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Conductive composites of polyamide-6 with polyaniline coated vegetal fiber

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ABSTRACT

Vegetal fibers, like curauá fibers, are used as reinforcement for thermoplastics in biocomposites, due to their low density and availability. Polyaniline can be deposited on the surface of fibers producing electrically conductive fibers. The conductivity of these PAni treated fibers suggest their use as antistatic agents. Composites of polyamide-6 with Pani-treated curaua fibers were prepared in a twin-screw extruder and specimens were obtained by transfer-molding. The electrical properties of the modified fibers and composites were measured and the mechanical properties were evaluated by tensile tests. The morphology of the composites, the fibrillation process and adhesion at the polymer/fiber interface were observed by scanning electron micrography. The ATR-FTIR showed that the most important bands of PAni were present in the modified fibers. The thermogravimetric results showed that the PAni-coated fibers present two distinct weight loss processes with a positive shift of the PAni degradation process, corresponding to a stabilization effect. The composite has a conductivity of 5×10^{-7} S cm^{-1}, three orders of magnitude higher than pure polyamide-6, and in the range of antistatic materials. The composites with PAni-coated fibers show better mechanical performance than the polymer matrix, and SEM shows good adhesion at the polymer/fiber interface.

1. Introduction

The modification of thermoplastics with conducting polymers with the aim to develop a processable and conducting material is known since 1985, when the first materials based in poly(vinyl chloride) and polypirrol were prepared [1]. Many blends and composites were prepared since than, using various thermoplastics and conducting polymers [2]. Nowadays, there is a tendency in use renewable raw materials in the preparation of composites reinforced with vegetable fibers. In the case of polyamide-6, a composite reinforced with curauá fibers were developed, substituting with advantage the traditional polyamide-glass fiber composites [3].

Polyamide-6 is an insulating matrix that generates accumulation of static electricity on its surface. The incorporation of a conducting polymer like polyaniline may decrease the surface electrical resistance, promoting a fast dissipation of static charge accumulated at the surface [4]. The addition of antistatic agents, however, has a significant effect on the properties of the product, especially mechanical properties [5].

The additives most used for reducing the surface resistivity of thermoplastics are glycerine stearate and glycerine monostearate in concentrations in the range of 0.05 to 2.5 wt% and in the presence of humidity. Another method to increase the superficial and volumetric conductivity of thermoplastics is by adding intrinsically conducting polymers, like polyaniline [6] and polypyrrol [7], or functional charges like carbon black [8], metallic fibers [9] and carbon fibers [10]. Anchoring conductive polyaniline on the surface of expandable polystyrene beads by swelling-based and in situ polymerization of aniline also provided a method for increased antistatic effect [11].

Industrial interest in filled electro-conductive polymer composites, which are comprised by a conductive filler and a polymer matrix, is growing quickly due to the variety of applications that could benefit from a material with the conductivity of a metal combined with the mechanical properties of a polymer.

In recent years a class of polymers, called intrinsically conducting polymers (ICP), has been extensively studied because of their interesting electrical properties, which can be used for technological applications such as: light-emitting diodes, electrostatic dissipation, electromagnetic interference shielding, smart windows, biosensors, chemical sensors, electromechanical and electrochromic devices, etc [12]. Among the conducting polymers, polyaniline (PAni) has been extensively investigated for several important reasons: the monomer is inexpensive, polymerization reactions are simple and the polymer has excellent environmental stability [13,14]. PAni can be obtained by chemical or electrochemical oxidation [15]. However, chemical oxidation is the better method when large amounts of PAni are needed [16]. With increasing industrial interest in PAni, synthesis by the chemical oxidation

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method has become a good candidate for its production on a pilot plant scale [17]. Ammonium peroxydisulfate (APS), $(NH_4)_2S_2O_8$, is the most used oxidant in PAni chemical syntheses, because it has good solubility in water, leading to high yields, and its byproducts are of easy disposal and low toxicity. Some works in the literature report that composites or PAni blends can have electrical conductivity at the range of antistatic materials [18].

The composites with conducting fibers have shown very promising results. The modification of curauá fibers with PAni nanoparticles was carried out for the first time by Souza et al. [19] aiming to construct a pressure sensor, since the resistivity of the treated fibers depends of the applied pressure. The authors report an increase of the conductivity of the fibers by 2500 times after modification with PAni particles.

The innovation in this work is the dispersion of curauá fibers coated with polyaniline in polyamide-6, by extrusion, to produce a material with a simultaneous improvement in mechanical and electrical properties. The aim is to use this material as an antistatic engineering plastic. Prior to deposition, the fibers, obtained from the curauá leaves, were milled and extracted with acetone to remove lignin, promote fibrillation and increase aspect ratio. These fibers were coated with polyaniline, PAni, by in situ polymerization in an acid medium. The composites were prepared in a mini-extruder to choose the best processing method for a good dispersion of the conductive fibers. After determination of the processing conditions, the composites were characterized by FTIR, thermogravimetry, mechanical properties, conductivity analysis, and scanning eletronic microscopy.

2. Experimental

2.1. Materials

The polyamide-6 used was Nylon – MAZMID C 380. The reagents used for the synthesis of PAni were: aniline (Vetec, 99%), hydrochloric acid (Synth, 37%) or p-toluene sulfonic acid (Merck, 99%), sodium chloride (Synth, 99%), ammonium peroxydisulfate (Synth, 98%) and cobalt sulfate hepta hydrated (Synth, 99%). The curauá fibers (CF) were supplied by Embrapa-PA (Belém do Pará-Brazil) and milled in a three knife rotary mill.

2.2. Curauá fiber-polyaniline preparation

Before the polymerization reaction of PAni, the aniline was distilled under vacuum at 130 °C for the elimination of oligomers and the milled curauá fibers were extracted with acetone in a soxhlet apparatus for 48 h. The modification of the fibers with polyaniline doped with hydrochloric acid followed the procedure described in the literature for the synthesis of the PAni [17]: 9 g of milled and extracted fibers were added to a solution of 400 ml of HCl (1 mol L^{-1}), NaCl (3 mol L^{-1}) and aniline (0.1 mol L^{-1}). The mixture was maintained under stirring at ambient temperature for one hour. Then, 160 ml of a solution containing $(NH_4)_2S_2O_4$ (0.3 mol L^{-1}), HCl (1 mol L^{-1}) and NaCl (3 mol L^{-1}) were added dropwise. The mixture was maintained in an ice bath under stirring for 4 h. Finally the solution was filtered and the precipitate was washed in 50% (v/v) alcoholic solution. For doping with p-toluene sulfonic acid (TSA) the same quantity of fibers were immersed in 400 ml of a solution 1 mol L of TSA and 0.1 mol L of aniline for one hour. The oxidizing agent was added in 160 ml of a solution containing 0.3 mol L of ammonium persulfate (PSA) and 1 mol L of TSA using the same conditions as the doping reaction with HCl. The filtration and washing also followed the procedure described above.

Table 1
Real contents of PAni at the curauá fibers calculated by the CHN analysis.

Sample (aniline concentration)	C (%)	H (%)	N (%)	PAni (wt%)
Curaua fiber	44.0	5.9	0.3	–
PAni	53.6	3.3	9.7	100
CF-PAni (0.05 mol L^{-1})	45.0	6.2	0.6	3.9
CF-PAni (0.10 mol L^{-1})	44.6	5.9	1.5	12.3
CF-PAni (0.15 mol L^{-1})	46.0	5.9	1.9	17.4
CF-PAni (0.20 mol L^{-1})	50.5	5.5	4.2	40.4
CF-PAni (0.50 mol L^{-1})	48.7	5.6	3.1	29.8

2.3. Processing conditions

Before processing, the curauá fibers coated with PAni (CF-PAni) were dried in a conventional oven at 80 °C for 4 h and the polyamide-6 was dried in a vacuum oven at 120 °C for 6 h. The composites were processed in a counter-rotating intermeshing twin-screw extruder with 3 heating zones (DSM explore 15 cm^3 micro compounder) coupled to a mini-injector (DSM explore 10 cm^3 transfer molding injector), to obtain the specimens. The temperature profile used from feed to die was 230, 235, 240 °C. The screw rotation speed, SRS, used was 250 rpm. The specimens were obtained by transfer molding at pressures of 600, 800 and 800 kPa, temperature profile 240 °C, and mold temperature of 60 °C. The composites PA-6/CF-PAni, CF-PAni only and PAni were prepared at the compositions shown in Table 1. The real concentration of PAni in the composites was calculated using the results provided by CHN elemental analysis. The real content of PAni was calculated as percentage of nitrogen in the CF-Pani subtracting the percentage of nitrogen in pure curaua fiber. Then, this result was compared with the percentage of nitrogen in pure PAni, Table 1.

2.4. Characterization techniques

The elemental composition of PAni, CF, and CF-PAni composites were determined by elemental analysis, using a Perkin Elmer 2400 analyzer.

For aditional characterization of the fibers, the ATR-FTIR spectra (IlluminatIR II Smiths, coupled to an optical microscope, Olympus BX51) were measured using an window area of 50 μm × 50 μm, in the region from 4000 to 650 cm^{-1}, resolution of 4 cm^{-1} and 64 scans. The properties of the fibers as reinforcement and antistatic additive were evaluated.

Electrical conductivity was measured by an adaptation of the Coleman method [20], using a Keithley 617 programmable electrometer and a four-probe sensor with gold contacts. For the measurements, the samples were pressed into pellets (ca. 1.2 cm of diameter and 0.5 mm of thickness) by applying a pressure of 1.2 Pa. Measurements were made in triplicate (three pellets) and show a high standard deviation due to the heterogeneity of the samples. The morphology of the CF-PAni composites was studied by scanning electron microscopy (SEM). The samples were maintained for 30 min in liquid N_2 before fracturing and were coated with Pt/Au (80:20) by sputtering. Composite samples were chosen from the specimens with mechanical properties closer to the average values of the mechanical tests. SEM analyses (Jeol, JSM–6360LV) were performed at an accelerating voltage of 25 kV.

The test specimens obtained by injection molding were conditioned, before the tests, for 48 h at 25 (±5) °C and 50 (±5) % relative humidity. The tensile tests were conducted according to ASTM D-638 for specimen type V in an universal testing machine (EMIC, DL2000), load cell of 5000 N, gauge length of 25.4 mm, displacement speed of 10 mm min^{-1}. Thermogravimetric analysis (TGA) were performed on ca. 7 mg samples under an argon flow of 50 ml min^{-1} at a heating rate of 10 °C min^{-1}, using a TA Instruments TGA TA2900.