



Wheat straw hemicellulose films as affected by citric acid



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ABSTRACT

Hemicelluloses have been extracted from wheat straw with an alkaline peroxide solution. Biodegradable films intended for food packaging have been produced from hemicelluloses mixed with glycerol and different concentrations of citric acid (as a crosslinking agent), with or without sodium hypophosphite (catalyst to the crosslinking reaction). A curing treatment at 150 °C has been carried out on the dried films in order to promote formation of ester bonds between citric acid and hemicelluloses. The crosslinking reaction, evidenced by FTIR spectra, improved water resistance and water vapor barrier properties of the films. On the other hand, the citric acid effects on film tensile properties were more consistent with those of a plasticizer than of a crosslinker, which might be ascribed to a flexible crosslinking. Sodium hypophosphite (SHP) did not affect the properties of crosslinked films. FTIR spectra indicated that some crosslinking reaction occurred even in a non-cured film.

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1. Introduction

In the last decades, an increasing interest from research institutes and industries in biopolymers from renewable sources is noticeable, and has been motivated by shortage of natural energy sources as well as the necessity of replacement of petroleum-based products, which is connected with demands for more environmentally friendly materials. In 2011, the global use of biodegradable plastics was 0.85 million metric tons. BCC Research recorded a global bioplastic demand of 1.1 million metric tons in 2013, expected to reach 1.4 million metric tons in 2014 and about 6 million metric tons in 2019, in a compound annual growth rate of 32.7% (BCC, 2014). According to studies by Helmut Kaiser Consultancy (2013), bioplastics are expected to cover approximately 25–30% of the total plastics market by 2020.

The worldwide wheat consumption has been estimated to be around 705 million tons in 2013/2014 (WASDE, 2014). Wheat straw and bran, which are abundant co-products of wheat crop, represent a valuable source of hemicelluloses, cellulose and lignin. In the European Union, some millions of tons of wheat straw and wheat

bran could be collected per year (Martel, Estrine, Plantier-Royon, Hoffmann, & Portella, 2010). Some of those co-products are used in animal feed and paper production, but the majority is discarded as waste, when it could be exploited to produce high-valued materials such as biodegradable (or edible) films for food packaging.

The hydrophilic nature of polysaccharide films provide them with good oxygen barrier properties, but their water vapor barrier and moisture resistance are poor (Giancone et al., 2011; Janjarasskul & Krochta, 2010). A high water solubility obviously affects the applicability of edible films, since a packaging material is not supposed to dissolve upon contact with water. Another problem which can result from polysaccharide hydrophilicity is swelling by water, leading the films to have their mechanical and overall barrier properties impaired (Sebti, Delves-Broughton, & Coma, 2003). The water resistance of a film can be improved by crosslinking, which consists of linking polymer chains by covalent (chemical crosslinking) or by weaker bonds (physical crosslinking), forming three-dimensional networks which reduce the mobility of the structure, usually enhancing its water resistance (reducing both water solubility and swelling by water) as well as its mechanical and barrier properties (Balaguer, Gómez-Estaca, Gavara, & Hernandez-Muñoz, 2011).

Dicarboxylic and polycarboxylic acids such as citric acid have been reported by several authors (Bonilla, Talón, Atarés, Vargas, &

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Chiralt, 2013; Coma, Sebti, Pardon, Pichavant, & Deschamps, 2003; Möller, Grelier, Pardon, & Coma, 2004; Olsson, Hedenqvist, Johansson, & Järnström, 2013) to act as crosslinking agents for polysaccharide films. One advantage of citric acid is that any unreacted acid is not only nutritionally acceptable but it can also act as a plasticizer (Chabrat, Abdillahi, Rouilly, & Rigal, 2012; Shi et al., 2008). The crosslinking mechanism is attributed to covalent intermolecular di-ester linkages between hydroxyl groups of the polysaccharide and two carboxyl groups of the crosslinker (Coma et al., 2003; Hashem, Sharaf, El-Hady, & Hebeish, 2013; Olsson, Hedenqvist, et al., 2013), as indicated in Fig. 1. In a first step (not shown in Fig. 1), carboxyl groups of the acid form cyclic anhydrides, which react further with the carbohydrate hydroxyls (Xiaohong & Yang, 2000). The reaction has been reported to be favored by a high temperature (typically above 100 °C) curing process on the dried films (Coma et al., 2003; Dastidar & Netravali, 2012; Olsson, Hedenqvist, et al., 2013, Olsson, Menzel, et al., 2013), although the crosslinking reaction has also been reported to take place at a relatively low temperature (70 °C) by Menzel et al. (2013). Sodium hypophosphite (SHP) acts as a catalyst for the reaction (Reddy & Yang, 2010; Salam, Pawlak, Venditti, & El-tahlawy, 2011) by weakening the hydrogen bonding between the carboxylic acid groups (Xiaohong & Yang, 2000), increasing the speed of formation of the cyclic anhydride intermediate (Feng, Xiao, Sui, Wang, & Xie, 2014; Garcia et al., 2014; Sauperl & Stana-Kleinschek, 2010) and allowing the reaction to occur at a lower temperature (Feng et al., 2014). Peng, Yang, and Wang (2012), when studying maleic acid crosslinking in cotton fabrics, suggested that SHP reacted to two maleic acid molecules already esterified with cellulose, forming a new crosslink between two cellulose molecules.

A previous study (Ruiz et al., 2013) has shown wheat straw hemicelluloses as a promising reinforcement material to κ -carrageenan/locust bean gum blend films. However, no previous study has been found describing the use of wheat straw hemicelluloses as a film matrix.

The objectives of this study were to evaluate some physical properties of films from wheat straw hemicelluloses as affected by citric acid contents, the presence of sodium hypophosphite and the curing step.

2. Materials and methods

2.1. Isolation of hemicelluloses

Wheat straw was milled to less than 0.5 mm in a Retsch Brinkmann ZM-1 centrifugal grinding mill (Retsch GmbH, Haan, Germany). The hemicellulose and α -cellulose contents of milled wheat straw were analyzed (in triplicate) as described by TAPPI

T203 cm-99 (TAPPI, 2009), and holocellulose, according to Yokoyama, Kadla, and Chang (2002).

100 g of milled straw were washed with 1 L of 0.2% (w/v) ethylenediamine tetraacetic acid (EDTA) solution at 90 °C for 1 h, to remove water soluble components and to chelate hydrogen peroxide (H_2O_2) decomposing metals. The hemicelluloses were extracted with an alkaline H_2O_2 solution (2% w/v, pH adjusted to 12.5 with potassium hydroxide) for 16 h at 50 °C, following the conditions as optimized by Fang, Sun, Salisbury, Fowler, and Tomkinson (1999) for hemicellulose extraction of wheat straw. The H_2O_2 was used to delignify the material, since preliminary tests indicated that films from non-delignified hemicelluloses (extracted by using KOH solutions in different concentrations) were cracking, not continuous structures. During an alkaline H_2O_2 treatment, the peroxide degrades in a reaction with the hydroperoxide anion (HOO^-), producing the highly reactive hydroxyl radical (HO^\bullet) which oxidizes lignin forming low molecular weight, water-soluble products (Fang et al., 1999).

The supernatant resulting from the subsequent centrifugation was vacuum filtered and its pH was adjusted to 5.0 with acetic acid. Ethanol was added to a concentration of 60%, the suspension was stirred for 30 min, left overnight at 4 °C, centrifuged, washed with ethanol 70%, centrifuged again, and left to dry at room temperature. The dried hemicelluloses were then milled to a fine powder by using a basic mill (A10, IKA GmbH, Germany).

2.2. Film formation

The hemicellulose powder was homogenized for 15 min in distilled water (5 g/100 mL) with 30% glycerol (w/w, on a hemicellulose basis), citric acid (5%, 10%, 20%, or 30% w/w on a hemicellulose basis), with or without SHP (50% w/w on a citric acid basis), by using a homogenizer (Ystral X10/25, Ballreichtar-Dottingen, Germany). Air bubbles were removed under vacuum, and the films were cast on petri dishes to a final dried thickness of 0.09 mm, left to dry at room temperature for 24 h, then conditioned (50% RH, 24 °C) in an environmental chamber (Weiss Gallenkamp, Loughborough, UK) for 24 h, so they had all similar moisture contents (between 11.91 and 12.32 g/100 g). The dried films were then subjected to a curing treatment at 150 °C for 10 min using a fan oven (Memmert, Schwabach, Germany). Apart from a control film (with no citric acid or SHP), three groups of films were prepared, namely, CA-C (those added with citric acid and cured), CA-NC (added with citric acid and not subjected to the curing treatment), and CA-C-SHP (added with citric acid and SHP, and cured).

The water vapor permeability (WVP) determination was modified from the method E96-05 (ASTM, 2005) for five circular samples (30 mm in diameter). The thicknesses of the samples were measured using a micrometer screw gauge (Moore & Wright, Sheffield, UK) to the nearest 0.01 mm at 5 random locations, and the average value was calculated. The test films were sealed as patches onto acrylic permeation cells (2.4 cm in diameter and 1 cm in height) containing 2 mL of distilled water. The cells were placed in a desiccator connected to two channels providing a steady flow of dried air (less than 1% RH) from a Balston 75–60 air drier at 24 °C, and were weighed 7 times over a 24-h period.

The water solubility determination was conducted on 2 cm \times 2 cm film pieces in quadruplicate, based on the method proposed by Ojagh, Rezaei, Razavi, and Hosseini (2010), with some modifications. Previously dried and weighed samples were immersed in 50 mL of distilled water for 6 h at 25 °C, under stirring (150 rpm). The dry weight of the remaining film pieces was obtained after filtration on previously dried and weighed filter paper, and it was used to calculate the insoluble matter as a percentage of the initial dry weight. All the dry weights (of the initial and final

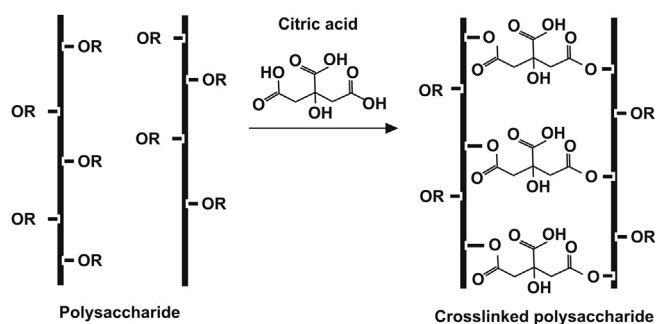


Fig. 1. Proposed mechanism for covalent crosslinking between citric acid and a polysaccharide.

Adapted from Hashem et al. (2013).

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