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Storage-induced changes in functional properties of glycerol plasticized – Soybean protein concentrate films produced by casting

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ABSTRACT

Aging of soybean protein concentrate (SPC) films plasticized by glycerol obtained by casting and stored at 25 ± 2 °C and 65 ± 2% relative humidity was systematically investigated over a period of 90 days. Aging promoted the reorganization of the secondary structure of protein fraction in SPC into others with prevalence of extended β-sheet conformation. Stabilizing interactions also progressed to increasing contribution of disulfide cross-links and Maillard aggregates through the carbohydrate fraction of SPC. Such time-dependent structural changes were ineffective in retaining glycerol within the films. This caused increased strength and stiffness with time. Water vapor permeability values increased up to 90th day due to micro-cracks created by film contractions during storage, which create more permeable structures which hamper the determination of oxygen permeability on aged films. As a general trend, films functional properties remained stable for two weeks under specific storage conditions preserving enough mechanical and barrier properties to act as efficient protective food packaging materials.

1. Introduction

Motivated by petroleum shortage and market demand for sustainable and cost – effective sources, vegetable proteins are regarded as potentially viable feedstock options to depleting ones for the design of food packaging films. The biological nature of such materials provides abundant raw supplies with constant composition and favorable costs, along with the distinctive ability of being converted into biomass and harmless by-products through microbial activity, under appropriate waste management infrastructures. Soybean proteins are appealing raw materials for food packaging films because of their aptitude of protecting foodstuffs due to their good mechanical properties and oxygen barrier at medium and low relative humidity, and their processing ability by diverse methods (Ciannamea, Stefani, & Ruseckaite, 2014). From a technological point of view, the potential of soybean proteins films as packaging materials require controlled lifetime of the macroscopic properties to become competitive to the commonly used synthetic polymers (Orliac, Rouilly, Silvestre, & Rigal, 2003). However, biopolymers, such as soybean proteins suffer aging. To limit aging, it is important to identify and understand the mechanisms and reasons for the time-dependent physical and chemical changes (Olabarrieta, Cho, et al., 2006).

Physical aging or structural relaxation of a glassy matrix occurs at temperature below the glass transition temperature (T_g) and it is related with the evolution from a non-equilibrium state (i.e. glassy state) toward the equilibrium accompanied by molecular rearrangements. Chemical aging, on the other hand, is associated with chemical reactions undergoing with time such as protein aggregation and thiol oxidation (Morel, Bonicel, Micard, & Guilbert, 2000; Olabarrieta, Cho, et al., 2006; Olabarrieta, Gällstedt, Ispizua, Sarasua, & Hedenqvist, 2006; Ullsten et al., 2009). Accordingly the understanding and control of the causes driving such variations is crucial in predicting and ensuring the long-term stability of the functional properties of protein films.

Changes upon aging such as those due to the migration/diffusion of low mass components (i.e., plasticizers, additives), protein aggregation, denaturation and/or thiol oxidation have been reported for protein – based films. Aging experiments conducted on wheat gluten and corn zein films containing polyethylenglycol or glycerol (Gly) as plasticizers revealed increased tensile strength occurred after 20 days of storage associated with plasticizer migration (Park, Bunn, Weller, Vergano, & Testin, 1994). The greater stability of whey protein isolate films

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plasticized with sorbitol over those plasticized with Gly during storage at 23 °C, 50% relative humidity (RH) for 120 days was correlated with the out – diffusion of the latter over time (Anker, Stading, & Hermansson, 2001). On the contrary, whey protein isolate films with Gly were reported to be more stable than their counterpart containing sorbitol due to the migration and crystallization of sorbitol (Osés, Fernández-Pan, Mendoza, & Maté, 2009). Color variations upon aging linked with non enzymatic browning were also observed in whey protein concentrate (Trezza & Krochta, 2000) and fish myofibrillar protein –based films plasticized with saccharose (Cuq, Gontard, Cuq, & Guilbert, 1996). Examples of time-induced brittleness of wheat gluten films plasticized with diverse plasticizers are reported in the literature (Gueguen, Viroben, Barbot, & Subirade, 1998; Micard, Belamri, Morel, & Guilbert, 2000; Olabarrieta, Cho, et al., 2006). Particularly, the decrease in ductility of vital wheat gluten films obtained at pH 4 over time was associated to the loss of plasticizing molecules due to a lower degree of protein aggregation at acidic pH (Olabarrieta, Cho, et al., 2006). Similar findings were accounted for glycerol-plasticized vital wheat gluten films containing 4.5 wt % natural or quaternary ammonium salt modified montmorillonite clay (Olabarrieta, Gällstedt, et al., 2006), extruded glycerol-wheat gluten with salicylic acid and sodium hydroxide (Ullsten et al., 2009) exposed to identical aging conditions (23 °C, 50% RH, 120 days) and compression-molded glycerol-plasticized wheat gluten films exposed to 0% RH and 50% RH for 24 days (Gällstedt, Mattozzi, Johansson, & Hedenqvist, 2004). Hernández-Muñoz, López-Rubio, del-Valle, Almenar, and Gavara (2004) reported changes in mechanical and color properties of gluten films plasticized with glycerol while those incorporated with sorbitol and thriethanolamine remained stable after 1 year of storage at 25 °C and 65% RH. Similarly, sunflower protein films plasticized with glycerol and triethylenglycol were stable over a 3-month aging period while lighter plasticizers were lost over time (Orliac et al., 2003). In addition to variations in tensile, barrier and color properties, antioxidant activity also evolved with time as reported by Jongjareonrak, Benjakul, Visessanguan, and Tanaka (2008) for fish skin gelatin films incorporated with BHT (butylated-hydroxy-toluene) or a-tocopherol, stored at 28 °C and 50% RH for several weeks. Despite the industrial significance of the aging problem, a limited number of studies on soybean protein – based films have been reported in the literature. One study carried out on glycerol-plasticized soybean protein isolate (SPI) films made from intensively mixed materials stored at 25 °C and 50% RH over 14 weeks revealed that films evidenced a sticky surface due to the out – diffusion of the plasticizer. Thickness, tensile strength as well as percentage of elongation at break barely varied with aging, except for 40%Gly-added films which experienced a reduction in elongation of about 45% (Cunningham, Ogale, Dawson, & Acton, 2000). Compression-molded SPI plastics modified by different plasticizers and exposed at 25 °C, 50% RH for 180 days, showed an excess of enthalpy relaxation and all plastics tended to be stiff and brittle upon storage, being the plastics with Gly fairly stable after 60 days (Mo & Sun, 2003).

The functional properties of freshly prepared soybean protein concentrate (SPC) films plasticized with glycerol were studied after processing by casting and compression molding in our previous work (Ciannamea et al., 2014). In order to evaluate whether the functional properties remained stable during the foreseen shelf life of the material, films were stored for 90 days at 25 ± 2 °C and 65 ± 2% RH. Variations on tensile properties, color, moisture content, total soluble matter as well as water vapor permeability were assessed and related with the evolution of the stabilizing interactions in SPC films over time.

2. Experimental

2.1. Materials

Soy protein concentrate (SPC, Solcom S 110) with an average particle size of 100 mesh, and a proximate composition of 7% moisture, 69% protein, 1% fat, 3% fiber, 5% ash and about 15% non-starch polysaccharides (mainly cellulose, non cellulose polymers and pectin polysaccharides), was provided by Cordis S.A. (Villa Luzuriaga, Buenos Aires, Argentina). Glycerol analytical grade (Gly, 98%) was purchased from Anedra (Buenos Aires, Argentina) and used as a plasticizer. TRIZMA/hydrochloric acid, glycine and Na_2EDTA (Biopack, Buenos Aires, Argentina), Sodium dodecyl sulfate (SDS) and urea (Anedra, Buenos Aires, Argentina), and 2-mercaptoethanol (Aldrich, St. Louis, USA) were used in solubility tests. Buffer solution pH 10 (Anedra, Buenos Aires, Argentina) was used to adjust the pH level of the film-forming solutions. Sodium azide (Na_3N, Anedra, Buenos Aires, Argentina) was applied to prevent microbial growth during total soluble matter assays. Calcium chloride ($CaCl_2$; Aldrich, St. Louis, USA) was used as desiccant for water vapor transmission measurements. Copper sulfate ($CuSO_4$) and potassium and sodium double tartrate tetrahydrate (Anedra, Buenos Aires, Argentina) were used as received to prepare Biuret reagent. Trichloroacetic acid (TCA, Biopack, Buenos Aires, Argentina) was used as received.

2.2. Methods

2.2.1. Film formation

All films were produced by casting from their film – forming solutions according to the conditions previously reported elsewhere (Ciannamea et al., 2014). SPC powder was manually mixed with suitable amounts of glycerol (30%, 40% and 50% on dry SPC basis) for 15 min. Pre-mixes (5 g/100 ml solution) were subsequently dissolved in pH 10 buffer solution (pH > isoionic point, pI ~ 4.5) under constant stirring at 70 °C on a hot plate (Cole-Parmer, USA) for 30 min. After mixing, dispersions were sonicated in an ultrasonic bath (Testlab, 160 W, 40 KHz) for 15 min to remove bubbles and subsequently poured into leveled Teflon-coated Petri dishes, equipped with Teflon frames (thickness 0.5 cm) to control the amount of film – forming solutions per area. A uniform film thickness (target thickness ~ 150 μm) was maintained by casting the same solid content (i.e. approximately 35 ml/150 cm^2, for SPC-30% Gly). Water was evaporated in an air-circulating oven (Memmert, Germany) at 25 °C until reaching constant moisture content (about 24 h), and then peeled-off from the molds. Films were cut into the desired shapes for further testing and stored in a controlled humidity chamber at 25 ± 2 °C and 65 ± 2% RH for 48 h, prior testing. Films were labeled as **SPCX** where **X** corresponds to the percentage (on dry SPC weight) of glycerol.

2.2.2. Aging

After casting and conditioning, films were stored in a climate chamber at 25 ± 2 °C and 65 ± 2% RH. Preliminary experiments had shown that films reached the equilibrium moisture content within the first 48 h of storage. Twenty films were cast from each formulation and samples of adequate shape were subjected to FTIR analysis, differentiate solubility tests, tensile properties, opacity, color, total soluble matter and water vapor permeability as well as morphological changes with time. Experiment was performed during 90 days. 'Un-aged' refers to 0 day stored samples.

2.2.3. Thickness

Film thickness was measured with a manual micrometer (0–25 ± 0.01 mm, Bta. China). Measurements were done at ten