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Changes of the dynamic properties of tamarind (*Tamarindus indica*) gel with different saccharose and polysaccharide concentrations

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Abstract

The dynamic properties (storage moduli, G' and loss moduli, G'') of tamarind gels and the influence of saccharose and polysaccharide concentrations were studied using model rings of 3 mm thickness and 20 mm diameter, prepared with three saccharose (55, 60 and 65% w/v) and three polysaccharide concentrations (1.5, 2.0 and 2.5% w/v). Small amplitude oscillatory measures were taken at 25°C in a PHYSICA LS 100 rheometer with parallel plate geometry. Results for the 9 gels showed the zone of linear viscoelasticity between 0.637 and 6.37 Pa of oscillatory shear stress. The mechanical spectra obtained after 24, 48 and 72 h evidenced the presence of syneresis with an increase in G' as a function of time. The effects of polysaccharide concentrations on gel viscoelasticity were greater than those of saccharose. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Rheology; Gel; Viscoelasticity; Tamarind seed; Polysaccharide

1. Introduction

Hydrocolloids (i.e. carrageenan, alginate, agar–agar, starches, gelatine and pectins) are high molecular weight macromolecules that are easily dissolved or dispersed in water, and under appropriate conditions can produce an increase in viscosity. For this property they are used as food thickeners, stabilizers and emulsifiers (Doublier & Thibault, 1988; Glicksman, 1969, 1982; Ian, 1993).

The polysaccharide extracted from tamarind seeds presents interesting properties (Bhattacharya, Bal, Mukherjee, & Bhattacharya, 1994; Shankaracharya, 1998). It represents between 46 and 48% of the barked seeds (Preciado, 1996). Its structure contains glucose, xylose and galactose units, in a molecular proportion of 3:2:1 with β1–4, β1–6 and β1–2 linkage (Mukherjee & Khan, 1959; Preciado, 1996; Whistler & Barkalow, 1993). This polysaccharide gelifies in aqueous phase with saccharose and when ethanol is added (Glicksman, 1986; Lang et al., 1992; Yamanaka, Yuguci, Urankawa, Kajiwara, Shirakawa, & Yamatoya, 2000).

This property of gelation makes it attractive to be used as additive in the food industry. The gel maintains its form and resists some shear; therefore, it is considered as a two-phase system constituted by a macromolecular three-dimensional solid net that retains a liquid phase. A molecular 'order' exists in the gel form which is differentiated from a molecular 'disorder' in water dispersions (Badui, 1996; Doublier & Thibault, 1998; Glicksman, 1969). The viscoelastic behavior of the gel is related with the solid-liquid nature. When the relative deformation and the shear rate are infinitesimal and dependent on time, it is possible that the relationship stress–strain can be described by a linear differential equation, that corresponds to a linear viscoelasticity behavior (Ferry, 1980). The general equation that describes this behavior can be developed using the Boltzmann superposition principle (Barbosa-Cánovas, Kokini, Ma, & Ibarz, 1996; Dealy & Wissbrun, 1990).

Several methods to study viscoelasticity are used to determine the relationships between stress, the relative deformation and the time given for a deformation. Oscillatory methods were used in this study. With this oscillatory measurement the relative deformation varies with time according to a sinusoidal relationship, because these viscoelastic materials show values of phase displacement between 0 and 90°, where the corresponding shear is the sum of the elastic (G') and viscous (G'') components. The aim of the present study was to evaluate the effect of the concentration of saccharose and polysaccharide on the viscoelasticity properties, storage moduli (G') and loss moduli (G''), of gels prepared with tamarind seed polysaccharide.

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Table 1
Different saccharose–polysaccharide concentrations used for tamarind gels preparation (S/P) = saccharose–polysaccharide (%)

11(55/1.5)	21(60/1.5)	31(65/1.5)
12(55/2.0)	22(60/2.0)	32(65/2.0)
13(55/2.5)	23(60/2.5)	33(65/2.5)

2. Materials and methods

The polysaccharide of tamarind seeds (*Tamarindus indica*) was obtained by the method proposed by Flores (1986). Commercial saccharose was from Industrial Primo, S.A. of C.V., Co.

2.1. Gelification

Polysaccharide dispersion was accomplished in distilled water, heating gradually until 60°C with continuous agitation. Saccharose was solubilized and the temperature was increased to 80°C, for 5 min. The sample obtained was cooled to 60°C and the dispersion was carefully poured into copper rings of 3 mm thickness and 20 mm internal diameter; subsequently, the gels were placed on a plastic plate after removal. Thereafter, the molds in the plate were left for an hour at room temperature and stored for 24 h at 10°C before proceeding to the rheological studies.

The gels were prepared with saccharose (55, 60 and 65% w/v) and tamarind polysaccharide (1.5, 2.0 and 2.5% w/v), then mixed at different proportions as shown in Table 1.

2.2. Small amplitude oscillation

Dynamic determinations were accomplished in a low shear PHYSICA LS 100 (Paar Physica, Germany) rheometer. The equipment was coupled to a water recirculation system with temperature control (Julabo F10, Germany) permitting a wide range of temperatures. The rheometer is regulated by a software Paar Physica ver 2.06 which analyzes information. Measurements were in triplicate at 25°C using parallel plate geometry (PP20), with a diameter of 20 mm, radius of 10 mm and gap of 3 mm. The sample was put on the lower plate (Peltier) and the gap was adjusted; then the measure was for a shear rate in the range 1.66×10^{-6}–$3.33 \times 10^{1}\ \mathrm{s}^{-1}$, a shear stress interval in the range 6.37×10^{-1}–6.37×10^{3} Pa was also considered.

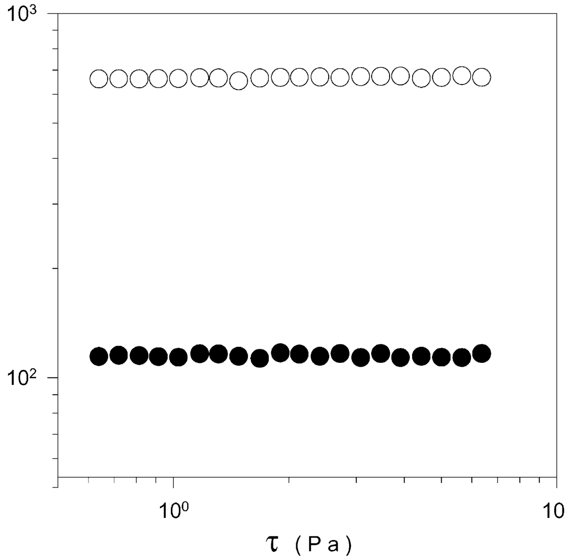

Fig. 1. Amplitude sweep on the storage moduli (G', ○) and loss moduli (G'', ●) for gel 21.

2.3. Linear viscoelasticity

To establish the zone of linear viscoelasticity of the gels, an oscillatory amplitude sweep was performed for each gel, at a temperature of 25 ± 0.1°C, 1.0 Hz frequency and an interval of oscillatory shear stress between 0.637 and 6.37 Pa. The graphics for storage moduli (G') and loss moduli (G'') were obtained according to the experimental oscillatory shear data. The linear zone is defined when independence of these moduli to an oscillatory shear stress is presented, then the value of shear stress is selected in the zone of linear viscoelasticity.

2.4. Aging of gels

The mechanical spectrum of the gels was obtained by a frequency sweep in an interval of 0.1–5.0 Hz, to the oscillatory stress selected in the zone of linear viscoelasticity. For gel evaluations, only one batch was prepared and the mechanical spectra were evaluated at 24, 48 and 72 h.

2.5. Mechanical spectrum of gels

The mechanical spectra of the nine gels were obtained by a frequency sweep between 0.1 and 5.0 Hz, for an oscillatory stress and this was selected in the zone of linear viscoelasticity. All measurements were done in triplicate.

2.6. Statistical analysis

Variance analysis was performed on all data obtained from the storage moduli (G') and loss moduli (G'') as a function of aging and also as a function of saccharose and polysaccharide concentration of each gel, with a statistical difference of $\alpha = 0.05$, using ver. 3.5 of Design Ease. Treatments for the times of 24, 48 and 72 h, for polysaccharide concentrations of 1.5, 2.0 and 2.5% and saccharose concentrations of 55, 60 and 65% were considered. The null hypothesis proposes, at average level, that G' or G'' were equal, independently of the treatment (aging or concentration). The calculated F was compared with the theoretical F (Walpole & Myers, 1997).

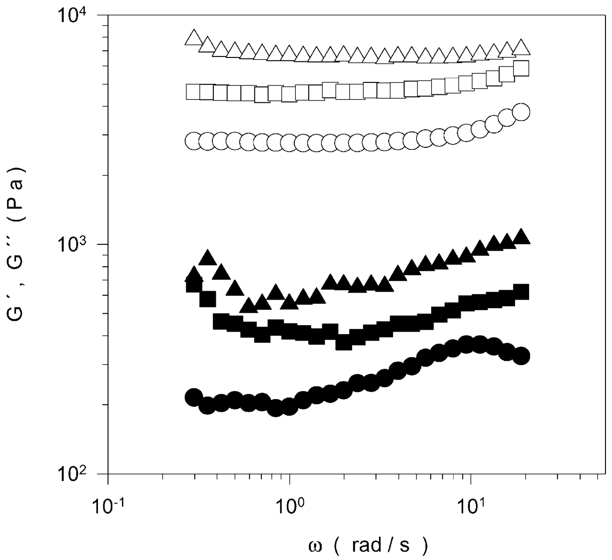

Fig. 2. Effect of aging time on the storage moduli (G', opened) and loss moduli (G'', closed) for the gel 23. 24 h (○, ●), 48 h (□, ■) and 72 h (△, ▲).

3. Results and discussion

The gels presented physical characteristics of a strong gel, self-supported and firm to touch. During and after the shear, in the rheometer, the gel preserved its macroscopic structure, and did not undergo syneresis.

3.1. Linear viscoelasticity

Fig. 1 presents the behavior of the storage moduli (G') and loss moduli (G'') as a function of oscillatory shears stress by an amplitude sweep at a frequency of 1.0 Hz for gel 21 (60% of saccharose and 1.5% of polysaccharide). This behavior was similar to the other gels, where G' prevailed over G'', i.e. the gels presented a viscoelastic behavior. It was also observed that the linear zone for low oscillatory shears is found in an interval of 0.637 and 6.37 Pa, where G' and G'' are independent of the shear.

3.2. Aging of the gel

Fig. 2 presents the evolution of G' and G'' for gel 23 (60% of saccharose and 2.5% of polysaccharide), as a function of frequency, at the aging time of 24, 48 and 72 h. All gels showed that G' was significantly greater than G'' in the employed frequency interval, indicating the predominance of the elastic character of the gels. Likewise, as aging time increased, G' and G'' tended to increase as well; i.e. the polymeric chains associate slowly and do not reach the equilibrium state in the 72 h evaluated. The mechanical spectrum obtained at 72 h presented a light concavity, and according to this effect, probably was produced by contraction of the molecules, and therefore syneresis was also observed (Clark & Farrer, 1995; Doublier & Thibault, 1988; Glicksman, 1969). Fig. 2 shows that G' is greater than G'', therefore, energy is stored and recovered in each oscillation cycle and only a small quantity is lost as heat (Ferry, 1980). Statistic analysis verifies that G' and G'' are different ($P > 0.05$).

For dispersions of 1% high methoxyl pectin added with 60% fructose, aged during two weeks, the values of G' and G'' increased in an order of 10^5–10^6 Pa for G', and 10^3–10^4 Pa for G'', in an interval from 1.0 to 4.0 rad s^{-1} of frequency, indicating that the gels prepared with tamarind seed polysaccharide present viscoelastic characteristic similar to high methoxyl pectin gels in the presence of fructose (Rao, Van Buren, & Cooley, 1993).

3.3. Mechanical spectrum of gels

Fig. 3 presents the effect of polysaccharide concentrations (1.5, 2.0 and 2.5%) on the dynamic modules for gels 11, 12 and 13. In the frequency interval employed, G' is greater than G'', and the elastic character of the gels prevail. Also G' is more independent of the frequency than G''. The dependency of the moduli related to frequency indicates the existence of a three-dimensional net without the possibility of breaking the union zones at any time (Goodwin & Hughes, 2000).

The mechanical spectrum presents characteristics of strong gels as classified by Clark and Ross-Murphy (1987), which indicates that the prevailing rheological behavior is more elastic than viscous. This behavior of G' and G'' was similar for gels 21, 22 and 23, as well as for gels 31, 32 and 33. Fig. 3 shows that, at high frequencies, G'' decreases probably due to hydrophobic interactions, contributing to the stabilization of junction zones as in systems containing pectin (Schmelter, Vreeker, & Klaffke, 2001).

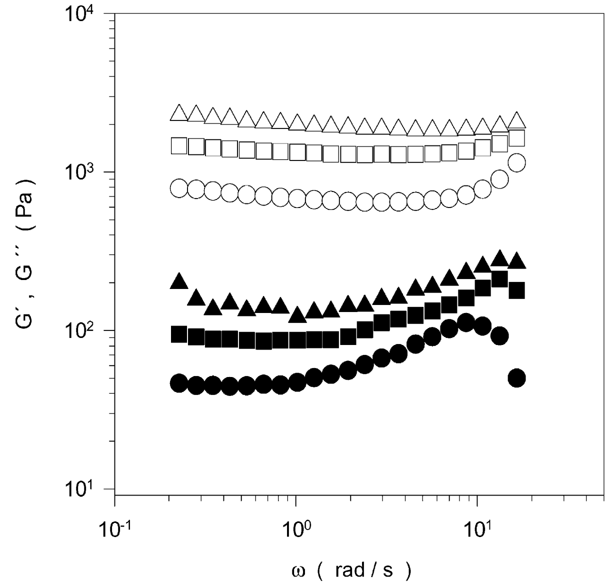

Fig. 3. Effect of polysaccharide concentration on the storage moduli (G', opened) and loss moduli (G'', closed) for the gels 11 (○, ●), 12 (□, ■) and 13 (△, ▲).

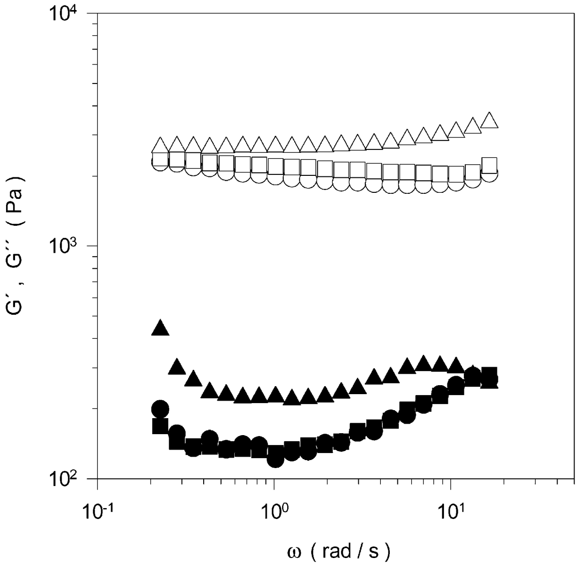

Fig. 4. Effect of saccharose concentration on the storage moduli (G', opened) and loss moduli (G'', closed) for the gels 13 (○, ●), 23 (□, ■) and 33 (△, ▲).

Fig. 4 shows the effect of saccharose concentration (55, 60 and 65%) on modules G' and G'' for gels 13, 23 and 33. G' is greater than G'', as in the previous cases. Saccharose concentration has a minimal effect on the magnitude of the moduli, the difference is small. Comparing Figs. 3 and 4, polysaccharide concentration has greater effect than saccharose concentration, modifying the elastic properties of the gels (Delgado, Salazar, & Ramos, 1998; Zirnsak, Boger, & Tirtaatmadja, 1999).

The variation intervals of G' and G'' for the gels are presented in Table 2. The difference in magnitude of G' is accordingly greater as the saccharose concentration increases, the upper value of the previous gel is always smaller than the lower value of the following gel. At medium saccharose concentration, there is not much difference with respect to G''.

The values of G' are between 10^2 and 10^3 Pa, and for G'' are between 10^1 and 10^2 Pa. These dynamic moduli of a gel based on tamarind seed polysaccharide with saccharose are greater than those reported for gels of 0.3% Kappa-carrageenan (Doublier, 1994) with values of 10^2 Pa for G' and of 10^1 Pa for G''. They are similar to alginate gels (1.4%) whose magnitudes are of 10^3 for G' and of 10^1 for G'' (Doublier, 1992) and to 10% corn starch gels which have a magnitude of 10^3 Pa for G' (Hansen, Hoseney, & Faubion, 1991).

Table 2
Variation range of the storage and loss moduli for the characteristic curves of each gel

Gel	G' (Pa)	G'' (Pa)
11	787–1140	46–50
12	1460–1635	94–179
13	2050–2290	198–267
21	895–1260	68–94
22	1445–1970	99–203
23	2215–2380	168–278
31	1290–1395	64–142
32	2000–2730	142–230
33	2705–3610	237–451

4. Conclusions

The gels of tamarind seed polysaccharide present a storage modulus greater than the loss modulus, with prevalence of the elastic character. The zone of linear viscoelasticity of the gels was in an interval of 0.637–6.37 Pa of oscillatory shears stresses. The dynamic moduli increase as a function of time. The relationship of the storage moduli (G') and the loss moduli (G'') with the frequency is characteristic of a strong gel, which can also be observed physically, and in this study its native macroscopic form was maintained even after the shears. Also, saccharose and polysaccharide concentrations have an effect on the viscoelastic characteristics of the gels. It seems that saccharose favors the association of the polymeric chains and increases the storage moduli, which could be evidence of a possible synergic effect.

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