Contents lists available at ScienceDirect

Polymer Testing

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

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

ARTICLE INFO

Article history: Received 10 May 2014 Accepted 15 June 2014 Available online 23 June 2014

Keywords: Intrinsically conducting polymer Polyaniline Coconut fibers Polyurethane

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.}6H₂O) 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.}6H₂O 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 showed a variation in electrical resistivity according to the compressive stress applied, indicating that these materials could be applied for pressure sensitive applications.

© 2014 Elsevier Ltd. All rights reserved.

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

http://dx.doi.org/10.1016/j.polymertesting.2014.06.005 0142-9418/© 2014 Elsevier Ltd. All rights reserved. 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).

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 PANIcoated 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 PANIcoated 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 (FeCl₃.6H₂O) 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 FeCl₃.6H₂O 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 (FeCl₃.6H₂O) (analytical grade, Vetec) and ammonium persulfate (APS) (NH₄)₂S₂O₈ (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 (FeCl₃.6H₂O) or ammonium persulfate (APS) (NH₄)₂S₂O₈ as oxidants. The samples were denominated as CF-PANI.FeCl₃ 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 $(0.2 \text{ mol } L^{-1})$ was then added. After 10 min the oxidant, FeCl₃.6H₂O or APS, dissolved in 0.028 L of distilled water, was slowly added. The polymerization was carried out using FeCl₃.6H₂O/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 FeCl₃.6H₂O (PANI.FeCl₃) and APS (PANI.APS).

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

Polyaniline-coated coconut fibers synthesized from FeCl₃.6H₂O were used as conductive filler in polyurethane derived from castor oil. The prepolymer and polyol (mass ratio of 1/2), and CF-PANI.FeCl₃ 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.FeCl₃ (denominated as PU/CF-PANI.FeCl₃) 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.FeCl₃ (namely PU/PANI.FeCl₃).

2.3. Characterization

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

were measured using the four-probe standard method with a Keithley 6220 current source to apply the current and a Keithley Model 6517A electrometer to measure the potential difference. For pure PU, CF and high-resistivity polymer composites, the volumetric conductivity measurements were performed using a Keithley 6517A electrometer connected to a Keithley 8009 test fixture. Measurements of each sample were repeated at least eight times at room temperature.

Micrographs of the CF, CF-PANI and PU/CF-PANI were obtained using scanning electron microscopy (SEM) on a Jeol model JSM-6390LV microscope. The samples were coated with gold and analyzed using an applied tension of 10 to 15 kV. The PU/CF-PANI composites were previously fractured in nitrogen.

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was performed on a Bruker

spectrometer, model TENSOR 27, in the range of wave numbers from 4000 to 600 cm^{-1} by accumulating 32 scans at a resolution of 4 cm⁻¹.

The thermogravimetric analysis (TGA) was performed on a STA 449 F1 Jupiter[®] (Netzsch) thermogravimetric analyzer. The samples were heated from 35 to 700 °C at a heating rate of 10 °C min⁻¹ under a nitrogen flow of 50 cm³ min⁻¹. The amount of PANI deposited onto the CF was calculated from the TGA curves, comparing the amounts of residue of CF-PANI.FeCl₃ or CF-PANI.APS composite with those of the CF and PANI prepared under the same conditions, according to Merlini, Ramôa and Barra [4].

Electrical sensitivity under pressure was evaluated on the PU/CF-PANI.FeCl₃ composites in a setup that consists of an electromechanical universal testing machine (Instron, Model 5969) coupled with an electrometer (Keithley 6517A) to acquire the resistivity data. An RJ45 interface and

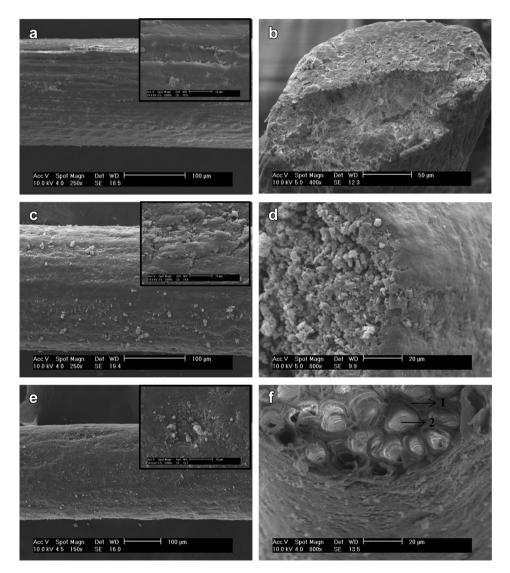


Fig. 1. SEM micrographs of surface at lower and higher magnification and cross-sections of pure CF (a and b), CF-PANI.FeCl₃ (c and d) and CF-PANI.APS (e and f). In the micrograph (f) the presence of the lumen (1) and the cell wall (2) is also evidenced.

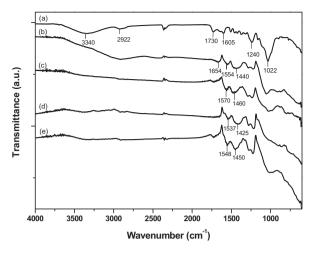
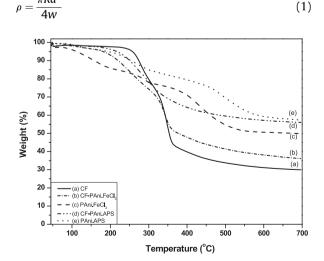


Fig. 2. FTIR of (a) uncoated coconut fibers, (b) PANLAPS, (c) CF-PANLAPS. (d) PANLFeCl₃ and (e) CF-PANLFeCl₃.

a GPIB were used to connect the Instron and electrometer to the computer, respectively. The tests were performed according to the methodology used by Merlini, Barra, Medeiros Araujo and Pegoretti [27]. The sample with a diameter of 22.5 mm and 400-800 µm thickness was placed between two circular electrodes confined in a cylinder made of poly(tetrafluoroethylene). The assembly was then placed between the testing plates of the universal testing machine. The electrodes were connected to the electrometer in order to measure the volume resistivity of the composite during controlled loading and unloading cycles. The samples were loaded up to 5 MPa at a loading rate of 1 MPa min⁻¹, the compressive stress was then released at the same rate. For each sample, loadingunloading sequences of 5 and 20 cycles were performed on different specimens. The electrical resistivity (p) values $(in \Omega cm)$ were calculated using Equation 1, where R is the measured resistance (Ω), *d* is the sample diameter (cm) and w is the specimen thickness (cm).



 πRd^2

Fig. 3. TG curves for (a) uncoated coconut fibers, (b) FC-PANI.FeCl₃, (c) PANI.FeCl₃ (d) FC-PANI.APS and (e) PANI.APS.

Table 1

TGA parameters of CF, PANI and CF-PANI, percentage of PANI on the conducting fibers and electrical conductivity.

Sample	Residue from TGA (%)	PANI content (%)	Electrical conductivity (S cm ⁻¹)
CF	29.95	_	$(3.13 \pm 0.27) \times 10^{-10}$
PANI.FeCl ₃	49.86	_	4.47 ± 0.39
PANI.APS	57.67	_	1.13 ± 0.23
CF-PANI.FeCl ₃	36.10	30.89	$(1.5 \pm 0.39) \times 10^{-1}$
CF-PANI.APS	56.01	94.17	$(1.9 \pm 0.35) \times 10^{-2}$

3. Results and discussion

3.1. Characterization of polyaniline-coated coconut fibers

SEM micrographs of the surfaces and cross-section of the uncoated coconut fiber, CF-PANI.FeCl₃ and CF-PANI.APS are shown in Fig. 1. CF was characterized by a slightly rough surface (Fig. 1 (a)) while on the CF-PANI surface the presence of PANI particles can be detected (Fig. 1 (c) and 1 (e)). More detailed morphologies of CF, CF-PANI.FeCl₃ and CF-PANI.APS are shown in Fig. 1 (b), (d) and (f), respectively. The micrograph on CF-PANI.FeCl₃ revealed that the polyaniline formed a compact and uniform layer completely covering the fiber coconut surface. On the other hand, CF-PANI.APS showed a uniform layer consisting of PANI particles lying close together. The cross-section morphology of the coconut fibers (Fig. 2 (f)) reveals the presence of a lumen (1) surrounded by the cell walls (2). The cell walls are made of crystalline cellulose microfibrils embedded in a hemicellulose and lignin matrix which links the cellulose microfibrils through hydrogen bonds, forming a threedimensional network [28].

Fig. 2 shows the FTIR spectra of the coconut fiber, PANI.FeCl₃, PANI.APS, CF-PANI.FeCl₃ and CF-PANI.APS. The FTIR spectrum of the coconut fibers reported in Fig. 2 (a) is typical of a lignocellulosic material, with broad absorption bands at 3340 cm⁻¹ and 2922 cm⁻¹ due to the stretching vibrations of the hydroxyl and C–H groups, respectively [4,28]. The bands at 1730 and 1605 cm⁻¹ can be ascribed to the C=O groups of the hemicellulose and lignin, respectively. The bands at 1240 cm⁻¹ and 1022 cm⁻¹ can be

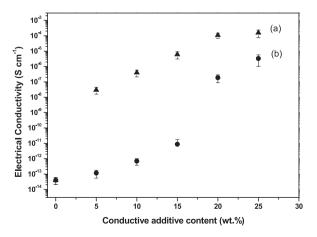


Fig. 4. Electrical conductivity as a function of conductive filler content (by weight) in the composites: (a) PU/CF-PANI.FeCl₃ and (b) PU/PANI.FeCl₃.

Table 2

Percolation parameters of CF-PANI.FeCl_3 and PANI.FeCl_3-loaded PU mixtures.

Conductive filler	<i>f</i> _p (wt.%)	Critical exponent (t)	Linear correlation coefficient (R)
PANI.FeCl ₃	14.0	5.4	0.99
CF-PANI.FeCl ₃	4.2	4.9	0.97

assigned to the C–O stretching vibration of the acetyl group of hemicelluloses and plane deformation of the aromatic C–H groups, respectively [29–32]. PANI.APS (Fig. 2 (b)) exhibits characteristic absorption bands at 1554 cm⁻¹ and 1440 cm⁻¹, assigned to the stretching vibrations of the quinoid and benzoid structures, respectively [33]. These bands for PANI.FeCl₃ (Fig. 2 (d)) are located at 1537 cm⁻¹ and 1425 cm⁻¹. The spectra for the CF-PANI.APS (Fig. 2 (c)) and CF-PANI.FeCl₃ (Fig. 2 (e)) show overlapped absorption bands related to the corresponding PANI, however, these bands are blue-shifted, probably due to the site-specific interaction of -N-H and -O-H groups of polyaniline and CF, respectively [25]. Additionally, the bending modes of the OH groups present on the CF disappear, suggesting that the coconut fibers were completely coated by a polyaniline laver.

The thermogravimetric curves of the coconut fiber, PANI.FeCl₃, PANI.APS, CF-PANI.FeCl₃ and CF-PANI.APS are shown in Fig. 3. According to Fig. 3 (a) the weight loss of the coconut fibers at 280 °C and 350 °C corresponds to hemicellulose and lignin degradation and the decomposition of

cellulose, respectively [20]. PANI.FeCl₃ and PANI.APS display three main steps of weight loss. For both samples, the first peak at around 125 °C is related to the elimination of water and small adsorbed molecules. The stages of weight loss at 290 °C and 430 °C for PANI.FeCl₃ and 250 °C and 500 °C for PANI.APS are assigned to the release of Cl counter ions and polymeric chain degradation, respectively. The TGA curves of the CF-PANI.FeCl₃ and CF-PANI.APS display similar behavior to that observed for the pure coconut fibers, however, the polyaniline-coated coconut fibers showed lower onset degradation temperatures which can be attributed to the loss of intermolecular hydrogen bonds of cellulose due to the presence of PANI [11].

Table 1 shows the TGA parameters for CF, PANI and their corresponding conducting fibers, the percentage of PANI on the coconut fiber surface and the electrical conductivity. The percentages of PANI on the CF surface calculated from the TGA curves were 30.89 and 94.17 wt.%, for CF-PANI.FeCl₃ and CF-PANI.APS, respectively. It is interesting to note that the electrical conductivity of the PANI-coated coconut fibers was not influenced by the amount of PANI incorporated on the fiber surface, since the CF-PANI composite prepared using APS displayed a higher amount of PANI (94 wt.%) on the fiber surface but an electrical conductivity lower than CF-PANI prepared using FeCl₃.6H₂O. Based on this result, we decided to focus the attention on the conducting fibers prepared with FeCl₃.6H₂O as a conductive filler for the polyurethane matrix due to their higher electrical conductivity and lower PANI content (31 wt.%) compared with CF-PANI.APS.

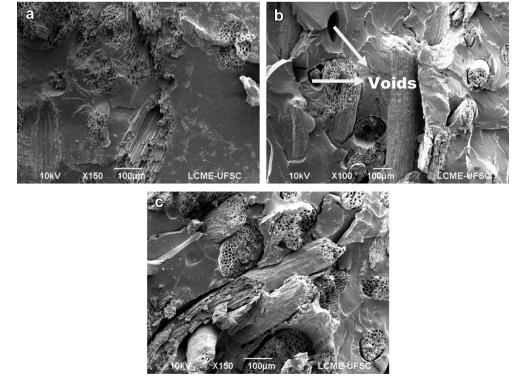


Fig. 5. Scanning electron micrographs of the PU/CF-PANI.FeCl3 composites with CF-PANI.FeCl3 content: (a) 15 wt.%, (b) 20 wt.% and (c) 25 wt.%.

3.2. Characterization of PU/CF-PANI.FeCl₃ and PU/PANI.FeCl₃ composites

Fig. 4 shows the electrical conductivity of PU filled with polyaniline-coated coconut fibers (PU/CF-PAN-I.FeCl₃) and pure PANI (PU/PANI.FeCl₃) as a function of the content of conductive additive. As the CF-PANI.FeCl₃ content increases, the electrical conductivity enhances significantly due to the formation of a conducting pathway through the PU matrix [4]. Similar behavior can

be observed for the PU/PANI.FeCl₃ composites prepared through the same process. However, the values for the electrical conductivity are lower than those found for the corresponding PU/CF-PANI.FeCl₃ composites, probably due to the lower aspect ratio of the PANI particles when compared with the CF-PANI. The PU/CF-PANI.FeCl₃ composites show higher electrical conductivity than that observed for PU filled with polypyrrole-coated banana fibers reported by this research group in a previous publication [4].

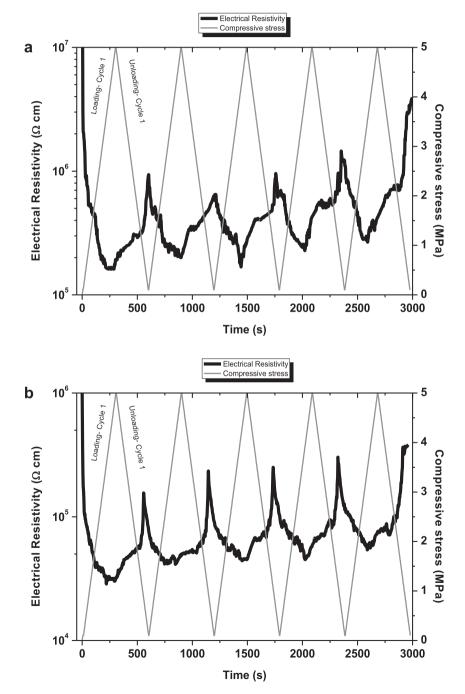


Fig. 6. Electrical resistivity as a function of compressive loading-unloading stress cycles applied to PU/CF-PANI.FeCl₃ composites with CF-PANI.FeCl₃ contents of (a) 20 wt.% and (b) 25 wt.%.

The data shown in Fig. 4 were fitted by the well-known percolation scaling law:

$$\sigma_{\rm f} = c (f - f_{\rm p})^{\rm t} \tag{2}$$

where, *c* is a constant, *t* a critical exponent, σ_f the conductivity, *f* the fraction of the conductive medium and f_p the fraction at the percolation threshold, expressed as a weight fraction.

The experimental data were used to construct a plot of σ versus log $(f - f_p)$ from which it is possible to estimate the percolation threshold of the system [9,34]. The values of f_p and t for the composites are given in Table 2. The lower f_p value for the PU/CF-PANI.FeCl₃ composite when compared to the PU/PANI.FeCl₃ may be associated with the high aspect ratio of the CF-PANI fibers dispersed in the PU matrix. It is well known that by increasing the aspect ratio of the conductive filler the percolation threshold can be decreased, i.e., a lower filler concentration is necessary to ensure physical contact between fibers when compared with spherical particles. Critical exponent values are higher than those predicted from classical percolation theory and can be explained by a tunneling-percolation process [35,36].

The SEM pictures of the PU/CF-PANI.FeCl₃ composite surfaces fractured under cryogenic conditions are shown in Fig. 5. In particular, in Fig. 5 (a) the fracture surface of the composite with 15 wt.% of CF-PANI.FeCl₃ clearly indicates that a good fiber-matrix adhesion is reached in this case. On the other hand, as the content of conducting fibers is increased, the presence of voids in the matrix and at the fiber/matrix interface can be observed (Fig. 5 (b) and (c)).

Fig. 6 shows the variation in the electrical resistivity of PU/CF-PANI.FeCl3 composites with 20 and 25 wt.% of CF-PANI.FeCl₃ subjected to five consecutive compressive loading-unloading stress cycles. Pure PU and PU/PANI.FeCl₃ composites with 5, 10 and 15 wt.% of CF-PANI.FeCl₃ content showed no change in the electrical resistivity when the compressive stress was applied. On the other hand, the compressive stress had an effect on the electrical resistivity of the PU/CF-PANI.FeCl3 composites containing a conducting fiber concentration above 20 wt.%. When the composites are subjected to compressive stress (loading cycle), the resistivity value decreases by about one order of magnitude. This behavior may be associated to the formation of new pressure-induced conducting pathways. Moreover, it is interesting to note that the initial resistivity value almost returns to its previous value after the sample loading is removed.

Fig. 7 shows the hysteresis effect on the stress-strain curves when the PU/CF-PANI.FeCl₃ composite with 25 wt.% of CF-PANI.FeCl₃ was subjected to 5 consecutive loading/unloading cycles. A residual irreversible strain can be observed after the first loading-unloading step which is probably related to the accommodation of the sample between the electrodes.

The dependence of the electrical conductivity on the compressive stress during 50 consecutive loading - unloading cycles performed on the PU/CF-PANI.FeCl₃ with 25 wt.% of CF-PANI.FeCl₃ is shown in Fig. 8. The loading-unloading process induces a slight difference in the relative conductivity between the first and the fiftieth cycles.

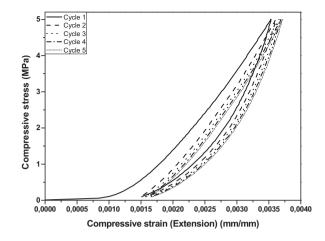


Fig. 7. Compressive stress as a function of compressive strain during 5 loading and unloading cycles for PU/CF-PANI.FeCl₃ composites with 25 wt.% of CF-PANI.FeCl₃.

This behavior is probably due to a breakdown in the conductive pathway and/or plastic deformation of the insulating polymer matrix during the loading and unloading cycles [10,37,38].

4. Conclusions

A conducting fiber based on CF-PANI was successfully obtained through the *in situ* oxidative chemical polymerization of ANI in the presence of CF using FeCl₃.6H₂O or APS as an oxidant. Scanning electron micrographs revealed that the CF surface was completely coated with a uniform PANI layer which led to an electrical resistivity quite similar to that of the pure PANI. AT-FTIR spectra revealed a strong intermolecular interaction between -N-H groups in the PANI ring and the -OH functional group in the CF. The CF-PANI.FeCl₃ fibers were chosen as a conductive filler to be incorporated into the PU matrix due to their higher electrical conductivity and the lower PANI content on the CF surface compared with the conducting fibers containing

10 -- Cycle 1 - -- Cvcle 2 - Cycle 10 - Cvcle 25 Cycle 50 Electrical Resistivity (Ω cm) 10⁵ 10 ò 2 3 4 5 Compressive stress (MPa)

Fig. 8. Electrical resistivity as a function of the loading and unloading cycle for PU/FC-PANI.FeCl₃ with 25 wt.% of FC-PANI.FeCl₃.

CF-PANI.APS. The PU/CF-PANI.FeCl₃ composites with 20 wt.% and 25 wt.% of CF-PANI.FeCl₃ content showed a variation in the electrical resistivity when compressive stress was applied. The results observed in this study open new possibilities for the use of conducting coconut fibers as a conductive filler in an insulating polymer. These results will be useful in the development of conducting polymer composites for sensor pressure applications.

Acknowledgements

The authors acknowledge the financial support of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) grant number 304090/2013-1, Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES) and Fundação de Amparo à Pesquisa e Inovação do Estado de Santa Catarina (FAPESC 3434/2012). Also, we extend our sincere gratitude to the Central Electronic Microscopy Laboratory, Federal University of Santa Catarina (LCME-UFSC).

References

- A. Varesano, L. Dall'Acqua, C. Tonin, A study on the electrical conductivity decay of polypyrrole coated wool textiles, Polymer Degradation and Stability 89 (2005) 125–132.
- [2] K.F. Babu, R. Senthilkumar, M. Noel, M.A. Kulandainathan, Polypyrrole microstructure deposited by chemical and electrochemical methods on cotton fabrics, Synthetic Metals 159 (2009) 1353–1358.
- [3] N. Onar, A.C. Aksit, M.F. Ebeoglugil, I. Birlik, E. Celik, I. Ozdemir, Structural, electrical, and electromagnetic properties of cotton fabrics coated with polyaniline and polypyrrole, Journal of Applied Polymer Science 114 (2009) 2003–2010.
- [4] C. Merlini, S.D.A.S. Ramôa, G.M.O. Barra, Conducting polypyrrolecoated banana fiber composites: preparation and characterization, Polymer Composites 34 (2013) 537–543.
- [5] J.H. Johnston, F.M. Kelly, J. Moraes, T. Borrmann, D. Flynn, Conducting polymer composites with cellulose and protein fibres, Current Applied Physics 6 (2006) 587–590.
- [6] F.M. Kelly, J.H. Johnston, T. Borrmann, M.J. Richardson, Functionalised hybrid materials of conducting polymers with individual fibres of cellulose, European Journal of Inorganic Chemistry 2007 (2007) 5571–5577.
- [7] F.G. Souza, G.E. Oliveira, C.H.M. Rodrigues, B.G. Soares, M. Nele, J.C. Pinto, Natural Brazilian Amazonic (Curauá) fibers modified with polyaniline nanoparticles, Macromolecular Materials and Engineering 294 (2009) 484–491.
- [8] P.A. Kumar, S. Chakraborty, M. Ray, Removal and recovery of chromium from wastewater using short chain polyaniline synthesized on jute fiber, Chemical Engineering Journal 141 (2008) 130–140.
- [9] C. Merlini, B.S. Rosa, D. Muller, L.G. Ecco, S.D.A.S. Ramoa, G.M.O. Barra, Polypyrrole nanoparticles coated amorphous short silica fibers: synthesis and characterization, Polymer Testing 31 (2012) 971–977.
- [10] C. Merlini, R.d.S. Almeida, M.A. D'Ávila, W.H. Schreiner, G.M.d.O. Barra, Development of a novel pressure sensing material based on polypyrrole-coated electrospun poly(vinylidene fluoride) fibers, Materials Science and Engineering B 179 (2014) 52–59.
- [11] D. Müller, J.S. Mandelli, J.A. Marins, B.G. Soares, L.M. Porto, C.R. Rambo, G.M.O. Barra, Electrically conducting nanocomposites: preparation and properties of polyaniline (PAni)-coated bacterial cellulose nanofibers (BC), Cellulose 19 (2012) 1645–1654.
- [12] J.A. Marins, B.G. Soares, K. Dahmouche, S.J.L. Ribeiro, H. Barud, D. Bonemer, Structure and properties of conducting bacterial cellulose-polyaniline nanocomposites, Cellulose 18 (2011) 1285–1294.
- [13] I. Cucchi, A. Boschi, C. Arosio, F. Bertini, G. Freddi, M. Catellani, Biobased conductive composites: preparation and properties of polypyrrole (PPy)-coated silk fabrics, Synthetic Metals 159 (2009) 246–253.
- [14] J. Molina, A.I. del Río, J. Bonastre, F. Cases, Electrochemical polymerisation of aniline on conducting textiles of polyester covered with polypyrrole/AQSA, European Polymer Journal 45 (2009) 1302–1315.

- [15] L. Dall'Acqua, C. Tonin, A. Varesano, M. Canetti, W. Porzio, M. Catellani, Vapour phase polymerisation of pyrrole on cellulosebased textile substrates, Synthetic Metals 156 (2006) 379–386.
- [16] J. Wu, D. Zhou, C.O. Too, G.G. Wallace, Conducting polymer coated lycra, Synthetic Metals 155 (2005) 698–701.
- [17] A. Varesano, C. Tonin, Improving electrical performances of wool textiles: synthesis of conducting polypyrrole on the fiber surface, Textile Research Journal 78 (2008) 1110–1115.
- [18] E. Mussatti, C. Merlini, G.M.D. Barra, S. Guths, A.P.N. de Oliveira, C. Siligardi, Evaluation of the properties of iron oxide-filled castor oil polyurethane, Materials Research 16 (2013) 65–70.
- [19] J.R. Araujo, C.B. Adamo, M.V. Costa e Silva, M.A. De Paoli, Antistaticreinforced biocomposites of polyamide-6 and polyaniline-coated curauá fibers prepared on a pilot plant scale, Polymer Composites 34 (2013) 1081–1090.
- [20] J.R. Araujo, C.B. Adamo, M.-A. De Paoli, Conductive composites of polyamide-6 with polyaniline coated vegetal fiber, Chemical Engineering Journal 174 (2011) 425–431.
- [21] F.G.d. Souza, P.H.S. Picciani, E.V.d. Rocha, G.E.d. Oliveira, Estudo das propriedades mecânicas e elétricas de fibras de curauá modificada com polianilina, Polímeros 20 (2010) 377–382.
- [22] F.G.d. Souza, L.O. Paiva, R.C. Michel, G.E. de Oliveira, Modificação da fibra de coco com polianilina e o seu uso como sensor de pressão, Polímeros 21 (2011) 39–46.
- [23] W.M. Hosny, A.H. Basta, H. El-Saied, Metal chelates with some cellulose derivatives: V. synthesis and characterization of some iron(-III) complexes with cellulose Ethers, Polymer International 42 (1997) 157–162.
- [24] C. Sasso, E. Zeno, M. Petit-Conil, D. Chaussy, M.N. Belgacem, S. Tapin-Lingua, D. Beneventi, Highly conducting polypyrrole/cellulose nanocomposite films with enhanced mechanical properties, Macromolecular Materials and Engineering 295 (2010) 934–941.
- [25] D. Muller, C.R. Rambo, L.M. Porto, W.H. Schreiner, G.M. Barra, Structure and properties of polypyrrole/bacterial cellulose nanocomposites, Carbohydrate Polymers 94 (2013) 655–662.
- [26] D. Beneventi, S. Alila, S. Boufi, D. Chaussy, P. Nortier, Polymerization of pyrrole on cellulose fibres using a FeCl3 impregnation- pyrrole polymerization sequence, Cellulose 13 (2006) 725–734.
- [27] C. Merlini, G.M.O. Barra, T. Medeiros Araujo, A. Pegoretti, Electrically pressure sensitive poly(vinylidene fluoride)/polypyrrole electrospun mats, RSC Advances 4 (2014) 15749.
- [28] C. Merlini, V. Soldi, G.M.O. Barra, Influence of fiber surface treatment and length on physico-chemical properties of short random banana fiber-reinforced castor oil polyurethane composites, Polymer Testing 30 (2011) 833–840.
- [29] F. Corrales, F. Vilaseca, M. Llop, J. Girones, J.A. Mendez, P. Mutje, Chemical modification of jute fibers for the production of greencomposites, Journal of Hazardous Materials 144 (2007) 730–735.
- [30] J.L. Guimarães, E. Frollini, C.G. da Silva, F. Wypych, K.G. Satyanarayana, Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil, Industrial Crops and Products 30 (2009) 407–415.
- [31] A.I.S. Brígida, V.M.A. Calado, L.R.B. Gonçalves, M.A.Z. Coelho, Effect of chemical treatments on properties of green coconut fiber, Carbohydrate Polymers 79 (2010) 832–838.
- [32] K. Bilba, M.A. Arsene, A. Ouensanga, Study of banana and coconut fibers botanical composition, thermal degradation and textural observations, Bioresource Technology 98 (2007) 58–68.
- [33] N.V. Blinova, J. Stejskal, M. Trchová, J. Prokeš, M. Omastová, Polyaniline and polypyrrole: a comparative study of the preparation, European Polymer Journal 43 (2007) 2331–2341.
- [34] M.E. Leyva, G.M.O. Barra, B.G. Soares, Conductive polyaniline–SBS blends prepared in solution, Synthetic Metals 123 (2001) 443–449.
- [35] S.D.A.S. Ramôa, G.M.O. Barra, R.V.B. Oliveira, M.G. de Oliveira, M. Cossa, B.G. Soares, Electrical, rheological and electromagnetic interference shielding properties of thermoplastic polyurethane/carbon nanotube composites, Polymer International 62 (2013) 1477–1484.
- [36] C. Grimaldi, T. Maeder, P. Ryser, S. Strässler, Critical behaviour of the piezoresistive response in RuO2–glass composites, Journal of Physics D: Applied Physics 36 (2003) 1341–1348.
- [37] G.M.O. Barra, R.R. Matins, K.A. Kafer, R. Paniago, C.T. Vasques, A.T.N. Pires, Thermoplastic elastomer/polyaniline blends: Evaluation of mechanical and electromechanical properties, Polymer Testing 27 (2008) 886–892.
- [38] F.G. Souza, R.C. Michel, B.G. Soares, A methodology for studying the dependence of electrical resistivity with pressure in conducting composites, Polymer Testing 24 (2005) 998–1004.