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Structure and properties of polypyrrole/bacterial cellulose nanocomposites

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ABSTRACT

An electrically conducting composite based on bacterial cellulose (BC) and polypyrrole (PPy) was prepared through *in situ* oxidative polymerization of pyrrole (Py) in the presence of BC membrane using ammonium persulfate (APS), as an oxidant. The electrical conductivity, morphology, mechanical properties and thermal stability of the composites obtained using APS (BC/PPy·APS) were evaluated and compared with BC/PPy composites prepared using as oxidant agent Iron III chloride hexahydrate ($FeCl_3{\cdot}6H_2O$). The morphology of the BC/PPy·APS composites is characterized by spherical conducting nanoparticles uniformly distributed on the BC nanofiber surface, while the composites produced with $FeCl_3{\cdot}6H_2O$ (BC/PPy·$FeCl_3$) is composed of a continuous conducting polymer layer coating the BC-nanofibers. The electrical conductivity of BC/PPy·$FeCl_3$ was 100-fold higher than that found for BC/PPy·APS composites. In order to understand the site-specific interaction between PPy and BC functional groups, both composites were characterized by Fourier transform infrared (attenuated total reflectance mode) spectroscopy attenuation reflectance (FTIR-ATR) and X-ray photoelectron spectrometry (XPS). The affinity between functional groups of PPy·$FeCl_3$ and BC is higher than that found for BC/PPy·APS composite. In addition, the tensile properties were also influenced by the chemical affinity of both components in the polymer composites.

1. Introduction

Intrinsically conducting polymers (ICPs), such as polypyrrole (PPy) and polyaniline (PAni)-coated fibers with functional properties have been studied extensively due to their potential in many technological application, such as electronic displays (Spinks, Xi, Zhou, Troung, & Wallace, 2004), *scaffolds* for tissue engineering (Castro, Polo, Labrato, Cañete, & Rama, 2010; Cucchi et al., 2009; Stewart, Liu, Clark, Kapsa, & Wallace, 2012), smart sensors and actuators (Al-Mashat, Tran, Wlodarski, Kaner, & Kalantar-Zadeh, 2008; Savage, 2009), among others. A literature overview reveals interesting results concerning the use of fibers, such as polyester (Molina, Del Río, Bonastre, & Cases, 2009), polyamide (Kaynak, Najar, & Foitzik, 2008), cotton (Onar et al., 2009), cellulose derivate (Beneventi, 2010; Kelly, Johnston, Borrmann, & Richardson, 2007; Mo, Zhao, Chen, Niu, & Shi, 2009), and others, as a templates for preparing conducting polymer coated fibrous matrixes.

In recent years, considerable attention has been focused on the preparation of polypyrrole or polyaniline-coated nanofibers network through electrospinning technique, given the possibility to produce new nanostructured composites with the combination of high surface area, light weight, flexibility, toughness, high mechanical strength, fast diffusion of gas or liquid molecules, capacity to entrap biomolecules and serve as carriers in biological medium with the electrical, optical and magnetic behavior of ICPs (Chronakis, Grapenson, & Jakob, 2006; Ismail, Min, & Kim, 2009; Lee, Bashur, Goldstein, & Schmidt, 2009; Li, Guo, Wei, MacDiarmid, & Lelkes, 2006; Suttar et al., 2007). Despite the wide use of electrospinning for fabrication of conductive nanofibrous composites (Choi, Lee, Choi, Jung, & Shim, 2010), this process commonly involves organic solvent evaporation, which imparts a significant environmental impact. Among eco-friendly nanofibrous materials, bacterial cellulose (BC) has also been used as insulating polymer template to develop conductive polymer composites, especially because of its biocompatibility, low density, and noticeable properties of cellulose even in a hydrogel form (Rambo et al., 2008). BC can be mass produced in a wide variety of shapes and sizes through the control of cellulose biosynthesis in aqueous solution. In addition, this material exhibits interconnected nanofibers network similar to those prepared through electrospinning method.

There are some reports concerning the preparation of polyaniline-coated BC composites through *in situ* oxidative polymerization of aniline in BC membrane, using ammonium persulfate (APS) or Iron III chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) (Hu, Chen, Yang, Liu, & Wang, 2011; Lee, Kim, & Yang, 2012a; Marins et al., 2011;

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Müller et al., 2012). Lee et al. have recently published a report dealing the production of nanostructured conductive PAni/BC composites through interfacial polymerization (Lee, Chung, Kwon, Kim, & Tze, 2012b).

On the other hand, it has been reported previously by our research group the production of conducting composite composed of BC and polypyrrole (PPy) through *in situ* pyrrole (Py) polymerization on BC nanofibers, using $FeCl_3{\cdot}6H_2O$ (Müller, Rambo, Recouvreux, Porto, & Barra, 2011b). However, the correlation between structure and mechanical properties of BC/PPy·$FeCl_3$ system is particularly unclear. Moreover, it is well known that under aggressive reaction condition, such as high amount of $FeCl_3$ and strong acid medium, cellulose can be subjected to acid hydrolysis and degradation (Beneventi, Alila, Boufi, Chaussy, & Nortier, 2006). Through control of the polymerization conditions it is possible to produce PPy-coated fibers without a noticeable reduction in their mechanical properties when compared with those of pristine fibers (Dall'Acqua, Tonin, Peila, Ferrero, & Catellani, 2004; Dall'Acqua et al., 2006). Ferrero, Napoli, Tonin, and Varesano (2006) have studied the polymerization rate of Py on fibers surface using APS in the presence of different organic dopants in order to obtain PPy-coated fiber with suitable electrical conductivity and mechanical properties. In this context, the aim of this work is to obtain BC/PPy·APS composites with good electrical conductivity and mechanical properties through *in situ* oxidative polymerization of Py using APS without an organic dopant. The morphology, electrical conductivity, thermal and mechanical properties of BC/PPy·APS composites were evaluated and also compared with BC/PPy·$FeCl_3$ composites. The influence on site-specific interaction between PPy and BC functional groups of these resulting composites was also investigated.

2. Materials and methodology

Pyrrole (Merck, analytical grade) was distilled under vacuum and stored in refrigerator. Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) (Vetec) and ammonium persulfate (APS) (Vetec) were used as received. The bacterial cellulose membranes were synthesized according to the procedure described in Rambo et al. (2008) by using the bacterial G. hansenii, ATC 558 232 strain in static culture conditions.

The polpypyrrole-coated bacterial cellulose composite (BC/PPy) was obtained through oxidative polymerization of pyrrole in

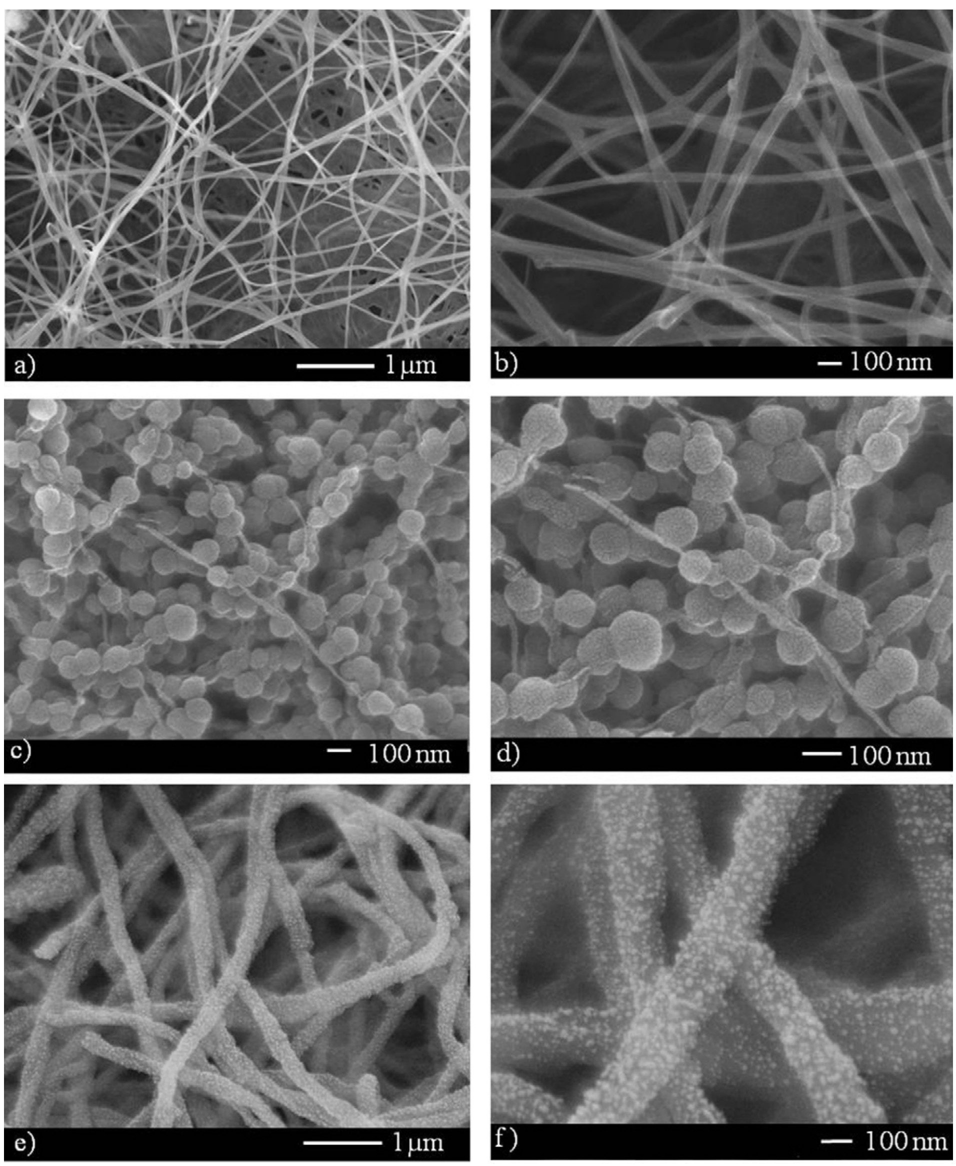

Fig. 1. FEG-SEM micrographs of (a and b) BC, (c and d) BC/APS and (e and f) BC/$FeCl_3$ samples.