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Rheological behavior of borate complex and polysaccharides

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ABSTRACT

In this work the rheological behavior of manioc starch (S) industrially modified and its blends with a xyloglucan (XG) in the presence of tetraborate (T) ions at pH 12 was described. At rotational measurements the viscosity values showed a good interaction between polysaccharides (20/5 g/l, respectively, to S and XG), which were highly modified by the presence of tetraborate (7 g/l) resulting in better pseudo or plasticity. To system S/XG/T at 20/5/7 or 40/10/14 g/l the rheological properties were dependent of polysaccharides/T concentration. Mixtures at 25/7 g/l performed a viscoelastic solution, and at 50/14 g/l a weak gel. After the temperature sweep analyses (heating and cooling), a more solid character was obtained. This performance could be explained as a result of total gelatinization process that benefits the structural reorganization and better interaction between polysaccharides and the tetraborate complex formed with the hydrocolloid. Also, it was observed that the S/XG/T system, after heating/cooling together with a shear stress, adopted a helical conformation similar to that obtained with amylose standard, since it was colored in blue with lugol. So, the interactions are related with the conformational change of S and XG and also with shear processes, which aid the reptation phenomena and improvement of the solid character.

1. Introduction

The polysaccharides are utilized in several industries as functional ingredients for controlling stability, structure, and texture of products. Xyloglucan is a water-soluble neutral polysaccharide, found in the primary cell walls of non-graminaceous (monocotyledons) and in the cotyledon of some dicotyledonous seeds, where it has functioned as a storage [1]. It is the commercial form extracted from *Tamarindus indica* (tamarindo) seeds which is used in cosmetic, biomedical and food applications [2–4]. One of the properties of xyloglucan is its high viscosity in aqueous solutions. This biopolymer shows a main chain with (1→4)-linked β-D-glucan, and in the side chains xylose units are linked to the glucose units in the C-6 position. Some of the xylose units are also substituted at C-2 by β-D-galactose units [5]. In the Federal University of Paraná (UFPR) considerable attention has been paid to the xyloglucan extracted from *H. courbaril* (jatobá) seeds obtained at different Brazilian locations, whose partial fine chemical structure and properties have been determined [6–11].

Other polysaccharide widely used is the starch, that is composed of anhydrous glucose units linked primarily through α-D-(1→4) glycosidic bonds. While the detailed fine structure has not been fully elucidated, it has been firmly established that starch is a heterogeneous material consisting of varying proportions of amylose and amylopectin [12,13]. Some properties of starch can be modified by the presence of hydrocolloids, to improve their rheological characters, since that mixture of polysaccharides in solution is different from pure systems [13,14]. The synergic interactions between starch and hydrocolloids are of great interest commercially, since they resulted in systems with different functionalities, new rheological characteristics or better textures using minor quantity of polysaccharides, properties which can possibly be used for other applications also [11,15]. Regarding the industrial potential in the processing of polysaccharides, the knowledge of the rheological behavior of starches and other biopolymers is very useful in quality/process control and equipment selection.

It is known that at alkaline pH, polysaccharides complex with borate ions forming some heterocyclic boron compounds [16–20]. In the literature it was related that the presence of borate ions in xyloglucan (tamarindo seeds) made up viscous and elastic solutions [21]. This effect was demonstrated previously by Ghose and Krisna [22]. The studies involving guar gum and hydroxypropyl guar (HPG) in high concentrations and pH variation related that the behavior of relaxation of a gel depends on the nature of links due to borate ions [23]. Other studies rheologically involving a complex of guar or hydroxypropyl guar with borate ions, showed that the chemical balance involving boric acid, borate ions free or associated with cis-diol sites of the polysaccharides chain, determines the number of links, and this balance is in function of temperature and pH [24]. Power et al. [25] studied the rheological behavior of the complex of HPG with borate ions, and the authors showed that despite the properties of guar and HPG being studied extensively by groups of rheology and industries of petroleum, a complete understanding of the behavior of these fluids

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Table 1
Composition and identification of the systems

System	Starch (g/l)	Xyloglucan (g/l)	Sodium borohydride (g/l)	Sodium tetraborate (g/l)
25S	25	–	0.1	–
25S/7T	25	–	0.1	7
5XG		5	0.1	–
5XG/7T	–	5	0.1	7
20S/5XG	20	5	0.1	–
20S/5XG/7T	20	5	0.1	7
50S/14T	50	–	0.1	14
40S/10XG/14T	40	10	0.1	14

and gels still is not clear. Rheological studies in the interaction of xyloglucan (XG) from *H. courbaril* seeds and borate ions were performed by Martin et al. [10], these authors observed that better viscoelasticity was related with greater M_w of XG. In the ^{11}B NMR spectrum, it was found that the interaction of borate ions with xyloglucan was through galactose units. Recently, the critical strain for the gel formulated with konjac glucomannan was found to be independent of borax concentration, while the yield stress firstly increased with increasing borax concentration and then decreased [26].

Considering the rheological properties, the aim of this work was to characterize the behavior of systems of manioc starch, xyloglucan, and its blends in the presence of borate ions by dynamic viscosity curves, to obtain more plastic properties.

2. Materials and methods

2.1. Materials

The xyloglucan (XG) was obtained by exhaustive aqueous extraction from pooled and milled *Hymenaea courbaril* seeds acquired from EMBRAPA/Natal/RN. The viscous extracts were purified by centrifugation. The polymer was obtained after precipitation with two volumes of 96% ethanol and washed with acetone [15]. Starch (S) from *Manihot utilissima* industrially modified (cross bounded) by pre-gelatinization was supplied by Corn Products Brasil Ingredientes Industriais Ltda, Balsa Nova, State of Paraná, Brazil, in which amylose content was related as 18%.

2.2. Swelling and solubility of starch

The swelling assay was made by the method of Leach et al. [27], using a 0.5% (w/v) solution. So, starting at 50 g/l, the solution was diluted with purified water to the correct concentration. Then it was centrifuged at 700 *g* for no more than 15 min. The volume of supernatant indicated the volume of water non-linked in the solution.

2.3. Determination of XG critical concentration

Solutions of starch (5 g/l) in water and XG (3 g/l) in 0.1 M sodium nitrite were prepared and diluted in water, which were utilized to determine, initially, the intrinsic viscosity [η], evaluated by extrapolation of reduced viscosity to the limit of zero concentration, where the linear coefficient is the [η]. Then, by slope of log specific viscosity versus log ($c\times[\eta]$), the values of critical concentration were determined.

2.4. Preparation of the isolated polysaccharide solutions, blends and complexes with borate ions

The starch (S) was solubilized in distilled water at 25 °C for 30 min and the xyloglucan (XG) in distilled water at 25 °C for 19 h. The S/XG blends, for example at 25 g/l, were obtained by adding the S solution (200 mg/5 ml) into the XG solution (50 mg/5 ml). The mixture was stirred for 20 min and sodium borohydrate was added, and then the pH of all solutions was adjusted for 12 with sodium hydroxide solution (40%, w/v). Sodium tetraborate (T) was added to obtain the S/T, XG/T or S/XG/T system. All the systems formulated are present in Table 1.

Table 2
Rheological parameters of the systems at 25 or 5 g/l evaluated by the Power law, Bingham and Herschel–Buckley models

Sample	R^2	χ^2	τ_o (Pa)	K (Pa s^n)	n	η (Pa s)
25S[a]	0.9979	0.0484	–	1.4384	0.5359	–
25S/7T[a]	0.9749	0.2873	–	2.0485	0.3915	–
5XG[a]	0.9998	0.0002	–	0.0615	0.8562	–
5XG/7T[a]	0.9998	0.0002	–	0.0663	0.8253	–
20S/5XG[a]	0.9870	0.1936	–	2.5776	0.5496	–
25S[b]	0.9972	0.0127	10.4894	–	–	0.0642
25S/7T[b]	0.9871	0.0029	10.7266	–	–	0.0139
5XG[b]	0.9992	0.0004	0.8266	–	–	0.0230
5XG/7T[b]	0.9998	0.0001	0.7863	–	–	0.0795
20S/5XG/7T[b]	0.9596	0.0702	20.5533	–		0.1184
20S/5XG/7T[c]	0.9993	0.1599	27.7621	23.1685	0.5372	–

[a] Power law ($\tau = K\gamma^n$).
[b] Bingham ($\tau = \tau_o + K\gamma^n$).
[c] Herschel–Buckley ($\tau - \tau_o = \eta\gamma$).

2.5. Rheological properties

Rotational experiments to the upward and downward curve had a duration of 2 min each one with shear rate ranging from 0 to 200 s^{-1}. The experimental data were mathematically evaluated and fitted according to the Herschel–Buckley model (Eq. (1)), Power law (Eq. (2)) or Bingham (Eq. (3)).

$$\tau = \tau_o + K\gamma^n \quad (1)$$

where, τ is the shear stress (Pa), τ_o is the yield stress (Pa), K is the consistency coefficient (Pa s^n), g is the shear rate (s^{-1}) and n is the flow behavior index of the fluid (dimensionless).

$$\tau = K\gamma^n \quad (2)$$

where, τ is the shear stress (Pa), K is the consistency coefficient (Pa s^n), g is the shear rate (s^{-1}) and n is the flow behavior index of the fluid (dimensionless).

$$\tau - \tau_o = \eta\gamma \quad (3)$$

where, τ is the shear stress (Pa), τ_o is the yield stress (Pa), η is the Bingham plastic viscosity (Pa s) and g is the shear rate (s^{-1}).

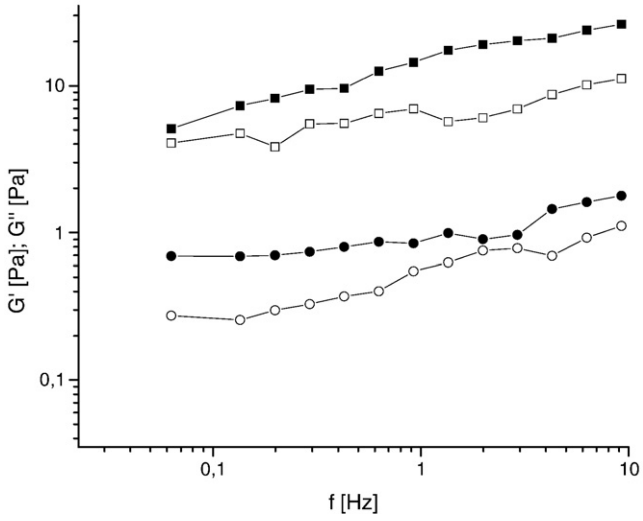

Fig. 1. Frequency (f) dependence of systems 25S/7T (modulus (G') — ●, (G'') — ○); and 20S/5XG/7T (modulus (G') — ■, (G'') — □), in Haake RS 600 rheometer, spindle PP 35 mm, 1 Hz, at 25 °C.