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The structural characteristics and rheological properties of Lebanese locust bean gum

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ABSTRACT

To characterize and study the rheological behavior of Lebanese locust bean gum (LBG), nine Lebanese carob varieties, including a wild type, were randomly collected from various sites and different altitudes of the Lebanese territories. After an extraction and purification ($_p$LBG) step, the obtained locust bean gum was submitted to several physic-chemicals (size distribution, charge and macromolecular weight) and rheological characterization in a wide range of temperature (25–55 °C). The obtained results showed that the gum yield (40–60%), the charge (−2.67 to −12.95), the size (56.37–92.23 nm), the weight–average molecular weight (535–826 kDa) and intrinsic viscosity [η] (7.25–10.76 dl/g) vary significantly depending upon the variety and the geographical localization. However, principal component analysis (PCA) indicated that the size and molecular weight are the most distinctive variables. The rheological investigation indicated that $_p$LBG exhibit Newtonian flow behavior at a concentration less or equal to 0.1% (w/v) and shear-thinning behavior for higher concentrations (0.5–2%). The effect of temperature on flow behavior was well fitted by Ostwald–de Waele model (power law model) and the flow behavior index (n) was less than 1 for all studied varieties; which means that LBGs had a pseudo-plastic flow. The all new knowledge obtained in this study on the Lebanese locust bean gum will open to these interesting macromolecules new niches in food and cosmetics applications.

1. Introduction

The evergreen carob (*Ceratonia siliqua*), a legume tree relatively common in the Mediterranean region, is grown today in many mild and semi-arid regions (Batlle and Tous, 1997), especially at low altitudes [0–300, sometimes 500, rarely 800 m]. Furthermore, certain in some countries, such as Lebanon, there are regional variations in the naming of this tree. Internationally, carob and locust bean are the best known names.

The economic importance of the crop comes from the industrial use of locust bean gum obtained from the seeds (Custódio et al., 2005). Besides economic importance, these species have great ecological significance in the reforestation of arid degraded areas and for limiting spread of fires (Barracosa et al., 2007).

Locust bean gum (LBG) or E410 is widely used as a thickener, gel strengthening in the food industry due to its ability to form viscous solutions (Richardson and Norton., 1998) at relatively low concentrations, which are only slightly affected by pH, added ions, and heat processing (Sittikijyothin et al., 2005). For this reason, the gum is used as a substitute for pectin and agar. This galactomannan (GM) is also used widely in pharmaceutical and cosmetic industries as a stabilizer and emulsifier, due to its high water binding capacity, emulsification properties and ability to form synergistic interactions with other components, such as carbohydrates or proteins, thereby increasing its viscosity (Wu et al., 2012; Rizzo et al., 2004; Sand, 1982). GM is a bland, notably white in color, nearly odorless powder and an excellent binder in cream and other soft cheeses. In ice cream, GM improves texture, adds body to the mixture, prevents lactose crystal formation (sandiness) and

Abbreviations: A1, Akkari 1; A2, Akkari 2; Ah, Ahmar; Bal, Baladi; Bar, Barri; cLBG, crude locust bean gum; Da, Dalton; G', elastic modulus; G'', viscous modulus; GC, commercial gum; GM, galactomannan; M/G, mannose to galactose ratio; J1, Jnoubi1; J2, Jnoubi2; K, consistency index or apparent viscosity; kDa, kilo Dalton; Kh, khachabi; Mw, molecular weight; n, flow behavior index; pLBG, purified locust bean gum; SM, Sandali Makdissi; $\eta *$, complex viscosity; [η], intrinsic viscosity; η, viscosity.

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reduces ice cream meltdown (Samil Kök, 2007). Moreover, to extend the shelf life of mandarins, LBG-based edible coatings were developed and optimized for postharvest storage (Rojas-Argudoa et al., 2009).

Lower-grade galactomannan (cLBG) sources are frequently used in canned products. These sources differ substantially from higher quality gum (pLBG), in composition as a result of high levels of non-galactomannan material (Samil Kök, 2007). For instance, the galactomannan (GM) in LBG is partially soluble in water, so the lowest viscoelastic properties correspond to the system prepared at room temperature; at this temperature, LBG is poorly hydrated. In contrast, when LBG is dissolved in water for at least 80 °C, G' and G'' are much higher (i.e., the viscous modulus G'' is approximately 25 times higher (Zárate-Ramírez et al., 2010), and therefore full solubility and delayed viscosification require heating to at least 80 °C, and maximum viscosity is obtained at 95 °C (Pollard et al., 2007; Lurueña-Martínez et al., 2004).

The carob galactomannan polysaccharides do not lead to gel formation and it is used generally as a thickening to obtain highly viscous aqueous solutions (Lazaridou et al., 2000). The rheological characterization of LBG is scarcely studied. The main model used to describe the rheological behavior of LBG are Ostwald–de Waele model (Dakia, 2008; Wu et al., 2009), cross model (Lopes Da Silva et al., 1992; Bourbon et al., 2010), carreau model (Sittikijyothin et al., 2005; Pollard et al., 2008) and the cascade model (Richardson et al., 1999). However, the Ostwald–de Waele model (power law model) is the most used in the case of the polymer studies.

All GM have the similar general structure that consists of a main chain of mannane on which there is a branching unit of galactose. They differ in their galactose content unit expressed by the mannose to galactose ratio (M/G), in the distribution of galactose units along the mannane chain and also in their molecular weight (Fox, 1992; Azero and Andrade (2002)), which results in differing solubilities (LBG 4:1, tara gum TG 3:1, guar gum (GG) 2:1 and fenugrec Gum (FG) 1:1) (Fernandes et al., 1992; Dea and Morrison, 1975; Batlle and Tous, 1997). Pollard et al. (2007), Lopes da Silva et al. (1996) and Azero and Andrade (2002) reported that the LBG galactomannan has a non-regular, non-statistically random distribution of D-galactose. It has random coil structure composed of linear 1,4-β-linked D-mannan backbone to which single D-galactosyl units are attached to the C6 of some of the D-mannosyl residues, thus, water solubility increases with increasing content of galactose, presumably because the galactose substituents inhibit solid-state packing of the mannan chains and contribute to conformational entropy in the solution state by freedom of rotation about the $(1 \rightarrow 6)$ linkages (Silveira and Bresolin, 2011).

In Lebanon, carob trees are abundant and distributed along the coastal lower hills. Lebanese carob pods are mainly used for the preparation of Dibs, a local molasses consumed by the Lebanese population, while the seeds are often thrown without any valorization. Recent studies indicated that the composition (carbohydrates, proteins, phenolic compounds, minerals, etc.) of different varieties of Lebanon carob varies considerably depending upon the variety and localization (Amira Haddarah et al., 2013); However, in our knowledge, no study has been done till now to characterize the rheological properties of the locust bean carob of the Lebanese varieties, despite the economic potential that could represent this plant for the country. Thus, the aim of the present work was to characterize the LBG of 9 Lebanese carob populations; study the viscometric properties as a function of temperature; and quantify the viscoelastic behavior since hydrocolloids promote specific rheological and textural properties when used as ingredients in the food industry.

2. Materials and methods

2.1. Materials

Nine carob bean varieties (A1, A2, Ah, Bal, Kh, J1, J2, SM and Bar) Lebanon were collected in August–September in 2009 from several regions of Lebanon (from north to south) where they grow naturally along the Lebanese coast at an altitude of 0–800 m. Selected regions were Akkar (Akkari1 and 2), Selaata (Baladi), Batroune (Ahmar), Bourjen (Khachabi), Blat (Sandali or Makdessi), Maaroub and Borj Rahal (Jnoubi 1 and 2), and Wadi Hojeir (wild variety). The samples were kept at 4 °C. The pods were crushed, and the seeds were manually separated.

2.2. Samples preparation

To obtain gum with high qualities and whitish color, an acid treatment was applied for decortication, which consisted of macerating 100 g of seeds in diluted sulfuric acid H_2SO_4/H_2O [60/40 ml] for 60 min at 60 °C in a preheated water bath while stirring periodically (Dakia et al., 2007, 2008). Extensive washing and rubbing were performed through a 2-mm metallic sieve to eliminate the charred hull. Next, the dehulled seeds were soaked in distilled water overnight to swell to make possible manual separation of germs from endosperms. After that, they were washed and dried in an oven at 105 °C for 4–5 h. Finally, endosperms were then milled with a laboratory miller (IKA-WERKE, MF10, 0.5 mm, Staufen Germany) to obtain the powdered, unpurified locust bean gum, or crude LBG (cLBG).

The quality of powdered, unpurified LBG depends on the milling process that sometimes darkens the powder, due to the high temperatures encountered during the process. This process determines the size and color of the end product. The color and particle size are also an indication of impurities (Samil Kök, 2007).

2.3. Preparation of solutions

Crude powdered endosperm or crude LBG was washed with ethanol and acetone (to control the microbiological load (Kawamura, 2008) on a sintered no. 3. The precipitation was initiated in an aqueous solution at a concentration of 1.3 g/100 ml (Bouzouita et al., 2007). The required amount of crude endosperm was gradually added to the distilled water, stirred gently for 2 h at room temperature, and was kept overnight at 4 °C to swell slowly. Afterwards, the solutions were heated to 80 °C in a water bath for 30 min with continuous agitation. The resulting solution was allowed to cool and centrifuged for 1 h at 10,000 rpm (20 °C) to remove the insoluble matter (Mannion et al., 1992). The supernatant or crude locust bean gum solution containing the solubilized galactomannan was collected for the purification process.

2.4. Purification of gum

The solubilized galactomannan was purified by precipitation with isopropanol. This process eliminates all unacceptable flavors of crude LBG and provides a clear and more stable solution, due to elimination of impurities and endogenous enzymes (Dea and Morrison, 1975). The galactomannan was precipitated from the crude LBG solution by pouring an excess of two volumes of isopropanol and allowing the mixture to stand for 30 min. The white fibrous matter was collected and filtered through a screen (53 μm) and subsequently washed twice with isopropanol and acetone. After a 48-h freeze-drying step, the obtained friable solid was crushed into a fine powder (purified locust bean gum). Bouzouita et al. (2007) reported that purification of LBG with isopropanol