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Physical and mechanical properties of compression molded and solution casting soybean protein concentrate based films

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ABSTRACT

Soybean protein concentrate-based films plasticized by glycerol were obtained by two processing methods: intensive mixing followed by compression molding and solution-casting. Film forming conditions such as molding temperature, molding pressure, drying conditions as well as glycerol level were determined. The effect of the forming method on the physical and mechanical properties of the resultant films was analyzed in terms of color, light transmission, tensile properties, water solubility and water vapor and oxygen barrier properties. Thermo-pressed soy protein concentrate films were significantly more transparent, less soluble, more stretchable and had lower water vapor permeability but greater oxygen permeability coefficient than solution casting films at the same plasticizer level. These results were associated with the intermolecular forces involved in the formation of the films. Hydrophobic interactions and hydrogen bonding dominated the formation solution-casting films, whereas disulphide bonding played a more important role in the formation of compression molded films, as revealed by solubility of obtained films in denaturing solutions and infrared spectroscopy. This study demonstrates that forming process plays a major role in determining the final properties of soy protein concentrate-based films and reveals the possibility of soy protein concentrate-glycerol mixtures to be transformed through thermo-mechanical processing into biodegradable films with potential application in food packaging.

1. Introduction

Biopolymers extracted directly from biomass, such as polysaccharides and proteins, have received much attention in recent years for the development of biodegradable materials for food packaging and are considered as potential substitutes of non-biodegradable polymers derived from oil, given their renewable origin and biodegradability (Song, Tang, Wang, & Wang, 2011). Among biopolymers, animal and vegetable proteins are of great interest for the production of food packaging films because of their relatively low cost, high availability as byproducts of food industry and agriculture and inherent biodegradability (Janjarasskul & Krochta, 2010; Mangavel et al., 2004; Paetau, Chen, & Jane, 1994; Reddy & Yang, 2013). An additional advantage is that proteins can be processed by diverse methods such as dissolution-solvent evaporation or thermo-mechanical methods to produce films with excellent oxygen barrier properties and suitable mechanical properties (Guerrero, Retegi, Gabilondo, & de la Caba, 2010; Hernandez-Izquierdo & Krochta, 2008; Krishna, Nindo, & Min, 2012; Mangavel et al., 2004; Reddy & Yang, 2013; Song et al., 2011).

Particularly, soy proteins are an interesting alternative for obtaining environmentally friendly materials. These proteins, in addition to being an abundant and renewable resource with high biodegradability, arouse further interest in Argentina, the third largest producer of soybeans after the United States and Brazil, with 48.8 million tons harvested in 2011. According to official data, the majority of soybean harvest in Argentina is used for the production of flour and oil, 28.6 and 7.1 million tons in 2011, respectively, exporting almost the total, making the country the largest global exporter of these products (Ministry of Agriculture, 2013). Considering that recycling rate of soybean protein into added value products other than food systems, such as adhesives and plastics is constantly increasing there is a great need to investigate new industrial uses for this protein.

Soy proteins mainly consist of four globulin fractions, characterized by the ultracentrifuge sedimentation rates: 2S, 7S, 11S and 15S, expressed in Svedberg units. Among them, the major fractions are glycinin (11S) and conglycinin (7S), representing 31% and 37% of the protein, respectively (Hettiarachchy & Eswaranandam, 2005;

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Kunte, Gennadios, Cuppett, Hanna, & Weller, 1997). Soy protein is available in various commercial forms, such as soybean flour (SF), soy protein concentrate (SPC) and soy protein isolate (SPI) (Song et al., 2011). SF contains about 40–60% protein, combined with fats and carbohydrates. SPC contains about 60–70% protein, a polyscaccharide fraction (8–15%) mainly composed of cellulose and pectic polysaccharides (linear hetero-polysaccharides containing free or esterified units based on galacturonic acid) and minor components such as fats (1%), fibers (1–3%) and ashes (3–5%). SPI contains more than 90% of protein (Janjarasskul & Krochta, 2010; Singh, Kumar, Sabapathy, & Bawa, 2008) and is the most widely soybean product used for film processing (Cunningham, Ogale, Dawson, & Acton, 2000; Kokoszka, Debeaufort, Hambleton, Lenart, & Voilley, 2010; Kunte et al., 1997; Paetau et al., 1994; Rhim, Gennadios, Handa, Weller, & Hanna, 2000; Rhim, Gennadios, Weller, Carole, & Hanna, 1998). However, SPI is relatively expensive for the potential production of materials on a large scale in comparison with SPC.

The functional properties of protein films are determined by their microstructure, which strongly depend on the protein structure and the processing method. Protein–protein interactions involved in the generation of the film will define the final properties. The type and number of interactions (electrostatic, hydrophobic, hydrogen bonding and disulfide bridges) will be established by amino acid composition, the average molar mass and the type and variables of the processing technology used to obtain the film. Broadly, two technologies are used to process proteins: the wet and dry methods (Hernandez-Izquierdo & Krochta, 2008; Reddy & Yang, 2013). Wet method (solution casting) first involves the dispersion or solubilization of the protein in a solvent and in a second step the suspension or film-forming solution is placed in a suitable mold and the solvent is evaporated under controlled conditions (Kunte et al., 1997; Mangavel et al., 2004). During this process the primarily polymer–polymer interactions are set, resulting in a stable three-dimensional network (Hernandez-Izquierdo & Krochta, 2008; Reddy & Yang, 2013). The result of the casting process depends mainly on the mixing conditions: temperature, time, type and concentration of solvent, plasticizer and pH, and the drying relative humidity and temperature (Gällstedt, Mattozzi, Johansson, & Hedenqvist, 2004; Monahan, German, & Kinsella, 1995). Most of the researches in protein based films use this method because it is simple, reproducible in most laboratories and useful as a first approximation to the formation of protein films. However, the drying step makes this method slow and discontinuous, making it infeasible for an industrial scale (Krishna et al., 2012; Reddy & Yang, 2013).

Although thermo-mechanical processing has received less attention, these technologies can use pre-existing equipment for thermoplastics with minimal modifications (Cunningham et al., 2000; Gällstedt et al., 2004; Krishna et al., 2012; Mangavel et al., 2004). Extrusion is a continuous and high performance process, advantageous for industrial scale (Krishna et al., 2012; Reddy & Yang, 2013). On the other hand, compression molding, which is usually assisted by a prior intensive mixing, is generally studied at laboratory scale as a precursor to continuous extrusion with the aim of determining the suitable processing conditions (Hernandez-Izquierdo & Krochta, 2008). During the thermo-mechanical processing, proteins disaggregate, denature and dissociate. These changes result in a complete restructuring of the protein molecules and allow them to recombine, crosslink and aggregate through specific links (Hernandez-Izquierdo & Krochta, 2008; Kuktaite et al., 2011). Particularly, glycinin (11S) has a quaternary structure composed of acidic and basic polypeptides, associated by disulfide bridges. During heat treatment 11S molecules unfold and part of the hydrophobic residues, SH groups and SS bonds are exposed. The intermolecular polymerization, which in turn leads to protein aggregation, may occur via these groups by the formation of disulfide bridges by oxidation of sulfhydryl groups and the reorganization of intramolecular disulfide bonds to intermolecular disulfide bonds through thiol–disulfide exchange reactions, resulting in an intermolecular network (Gällstedt et al., 2004; Lodha & Netravali, 2005). Parameters such as temperature, pressure, time and plasticizers determine the degree of conformational changes, protein aggregation and chemical crosslinking that take place during processing (Gällstedt et al., 2004; Ullsten et al., 2009). The crosslinking via SH and SS groups is highly dependent on temperature, therefore processing temperature will have significant effects on the final properties of the films (Kim, Weller, Hanna, & Gennadios, 2002; Park, Scott Whiteside, & Cho, 2008; Rhim et al., 2000; Sun, Song, & Zheng, 2008). A greater degree of crosslinking in the network will result in films with higher microstructures density, decreased solubility and improved mechanical strength and barrier properties (Mo & Sun, 2002; Ustunol & Mert, 2004).

The combination of bonds and interactions established between protein chains cause protein based films to be fragile and brittle (Sothornvit & Krochta, 2001). Therefore, is usually necessary to add plasticizers to reduce interactions between protein chains in order to improve their processability and the mechanical properties of the final material. Plasticizers increase chain mobility by reducing interactions between proteins and replacing them with protein–plasticizer interactions (McHugh & Krochta, 1994). Consequently, they increase the flexibility and reduce the brittleness of the films. However, the increased mobility of the chains also causes an increase in the diffusion coefficient of water vapor and oxygen, and as well lowers the mechanical strength of the films. Therefore, the content of plasticizer must be optimized to produce films with desirable mechanical strength, reducing the adverse effect on its properties (Hernandez-Izquierdo & Krochta, 2008; Hettiarachchy & Eswaranandam, 2005). Plasticizers used in biopolymers include polyols, such as sorbitol, glycerol and glucose, among others (McHugh & Krochta, 1994; Rhim et al., 2000; Singh et al., 2008; Sothornvit & Krochta, 2001). Among these plasticizers, glycerol (Gly) is one of the most widely used in protein processing. Soy proteins plasticized with Gly have good processing properties with good final properties (Sothornvit & Krochta, 2001).

The objective of this work was to study the effect of the processing method on the physicochemical, mechanical, and functional barrier of SPC based films. Two methods were used and compared, the traditional method of casting and intensive mixing followed by compression molding. For both methods, the influence of the addition of varying amounts of glycerol on the final properties was also studied.

2. Materials and methods

2.1. Materials

Soy protein concentrate (SPC, Solcom S 110) with an average particle size of 100 mesh, and proximate composition of 7% moisture, 69% protein, 1% fat, 3% fiber, 5% ash and about 15% non-starch polysaccharides (NSP, mainly cellulose, non cellulose polymers and pectin polysaccharides), was kindly 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. Sodium hydroxide (NaOH, Anedra) was used to produce pH 10 solution. TRIZMA/hydrochloric acid (Biopack; Buenos Aires, Argentina), glycine (Biopack) Na_2EDTA (Biopack), sodium dodecyl sulfate (SDS; Anedra), urea (Anedra) and 2-mercaptoethanol (Aldrich, St. Louis, USA) were used for