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Effect of thermo-pressing temperature on the functional properties of bioplastics made from a renewable wheat gliadin resin

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ABSTRACT

In this work a new methodology based on thermo-pressing a resin made from gliadins and glycerol has been developed to obtain water resistant films. The effect of processing temperature was studied on the functional properties of the films. The results of SDS-PAGE analysis of the molecular weight profiles of the resulting films were indicative of disulfide/sulfhydryl interchange reactions giving rise to the formation of intermolecular disulfide bonds between the gliadin units. These reactions augmented the degree of cross-linking of the matrix, which increased with thermo-pressing temperature, as evidenced by the residual reaction enthalpy values determined by MDSC as well as by cross-linking density values determined from tensile tests. In consequence the films produced at high temperature had better water resistance upon immersion, greater maximum tensile strength and Young's modulus values, and lower water vapor and oxygen permeabilities compared with cast films. Based on the analytical test results, thermo-pressing the resin in successive time/force steps along with a temperature of 130 °C produced gliadin films with improved properties.

1. Introduction

The development of renewable materials that can be applied in different fields of technology, such as packaging, is a topic of growing interest. These materials have their origin in biopolymers obtained directly from biomass and food industry by-products. Nevertheless, for economic and technical reasons breaking into the packaging market is a challenge (Guilbert & Gontard, 2005). Currently, food packaging is still dominated by plastics derived from petroleum, particularly polyolefins, though renewable polymers like poly(lactic acid) and blends of starch and synthetic polymers have been able to successfully exploit a niche in the food market as utensils for fast-food outlets (Marron, Bolck, Saari, & Degli-Innocenti, 2000). Many proteins from different sources have good film-forming properties when processed under so-called 'wet conditions' and thus can be good candidates for developing films and coatings for use in food packaging (Ayhllon-Meixueiro, Vaca-Garcia, & Silvestre, 2000; Hernandez-Munoz, Kanavouras, Ng, & Gavara, 2003; Mauri & Añón, 2008; Tihminlioglu, Atik, & Ozen, 2011). These protein polymers are grease resistant and are also excellent barriers to oxygen and volatile compounds at low and intermediate humidity levels (Gennadios, Hanna, & Kurth, 1997). Moreover, most of these proteins are suitable for heat processing, thereby broadening the range of applications available in food packaging and other technical fields (Hernandez-Izquierdo & Krochta, 2008).

Wheat gluten has been the subject of considerable attention as a renewable and biodegradable material which can be converted into films using standard techniques employed in the manufacture of plastics, such as casting, heat molding, extrusion, etc. Several studies have explored the feasibility of obtaining gluten films by dry processes such as extrusion or compression molding in which proteins are processed in the dry state taking advantage of their thermoplastic properties (Chen, Reddy, Wu, & Yang, 2012; Cuq, Boutrot, Redl, & Lullien-Pellerin, 2000; Mangavel et al., 2004; Redl, Morel, Bonicel, Vergnes, & Guilbert, 1999; Sun, Song, & Zheng, 2008). Processing of gluten using heat combined with pressure and shear modifies the protein structure to create a covalently cross-linked network through the formation of SH/SS interchain reactions between cysteine residues (Morel, Redl, & Guilbert, 2002). During gluten film formation by dry processes, the proteins clump together, forming large aggregates, limiting polymer processability (Morel et al., 2002). Some efforts to improve gluten protein processability in the dry state have been made, including for example the use of

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salicylic acid as a scorch retarder and radical scavenger that acts to lower the degree of protein aggregation/cross-linking, thereby helping to yield flat sheets by extrusion (Ullsten et al., 2009). Gluten film formation by dry processes requires previous steps, including making up a mixture of gluten powder, water and a plasticizer which is commonly glycerol.

Gliadins are monomeric proteins of gluten which lack intermolecular disulfide bonds. They can be extracted from gluten using ethanolic solutions, in which they have long-term stability and show excellent film-forming properties (Hernandez-Munoz & Hernandez, 2001; Hernandez-Munoz et al., 2003). Given the absence of intermolecular disulfide bonds, it is reasonable to expect that the thermal processing of gliadins into films will be easier than that of gluten, avoiding the formation of large aggregates under heating, shear and pressure.

In this work gliadins have been employed for obtaining a bio-resin capable of being transformed directly into films by thermo-pressing. This methodology avoids the current step of mixing components for the formation of gluten films. The effect of the pressing temperature during film processing on the cross-linking and thermal properties of the protein matrix has been studied. Water resistance, barrier, mechanical and optical properties of the films have been evaluated and the results are discussed with reference to the degree of cross-linking achieved.

2. Materials and methods

2.1. Reagents

Crude wheat gluten, glycerol, ethanol, and all other reagents were supplied by Sigma (Madrid, Spain).

2.2. Preparation of the gliadin-rich resin fraction

The gliadin-rich fraction was extracted from wheat gluten according to the method described by Hernandez-Munoz and Hernandez (2001). Briefly, 100 g of wheat gluten was dispersed in 400 mL of an ethanolic solution (280 mL of ethanol and 120 mL of water), stirred overnight at room temperature and subsequently centrifuged at 5000 rpm for 20 min at 20 °C. The supernatant containing the gliadin-rich fraction was collected and used as the film-forming solution. The amount of protein extracted was around 12–14 g of protein/100 g of solution. Glycerol was added as a plasticizer to the film-forming solution at a ratio of 25 g/100 g of dry protein and stirred for 30 min. The mixture was left to evaporate under continuous stirring and then placed in a thermostatic chamber at 37 °C until the solvent had completely evaporated. The resin thus obtained was frozen using liquid nitrogen and ground to a fine powder in a Moulinex grinder.

2.3. Film formation

Gliadin resin containing glycerol was stored at 52.9% RH, whereas the resin without glycerol was kept at 90% RH and 25 °C prior to thermo-pressing. The moisture content of the resin was evaluated according to the method described by Hernandez-Munoz et al. (2003). The moisture content of the gliadin resin with glycerol conditioned at 52.9% RH was 59.5 ± 0.7 (g of water/100 g of dry resin) whereas the moisture content of gliadin resin without glycerol and conditioned at 90% RH was 20.9 ± 0.8 (g of water/100 g of dry resin). Films were fabricated by placing 0.9 g of resin between two Teflon®-coated aluminum sheets to obtain 110 ± 10 μm thick films. This assembly was compressed on a Carver 4128 hydraulic press (Wabash, IN, USA) and heated to temperatures between 70 °C and 150 °C. Various values of time and applied force were assayed to identify the best processing conditions to obtain homogeneous films lacking holes. For all samples, force was first applied at 4 t for 1 min, then at 14 t for 2 min, and finally at 22 t for 9 min. Gliadin films obtained by casting were used as the control. To make cast films, glycerol was added to a solution of the film-forming solution (25 g/100 g of protein) for obtaining plasticized films. Measured volumes of the film-forming solution with or without glycerol were then poured onto a horizontal Pyrex tray and the solvents were allowed to evaporate at 37 °C for 24 h. Dried films were peeled off the casting surface. Unplasticized films were prepared without glycerol addition.

Film thickness was measured with a digital micrometer (Mitutoyo, Kanagawa, Japan) with a 2 μm sensitivity. Mean thickness was calculated from measurements taken at five different locations on each film sample.

2.4. Sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE)

The molecular weight distributions of proteins present in gliadin films were analyzed by SDS-PAGE performed in a vertical electrophoresis unit (Bio-Rad Laboratories, Hercules, CA, USA). The procedure employed was based on that of Laemmli (Laemmli, 1970) with some minor modifications (Ng & Bushuk, 1987) and adapted to gliadin films by Hernández Muñoz et al. (2003). A molecular weight standard protein mixture composed of myosin (199 kDa), β-galactosidase (116 kDa), bovine serum albumin (97 kDa), ovalbumin (53 kDa), carbonic anhydrase (37 kDa), soybean trypsin inhibitor (29 kDa), lysozyme (20 kDa) and aprotinin (7 kDa) was run.

2.5. Water uptake and weight loss

Triplicate film specimens of 7 cm^2 were dried over silica gel in a desiccator for 10 days. At this point the moisture content in the film samples was assumed to be close to zero. Samples (<150 mg) were accurately weighed (initial dry weight, W_d^i) and immersed in test tubes containing 10 mL of 0.1 M sodium phosphate buffer (pH 7). The tubes were shaken in an orbital shaker at 180 rpm at 25 °C for 24 h. The film specimens were then removed from the solutions, blotted with absorbent paper and weighed (final wet weight, W_w^f). After weighing, film samples were put back in the desiccator until constant weight was achieved (final dry weight, W_d^f). The percentage of water uptake and weight loss of the films were calculated as:

$$\text{Water uptake}(\%) = \frac{W_w^f - W_d^f}{W_d^f} \cdot 100 \quad (1)$$

$$\text{Weight loss}(\%) = \frac{W_d^i - W_d^f}{W_d^i} \cdot 100 \quad (2)$$

2.6. Water vapor permeability

WVP tests were carried out at a 0–50% RH gradient and at 23 °C using 10 cm^2 aluminum permeability cups (Elcometer, Manchester, England), in accordance with ASTM E96-10 (ASTM, 2010). The cups were filled with 7 g of silica gel and the film to be tested was held in place with a flat Viton ring, an aluminum ring and three press-screws. The cups were then stored in a desiccator containing a saturated aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and weighed daily. The samples were prepared in quadruplicate and weighed daily.