Composites Science and Technology 88 (2013) 106–112

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Crystallinity, oxidation states and morphology of polyaniline coated curauá fibers in polyamide-6 composites

J.R. Araujo [a], C.B. Adamo [b], E. De Robertis [a], A. Yu. Kuznetsov [a], B.S. Archanjo [a], B. Fragneaud [a], C.A. Achete [a], M.-A. De Paoli [b,*]

[a] *Instituto Nacional de Metrologia, Qualidade e Tecnologia, Av. Nossa Senhora das Graças, 50, 25250-020 Duque de Caxias, RJ, Brazil*
[b] *Institute of Chemistry, University of Campinas-Unicamp, P.O. Box 6154, 13083-970 Campinas, SP, Brazil*

ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form 12 August 2013
Accepted 29 August 2013
Available online 8 September 2013

Keywords:
A. Coating
A. Short–fiber composites
B. Surface treatments
D. Photoelectron spectroscopy
E. Extrusion

ABSTRACT

Polyaniline (PAni) is one of the most studied conductive polymers due to its ability to exist in various redox states. The possibility of depositing PAni on vegetable fibers and incorporating this in polymeric matrices, such as polyamide-6, enables production of antistatic reinforced materials. In this work, polyaniline was deposited on fiber surfaces on a pilot plant scale and the composites were prepared by extrusion. The microstructures of the polyaniline coated curauá fibers and polyamide-6 were characterized by X-ray diffraction (XRD) measurements and the crystallinity degree of the polyamide-6 was evaluated by differential scanning calorimetry and XRD. Atomic force and electron scanning microscopies were employed to observe the distribution and morphology of the PAni nanoparticles. The oxidation states of PAni were determined by X-ray photoelectron spectroscopy. The results showed that polyaniline supported on the fibers presents amorphous domains and nanometer scale sizes.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Antistatic materials have very diverse technological applications. Their main purpose is to dissipate static electricity accumulated on the surface of a polymer, reducing the risk of sparks. Previous studies have shown that curauá fibers act as a reinforcing agent for thermoplastic matrices, such as polyethylene [1,2], polypropylene [3] and polyamide-6 [4,5]. There are numerous studies in the literature reporting the electrical properties of polyaniline emeraldine salt [6–8], as well as its application in blends [9,10], but there are only a few studies about composites constituted of vegetal fibers and conducting polymers [10–13].

Composites of polyamide-6 (PA-6) reinforced with curauá fibers were studied for the first time by Santos et al. [4] aiming at glass fiber replacement. These authors reported that the reinforcement effect in PA-6 was obtained with 20 wt% of curauá fibers, if suitable processing equipment and conditions are used. The modification of the surface of curauá fibers with polyaniline nanoparticles was performed for the first time by Souza et al. by *in situ* preparation of the polyaniline in the presence of the curauá fibers [11]. The incorporation of PAni on the fibers allowed a 2500 times increase in the electrical conductivity of the fibers. Blends of PAni and PA-6 were also prepared by Schettini et al. [10], comparing casting and *in situ* polymerization methods. These authors reported that the conductivity values for the blends prepared by both methods are in the range of antistatic materials.

A previous work demonstrated that polyaniline coated curauá fibers (CF-PAni) are efficient in promoting conductivity in a composite with polyamide-6 prepared in a mini-extruder [5]. This publication shows that the percolation threshold was reached with a very low content of PAni on the fibers (1–2 wt%) and, with 12 wt.% of PAni, the conductivity was quite similar to the conductivity of pure PAni.

The aim of this study is to evaluate how polyaniline and the polyaniline coated curauá fibers affect the microstructural, morphological and thermal properties of PA-6 and of the pristine curauá fibers. The oxidation state of the PAni was observed by XPS through the identification of the percentage of amine, imine and charged nitrogens present in the conducting polymer. The choice of the amount of polyaniline on the curauá fibers (12 wt.%) was based on a previous work in which the optimal results for mechanical and electrical properties were obtained [5]. Higher polyaniline content was used in DSC studies in order to evaluate the effect of PAni on the phase transitions of PA-6.

2. Materials and methods

2.1. Materials and reagents

Polyamide-6 (Nylon – MAZMID C 380, Mazzaferro Ind. e Com. de Polímeros e Fibras), aniline (Vetec, 99%), p-toluenesulfonic acid,

---

* Corresponding author. Tel.: +55 19 35213075.
E-mail address: mdepaoli@iqm.unicamp.br (M.-A. De Paoli).

0266-3538/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compscitech.2013.08.039

p-TSA, (Merck, 99%), ammonium persulfate (Synth, 98%) and heptahydrated copper sulfate (Synth, 99%) were used in this work. The curauá fibers were supplied by Embrapa-PA (Belém do Pará-Brazil), milled in a three knife rotary mill (Rone, NFA 1533), extracted with acetone in a Soxhlet apparatus for 48 h and dried at room temperature. The extraction aims to eliminate part of the lignin and promote fibrillation of the microfibril bundles. The average fiber length was calculated using "Image Pro-Plus" software for image treatment, with a sampling of 400 fibers. The fiber length varied from 3 to 7 mm.

2.2. Synthesis of polyaniline coated fibers on a pilot-plant scale

PAni synthesis and curauá fibers coating with PAni was done according to previously published studies [5,14]. The basic experimental procedures consisted of the following steps. The commercial sample of aniline was distilled under vacuum at 130 °C. The homogeneous mixture of milled fibers (300 g) in an aqueous solution of p-toluene sulfonic acid (p-TSA, 1.0 mol L^{-1}) and aniline (0.1 mol L^{-1}) was formed by stirring for 1 h at room temperature. Afterwards, 2 L of a 1 mol L^{-1} aqueous solution of p-TSA and 0.3 mol L^{-1} of oxidizing agent, $(NH_4)_2S_2O_4$ were added dropwise, while the mixture was kept under mechanical stirring at −5 °C by pumping a cooling solution through the reactor jacket. After the color of the reaction mixture became dark green, it was removed from the reactor, filtered and washed with a 2:5 (v/v) water:ethanol solution.

The amount of PAni coated on the fibers was calculated using the results provided by CHN elemental analysis [5]. The nitrogen content in the coated samples defines the amount of PAni on the fiber. Different contents of coated fibers in poliamide-6 (0, 5, 10 15 wt.%) and different concentrations of PAni on fibers (12, 30 and 40 wt.%) were tested, as shown in Table 1.

2.3. Processing conditions

PA-6/CF-PAni composites were prepared by testing various conducting fiber contents, Table 1. Before processing, PA-6 was dried in a vacuum oven at 120 °C for 4 h and the modified fibers were dried in a vacuum oven at 60 °C for 2 h. Composites were processed in a co-rotating intermeshing twin-screw extruder (Coperion Werner & Pfleiderer ZSK 26, Germany, $L/D = 44$). The temperature profile used (from feed to die) was 200–220 °C with a screw rotation of 300 rpm. The PA-6 matrix was fed using a gravimetric dosimeter (5 kg/h) connected to the main feeding funnel whilst the fibers were fed using a side-feeder at a rotation speed of 250 rpm.

2.4. Testing and characterization

The wide angle X-ray diffraction patterns were collected on a Bruker AXS D8-Focus diffratometer in reflection Bragg–Brentano geometry, using Cu Kα (Ni filter) with 2Θ steps of 0.02° and acquisition times of 15 s/step. The basic approach to calculate the crystallinity degree of polymers from the X-ray diffraction data is to obtain the ratio between the integrated intensity of the crystalline phases and the integrated intensity of the whole diffractogram. In a sample with completely random orientation of crystallites, the area under the peaks in a diffraction pattern is directly proportional to the integrated intensity [15]. The crystalline/amorphous phase ratio was estimated using Eq. (1), where A_a is the area of the diffraction peak related to an amorphous component and A_c is the residual area below Bragg peaks of the crystalline phases. The respective areas were determined using TOPAS-Academic software [16]. Two diffraction peak profiles were described by two independent pseudo Voigt functions. The amorphous component was modeled by a split pseudo Voigt function. All parameters of the fitting functions were allowed to vary.

Table 1
PA-6/CF-PAni composites formulations prepared in the twin-screw extruder.

Sample	PA-6 (wt%)	CF-PAni (wt%)	PAni[a] (wt%)	PAni doping
PA-6	100	0	0	–
PA-6/5CF-PAni	95	5	12	p-TSA
PA-6/10CF-PAni	90	10	12/30/40	p-TSA
PA-6/15CF-PAni	85	15	12/30/40	p-TSA

[a] Relative amount of PAni on fiber.

$$X = \frac{A_c}{A_c + A_a} \cdot 100\% \qquad (1)$$

The samples used for DSC analysis were cut from the extruded pellets in order to have a weight of 7 mg. After weighing, the samples were dried in an oven for 1 h at 100 °C. Samples were placed in hermetic T0 low mass aluminum pans. DSC analyses were performed in a DSC Q2000 from TA Instruments between −50 and 350 °C, under a nitrogen flow of 50 mL min^{-1} at a heating/cooling rate of 10 °C min^{-1}. The degree of crystallinity was estimated also from DSC measurements using the following equation:

$$X = \frac{\Delta H_m}{\Delta H(100\%)} \times \frac{100}{1 - w} \qquad (2)$$

In this equation, ΔH_m corresponds to the enthalpy of fusion of PA-6 taken from the experimental results, ΔH (100%) corresponds to the enthalpy of fusion of pure PA-6, used as reference ($\Delta H_m = 235$ J g^{-1}) [17] and w corresponds to the mass fraction of fibers in the composites.

SEM images were collected in a Nova Nanolab 600 dual beam microscope working at 5 keV accelerating energy and 50 pA beam current. Atomic force microscopy was performed on a JPK NanoWizard AFM operating in intermittent contact mode, using a phosphorus n-doped silicon cantilever having a resonance frequency around 84 kHz and constant force around 3 N/m.

XPS analyses were performed in ultra-high vacuum (pressure 10^{-8} Pa) using Al Kα $h\nu = 1486.7$ eV) as X-ray source, with power given by emission of 20 mA, at a voltage of 12.5 kV. For the element nitrogen, the high-resolution spectra were obtained with an analyzer pass energy of 20 eV and steps of 0.05 eV. The binding energies were referred to the carbon 1s level, set as 284.6 eV.

3. Results and discussion

3.1. X-ray diffraction measurements (XRD)

X-ray diffraction is routinely used for the determination of the crystallinity degree of polymeric compounds [18,19]. Fig. 1 shows the collected diffraction pattern of polyamide-6 (PA-6). Two crystalline structural modifications of PA-6 are known: monoclinic α-phase and hexagonal/pseudo-hexagonal γ-phase [20]. Polymeric chains of PA-6 in these structures are joined by hydrogen bonds that can be oriented parallel (α-phase) or anti-parallel (γ-phase) in relation to each other. Different factors determine the phase composition of PA-6 during crystallization from melt [21]. In particular, the crystallization at temperatures above ~190 °C results in formation of only α-phase [22]. The single crystalline α-phase expected from the thermal treatment of PA-6 of our study was indeed observed in the obtained diffraction patterns. Two strong diffraction peaks at 20.66° and 24.26°, denoted as α_1 and α_2, respectively, are characteristic of a monoclinic polymorph of PA-6 [17]. The calculated degree of crystallinity of PA-6 is 39%.

Download English Version:

https://daneshyari.com/en/article/820474

Download Persian Version:

https://daneshyari.com/article/820474

Daneshyari.com