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Characterization of galactomannans extracted from seeds of *Gleditsia triacanthos* and *Sophora japonica* through shear and extensional rheology: Comparison with guar gum and locust bean gum

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ABSTRACT

The rheological behaviour, under steady and dynamic shear and extensional conditions, of two non-conventional galactomannans isolated from *Gleditsia triacanthos* and *Sophora japonica* is determined and compared to those of locust bean gum and guar gum.

The studied galactomannans exhibit shear-thinning behaviour in the range of concentrations and shear rates evaluated. For similar concentrations and shear rates, the guar gum exhibits the highest viscosities. Experimental data in steady shear was correlated with the Cross model, which provided a good description of viscosity shear rate data. Under oscillatory shear, all gum solutions exhibited a behaviour typical of random-coil polysaccharide solutions.

The extensional rheology experiments showed that by increasing the polymer concentration and decreasing the temperature, the relaxation times, elastic moduli and rupture times increase.

These findings lead to the conclusion that *G. triacanthos* and *S. japonica* galactomannans can be used as efficient thickening hydrocolloids as alternative to conventional galactomannans.

1. Introduction

Galactomannans, storage polysaccharides isolated from the seed endosperm of some Leguminosae, are composed of a linear mannan main chain with side chains of a single galactose (Dea & Morrison, 1975).

The two galactomannans of major commercial importance are Guar Gum (GG) from *Cyamopsis tetragonolobus* and Locust Bean Gum (LBG), from *Ceratonia siliqua,* which have mannose/galactose ratios (M/G) of 1.8:1 and 3.5:1 (Dakia, Blecker, Roberta, Watheleta, & Paquota, 2008) and molecular weight in the range of 0.697×10^6–0.94010^6 Da (Parvathy, Nuggehalli, & Tharanathana, 2007) and 0.856×10^6–1.20×10^6 Da (Dakia et al., 2008), respectively. They are extensively applied in the food industry as thickening and stabilizing agents, due to their low cost and wide range of functional properties (Cheng, Brown, & Prud'homme, 2002).

Galactomannans have the ability to form very viscous solutions at low concentrations, which are lightly affected by pH, addition of electrolytes and heat processing (Sittikijyothin, Torres, & Gonçalves, 2005). These solutions usually exhibit a non-Newtonian behaviour, in which the viscosity decreases with the increase of shear rate (Garti, Madar, Aserin, & Sternheim, 1997). The Cross (1965) model has been successfully used to describe the shear-thinning behaviour of most galactomannans (da Silva, Gonçalves, & Rao, 1992; Sittikijyothin et al., 2005). When associated with other polysaccharides, such as xanthan gum and kappa-carrageenan, galactomannans can form gels with new properties (Andrade, Azero, Luciano, & Gonçalves, 2000; Azero & Andrade, 2006; Bresolin, Milas, Rinaudo, Reicher, & Ganter, 1999; Casas, Mohedano, & Garcia-Ochoa, 2000; Fernandes, Gonçalves, & Doublier, 1991 and Hernandez, Dolz, Dolz, Delegido, & Pellicer, 2001).

Their functional properties are connected to their molar mass and structural features: the solutions' viscosity depends mainly on the molar mass while the synergistic interactions seem to be determined by the mannose/galactose ratio (M/G) and fine structure of galactomannan chain (Dea, Clark, & McCleary, 1986; Fernandes et al., 1991; Schorsch, Gamier, & Doublier, 1997).

Since the hydrocolloids are used to modify textural attributes, the study of their rheological behaviour is essential as it is recognized that rheological properties play an important role in process

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design, evaluation and modelling. Furthermore, rheological data is required for calculation in any process involving fluid flow (e.g. pump sizing, extraction, filtration, extrusion, purification) and play an important role in the analyses of flow conditions in food processes such as pasteurization, evaporation, drying and aseptic processing (Marcotte, Taherian, Trigui, & Ramaswamy, 2001).

While considerable work has been published on the rheological characterization of LBG and GG under shear flow (Choi & Yoo, 2008; Doublier & Launay, 1981; Patel, Ranjan, & Patel, 1987; Sittikijyothin et al., 2005), the work done with non-traditional sources of galactomannans is scarce.

Mazzini and Cerezo (1979) first reported the presence of galactomannans in the seeds of *Gleditsia triacanthos* (a Leguminosae). This species can tolerate a wide range of climatic and soil conditions (Blair, 1990) and is spread in America, Middle Europe and Mediterranean countries (Üner & Altınkurt, 2004). Its seeds are composed of testa (27%), embryo (29%) and endosperm (34%) and galactomannans are the main polysaccharide constituents of the endosperm (Manzi, Mazzini, & Cerezo, 1984). The galactomannan of *G. triacanthos* used in this study was previously characterized in terms of M/G ratio, intrinsic viscosity and viscosity average molar mass and the obtained values were 2.82:1, 1042 ml/g and 1.62×10^6 Da, respectively (Cerqueira et al., 2009). *Sophora japonica* (also a Leguminosae) is native from China, where it is widely cultivated and used as a hemostatic agent in traditional medicine and is currently spread all over the word (Ishida, Umino, Tsuji, & Kosuge, 1989; Tang, Lou, Wang, & Zhuang, 2001). The galactomannan extracted from *S. japonica* used in this study has been previously characterized and exhibits an unusually high M/G ratio (5.75:1), an intrinsic viscosity of 1001 ml/g and a viscosity average molar mass of 1.34×10^6 Da (Cerqueira et al., 2009).

Extensional rheology can be used to complement data obtained from conventional shear rheometers and to fully characterize fluid properties (Odell & Carrington, 2006). It is much less studied, partly due to difficulties in creating a pure extensional flow. However, the extensional component is an important part of many food-processing operations, and it may be also very useful for consumer perception studies and quality evaluation of food products. Operations such as mixing, homogenization, sheeting, extrusion, extrudate expansion, baking expansion, flow in and out of constrictions and coating are all examples of processes with significant extensional component. From the consumer's standpoint, spreadability, pourability, mouthfeel, stinginess and stretchability are important attributes where extensional rheology dominates the textural perception (Padmanabham, 2003). An extensional deformation differs significantly from a shear deformation. During a shear deformation, the particles within the flowing body move in the same direction and slide over each other, while during an extensional deformation, as the material is either stretched or compressed, the particles within the fluid will either move away or towards each other (Chan et al., 2007). Contrary to shear rheology, in extensional measurements the cross-sectional area of the sample undergoes a modification as a consequence of the exponentional change in length. Therefore, the extensional rheology allows the evaluation of interfacial multicomponent phenomena (Steffe, 1996).

The extensional properties of a fluid can be quantified by various means, including a Capillary Break-up Elongation Rheometer (CaBER), as in the present work. The rheological analysis with a CaBER is based on the formation of an unstable fluid filament by imposing a rapid axial step-strain of prescribed magnitude. The filament is then allowed to relax until breakup under the action of its own dynamics. The relaxation and decay of the necked sample is governed by different forces, e.g. viscous, elastic, gravitational and capillary forces (Sujatha, Matallah, Banaai, & Webster, 2008). This technique allows the creation of a pure extensional flow and can be applicable to fluids over a wide range of viscosities.

Little is known about the extensional behaviour of galactomannans. In the present work, two non-conventional galactomannans were isolated from *G. triacanthos* and *S. japonica* seeds, and their rheological behaviour, in steady and dynamic shear and in extensional conditions was determined and compared with those of guar gum and locust bean gum, in order to investigate their effectiveness as alternative thickening hydrocolloids. The flow curves of each gum have been correlated with the Cross model.

The results of this study will contribute to the research of novel renewable sources of hydrocolloids, as alternatives to the traditional ones, and to the development of novel foods, addressing the claims of the modern consumer.

2. Materials and methods

2.1. Materials

The pods of *G. triacanthos* (M/G = 2.81:1, Cerqueira et al., 2009) and *S. japonica* (M/G = 5.75:1, Cerqueira et al., 2009) were collected in the Botanic Garden in Porto, Portugal, during April 2006 and February 2008, respectively. The seeds were manually separated and kept in a cool, dry place until further commercial use. Commercial Guar Gum (GG) (Viscogum, Cargill) (M/G = 1.8:1, Dakia et al., 2008) and commercial Locust Bean Gum (LBG) (Genu gum type RL-200V, CP Kelco) (M/G = 3.5:1, Dakia et al., 2008) were used as control.

2.2. Methods

2.2.1. Polysaccharide extraction and purification

The extraction of polysaccharide from *G. triacanthos* and *S. japonica* was performed according to Cerqueira et al. (2009). Briefly, the extraction of galactomannans from *G. triacanthos* was performed with ethanol and distilled water. In this process, the seeds were mechanically broken, the endosperm was separated from the germ and the hull and was suspended in ethanol (purity 99.8%, Riedel-de Haën, Germany) to inactivate the enzymes and to eliminate low-molecular-weight compounds (Egorov, Mestechkina, & Shcherbukhin, 2003; Egorov, Mestechkina, & Shcherbukhin, 2004). Following this step, distilled water was added and the suspension was mixed in a blender.

The extraction procedure of galactomannan from the seeds of *S. japonica* required an acidic pretreatment in order to effectively separate the hull from the endosperm. The seeds were peeled using sulfuric acid (purity 98%, Fluka, Germany) (1:1) in a water bath at 100 °C for 1.5 h. After the endosperm removal and after its treatment with ethanol, water was added to it and the mixture was heated at 80 °C.

The purification process of both galactomannans included a filtration through a nylon net followed by a centrifugation step at 3800 g (Sigma 4 K, B.Braun, Germany) during 20 min at 20 °C. The precipitation of galactomannan was achieved by adding the supernatant to ethanol (purity 99.8%, Riedel-de Haën, Germany) at a ratio of 1:2. The precipitated galactomannan was lyophilized and kept in a dry place until further use (Cerqueira et al., 2009).

2.2.2. Solution preparation

The required quantity of powdered gums was added to the appropriate amount of distilled water in the presence of sodium azide (5 ppm) in order to prevent bacterial degradation. The dispersions of the four gums were stirred at room temperature overnight; the dispersions of locust bean gum, *S. japonica* and *G. triacanthos* gums were also subjected to a further stirring period (1 h) at a higher temperature (80 °C) in order to ensure their complete solubilization.

The solutions were centrifuged for 1 h at 20,000 rpm and the supernatants were recovered. The final polymer concentrations were determined as total solids dried at 105 °C until constant weight.

2.2.3. Chemical analyses

Moisture content was determined according to AOAC standards (1975), protein content was assessed using Bradford's method (Bradford, 1976) and ash content was evaluated by heating the sample in a muffle furnace at 500 °C for 8 h followed by cooling and weighing (Ranganna, 1977).

2.2.4. Rheological properties

2.2.4.1. Shear rheological tests. All rheological shear measurements were carried out at 25 °C, with a TA Instruments AR-G2 controlled-stress rheometer, using parallel plates (25 mm diameter and 1 mm gap). Steady-state flow curves were obtained working in controlled-stress mode, over the shear rate range of 0.01–1000 s^{-1}.

Frequency sweeps were performed in the 0.1–100 rad s^{-1} range and the strain was fixed at 5% in order to assure that the working conditions lied in the linear viscoelastic region. In fact, before performing frequency spectra, the linear viscoelastic region was determined and the appropriate strain was selected, by means of strain sweeps conducted at a constant frequency (6.279 rad s^{-1}) and variable strain ranging from 0.01 to 10%. This type of test determines the maximum deformation attainable for a system without structural failure.

For each sample and due to the non-destructive character of oscillation measurements of low frequency, the mechanical spectra preceded the flow curves. All the measurements were performed in triplicate.

2.2.5. Extensional rheological tests

Extensional rheology tests were carried out using a Haake CaBER-1 extensional rheometer (Thermo Haake GmbH, Karlsruhe, Germany), equipped with two 6 mm circular parallel plates. In order to minimize the influence of gravity and shear flow during the early stages of stretch, plates were set at an initial gap of 2 mm, resulting in an aspect ratio (initial length to radius, L/R) equal to 0.33. Fluid samples were carefully loaded between the plates using a syringe to ensure the absence of trapped air within the sample cylinder, or between the sample and the plates. The upper plate was suddenly raised to a pre-set height of 6 mm to create a filament and a laser beam aiming at the middle point of the filament monitored the changes in diameter. All extensional tests were repeated at least six times and their average was taken for analysis.

The sample temperature (25, 40, 50, 60 and 80 °C) was controlled by a water bath circulating underneath the plates with an accuracy of 0.1 °C. Prior to testing, samples were thermally equilibrated in a water bath to testing temperature.

The surface tensions of fluid samples, required for the relaxation time calculation, were determined using a Surface Tensiometer K6 (KRUSS Gmbh, Germany), using a Platinum–Iridium Du Nouy ring, at the testing temperature. All the measurements were performed in triplicate. For decreasing concentrations, the surface tension is in the range of 0.068–0.073 N/m for locust bean gum, 0.056–0.064 N/m for guar gum, 0.044–0.050 N/m for *G. triacanthos* galactomannan and 0.038–0.043 N/m for *S. japonica* galactomannans.

3. Results and discussion

3.1. Chemical analyses

The composition of the gums is given in Table 1. The purification process was sufficient to eliminate ash and proteins in *G. triacanthos* and *S. japonica* galactomannans, thus providing final products with a quality comparable to commercial gums (locust bean gum and guar gum).

Table 1
Moisture, ash and protein of Locust Bean Gum (LBG), Guar Gum (GG), *G. triacanthos galactomannan* and *S. japonica* galactomannan (±95% confidence interval).

Galactomannans	%Moisture	%Ash	% Protein
LBG	11.38 ± 0.01	0.16 ± 0.01	0.01 ± 0.007
GG	11.70 ± 0.03	0.72 ± 0.01	0.05 ± 0.030
G. triacanthos	10.17 ± 0.01	0.08 ± 0.01	0.07 ± 0.023
S. japonica	13.39 ± 0.02	0.32 ± 0.02	0.06 ± 0.015

3.2. Steady–shear properties

The effect of shear rate on viscosity, at 25 °C, for locust bean, guar, *G. triacanthos* and *S. japonica* gum solutions of different concentrations is shown in Fig. 1. The values of viscosity at low shear rates are an indication of the consistency in mouth of the product (Morris & Taylor, 1982), while the values of viscosity at high shear rates are an indication of the viscosity of the product during processing operations (e.g. when it is pumped) (Dakia et al., 2008). In all cases, a shear-thinning behaviour was observed that may be regarded as arising from modifications in the macromolecular organization of the solution as the shear rate changes. With increasing shear rate, the disruption predominates over formation of new entanglements, molecules align in the direction of flow and the viscosity decreases (Dakia et al., 2008; Sittikijyothin et al., 2005).

For similar concentrations and shear rates, the guar gum exhibits the highest viscosities. The flow curves obtained for guar and locust bean gums are in good agreement with the results reported in the literature (Andrade, Azero, Luciano, & Gonçalves, 1999; Sittikijyothin et al., 2005; Wientjes, Duits, Jongschaap, & Mellema, 2000).

Experimental data in steady shear was modelled with the Cross (1965) model (Eq. (1)):

$$\eta = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{\left[1 + (\tau\,\gamma)^m\right]} \tag{1}$$

where $\dot{\gamma}$ is the shear rate (s^{-1}), η is the viscosity (Pa.s), η_0 is the zero-shear rate viscosity (Pa.s), η_∞ is the infinite shear rate viscosity (Pa.s), τ (s) is a time constant, and m is a dimensionless constant. Since the high shear rate Newtonian viscosity was never approached in this study, the above equations were simplified, assuming $\eta_0 >> \eta_\infty$ (Eq. (2)).

$$\eta = \frac{\eta_0}{\left[1 + (\tau\,\gamma)^m\right]} \tag{2}$$

From Fig. 1 and Table 2 it can be seen that the experimental data of all the studied galactomannans were adequately described by this model, as indicated by the magnitudes of the regression coefficient, R^2.

In all cases, due to the increase of the shear-thinning behaviour with concentration, the values of ς_0 and τ increase with increasing concentration. The magnitude of zero-shear rate viscosity is a macroscopic representation of the microstructural nature of biopolymers; a higher value of ς_0 indicates the establishment of a greater number of links between the biopolymer molecules and depends on the molar mass and on interchain interactions (junctions zone). The parameter τ corresponds to the structural relaxation time and its increase with concentration is due to an increase of the chains' entanglement density. As a result, the freedom of

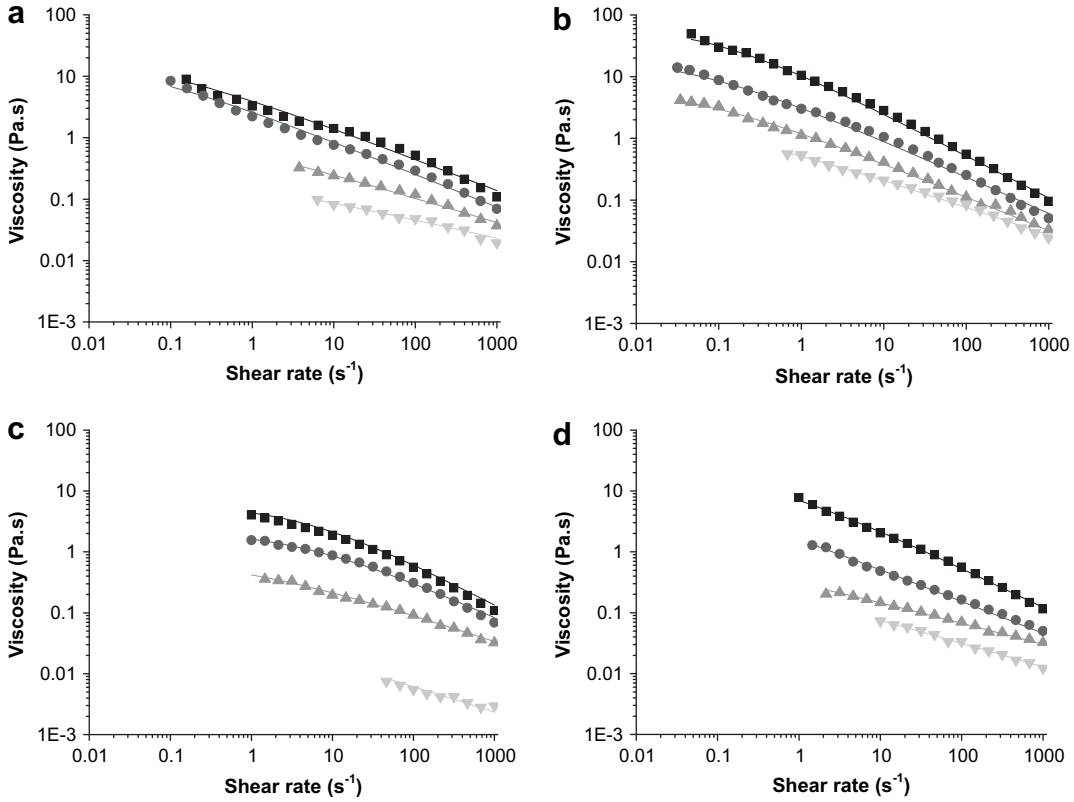

Fig. 1. Flow curves of galactomannan solutions at different concentrations (wt%), at 25 °C; (a) commercial locust bean gum, 1% (■), 0.8% (●), 0.6% (▲) and 0.4% (▼); (b) commercial guar gum, 0.97% (■), 0.78% (●), 0.58% (▲) and 0.39% (▼); (c) *galactomannan of Gleditsia triacanthos*, 0.94% (■), 0.75% (●), 0.56% (▲) and 0.38% (▼); (d) galactomannan of *Sophora japonica*, 0.96% (■), 0.77% (●), 0.58% (▲) and 0.38% (▼); The full line represents the best fits of the cross model.

movement of individual chains is progressively restricted and consequently increases the time needed to form new entanglements to replace those destroyed by the external deformation. Therefore, the shear rates values for which the behaviour becomes shear-thinning decrease as the concentration increases. Values of the dimensionless exponent m tending to zero, describes an increasing Newtonian behaviour, while fluids with shear-thinning behaviour exhibit m tending to 1. The parameter m obtained for the studied galactomannans assumes values between 0.5 and 0.6, which are the typically expected values for polymer solutions.

3.3. Dynamic shear properties

The frequency sweeps for all galactomannan solutions are shown in Fig. 2. At low frequencies, the viscous modulus G'', related to the viscous response of the system, is higher than the elastic modulus G', i.e. the system shows a liquid-like behaviour until a crossover frequency after which it is reversed and the elastic response prevails. As expected, for all galactomannans, the frequency at which G' and G'' become equal to each other moves to lower values as the concentration increases, as a consequence of

Table 2
Magnitudes of the cross model parameters for steady simple shearing, obtained for commercial Locust Bean Gum (LBG), commercial Guar Gum (GG), galactomannan of *G. triacanthos* and galactomannan of *S. japonica* (±95% confidence interval).

Galactomannan	Concentration/%	η_0/Pa.s	T/s	m	R^2
LBG	1	24.74 ± 0.01	26.44 ± 5.08	0.505 ± 0.030	0.96281
	0.8	21.99 ± 1.01	25.33 ± 6.08	0.551 ± 0.014	0.97571
	0.6	5.60 ± 1.15	16.00 ± 3.34	0.415 ± 0.059	0.9723
	0.4	1.46 ± 0.01	9.91 ± 0.49	0.320 ± 0.003	0.98791
GG	0.97	48.00 ± 0.08	32.50 ± 0.17	0.683 ± 0.003	0.97961
	0.78	26.00 ± 0.02	22.00 ± 0.01	0.588 ± 0.007	0.97871
	0.58	7.30 ± 0.01	20.00 ± 0.01	0.551 ± 0.004	0.99346
	0.39	2.30 ± 0.03	15.30 ± 0.01	0.460 ± 0.007	0.99532
G. triacanthos	0.94	22.24 ± 0.03	18.99 ± 0.18	0.456 ± 0.004	0.9898
	0.75	20.06 ± 0.34	13.99 ± 5.01	0.512 ± 0.030	0.9823
	0.56	4.74 ± 0.05	11.99 ± 4.09	0.548 ± 0.006	0.9758
	0.38	3.74 ± 0.01	5.99 ± 1.00	0.508 ± 0.016	0.9516
S. japonica	0.96	30.43 ± 2.10	26.99 ± 0.08	0.608 ± 0.080	0.9899
	0.77	24.74 ± 0.01	23.02 ± 0.08	0.588 ± 0.009	0.9710
	0.58	6.74 ± 0.45	11.99 ± 1.21	0.598 ± 0.005	0.9579
	0.38	2.74 ± 0.23	11.99 ± 2.08	0.618 ± 0.034	0.9878

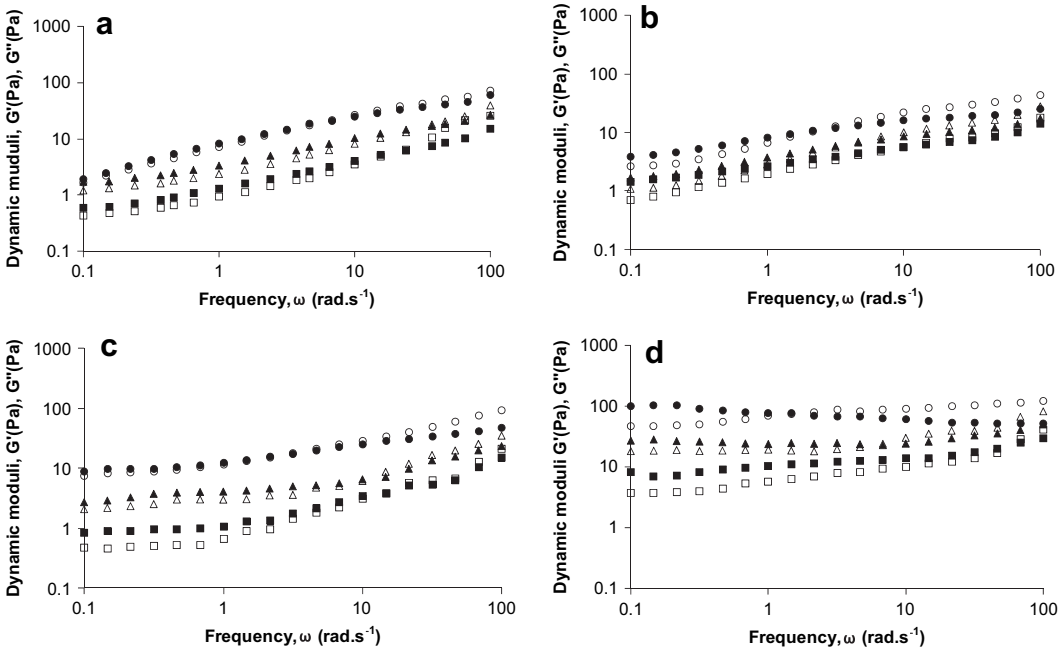

Fig. 2. Mechanical spectra of; (a) commercial locust bean gum, 1% (○,●), 0.8% (▲,△), 0.6% (□,■); (b) commercial guar gum, 0.97% (○,●), 0.78% (▲,△), 0.58% (□,■); (c) galactomannan of *Gleditsia triacanthos*, 0.94% (○,●), 0.75% (▲,△), 0.56% (□,■); (d) galactomannan of *Sophora japonica*, 0.96% (○,●), 0.77% (▲,△), 0.58% (□,■) at 25 °C (G': open symbols, G'': full symbols).

increasing relaxation times. This feature was found for several other random-coil polysaccharide solutions in the same concentration range (Brummer, Cui, & Wang, 2003; Sittikijyothin et al., 2005). The *S. japonica* galactomannan solutions exhibit a more pronounced elastic behaviour, with higher values of both G' and G'', compared with the other galactomannan solutions, a reflection of the larger network development in *S. japonica* solutions, due to its high M/G ratio.

3.4. Extensional properties

Fig. 3 represents the results of extensional rheology, where the filament diameter *vs*. time profiles for the solutions of the four studied galactomannans (guar gum, locust bean gum, *G. triacanthos* and *S. japonica*) are shown. All experiments were conducted at 25 °C using a CaBER rheometer.

From Fig. 3 it can be observed that the polymer filament passes through four stages: the rest phase, the filament stretch phase, the relaxation phase and the breaking of the filament (as illustrated in Fig. 3 a) for 1% of LBG). The filament evolution is basically controlled by the balance of surface tension and viscous/elastic forces: viscous forces tend to stabilize the filament, while surface tension acts to destabilize it, causing the rapid decrease of the diameter until the filament breaks apart. The shape of the filament diameter *vs.* time curve and the time of breakup provide information about the extensional rheological properties of fluids. It was found that the increase of biopolymer concentration leads to a delay in filament breakup and that, for the same concentrations, the highest breakup times were obtained for the *S. japonica* galactomannan, followed by *G. triacanthos* galactomannan, guar gum, locust bean gum. These results show that the solutions of *S. japonica* galactomannan are more elastic fluids and that LBG solutions, at low concentrations, approach a Newtonian fluid behaviour.

An elastocapillary force balance predicts that the filament radius decays exponentially in time (Rodd, Scott, Cooper-White, and Mckinley (2005)):

$$\frac{R_{\mathrm{mid}}(t)}{R_0} = \left(\frac{GR_0}{2\sigma_s}\right)^{1/3} \exp\left[-\frac{t}{3\lambda_1}\right] \tag{3}$$

where R_{mid} is the midpoint radius, R_0 is the radius at the time zero, G is the elastic module, σ_S is the surface tension, t is time and λ_1 is the polymer relaxation time. This relationship has been utilized to determine the relaxation time for many different polymeric solutions over a range of concentrations and molecular weights (Anna & McKinley, 2001; Bazilevskii, Entov, Lerner, & Rozhkov, 1997; Bazilevsky, Entov, & Rozhkov, 1990; Entov & Hinch, 1997; Liang & Mackley, 1994; Stelter, Bunn, Yarin, Singh, & Durst, 2000).

Eq. (3) was initially used to predict the behaviour of solution galactomannans for all the studied concentrations and temperatures; however, a poor fit of this equation to the experimental data was observed for the highest concentrations and for the lowest temperatures, as shown in Fig. 4 a) for 1% locust bean gum at 25 °C (concentration, gum and temperature taken as example), revealing the involvement of another physical mechanism. To include this mechanism and consequently, obtain a better fit to experimental data, Eq. (3) was modified and the existence of a second relaxation time (λ_2) was considered:

$$\frac{R_{\mathrm{mid}}(t)}{R_0} = \left(\frac{GR_0}{2\sigma_s}\right)^{1/3} \exp\left[-\frac{t}{3\lambda_1}\right] + \left(\frac{GR_0}{2\sigma_s}\right)^{1/3} \exp\left[-\frac{t}{3\lambda_2}\right] \tag{4}$$

Fig. 4 b) clearly shows the improvement of the fitting provided by the addition of a second term to Eq. (3). For concentrations lower than 0.4 the fit obtained by using of Eq. (3) or Eq. (4) is similar (see Fig. 4c) and d)). Table 3 show the physical parameters obtained at different concentrations in the relaxation phase, at 25 °C, calculated based on Eq. (4). It can be observed that both the elastic modulus and the relaxation times decrease with decreasing polymer concentration. The highest values of these parameters were obtained for the *S. japonica* galactomannan which reflect the development of a larger network structure due to the presence of expanded molecules that allow the establishment of numerous associations polymer–polymer, as mentioned before.

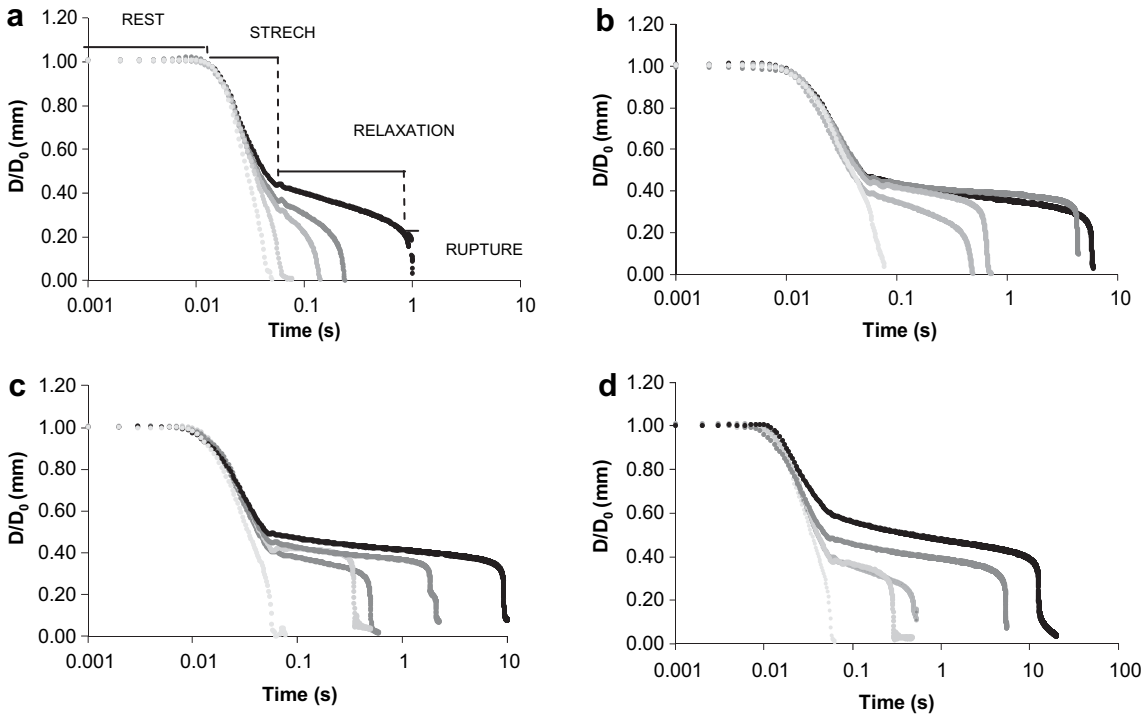

Fig. 3. Comparison of filament diameter vs. time profiles of different galactomannans solutions; (a) Locust bean gum, 1% (●), 0.8% (●), 0.6% (●), 0.4% (●) and 0.2% (●); (b) guar gum, 0.97% (●), 0.78% (●), 0.58% (●), 0.39% (●) and 0.19% (●); (c) galactomannan of *Gleditsia triacanthos*, 0.94% (●), 0.75% (●), 0.56% (●), 0.38% (●) and 0.19% (●) and (d) galactomannan of *Sophora japonica*, 0.96% (●), 0.77% (●), 0.58% (●), 0.38% (●) and 0.19% (●). All experiments were conducted at 25 °C using a CaBER rheometer.

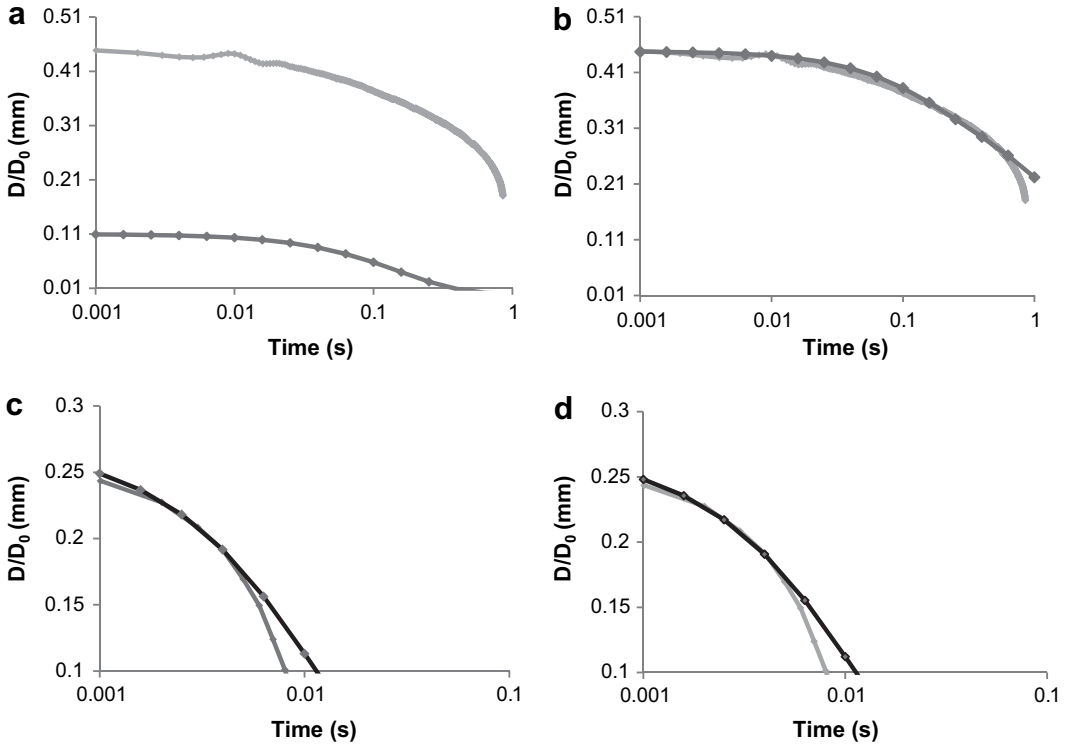

Fig. 4. Fitting of Eq. (3) and Eq. (4) to experimental data of locust bean gum solutions, at 25 °C; (a) fit of Eq. (3) to 1% LBG solution, (b) fit of Eq. (4) to 1% LBG solution, (c) fit of Eq. (3) to 0.4% LBG solution, (d) fit of Eq. (4) to 0.4% LBG solution (experimental data: ♦, best fit of the Eq. (3) or Eq. (4) to the experimental data: ◆).

Table 3
Physical parameters of galactomannans solutions, at 25 °C, in extensional rheology (±95% confidence interval).

Galactomannan	Concentration/%	*G*/*Pa*	λ_1/s	λ_2/s
LBG	1	4.07 ± 0.01	0.054 ± 0.006	0.780 ± 0.010
	0.8	2.97 ± 0.01	0.030 ± 0.003	0.350 ± 0.010
	0.6	2.22 ± 0.01	0.015 ± 0.006	0.070 ± 0.020
	0.4	1.28 ± 0.02	0.004 ± 0.003	0.002 ± 0.001
	0.2	0.97 ± 0.01	0.003 ± 0.001	0.001 ± 0.001
GG	0.97	4.14 ± 0.06	0.058 ± 0.009	4.200 ± 0.050
	0.78	3.38 ± 0.01	0.047 ± 0.002	2.200 ± 0.010
	0.58	3.31 ± 0.03	0.043 ± 0.002	0.090 ± 0.010
	0.39	2.02 ± 0.02	0.025 ± 0.007	0.003 ± 0.001
	0.19	1.20 ± 0.01	0.015 ± 0.009	0.001 ± 0.001
G. triacanthos	0.94	5.73 ± 0.13	0.059 ± 0.002	5.200 ± 0.080
	0.75	3.72 ± 0.05	0.049 ± 0.001	3.170 ± 0.090
	0.56	2.78 ± 0.13	0.026 ± 0.001	0.270 ± 0.020
	0.38	2.26 ± 0.09	0.009 ± 0.001	0.008 ± 0.001
	0.19	1.23 ± 0.09	0.006 ± 0.002	0.002 ± 0.002
S. japonica	0.96	8.07 ± 0.23	0.077 ± 0.006	12.000 ± 0.05
	0.77	4.71 ± 0.09	0.057 ± 0.004	4.170 ± 0.010
	0.58	3.52 ± 0.11	0.058 ± 0.004	0.420 ± 0.010
	0.38	2.00 ± 0.04	0.009 ± 0.003	0.004 ± 0.001
	0.19	1.98 ± 0.04	0.008 ± 0.002	0.002 ± 0.001

Table 4
Physical parameters of galactomannans solutions, at different temperatures (±95% confidence interval).

Galactomannan	Temperature (°C)	*G* (Pa)	λ_1 (s)	λ_2 (s)
1% LBG	25	4.07 ± 0.01	0.054 ± 0.002	0.78 ± 0.01
	40	2.97 ± 0.07	0.012 ± 0.009	0.46 ± 0.02
	50	2.22 ± 0.07	0.010 ± 0.004	0.31 ± 0.01
	60	1.25 ± 0.09	0.004 ± 0.006	0.08 ± 0.01
	80	0.97 ± 0.01	0.003 ± 0.007	0.06 ± 0.02
0.97% GG	25	4.14 ± 0.06	0.058 ± 0.007	4.20 ± 0.05
	40	3.38 ± 0.12	0.035 ± 0.006	4.00 ± 0.11
	50	3.31 ± 0.02	0.018 ± 0.003	3.50 ± 0.10
	60	1.99 ± 0.01	0.010 ± 0.002	1.40 ± 0.10
	80	1.22 ± 0.01	0.008 ± 0.002	0.90 ± 0.08
0.94%	25	5.73 ± 0.13	0.059 ± 0.002	5.20 ± 0.08
G. triacanthos	40	3.24 ± 0.01	0.036 ± 0.004	4.17 ± 0.05
	50	2.59 ± 0.02	0.030 ± 0.008	3.99 ± 0.03
	60	2.38 ± 0.11	0.018 ± 0.006	2.40 ± 0.02
	80	1.32 ± 0.01	0.017 ± 0.004	2.00 ± 0.01
0.96% *S. japonica*	25	8.07 ± 0.23	0.077 ± 0.006	12.00 ± 0.05
	40	5.43 ± 0.02	0.045 ± 0.013	7.00 ± 0.04
	50	3.20 ± 0.05	0.040 ± 0.010	4.50 ± 0.05
	60	2.41 ± 0.10	0.015 ± 0.004	2.92 ± 0.11
	80	1.82 ± 0.23	0.010 ± 0.008	2.80 ± 0.16

The existence of two relaxation times may be due to the structure of the studied polysaccharides, since besides the expansion of the polymeric chains, the existence of the interactions between the chains delays the relaxation phase. In this case λ_1 represents a time scale associated with elongation or stretching of polymer molecules (unravelling the polysaccharide chains) (Duxenneuner, Fisher, Windhab, & Cooper-White, 2008) and λ_2 possibly refers to the destruction of the links between the chains. As the concentration decreases, λ_2 becomes more and more insignificant as a consequence of a greater freedom of movements of individual chains.

Fig. 5 shows the effect of temperature on the variation of filament diameter with time for the 1% solutions of the four galactomannans. It can be seen that in all cases, as the temperature raises from 25 °C to 80 °C the breakup time decreases and the solutions' behaviour comes close to Newtonian fluid behaviour.

Table 4 show the physical parameters obtained at different temperatures in the relaxation phase for galactomannan solutions with similar concentrations and it can be observed that both the relaxation time and the elastic modulus decrease as temperature increases. With the increase of temperature there is a more effective destruction of the links between the chains (rupture of H-bonds involved in the interchain interactions) and, consequently, the mobility of the chains increases. It can also be observed that the

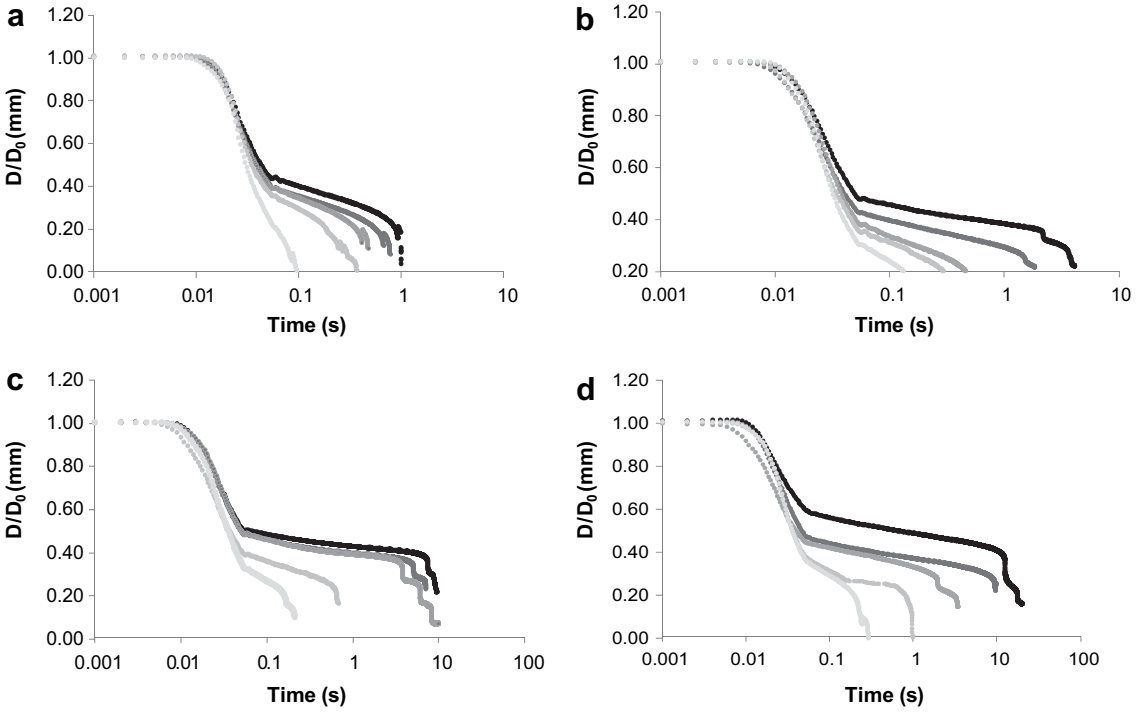

Fig. 5. Variation of the normalized filament diameter with time for the different galactomannans solutions (1%) at different temperatures: (a) locust bean gum; (b) guar gum; (c) galactomannan of *Gleditsia triacanthos* and (d) galactomannan of Sophora japonica, 25 °C (●), 40 °C (●), 50 °C (●),60 °C (●), 80 °C (●).

S. japonica galactomannan exhibits the highest values of these parameters at all studied temperatures, followed by *G. triacanthos*, guar gum and locust bean gum. This indicates that the interchain interactions established by *S. japonica* and *G. triacanthos* galactomannan chains among them are more resistant to temperature when compared to the ones established by the guar gum and locust bean gum.

The values for the breakup times of the polymer solutions' filaments are not shown, because it was observed that the measurements in CaBER rheometer were not satisfactorily reproducible. For the same solution, the relaxation patterns obtained were similar, however the absolute values of filament breakup times were significantly different (error percentage in the range of 70%).

4. Conclusions

The obtained results showed that all the studied galactomannans exhibited a shear-thinning behaviour in the range of concentration and shear rates studied. Experimental data obtained under steady shear were correlated with the Cross model and this model described well the viscosity shear rate data of all galactomannan solutions. The dynamic shear experiments showed that the galactomannan of *S. japonica* leads to more elastic solutions compared with the other studied galactomannans, which could be an attractive for the use of this gum in some food applications.

The extensional rheology showed that the breakup time, relaxation time and elastic modulus decreased with decreasing polymer concentration and with increase temperature. The higher values of these parameters were obtained for *S. japonica* galactomannan and are in agreement with shear rheology results.

The obtained results indicate that the galactomannans of *G. triacanthos* and *S. japonica* may offer an excellent alternative for guar and locust bean gums as thickening agents.

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