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Brea Gum (from *Cercidium praecox*) as a structural support for emulsion-based edible films

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ABSTRACT

Brea gum (BG) is an exudate gum obtained from the *Cercidium praecox* tree. It is an acidic polysaccharide, made up of 75 g/100 g of hydrolysable sugars, such as L-arabinose, D-xylose, D-glucuronic acid and 4-O-methyl-D-glucuronate. The purpose of this study was to investigate the role of BG as a structural agent in the formulation of emulsion based films. Beeswax (BW) and glycerol (Gly) were added as moisture barrier and plasticizer, respectively. Mechanical and optical properties, microstructure and water vapour permeability were studied. The concentration of BW and Gly was ranged from 0 to 40 g/100 g in a dry basis with respect to BG. We found that, regardless the BW concentration, films with 0 g/100 g Gly were too brittle and they could not be handled. In contrast, films with 40 g/100 g Gly were too tacky and gummy, consequently they could not be unpeeled. Only those films with 20 g/100 g Gly (and 0, 20 and 40 g/100 g of BW) were assayed. Increasing BW concentration resulted in better vapour permeability, to the detriment of its mechanical properties; meanwhile it had no influence in colour parameters. BG may be considered to be a structural support for emulsion based films, being 20 g/100 g of Gly the satisfactory amount of plasticizer.

1. Introduction

With the prospect of environmental problems and a global energy crisis looming, fully green ecomaterials based on biomacromolecules have increasingly attracted researchers' interest due to their advantages: low cost, renewable resource, and biodegradability (Song & Zheng, 2014). Edible films are able to reduce the amounts of non-renewable conventional synthetic polymer packaging materials, and use ingredients of agricultural derived products.

An edible coating or film has been defined as a thin and continuous layer of edible material formed on food that can be ingested by the consumer (Wu, Weller, Hamouz, Cupett, & Schnepf, 2002). The coatings are directly applied by dipping or spraying on food, so the coating is formed during a drying step, while edible films are produced on a cast, and applied onto the food (Dangaran, Tomasula, & Qi, 2009).

Ideal edible films have a great potential for enhancing food quality, safety and stability and are used as carrier for functional active substances. They can also act as a barrier for moisture transmission, solutes and/or gases and can provide mechanical protection. The most commonly used materials for edible film production are biopolymers such as polysaccharides and proteins (Liu, 2005; Ponce, Roura, del Valle, & Moreira, 2008). Such natural polymers can be effective as gas barriers (O_2 and CO_2) (Baldwin, Nisperos-Carriedo, & Baker, 1995), having suitable mechanical and optical properties but being highly sensitive to moisture and exhibiting poor water vapour barriers (Guilbert, Gontard, & Gorris, 1996). On the contrary lipid component, such as sunflower oil or beeswax, can serve as a good barrier to water vapour permeability (Pérez-Gago & Krochta, 2005; Garcia, Martino, & Zaritzky, 2000). Film forming solutions frequently include plasticizers (Wu et al., 2002) like sorbitol and glycerol, which reduce internal hydrogen bonding while increasing intermolecular spacing (Hernandez-Izquierdo & Krochta, 2008). Therefore, it is quite a well-established concept to combine different biopolymers and lipids for food packaging.

Many types of polysaccharides were used for film production including exudate gums, which are produced by many trees and shrubs as a natural defence mechanism, particularly in semiarid regions. When the bark is injured, an aqueous gum solution is exuded to seal the wound. This solution dries in contact with air

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and sunlight, to form hard, glass-like lumps which can easily be collected (Verbeken, Dierckx, & Dewttlinck, 2003). Some gums used for making edible films were Arabic gum (Ali, Maqbool, Ramachandran, & Alderson, 2010), Mesquite gum (Bosquez-Molina, Guerrero-Legarreta, & Vernon-Carter, 2003) and Brea gum (Bertuzzi & Slavutsky, 2013).

Brea gum (BG) is a hydrocolloid exudate obtained from *Cercidium praecox* (Brea tree); which grows in semi-arid regions in South America (Bertuzzi, Slavutsky, & Armada, 2012). BG is defined as an acidic polysaccharide, made up of 75 g/100 g of hydrolysable sugars, such as L-arabinose, D-xylose, D-glucuronic acid and 4-O-methyl-D-glucuronate (De Pinto, Rodriguez, Martinez, & Rivas, 1993), and having no starch, dextrin or tannins. These carbohydrates are in association with approximately 8 g/100 g of protein, which may indicate the presence of proteoglycans (Majewska-Sawka & Nothnagel, 2000) which are crucial for the functionality of the gums, mainly for their emulsifying properties. Moreover, it has been proved that this gum is safe (Von Müller, López, Eynard, Aldo, & Guzmán, 2009), having been incorporated as a food additive in the Argentinian Food Code.

The BG has great economic, social and environmental importance in Argentina. Since it has similar properties to the Arabic gum, which Argentina imports, the exploitation of this gum could lead to significant profits for the country. Furthermore it could also represent an alternative income for indigenous communities, which currently harvest the gum. From an environmental point of view, this tree can be a groundbreaking element in the recovery of desert land.

Accordingly, the objective of this research was to obtain edible films from BG, with different concentration of beeswax and glycerol, and to study their mechanical and optical properties and their water vapour permeability.

2. Materials and methods

2.1. Materials

The BG was collected as small drops, and kindly provided by an indigenous community from Tartagal (Salta, Argentina).). The purification was done following these steps: the gum was dissolved in distilled water at 17 g/100 g and stirred with mechanical stirrer (Thorbell model HS30SE, Argentina) for 3 h, then kept overnight at 4 °C. After that, the solution was stirred again for 1 h, and centrifuged at 2000 g for 20 min. The supernatant was filtered by 0.45 mm filter paper, and the permeate was analysed in solid content (105 °C for 2 h) or freeze dried and kept at −18 °C for future experiments. The beeswax (BW) was obtained from a local producer of Santa Fe (Santa Fe, Argentina). This beeswax was melted at 60 °C and filtered through a mesh strainer before the experiments were conducted.

2.2. Experimental design

An experimental design with 2 variables: Glycerol (Gly) and BW concentrations, in 3 levels: −1, 0, +1 (design 3^2) was carried out. These levels correspond to 0 g/100 g (−1), 20 g/100 g (0) and 40 g/100 g (+1) on a dry basis of Gly and BW in each formulation with respect to BG, which remained constant 10 g/100 g (Table 1).

2.3. Preparation of film-forming solutions

GB was dissolved in distilled water at 19 g/100 g, 24 h before being used. Gly (Cicarelli, Argentine) and BW were added at 0, 20 and 40 g/100 g dry solid basis with respect to BG, potassium sorbate (Anedra, Argentina) was added as an antimicrobial agent (0.12 g/100 g), and Tween 80 (Anedra, Argentina) was used as an emulsifier. In order to melt the BW and form the emulsion, film-forming solutions were heated at 90 °C for 30 min in a water bath. The emulsions were obtained by homogenization at 90 °C using a Waring Blender 8010 EG (Waring Products, USA) for 4 min at high speed. After, the exact amount of each system to reach 1 g of solid per plate was placed in polyethylene Petri dishes (diameter 8.5 cm). Films were dried at 40 °C for 5 h, and then were placed at room temperature for 8 h. After that, the dried films were fitted out at 32 °C and 75.1 g/100 g of relative humidity for at least 3 days before characterization.

Table 1
Concentrations in dry basis of Gly and BW (−1, 0, +1 are the levels of the two factors).

Formulation	Wax (g/100 g)	Glycerol (g/100 g)
1	20 (0)	0 (−1)
2	20 (0)	20 (0)
3	20 (0)	40 (+1)
4	0 (−1)	0 (−1)
5	0 (−1)	20 (0)
6	0 (−1)	40 (+1)
7	40 (+1)	0 (−1)
8	40 (+1)	20 (0)
9	40 (+1)	40 (+1)

2.4. Optical microscopy

Emulsions were observed by means of optical microscopy (Leica DM Microsystems Inc., Germany). A drop of each forming film solution was put onto clean dry slides, and observed in 10X.

2.5. Film thickness

Film thickness was measured with a precision digital micrometer (Testing Machine Inc., USA). For each film, 9 thickness measurements were taken in different parts of the film chosen randomly and averaged.

2.6. Water solubility

Films were dried at 70 °C for 24 h, and then were immersed in 100 mL of distilled water for 24 h at 32 °C. Finally, the samples were removed, filtered through a 0.5 μm paper filter, and the remaining pieces were dried at 70 °C to constant weight (final dry weight). Water solubility (WS) was calculated by using the following equation:

$$WS(g/100g) = (initial\ weight - final\ weight)/initial\ weight \times 100 \quad (1)$$

Determinations were performed in quintupled.

2.7. Transparency

Film transparency was carried out according to the procedure reported by Han and Floros (1997) with a spectrophotometer Jenway 7305 (Staffordshire, UK). Film samples were cut in rectangular strips and placed in the interior of the spectrophotometer cell. The transparency of the films was calculated by the Eq. (2):

$$\text{Transparency} = \log(\%T_{600}/b) \quad (2)$$

Where $\%T_{600}$ is the Transmittance at 600 nm and b is film thickness