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Combination of high-pressure treatment, mild heating and holding time effects as a means of improving the barrier properties of gelatin-based packaging films using response surface modeling

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ABSTRACT

The optimum combination of high-pressure (HP), mild temperature application and holding time on pigskin-derived, gelatin-based, film-forming solutions to improve the barrier properties of packaging films was determined using response surface methodology. Results showed that the variable response oxygen transmission rate (OTR) decreased significantly using a combination of temperature, time, and the interaction between pressure and time. The determined optimum conditions to minimize the OTR were high pressure treatment (600 MPa) and holding time (30 min), while maintaining the temperature at 20.5 °C. In parallel, films obtained at the optimum conditions (OPT) were characterized for structural, thermal, mechanical, water vapor transmission rate (WVTR) and color properties. OPT films were significantly affected by mechanical (TS), thermal (T_m), WVTR properties and redness a^* values compared to untreated control samples. Overall, a combination of HP, mild temperature and holding time on film-forming solutions showed interesting potential in altering film characteristics, especially in the enhancement of barrier properties.

Industrial relevance: Results obtained in this study are of considerable importance for the film development and the shelf-life of food products packaged in films treated with the methodology used in the current work. The oxygen permeation through the film packaging can lead to a degradation of the quality attributes of the food products influencing microbial development as well chemical and enzymatic degradation pathways. Oxygen is responsible for oxidative rancidity of unsaturated fats with the development of undesirable flavors and aromas and a loss in vitamin C. The package oxygen permeability plays a key role in affecting the internal partial pressure of a packaging system and for this reason the oxygen permeability is probably the property mostly tested for the different packaging materials. Within this contest, the industrial relevance of this study is significant, since the results showed a potential application of a combination of high-pressure, mild treatment and holding time to increase barrier properties in bio-sourced packaging films thus extending the shelf-life of foodstuffs.

1. Introduction

Gelatin is a protein derived by partial hydrolysis of animal collagen and sourced globally from pigskin (46%), bovine hide (29.4%) and bones (23.1%) (Gómez-Guillén et al., 2009). However, fish gelatin now represents a real alternative to mammalian gelatins, due to the development of vegetarianism, halal and kosher markets as well as the concern about bovine spongiform encephalopathy (BSE) (Nur Hanani, Roos, & Kerry, 2012). See, Hong, Ng, Wan Aida, and Babji (2010) estimated global gelatin use to be 326,000 tons and have reported that commercial demand is anticipated to increase into the future. Gelatin is characterized by a unique sequence of amino acids; possessing a high level of glycine, proline and hydroxyproline. In particular, pigskin-derived gelatine (PSG) possesses a content of proline and hydroxyproline of around 30%, which is considerably higher when compared with that provided by fish gelatins (Karim & Bhat, 2009). Gelatin has been widely used for application within the food industry as a highly functional ingredient and more recently has received attention with respect to its ability to form films. Such investigation has taken place due to the ease of use, wide source range, free availability, potential biodegradability and compostability, relatively low cost and of course, its excellent film forming capabilities. The previous statement is underpinned by the vast amount of research published to date on the use of gelatin for film application (Arvanitoyannis, Kolokuris, Nakayama,

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Yamamoto, & Aiba, 1997; Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997; Cao, Fu, & He, 2007; Eastoe & Leach, 1997; Núñez-Flores et al., 2012; Rivero, García, & Pinotti, 2009; Wang, Auty, Rau, Kerry, & Kerry, 2009).

When used for film manufacture, gelatin produces clear, flexible and strong films through the use of a casting process or following extrusion, after dissolution in water and in presence of suitable plasticizers (Gennadios, McHugh, Weller, & Krochta, 1994; Nur Hanani, Beatty, Roos, Morris, & Kerry, 2012; Nur Hanani, McNamara, Roos, & Kerry, 2013). As a potential food packaging material, gelatin films are mainly deposited as coatings to extend the shelf-life of perishable foods, especially protecting them from oxygen, light, and moisture exchange (Farris, Schaich, Liu, Piergiovanni, & Yam, 2009; Villegas, O'Connor, Kerry, & Buckley, 1999). In fact, gelatin is known to produce biodegradable films which possess excellent gas barrier properties (Giménez, Gómez-Estaca, Alemán, Gómez-Guillén, & Montero, 2009). Impermeability to gases is typically a very important attribute for the vast majority of films used for food packaging applications. In particular, oxygen is responsible for many deteriorative processes occurring in packaged foods and its presence can drive to undesiderable modifications of food products leading to safety, organoleptic and nutritional-loss issues. For example, changes in color, degradation of various vitamins and development of rancid flavors are directly linked to the presence of oxygen as is the promotion of aerobic microbial growth and several enzyme catalyzed reactions, all of which are responsible for the reduction in shelf-life of oxygen-sensitive foods. Gelatin-based films generally have good gas barrier properties. However, protein-based films like gelatin are highly sensitive to moisture and exhibit poor water vapor barrier properties (Guilbert, Gontard, & Gorris, 1996; Wang, Liu, Kerry, & Kerry, 2007).

HP treatment has been increasingly used for the preservation and processing of food. This alternative technology is used to preserve a variety of food materials without the requirement for excessive levels of heat, thereby making it a minimal processing technology. HP processing has been found to disrupt the quaternary and tertiary structure of globular proteins, with little influence on secondary structures, but accompanied by the formation of new hydrogen bonds. In particular, the interactions between hydrogen bonds are favored under HP conditions since this treatment induces a small negative volume change (Galazka, Dickinson, & Ledward, 2000). The effects of HP treatment depend upon the pressure applied, as well as on other parameters such as: temperature, holding time and molecular size of the protein (Nguyen & Balasubramaniam, 2011).

Research on the application of HP in the food packaging area is generally related to the compatibility of this technology with existing ready-to-use packaging materials, but it has rarely been used as a technology to improve food-based ingredient formulations for film manufacture in an attempt to improve the mechanical and barrier properties of films produced following subsequent film-manufacture. In fact, effects of HP treatment on synthetic or conventional packaging film properties such as seal integrity, mechanical properties plus oxygen and water permeability, and its impact on migration of volatile compounds from packaging materials to foodstuffs have only been recently reported (Bull, Steele, Kelly, Olivier, & Chapman, 2010; Dobiáš, Voldřich, Marek, & Chudáčková, 2004; Eisenbrand, 2005; Galatto et al., 2008; Rivas-Cañedo, Nuñez, & Fernández-García, 2009). However, the majority of these studies examined the effects of HP processing on formed film properties, rather than film formulations prior to film manufacture. Results obtained from these studies showed that HP treatments up to 600 MPa affected the functional properties of films examined with respect to processing temperature and time. For the majority of samples examined, an increase in the permeance to oxygen and water vapor was reported with an accompanied loss of sealability, along with a significant increase in the migration of compounds from plastic materials. To our knowledge, there are only few studies that have assessed the effects of HP treatment on biopolymer-based solutions or gelled systems prior to forming food packaging films (Bi et al., 2004; Montero, Fernández-Díaz, & Gómez-Guillén, 2002). The objective of this study was to investigate the use of a combination of HP, mild heat treatments and holding time on PSG film-forming solutions and the subsequent assessment of the resulting films with respect to film properties.

2. Experimental

2.1. Materials

PSG Bloom 180 (average molecular weight 1×10^5 Da) was used as the basal material for all film matrices (Healan Ingredientes Ltd., York, UK). Glycerol (Cahill May Roberts Ltd., Dublin, Ireland) was used as plasticizer. A 0.1 M NaOH (Lab Pak Ltd.., Filongley, UK) was used for the adjustment of the pH.

2.2. Preparation of films

Dry PSG was dissolved in distilled water (10% w/w) by heating at 90 °C in a water bath (SW23, Julabo USA Inc., Allentown, PA, USA) for 30 min. Successively, the solution was cooled to 30 °C and the pH was adjusted to 8.0. After pH adjustment, glycerol was added under constant stirring at a concentration of 33% w/w dry matter. The solution was transferred into vacuum pack pouches, cooled in icy water (1:3 ice:water), vacuum packed and treated at different combinations of pressure, temperature and holding time in a Stansted Fluid Power Iso-Lab 900 Power HP Food Processor (Stansted Fluid Power Ltd., Stansted, UK). The pressure vessel had a 2 L capacity and an internal diameter of 100 mm. A mixture of ethanol–castor oil (90:10) was used as the pressure transmitting medium and the rates of compression and decompression were both set at 300 MPa min^{-1}. The temperature of the pressure transmitting medium (ethanol–castor oil) inside the HP chamber was maintained constant with a heating jacket surrounding the pressure chamber. Before casting, HP-treated or untreated PSG film forming solutions were set to 40 °C, and then solutions casted onto leveled acetate sheets using a Micron II film applicator (Gardco, FL, USA) and dried for 48 h at 20 °C.

2.3. Film thickness and conditioning

Film thickness was measured using a digital micrometer (Käfer Digital Thickness gauge, Käfer Messuhrenfabrik GmbH & Co., Villingen-Schwenningen, Germany) with an accuracy of 0.001 mm. Before measurement, films were preconditioned for at least 48 h in an environmental chamber set at 23 °C and 50% relative humidity.

2.4. Oxygen transmission rate (OTR) measurement

The OTR was performed as described by Molinaro et al. (2013). Briefly, Perspex™ cups were stored under controlled temperature (23 °C) and relative humidity (50%) and a constant air velocity of 152 m/min maintained over the cups to ensure uniform air movement across the cells. The oxygen concentration was calculated according the following equation (Siró, Plackett, & Sommer-Larsen, 2010):

$$OTR = V * (slope/100) * 24 * (10000/A) \quad (1)$$

where OTR is expressed as ml m^{-2} day^{-1}, V is the volume of the receiving chamber and A is the area of the film available for gas permeation. Results presented are an average of three replicates.

2.5. Design of experiments (DoE)

The experiment was carried out using a Box–Behnken design (BBD) response surface methodology (RSM) (Statgraphics software version XV, Statpoint Technologies Inc., Warrenton, VI, USA). The statistical experiment design was an independent, rotable quadratic design where