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Physical and bioactive properties of corn starch – Buttermilk edible films

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ABSTRACT

The effect of incorporating different ratios of both non-heated and heated (95 °C) buttermilk (BM) to corn starch (CS) films was analysed in terms of its structural, mechanical, barrier, optical and bioactive properties. The properties of the film forming dispersions (particle size distribution, ζ-potential and rheological behaviour) were also analysed. As the BM increased in the blend, both the average particle size and the apparent viscosity of the film forming dispersions were reduced. The low degree of compatibility between both materials resulted in heterogeneous structures, where an interpenetrated protein phase in the starch matrix was observed as a result of the protein gelation when BM was heated. This affected the mechanical and barrier properties giving rise to more resistant and extensible, and less permeable films than in non-heated BM. Only films formulated with heated BM exhibited antioxidant activity, probably due to the release of the antioxidant peptides during thermal treatment of proteins. BM did not have any effect on the growth of *Listeria innocua*.

1. Introduction

Currently, most of the plastics used are petroleum-derived (Saiah et al., 2009) and about a third of the world's plastic production goes into packaging applications (Wiles, 2005). The use of these non-biodegradable materials represents a huge worldwide environmental problem (Azeredo, 2009), since these materials are highly polluting and their recycling implies a great expense (Sánchez-García et al., 2008). To face up to this situation, much research work has been focused on the substitution of synthetic plastics by biodegradable polymers (biopolymers) obtained from renewable resources (Saiah et al., 2009), the use of which would reduce the environmental impact of petroleum plastics (Sánchez-García et al., 2008).

Of the renewable sources with film-forming ability, polysaccharides are the most abundant (Carvalho, 2008). Starch is often used due to its low cost and easy availability (Cuq et al., 1997; Carvalho, 2008). Native starch becomes thermoplastic after heat treatment with plasticizers, with properties similar to those of common synthetic polymers. The material obtained is called thermoplastic starch (TPS).

The development of biodegradable packaging materials with adequate physical properties (mechanical and water and gas barrier), with antimicrobial or antioxidant activity, is especially relevant for food preservation. This stems both from reasons related to environmental aspects and from consumer demand for safe and high quality products. The incorporation of active compounds into food packaging increases the efficiency of food preservation. Packaging becomes the vehicle for preservatives or compounds of interest from a nutritional point of view, such as nutraceuticals.

Several authors have developed and characterised edible films based on starch of different origins containing diverse bioactive ingredients (Pyla et al., 2010; Kechichian et al., 2010; Shen et al., 2010; Mathew and Abraham, 2008). Buttermilk is a by-product of the butter-making process, which is spray-dried to obtain a commercial powder, whose principal compounds are lactose, proteins, fat and mineral salts. The breaking of the fat globule membrane during the process releases a high quantity of proteins and membrane peptides with bioactive properties, such as antioxidants and others with physiological effects (Affolter et al., 2010; Michalski and Januel, 2006). Previous studies have pointed out the antioxidant role of buttermilk, (Wong and Kitts, 2001, 2003), and of different dairy peptides (Pihlanto, 2006). Both lactoferrin and its derived peptide lactoferricin have been reported to have bactericidal, fungicidal, and antiviral activities (Van der Kraan Marieke et al., 2004). The heat treatment of buttermilk leads to the inactivation of its native flora and could release antimicrobial peptides from milk proteins (Mills et al., 2011).

No previous studies have been found into the use of buttermilk to form films, despite their bioactive properties and high protein content (whey protein) with film-forming ability. The other compounds, lactose and minerals, would act as plasticizers which can reduce the requirements of other agents to this end. Likewise,

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the blend of buttermilk with other film-forming compounds, such as starch, might improve the functional properties of the film and its bioactivity.

The objective of this work was to analyse the effect of buttermilk incorporation on the properties of the film-forming dispersions and the physical (mechanical, barrier, optical) and microstructural characteristics of corn starch films. The impact that heat treatment has on films containing buttermilk was analysed. The antioxidant and antimicrobial activities of the films were also tested.

2. Materials and methods

2.1. Raw materials

Corn starch (CS) and buttermilk (BM), supplied respectively by Roquette Laisa España, SA (Valencia, Spain) and Lactotecnia, S.L. (Barcelona, Spain), were used to obtain the films. BM composition was: lactose (51%), proteins (31%), fat (7%) and salts (7%). Glycerol and magnesium nitrate were purchased from Panreac Química S.L.U. (Barcelona, Spain). The reactants for the antioxidant capacity assay – Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), $K_2S_2O_8$ and ABTS (202-azino-bis-[3-etilbenzotiazol-6-sulphonic acid]) – were supplied by Sigma–Aldrich (Madrid, Spain). For the antimicrobial activity analysis, stock culture of *Listeria innocua* (CECT 910) was supplied by the Spanish Type Culture Collection (CECT, Burjassot, Spain). Tryptone Soy Broth, Agar bacteriological and tryptone phosphatewater were provided by Scharlab, (Barcelona, Spain). NaCl was purchased from (Panreac, Barcelona, Spain).

2.2. Preparation of film forming dispersions (FFD)

CS was dispersed at 3% (w/w) in distilled water and stirred for 5 min at room temperature. Then the dispersion was heated at 95 °C for 30 min to induce starch gelatinization and cooled down under running water to reach room temperature. Glycerol was added as a plasticizer in a CS:glycerol ratio of 1:0.25 (Jiménez et al., 2012; Talja Riku et al., 2007; Teixera et al., 2007). Distilled water was added to adjust the concentration, and homogenisation was carried out in a rotor–stator ultraturrax (DI25, Janke and Kunkel, Germany) at 13,500 rpm for 4 min. CS dispersion was degasified for 15 min at room temperature by means of a vacuum pump (MZ 2C NT, Vacuubrand GMBH + CO KG, Wertheim, Germany). BM (3% w/w) was dispersed in distilled water and stirred for 5 min at room temperature. Glycerol was added in a BM:glycerol ratio of 1:0.25, and the dispersion was stirred at room temperature for another 10 min. Finally, both suspensions were mixed in four different CS:BM w/w ratios (1:0, 0.75:0.25, 0.50:0.50, 0.40:0.60) and kept under stirring at room temperature for 10 min.

A second series of FFDs was prepared with the aim of testing the effect that heat treatment had on buttermilk. In this case, both dispersions were mixed prior to heating them for 30 min at 95 °C. The resulting formulations were referred to as $CS_{0.75}$:$BM_{0.25}$ Q, $CS_{0.50}$:$BM_{0.50}$ Q and $CS_{0.40}$:$BM_{0.60}$ Q.

2.3. Characterisation of the film-forming dispersions

2.3.1. Particle size, pH and ζ-potential

The particle size analysis of the FFDs was carried out by using a laser scattering instrument (MasterSizer 2000, Malvern Instruments, UK). The samples were dispersed in distilled water at 2000 rpm until an obscuration rate of 8–10% was obtained. The Mie theory was applied by considering a refractive index of 1.52 and absorption of 0.1. Three samples of each FFD were measured at 25 °C. Two average diameters were obtained: the area-volume mean diameter ($d_{3,2}$), which is related to the average surface area of droplets exposed to the continuous phase per unit volume of emulsion, and the volume-length diameter ($d_{4,3}$), which is the sum of the volume ratio of droplets in each size-class multiplied by the mid-point diameter of the size-class.

$$d_{3,2} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

$$d_{4,3} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (2)$$

The pH of the FFDs was measured in triplicate at 25 °C by using a pH-meter (SevenEasy, Mettler-Toledo, S.A.E, Barcelona, Spain). Prior to the measurement of Zeta potential (ζ-potential), FFDs were diluted to a droplet concentration of 0.02% (w/v) using distilled water. ζ-potential was determined in triplicate by measuring the electrophoretic mobility of the dispersed particles in a charged field by using ZetaSizer equipment (Nano-Z, Malvern Instruments, UK). The Smoluchowsky mathematical model was used by the software to convert the electrophoretic mobility measurements into ζ-potential values.

2.3.2. Rheological behaviour

The rheological behaviour of the FFDs was analysed in triplicate at 25 °C by means of a rotational rheometer (HAAKE RheoStress 1, Thermo Electric Corporation, Germany) with a type ISO 3219 Z34DIN sensor system of coaxial cylinders. Rheological curves were obtained after a stabilization time of 5 min at 25 °C. Shear stress (σ in Pa) was measured as a function of shear rate ($\dot{\gamma}$ in s^{-1}) from 0 to 512 s^{-1} in the following way: 5 min to reach the maximum shear rate and 5 min to attain zero shear rate. The power law model (Eq. (3)) was applied to determine both the consistency index (K in Pa s^n) and the flow behaviour index (n). Additionally, the apparent viscosity (η_{ap}) at 100 s^{-1} was determined.

$$\sigma = K \cdot \dot{\gamma}^n \quad (3)$$

2.4. Film preparation

FFDs were poured onto framed and levelled polytetrafluorethylene (PTFE) plates (15 cm diameter) and were dried for at least 24 h under natural convection at 25 °C and 45(±2)% relative humidity (RH). Film thickness was controlled by pouring the amount of FFD onto the PTFE plate that would provide a surface density of solids of 56 g/m^2. Dry films were peeled off the casting surface and preconditioned for 14 days in desiccators at 25 °C and 54% RH, by using an oversaturated $Mg(NO_3)_2$ solution.

2.5. Film characterisation

2.5.1. Film thickness

A hand-held digital micrometer (Electronic Digital Micrometer, Comecta S.A., Barcelona, Spain) was used to measure film thickness to the nearest 0.0001 mm. This was measured in triplicate for samples submitted to mechanical tests and water vapour permeability analyses.

2.5.2. Microstructure

Cross-section images of the films were obtained by using Scanning Electron Microscopy (SEM) with a JEOL® microscope, model JSM-5410. The samples were immersed in liquid nitrogen and cryofractured. After gold coating, the samples were observed using an accelerating voltage of 10 kV.