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Water barrier properties of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse

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ABSTRACT

Water transport in edible films based on hydrophilic materials such as starch, is a complex phenomenon due to the strong interaction of sorbed water molecules with the polymeric structure. Cellulose nanocrystals (CNC) were obtained from sugarcane bagasse. Starch and starch/CNC films were formulated and their water barrier properties were studied. The measured film solubility, contact angle, and water sorption isotherm indicated that reinforced starch/CNC films have a lower affinity to water molecules than starch films. The effects that the driving force and the water activity (a_w) values at each side of the film have on permeability were analyzed. Permeability, diffusivity, and solubility coefficients indicated that the permeation process depends mostly on the tortuous pathway formed by the incorporation of CNC and therefore were mainly controlled by water diffusion. The interaction between CNC and starch chain is favoured by the chemical similarities of both molecules.

1. Introduction

Polysaccharides such as starch, cellulose derivates and plant gums have been studied as edible films and coatings in food packaging and preservation (Kester & Fennema, 1986). Generally, the main functional properties of these hydrophilic materials depend strongly on their water content and therefore on the surrounding humidity. The relationship between water activity (a_w) and the moisture content of a material is explained by means of its moisture sorption isotherms. Water permeability depends on its solubility and diffusivity, the former is obtained from water sorption isotherms while the latter is related to the diffusion path of water molecules in the film matrix. In addition, water also acts as a plasticizer for hydrophilic materials and a swelling process occurs affecting the barrier properties, which depend strongly on water content (Bertuzzi, Armada, & Gottifredi, 2003).

Nanotechnology focuses on the characterization, fabrication and manipulation of biological and nonbiological structures smaller than 100 nm. The design of internal micro or nanoscale structures can improve the functional properties, morphology and stability of the polymer matrix used in edible films and coatings (Azeredo, 2009). Cellulose is the most abundant renewable polymer in the world; it is found in plant cell walls, and it can also be synthesized by some bacteria. Its reinforcing property is remarkable (Tashiro & Kobayashi, 1991). Basically two types of nanoreinforcements can be obtained from cellulose: microfibrils and whiskers. In the case of plants or animals, the cellulose chains are synthesized to form microfibrils (or nanofibres), which are bundles of molecules that are elongated and stabilized through hydrogen bonding (Wang & Sain, 2007). The microfibrils have nanosized diameters (2–20 nm, depending on the origin), and their lengths are in the micrometre range (Azizi Samir, Alloin, Sanchez, & Dufresne, 2004; Oksman, Mathew, Bondeson, & Kvien, 2006). Each microfibril is formed by aggregation of elementary fibrils, which are made up of crystalline and amorphous parts. The crystalline parts, which can be isolated by several treatments, are the whiskers, also known as nanocrystals (CNC), nanorods, or rodlike cellulose microcrystals (Azizi Samir et al., 2004; Dujardin, Blaseby, & Mann, 2003), with lengths ranging from 500 nm up to 1–2 μm, and about 8–20 nm or less in diameter (Azizi Samir et al., 2004; Lima & Borsali, 2004), resulting in high aspect ratios. Each microfibril can be considered as a string of whiskers connected by amorphous domains (which act as structural defects), and having a modulus close to that of a crystal of native cellulose (about 150 GPa) and a strength of about 10 GPa

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(Helbert, Cavaillé, & Dufresne, 1996). These values are only about seven times lower than those of single walled carbon nanotubes (Podsiadlo et al., 2005).

Bagasse is the by-product obtained after sucrose extraction from the sugar cane plant. It has a high proportion of cellulose, which can be readily isolated from the other components namely lignin and hemicelluloses. The cellulose is obtained from bagasse by a pulping process (Zanin et al., 2000). Bondeson and Oksman (2007), Paralikar, Simonsen, and Lombardi (2008), Svagan, Hedenqvist, and Berglund (2009) and Belbekhouche et al. (2011) obtained nanocomposites based on different polymer matrices reinforced with cellulose fibres or whiskers. Kvien, Sugiyama, Votrubec, and Oksman (2007) and Savadekar and Mhaske (2012) studied the effect of CNC incorporation on thermoplastic starch matrix and found that the incorporation of nanofillers improved their barrier and mechanical properties.

The description and prediction of water vapour transport through hydrophilic films are extremely complex. The complexity is due to the nonlinear behaviour of water sorption isotherms and the water content dependency on diffusivity at high water activities. Water vapour transmission rate of hydrophilic films varies nonlinearly with water vapour pressure (Wiles, Vergano, Barron, Bunn, & Testin, 2000) at water activities higher than 0.55. At lower water activities, Wiles et al. (2000) and Debeaufort, Voilley, and Meares (1994) reported a linear dependence of water vapour transmission rate with water vapour pressure. Larotonda, Matsui, Sobral, and Laurindo (2005) and Müller, Yamashita, and Borges Laurindo (2008) investigated the influence of the diffusion coefficient (D_{eff}), the water vapour permeability (P) and the solubility coefficient of water (β) in different polymers. The β value, called film hydrophilicity, can be calculated from the first derivative of the water sorption isotherm (represented by GAB model fit) in relation to a_w, divided by the water vapour pressure (p_w) at the sorption isotherm temperature. The average β values for each range were determined and represented by β'. Water vapour permeability can be obtained using the ASTM E96 method (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007). The diffusivity coefficient can be obtained from solubility and permeability coefficients (Larotonda et al., 2005).

The aim of this work was to determine the effect of variations of assay parameters such as water vapour gradient (permeation process driving force) and water vapour pressure values at each side of the film on water vapour permeability of starch/CNC nanocomposite films.

2. Materials and methods

2.1. Materials

Commercial and food grade corn starch (Unilever, Argentina) was used as the polymeric matrix for film formulation. Sugarcane bagasse was kindly supplied by Ingenío Río Grande (Jujuy, Argentina). Glycerol (Mallinckrodt, USA) was added as plasticizer. Ethylene glycol anhydrous (water content <0.003%) (Mallinckrodt, USA) was used for density determinations. P_2O_5 (Mallinckrodt, USA) was utilized as desiccant and saturated solution of $Mg(NO_3)_2$ (Mallinckrodt, USA) was used to obtain 53% RH. NaOH (Merk, Argentina) and $NaClO_2$ (Clorox, Argentina) were employed to obtain cellulose fibres. H_2SO_4 (Cicarelli, Argentina) was used in the acidic hydrolysis of cellulose fibres in order to obtain CNC. All salts used to achieve different relative humidity ambient (% RH) were provided by Aldrich (USA).

2.2. Preparation of CNC

Cellulose fibres (CF) were obtained by alkaline hydrolysis. 10 g of sugarcane bagasse were hydrolysed with 100 mL of NaOH (6%) at 60 °C for 4 h using a shaker. Next, the fibres were filtered to remove the excess of NaOH and washed with 200 mL of distillate water. Bleaching process consisted in the introduction of the material into a flask containing 200 mL of $NaClO_2$ (30%) and its shaking during 24 h at room temperature. After that, the fibres were filtered and washed with distilled water until neutral pH. The cellulose fibres were dried at 50 °C until constant weight. The cellulose, lignin and hemicelluloses contained in baggase were determined by means of the techniques proposed by Geoering and Van Soest (1970) using a Fibre Analyzer (ANKOM Technology Fiber Analyzer Model 220, USA). CNC were extracted from cellulose fibres, according to the methodology proposed by Bondeson, Mathew, and Oksman (2006). About 10 g of fibres were dispersed in 200 mL of H_2SO_4 (64%) into a flask under mechanical stirring. Hydrolysis was performed at 40 °C under vigorous stirring during 3 h. The excess of H_2SO_4 was removed from the resulting suspension by centrifugation at 800 rpm during 10 min. After that, the suspension was dialyzed against distilled water using a cellulose membrane until the pH reached 6–7. The resulting suspension was introduced into an ultrasonic bath for 1 h and stored in a refrigerator.

2.3. Film preparation

Film-forming solution was prepared by mixing starch (4%), glycerol (20% dry weight), water, and an appropriate amount of CNC suspension (prepared as was described in Section 2.2) in order to obtain a CNC concentration of 3% dry weight. The resulting dispersion was kept 60 min in an ultrasonic bath. Dispersions were gelatinized in a shaking water bath at 78–80 °C during 10 min. This procedure ensured disintegration of starch granules and formation of a homogeneous dispersion. The resulting dispersion, while still hot, was poured on polystyrene plates. Then, they were placed in an air-circulating oven at 35 °C and 53% RH for 15 h. After that, plates were removed from the oven and films were peeled off.

2.4. Characterization of CNC. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD)

CNC powder and cellulose fibres were analyzed. X-ray diffraction spectra were carried out in a diffractometer Rigaku Mini Flex (Japan), using a Cu kα radiation, 40 kV and 20 mA over an angular range 1–40° with step size 0.02. Samples were previously conditioned at a relative humidity of 53% and 25 °C.

CNC powder and cellulose fibres were examined by SEM utilizing a JEOL JSM 6480 LV scanning microscope. Samples were stored at 25 °C over silica gel. Powder samples were mounted on bronze stubs and coated with gold plasma. Samples were observed using an accelerating voltage of 20 kV.

An aliquot of CNC suspension was diluted and sonicated for 5 min (Branson 450 sonifier). A drop of this resultant diluted suspension was deposited on a carbon microgrid net (400 meshes) and the grid was stained with a 1.5% solution of uranyl acetate and dried at room temperature. Transmission electron micrographs (TEM) images were obtained using a JEOL JEM-1011 HR transmission electron microscope with an acceleration voltage of 80 kV.

2.5. Scanning electron microscopy (SEM) of starch/CNC films.

Cross-sections of starch/CNC films were examined by SEM using a JEOL JSM 6480 LV scanning microscope. For cross-section observations, films were cryofractured by immersion in liquid nitrogen.