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Bio-composites of cassava starch-green coconut fiber: Part II—Structure and properties

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ABSTRACT

Development of any new material requires its complete characterization to find potential applications. In that direction, preparation of bio-composites of cassava starch containing up to 30 wt.% green coconut fibers from Brazil by thermal molding process was reported earlier. Their characterization regarding physical and tensile properties of both untreated and treated matrices and their composites were also reported. Structural studies through FTIR and XRD and thermal stability of the above mentioned composites are presented in this paper. FT-IR studies revealed decomposition of components in the matrix; the starch was neither chemically affected nor modified by either glycerol or the amount of fiber. XRD studies indicated increasing crystallinity of the composites with increasing amount of fiber content. Thermal studies through TGA/DTA showed improvement of thermal stability with increasing amount of fiber incorporation, while DMTA showed increasing storage modulus, higher glass transition temperature and lower damping with increasing fiber content. Improved interfacial bonding between the matrix and fibers could be the cause for the above results.

1. Introduction

A number of bio-polymers based on renewable resources such as starch, cellulose, soya, polylactic acid, polyhydroxy alkanoates, among others, have been investigated as alternate materials to conventional synthetic polymers. This is because some of these materials are less environmental friendly [Ma, Yu, & Kennedy, 2005]. Of these, starch is the most promising material for the production of biodegradable plastics and their composites, because it is natural, abundant, sustainable and biodegradable in addition to being capable of exhibiting thermoplastic in behavior under the action of high temperature and shear stress [Mo, Zhong, Liang, & Yu, 2010]. Materials produced using such material are characterized by their high solubility in water, high hygroscopy, poor melting point, faster aging due to retrogradation (a process in which the amylase and amylopectin chains realign themselves making the liquid starch turn to gel) and lower mechanical properties in comparison with the materials based on synthetic polymers. Besides these aspects, starch is one of the most difficult materials to process, because of its brittleness. Therefore, it requires addition of some plasticizers to make it suitable for engineering applications [Satyanarayana, Carbajal, & Wypych, 2009]. In fact, a number of studies on various aspects such as chemical composition, changes in chemical structure, thermal properties and X-ray diffraction studies (for crystallinity) of different types of starches (both natural from different botanical sources and modified starches) and in some cases their bio-composites even with the incorporation of nanofibrils have been carried out [Damager, Engelsen, Blennow, Møller, & Motawia, 2010; Gómez, Torres, Nakamatsu, & Arroyo, 2006; Kaewtatip & Thongmee, 2012; Ma, Chang, Yu, & Stumborg, 2009; Prachayawarakorn, Sangnitidej, & Boonpasith, 2010; Sarifuddin, Ismail & Ahmad, 2012; Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005; Teixeira et al., 2009].

In addition to improving the processability of starch (continuous phase named matrix), its mechanical properties can be enhanced by

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the incorporation of plant-based fibers (kenaf, jute, sisal, coconut fiber, sugarcane fiber, bagasse, etc., or cellulose fibers of wood from eucalyptus or coniferous *Pinus*) to obtain composites called "bio-composites" or "green composites" [Avérous & Halley, 2009; Mohanty, Misra, & Drzal, 2002]. Such composites are completely biodegradable and compostable and therefore considered "environmentally friendly" since, at the end of their useful life, they can be discarded without causing any damage to the environment [Dobircau et al., 2009]. The use of natural fibers to reinforce brittle polymers is not only a good alternate application for these agro-products (which would otherwise go to waste), but also clear advantages because of their renewability, abundant availability, biodegradability and relative low cost [Kuciel & Liber-Knec, 2009].

These new materials, which include bio-composites of cassava starch and green coconut fibers, would fulfill the sustainable development perspectives and current ecological design of safe environment [Avérous & Digabel, 2006; John & Thomas, 2008; Lomelí et al., 2011]. Such bio-composites have been used in products that can be discarded after use, as well as in products having longer lifetimes preferably for interior applications [John & Thomas, 2008].

Besides the great advantages of using bio-composites as described above, our interest in this material is also due to the following facts: (i) Brazil has the highest production and yield per hectare of starch production in Latin America, particularly cassava or tapioca ('mandioca' in Portuguese) starch; (ii) coconut is an important crop in northeastern Brazil, which produces abundant fibers resulting from discarded green coconuts [Tomczak, Sydenstricker, & Satyanarayana, 2007]; and (iii) in recent years, Brazil has been in the forefront of the use of industrial wastes for value addition [Satyanarayana et al., 2009]. The present authors have previously carried out studies to understand processing–property–structure correlations of bio-composites of cassava starch reinforced with 5–30 wt.% of fibers from green coconuts (hereafter called 'coir fibers') using glycerol as plasticizer. The first part of this study reported [Lomelí et al., 2011] the preparation of the above composites by compression (thermo) molding process and their characterization regarding tensile properties, and water sorption characteristics both before and after thermal treatments of the matrix and its composites. It was possible to prepare composites free of fiber agglomeration with the incorporation of up to 30% coir fibers. It was observed that both tensile strength (TS) and Young's modulus (YM) of the thermoplastic starch (TPS) increased with the incorporation of coir fibers; those of composites increased with increasing amount of fibers as well as with the thermal treatment. It was observed that treated TPS matrix showed 207%, 410.8% and 221.9% enhancement in tensile strength, Young's modulus and maximum load respectively, over the corresponding values of untreated TPS matrix. Similarly, in the case of composites containing 30% w/w of fibers, the enhancement of Young's modulus and tensile strength are 212.2% and 366.7% respectively, for the treated TPS composites over the untreated TPS composites. These results were explained as due to better fiber-matrix interface obtained by good adhesion between the fiber and the matrix as observed in their fractographs. On the other hand, water uptake, swelling and moisture absorption of TPS decreased with the incorporation of fibers, attributed to better interfacial bonding between the matrix and fibers as well as the hindrance to absorption caused by the fibers.

In the present paper, structural [through Fourier transform infra red spectroscopy (FTIR) and X-ray diffraction (XRD) techniques] and thermal studies [through differential thermal analysis/differential thermo-gravimetry (DTA/DTG) and thermo-mechanical analysis (DMTA)] of the thermoplastic cassava starch (TPS) and its composites containing 5–30 wt.% of coir fibers are reported. It is hoped that these results along with those reported in Part I [Lomelí et al., 2011] will contribute to the understanding of the relationship between composition of composite materials and properties of these materials. This information could be used to propose practical applications for this bio-composite, which would have the additional benefits of enhanced use of coir fibers and generating employment along with economic advantages for all the coconut growing countries of the world.

2. Experimental

2.1. Materials

The native cassava starch (*Manihot esculenta*) used in this study was donated by J. A. Pasquini and Cía Ltda., Nova Esperança, Paraná, Brazil. The coir fibers were donated by COOBCOCO, a street scavengers cooperative in Fortaleza, Ceará state, in north eastern Brazil. Commercial grade glycerol used as plasticizer was donated by Labsynth, São Paulo, Brazil.

2.2. Methods

2.2.1. Preparation of composites

The method has been described previously [Lomelí et al., 2011]. Briefly, the coir fibers were first dried followed by milling and sieving to obtain fibers with an average length of about 10 mm. Then, the cassava starch was mixed thoroughly with 30 wt.% of glycerol in a plastic bag until a homogeneous mixture was obtained. Into this, 5–30 wt.%[2] previously prepared coconut fibers in steps of 5 wt.% were mixed using an industrial mixer (Hobart) at high speed to obtain a good dispersion of the fibers in the starch. These mixtures were then transferred to plastic bags for storage until the preparation of the composite laminates. This material was then poured into a stainless steel mold (170 mm × 170 mm × 3 mm), which was placed in a hydraulic press (Solab make) with a heating system and controlled cooling apparatus to obtain the laminates. Laminates of matrix (cassava starch + glycerol) were also prepared for comparison. Laminates of both the TPS matrix and their composites were prepared with the processing conditions of 160 °C and 410.4 kgf cm^{-2} applied pressure for about 50 min.

2.2.2. FTIR analysis

The native starch was chemically characterized by FTIR spectroscopy in a Bio-Rad Excalibur instrument. The starch spectrum was obtained using the potassium bromide disk technique.

In the case of bio-composites samples, the FTIR analyses were performed in a Vertex Excalibur spectrophotometer by means of the ATR (attenuated total reflectance) technique. All IR spectra were the average of 64 scans with a resolution of 4 cm^{-1} within a frequency of 4000–700 cm^{-1}.

2.2.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) studies were carried out using a Shimadzu diffractometer (Model XRD 7000), with monochromatic Cu Kα radiation (λ = 1.5418 Å), at operating conditions of 40 keV and 20 mA to determine the crystallinity of the materials.

All samples were dried at 60 °C during 8 h, and the composites specimens used had dimensions of 40 mm × 20 mm × 0.3 mm, while the starch sample was in powder form. The analysis was carried out in the 2θ angle range of 2.5–60° with a scanning speed of 1°/min. The relative crystallinity of starch and composites was calculated according to Eq. (1) proposed by Frost, Kaminski, Kirwan, Lascaris, and Shanks (2009), based on the deconvolution calculus

[2] Throughout this paper, the composition of composites is in wt.% unless otherwise mentioned.