

Relationship between galactomannan structure and physicochemical properties of films produced thereof

V. R. F. Dos Santos¹ · B. W. S. Souza² · J. A. Teixeira³ · A. A. Vicente³ · M. A. Cerqueira^{1,3}

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Abstract In this work five sources of galactomannans, *Adenanthera pavonina*, *Cyamopsis tetragonolobus*, *Caesalpinia pulcherrima*, *Ceratonia siliqua* and *Sophora japonica*, presenting mannose/galactose ratios of 1.3, 1.7, 2.9, 3.4 and 5.6, respectively, were used to produce galactomannan-based films. These films were characterized in terms of: water vapour, oxygen and carbon dioxide permeabilities (*WVP*, *O₂P* and *CO₂P*); moisture content, water solubility, contact angle, elongation-at-break (*EB*), tensile strength (*TS*) and glass transition temperature (*T_g*). Results showed that films properties vary according to the galactomannan source (different galactose distribution) and their mannose/galactose ratio. Water affinity of mannan and galactose chains and the intermolecular interactions of mannose backbone should also be considered being factors that affect films' properties. This work has shown that knowing mannose/galactose ratio of galactomannans is possible to foresee galactomannan-based edible films properties.

Keywords Edible packaging · Polysaccharide · Transport properties · Mechanical properties · Thermal properties

Introduction

Edible film is a thin layer of an edible material which can be placed on or between food components (Falguera et al. 2011) and can be used with a multipurpose objective (e.g. restrict of moisture loss, control of gas permeability, decrease microbial activity and control the release of functional compounds) while being a fully biodegradable, environmental-friendly packaging system (Arvanitoyannis et al. 1997). Edible films are envisaged to reduce the amount of synthetic packaging used in some specific applications (Mikkonen et al. 2007), however the cost of the edible materials used and the difficulty of up-scaling the process lead to difficulties in using these edible films as packaging materials.

The growing interest on identifying new natural sources for edible films production originated a great number of works showing the possible applications of these materials, being polysaccharides such as starch, chitosan, carrageenan, and galactomannans among the most studied materials for edible films production (Bozdemir and Tutas 2003; Mikkonen et al. 2007; Kristo and Biliaderis 2007). In the last years, have been given special attention to galactomannan polysaccharides from *Leguminosae* seeds due to their interesting properties when compared with other polysaccharide sources (Aydinli and Tutas 2000; Cerqueira et al. 2009a; Mikkonen et al. 2007; Saurabh et al. 2013). The physicochemical properties of galactomannans varies among species, being the ratio mannose/galactose of the galactomannan chain one of the most used variables to predict their final properties. They are water soluble polysaccharides forming highly viscous and stable aqueous solutions (Mikkonen et al. 2007). Featuring different physicochemical properties, galactomannans are a versatile material used for many applications (e.g. stiffeners and stabilizers of emulsions) (Stephen et al. 2006). They are not

✉ M. A. Cerqueira
miguelcerqueira@deb.uminho.pt

¹ Improveat, Ltd. Spinpark – Centro de Incubação de Base Tecnológica, S. Cláudio de Barco, 4805-017 Guimarães, Portugal

² Departamento de Engenharia de Pesca, Universidade Federal do Ceará, Campus do Pici, Fortaleza, Ceará, Brazil

³ Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

toxic which allows their use in the textile, pharmaceutical, biomedical, cosmetics and food industries (Kapoor and Srivastava 2005; Saha and Bhattacharya 2010). The four primary plant sources of galactomannans are locust bean gum (*Ceratonia siliqua* L.), guar (*Cyamopsis tetragonolobus*), tara plant (*Caesalpinia spinosa*) and fenugreek (*Trigonella foenum-graecum*) (Prajapati et al. 2013). Recently, several works characterized galactomannan films regarding their barrier, mechanical and thermal properties, showing the influence of plasticizers and oil on their properties, and their potential application in food products (Aydinli and Tutas 2000; Bozdemir and Tutas 2003; Cerqueira et al. 2009a; Cerqueira et al. 2011).

Galactomannans are built up of a β -(1–4)-D-mannan backbone with single D-galactose branches linked α -(1–6) (Blibech et al. 2013). They differ from each other mainly by the M/G ratio and fine structure (McCleary et al. 1985; Stephen et al. 2006). This molar ratio varies with plant origin typically in the range of 1.0–1.1/1.0, 1.6–1.8/1.0, 3.0/1.0 and 3.9–4.0/1.0 for fenugreek, guar, tara, and locust bean gums, respectively (Dea and Morrison 1975; Mudgil et al. 2011); these values vary within the same species due to different metabolic processes of the plant, environmental factors and to the extraction method used (Cerqueira et al. 2009b; Chaires-Martínez et al. 2008; Reid and Meier 1970).

Differences in the fine structure are also pointed as an important factor regarding the final properties of galactomannans. The distribution of D-galactose groups along the mannan chain can have a significant effect on the properties of the galactomannans (Dea et al. 1986b). The distribution of D-galactosyl groups along the mannan chain is a consequence of the *in vivo* synthetic mechanism and is represented in Fig. 1. This mechanism varies from species to species depending on structural differences around the active sites of the enzymes (Dea et al. 1986a).

Several works have described the behaviour of different sources of galactomannans in aqueous solution, showing the influence of galactomannan structure on their final properties (Cerqueira et al. 2011; Prajapati et al. 2013). Moreover, the presence of salts or other biopolymers was extensively studied, and it has been shown that solubility, rheology and thermal behaviour are significantly changed with their addition (Cerqueira et al. 2011; Dea et al. 1986a; Mikkonen 2009). However, it is still unexplored the way that galactomannan structure can influence the properties of edible films (i.e. upon solvent evaporation).

This work explores and provides an insight of the influence of mannose/galactose ratio and fine structure of galactomannans on physicochemical properties of edible films prepared thereof.

Experimental

Film preparation

Five sources of galactomannans have been used for films preparation. Guar gum (GG) and Locust bean gum (LBG) with G/M ratios of 1.7 and 3.4, respectively, were purchased from Sigma-Aldrich (USA). *Adenanthera pavonina* (AP), *Caesalpinia pulcherrima* (CP) and *Sophora japonica* (SJ) gums with G/M ratios of 1.3, 2.9 and 5.6, respectively, were obtained as described by Cerqueira et al. (2009b). Films were prepared adding 1.5 g of galactomannan powder to 100 mL of distilled water at 25 ± 1 °C and left in agitation during 24 h. Afterwards the solutions were heated to 60 °C in a thermostatic bath with stirring and left in agitation for 2 h. 0.5 g of glycerol (Panreac, Barcelona, Spain) was then added to the solution and left in agitation for 1 h. After this, the solution was left overnight at room temperature with agitation. The films were prepared casting 28 mL of each galactomannan solution onto 9 cm diameter plastic Petri dishes. The films were dried in an oven at 35 °C for 16 h yielding a film thickness, measured by a micrometre (293–561, Mitutoyo, USA), of approximately 70 μ m. The films were peeled and left to stabilize at 25 ± 1 °C and 53 % RH $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ before analyses.

Water vapour permeability

Water vapour permeability (*WVP*) was determined gravimetrically following the methodology used by Martins et al. (2012) adapted from the ASTM E96-95 (1992) method. Three samples were cut from each film. Each sample was sealed on a permeation cell (cup containing distilled water at 100 % RH; 2.337×10^3 Pa vapour pressure at 20 °C), and placed in a desiccator containing silica gel (0 % RH; 20 °C). The water transferred through the test films was determined from cup weight loss over time. The steady state of weight loss was reached after 10 h. Experiments were performed in triplicate for each film formulation.

Oxygen and carbon dioxide permeability

Oxygen permeability (*O₂P*) and carbon dioxide permeability (*CO₂P*) were determined following the method used by Cerqueira et al. (2009a) based on the ASTM D3985-02 (2001) method. The films were sealed between two chambers, having each one two channels. In the lower chamber O₂ (or CO₂) was supplied at a controlled (J & W Scientific, ADM 2000, USA) flow rate to maintain its pressure constant in that compartment. The other chamber was purged by a stream of nitrogen, also at controlled flow. Nitrogen acted as a carrier for the O₂ (or the CO₂). In the case of O₂P measurement, the flow

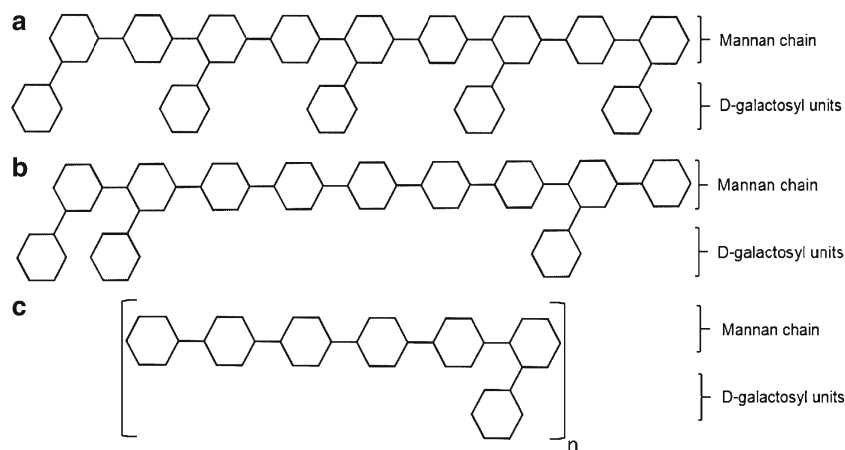


Fig. 1 Schematic representation of typical distribution of D-galactose units along the mannan chain in three galactomannans with distinct M/G content and fine structures: **a** Regular and statistically random distribution of D-galactose with low to medium M/G content (e.g. *Caesalpinia pulcherrima* galactomannan); **b** Non-regular, non-

statistically random distribution of D-galactose (e.g. *Ceratonia siliqua* galactomannan); **c** Regular and statistically random distribution of D-galactose with a high M/G content (e.g. *Sophora japonica* galactomannan)

leaving this chamber was connected to an O₂ sensor (Mettler Toledo, Switzerland) which measured the O₂ concentration in that flow on-line. In the case of CO₂P measurement the flow leaving this chamber was collected in a syringe for CO₂ quantification. To determine CO₂ concentration, 0.5 mL of sample was injected in a gas chromatograph (Chrompack 9001, Middelburg, Netherlands) at 110 °C with a column Porapak Q 80/100 mesh 2 m × 1/8" × 2 mm SS, using a flame ionization detector (FID) at 110 °C. Helium at 23 mL min⁻¹ was used as carrier gas. A standard mixture containing 10 % CO₂, 20 % O₂ and 70 % N₂ was used for calibration. The flows of the two chambers were connected to a manometer to ensure the equality of pressures (both at 1 atm) between both compartments. As the O₂ (and the CO₂) was carried continuously by the nitrogen flow, it was considered that partial pressure of O₂ (and the CO₂) in the upper compartment is null, therefore ΔP is equal to 1 atm. Three replicates were obtained for each sample, in each case (O₂P and CO₂P).

Water solubility and moisture content

The solubility in water (*S*) was determined according to Casariego et al. (2009). Samples of each galactomannan film (2.0 cm in diameter) were immersed in a cup with 50 mL of distilled water that were then kept under mechanical shaking (70 rpm) at 20 °C for 24 h. After this period, the samples were removed from the solution and dried to constant weight in an oven at 105 °C for 24 h. The initial dry mass was determined knowing the moisture content of sample. Moisture content was determined by drying the films at 105 °C during 24 h (until the equilibrium weight was attained). Three replicates were obtained for each sample.

Contact angle

Water contact angle (°) of the film surface was measured according to Kwok and Neumann (1999) in a face contact angle meter (OCA 20, Dataphysics, Germany) using the sessile drop method. A 2 µL droplet of ultra pure water was placed on the horizontal surface of the galactomannan films, with a 500 µL syringe (Hamilton, Switzerland), with a needle (0.75 mm diameter). Nine replicates of contact angle measurements were performed at 20.5 ± 0.3 °C.

Tensile strength and elongation-at-break

Tensile strength (*TS*) and elongation-at-break (*EB*) were measured according to Cerqueira et al. (2009a) with an Instron Universal Testing Machine (Model 4500, Instron Corporation) following the guidelines of ASTM D 882-91 (1991). The initial grip separation was set at 30 mm and the crosshead speed was set at 5 mm min⁻¹. *TS* was expressed in MPa and was calculated by dividing the maximum load (in N) by the initial cross-sectional area (in m²) of the specimen. *EB* was calculated as the ratio of the final length at the point of sample rupture to the initial length of a specimen (30 mm) and expressed as a percentage. According to the ASTM standard, film strips with a length of 45 mm and a width of 20 mm were used. *TS* and *EB* tests were replicated seven times for each sample.

Glass transition temperature

Glass transition temperature (*T_g*) was determined using a Differential Scanning Calorimetry (Shimadzu DSC-50, Shimadzu Corporation, Kyoto, Japan) calibrated with Indium as standard. Ca. 10 mg of the sample was placed in aluminium DSC pans (Al crimp Pan C.201-52943). The

measurements were performed between -100 and $250\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, being T_g determined at the second heating run.

Statistical analyses

Statistical analyses were performed using Analysis of Variance (ANOVA) and Tukey test ($p < 0.05$) was used to determine any significance of differences between specific means (SigmaPlot 11.0 2008, Germany).

Results and discussion

Permeability to gases

Table 1 shows permeability values of the films where is showed that WVP and CO_2P values follow the same pattern according to the type of galactomannan used. WVP values increase for higher values of M/G ratio until an M/G ratio of approximately 3 (LBG films). WVP values obtained for AP films are in agreement with values obtained by Cerqueira et al. (2009a) for films produced with the same source of galactomannan using different concentrations of glycerol (ranged between 4.89 and $8.10 \times 10^{-11}\text{ g m}^{-1}\text{ Pa}^{-1}\text{ s}^{-1}$). For GG and CP films, which have M/G ratios of 1.7 and 2.9, the WVP values increase ($p < 0.05$) to 10.45 and $10.69 \times 10^{-11}\text{ g m}^{-1}\text{ Pa}^{-1}\text{ s}^{-1}$, respectively. The higher values of WVP for increasing M/G ratio can be explained by the decrease in galactose content which leads to a better hydration of the inter-chain space and promote the diffusion of water molecules. Chandrasekaran et al. (1998) conducted an X-ray diffraction test with a prototype mannan chain with eight galactose units as side chains. They sequentially depicted the galactose units and concluded that gaps in the middle of the structures were immediately noticeable. This led to a disruption of the crystalline arrangement and the surrounding water moved in to the gaps and caused hydration (Chandrasekaran et al. 1998).

For higher M/G ratios galactomannan-based films present a distinct behaviour, being observed the decrease of WVP values for higher M/G ratios. WVP values for LBG and SJ

galactomannan films were 9.16 and $8.06 \times 10^{-11}\text{ g (m Pa s)}^{-1}$, respectively. In the case of SJ galactomannan, with an M/G ratio of 5.6, the low content of galactose results in a galactomannan chain with a great number of free mannan units. This causes a denser packing of the galactomannan chains, being more difficult for the water molecule to diffuse (Chandrasekaran et al. 1998; Kurt and Kahyaoglu 2014). This phenomenon can explain the fact that films with M/G values higher than 3 have gradually lower values of WVP , where the progressive increase of the free mannan units increases the intermolecular forces between mannan backbones.

CO_2P presented values ranging between 28.74 and $42.90 \times 10^{-15}\text{ g m (Pa s m}^2)^{-1}$, and follows the same pattern of WVP . CO_2P values increase from AP films to CP films, where CP presents an M/G ration of 2.9. CO_2P values start to decrease for films of LBG and SJ galactomannas (Table 1). O_2P values range from 1.64 to $2.94 \times 10^{-15}\text{ g m (Pa s m}^2)^{-1}$ (Table 1) being clear the influence of M/G content on the obtained values. Cerqueira et al. (2009a) mentioned that the galactomannan source seems to have an effect in the O_2P of galactomannan films, where lower M/G ratios lead to higher values of O_2P for films of AP, GG and CP galactomannans. For higher values of M/G ratios O_2P values of films start to rise. Actually, SJ films, which have an M/G ratio of 5.6, present the highest value of O_2P of all tested films.

Solubility, water content and contact angle

Food applications may require water insolubility to enhance product integrity and water resistance, or good water solubility if the film is meant to be dissolved quickly (Ghasemlou et al. 2011; Wan et al. 2015). The sensitivity of films to water can be evaluated by measuring solubility, water content and contact angle.

The solubility values obtained for AP, GG and CP galactomannan films were 64.39, 81.08 and 92.75 %, respectively (Table 2), while for LBG and SJ films the solubility values were 26.80 and 44.35 %, respectively, showing that high M/G ratio leads to films with lower solubility. These values are in agreement with the results obtained for other polysaccharide-based films. Ghasemlou et al. (2011) reported

Table 1 Values of mannose/galactose ratio (M/G), water vapour (WVP), carbon dioxide (CO_2P) and oxygen permeabilities (O_2P) for galactomannan-based films

Galactomannan film	M/G	$WVP \times 10^{-11}\text{ g m}^{-1}\text{ Pa}^{-1}\text{ s}^{-1}$	$CO_2P \times 10^{-15}\text{ g m (Pa s m}^2)^{-1}$	$O_2P \times 10^{-15}\text{ g m (Pa s m}^2)^{-1}$
AP	1.3	6.78 ± 0.63^a	28.81 ± 2.36^a	2.79 ± 0.14^a
GG	1.7	10.45 ± 0.32^b	37.06 ± 0.93^b	1.85 ± 0.08^b
CP	2.9	10.69 ± 0.75^b	42.90 ± 2.46^b	1.64 ± 0.08^b
LBG	3.4	9.16 ± 0.70^{bc}	37.16 ± 4.22^b	1.75 ± 0.31^b
SJ	5.6	8.06 ± 0.29^{ac}	28.74 ± 3.70^a	2.94 ± 0.08^a

^{a-c} Means ($n = 3$ for WVP and CO_2P , $n = 7$ for O_2P) in the same column with different superscripts are statistically different ($p < 0.05$)

Table 2 Values of mannose/galactose ratio (M/G), solubility, contact angle and water content

Galactomannan film	M/G	Solubility (%)	Contact angle (°)	Water content (%)
AP	1.3	64.39 ± 2.23 ^a	65.22 ± 1.26	9.07 ± 0.34
GG	1.7	81.08 ± 7.78 ^{ab}	82.88 ± 4.09	7.80 ± 0.60
CP	2.9	92.75 ± 0.96 ^b	96.03 ± 6.30	6.81 ± 0.34
LBG	3.4	26.80 ± 8.82 ^c	76.40 ± 1.48	8.99 ± 0.09
SJ	5.6	44.35 ± 12.77 ^c	65.16 ± 13.23	8.01 ± 1.32

^{a-c} Means ($n = 2$ for water content, $n = 3$ for solubility and $n = 9$ for contact angle) in the same column with different superscripts are statistically different ($p < 0.05$)

that kefiran films plasticized with glycerol presented a solubility of 28.88 %, while Jouki et al. (2013) for cress seed gum films with glycerol presented solubility values ranging from 48.30 to 54.12 %. Kurt and Kahyaoglu (2014) presented solubility values of 75.94 and 57.87 % for GG and LBG films, respectively. It is known that the presence of a plasticizer like glycerol, an hydrophilic molecule, leads to a reduction of the hydrophobicity of polysaccharide-based films (Ahmadi et al. 2012; Ghasemlou et al. 2011). Also, the crystalline arrangement of galactomannan films can influence their water solubility; according to Chandrasekaran et al. (1998) the removal of D-galactosyl units from the mannan chain induces a change in their crystallinity leading to hydration that will influence water solubility. This can explain the low solubility of LBG and SJ films and the higher solubility values for the three films (AP, GG and CP) with more galactose content. For galactomannan films with higher M/G ratio, the more hydrophobic mannan chains will contribute to decrease films water solubility (Mikkonen 2009). This happens due the low galactose content and the consequent denser packing of the mannan chains which generate stronger inter-chain connections and consequently more water-resistant films. These results are in agreement with *WVP* values (please see *Permeability to gases* section) where CP films present the highest *WVP* value. Indeed, it is widely known that permeability is influenced by the diffusion coefficient and solubility.

A different behaviour is observed for contact angle and water content values. Results showed a lower water affinity for CP films, when contact angle and water content are measured. Contact angle and water content provide information regarding the sorption of water molecules to the film structure, being also related with the hydrophobicity of the film surface, thus being lower for CP films.

Mechanical and thermal properties

Figure 2 shows the values of tensile strength (*TS*) and elongation-at-break (*EB*) for the films for increasing M/G ratios. *EB* increases (36.58, 50.76 and 69.72 %) with the

increase of the M/G ratio for AP, GG and CP films, respectively. For higher M/G ratios the *EB* values drop to 47.34 and 40.34 % for LBG and SJ films, respectively.

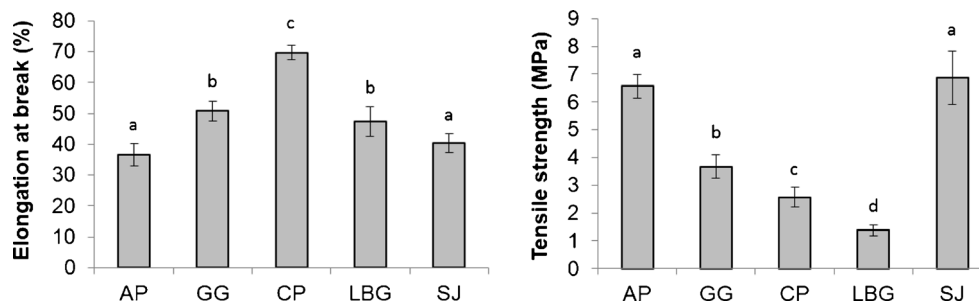
TS values follow the inverse of those obtained for *EB*; they are high at low M/G ratios, rising again for high M/G ratios. *TS* values were 6.56, 3.67, 2.56, 1.37 and 6.86 MPa for AP, GG, CP, LBG and SJ films, respectively. Results are in agreement with published works for other galactomannan- and polysaccharide-based films. Saurabh et al. (2013) presented *TS* values of 6 MPa for GG films plasticized with glycerol at 40 % w/w of polysaccharide. Cerqueira et al. (2009a) reported *TS* values from 2.5 to 4 MPa for films of AP and CP galactomannans with varying glycerol concentrations. Mikkonen (2009) performed a stepwise enzymatic modification with α -galactosidase to remove galactose side groups from a GG galactomannan and concluded that the depletion of galactose from the mannan chain makes the subsequent films to have higher *EB* values, ranging between 4 and 55 % for GG films and between 10 and 70 % for LBG films, depending on the plasticizer concentration (Mikkonen et al. 2007). Kurt and Kahyaoglu (2014) reported a *EB* value of 37.2 % for salep glucomannan films whereas Mali et al. (2005) obtained *EB* values between 10.3 and 47.0 % for yam starch-based films. Tavares et al. (2005) stated that a high number of D-galactosyl units seems to obstruct galactomannan-galactomannan interactions. In the present work this obstruction seems to create more flexible films for the AP, GG and CP galactomannans. Consequently, *TS* values for these three films decrease with the increase of *EB* values. Similar results were described in the work of Cerqueira et al. (2009a, b), where for AP films with concentrations of glycerol ranging between 0.5 and 1.5 % the *EB* increased and *TS* decreased with the increase of glycerol concentration.

Higher values of *TS* for SJ films can be explained by the denser packing of the mannan chains. Kurt and Kahyaoglu (2014) found that glucomannan-based films had higher tensile strengths compared to GG and LBG films. This occurred mainly because of the acetyl groups of glucomannan, which are smaller than those of galactomannan, resulting in higher hydrogen bonding frequency. The depletion of galactose probably enables side chains to pack and to establish hydrogen bonds more easily, thus increasing *TS* values.

The values of T_g of edible films can be used to clarify whether the film is brittle or rubbery and at which temperature this transition happens (Mali et al. 2005). Antoniou et al. (2014) tested the thermo mechanical properties of tara gum films for different concentrations of glycerol. For a concentration of 0.15 % they found one T_g peak at -46.7 °C, and with the increase of the plasticizer to 0.30 % two T_g peaks were clearly noticeable.

In the present work the films were plasticized with 0.5 % of glycerol and only one T_g peak was found. The values of T_g were -66.7 , -69.5 and -71.3 °C for AP, GG and CP films,

Fig. 2 Elongation-at-break and tensile strength of AP, GG, CP, LBG and SJ galactomannan films with an M/G ratio of 1.3, 1.7, 2.9, 3.4 and 5.6, respectively. *a–d* Means (*n* = 7) in the bars with different superscripts are statistically different (*p* < 0.05)



respectively. The M/G ratio and the fine structure of the polymer chain have an important role in the T_g values, as verified by Chaires-Martinez et al. (2008). Mikkonen et al. (2007) found two T_g peaks for native GG films with glycerol and one T_g peak for a depleted GG galactomannan film. The T_{g1} of the native GG film was $-64\text{ }^\circ\text{C}$, which is identical to the T_g found for GG films in this work (Table 3). Regarding the T_{g2} of Mikkonen’s work for galactomannan films, it was found that it decreases with depletion of galactose units. They verified that with the increase of the M/G ratio the value of T_g decreases, and this has also occurred for the three galactomannans with the lowest M/G ratios in the present work. For LBG and SJ films T_g starts to increase to values of -63.53 and $-65.34\text{ }^\circ\text{C}$, respectively. The distribution of the galactose units in the mannan chain can affect T_g values (Bresolin et al. 1998; Chaires-Martínez et al. 2008) and can explain the increase of those values for galactomannan films with higher M/G content.

Galactomannan structure

From the presented results it is clear that the structure of galactomannans has a strong influence in films properties. There are three main characteristics to be taken into account for the formulation of galactomannan films with tailored properties: the M/G ratio, molecular weight and the distribution of the D-galactosyl units along the mannan chain. These three characteristics are closely related and should not be evaluated separately.

In this work only the M/G ratios were evaluated and it can be concluded that for films of galactomannans with lower M/

G ratios, and well-distributed galactose units along the mannan chains, is expected low *WVP*, solubility and *EB* values. This can be explained by the high galactose content of AP and GG, where mannan chains are not easily accessible for inter-chain associations. Moreover, according to Chandrasekaran et al. (1998), water would not be able to enter the inter-chain space because of the highly branched galactomannans. The same authors report that when galactose is removed holes will be formed between the chains and water will enter the gaps formed by this depletion, leading to higher values of *WVP* and solubility as well as to the increase of *EB* due to the plasticizing effect of water. This explains the variation of these properties for the films with intermediate M/G content. For low galactose content and consequently high M/G ratio there will be free mannan chains to interact with each other. Dea et al. (1986b) describes this stronger interactions for low galactose content galactomannans and for those which have high frequency of unsubstituted blocks of at least 6 mannans. The properties of the films studied in the present work are in agreement with these premises. For films based in galactomannans with higher M/G ratio, mannan chains get closer and stronger inter-chain linkages are formed leading to a “repelling” effect towards water. When evaluating the AP and SJ galactomannans (which have the lowest and highest M/G content, respectively) films properties, it is possible to state that they have similarities in every analysed property. This can be due to the statistically random distribution of D-galactosyl units in the SJ galactomannan backbone. The LBG films present a solubility of 31.39 % and a *TS* of 1.37 MPa, while SJ films present a solubility of 51.67 % and a *TS* value of 6.86 MPa. The comparison of LBG and SJ galactomannans’ behaviour in solution showed that LBG has stronger inter-chain interactions than SJ (Dea et al. 1986a). This happens because of the non-statistically random distribution of galactose in the LBG galactomannan. For galactomannans having this kind of fine structure the interactive properties are mainly associated with the unsubstituted regions of the mannan backbone (Dea et al. 1986b) which leads to distinct film properties. For example in mechanical and thermal analysis the LBG films showed unexpected values if based solely in the criterion of M/G ratio. Thus the different fine structure of this galactomannan seems to have an

Table 3 Values of mannose/galactose ratio (M/G), glass transition temperatures (T_g) for the AP, GG, CP, LBG and SJ galactomannan films

Galactomannan film	M/G	T_g ($^\circ\text{C}$)
AP	1.3	-66.27 ± 3.34
GG	1.7	-69.75 ± 2.50
CP	2.9	-71.13 ± 5.38
LBG	3.4	-63.53 ± 2.49
SJ	5.6	-65.34 ± 5.95

important effect in the properties described and further studies should be performed in order to relate fine structure and final properties of galactomannan-based films.

Conclusion

It is possible to produce films with predetermined properties taking into account the different galactomannan sources. Water affinity of the films, as expected for polysaccharide-based films, has a great influence in their final properties. This work has shown that mannose/galactose ratios influences galactomannan-based edible films' final properties. It can thus serve as a guide for the use of galactomannans as alternatives to non-edible coatings and may also be a guide for the study of the influence of galactomannans structure in edible film properties.

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References

- Ahmadi R, Kalbasi-Ashtari A, Oromiehie A, Yarmand M, Jahandideh F (2012) Development and characterization of a novel biodegradable edible film obtained from psyllium seed (*Plantago ovata* forsk). *J Food Eng* 109(4):745–751. doi:10.1016/j.jfoodeng.2011.11.010
- Antonίου J, Fei L, Hamid M, Haroon JQ, Fang Z (2014) Physicochemical and thermomechanical characterization of tara gum edible films: effect of polyols as plasticizers. *Carbohydr Polym* 111:359–365. doi:10.1016/j.carbpol.2014.04.005
- Arvanitoyannis I, Eleni P, Atsuyoshi N (1997) Edible films made from sodium caseinate, starches, sugars or glycerol part 1. *Carbohydr Polym* 31:179–192. doi:10.1016/S0144-8617(96)00123-3
- Aydinli M, Tutas M (2000) Water sorption and water vapour permeability properties of polysaccharide (locust bean gum) based edible films. *LWT Food Sci Technol* 33(1):63–67. doi:10.1006/fstl.1999.0617
- Blibech M, Maktouf S, Chaari F, Zouari S, Neifar M, Besbes S, Ellouze-Ghorbel R (2013) Functionality of galactomannan extracted from tunisian carob seed in bread dough. *J Food Sci Technol* 52:1–7. doi:10.1007/s13197-013-0966-2
- Bozdemir OA, Tutas M (2003) Plasticiser effect on water vapour permeability properties of locust bean gum – based edible films. *Turk J Chem* 27:773–782
- Bresolin TMB, Milas M, Rinaudo M, JLMS G (1998) Xanthan–galactomannan interactions as related to xanthan conformations. *Int J Biol Macromol* 23(4):263–275. doi:10.1016/S0141-8130(98)00061-0
- Casariogo A, Souza BWS, Cerqueira MA, Teixeira JA, Cruz L, Díaz R, Vicente AA (2009) Chitosan/clay films' properties as affected by biopolymer and clay micro/nanoparticles' concentrations. *Food Hydrocoll* 23(7):1895–1902. doi:10.1016/j.foodhyd.2009.02.007
- Cerqueira MA, Lima AM, Teixeira JA, Moreira RA, Vicente AA (2009a) Suitability of novel galactomannans as edible coatings for tropical fruits. *J Food Eng* 94(3–4):372–378. doi:10.1016/j.jfoodeng.2009.04.003
- Cerqueira MA, Pinheiro AC, Souza BWS, Lima AM, Ribeiro C, Miranda C, Teixeira JA, et al. (2009b) Extraction, purification and characterization of galactomannans from Non-traditional sources. *Carbohydr Polym* 75(3):408–414. doi:10.1016/j.carbpol.2008.07.036
- Cerqueira MA, Bourbon AI, Pinheiro AC, Martins JT, Souza BWS, Teixeira JA, Vicente AA (2011) Galactomannans use in the development of edible films/coatings for food applications. *Trends Food Sci Technol* 22(12):662–671. doi:10.1016/j.tifs.2011.07.002
- Chaires-Martínez L, Salazar-Montoya JA, Ramos-Ramírez EG (2008) Physicochemical and functional characterization of the galactomannan obtained from mesquite seeds (*Prosopis pallida*). *Eur Food Res Technol* 227(6):1669–1676. doi:10.1007/s00217-008-0892-0
- Chandrasekaran R, Radha A, Okuyama K (1998) Morphology of galactomannans: an X-Ray structure. *Carbohydr Res* 306:243–255
- Dea ICM, Morrison A (1975) Chemistry and Interactions of Seed Galactomannans. *Adv Carbohydr Chem Biochem* 31:241–312. doi:10.1016/S0065-2318(08)60298-X
- Dea ICM, Clark AH, McCleary BV (1986a) Effect of galactose substitution patterns on the interaction properties of galactomannans. *Carbohydr Res* 147:275–294
- Dea ICM, Clark AH, McCleary BV (1986b) Effect of the molecular fine structure of galactomannans on their interaction properties — the role of unsubstituted sides. *Food Hydrocoll* 1(2):129–140. doi:10.1016/S0268-005X(86)80015-7
- Falguera V, Quintero JP, Jimenez A, Aldemar J, Ibarza A (2011) Edible films and coatings- structures, active functions and trends in their use. *Trends Food Sci Technol* 22(6):292–303. doi:10.1016/j.tifs.2011.02.004
- Ghasemlou M, Khodaiyan F, Oromiehie A (2011) Physical, mechanical, barrier, and thermal properties of polyol-plasticized biodegradable edible film made from kefiran. *Carbohydr Polym* 84(1):477–483. doi:10.1016/j.carbpol.2010.12.010
- Jouki M, Khazaei N, Ghasemlou M, Hadinezhad M (2013) Effect of glycerol concentration on edible film production from cress seed carbohydrate gum. *Carbohydr Polym* 96(1):39–46. doi:10.1016/j.carbpol.2013.03.077
- Kapoor VP, Srivastava M (2005) Seed galactomannans: an overview. *Chem Biodivers* 2:295–317. doi:10.1002/cbdv.200590013
- Kristo E, Biliaderis CG (2007) Physical properties of starch nanocrystal-reinforced pullulan films. *Carbohydr Polym* 68(1):146–158. doi:10.1016/j.carbpol.2006.07.021
- Kurt A, Kahyaoglu T (2014) Characterization of a new biodegradable edible film made from salep glucomannan. *Carbohydr Polym* 104:50–58. doi:10.1016/j.carbpol.2014.01.003
- Kwok DY, Neumann AW (1999) Contact angle measurement and contact angle interpretation. *Adv Colloid Interface* 81(3):167–249. doi:10.1016/S0001-8686(98)00087-6
- Mali S, Grossmann MV, García MA, Martino MN, Zartzyk NE (2005) Mechanical and thermal properties of yam starch films. *Food Hydrocoll* 19(1):157–164. doi:10.1016/j.foodhyd.2004.05.002
- Martins JT, Cerqueira MA, Bourbon AI, Pinheiro AC, Souza BWS, Vicente AA (2012) Synergistic effects between K-carrageenan and locust bean gum on physicochemical properties of edible films made thereof. *Food Hydrocoll* 29(2):280–289. doi:10.1016/j.foodhyd.2012.03.004

- McCleary BV, Allan HC, Dea ICM, Rees DA (1985) The fine structures of carob and guar galactomannans. *Carbohydr Res* 139:237–260. doi:10.1016/0008-6215(85)90024-2
- Mikkonen KS (2009) Mannans as film formers and emulsion stabilizers. University of Helsinki
- Mikkonen KS, Rita H, Helén H, Talja RA, Hyvonen L, Tenkanen M (2007) Effect of polysaccharide structure on mechanical and thermal properties of galactomannan-based films. *Biomacromolecules* 8: 3198–3205. doi:10.1021/bm700538c
- Mudgil D, Barak S, Khatkar BS (2011) Guar gum: processing, properties and food applications—a review. *J Food Sci Technol* 51:409–418. doi:10.1007/s13197-011-0522-x
- Prajapati VD, Jani GK, Moradiya NG, Randeria NP, Nagar BJ, Naikwadi NN, Variya BC (2013) Galactomannan: a versatile biodegradable seed polysaccharide. *Int J Biol Macromol* 60:83–92. doi:10.1016/j.ijbiomac.2013.05.017
- Reid JSG, Meier H (1970) Formation of reserve galactomannan in the seeds of *trigolella foenum-graecum*. *Phytochemistry* 9:513–520. doi:10.1016/S0031-9422(00)85682-4
- Saha D, Bhattacharya S (2010) Hydrocolloids as thickening and gelling agents in food: a critical review. *J Food Sci Technol* 47(6):587–597. doi:10.1007/s13197-010-0162-6
- Saurabh CK, Gupta S, Bahadur J, Mazumder S, Variyar PS, Sharma A (2013) Radiation dose dependent change in physiochemical, mechanical and barrier properties of guar gum based films. *Carbohydr Polym* 98(2):1610–1617. doi:10.1016/j.carbpol.2013.07.041
- Stephen AM, Phillips GO, Williams PA (2006) Food polysaccharides and their applications, 1st edn CRC Press
- Tavares C, Monteiro SR, Moreno N, Lopes da Silva JA (2005) Does the branching degree of galactomannans influence their effect on whey protein gelation? *Colloids Surf A* 270-271:213–219. doi:10.1016/j.colsurfa.2005.06.014
- Wan J, Liu C, Liu W, Tu Z, Wu W, Tan H (2015) Optimization of instant edible films based on dietary fiber processed with dynamic high pressure microfluidization for barrier properties and water solubility. *LWT Food Sci Technol* 60(1):603–608. doi:10.1016/j.lwt.2014.07.032