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Conducting and magnetic mango fibers

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ABSTRACT

This paper presents a new magnetic material, obtained from the modification of mango (*Mangifera indica* L.) fibers with polyaniline (PAni). The obtained materials were characterized through wide-angle X-ray scattering, scanning electron microscopy, Fourier transform infrared spectroscopy, and ultraviolet–visible spectroscopy. Additionally, the electrical resistivity and magnetic behavior of the obtained samples were evaluated with the help of volume resistivity measurements assisted by probability density function analysis and magnetic force tests. The materials presented good electrical and magnetic properties. For instance, in the best case, fibers modified with PAni are approximately 120,000 times more conductive than raw mango fibers. In addition, mango fibers modified with PAni were increasingly attracted by the magnetic field, presenting magnetic force and magnetic susceptibility equal to 6.69 ± 0.05 mN/g (at 872 ± 4 Gauss) and $(2.48 \pm 0.04) \times 10^{-4}$ m^3 kg^{-1}, respectively. As a consequence, modification of mango fibers with PAni constitutes a very promising way for the preparation of green magnetic devices.

1. Introduction

Among the many renewable sources used for the preparation of new materials with remarkable properties, natural fibers have been frequently investigated (Hossain et al., 2014; Kengkhetkit and Amornsakchai, 2012; Le Moigne et al., 2014; Macías-García et al., 2012; Rahatekar et al., 2009), given the interesting properties such as good strength and low density associated to low cost and availability of most natural fibers (Mulinari et al., 2011; Souza et al., 2014, 2009). Particularly, the use of mango seed fibers for the preparation of polymer-based devices is very interesting since mango (*Mangifera indica* L., family Anacardiaceae) is an abundantly available natural material consumed all over the world (Kulkarni and Rathod, 2014; Yang and Li, 2013). Mango grows in almost all tropical and subtropical regions of the world and about 27 million tons of this fruit are produced annually (Iqbal et al., 2009). Brazil alone produces about 5% of the mango consumed, being one of the eight largest producers in the world (Henrique et al., 2013). Besides mango's use in animal feed (Kittiphoom, 2012), mango fibers are also useful as an antioxidant (Vergara-Valencia et al., 2007), a biosorbent (Alencar et al., 2012), and a stabilizer in silver nanoparticles synthesis (Yang and Li, 2013). In spite of its interesting uses, mango is a still an underutilized natural resource (Vergara-Valencia et al., 2007) that is mainly discarded by the mango juice industry (Alencar et al., 2012).

Fibers from mango seed, like other vegetable fibers (Young, 2002), are mainly constituted of cellulose (Chun et al., 2013; Macedo et al., 2010). As demonstrated elsewhere (Souza et al., 2014), the properties of vegetable fibers can be modified by *in situ* aniline polymerization, producing sensitive materials practically in one step (Souza et al., 2009a, 2009, 2014). Polyaniline is the oldest known synthetic organic polymer (Letheby, 1862; Souza et al., 2008d). It can exist in several oxidation states, such as leucoemeraldine, emeraldine and pernigraniline, and different protonation degrees (MacDiarmid and Epstein, 1989, 1994, 1995). Among possible oxidation states, due to the higher electrical conductivity of the protonated form, the emeraldine one is the most important. Emeraldine can be isolated in the insulating or conducting forms, named emeraldine base and emeraldine salt (Dimitriev, 2001; Jamadade et al., 2010; Javadi et al., 1989; Lee et al., 2009; Wang, 2002), respectively (Duboriz and Pud, 2014; MacDiarmid

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and Epstein, 1995), which can be identified by their characteristic bluish and greenish colors (Duboriz and Pud, 2014; Souza and Soares, 2006). Polyaniline is frequently a good choice for manufacture of sensitive devices (Rahaman et al., 2013; Souza et al., 2008b, 2009, 2010b, 2011), because of its low cost, very good electrical and electronic properties and easy preparation (Alizadeh et al., 2011; Kar et al., 2011; Ram and Palaniappan, 2004; Souza et al., 2006, 2008a,c, 2010b).

In this work, mango fibers are modified with polyaniline by *in situ* aniline polymerization. To the best of our knowledge, mango fibers have never before been modified by polymerization of aniline. The obtained materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and ultraviolet–visible spectroscopy (UV–vis). The electrical resistivities were studied with the help of probability density function analysis (Souza et al., 2005; Souza and Varela, 2012). Additionally, modified fibers were studied using the magnetic force test (Souza et al., 2013). The obtained materials presented good electrical and magnetic properties, constituting a very promising material for the manufacture of a new generation of magnetic devices.

2. Experimental

2.1. Materials

Aniline, sulfuric acid, ammonium peroxydisulfate (APS), hydrogen peroxide (32 vol%) and cobalt(II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), were purchased from Sigma–Aldrich, Brazil. All reactants were used as received. Mango fibers with average fiber length of 3 cm were kindly supplied by Arte em Forminhas, Brazil.

2.2. Preparation of mango fibers modified with polyaniline

Mango fibers (3.0531 g) were treated with 5.0 ml of aqueous H_2O_2 solution for 20 min at 25 ± 2 °C. Then, fibers were washed at least five times with distilled water. Fibers were then immersed in 50.0 ml of sulphuric acid (1 M), and 0.4894 ml of aniline was carefully added into the acidic medium with the fibers. The resulting medium was cooled, using an ice bath and after 2 h, 10 ml of aqueous H_2SO_4 solution (1 M), also containing the desired amount of APS, was added into the mixture under continuous stirring. The aniline/oxidizer molar ratio was always kept equal to 1:1. The total polymerization time was kept equal to 3.5 h under stirring. The polymerization was terminated by pouring the reacting mixture into ethanol. Fibers were washed more five times with distilled water and dried under continuous vacuum for 2 days at 25 ± 2 °C.

2.3. Characterization

2.3.1. SEM

The morphology of mango fibers was determined by SEM on JEOL equipment (model JSM-5300) with acceleration of 10 kV. The micrographs of natural and modified mango fibers were taken from samples fixed with carbon adhesive tape. All samples were coated with a thin layer of gold.

2.3.2. FTIR

FTIR analyses were performed in a Nicolet iN10 Spectrometer, using an Attenuated Total Reflectance (ATR) device, using 24 scans with a resolution of 4 cm^{-1} in the range 4000–675 cm^{-1}.

2.3.3. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

Simultaneous TGA and DTA of the materials were performed using a PerkinElmer Pyris STA 6000 thermogravimetric analyzer. The samples were heated from 25 to 700 °C using a heating rate equal to 20 °C/min under nitrogen flow (20 ml min^{-1}). Indium was used as the reference material for the DTA study. The average mass used in experiments was equal to 10 ± 2 mg.

2.3.4. Direct estimation of cellulose hemicellulose, and lignin

The direct estimation of cellulose, hemicellulose, and lignin present in the raw and modified fibers followed the procedure described by Moubasher et al. (1982). In a typical procedure, 2 g of the fibers were washed in ethanol and dried in an oven at 40 °C overnight. The obtained material was divided into two equal parts. One part was considered as fraction A. The second part was treated with a KOH solution (24%) for 4 h at 30 °C, and soon afterwards the medium was filtered, the residue was washed with distilled water, and then dried at 80 °C overnight; the dry weight was taken as fraction B. The same sample was treated with 72% H_2SO_4 for 3 h. The obtained medium was filtered and H_2SO_4 was removed by washing with distilled water and drying at 80 °C in an oven overnight; the dry weight was taken as fraction C. The difference in weight between fraction A and fraction B corresponded to the total hemicellulose content in the curaua fibers. Fraction C was considered to be the lignin content of the fibers, whereas the weight difference between fraction B and fraction C was calculated as the cellulose content inside the fibers.

2.3.5. XRD

X-ray diffraction experiments were performed using a Rigaku Miniflex X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) in a 2θ range from 2° to 80° by the fixed time (FT) method. The steps used were equal to 0.05° and a time of 1 s, and a tube voltage and a current equal to 30 kV and 15 mA, respectively, were used. The radiation used was CuKα = 1.5418 Å.

2.3.6. UV–vis

Ultraviolet–visible spectral analyses were carried out in a Varian UV–vis Spectrometer Model CARY 100 using samples collected directly from the reaction system soon afterwards the removal of the modified fibers. Aliquots of 1 ml of the polyaniline solution were dispersed into 15 ml of deionized water prior to analyses.

2.3.7. Volume resistivity

ASTM D257 procedure was used for determination of the volume conductivity, Vc. All measurements were performed with a Keithley 6517-B electrometer, as described previously (Souza et al., 2008a,e, 2010a). The total sampling time and the electrification time were equal to 2 and 1 min, respectively. Around 120 measurements were performed during the electrification time. In addition, each material was tested in triplicate.

2.3.8. Magnetic force and magnetic susceptibility tests

Magnetic force tests were performed according to the analytical procedure developed in our laboratory (Souza et al., 2013). In this test, the magnetic force (mN) is presented as a function of the magnetic field (Gauss). As a reference, the magnetic force of a standard sample ($CoCl_2{\cdot}6H_2O$) was calculated according to this method. Samples were also tested using a Johnson-Matthey Mark I magnetic susceptibility balance. Tests were carried out at 23 ± 2 °C.

3. Results

Mango fibers are colorless. After the aniline polymerization, the mango fibers become greenish, a strong indicative of the protonated polyaniline presence. In addition, the observed green color increases with reaction time. Fig. 1 shows SEM micrographs of the mango fibers before and after modification with polyaniline. Fig. 1(a) shows the characteristic microstructural defects of the raw