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Material properties

Polyaniline-coated coconut fibers: Structure, properties and their use as conductive additives in matrix of polyurethane derived from castor oil

Claudia Merlini [a, *], Guilherme M.O. Barra [a, *], Débora P. Schmitz [a], Sílvia D.A.S. Ramôa [a], Adriana Silveira [a], Thiago Medeiros Araujo [b], Alessandro Pegoretti [b]

[a] Polymer and Composites Laboratory, Mechanical Engineering Department, Federal University of Santa Catarina (UFSC), Florianópolis, SC, Brazil
[b] Department of Industrial Engineering, University of Trento, 38123 Trento, Italy

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ABSTRACT

Electrically conducting fibers based on coconut fibers (CF) and polyaniline (PANI) were prepared through *in situ* oxidative polymerization of aniline (ANI) in the presence of CF using iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) or ammonium persulfate (APS) as an oxidant. The PANI-coated coconut fibers (CF-PANI) displayed various morphologies, electrical conductivities and percentages of PANI on the CF surface. For both systems, a PANI conductive layer was present on the CF surface, which was responsible for an electrical conductivity of around 1.5×10^{-1} and 1.9×10^{-2} S cm^{-1} for composites prepared with $FeCl_3.6H_2O$ and APS, respectively; values that are similar to that of pure PANI. In order to modify the structure and properties of polyurethane derived from castor oil (PU) both CF-PANI and pure PANI were used as conductive additives. The PU/CF-PANI composites exhibited higher electrical conductivity than pure PU and PU/PANI blends. Additionally, the PU/CF-PANI composites showed a variation in electrical resistivity according to the compressive stress applied, indicating that these materials could be applied for pressure-sensitive applications.

1. Introduction

Intrinsically conducting polymers (ICPs) offer very attractive electrical, optical and magnetic properties which can be used to expand scientific knowledge and develop technological applications. However, poor mechanical properties and processing difficulties have hampered their commercial use [1]. In the past three decades, several techniques have been developed to overcome these limitations. One of the most successful approaches is the coating of conducting polymers such as polypyrrole (PPy) or polyaniline (PANI) onto fiber surfaces. ICP-coated fibers can be commonly prepared through the *in situ* oxidative polymerization of pyrrole or aniline in the presence of a suitable fiber using an electrochemical technique [2] or an appropriate oxidant [3]. The deposition of an ICP onto a fiber surface provides the possibility of obtaining a new hybrid material displaying the functional properties of the fiber as well as the properties associated with the ICP [4–6]. The resulting conducting fibers can be of potential interest for several technological applications [3,7,8] or they can be incorporated into insulating polymer matrices to produce

* Corresponding authors. Department of Mechanical Engineering, UFSC – Campus Universitário Trindade, Caixa Postal 476, 88040-900, Florianópolis, SC, Brazil. Tel.: +55 48 3721 4019.
E-mail addresses: claudiamerl@yahoo.com.br (C. Merlini), g.barra@ufsc.br (G.M.O. Barra).

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conducting polymer composites with a low percolation threshold [4–6,9].

Different fibers have been employed to prepare conducting composites, for example, electrospun polymer fibrous mats [10], bacterial cellulose nanofibers [11,12], banana fibers [4], silk [13], polyester [14], viscose, lyocell [15], lycra [16], wool [17], cotton [2,3] and short amorphous silica fibers [9]. However, less attention has been dedicated to vegetal fibers for this purpose. These materials are good candidates because they are obtained from renewable sources and sometimes from residues generated during the transformation of natural resources into finished products [4,18]. Among plausible candidates, coconut fibers (*Cocos nucifera L.*) constitute an interesting alternative because they are available throughout the tropical regions and can be extracted from the fruit after the consumption of coconut water (a natural drink very popular in Brazil). Some publications in the literature have reported the preparation of ICP-coated vegetal fibers and their use for different applications. Kumar et al. [8] reported the preparation of PANI-coated jute through *in situ* aniline polymerization in the presence of jute fibers. The resulting composite was used as an absorbent material to remove hexavalent chromium (Cr(VI)). Araújo et al. [19,20] have employed PANI-coated curauá fibers as either a reinforcement or conductive filler to improve the electrical conductivity and mechanical properties of polyamide-6. According to the authors, the polyaniline-coated curauá fibers act simultaneously as antistatic additive and reinforcing filler for the polyamide-6 matrix. Souza et al. [7,21,22] have reported three studies concerning the *in situ* preparation of PANI nanoparticles in the presence of curauá and coconut fibers. According to the authors, the PANI-coated curauá or coconut fibers showed adequate compression sensitivity and they can be used as a pressure-sensing material. However, to the best of our knowledge, no studies on the use of PANI-coated coconut fibers as conductive filler in polymer matrices for pressure-sensitive applications, for instance, have been reported in the literature. Furthermore, all studies reported in the literature on the preparation of PANI-coated vegetal fibers have employed ammonium persulfate (APS) as an oxidant. On the other hand, iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) is also a good oxidant for producing these conducting fibers because, in aqueous solutions, iron (III) creates aquo-hydroxyl complexes some of which can be adsorbed onto a cellulose surface [23,24]. Under these conditions, the polymerization takes place preferentially on the fiber surface to form a conducting polymer layer that fully coats the cellulose fibers [4–6,11,25,26].

Considering the reported advantages of $FeCl_3.6H_2O$ and the possibility of using PANI-coated coconut as conducting filler in polymer matrix for pressure-sensing applications, the objective of this study was to develop conducting fibers through *in situ* oxidative polymerization of aniline (ANI) onto the surface of coconut fibers (CF) using iron (III) chloride hexahydrate. In order to evaluate the influence of the oxidant on the structure and properties of the polyaniline-coated coconut fiber (CF-PANI), APS was also employed in the ANI polymerization on the CF surface. The resulting CF-PANI was incorporated in a thermosetting polyurethane (PU) derived from castor oil in order to produce a conducting polymer composite with suitable properties for pressure-sensing applications.

2. Experimental

2.1. Materials

Coconut fibers (CF) were kindly supplied by a rural research agency in Santa Catarina, southern Brazil (EPAGRI-*Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina*). Aniline (ANI) (analytical grade, Merck) was distilled under vacuum and stored in a refrigerator. Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) (analytical grade, Vetec) and ammonium persulfate (APS) $(NH_4)_2S_2O_8$ (Nuclear) were used without purification.

The polyol derived from castor oil (IMPERVEG® UG 132 A) with molar mass of 928 g mol^{-1} and the pre-polymer (IMPERVEG® UG 132 B) were acquired from IMPERVEG® *Comércio e Prestações de Serviço Ltda*.

2.2. Preparation of PANI-coated coconut fibers (CF-PANI)

PANI-coated coconut fibers (CF-PANI) with a length of 10 mm were prepared through *in situ* oxidative polymerization. The reactions were performed in the presence of HCl aqueous solution using iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) or ammonium persulfate (APS) $(NH_4)_2S_2O_8$ as oxidants. The samples were denominated as CF-PANI.$FeCl_3$ and CF-PANI.APS, respectively. Firstly, 0.5 g of CF was immersed in 0.028 L of HCl aqueous solution (0.1 mol L^{-1}) under stirring at room temperature and aniline (0.2 mol L^{-1}) was then added. After 10 min the oxidant, $FeCl_3.6H_2O$ or APS, dissolved in 0.028 L of distilled water, was slowly added. The polymerization was carried out using $FeCl_3.6H_2O$/ANI and APS/ANI molar ratios of 3/1 and 1/1, respectively. After 6 h, the CF-PANI composites were washed with the aqueous HCl solution in order to extract the byproducts and residues of the reaction and vacuum dried at room temperature. For comparison, pure PANI samples were also synthesized using similar methodologies, with $FeCl_3.6H_2O$ (PANI.$FeCl_3$) and APS (PANI.APS).

2.2.1. Preparation of PU/CF-PANI and PU/PANI composites

Polyaniline-coated coconut fibers synthesized from $FeCl_3.6H_2O$ were used as conductive filler in polyurethane derived from castor oil. The prepolymer and polyol (mass ratio of 1/2), and CF-PANI.$FeCl_3$ were blended in a reactor under vacuum for 5 min. This mixture was poured into a metallic mold and subjected to compression molding at 10.7 MPa at room temperature for 4 hours. Composites with randomly-oriented CF-PANI.$FeCl_3$ (denominated as PU/CF-PANI.$FeCl_3$) with weight fractions of 5, 10, 15, 20 and 25 wt.% were obtained. Composites containing only pure PANI were also prepared using the same weight fractions of PANI.$FeCl_3$ (namely PU/PANI.$FeCl_3$).

2.3. Characterization

The electrical conductivity of the PANI, CF-PANI and high-conductivity PU/CF-PANI and PU/PANI composites