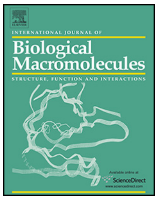
International Journal of Biological Macromolecules 96 (2017) 550–559

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac



Structure impact of two galactomannan fractions on their viscosity properties in dilute solution, unperturbed state and gel state☆

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ARTICLE INFO

Article history:
Received 19 July 2016
Received in revised form
19 December 2016
Accepted 21 December 2016
Available online 26 December 2016

Keywords:
Galactomannans
Viscosity
Structure
Rheology

ABSTRACT

Two fractions of carob galactomannans (GM25 and GM80) were extracted at respectively 25 °C and 80 °C from crude locust bean gum. Those fractions having slightly different chemical structures, previously characterized, were studied for their viscosity properties over a wide range of concentrations: diluted solution, unperturbed state and gel state. For each of the physical properties, links to the chemical fine structure could be established, expanding knowledge on the topic: in dilute solution, GM25 is more soluble in water while GM80 seems to tend to self-association due to its structure as highlighted by intrinsic viscosity measurements ($[\eta]_{GM25} = 9.96\,\mathrm{dL\,g^{-1}}$ and $[\eta]_{GM80} = 4.04\,\mathrm{dL\,g^{-1}}$). In unperturbed state, initial viscosities η_0 were more important for GM80 fractions at 1% and 2% due to greater hyperentanglements ($\eta_{0(GM80,1\%)} = 9.9$ Pas; $\eta_{0(GM80,2\%)} = 832.0$; Pa.s $\eta_{0(GM25,1\%)} = 3.1$ Pas; $\eta_{0(GM25,2\%)} = 45.1$ Pas). In gel state, hydrogels obtained from GM80 were also stronger (hardness GM80 (2%) = 0.51 N and hardness GM25 (2%) = 0.11 N), suggesting a much more important number of junction areas within the gel network. The findings discussed herein demonstrate the potential for new applications.

1. Introduction

Locust bean gum (LBG) is a food additive (E410) used mainly in the industry for its rheological, texturing and gelling properties [1]. LBG is made from the endosperm of the seeds of the carob tree (*Ceratonia siliqua* L.). The endosperm is composed of reserve polysaccharides (hemicelluloses) called galactomannans. Galactomannans consist of a β-(1 → 4)-D-mannopyranosyl backbone substituted to varying degrees at α-(1 → 6) with single D-galactopyranosyl residues [2]. The basic structure is the same for all galactomannans. Three elements, however, allow distinction between these polysaccharides: (i) the degree of galactose substitution (DS_{Gal}), (ii) the molecular weights, and (iii) the distribution pattern of galactosyl substituents along the main chain of mannans [3]. The fine structure of galactomannans of locust bean is most likely composed of "smooth" zones (lowly substituted) and "hairy" zones, i.e. much denser in side-galactosyls, without being systematically adjacent [4]. In the industrial production process of LBG [5], the purification step has a major influence on the composition and properties of gums. During clarification, the dissolution temperature is a crucial parameter which influences the average chemical structure of the resulting gum, also correlated to the viscosity observed in aqueous solution or dispersion [1]. In dilute solutions, the intrinsic viscosity is influenced by the fine chemical structure of galactomannans [4], itself defining the conformation of the polymer coil. The degree of space occupancy of a coil present in a polymer solution at a given concentration (C) may be characterized by the dimensionless "coil overlap parameter" $C[\eta]$ [6]. Double logarithmic plots of specific viscosity (η_{sp}) versus $C[\eta]$ for a range of random coil polysaccharides were found to closely superimpose over one another, and fall into two linear regions, with an abrupt change in slope, when critical concentration C^* is reached. C^* depends on the hydrodynamic volume and corresponds to the transition from dilute to semi-dilute solutions, when concentration increases. It appears that the volume occupied by the isolated polymer coils decreases with concentration.

☆ This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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http://dx.doi.org/10.1016/j.ijbiomac.2016.12.057
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At concentrations greater than C^*, the polymer coils compress. This compression continues until the polymer chains have reached their limiting size at C^{**}, providing a regime called unperturbed state [7]. At $C > C^{**}$ the limited size coils have to interpenetrate more and more [8]. The existence of this second transition at C^{**}, which marks the onset of the concentrated regime, was predicted from scaling arguments by de Gennes [9]. The magnitude of these two transitions will therefore depend upon solvent quality as well as hydrodynamic volume, with more chains increasing the breadth of the semi-dilute region [10]. The distinction between C^* and C^{**} is however not always visible graphically [11] and the transition between the dilute and the concentrated regimes is then generally designated by C^*. Thus in concentrated regime, an increasing concentration in polymers promotes the overlapping of the macromolecular chains and the appearance of entanglement [12]. In these concentrated states other approaches are needed to study the behavior of polymers such as the dynamic viscosity or the viscoelasticity. A viscous solution of LBG can finally generate a gel state when the polymer concentration in the concentrated regime increases or when a contracted hydrogel is formed after the solution was subjected to several freeze-thaw cycles [13–15].

The present study aims to establish links between the structural differences of two fractionated carob galactomannans samples (99.9% pure), previously fully characterized, and their viscosity properties over a wide range of polymer concentrations, under: (i) dilute solutions; (ii) unperturbed state; (iii) gel state. The objective is to assess the impact of small structural differences on the physical behavior of these macromolecules and thus to improve the global knowledge about the macromolecular phenomena that determine coil polymer viscosity, as well as the structure-function relationship of galactomannans and their potential industrial applications.

2. Materials and methods

2.1. Materials

Crude locust bean gum (CLBG) was obtained from PFW Ltd. (Greenford, UK) as the product sold under the trade mark name HERCOGUM N1. All others chemicals were purchased from commercial suppliers and used as received. A purified hot extract (GM80) and a purified cold extract (GM25) were obtained respectively from 80 °C and 25 °C subtractive fractionation treatment of the CLBG sample. Fractionation, analyses of composition and structures determination have been carried out for and as describe in our previous study [4], resulting in two fully-characterized-fractions that were used as starting material in the present study.

2.2. Viscosity and physical properties in solution/dispersion

Three main physical properties of galactomannans in solution/dispersion, which are of interest for industrial potential applications, were investigated.

2.2.1. Intrinsic viscosity and coil overlap parameter

The specific viscosity (η_{sp}) of a polymer is a dimensionless characteristic: $\eta_{sp} = (\eta_o - \eta_s)/\eta_s$ (Eq. (1)), where η_s is the viscosity of the solvent in the absence of polymer and η_0 is the viscosity of the solution containing a given concentration of dissolved polymer. The intrinsic viscosity $[\eta]$ (mL/g) is defined as follows: $[\eta] = \lim_{c \to 0}(\eta_{sp}/C)$ (Eq. (2)). To determine $[\eta]$, dilute solutions (0.01–0.50 g/100 mL) of LBG were prepared by mixing the appropriate amount of GM25 and GM80 fractions in distilled water at 90 °C, under mechanical stirring for 3 h and cooled to room temperature before measurements at 25 °C. Specific viscosities (η_{sp}) were measured with a Desreux-Bischoff capillary viscosimeter. The Huggins equation was applicable and was used to calculate the intrinsic viscosities $[\eta]$: $\eta_{sp}/C = [\eta] + \lambda_H[\eta]^2 C$ (Eq. (3)), where C is the concentration and λ_H the Huggins constant. Another relation, the Kraemer equation, based on the relative viscosity (η_r), in dilute solutions where the specific viscosity is much less than 1, may be constructed: $\ln(\eta_r)/C = [\eta] + \lambda_K[\eta]^2 C$ (Eq. (4)), where λ_K is the Kraemer constant. A plot of the inherent viscosity, extrapolated to zero concentration, yields the intrinsic viscosity $[\eta]$. Values of intrinsic viscosity were used to construct a double-logarithmic plot of specific viscosity versus $C[\eta]$ to determine the transition at the critical concentration (C^*) between the dilute and the concentrated regimes – which is characteristic of many polymer solutions – and the scaling laws obtained by the slopes of the regression lines of semi-dilute and dilute solution.

2.2.2. Viscosity and viscoelasticity

Rheological properties of carob gum were characterized at 25 °C on carob gum dispersions prepared as follows: 0.5%, 1% and 2% on a dry weight basis in distilled water, 1 M NaOH or 1 M NaCl at 90 °C, under mechanical stirring for 3 h and cooled to room temperature before measurements. Rheological measurements were performed using a rheometer MCR 302 (Anton Paar, Graz, Austria) equipped with a temperature control system and with a cone and plate geometry (0.996° cone angle, 49.975 mm plate diameter, 102 μm gap). Each sample (approximately 3 mL) was placed in the sensor system for measurement at 25 °C. The dynamic viscosity η (Pa.s) of semi-dilute solutions is defined as followed $\eta = \sigma/\gamma$ (Eq. (5)) with σ the shear stress (Pa) and γ the shear rate (s^{-1}). Dynamic viscosity curves were obtained with the following program: from 0.1 to 1000 s^{-1} with 5 points measured per decade (Log). Zero-shear viscosity (η_0) and shear rate at which viscosity is reduced to $\eta_0/2$ ($\gamma_{1/2}$) are obtained from the equation of Morris [16]: $\eta = \eta_0/[1 + (\gamma/\gamma_{1/2})]^{0.76}]$ (Eq. (6)). Oscillatory tests were performed at 25 °C using the same equipment. Variations in G' (storage modulus – elastic component), G'' (loss modulus – viscous component) and η^* (complex viscosity) were recorded as a function of frequency, thus obtaining the characteristic mechanical spectra. Frequency sweeps from 0.1 to 30 Hz were performed at constant strain within the linear viscoelastic range ($\gamma = 0.5\%$). All the measurements were performed at least in duplicate. Brookfield silicone oils respectively 9.2, 95.5 and 4950 cp were used as newtonian behavior references. Hyperentanglement highlighting was characterized by preparing solutions of galactomannans in alkali (1 M NaOH) and comparing their viscosity before and after neutralization with HCl. Experimentally, the volume changes during neutralization were measured, and the polysaccharide concentration in the alkali solution was adjusted to the same value by addition of the appropriate volume of 1 M NaOH. Comparison was also made with the same concentration of galactomannan dissolved directly in 1 M NaCl.

2.2.3. Analysis of hydrogels with the texture analyzer

Dilute solutions (0.05–2 g/100 mL) of LBG were prepared by mixing the appropriate amount of GM25 and GM80 fractions in distilled water at 90 °C, under mechanical stirring for 3 h and cooled to room temperature before three freeze-thaw cycles (−20 °C). If present, the excess water released during the operation was removed before measurements at 25 °C. A sample with a height of 10 mm was placed in a cylindrical vessel in stainless steel (40 mm inner diameter). Gelled sampled were prepared by wire-cutting standard-sized cylinder shape (fitted to the vessel) while viscous samples and water were simply poured into the vessel to the desired height. Samples were analyzed with a TA-XT2 texture analyzer (Stable Micro-Systems, Haslemere, UK). Instrumental texture profile analysis (TPA) methodology consists of compressing the gel sample twice in a reciprocal motion. TPA was performed by means of a 15 mm diameter flat circular probe, penetrating twice for 5 s