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Starch/PVA-based nanocomposites reinforced with bamboo nanofibrils

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ABSTRACT

This work aimed to evaluate the effect of including different concentrations of bamboo nanofibrils on physical, mechanical, morphological and structural properties of nanocomposites from cassava starch and polyvinyl alcohol (PVA). Nanocomposites were prepared with blends of starch/PVA and nanofibrils of bamboo. Chemical pre-treatments and mechanical defibrillation were used to obtain the nanofibrils. The mixture containing 3% of starch and 4% of PVA in the proportion of 20/80 (starch/PVA) were chosen after preliminary testing. Atomic force microscopy (AFM) and transmission electronic microscopy (TEM) were used to characterize the bamboo nanofibrils. Microstructure of the nanocomposites was evaluated using scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Physical and mechanical properties were also evaluated. Results showed that pre-chemical treatments increased the content of the alpha-cellulose in bleached pulp by approximately 112% in relation to the native fiber. Increasing the number of passages through the defibrillator reduced the average diameter of the bamboo nanofibrils (from 82 ± 29 nm to 10 ± 6 nm). Addition of 6.5% nanofibrils improved the tensile strength and elongation at the break of the nanocomposite by 24 and 51%, respectively, but reduced the tensile modulus by 40% in relation to control (unreinforced) blend. Nanofibrils decreased the transparency of the nanocomposite films. The water vapor permeability and water solubility of the nanocomposite containing high contents of nanofibrils decreased up to 20% and 30%, respectively, in relation to the control blend.

1. Introduction

Ecological concern has increased the interest on natural and renewable materials, making plant fibers and biodegradable polymers an interesting and secure alternative for development of new materials. Most common biodegradable polymers are obtained from polysaccharides and polyesters. Between the polysaccharides, thermoplastic starch (TPS) has been largely used, despite presenting some disadvantages, such as strong hydrophilicity, poor mechanical properties in comparison to conventional polymers and variations of post-processing properties. Some strategies have been presented to improve these properties, including the use of blending (Mohanty et al., 2000; Averous and Boquillon, 2004; Olobarrieta, 2005).

Several studies have examined blending starch with other polymers due to the relative facility of obtaining materials with desirable properties with no need to significant changes or investments on the conventional process. Thus, polymeric blends are a versatile technological solution to obtain polymeric materials with myriad specifications at relatively low cost using combinations of polymers with properties of interest (Utracki, 1989; Ishiaku et al., 2002). Many types of biodegradable PVA-based composites have been prepared through mixture with starch (Follain et al., 2005; Lawton, 1996; Siddaramaiah et al., 2004; Cinelli et al., 2006; Zhai et al., 2003; Khan et al., 2006). Chemical modification, including cross linking with glutaraldehyde and epichlorohydrin, has also been used by several authors to improve the physical properties

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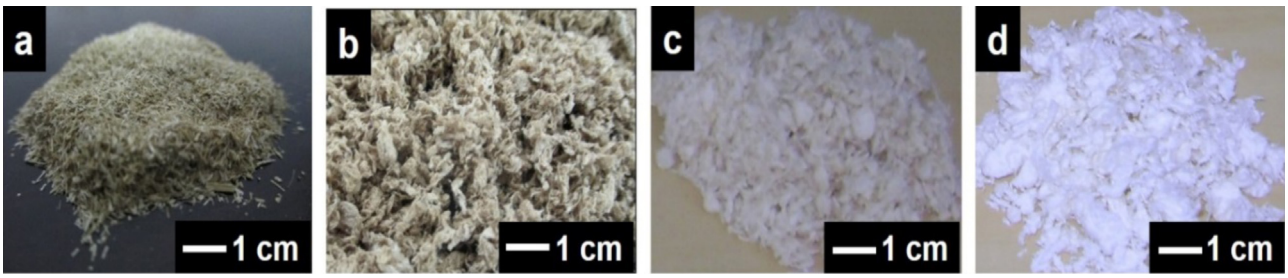

Fig. 1. Visual appearance: (a) ground bamboo native fiber; (b) refined pulp without bleaching; (c) refined pulp bleached for one time (1×); and (d) refined pulp bleached for two times (2×).

and limitations of these polymers (Nabar et al., 2006; Beliakova et al., 2004; Ramaraj, 2007; Sreedhar et al., 2006).

In recent years, nanofibrils and nanocrystals obtained from plant fibers have been studied as reinforcement in starch-based nanocomposites. The use of these two types of cellulosic nanoreinforcements in polysaccharides matrices has increased because of their great affinity. Large specific surface area, high aspect ratio and high capacity to form structured nets make cellulosic nanofibrils excellent low-cost and non-toxic reinforcement agents (Chang et al., 2010; Chang et al., 2010). This class of materials presents micrometric lengths and nanometric widths, leading to interest potential for several applications, including drugs (Villanova et al., 2011), dietary food (Okiyama et al., 1993), special papers (Nguyen and Tan, 2009), reinforcement in packaging/films (Siro and Plackett, 2010; Syverud et al., 2011) and polymeric matrices (Orts et al., 2005; Azizi Samir et al., 2005; Siqueira et al., 2010).

The present work aimed to evaluate the effect of including various concentrations of bamboo nanofibrils on mechanical, morphological, structural and physical properties of cassava starch/PVA-based nanocomposites.

2. Materials and methods

2.1. Materials

Commercial unbleached refined bamboo cellulose pulps from *Bambusa Vulgaris* Schrad (around 2 years of age), were obtained from CEPASA – Celulose e Papel de Pernambuco S/A, Jaboatão dos Guararapes, Brazil. The bamboo pulp was produced by the soda-anthraquinone process (NaOH-AQ), with approximately, 18% NaOH and 0.03% anthraquinone ($C_{14}H_8O_2$) per unit of solid mass, pH between 12 and 13, and with a fiber yield estimated in 46%. After batching in a Pandia continuous digester at 6–7 bar and 170 °C for 45 min, samples were disk refined until a Schopper Riegler (SR) index of around 25–30.

Composite matrix was formed by: modified cassava starch – FMM (Cargill, lot 1,209,035, type A), crystallinity index (CI) of around 45% and amylopectin content of 85%; polyvinyl alcohol – PVA (Sigma–Aldrich, lot MKBK3473V), with molecular weight (Mw) of 130.000 g/mol, 99% hydrolyzate; and liquid glycerol (Sigma–Aldrich) as plasticizer agent, with Mw of 92.09 g/mol, ≥ 99% concentration and density of 1.26 g/mL.

2.2. Pre-treatment and characterization of the bamboo pulp

Before obtaining bamboo nanofibrils, the refined pulp sample was subjected twice to alkaline treatment as proposed elsewhere (Corradini et al., 2006) followed by bleaching (Pereira et al., 2010) but maintaining the pH at 11 in order to prevent brightness reversion. Before repeating or starting a new treatment, samples were washed with tap water until the pH becomes neutral. In order to calculate fiber yield, the samples were oven dried at 60 °C for 24 h and weighted before and after each treatment.

Chemical composition of the refined pulps, with and without treatments, was determined. Sample preparation for chemical analysis followed the procedures described in T264 cm-97 (TAPPI, 1999a) and T257 cm-97 (TAPPI, 1999b) standards. The percentage of holocellulose (cellulose + hemicelluloses) was determined as described in T9 m-54 (TAPPI, 1999c). The contents of alpha-cellulose and lignin (insoluble in acid) were estimated according to T203 cm-99 (TAPPI, 1999d) and T222 cm-88 (TAPPI, 1999e) standards, respectively. The content of hemicelluloses was calculated from the difference between the values of holocellulose and alpha-cellulose, and the contents of ash and extractives were calculated in accordance with T211 cm-93 (TAPPI, 1999f) and T204 cm-97 (TAPPI, 1999g) standards, respectively. The procedure for determining solubility in ethanol–toluene (1:2, v/v) was conducted for 6 h in ethanol/toluene and 4 h in ethanol. All determinations were performed in triplicate.

After pre-treatment and characterization, the native fiber and refined pulp without bleaching were called FNA and PRST, respectively, and the pulp twice alkaline treated and bleached were called PRM2 and PRM2B2, respectively. Fig. 1a–d show the ground bamboo native fiber, refined pulp without bleaching, refined pulp bleached for one time (1×) and refined pulp bleached for two times (2×).

2.3. Production of bamboo nanofibrils

Bamboo nanofibrils were obtained by mechanical defibrillation of the pre-treated (twice alkaline treated and twice bleached) refined pulp fibers using a Super Masscolloider Masuko Sangyo MKCA6-3 defibrillator at 1500 rpm (Ifuku et al., 2010). Initially, the bamboo pulp was immersed (at 1.2% w/v concentration) in water for 48 h for hydration to guarantee the swelling of the fiber cell wall. The gap between the silicon carbide stones in the defibrillator was adjusted to 100 μm (Nakagaito and Yano, 2004) and suspensions from refined/bleached fibers were fed several times until form a gel, which began to happen after 15 passages through the defibrillator (Bufalino et al., 2014; Guimarães Junior et al., 2015). The number of passages adopted for this study was 5 and 30, and the electric current consumed was kept at 6 A. Sonication was applied after defibrillation, for 30 min, using a Branson sonicator with a 13 mm tip, at 450 W (25% amplitude) and 20–25 KHz, which led to 840 J/mL energy.

The suspensions were called NRB5x and NRB30x for nanofibrils obtained after 5 and 30 passages through the defibrillator, respectively. Fig. 2 shows the steps of production the bamboo nanofibrils from the solution of bleached refined pulp until obtaining the gel after 30 passages through the mechanical defibrillator.

2.4. Characterization of the bamboo nanofibrils

Transmission electron microscopy (TEM) was performed in order to evaluate the morphology of bamboo nanofibrils, using a