Relation between concentration and shear-extensional rheology properties of xanthan and guar gum solutions

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ABSTRACT

The influence of concentration on the shear and extensional rheology properties of aqueous solutions of xanthan and guar gums was studied in this work. Shear rheology involved small amplitude oscillatory shear (SAOS), flow curves and transient flow, while the extensional rheology was analyzed using hyperbolic contraction flow. In addition, the mechanical properties during solutions manufacture were monitored in situ through the evolution of torque with processing time by mixing rheometry. The results showed that the hydrocolloids exert a great influence on the process rheokinetics and on the resulting rheological response. SAOS tests showed that the xanthan gum solutions behaved as weak gels, whereas guar gum solutions suggest the presence of entanglement and the formation of a viscoelastic, gel-like structure. All the systems exhibited shear-thinning behaviour. Guar gum solutions obeyed the Cox-Merz rule, with some divergence at high rates for the more concentrated solutions, while the Cox-Merz rule was not followed for xanthan gum in the range of concentration studied. The extensional viscosity exhibited an extensional-thinning behaviour within the strain range used and all solutions were characterized by a high Trouton ratio.

Keywords: Polysaccharides solutions; Viscoelasticity; Flow behaviour; Shear thickening

1. Introduction

Nowadays, polysaccharides play a leading role as large source of biomass based materials useful for various applications (Lapasin & Pricl, 1995). They can be processed in different ways and their ability to form solutions and gels under specific conditions is the basis for important applications within areas such as cosmetic, biomedical, pharmaceutical and food technology (Tombs & Harding, 1998). The rheological properties of these materials depend on the nature of its components and the molecular interactions between the polymer and solvent, in the product and during its processing. Hence, it is possible to obtain novel products by proper selection of the ingredients, but also by process optimization. Guar gum (GG) is a water-soluble galactomannan from the endosperm portion of the guar bean (*cyamopsis tetragonoloba*) (Mudgil, Barak, & Khatkar, 2012; Szopinski, & Luinstra, 2016). Guar gum molecule has a backbone composed of a linear chain of β-1,4-linked mannose units with randomly attached α-1,6-linked galactose units. The mannose-to-galactose ratio in guar gum ranges from 1.6 and 1.8, varying with the source (Cheng, & Prud'homme, 2000) and this ratio is important in determining the mechanical properties of the solutions (Sittikijyothin, Torres, & Gonçalves, 2005). It can be utilized as stabilizing and thickening agent to form solutions in a broad range of concentrations in several industries such as food, agriculture, cosmetics, textile etc. (Miquelim, & Lannes, 2009). It has been extensively used in a range of applications because of its unique ability to produce viscous solutions with tuneable mechanical properties. Xanthan gum (XG) is a polysaccharide secreted by Xanthomonas campestris and composed of a (1→4) linked β-D-glucan (cellulose) backbone that is substituted on the O-3 position of alternating glucose residues by charged trisaccharide side chains of β-D-mannospyranosyl-(1→4)-β-D-glucuronopyranosyl-(1→2)-6-O-acetyl-β-D-mannospyranosyl (Choi, & Yoo, 2009;

Sworn, 2000). Xanthan gum is soluble in hot or cold water, and solutions exhibit a large increase in the viscosity at low concentrations, and exhibit a pronounced shear-thinning behaviour. Commonly used as a food thickening agent and a stabilizer and due to its rheological properties it has been utilized in a wide range of industrial applications (Sworn, 2000). The rheological properties of guar and xanthan gum solutions are useful to understand the polysaccharide structure and to investigate its potential functionalities in a wide range of engineering applications. Traditionally, the rheological properties of guar and xanthan gum aqueous solutions have been determined through flow curves and small amplitude oscillatory shear (Tako, & Nakamura, 1985; Abdulrahman, Alquraishi, & Fares Alsewailem, 2012). In recent years, extensional rheology has received increasing attention since it is crucial for many polymer processing operations, consumer perception and product quality and due to experimental techniques have evolved and become widely available. For instance, industrial applications often involve extensional flow in addition to shear flow. In some cases, the extensional deformation dominates, as it is the case of a flow through a contraction, or a melt stretched during film blowing or between rotating rollers (Piermaría, Bengoechea, Abraham, & Guerrero, 2016). Studies have shown that a food bolus is subject to both shear and extensional flow during mastication when the bolus is compressed between the tongue and the soft palate (Hasegawa, Otoguro, Kumagai, & Nakazawa, 2005; Salinas-Vázquez, et al., 2014), and that fluid elasticity contributes to safe swallowing (Nyström, et al., 2015). Different experimental methods have been employed for quantifying the extensional viscosity. Techniques for elongation of melts was developed early by Meissner (1972) and Münstedt (1979) (Meissner, 1972; Münstedt, 1979). Filament Stretching is a well-established laboratory technique (Sridhar, Tirtaatmadja, Nguyen, & Gupta, 1991; Bach, Rasmussen, & Hassager, 2003), and the similar technique of Capillary Breakup (CABER) is commercially available (Entov, & Yarin, 1984; Anna, &

McKinley, 2001). A spinline measurements can also be used to obtain qualitative extensional data, and the material in form of a fibre, is then drawn with a drum and the drawn profile of the material is captured by a camera. The required tensile force is measured and together with the captured shape the extensional viscosity can be evaluated. Furthermore, contraction flows exerts extensional stress in a fluid and by pushing it through a hyperbolic nozzle designed to give a constant extension rate and measuring the required pressure drop the extensional behaviour can be determined. Hyperbolic Contraction Flow is the method used in the present work and it has been used successfully for many systems such as suspensions (Moberg, Rigdahl, Stading, & Bragd, 2014), dough/dairy products (Berta, Gmoser, Krona, & Stading, 2015), commercial thickeners (Qazi, et al., 2017), food systems (Berta, Muskens, Schuster, & Stading, 2016; Berta, Wiklund, Kotz, & Stading, 2016; Oom, Pettersson, Taylor, & Stading, 2008) and polymer melts (Köpplmayr, et al., 2016). The advantages of this technique are that it can create a controlled extensional flow and is suitable for medium-viscosity fluids where melt elongation techniques or capillary breakup are not suitable. Therefore, the objective of this work was to study the influence of concentration on the shear and extensional rheology properties of aqueous solutions of xanthan and guar gum. This rheological study involves small amplitude oscillatory shear (SAOS), steady shear flow and transient flow. The extensional rheology determined in order to improve the understanding of the rheological behaviour of these solutions in extensional flow to allow them to be used more efficiently.

2. Experimental

2.1. Materials and sample preparation

Food grade powders of xanthan (X, Danisco, Sweden) and guar (G, Sigma-Aldrich, India) were used as the gelling agent. Aqueous solutions of xanthan and guar gums at

concentrations of 1, 1.5 and 2 wt.% were prepared in distilled water by stirring at 900 rpm on a magnetic stirrer for 4 h at room temperature (20 - 23ºC). Finally, the solutions to be studied were left to stand for overnight at 4ºC for complete hydration of the biopolymer and removal of the remaining bubbles. Sodium azide was added to the solution to prevent the growth of microorganisms.

2.2. Rheological characterization

2.2.1 Shear rheology

Rheological measurements were carried out in controlled-strain rheometer (ARES-G2, TA Instruments, New Castle, USA), using a parallel plate geometry (40 mm diameter, 1 mm gap). Small-amplitude oscillatory shear (SAOS) measurements, inside the linear viscoelasticity regime, were performed in a frequency range between 10^{-2} and 10^{2} rad/s. Strain sweep tests, at a frequency of 6.23 rad/s, were first performed to determine the linear viscoelastic regime. Flow curves in shear flow were measured in the range 10^{-2} to 100 s^{-1}, according to a step-ramp of increasing shear rates (Torres, Hallmark, & Wilson, 2014). Viscosity was calculated in each step after a maximum shear time of 300 s, unless the steady-state response had been previously achieved within 1% tolerance. Transient shear stress experiments were performed at different constant shear rates (0.01, 0.1, 1, 10 and 50 s^{-1}). The shear stress evolution was monitored until steady-state was reached. In order to ensure accurate results, at least three replicates were conducted for every sample/test. Figures present the average values ± one standard deviation (SD). The upper plate rim was covered with a thin layer of mineral oil (Dow Corning 200, 20 cSt) to prevent water evaporation. In addition, in situ torque measurements during the polysaccharide solutions were monitored using a rheomixer experimental setup in order to follow the solution efficiency. The device setup consisting of a cup (40 mm diameter, 71 mm height) and a stirring arrangement (four-blade mixing head, 30 mm diameter)

coupled with the transducer of a controlled-stress Haake RS600 rheometer (Germany). This tool, successfully used in mixing applications (Martín-Alfonso, & Franco, (2014), allows on-line monitoring of the evolution of torque with time, thus studying the kinetics of the mixing process.

2.2.2 Extensional rheology

Extensional viscosity was measured using a Hyperbolic Contraction Flow rig (Nystrom, 2015; Stading, & Bohlin, 2001) mounted on an Instron 5542 Universal Testing Instrument (Instron Corporation, Canton, MA, USA). Measurements were performed at room temperature using a die with inlet radius of 15 mm and outlet radius of 1 mm, imposing a total Hencky strain of 7.7 to the samples. The extensional strain rates were in the same range of continuous shear flow measurements, 0.5-30 s^{-1}, and the data was evaluated as described previously (Nystrom, 2015; Binding, 1988). The transient extensional stress was monitored until a stable plateau value was reached from which the steady-state, and the transient extensional viscosity was calculated as described by Wikstrom and Bohlin (1999). The Power-law parameters acquired with the continuous shear measurements were used to calculate the extension rates, the Hencky strain and to compensate for the shear stress contribution to the total stress (Wikstrom, & Bohlin, 1999). At least two replicates were performed on fresh samples.

3. Results and discussion

3.1. Rheological properties during processing and linear viscoelasticity

In order to study the influence of gum concentration on the rheological properties of solutions and the evolution of the degree of solution of the gum in the water, different samples with 1, 1.5 and 2 wt.% gum concentration were processed. **Fig. 1** shows the evolution of torque during processing of solutions prepared in the Rheomixer as a function of gum concentration. Attending to the evolution of torque, the system to form

a physically stable solutions may be divided in different steps. The first monitored torque values correspond to those obtained just agitating the solvent (stage 1). When gum was added, a sudden increase in torque was noticed and then still increase more gradually as hydrocolloids were being intimately dispersed in the solvent (stage 2). Finally, once the polysaccharide was totally well dispersed, torque tends to constant values (stage 3). At this time, the mixing process was considered to be finished. The experimental torque value with time was successfully fitted to the following equation:

$$\frac{M - M_\infty}{M_0 - M_\infty} = \frac{1}{1 + \left(\frac{t}{t_{1/2}}\right)^p} \quad (1)$$

where M_0 and M_∞ are the torque values right after the polysaccharide addition and at the final step of the process, respectively, $t_{1/2}$ is the time necessary to reach an increase in torque of 50% after the polysaccharide addition, and 'p' is a parameter related to the slope of the rheokinetic curve. The values of fitting parameters are shown in **Table 1**. It can be observed that both lower 'p' and higher $t_{1/2}$ values were obtained with increasing polysaccharide concentration. Interestingly, the increase in torque values was more gradual when dispersing guar gum, thus yielding higher $t_{1/2}$ values. Hence, these results may shed light that the type of hydrocolloids exerts a great influence on the rheokinetic process. Finally, as could be expected, an increased hydrocolloid concentration produce an increase the torque values. The final torque values linearly increase with hydrocolloid content as can be observed in the graph alongside in **Fig. 1**.

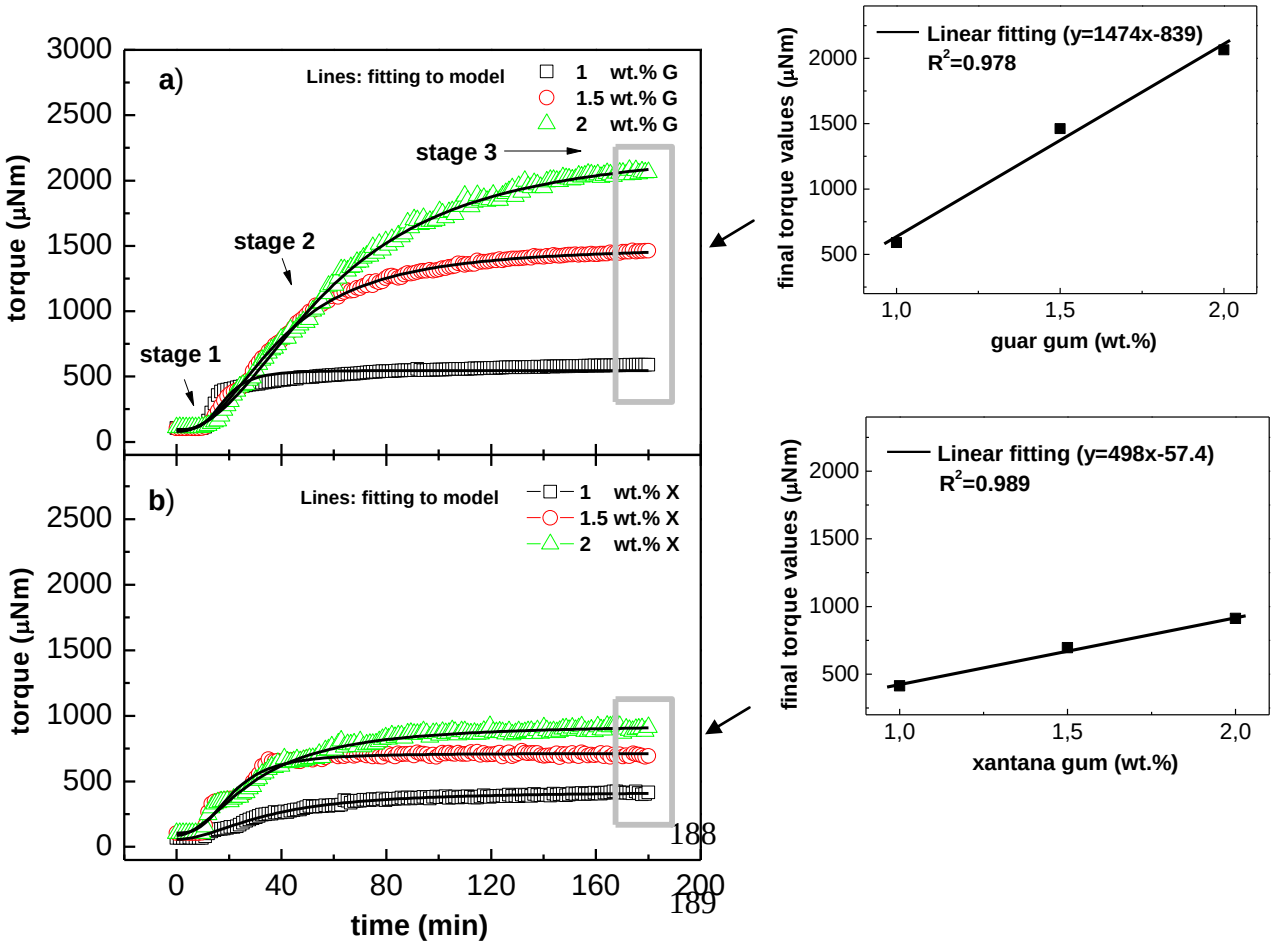


Fig. 1. Evolution of torque with time during processing of solutions as function of gum concentrations: a) guar, b) xanthan. The experimental data is fitted to Eq. (1).

Table 1

Fitting parameters corresponding to equation (4), for solutions manufactured in the 'rheomixer'.

Sample	M_0 (μNm)	M_∞ (μNm)	$t_{1/2}$ (s)	p	R^2
1 wt.% guar	95.2±3.41	546.4±4.26	18.3±0.40	3.86±0.02	0.988
2 wt.% guar	79.6±4.73	1495.5±3.73	39.8±0.20	2.25±0.02	0.997
3 wt.% guar	86.1±8.61	2279.3±14.3	58.7±0.46	2.07±0.03	0.998
1 wt.% xanthan	57.2±3.06	423.5±2.36	34.7±0.46	1.88±0.05	0.994
2 wt.% xanthan	105.6±10.08	712.7±3.18	21.3±0.47	2.89±0.14	0.986
3 wt.% xanthan	86.5±9.88	935.9±6.38	30.4±0.56	1.92±0.06	0.991

Solutions were studied under oscillatory shear conditions, in order to define the upper limit of the linear viscoelastic range (LVR) and determine the mechanical spectrum for each sample. **Fig. 2** shows storage and loss moduli dependence on strain amplitude. As long as the strain amplitude is small, G' and G'' curves present a constant plateau value. Here, the structure of the sample is only slightly perturbed, with it is viscoelastic response within the linear region (LVR) until a certain critical value (γ_c). This transition from the linear to the non-linear viscoelastic regimes may be described by the Soskey–Winter equation, applied to the both moduli, values ($r^2 > 0.995$):

$$\frac{G}{G_0} = \frac{1}{1 + b\gamma^n} \quad (2)$$

where G_0 represents the limiting values of the modulus (G' or G'') in the linear viscoelastic regime, γ is the strain and b and n are adjustable parameters. The critical strain value γ_c marking the upper limit of the linear viscoelastic regime was arbitrarily set in correspondence with $G/G_0=0.95$. It is worth noting that G' was clearly more sensitive than G'' in the detection of the onset of nonlinear viscoelastic response. As expected, both moduli increase with increasing polysaccharide concentration, consistent with an increasing degree of association among macromolecules. Critical strain does change significantly with polysaccharide concentration, since its value is generally between 14 and 99%. As shown in **Fig. 2**, xanthan gum solutions show a somewhat longer LVR compared to guar, indicating the network is less prone to yielding.

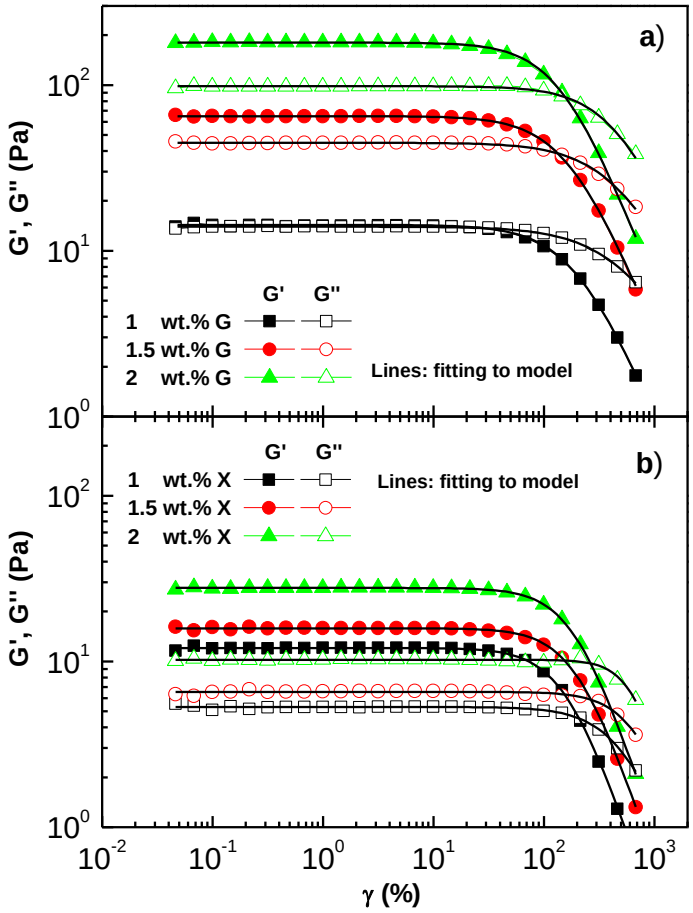


Fig. 2. Storage (G′) and loss (G″) moduli as a function of strain for gum solutions with different concentrations: a) guar, b) xanthan.

Fig. 3 shows the mechanical spectra (G' and G'' vs. angular frequency) of guar and xanthan aqueous solutions. Storage and loss moduli values (G' and G'') of the guar gum solutions (**Fig. 3a)** increased with angular frequencies and concentration, as expected. At low angular frequency the viscous component is dominant, but the increase on G'' with frequency increased is lower than the increase on G'. Therefore, a crossover point at a characteristic frequency of the polymer at concentrations and two regions dependent on concentration were observed, being the region at high frequencies shorter as concentration decreased. The crossover frequency point is an indication of the inverse of the polymer solution relaxation time and decreased from 6.3 rad/s to 1 rad/s as the concentration increased from 1 wt.% to 2 wt.%. This behaviour is typical of low

concentrated macromolecular solutions showing an apparent fluid character with a tendency to a crossover in the high frequency regime. Similar results were founded by Chenlo, Moreira, & Silva, (2010). On the other hand, the mechanical behaviour of xanthan gum solutions is reported in **Fig. 3b**. The linear viscoelasticity response is qualitatively similar for all the solutions studied, where the storage modulus G' remains higher than the loss modulus G'' (G' > G''), which means that the elastic response is consequently higher than the viscosity response. Values between of 0.20 to 0.25 were obtained for the slope of all the G' vs. ω curves. Hence, the solutions studied exhibited weak-gel viscoelastic behaviour as demonstrated by this slope value and by the fact that G' values lay above those of G''. These results were consistent with those previously reported for xanthan gum solutions (Choi et al., 2014; Carmona, Ramírez, Calero, & Muñoz, 2014; Choppe, Puaud, Nicolai, & Benyahia, 2010).

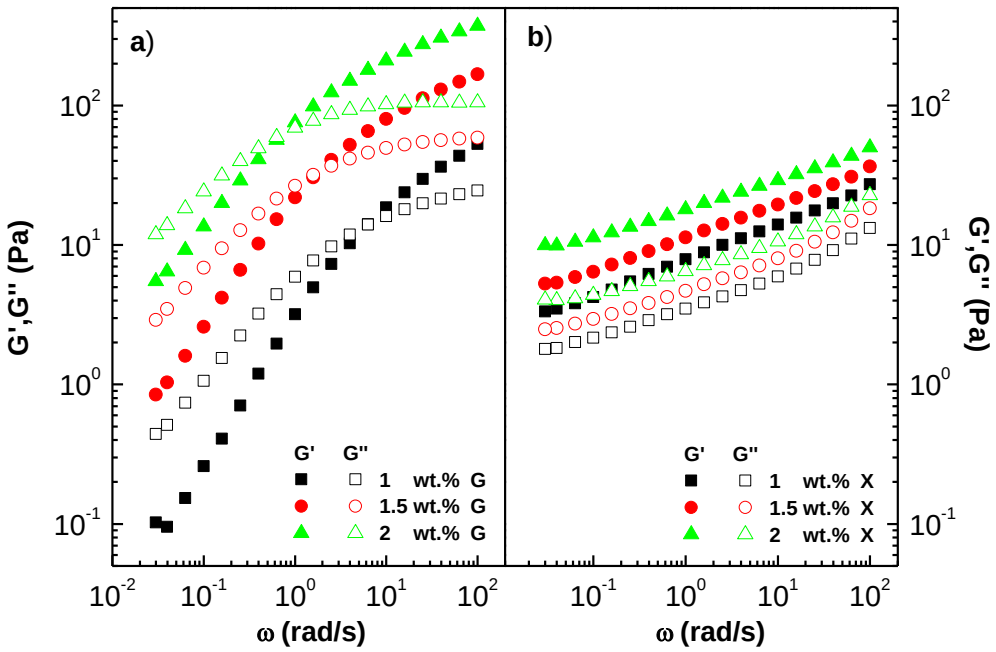


Fig. 3. Frequency dependence of the storage (G') and loss moduli (G''), in the linear viscoelasticity region, for aqueous gum solutions as a function of gum content.

244 *3.2. Flow behaviour*

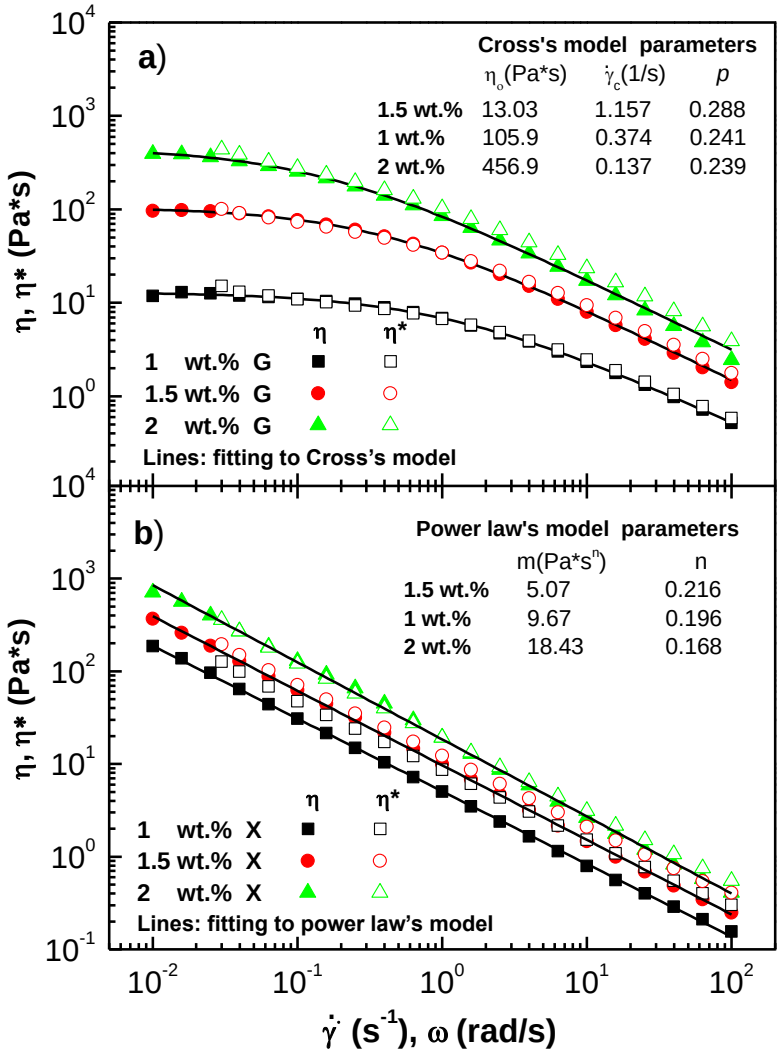
245 Flow curves for guar gum solutions as function of concentration are shown in the form
246 of flow curves in **Fig. 4a**. The apparent viscosity at each shear rate increases noticeably
247 with polymer concentration. In all cases, the solutions exhibit shear thinning behavior at
248 rates $>10^{-1}$ while at a lower rate the curves approach the Newtonian plateau. These
249 experimental data were fitted by the Cross model ($R^2 > 0.998$).

250
$$\eta = \frac{\eta_0}{\left(1 + \frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^{1-p}} \quad (3)$$

251 where η_o is the low-shear Newtonian viscosity, $\dot{\gamma}_c$is the critical shear rate for the onset
252 of shear-thinning response and *p* is a parameter related to the slope of the power-law
253 region. The values of these parameters are shown in **Fig. 4a**. The η_o values increased
254 significantly with increasing gum concentration, while $\dot{\gamma}_c$ values gradually decrease
255 with the concentration and the values of the slope, *p*, were quite similar. The variation
256 in η_o and $\dot{\gamma}_c$ values confirms the effect of the concentration on both the viscosity at low
257 frequencies and the beginning of the shear thinning region. The increase of η_o with
258 polymer concentration indicates the establishment of a greater number of links between
259 the biopolymer molecules and depends on the molar mass and on interchain
260 interactions. These results were consistent with those previously found for other guar
261 gum solutions (Torres, Hallmark, & Wilson, 2014; Duxenneuner, Fischer, Windhab, &
262 Cooper-White, 2008). Xanthan gum solutions showed shear thinning behavior without
263 any indication of a Newtonian plateau for $\dot{\gamma}_{>0.01}$ and were better fitted by the Ostwad-de
264 Waele Power law in the shear rate range studied ($R^2 > 0.995$):

$$\eta = m\dot{\gamma}^{n-1} \quad (4)$$

where “m” is a parameter related to the consistency of the sample and “n” is the slope of the shear thinning region. The fitted parameters are shown in **Fig. 4b**. Values of the consistency index clearly increases with xanthan gum concentrations, while the values of the flow index gradually decrease with the concentration showing that shear thinning is induced by the presence of xanthan gum in solution. In addition, **Fig. 4** provides a comparison between complex viscosity, derived from SAOS measurements and steady shear viscosity. As can be observed, guar gum solutions obeyed the Cox-Merz rule (Cox, & Merz, 1958), $|\eta^*(\omega)| \approx \eta(\dot{\gamma})$ where $\omega = \dot{\gamma}$, relating the apparent viscosity (steady shear flow) and the magnitude of the complex viscosity (oscillatory shear flow) at a given frequency and shear rate. There is a divergence in behaviour at high rates for the more concentrated solutions, probably due to entanglements. The deviation is related to the elastic gel-like structure, which is not affected during oscillatory measurements, but is broken during steady shear tests such that the measured magnitude of the complex viscosity is larger than the apparent viscosity. Similar behaviour has been reported by Torres et al. (2014), who also found that the largest deviations occurred at higher angular frequencies and shear rates. On the other hand, the Cox-Merz rule was not followed throughout the xanthan gum concentrations studied. The departure from Cox-Merz rule confirms the occurrence of a structured system, supporting that the weak-gel structure was clearly set. These results were consistent with those previously reported (Carmona, et al., 2015).



286

287 **Fig. 4.** Comparison between steady-state and complex viscosities for aqueous gum

288 solutions.

289 *3.3. Transient flow*

290 **Fig. 5** shows selected shear stress vs. shear time plots for aqueous gum solutions

291 containing 1.5% wt. gum at several constant shear rates. In all cases, a non-linear

292 viscoelastic response was observed with two distinct regions: the first one comprised

293 between the onset of the transient test and the maximum shear stress, the so-called stress

294 overshoot (τ_{max}), and the second one ranging between this maximum and the

295 equilibrium or steady-state shear stress (τ_{eq}). The shear-induced structural modifications

observed during stress growth experiments involve two opposite processes. The first part of these curves is mainly result of the well-known viscoelastic response, being the elastic deformation the prevailing component. This results in an almost linear increase of shear stress with time at the beginning, and an increasing non-linearity as shear time approaches the characteristic time defined by the stress overshoot. It is worth pointing out that the magnitudes of the stress overshoot seem to be strongly dependent on both the time and the shear rates applied to the sample **(**see **Fig. 5)**. Once the stress overshoot is reached, the structural breakdown due to the shear flow process takes the main role. As a result, the shear stress, or the apparent viscosity, monotonically decreases in this region. This transient evolution continues until the steady state level is reached, which indicates that the time-dependent shear-induced microstructure become stable for the shear rate applied.

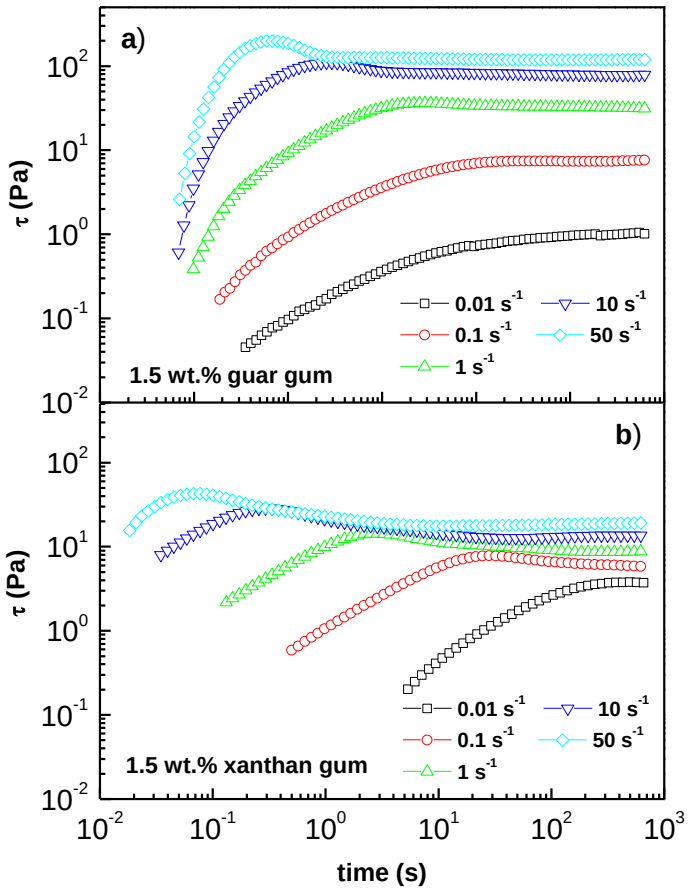
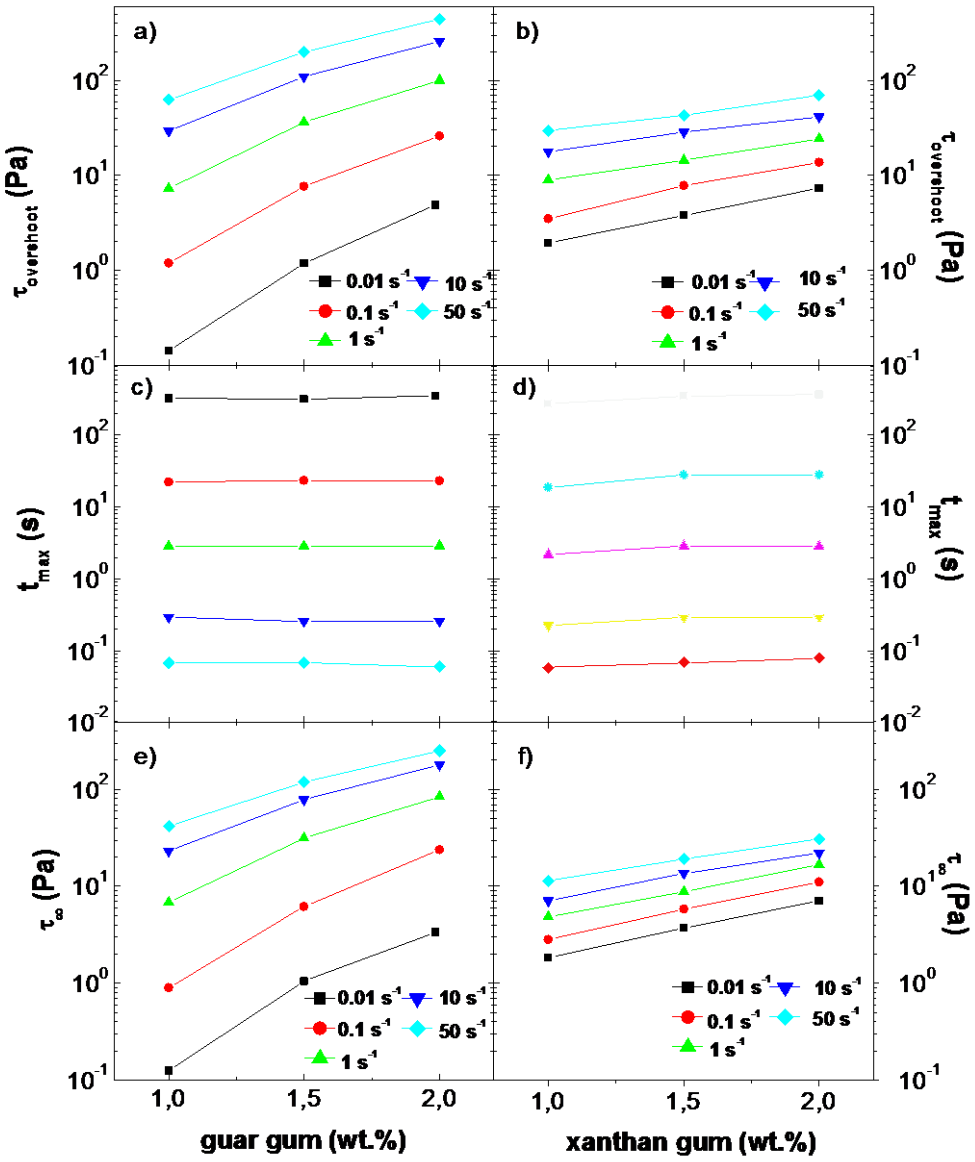


Fig. 5. Shear stress-growth curves, in a range of constant shear rates comprised between 0.01 and 50 s^{-1}, for selected aqueous gum solutions.

Fig. 6 shows the values of same relevant characteristics parameters, derived from analysis of stress grown curves, i.e., stress overshoot (τ_{max}), equilibrium or steady-state stress value (τ_{eq}), and elapsed time necessary to reach the stress overshoot for aqueous gum solutions. As expected, the stress overshoot and the equilibrium shear stress increased with the gum concentration. Guar gum solutions show higher stress overshoot values than xanthan gum solutions at all shear rates, excepting the sample with lower gum concentration. However, t_{max}, which is related to the beginning of the structural breakdown process, was larger for solutions containing xanthan gum. This implies that xanthan gum solutions induces structural networks that are able to resist higher deformations.



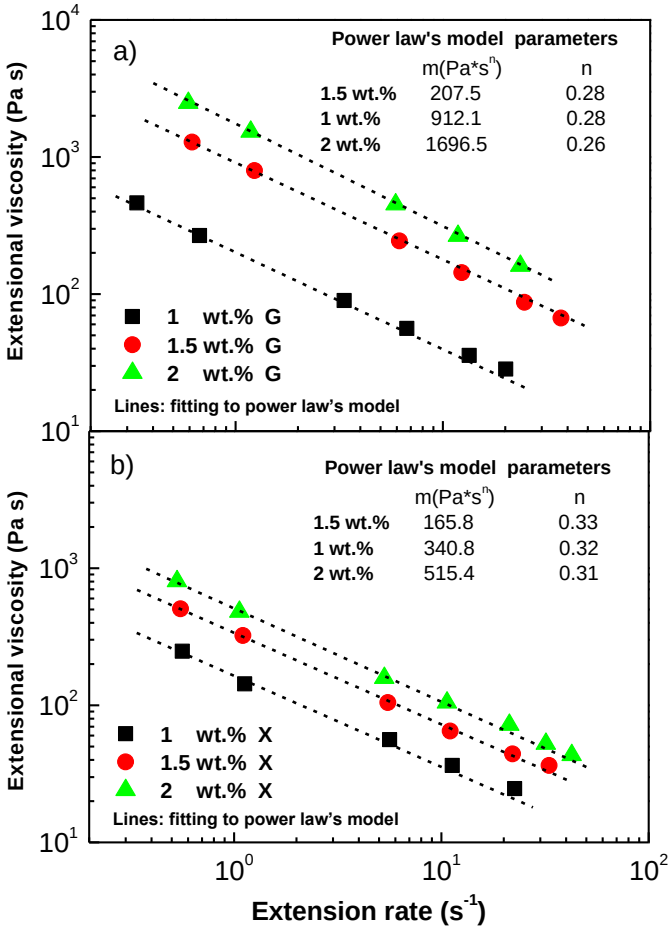
321

322 **Fig. 6.** Evolution of: a) the equilibrium shear stress, b) the stress overshoot, c) the time
323 for the overshoot and d) the amount of overshoot, as function of gum content.

324 *3.4. Extensional flow*

325 The extensional viscosity for the different gum solutions as a function of the strain rate
326 are shown in **Fig. 7**. The extensional viscosity decreased with increasing extensional
327 strain rate, and it also decreased with lower gum concentration. As can be observed,
328 guar solutions present higher viscosity than xanthan solutions on the whole range of

extensional rate studied, similar results were found by shear rheology. These curves give evidence of a clear extension thinning behavior, and they could be fitted by the Power law model for both solutions. The results for both guar and xanthan solutions are presented in **Fig. 7**. The flow index values for the extensional measurements, "n", is consistent irrespective of gum concentration unlike those obtained in shear. Trouton ratio (η_e/η) estimates the departure of ratio of extensional to shear viscosity from its Newtonian counterpart, which is 3 for the Newtonian fluids (Berta, Wiklund, Kotz, & Stading, (2016). In this this case, this value were taken at reference of 5 s^{-1}, shear rate/extensional strain rate since in the model it indicates the n coefficients are similar for the extension and shear curves. Trouton ratio for guar solutions was about ~20 and for xanthan solutions were about ~40, i.e. higher than 3 for all the solutions which confirms the elastic nature of the samples. Similar results were found by Qazi et al., (2017) for commercial gum or starch-based thickeners and by Torres et al., (2014) for natural giesekus fluids.



343

344 **Fig. 7.** The extensional viscosity as a function of the extensional strain rate for aqueous
345 guar (a) and xanthan (b) solutions.

346 **4. Concluding remarks**

347 The shear and extensional rheology of aqueous solutions of guar and xanthan gum with
348 concentrations has been studied over the range 1-3 wt.%. Preparations of solutions were
349 followed through the evolution of torque with processing time by using the mixing
350 rheometry technique. Different stages subsequently related to gum addition, solution
351 and further blending can be distinguished. The increase in torque values is more gradual
352 when using guar gum and these results reveal that the type of hydrocolloids exerts a
353 great influence on the process rheokinetics and resulting rheological response. The
354 critical shear strain for linear response increased with gum concentration and xanthan

gum solutions show a somewhat longer LVR compared to guar, indicating the network is less prone to yielding. SAOS tests within the linear viscoelastic region showed that xanthan gum solutions studied behaved as a weak gel, whereas guar gum solutions suggest the presence of entanglement and the formation of an elastic, gel-like structure. The viscoelastic moduli values of both solutions markedly increased with total polysaccharide concentration, maintaining the shape of the mechanical spectra. All the systems exhibited shear-thinning behaviour. Flow curves were fitted to the Cross and Power law models and the fitting parameters values were depend of the gum concentration. Guar gum solutions obeyed the Cox-Merz rule, although with a divergence at high rates for the more concentrated solutions, while the Cox-Merz rule was not followed throughout the xanthan gum concentrations studied. These results indicated the occurrence of a more developed structure. Transient stress data with time at different constant shear rates of solutions showed typically non-linear viscoelastic response, with a shear stress overshoot during the first stages of flow followed by a steady state. The overshoot and steady-state stresses increased with the gum concentration, whereas the time at which the stress overshoot occurs is only lightly affected by the gum content. The extensional flow curves determined by Hyperbolic Contraction Flow showed extension thinning behavior. The Trouton ratios were an order of magnitude higher than the lower limit for Newtonian fluid, likely due to the elasticity induced by the polysaccharides.

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