composite or conductive paper and thus, the relationship structure–properties of the neat and hybrid PANI particles was not systematically studied. Thus, the main goal of this work is to obtain and characterize hybrid particles with similar or higher conductivity than that of PANI using nanocellulose fibersas nucleating/reactive particles during the sonochemical synthesis.

2. Experimental

2.1. Preparation of cellulose nanofibers

Aqueous suspensions of cellulose crystals were prepared from commercial microcrystalline cellulose (Aldrich, cat. No. 31,069-7) by acid hydrolysis, using an optimized procedure [18]. The microcrystalline cellulose was mixed with aqueous sulfuric acid (64 wt%) in a ratio of microcrystalline cellulose to acid of 1:8.75 g/ml. The mixture was then held at 45 °C for 0.5 h under strong stirring. The resulting suspension was diluted with an equal volume of water and dialyzed using a cellulose dialysis membrane (Spectra/Por 2, SpectrumLabs, Unitek de Argentina, molecular weight cut off = 12–14,000 daltons) to pH = 5–6 to eliminate the excess of acid. The final suspension was stabilized by ultrasonic treatment (0.5 h, Elmasonic P 60H, Elma). The concentration of this suspension was determined by drying aliquots of known volume and determining the fiber weight.

2.2. Synthesis of PANI and PANI-cellulose nanofibers

PANI fibers were synthesized by the sonochemical method proposed by Jing et al. [10] and adapted with small modifications. Aniline (ANI, Carlo Erba) was doubly distilled in presence of zinc powders. Ammonium persulfate (APS, Anedra, RA-ACS-) and hydrochloric acid (HCl, 36–37 wt%, Anedra, RA-ACS) were used as received. In a typical procedure, a 0.2 mol/L solution of ANI in aqueous HCl (1 mol/L) was prepared in a beaker and sonicated by placing the beaker in an ultrasonic cleaning bath (Elmasonic P 60H, Elma), using a power of 160 W and operated at 37 kHz. Then, 0.2 mol of APS were dissolved in 100 ml HCl (1 mol/L) and dropwise added to the ANI containing beaker, which was kept at 25 °C during the 4 h of reaction. After that, the acid suspension was dialyzed using the membrane until the dialyzed water became colorless. PANI was doped in HCl solution (1 mol/L, ~2 g PANI in 50 ml) for 3 h with magnetic stirring. Finally, PANI was separated from the HCl solution by ultra-centrifugation (20 min at 12,000 rpm), washed once with distilled water and freeze-dried to yield a green powder.

The same procedure was used to synthesize PANI coated nanocellulose (PANI-NC) fibers, but in this case the nanocellulose fiber suspension (1 g/L) was previously dispersed in the ANI solution by ultrasonication. A ratio of 9.3 g ANI/g nanocellulose particles was used during synthesis.

2.3. Characterization techniques

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of PANI particles and PANI-NC hybrid particles (prepared as KBr pellets) were recorded using a ThermoScientific Nicolet 6700 FTIR spectrometer in transmission mode at 32 scans with a resolution of 4 cm^{-1}.

2.3.2. Thermogravimetric analysis (TGA)

Thermogravimetric tests were performed in a TGA-50 Shimadzu Thermogravimetric Analyzer at a heating rate of 10 °C/min under nitrogen atmosphere.

2.3.3. X-ray diffraction (XRD)

XRD patterns were recorded between 2° and 60°, at a scanning rate of 1°/min by using a PANalytical X'Pert Pro diffractometer equipped with Cu Kα radiation source (λ = 0.1546 nm), operating at 40 KV and 40 mA as the applied voltage and current, respectively.

2.3.4. UV–Visible spectroscopy (UV–Vis)

UV–Visible spectra of diluted suspensions of PANI and PANI-NC fibers (10 ppm) in 0.1 mol/L aqueous HCl solution and 0.1 mol/L aqueous NaOH solution, in the wavelength range 300–1000 nm, were obtained using an Agilent UV–VIS spectrometer, model 8453.

2.3.5. Field emission scanning electron microscopy (FESEM)

The surface morphology of PANI and PANI-NC fibers films was investigated using a field emission scanning electron microscope (Zeiss, model Leo 982 Gemini) at 3 kV. Sample specimens were prepared by depositing a very diluted drop of filler suspension in water onto a FTO glass, followed by spreading with nitrogen flow and finally drying at room conditions.

2.3.6. Transmission electron microscopy (TEM)

Internal morphology of PANI-NC particles was analyzed using a transmission electron microscope (Philips CM 200 UT, with ultratwin lens for high resolution images) at 200 keV, using a dilute aqueous dispersion of particles deposited onto carbon grids.

2.3.7. Rheological tests

The complex viscosity curves of diluted fiber suspensions (3 wt%) as a function of the angular frequency were obtained using an Anton Paar, Physica MCR rheometer. Frequency sweeps from 0.1 to 500 s^{-1} using cone and plate geometry (25 mm diameter) were performed at 25 °C. The applied deformation was kept at 10%.

2.3.8. Electrical properties

A Keithley 199 System DMM/Scanner multimeter was used to measure the DC electrical conductivity on PANI and PANI hybrids pellets. The multimeter automatically calculates resistance in the four-point probe configuration. Conductivity was calculated using the relationship:

$$\sigma = \frac{L}{RA}$$

where *R* is the resistance of the pellet calculated by the instrument, *A* the electrode surface, and *L* the electrode spacing (about 1.7 mm in this work). The pellets were prepared using about 0.6 g of particles, applying a pressure of 5 ton/m^2 and then were gold sputtered.