



Wheat straw hemicelluloses added with cellulose nanocrystals and citric acid. Effect on film physical properties

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ABSTRACT

Wheat straw has been used as a source of hemicelluloses (WSH) and cellulose nanocrystals (CNC) for the elaboration of biodegradable films. Different films have been formed by using WSH as a matrix and different contents of CNC and citric acid. The predominant hemicelluloses were arabinoxylans. CNC reinforced the films, improving tensile strength and modulus, water resistance and water vapor barrier. Citric acid, on the other hand, presented concomitant plasticizing and crosslinking effects (the latter also evidenced by FTIR), probably due to a crosslinking extension by glycerol. The use of 5.9 wt% CNC and 30 wt% citric acid was defined as optimal conditions, resulting in minimum water sensitivity and permeability, while maintaining a good combination of tensile properties. Under those conditions, the films presented enhanced modulus, elongation, water resistance, and barrier to water vapor when compared to the control WSH film, and might be used for wrapping or coating a variety of foods.

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1. Introduction

The petroleum-derived polymers have been presented to the world in the early 20th century as mediocre substitutes for natural materials such as silk and rubber, but have been engineered since then to become mainstream materials of low-cost and superior properties, accounting for the declining use of natural polymers. However, a transition from petrochemistry to bioeconomy, involving the renaissance of renewable polymers, is expected at the 21st century (Mülhaupt, 2013). The reasons for this shift are related to the non-renewability, the overall environmental impacts, and the lack of biodegradability of the petroleum-derived polymers. The modern polymer technology has been thus increasingly focused on green routes.

Biorefining may be defined as the sustainable processing of biomass into products and/or energy. The biorefinery concept embraces technologies able to separate biomass resources (such as food industry by-products) into their building classes of molecules

(such as polysaccharides, proteins, phenolic compounds, and triglycerides) which are then converted to value added products such as biomaterials and energy carriers in an integrated way so as to maximize the economic value of the biomass while reducing waste production (Cherubini, 2010; Thomsen, 2005).

The world wheat consumption for 2015/2016 was around 710 million tons (WASDE, 2016). Wheat straw, an abundant wheat co-product which is treated mostly as waste, is a source of cell wall polysaccharides such as hemicelluloses (mainly xylans) and cellulose (Jacquemin et al., 2015). Considering that the production of 1 kg of wheat grain generates an average of 1.3 kg of straw (Montane, Farriol, Salvado, Jollez, & Chornet, 1998), the world annual generation of wheat straw may be estimated as about 920 million tons. Although part of the wheat straw is already used (e.g. for animal feed and paper production), the majority is usually treated as waste, when it could instead be used to produce high-valued materials such as biodegradable films to be used as greener alternatives to conventional food packaging materials.

Biodegradable films have been produced from a variety of biopolymeric matrices, including polysaccharides. However, polysaccharide films have usually poor tensile properties, besides being highly permeable to water vapor and sensitive to water

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(because of the hydrophilic nature of polysaccharides). Cellulose nanocrystals (CNCs), which are needlelike crystals measuring 4–25 nm in diameter and 100–1000 nm in length (Jonoobi et al., 2015), have been reported to improve overall physical properties of polysaccharide films, especially tensile properties, due to the high strength and stiffness of individual nanocrystals (Cho & Park, 2011) as well as to mechanical percolation yielded by hydrogen bonding interactions between CNCs (Favier et al., 1995). CNCs are usually extracted by chemical treatments such as acid hydrolysis, which may be preceded by pretreatments such as steam explosion in order to fractionate the lignocellulosic material into its biopolymer components (Abdul Khalil, Bhat, & Yusra, 2012).

Another way to improve physical properties of polysaccharide films is by crosslinking, which consists of linking polymer chains by covalent or non-covalent bonds, forming three-dimensional networks with reduced mobility, which results in improved water resistance, and usually improved tensile and barrier properties (Balaguer, Gómez-Estaca, Gavara, & Hernandez-Muñoz, 2011). Citric acid has been reported to crosslink polysaccharides (Bonilla, Talón, Atarés, Vargas, & Chiralt, 2013; Olsson, Hedenqvist, Johansson, & Järnström, 2013a), while non-bonded citric acid may also act as a film plasticizer (Chabrat, Abdillahi, Rouilly, & Rigal, 2012; Ortega-Toro, Collazo-Bigliardi, Talens, & Chiralt, 2016; Shi et al., 2007). The crosslinking mechanism of citric acid is ascribed to covalent di-ester linkages between hydroxyl groups of two different polysaccharide chains and two carboxyl groups of citric acid (Coma, Sebti, Pardon, Pichavant, & Deschamps, 2003; Olsson et al., 2013a). The reaction is favored by curing the films at temperatures above 100 °C (Dastidar & Netravali, 2012; Olsson et al., 2013a, 2013b).

In a previous study from our group (Azeredo et al., 2015), citric acid was reported to improve water vapor barrier and water sensitivity of wheat straw hemicellulose films (suggesting a plasticizing effect), while the overall tensile properties of the films have been impaired by citric acid. In this study, both citric acid and cellulose nanocrystals (CNCs) have been used as additives to wheat straw hemicellulose films, in an attempt to combine crosslinking and reinforcing effects to improve not only the water resistance of the films but also their tensile properties.

2. Materials and methods

2.1. Isolation and characterization of wheat straw hemicelluloses (WSH)

Wheat straw was milled to 0.5 mm in a Retsch Brinkmann ZM-1 centrifugal grinding mill (Retsch GmbH, Haan, Germany). 100 g milled straw were washed with 1 L ethylenediamine tetraacetic acid (EDTA) solution (0.2%, w/v) at 90 °C for 1 h, to remove water soluble components and to chelate H₂O₂ decomposing metals. The hemicelluloses were then extracted with an alkaline H₂O₂ solution (3% w/v, pH adjusted to 12.5 with KOH) for 16 h at 50 °C, conditions modified from those previously optimized by Fang, Sun, Salisbury, Fowler, & Tomkinson, 1999. The supernatant from the subsequent centrifugation was vacuum filtered and had its pH adjusted to 5.0 with acetic acid. Ethanol was added to a concentration of 60 vol%, the suspension was stirred for 30 min, left for 16 h at 4 °C, centrifuged, washed with ethanol 70 vol%, centrifuged again, and left to dry at 24 °C. The dried WSH were then milled to a fine powder (particle size, 0.25 mm) by using a basic mill (A10, IKA GmbH, Germany).

The neutral sugar composition of WSH was determined by gas chromatography-flame ionization detection (GC-FID). A 10 mg sample of WSH was hydrolyzed with trifluoroacetic acid 4 M for 6 h at 100 °C. The hydrolyzed WSH and the monosaccharide standards

were acetylated with acetic anhydride and piridin (2:1, v/v), and the alditol acetates were dissolved in chloroform. The analyses were conducted in a Shimadzu GC-2010 Plus (Shimadzu, Japan) with a VF5-MS column (0.25 μm, 0.25 mm × 60 m). The injected volume was 1 μL with a 1:20 split ratio. Nitrogen was used as carrier gas, whose flow was 0.83 mL/min. The oven temperature was increased from 190 to 230 °C at 4 °C min⁻¹, then it was held at 230 °C for 12 min. The peaks were identified by comparing retention times with those obtained by injections of pure standards.

The hemicellulose and α-cellulose contents of milled wheat straw and the isolated WSH were determined (in triplicate) based on TAPPI T203cm-99 (TAPPI, 2009), and the lignin contents, according to TAPPI, 2004.

2.2. Isolation of cellulose nanocrystals

Chipped wheat straw (1 kg each run) was steam exploded at 210 °C for 10 min using a Cambi™ Steam Explosion Pilot Plant (Cambi, Asker, Norway) with a sealed 30 L vessel. The contents of the heating chamber were then released into a cyclone (to separate biomass from steam), and the solids were deposited in a hopper with 6.6 L hot water. The heating chamber was then pressurized again twice to 2–3 bar in order to dislodge any residual material. The resulting steam-exploded slurry was collected, filtered through a 100 μm nylon mesh, dried (60 °C, 24 h) and milled to 0.5 mm.

The dried steam-exploded slurry was then submitted to acetosolv pulping and alkaline-peroxide bleaching, as described by Nascimento et al. (2014), with some modifications. It was cooked in an aqueous solution of 93 wt% acetic acid and 0.3 wt% HCl, at a 1:10 ratio (w/v slurry: solution), under reflux at 110 °C for 3 h in a round-bottom flask. The mixture was filtrated (in a 28 μm mesh) to separate the black liquor from the acetosolv pulp (AP). The AP was washed with acetic acid (99.7%) until the washing liquid was colorless, dried (60 °C, 24 h), and bleached with a solution of 5 wt% H₂O₂ and 4% (w/v) NaOH at 70 °C, at a 1:10 (w/v) AP: solution ratio, for 3 h. The material was then vacuum-filtered, washed with distilled water until its pH was equal to that of the washing water, oven-dried at 60 °C for 24 h, and the bleaching procedure was repeated, producing the bleached acetosolv pulp (BAP).

The cellulose nanocrystals (CNCs) were finally extracted from the BAP by an acid hydrolysis, as described by Nascimento et al. (2014) with modifications. The BAP was stirred in a H₂SO₄ solution (50 wt%) at 45 °C for 60 min, at a 1:20 ratio (w/v, BAP: solution). The reaction was halted by adding 10 times the volume of cold (10 °C) deionized water. The suspension was submitted to three cycles of centrifugation at 2520 g for 30 min in a Beckman JS-4.2 centrifuge (Beckman Coulter, Brea, USA). After each centrifugation, the suspension was sonicated for 4 min in a probe Branson sonicator (Digital Sonifier 250, Branson Ultrasonics, Danbury, USA) at 20 kHz in order to prevent CNC aggregation. After the third centrifugation, the supernatant was a bit turbid (instead of the previous supernatants, which were clear), indicating that the CNCs were beginning to migrate to the supernatant. The suspension was then dialyzed with distilled water until it reached a pH of 6–7 (approximately 48 h, with four changes of water). The solid content of the dialyzed CNC suspension was determined by gravimetry after drying at 105 °C until constant weight in a drying oven (Memmert, Schwabach, Germany).

2.3. Characterization of cellulose nanocrystals

For the transmission electron microscopy (TEM) images, previously sonicated CNC suspensions were placed onto Formvar/carbon coated grids and negatively stained with 2% uranyl acetate. The samples were imaged using a Tecnai 20 Transmission Electron Microscope (FEI, Hillsboro, USA), with an acceleration voltage

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