



## Thermo-mechanical and hydrophilic properties of polysaccharide/gluten-based bioplastics



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### ABSTRACT

The influence of adding different polysaccharides (locust bean gum, LBG; methyl cellulose, MC; and carboxymethyl cellulose, CMC) to gluten-based biodegradable polymeric materials was assessed in this work. Gluten/polysaccharide/plasticiser bioplastics were prepared at different polysaccharide concentrations (0–4.5%) and pH values by mixing in a two-blade counter-rotating batch mixer (at 25 °C under adiabatic conditions) and thermomoulding at 9 MPa and 130 °C. Bioplastic probes were evaluated through dynamic mechanical thermal analysis, tensile strength and water absorption capacity tests. Results pointed out that a moderate enhancement of the network structure may be achieved by adding polysaccharide at a pH close to the protein isoelectric point (pH 6), which also conferred a further thermosetting capacity to the system. Moreover, the addition of MC and CMC was found to significantly enhance material elongation properties. However, the presence of charges induced by pH led to a higher incompatibility between the polysaccharide and protein domains forming the composite. The pH value played a relevant role in the material water absorption, which significantly increased under acidic or basic conditions (particularly at pH 3).

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### 1. Introduction

The global consumption of plastic in 2011 was almost 200 million tonnes with an annual growth of approximately 5% (Raphael & Yang, 2013). In this context, conventional plastics continue to dominate the market since, among other reasons, petroleum-based production benefits from large economies of scale and mature technologies. However, although bioplastic only constitutes a small part of the plastic consumption, production capacity will triple from 3.5 million tonnes in 2011 to nearly 12 million tonnes in 2020. With an expected total polymer production of about 400 million tonnes in 2020, the bio-based production should increase from 1.5% in 2011 to 3% in 2020 (Dammer, Carus, Raschka, & Scholz, 2013). Moreover, there exists a great interest in the utilisation of renewable biomass for the production of goods manufactured as an alternative to synthetic polymers, in order to reduce consumption

of petrochemical feedstock and diminish environmental pollution. Therefore, bioplastics (biobased products) are marketed as offering potential environmental advantages over conventional plastics, along with some economic benefits (Iles & Martin, 2013).

Proteins, lipids and polysaccharides have been proposed as biopolymers sources to obtain biodegradable plastic materials for many years (Averous, 2004; De Graaf, 2000; Hernandez-Izquierdo and Krochta, 2008; Irissin-Mangata, Bauduin, Boutevin, & Gontard, 2001; Siracusa, Rocculi, Romani, & Dalla Rosa, 2008). Most studies based on proteins have used plant proteins (i.e. from corn, wheat gluten or soy) to manufacture bioplastics since they are relatively inexpensive and environmentally friendly (Cuq, Boutrot, Redl, & Lullien-Pellerin, 2000; Jerez, Partal, Martinez, Gallegos, & Guerrero, 2005; Kim, 2008; Pomet, Redl, Morel, Domenek, & Guilbert, 2003; Reddy & Yang, 2013; Zheng, Tan, Zhan, & Huang, 2003). In particular, wheat gluten is a vegetable protein obtained as an agricultural by-product, which is considered a promising material due to their abundance, relatively low cost, good biodegradability and suitable material properties (Bengoechea, Arrachid, Guerrero, Hill, & Mitchell, 2007). In addition, gluten proteins show fast degradation rates and can be processed by thermoplastic methods with the aid of plasticisers (Chen, Reddy, Wu, & Yang, 2012;

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Zarate-Ramirez, Martinez, Romero, Partal, & Guerrero, 2011; Zhang & Mittal, 2010). Without such plasticising agents, gluten films are brittle and difficult to process and handle (Jerez et al., 2005). The most common plasticisers, among a wide variety, are water and glycerol. Previous results on glycerol/gluten-based bioplastics have pointed out a relevant effect of both processing and formulation on material properties, yielding a wide range of swelling and release behaviours (Gomez-Martinez, Partal, Martinez, & Gallegos, 2009, 2013; Lagrain, Goderis, Brijs, & Delcour, 2010). Furthermore, the addition of polysaccharides to protein/plasticiser blends also may play a role, due to the relevance of non-covalent protein–polysaccharide interactions that can be used to design and fabricate materials with novel or improved properties. In fact, due to the difference between the elemental composition of proteins (covalent bonds between hundreds of amino acids) and polysaccharides (covalent bonds between monosaccharides with ramifications), their mixtures can evidence a wide variety of two- and three-dimensional structures with different physico-chemical and rheological properties (Schmitt, Aberkane, & Sanchez, 2009).

Regarding polysaccharides, starch is widely used as a packaging material, usually mixed with biodegradable polyesters (Siracusa et al., 2008). However, there are other works that study the combination between these two different kinds of biopolymers, protein and polysaccharide, in order to improve the properties of the film due to their different physical properties and interactions. Several authors found that using a polysaccharide in combination to protein led to improved barrier properties by reducing permeability. This included films consisting of starch and gelatin (Aguilar-Mendez, Martin-Martinez, Tomas, Cruz-Orea, & Jaime-Fonseca, 2008), starch/alginate and milk proteins (Ciesla, Salmieri, & Lacroix, 2006), as well as whey protein-based films containing pectin or alginate (Parris, Coffin, Joubran, & Pessen, 1995), methylcellulose (Erdohan & Turhan, 2005) and pullulan (Gounga, Xu, & Wang, 2007). In addition to this enhancement in barrier properties, Coughlan, Shaw, Kerry, and Kerry (2004) also found higher tensile properties (tensile strength, elasticity modulus and elongation at break) by adding polysaccharide (particularly alginate) to whey protein. Lee, Shim, and Lee (2004) also found an improvement in tensile strength but at the expense of a reduction in elongation, by adding gellan gum to gelatin. On the other hand, Oses et al. (2009) found the opposite effect by adding mesquite gum to whey protein, which may be regarded as a typical plasticising effect that leads to a reduction of the interaction between protein molecules, thereby increasing flexibility (i.e. extensibility). Moreover, some authors have found improved elongational properties and water vapour permeability in film formulated by gluten proteins and chitosan (Park & Bae, 2006), cellulose acetate phthalate (Fakhouri, Tanada-Palmu, & Grosso, 2004; Zuo, Song, & Zheng, 2009) or methylcellulose (Zuo et al., 2009).

Most of the above-mentioned contributions are based on films processed by casting, thereby presenting some limitations related to its commercial applications as compared to other processing techniques such as extrusion or injection moulding. In any case, further research attention should be paid to the application of such thermomechanical processing techniques to obtain improved biodegradable polymeric materials.

It is generally regarded that incorporation of polysaccharides into protein matrices may extend their functional properties (Coughlan et al., 2004; Turgeon & Beaulieu, 2001; Zaleska, Ring, & Tomasik, 2000). Schmitt, Sanchez, Desobry-Banon, and Hardy (1998) have shown that protein–polysaccharide complexes gel more effectively than polysaccharides or proteins alone, which has been attributed to the simultaneous presence of the two biopolymers, as well as to the structure of the complexes. Likewise, as indicated by Zaleska et al. (2000) it is possible to manipulate

combinations of polysaccharide and protein component films to adjust water-vapour resistance or structural strength.

On these grounds, the overall objective of this work has been to evaluate the influence of the addition of different polysaccharides (locust bean gum, LBG; methyl cellulose, MC; and carboxymethyl cellulose, CMC) on the rheological and mechanical properties of WG/GL/polysaccharide/water blends subjected to thermoplastic compression moulding. Likewise, the influence of polysaccharide concentration and pH was analysed. The properties of the bioplastics obtained were evaluated by dynamic mechanical thermal analysis, tensile strength tests and water absorption capacity. This study would contribute to evaluate the potentials of adding a polysaccharide to gluten/plasticiser systems in order to develop bioplastics with enhanced tensile mechanical properties and tailored hygroscopic characteristics.

## 2. Material and methods

### 2.1. Materials

Wheat gluten, WG (83 wt% protein, 3 wt% lipid, 1 wt% ash, 8 wt% moisture and 10 wt% starch), was provided by Productos Riba S.A. (Granollers/Barcelona, Spain). Glycerol (GL), from Panreac Química S.A.U. (Castellar del Vallés/Barcelona, Spain), and distilled water were used as protein plasticisers. Polysaccharides such as locust bean gum, methyl cellulose and carboxymethyl cellulose (respectively, referred to as LBG, MC and CMC) were provided by Sigma–Aldrich (St. Louis, MO, USA).

### 2.2. Sample preparation

The WG/GL/polysaccharide/water systems consisted of 50 wt% gluten, 18 wt% glycerol, 0–4.5 wt% polysaccharide and 32–27.5 wt% water, depending on the percentage of polysaccharide. All the components were mixed in a two-blade counter-rotating batch mixer turning at a 3:2 differential speed (Rheomix 3000p; ThermoHaake, Karlsruhe, Germany). Mixing process was carried out at 25 °C and 50 rpm for 20 min under adiabatic conditions. Each polysaccharide was properly dispersed by the standard protocol described by Garnier et al. (1995) and Murray (2009) prior its addition. Native pH was generally found around 6, which corresponds to the isoelectric point (IEP) of gluten proteins. Furthermore, different pH values were used by adding NaOH or HCl 2 M solutions. The pH value was measured by a Crison pH 25 pH meter using a puncture electrode (Crison Instruments S.A., Barcelona, Spain).

Bioplastic probes were prepared from the dough-like materials obtained after the mixing process through thermo-moulding at 9 MPa and 130 °C for 10 min. Two types of moulds were used to prepare the probes: a 50 mm × 10 mm × 3 mm rectangular shape mould and a type IV probe defined by ASTM D638-99 (American Society for Testing Materials, 2005). All the probes (rectangular and type IV) were transferred into recipients at 53% relative moisture and allowed to reach moisture equilibrium at room temperature for at least 2 weeks before testing. The desired relative humidity was achieved by means of a desiccator, using a saturated solution of Mg(NO<sub>3</sub>)<sub>2</sub>. The values of the actual moisture of each sample were determined by evaporating the water at 105 °C to constant weight (Association of Official Analytical Chemists, 2005).

### 2.3. Dynamic mechanical temperature analysis (DMTA)

DMTA tests were carried out with a RSA3 (TA Instruments, New Castle, DE, USA), on rectangular probes using dual cantilever bending. All the experiments were carried out at constant frequency (1 Hz) and strain (between 0.01 and 0.3%, within the linear

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