RHEOLOGICAL PROPERTIES OF SODIUM ALGINATE SOLUTIONS

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A lot of chemical and others industries use non-Newtonian fluids in their processes.[1] One of the most important characteristics is the influence of shear rate on the fluid viscosity. In this work, we present the rheological properties of aqueous sodium alginate (NaAlg) solutions.

The molecular weight of this polymer was calculated using Huggins and Kramer equations and its intrinsic viscosity was determined for the polymer. The apparent viscosity and the influence of shear rate on polymer concentration in aqueous solutions were measured. The effect of solvent on rheological behaviour was also studied.

Dynamic viscoelastic moduli, thixotropy and oscillatory dynamic tests also showed the nature of the NaAlg solutions.
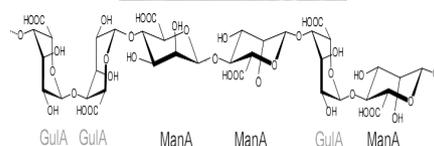
INTRODUCTION[*]

Alginate is a polysaccharide occurring in a large amount in nature,[1] this biopolymer is extracted primarily from brown algae. It has been used in the biotechnology industry as a thickening agent, a gelling agent and a colloidal stabilizer. Alginate also has a unique capacity to be used as a matrix for the entrapment and/or delivery of a variety of molecules or particles,[2] although alginate is biocompatible; they are known to be resistant to biodegradation.[3]

Alginate is linear copolymers composed of two monomeric units, β-1-4-linked d-mannuronic acid (M) and α-1-4-linked L-guluronic acid (G).[4] The chemical composition and sequence of M and G residues depend on the source from which the alginate has been extracted.[5] The most useful property of alginates are their ability to react with polyvalent metal cations, specifically calcium ions, to produce strong gels or insoluble polymers.[6,7]

Structural and mechanical proprieties of alginate solution can be tuned by adjusting the ionic strength of the gelification medium or the calcium source.[8,9]

The molecular weight of commercially available sodium alginates will seldom be higher than 500,000 g/mol. The molecular weight of native alginate is not known since degradation occurs during the extraction. The polydispersity index is given by ratio $\overline{M_W}/\overline{M_N}$ and provides an evolution of the polydispersity of the sample. Typically, alginate samples have a polydispersity index ranging from 1.5 to 3, although values as high as 6 have also been repoted.[10]

In previous papers, we described the sodium alginate solution properties and used it in after work to obtain hydrogels that would serve as material in the wastewater treatment. To fit the experimental data, the power law (Ostwald de Weale model) was used. This model was chosen for its simplicity and its good fit with the experimental data.
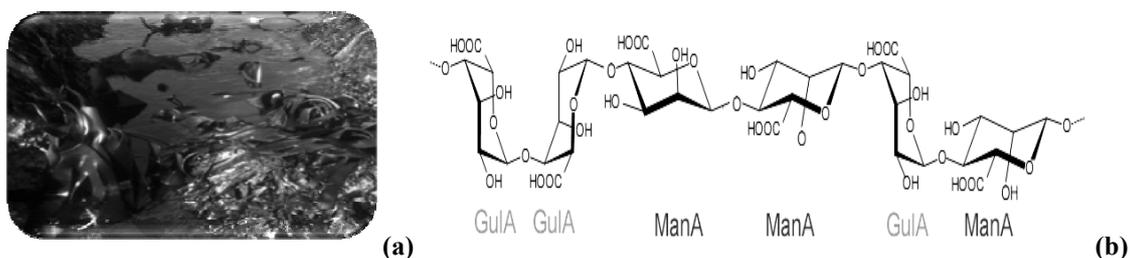
Fig. 1 – (a) Brown algae (Laminaria digitaria) (b) Chemical blocks structures of alginate.[11]

MATERIALS AND METHODS

Technical sodium alginate (NaAlg) sample (Lot# 4889401) purchased from Prolabo (France). NaAlg allow for preparation of aqueous solutions only at low concentration, usually less than 3wt%. Sodium chloride purchased from Prolabo. Distilled water was used to form all the aqueous solutions needed in these investigations.

Solutions were prepared by mixing the appropriate amount of sodium alginate with distilled water or else with 0.1M NaCl. Then, the mixture was heated on a hot-plate at 70°C, with an aid of continuous stirring for one hour. No adjustments of pH were made. The measured solution pH was between 5 and 5.5.[12]

1. Determination of intrinsic viscosity of alginate

The intrinsic viscosity [η] is a characteristic property of a single macromolecule in a given solvent and is a measure of the hydrodynamic volume occupied by the polymer itself. It depends primarily on the molecular weight (M_W), the chain rigidity and the solvent quality. For the anionic polyelectrolytes under study, the presence of macro-ions and counter-ions in aqueous media causes coil expansion by intrachain electrostatic repulsion and extra dissipation of energy, thus explaines why the intrinsic viscosity of a polyelectrolyte can be much higher than that of a neutral rodlike macromolecule of equal size. Thus, [η] usually increases with increasing charge density of the macroion.[13]

SmidsrØd (1970)[14] demonstrated that the intrinsic viscosity of different alginates at infinite ionic strength was independent of the counter-ion used and representative of the uncharged alginate molecule, being also identical to that obtained for the alginic acid formed in 0.1M HCl, when the macromolecule contains no charged groups. This way, the intrinsic viscosity is correlated to the average molecular weight via the well-known Mark-Houwink equation.

The polymer solutions were prepared by dissolution of a known amount of polymer in water or in 0.1M NaCl solution, because in literature based Mark-Houwink constants[15] were determined using this solvent to prevent the polyelectrolyte expansion in solution when using size exclusion chromatography to determine these constants.

The viscosimetry measurements on dilute solutions were performed on an Ubbelhode capillary viscosimeter (constant=1.08828 mm^2/s^2, Schott type S01.40/IV, 0.40 mm in diameter and 10.0 cm length)[16] that was immersed in a water bath previously equilibrated at 20°C±0,1°C. The NaAlg aqueous solutions used were in the range of 0 to 20g/L. These concentration intervals were used so as to obtain solutions of similar viscosity.

2. Rheological experiments

Aqueous solutions of polymers were prepared by gentle stirring for 24 h. Samples were subsequently centrifuged (20 min, 200 rpm) to get rid of entrapped air bubbles, and were then stored over the night before rheological measurements were performed. To carry out these measurements, an Auton Paar (MCR 301) rheometer using a cone-and-plate geometry, with a cone angle of 1°and a diameter of 50 mm. The samples were introduced on to the plate for 5 min to eliminate residual shear history, and then carry out experiments immediately. The measuring device was equipped with a temperature unit that gave good temperature control (20±0.05°C) over an extended time in this work. Steady shear and dynamic studies were executed at 20 °C. Also, oscillatory experiments were performed within the linear viscoelasticity

region, where storage (G$^{'}$) and loss (G$^{''}$) moduli are independent of the stress magnitude.

RESULTS AND DISCUSSION

1) Biopolymer characterization

a) FTIR spectroscopy

For identification of the polymer, infrared spectroscopy was used. FT-IR spectra of samples were taken in KBr pellets using an FT-IR spectrophotometer. The IR spectra obtained for the Na-Alg in the 600-4000 cm^{-1} range, is shown in Fig. 2. The spectra of this polysaccharide, presented two strong peaks at 1619 and 1420 cm^{-1} due to the asymmetrical and symmetrical–COO− stretching vibrations of the free carboxyl group as observed by Huang *et al.* (1999).[17] Characteristic absorption peaks around 2909 cm^{-1} due to C–H stretching and a band appeares at 3500 cm^{-1} for the hydroxyl group.[18]

FT-IR spectra were used to determinate the M/G ratio though characteristic absorbance peaks at 1036 and 1086 cm^{-1}. The average absorbance ratio (A1036/A 1086) for NaAlg was 0.97. This result agrees with results of Vivian Florian-Algarin and Aldo Acevedo (2010). [12]

b) Thermogravimetic analysis (TGA) and Differential Scanning Calorimetry (DSC)

This work will investigate the properties of mass (using TGA) and enthalpy (using DSC) of sodium alginate, as they relate the thermal stability and the changes in their decomposition pathways. All thermoanalytical experiments were carried out under atmospheric pressure.

Thermic analysis performed in a NETZSCH STA 409 PC/PG Luxx (Leading Thermal Analysis). Thermogravimetic analysis (TGA) was carried under an inert nitrogen atmosphere at a 2°C/min temperature ramp shows a weight decrease of 15,23% from 20°C to 250°C, which was associated to the water loss (Fig. 3). According to such a results, the salt decomposed by dehydration followed by degradation to Na_2CO_3 and a carbonized material that decomposes slowly from 500-550 °C in N_2 (Fig. 3). According to J. Soares (2004)[19] the Na_2CO_3 decomposition is dependent of the sample holder and atmosphere used. In this work such decomposition appeared above 550 °C in agreement with the findings of those author using Pt crucible and N_2 atmosphere. A vigorous liberation of CO_2 was observed while a dark insoluble residue remained in the test tube, in both cases.

The DSC curves of NaAlg under N_2 was measured at heating rate 10°C/min. In Fig. 3, the NaAlg presented a first endothermic peak around 100 °C attributed to the water release. The second and third exothermic peaks with a maximum at 238.1 and 368.3 to 394.8°C (depending on the heating rate) may be attributed to the decomposition of the biopolymer and formation of the respective carbonate, which is in agreement with TG curves. The degradation peak of sodium alginate has been previously reported in the literature in this temperature range.[20]
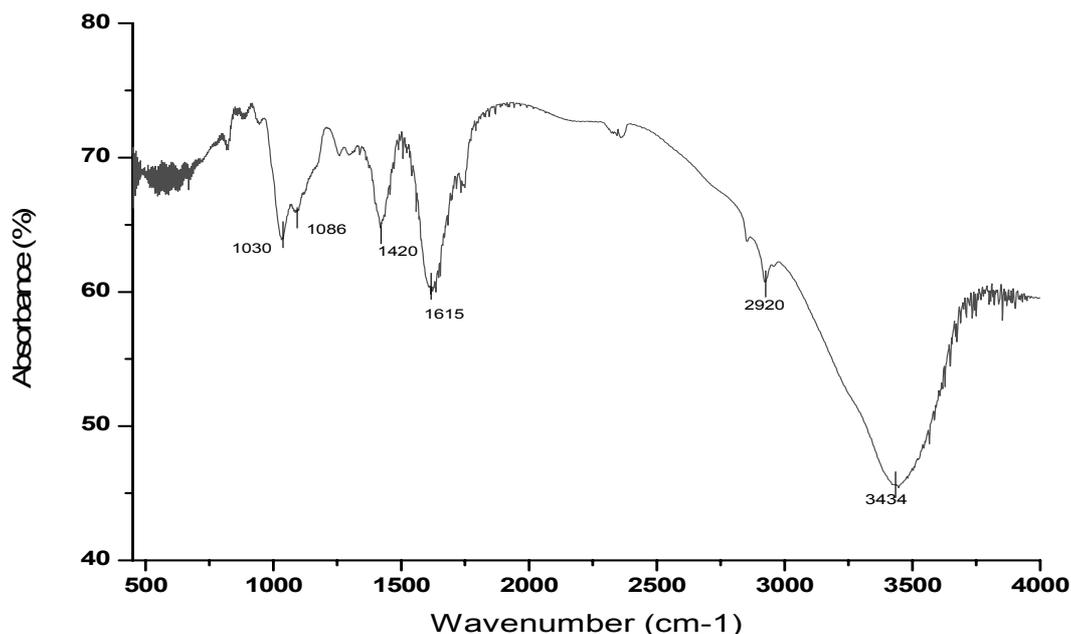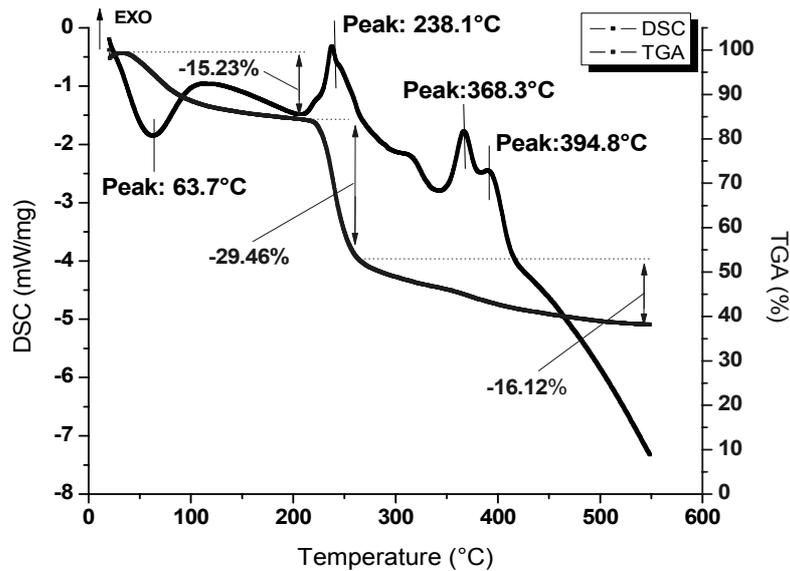

Fig. 2 – FT-IR spectra of Na-Alg.

Fig. 3 – DSC and TGA spectra of Na-Alg.

2) Average molecular weight of sodium alginate

The determination of molecular weight, Mv, from intrinsic viscosity is made through the viscometric equation for that system.[19] The molecular weight was determined using the corresponding Mark-Houwink equation (Eq. (i)).

$$[\eta] = K M_v^a \qquad \text{(i)}$$

Where K and *a* are the Mark-Houwink constants which depend on the polymer-solvent-temperature system. For these polymer, this constants were obtained from the literature.[21-22] For alginates from M. Pyrifera in 0.1M NaCl and 298 K viscometric constants are: $K = 7.3\ 10^{-3} cm^{-3}/g$ and $a = 0.92$.[23]

The value of the molecular weight of the biopolymer used in this study was not known. To characterize this biopolymer, the average molecular weight was calculated. For this, it was necessary to determine the intrinsic viscosity obtained by combined application of Huggins and Kraemer equations (ii) and (iii).[24-25] A similar technique was sodium alginate applied by Chuah *et al.* (2001)[26], and also by Diego Gomez-Diaz & José M.Navaza (2002).[20]

Huggins $\quad \dfrac{\eta_{ssp}}{c} = [\eta] + K'[\eta]^2 C,\qquad$ **(ii)**

Kraemer $\quad \dfrac{\ln \eta_{rel}}{c} = [\eta] - K''[\eta]^2 C,\qquad$ **(iii)**

Where:

$$[\eta] \equiv \lim_{C \to 0} \frac{\eta - \eta_s}{\eta_s C} = \lim_{C \to 0} \frac{\eta_{ssp}}{c} \qquad \text{(iv)}$$

Where: η is the viscosity of the solution, η_s that of the pure solvent, C the polymer concentration and η_{sep} the so-called specific viscosity (see nomenclature in Table 1).

The intrinsic viscosity is a measurement of the hydrodynamic volume of the polymer at infinite dilution. The values of $[\eta]$ are obtained by extrapolation of the reduced viscosity curve to zero polymer concentration using the Huggins equation.[24]

Different concentrations of sodium alginate were prepared to unsure good accuracy and linearity of extrapolation to zero concentration. Figs. 4, 5 show reduced and inherent viscosity versus alginate concentrations.

Table 2 shows the intrinsic viscosity values, the Mark-Houwink constants and the average molecular weight calculated for this polymer in distilled water and 0.1M NaCl solution.

3) Rheological behavior of aqueous solutions of sodium alginate

The rheological characterization of a material generally comprises both studies in the flow and oscillatory modes.

a) Flow mode

A small number of studies have touched the rheological behaviour of different kind of

biopolymers solutions.[26] These works concluded that these solutions have non-Newtonian and pseudoplastic behaviour in practically all cases. These results agree with results of Cheng *et al.* (1999)[27] and Diego Gomez-Diaz and José M.Navaza (2002).[20] The viscosity decreased when the shear rate increased. The same behaviour was shown for all solutions, the viscosity must decrease. The experimental data were fitted with the Ostwald's equation (v). The rheological parameters had been calculated using linearized equation (v). The variation in its typical parameters presented in Fig. 6; it was observed that the behaviour index, *n*, for sodium alginate was less that 1.2, and so, it must be that these solutions have pseudoplastic behaviour.

$$\tau = k.\gamma^n \qquad \textbf{(v)}$$

Table 1

Nomenclature of solution viscosity [28]

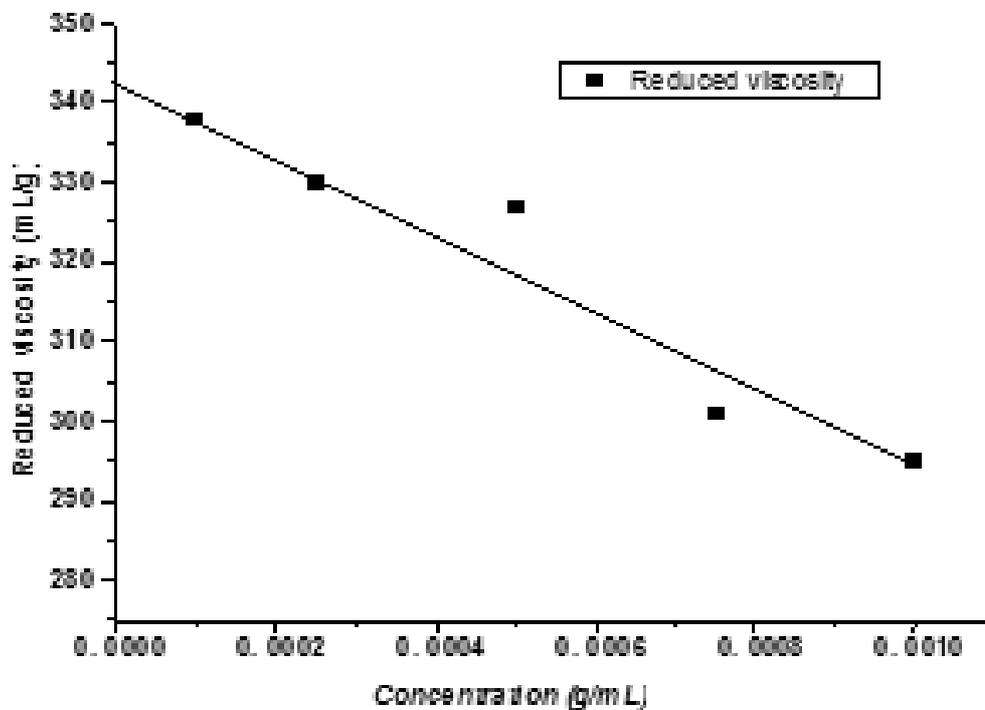| Common name	Name recommended by the International Union of Pure and Applied Chemistry	Symbol and defining equation
Relative viscosity	Viscosity ratio	$\eta_{rel} = \dfrac{\eta}{\eta_s}$
Specific viscosity		$\eta_{sep} = \eta_{rel} - 1 = \dfrac{\eta - \eta_s}{\eta_s}$
Reduced viscosity	Viscosity number	$\eta_{rel} = \dfrac{\eta_{sep}}{C}$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \dfrac{\ln \eta_{rel}}{C}$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \left(\dfrac{\eta_{sep}}{C}\right)_{C \to 0} = \left(\dfrac{\ln \eta_{rel}}{C}\right)_{C \to 0}$

Fig. 4 – The plot of reduced viscosity of sodium alginate aqueous solutions versus concentration using Huggins equation: NaAlg is prepared in distiller water.
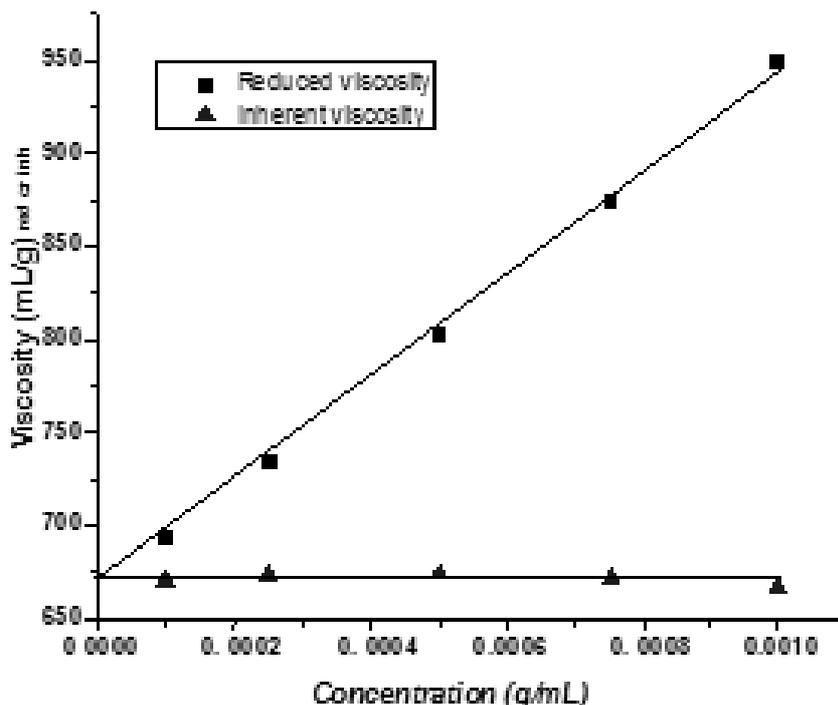
Fig. 5 – Determination of intrinsic viscosity of alginate using Huggins and Kramer equations: NaAlg is prepared in 0.1M NaCl.

Table 2

Values of intrinsic viscosity, Mark-Houwink constants and average molecular
weight of aqueous alginate solutions

Solvent	$[\eta]$ (ml/g)	Mark-Houwink constants		Molecular Weight (KD)
		K (mL/g)	α	
Distiller water	345.4	-	-	**345.4**
0.1M NaCl	676.4	7.30×10^{-3}	0.92 [21]	**250.5**

b) *Effect of solvent on polymer rheology*

The effect of solvent on the rheological behaviour of the polymer solutions was also studied. According to Fig. 6, it was possible to deduct the evolution of the relative viscosity as a function of the shear rate of alginate in diluted solutions were prepared in 0.1M NaCl and in distiller water. Obviously, as usual for polyelectrolyte, the viscosity decreases as the ionic strength increases. These results agree with studies of Rousseau *et al.* (2004).[2] The influence of the variable of solvent on the Ostwald's parameters are shown in Table 3. In this way, the concentration was set to 2wt%.

Fig. 6 depicts the effect of shear rate on the viscosity for 2wt% alginate solutions in presence and in absence of salt. In all cases, shear-thinning features are detected in the low to the high rate region, the produced fluid exhibited similar strong shear thinning behaviour.

Table 3 shows the rheological power-law dependency expressed by $\tau = k . \gamma'^{n}$ of alginate aqueous solution, where τ is viscosity [Pas], γ is shear rate [s^{-1}], K is the consistency constant [Pa.s] and n is the power law-index.

Therefore, a minimum value of the viscosity is found when the alginate is soluble in 0.1M NaCl with a reduction in the viscosity in comparison with the salt-free solution. The upturn at higher amount of supporting salt might be due to the formation of intermolecular junctions when the concentration of monovalent salt is high enough.[29]
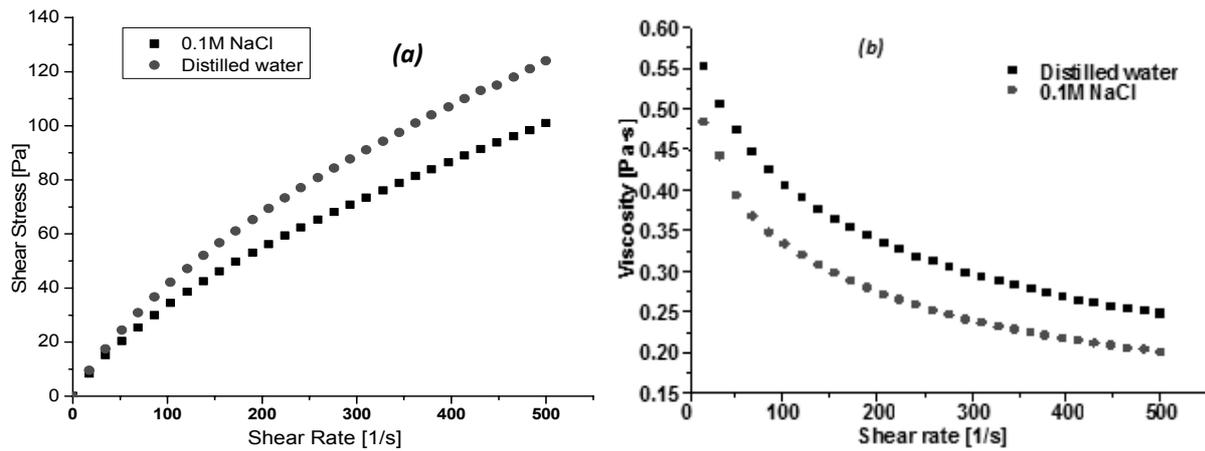
Fig. 6 – Influence of solvent on the rheological parameters n, k (a) and the viscosity (b).

Table 3

Influence of solvent on the rheological parameters (n, k).

Solvent	*k*	*n*	*R²*
Distilled water	1.828	0.816	**0.976**
0,1M NaCl	1.472	0.681	**0.977**

In the inset plot in Fig. 6b, we can easily observe the trend of viscosity with the salting out effect, where we can observe a decrease in the viscosity of the solution if the biopolymer is added the salt. Indeed, to obtain the formation of these polymers, we speculated that the viscosity of alginates depends strongly upon the ionic strength of the solution,[30] but its exact relationship to the ionic strength has not yet been established. These results agree with results of Ramón *et al* (2010).[31]

Sodium alginate, like basically all the monovalent salts of alginate, is highly soluble in water owing to the favorable entropic contribution from the free countreions. This consideration leads immediately to identification of the presence of high amount of supporting salt as a limiting condition for the solubilization of the polyanion. In fact, the addition of 1:1 salts will progressively disfavor the solubility of the alginate chain, leading eventually to phase separation. The salting-out effect can be efficiently used for the fractionation of alginates. In addition, concentration of supporting salt even lower that 0.1M slows down the kinetics of dissolution of alginate particles and limits their solubility, automatically, it slows down the rheology characterization of alginate solution.[10] These experimental results explain that the solutions have more non-Newtonian behaviour when the conditions used (solvent, ionic strength) changed. In relation to consistency index, k, the solvent nature caused a decrease in its value if there is the salt in alginate solution.

c) Effect of alginate concentrations on polymer rheology

The variation and influence of alginate concentrations on the rheological parameters was illustrated in Table 4; it was observed that the behavior index, *n*, for sodium alginate was less than 1.2. These experimental results explain when the concentration increased.

In the flow mode, the alginate solution at different concentration exhibited typical shear thinning behaviour with a non-Newtonian in the range of higher shear rates (1-500 s⁻¹).[32] This behaviour due to alignment of molecules in the flow (see Fig. 7).[33]

Table 4

Influence of alginate concentrations on the rheological parameters n, k

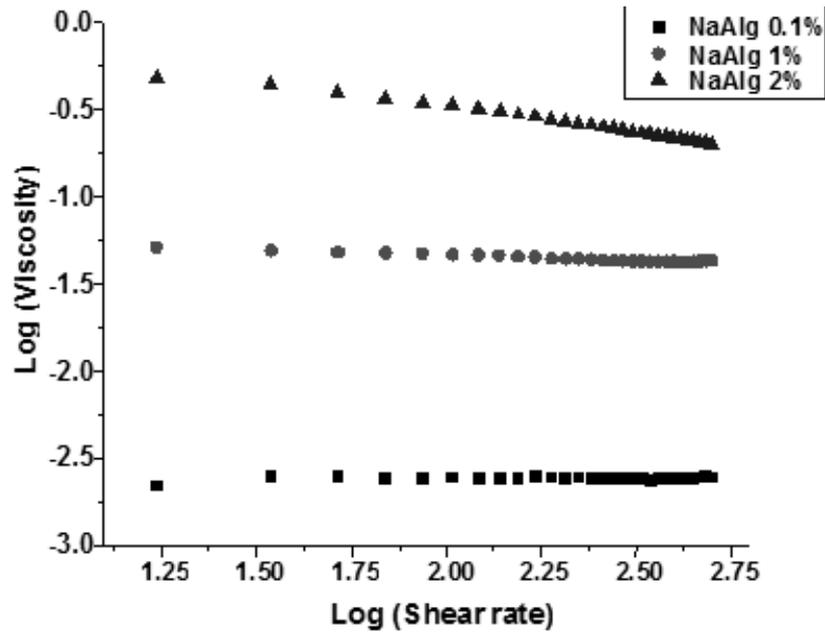| [Alginate] (g/L)	*k*	*n*	*R²*
1	0.002	1.008	**0.999**
10	0.057	0.952	**0.999**
20	1.472	0.681	**0.977**

Fig. 7 – Cone and plane: Flow-curves for different sodium alginate concentration in 0.1M NaCl.
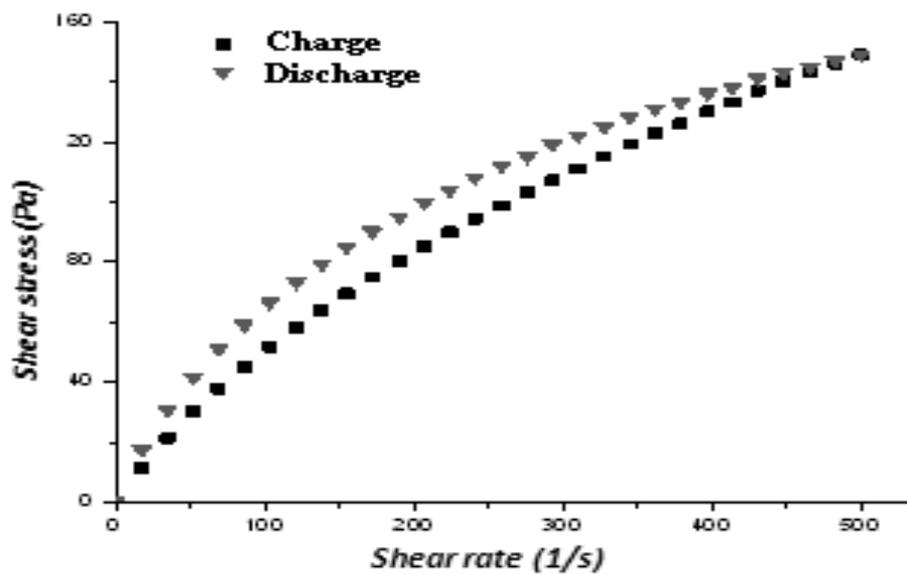

Fig. 8 – Hysteresis of Cone and plate for sodium alginate (2%).

d) Hysteresis experiment

A hysteresis experiment is used to determine how a macromolecule behaves as it suffers transitions from rheological non-steady-state to rheological steady-state phase and vice versa. An aqueous alginate sample was run in both geometries from low-to-high shear rates followed immediately after by a high-to-low run. In this experiment, the range of shear rate was from 0 to $500s^{-1}$. Fig. 8 shows the hysteresis (charge-discharge) for the rheometer geometry.

It is observed that the slop of discharge higher than the slop of charge. Based on these results the fluid presents a hysteresis buckle, so it exhibits typical anti thixotropy behaviour.

e) Oscillatory flow

Experiments in the oscillatory regime were performed with only one of its kind of sodium alginate concentration; it was the amount 2 wt%, and the results were compared with those corresponding to the polymer in literature.
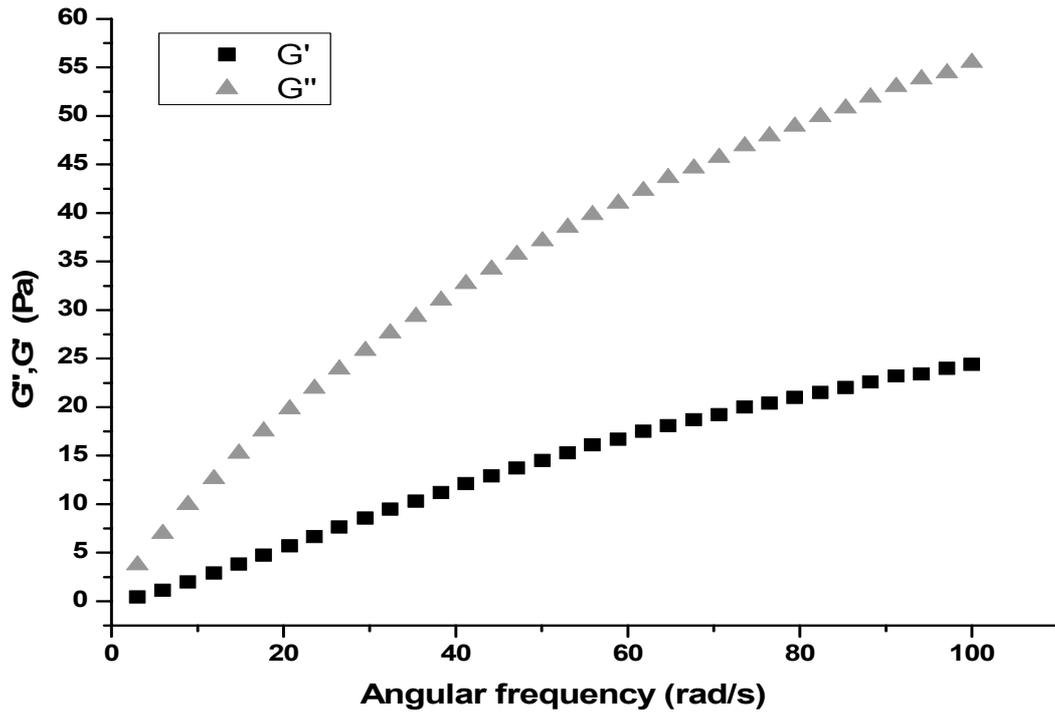
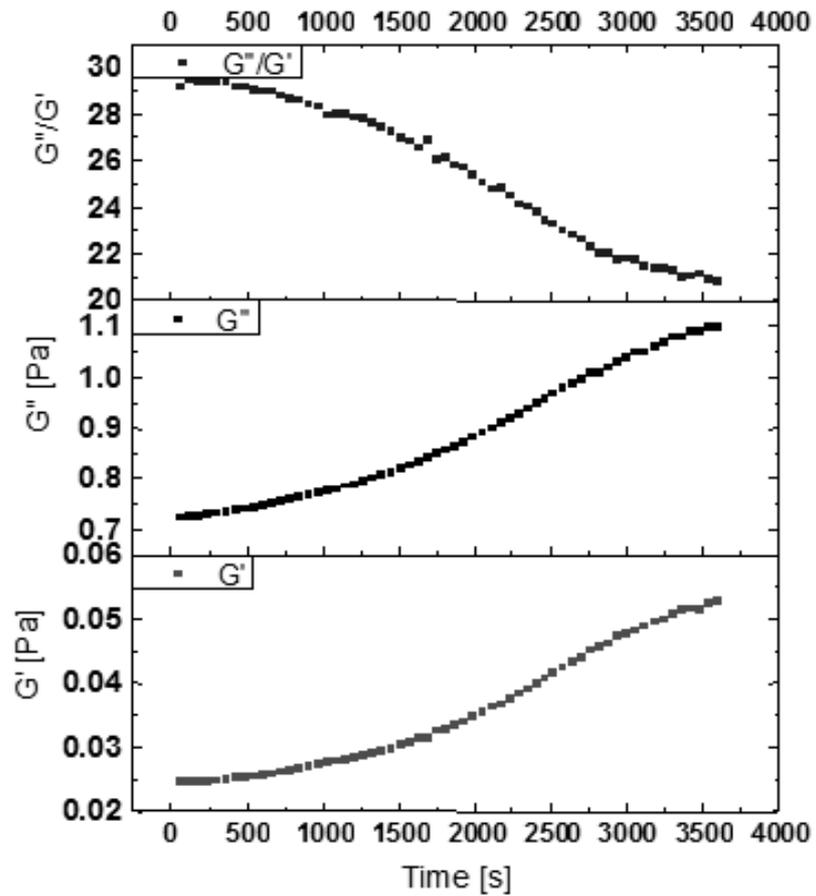Fig. 9 – Elastic (G') and viscous (G'') moduli as a function of angular frequency for 2wt% alginate.

Fig. 10 – Variation of viscoelastic moduli (G' and G'') and tan δ (G''/ G') as a function of the time.

The slopes of G' and G'' versus ω (log/log coordinates) were close to 1 and 1.5, respectively (results not shown), in agreement with theoretical predictions. Fig. 9 shows typical mechanical spectra for solutions of Na-alginate (20 g/L). A classical behaviour was observed, with G' and G'' increasing with the frequency. With this polymer, viscous solutions were obtained, with the loss moduli G'' higher than the storage moduli G', both being frequency-dependent; they decreased more markedly in the low frequency-range for this biopolymer. This would reflect an increasing number of loose chains end due to their random dimerization into heterogeneous network.[34] These solutions exhibit typical viscoelastic behaviour. The viscoelastic nature of the alginate-based networks, like the other polysaccharide-based systems, can be explored by dynamic measurements which allow determination of the elastic (G') and loss (G'') moduli.

With this solution, it was obtained that the viscous behaviour (G''> G') was predominant. Where the viscous moduli G'' higher than the elastic moduli G' both being frequency dependent. These solutions exhibit typical viscoelastic behaviour (see Fig. 10).

CONCLUSIONS

This study concluded that aqueous solutions of sodium alginate exhibited shear-thinning non-Newtonian flow behaviour. It was observed that a smaller quantity of alginate produces a more marked shear-thinning. For this reason the alginate will be more appropriate to use as a thickening agent.

The effect caused by the polymer concentration is an increase in the apparent viscosity. The behaviour parameter, n, decreased when the polymer concentration increased.

There is an important parameter determining and limiting the rheological proprieties of alginate, predominantly in water. It is the solvent nature. Obviously, any change in an alginate solution, generally will have a profound effect, especially on polymer chain extension and solution viscosity. At high and/or low ionic strength, the shear-thinning non-Newtonian also will be affected.

The experiments with sodium alginate concentration (20g/L), in the oscillatory regime showed that the polymer exhibit typical viscoelastic behaviour.

Abrreviations

NaAlg: Sodium alginate
M: Mannuronic acid
G: Guluronic acid
DP: Degree of polymerization
wt%: Weight percentage
G': Storage moduli
G'': Loss moduli
TGA: Thermogravimetic Analysis
DSC: Differential Scanning Calorimetry
η: Intrinsic viscosity (L.g^{-1})

η_{red} : Reduce viscosity (L.g^{-1})

η_{inh} : Inherent viscosity

η_{sp} : Specific viscosity

η: Viscosity of the solution

η_0 : Viscosity of solvent

K and α : Mark-Houwink constants (mL/g)
K_v : Constant dependant to polymer and of solvent
C: Concentration of solution (g.L^{-1})
M_w : Molecular weight (Da)

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