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Influence of glycerol and water activity on the properties of compressed egg white-based bioplastics

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ABSTRACT

In this paper, the effects of glycerol (35%, 40% and 45%) and water activity (0.34 and 0.48) on the physical, mechanical and morphological properties of compressed egg white-based bioplastics are investigated. Lighter, more reddish and less yellowish sheets with a decreased thickness and second-order transition temperature, improved mechanical properties (increased flexibility and decreased rigidity and stiffness) and constant moisture content can be obtained by increasing water activity. Increasing the GLY content results in the same type of changes but to a lesser extent and increased moisture content. Increasing both, water activity and GLY, leads to a more pronounced effect for some properties. This study demonstrates that compressed egg white-based bioplastics with desired properties can be obtained by adjusting water activity and GLY content during their synthesis.

1. Introduction

Government, industry, and consumers are more and more interested in ways to reduce the municipal solid waste resulting from use of plastics and to decrease the dependence of plastics on petrochemical sources (Kim, 2008; Koutsimanis et al., 2012; Mohanty and Misra, 2002). This has led to the intensification of research to develop plastics that are biodegradable and made from renewable resources. These plastics are currently known as bioplastics (Stevens, 2002).

Proteins offer great potential for the production of bioplastics (González-Gutiérrez et al., 2010; Guerrero et al., 2011). Proteins are molecules comprised of hundreds of amino acids and have the capability of forming both weak and strong linkages that result in a three-dimensional network stabilized by low-energy interactions and strengthened by covalent bonds (Pommet et al., 2003). Protein-bioplastics can be obtained by direct mixing of the proteins with a plasticizer under low moisture conditions, and subsequent exposure to heat and pressure using compression or extrusion processes (Hernandez-Izquierdo and Krochta, 2008a). Plasticizers are incorporated to modify the three-dimensional structure of the proteins through the reduction of intermolecular forces which facilitates the mobility of the protein chains and thereby eases processability (Di Gioia and Guilbert, 1999). Plasticizers can also reduce protein decomposition during processing by decreasing the transition temperatures. This results from an increase in the free volume of the protein network which facilitates chain mobility (Verbeek and Van Den Berg, 2010). In addition, plasticizers promote the flexibility and reduce the brittleness of a film or sheet (Sothornvit and Songtip, 2010; Sothornvit et al., 2007; Cunningham et al., 2000).

Water and glycerol are two well-known plasticizers used with proteins (Pommet et al., 2005; Slade and Levine, 1993; Sobral and Habitante, 2002; Sothornvit et al., 2007). Their effectiveness results from their small size which allows them to be easily interposed between the protein chains which decreases the forces holding the chains together (Di Gioia and Guilbert, 1999). Although water and glycerol are needed to improve protein matrix processability and to overcome film/sheet brittleness, the amount used can greatly affect the properties of the resulting film or sheet. Differences in mechanical properties, color, thermal behavior, and morphology in extruded and compressed protein-based sheets and films have been attributed to differences in water and glycerol contents (Hernandez-Izquierdo et al., 2008b; Sothornvit et al., 2007; Sothornvit and Krochta, 2005; Sothornvit et al., 2002; Zhang et al., 2001). Therefore, understanding the impact of plasticizer type and content on the properties of the protein-based bioplastic is necessary in order to improve the properties and suitability of these plastics for specific applications. This understanding can create bioplastics with desired properties.

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Recent studies have shown that it is feasible to produce bioplastics from egg white proteins (Jerez et al., 2007; Lee et al., 2013). Egg white-based bioplastics have been reported to be easily processed at low temperatures (Jerez et al., 2007). Sheets of egg white-based bioplastic have been manufactured by thermo-mechanical compression and have been described as highly transparent and highly elastic (González-Gutiérrez et al., 2010). Given these advantages and that egg protein meets food grade standards (Kreider, 2012), this bioplastic has potential as a material for biodegradable packaging and other plastic products. To date, only a few reported studies have been focused on egg white-based bioplastics (Jerez et al., 2007; González-Gutiérrez et al., 2010; González-Gutiérrez et al., 2011). These studies have been limited to one glycerol content and water activity and therefore, there is no systematic information in the literature about the effects of differing glycerol and water activities on the properties of egg white-based bioplastics. The goal of this study was to understand the effect of glycerol contents and water activities and of their interactions on the properties of sheets made of egg white-based bioplastics. The mechanical and thermo-mechanical properties, morphology, optical properties, and thermal behavior of these bioplastic sheets have been investigated. Understanding these properties brings us closer to useful applications of sheets and film made from this bioplastic.

2. Experimental section

2.1. Materials

Desugared, spray dried egg white protein (EWP) powder (82.1 ± 0.61% protein, 0.37 ± 0.17% fat, 6.04 ± 0.20% ash, and 3.51 ± 0.22% moisture determined by proximate analysis) was obtained from Rose Acre Inc. (Seymour, IN, United States). Glycerol (GLY) was obtained from Sigma–Aldrich, Inc. (St. Louis, MO, Unites States). Magnesium chloride ($MgCl_2$) and sodium nitrate ($NaNO_3$) were supplied by Columbus Chemical Industries Inc. (Columbus, WI, United States). Standard saturated salt solutions of 0.30 ± 0.01 and 0.50 ± 0.01 water activities were purchased from Decagon (Decagon Devices Inc., Pullman, WA, USA).

2.2. Methods

2.2.1. Preparation of EWP sheets

2.2.1.1. Preparation of egg white-based mixtures. EWP–GLY–water mixtures with GLY contents of 35%, 40% and 45% (w/w) were prepared by intensive mixing of EWP and GLY for 10 min using a mortar and pestle, and posterior pre-conditioning to water activities of 0.34 ± 0.01 and 0.48 ± 0.02 at 23.1 ± 0.1 °C. The pre-conditioning was performed by placing the mixtures into aluminum dishes and then storing for 3 days in closed environments maintained at 34% and 55% RH. A closed storage containers containing a saturated solution of $MgCl_2$ was used to condition the mixtures to 34% RH (0.34 ± 0.01 water activity). A room conditioned at 55 ± 5% RH was used to condition the mixtures to 0.48 ± 0.02 water activity. Three replicates were prepared per GLY content and per pre-conditioning condition. The water activity of the mixtures was verified using an AquaLab model CX-1 (Decagon Devices Inc., Pullman, WA, USA). The instrument was allowed to warm up for one hour and then calibrated with standard saturated salt solutions of 0.30 ± 0.01 and 0.50 ± 0.01 water activity.

2.2.1.2. Preparation of egg white-based sheet. Egg white-based mixtures resulting from combinations of 35%, 40% and 45% GLY and 0.34 and 0.48 water activity were converted into sheets using a thermo-mechanical procedure at a residence time of 8 min, and a pressure of 2.0 MPa (Model-M, Carver Laboratory Press, Carver Inc., Wabash, IN, USA). EWP–GLY–water mixtures were compressed at 128 °C. Mixtures were placed between aluminum foil sheets while pressing to prevent the molten material from sticking to the metal plates. Samples were cut into 5 × 10 cm strips and then repressed under the above conditions to obtain EWP sheets with a thickness close to that of current commercial sheets. Each of the EWP–GLY–water mixtures was replicated three times. EWP sheets were obtained from the replicates and conditioned at 55% RH and 23 °C for 3 days prior to use.

2.2.2. Moisture content determination

The moisture content of the EWP sheets was determined according to the Official Methods of Analysis AOAC International (2006), AOAC INTERNATIONAL, Gaithersburg, MD, USA, Official Method 937.01. The samples were placed into a vacuum oven (70 °C and 50 mmHg vacuum) for 24 h and then equilibrated to room temperature inside a desiccator. Three different EWP sheets per type sheet were tested.

2.2.3. Thickness determination

The thickness of EWP sheets was measured at five random positions using an electronic digital micrometer (Fowler® 0–1″ Digital Counter Micrometer, Port Washington, NY, USA). A mean thickness from three different sheets was calculated.

2.2.4. Thermal characterization

2.2.4.1. Differential scanning calorimetry. The second-order transition temperature of the EWP sheets was determined by using a differential scanning calorimeter (DSC Q100; TA Instruments, Newcastle, DE) with a liquid nitrogen cooling system. An amount between 7 and 10 mg of each type of sheet was hermetically sealed in an aluminum pan (TA Instruments, Newcastle, DE, USA), equilibrated to 0 °C, and then heated to 200 °C at a rate of 20 °C/min. During each run, the DSC cell was flushed with nitrogen at 70 ml/min to maintain an inert environment. The instrument was calibrated using pure indium. TA analysis software was used to do the data analysis in accordance with ASTM D3418 (ASTM, 2008). Samples from three different EWP sheets were evaluated.

2.2.4.2. Thermogravimetric analyses. The decomposition temperature of the EWP sheets was determined using a thermogravimetric analyzer (TGA Q50; TA Instruments, Newcastle, DE, USA). An amount between 7 and 10 mg of each EWP sheet was placed in an aluminum pan (TA Instruments, Newcastle, DE, USA) and then heated from 25 to 300 °C at a rate of 20 °C/min. The percent weight loss of each sample as a function of temperature under a nitrogen-air (40–60%) atmosphere was analyzed. Samples from three different EWP sheets were evaluated.

2.2.5. Mechanical characterization

2.2.5.1. Dynamic mechanical analyses. A dynamic mechanical analyzer (DMA Q800; TA instruments, New Castle, DE, USA) was used to measure the thermo-mechanical properties of the EWP sheets. The sheets were cut into rectangular specimens of 1.6 × 0.5 cm and then tested using the tension mode, frequency 1 Hz and amplitude 20 μm, over a temperature range of 25–150 °C at a heating rate of 5 °C/min under the DMA-multi-frequency-strain operational mode in accordance with ASTM D4065 (ASTM, 2006). The storage modulus (E') and tan delta ($\tan\delta$) were determined. Samples from three different EWP sheets were evaluated.

2.2.5.2. Tensile analyses. EWP sheets were cut into several rectangular pieces of 10 × 1.0 cm each. The elongation at break (E_b), tensile strength (σ_{max}), and modulus of elasticity (E) of each piece were measured according to ASTM D882 (ASTM, 2010) using an Instron Universal Testing Machine UTS SFM – 20 (United Calibration