

Effect of Salt on the Rheological Properties of Low-in-Fat O/W Emulsions Stabilised with Polysaccharides

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The droplet size distribution, stability, flow and viscoelastic properties of 35% oil-in-water emulsions stabilised with 1% w/w Tween 60 and: (i) 5% potato starch (PS), (ii) 5% potato starch and 0.5% xanthan gum (PS + XG), or (iii) 1% xanthan gum (XG), with and without the addition of 0.5M NaCl were studied. Visual inspection of the emulsions that contained a XG and PS + XG, with and without NaCl, showed that they remained stable after 6 months. Emulsions stabilised with PS (without salt) showed an incipient interface after four months storage, while those containing 0.5 M NaCl destabilised within a month. The presence of NaCl did not affect droplet size distribution. Microscopic observations showed that all the emulsions flocculated. The rheological properties of these emulsions were characterised on a controlled-stress rheometer. The linear viscoelasticity was determined by oscillatory measurements that revealed the systems that exhibited weak gel-like properties. The addition of NaCl to the systems caused a decrease of viscosity, storage modulus and of loss modulus for emulsions containing PS and PS + XG while it did not affect emulsions prepared with XG alone. The viscoelastic linear behaviour was described according to the Maxwell generalised model and the discrete relaxation time spectra of the emulsions by means of the BSW-CW model.

Key Words: oil-in-water emulsions, starch, hydrocolloids, viscosity, linear viscoelasticity, relaxation

INTRODUCTION

Stability is the most important factor to be considered in emulsion technology. When oil content is reduced, and droplet concentration decreases, creaming velocity rises. Thus, polysaccharides are added to food emulsions to stabilise emulsion droplets against creaming and to modify their textural properties. The addition of polysaccharides stabilises the emulsion by either enhancing the viscosity of the continuous phase or, in concentrated emulsions, forming a weak gel-like particulate network that imparts additional elastic properties to the whole system, so that emulsion creaming is strongly inhibited (Dickinson et al., 1994; Parker et al., 1995; McClements, 1999, 2000). Their efficiency depends on polymer concentration in the aqueous phase as well as on the structural features of the aqueous polymer system. The effectiveness of polysaccharides for enhancing the viscosity of aqueous

solutions depends on the size and shape of its molecules and conformations they adopt in the solvent (BeMiller and Whistler, 1996).

Although sorbitan fatty acid esters (Spans) and the corresponding polyoxyethylene (POE) adducts (Tweens) have applications as emulsifiers in the food industry (Owusu Apenten and Zhu, 1996), Quintana et al. (2001a) reported that 40% oil-in-water emulsions prepared with those emulsifiers without the addition of any thickening agent showed an incipient interface after 24 h. Moreover, addition of NaCl raised creaming rates resulting in decreased stability.

Xanthan gum (XG), guar gum and potato starch (PS) are some of the hydrocolloids that may be added to the aqueous phase of food emulsions to increase their viscosities. Xanthan's commercial success is due to its high viscosity, salt tolerance, thermal stability, and food compatibility (Kwon et al., 1987). Potato starch presents important characteristics that make it particularly suitable for many industrial food applications: a high consistency on pasting followed by a decrease in viscosity on further heating and agitation, low gelatinisation temperature, and a medium to low tendency to retrograde (BeMiller and Whistler, 1996). In a previous work Quintana et al. (2001b) reported that 40% oil-in-water emulsions stabilised with 1% Tween 60 that contained PS, XG, a mixture of both, or a mixture of xanthan and guar gums remained stable after 6 months,

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while emulsions containing 1% guar gum destabilised in a three-month period. Guar gum alone did not improve emulsion stability because it did not contribute to form a gel like matrix. Besides, the presence of NaCl, a frequent component of food emulsions, can destabilise the system and alter its rheological properties (Kokini and Fischbach, 1988; Yilmazer and Kokini, 1992; Chiralt et al., 1994; Dickinson et al., 1994; Quintana et al., 2001a).

The objectives of the present work were: (i) to establish the effect of PS and XG, on the viscoelastic properties and stability of 35% oil-in-water emulsions stabilised with ethoxylated-60-sorbitan monostearate (Tween 60); (ii) to analyse the effect of the addition of NaCl; and (iii) to model the rheological data within the linear viscoelastic range.

MATERIALS AND METHODS

Materials

Commercial 100% sunflower oil (Koipesol, Spain) was purchased from a local supermarket and used without further treatment. TweenTM60 (T60, ethoxylated-60-sorbitan monostearate) emulsifier, analytical grade NaCl and potato starch (S-4251, lot 123H0866) were purchased from Sigma Chemical Co. (St. Louis, MO). Food-grade commercial preparation of xanthan (Keltrol T, Kelco, San Diego) was used. Distilled and deionised water was used in all solutions and emulsions.

Preparations of the Emulsions

Food emulsions (35% w/w oil-in-water) were stabilised with 1% w/w T60, that was always incorporated to the aqueous phase prior homogenisation at room temperature. Lab-scale manufacture of emulsions was carried out using an Ultra Turrax T-25 homogeniser (Ika, Steufen, Germany). Sunflower oil was added slowly to the aqueous phase containing the remaining ingredients at room temperature. Emulsions were prepared at 11500 rpm for 4 min without thermal control during homogenisation; they were stored at 5°C for 24 h and then equilibrated at 25°C for 1 h before testing. The tested thickeners were: (i) 1% w/w xanthan gum (XG), (ii) 5% w/w potato starch (PS), and (iii) 5% PS + 0.5% XG. Clear gum dispersions were prepared by dissolving the powdered gum in water, while gently stirring for 3 h. Starch was suspended in water or in 0.5% XG and samples were heated at 90°C for 30 min. All gum and starch dispersions were let stand overnight at 5°C.

The effect of ionic strength was also considered adding NaCl to the 35% w/w oil-in-water emulsion to obtain a 0.05 M concentration in the aqueous phase (approximately 2% w/w emulsion). Emulsions prepared

to observe stability also contained 0.01% sodium azide as an antimicrobial agent.

Methods

Droplet Size Distribution

Mean droplet size and droplet size distribution of emulsions were determined by static light scattering using a Malvern Mastersizer model X (Malvern Instruments Ltd., Malvern, Worcester, UK). Sauter average diameter, $D[3,2]$, was calculated for each sample as follows:

$$D[3,2] = \frac{\sum_{i=1}^N (n_i d_i^3)}{\sum_{i=1}^N (n_i d_i^2)} \quad (1)$$

where d_i = droplet diameter, N = total number of droplets, n_i = number of droplets having d_i diameter.

Aliquots of fresh samples were observed after a 1:20 dilution with distilled water on a microscope (Leica DC100 microscope equipped with a digital camera).

Visual Stability

Two (100 mL) aliquots of each emulsion were carefully poured in 100 mL glass graduated cylinders and stored at 20°C in a temperature-controlled room. These samples were periodically observed and the time at which an oil–water interface appeared at the bottom of the cylinder determined the stability period.

Rheological Tests

All samples were left for 10 min before running any measurements in order to allow some stress relaxation and to reach the test temperature of 25°C. Samples were covered with a thin film of silicone oil to avoid evaporation during the measurements. Roughed plates were used to avoid wall slip errors in steady flow tests (Franco et al., 1998). According to Sánchez et al. (2001), in emulsions, the region at which wall slip is more apparent is associated with the shear-induced deflocculation process that leads to a decrease in the viscosity. On the contrary, it has been reported that wall slip.

The steady flow behavior (viscosity, η vs. shear rate, $\dot{\gamma}'$) was studied on a controlled stress rheometer RS 100 (Haake, Germany) using a serrated plate-and-plate geometry (35 mm diameter, 1 mm gap). The flow measurements were obtained by imposing a ramp of shear stresses in a range between 2 and 100 Pa and waiting until the slope of the resulting shear rate versus time was less than 0.001% at each point, so it can be assumed that steady-state was almost attained.

Dynamic rheological assays (storage moduli G' , loss moduli G'' vs. frequency, ω) were done in a controlled stress rheometer RS 150 (Haake, Germany) using a

smooth plate-and-plate geometry (60 mm diameter, 1 mm gap). Frequency ranged from 0.0428 to 92.32 rad/s. Oscillatory test were conducted at a frequency of 6.28 rad/s varying the amplitude of the stress applied on the samples in order to search the linear viscoelastic region.

Two replicates of each test were performed.

RESULTS AND DISCUSSION

Droplet Size Distribution and Stability

Visual inspection of the emulsions that contained XG and PS + XG, with and without NaCl added, showed that they remained stable after 6 months. Emulsions stabilised with PS (without salt) showed an incipient interface after four months of storage, while those containing 0.5 M NaCl destabilised within a month. In a previous study, 40% oil-in-water emulsions were stabilised with 1% Tween 60, without the presence of any thickener, and with NaCl added (0.05–0.2 M) showed a

sharp interface between the creaming zone and the particle-free serum below that was clearly visible with the naked eye after a few minutes (Quintana et al., 2001a). Besides, Dickinson et al. (1994) found that, for 18% o/w emulsions with 0.05 M NaCl, the rate of creaming is substantially reduced and the oil content in the developing cream layer is also significantly lower when xanthan content is increased from 0.017 to 0.6%. On further increasing xanthan content to 0.7% the creaming is completely inhibited over the observation.

A bimodal droplet size distribution was observed on a Malvern MasterSizer-X equipment. Average Sauter diameters were not significantly modified in emulsions containing starch or XG (Figure 1 a). The presence of NaCl did not affect droplet size distribution (Figure 1 b); $D[3,2]$ values were in all cases between 2.6 and 3.5 μm . Yilmazer and Kokini (1992) reported that the addition of 1% or 2% of NaCl to 0.4% XG emulsions did not cause any change in mean droplet size upon aging.

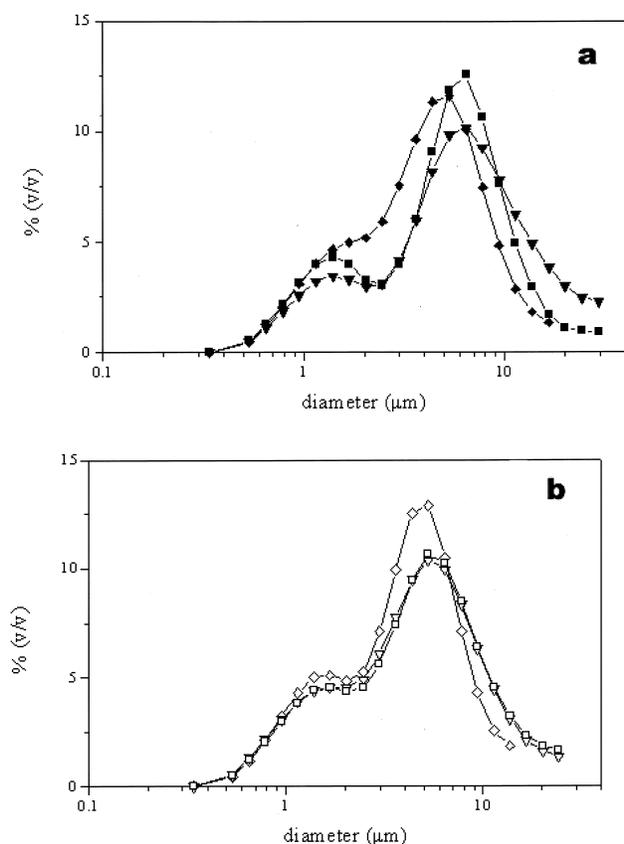


Figure 1. Droplet size distributions for emulsions prepared with different polysaccharides. (a) \blacktriangledown 5% PS + 0.5% XG, $D[3,2] = 3.39 \mu\text{m}$; \blacksquare 1% XG, $D[3,2] = 3.02 \mu\text{m}$; \blacklozenge 5% PS, $D[3,2] = 2.72 \mu\text{m}$; (b) ∇ 5% PS + 0.5% XG + 0.05 M NaCl, $D[3,2] = 2.87 \mu\text{m}$; \square 1% XG + 0.05 M NaCl, $D[3,2] = 2.94 \mu\text{m}$; \diamond 5% PS + 0.05 M NaCl $D[3,2] = 2.68 \mu\text{m}$.

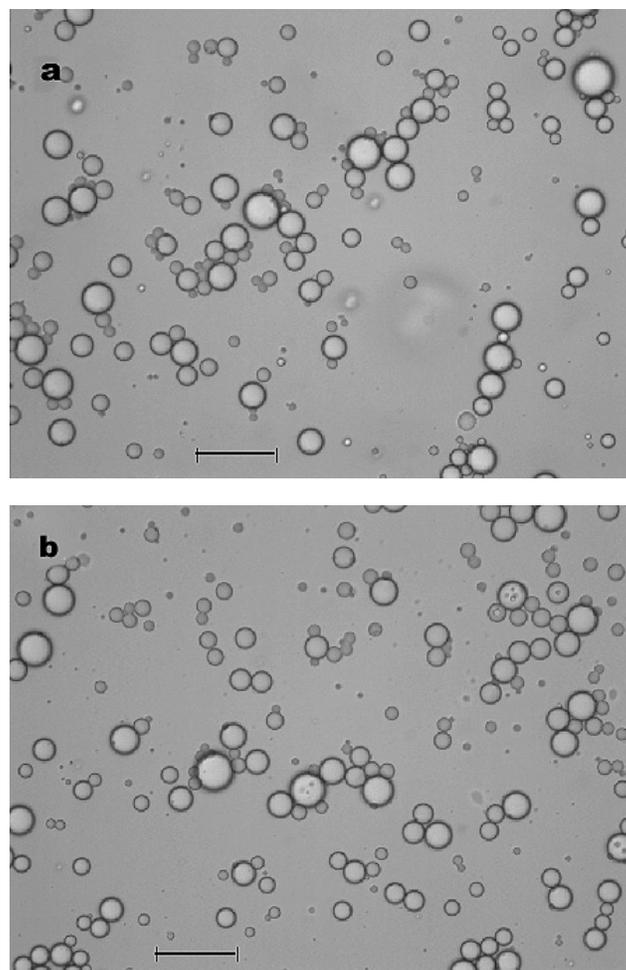


Figure 2. Flocculated oil droplets of a 35% oil-in-water emulsion with 1% Tween 60 containing. (a) 1% XG; (b) 1% XG + 0.05 M NaCl. The bar represents 20 μm .

Microscopic observations showed that all the emulsions flocculated (Figure 2). This aggregation could be explained in terms of depletion flocculation caused by the presence of individual non-adsorbing molecules (Walstra, 1996; McClements, 1999, 2000).

Steady-State Flow Measurements

All the emulsions showed shear-thinning behaviour over a wide range of shear rates (Figures 3 a–c). Thus, the flow curves present a power-law decrease in viscosity followed by a tendency towards a plateau which corresponds to a high-shear limiting viscosity, as may be seen in Figures 3 a and b for emulsions formulated with 5% PS or 5% PS + 0.5% XG, both with NaCl. The Sisko model (Equation (2)), which may be used to fit this type of rheological behaviour, was applied on the experimental flow curves of these emulsions (Figures 3 a and b):

$$\eta = \eta_{\infty} + k_s \cdot (\dot{\gamma}')^{n-1} \quad (2)$$

where, η_{∞} is the high-shear limiting viscosity, n is a flow-index-type parameter and $\dot{\gamma}'$ is the shear rate. In addition to the above described zones, a tendency to a Newtonian region has been found at low shear rates for emulsions that contained 5% PS, 5% PS + 0.5% XG, 1% XG, or 1% XG with NaCl (Figures 3 a–c). The Cross model, which has been successfully used to describe the flow properties of XG solutions (Rodd et al., 2000) was fitted satisfactorily to the flow behaviour of these emulsions:

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty}) / (1 + (\tau \cdot \dot{\gamma}')^m) \quad (3)$$

where η_0 is the limit viscosity at zero-shear rate, m is a dimensionless exponent and τ is a relaxation time equal to the reciprocal of the $\dot{\gamma}'$ value when $\eta = (\eta_0 + \eta_{\infty})/2$.

When both $\eta \ll \eta_0$ and $\eta \gg \eta_{\infty}$, Equation (2) predicts a power-law behavior ($\eta = k (\dot{\gamma}')^{n-1}$) with $n = (1 - m)$ and $k = \eta_0 (\tau)^{-m}$ (Launay et al., 1986). In these emulsions, oil droplets are dispersed in a continuous phase that has weak gel-like characteristics due to the presence of PS (Clegg, 1995), being the rheological properties usually governed by the properties of the continuous phase. The values of η_0 obtained for the tested systems were fitted with the Cross model (Figures 3 a–c). The addition of salt produced a significant decrease in the flow curves of the emulsions that contained PS and a less marked effect on those with PS + XG. In both cases, an asymptotic value of η_0 was not observed within the range of the tested shear rates and for that reason the Sisko model was applied to these systems, as it was previously mentioned. The η_0 values obtained for emulsions with 5% PS ($\eta_0 = 9.3 \cdot 10^4$ Pa s), or 5%

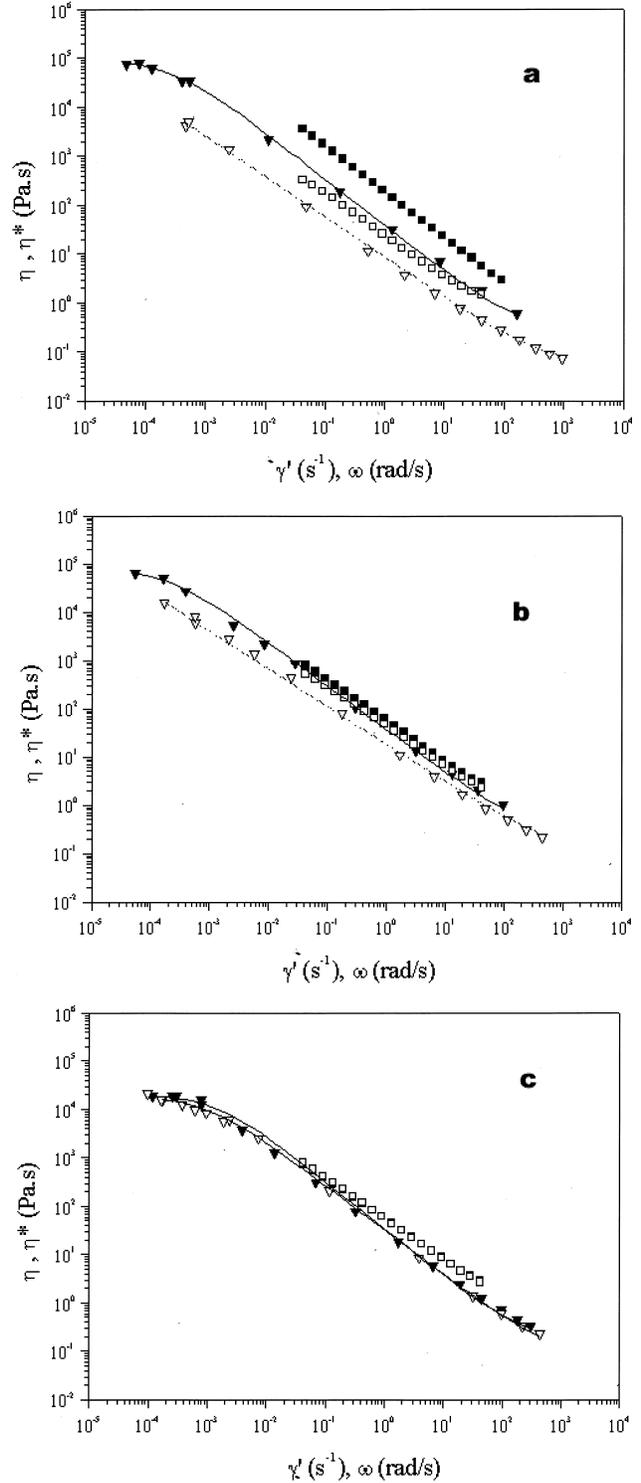


Figure 3. Steady-state and dynamic flow curves for 35% oil-in-water emulsions stabilised with 1% Tween 60. Steady state viscosity, η ($\blacktriangledown, \triangledown$) and dynamic viscosity, η^* (\blacksquare, \square). Solid line corresponds to Cross model, dotted line represents Sisko model. (a) $\blacktriangledown, \blacksquare$ 5% PS ($\eta_0 = 9.3 \times 10^4$ Pa s); \triangledown, \square 5% PS + 0.05 M NaCl; (b) $\blacktriangledown, \blacksquare$ 5% PS + 0.5% XG ($\eta_0 = 8.7 \times 10^4$ Pa s); \triangledown, \square 5% PS + 0.5% XG + 0.05 M NaCl; (c) $\blacktriangledown, \blacksquare$ 1% XG ($\eta_0 = 2 \times 10^4$ Pa s); \triangledown, \square 1% XG + 0.05 M NaCl ($\eta_0 = 2 \times 10^4$ Pa s).

PS + 0.5% XG ($\eta_o = 8.7 \cdot 10^4$ Pa s) were higher than those containing XG. For emulsions with 1% XG or 1% XG with NaCl η_o was 2.0×10^4 Pa s, thus the presence of salt did not affect flow curves of the emulsions containing only XG as a thickener.

The rheology of many food colloids is dominated by the behaviour of the hydrocolloid stabiliser. The addition of 0.5% of XG to water increases the viscosity by a factor of 10 at high shear rates and by a factor of 10^5 at low shear rates (Rodd et al., 2000). Under low shear rates, weak non-covalent interactions between aligned xanthan molecules led to a tenuous gel-like network capable of supporting emulsion droplets; the weak network is progressively broken down by increasing shear rates (Rodd et al., 2000) and the rheological behaviour is essentially independent of salt concentration (Pettitt, 1980; Dickinson and Stainsby, 1982). In emulsions containing PS, although NaCl was added after gelatinisation and thus it did not affect the degree of gelatinisation, salt ions competed with the amylose and amylopectin molecules for the existing water affecting the polymer-solvent and polymer-polymer interactions that decreased entanglements and reduced the strength of the system (Mc Clements, 2000).

Dynamic Tests (Linear Viscoelasticity)

A maximum stress amplitude of 2 Pa guaranteed linear viscoelastic behaviours for the samples that contained XG and PS + XG, both with and without salt added, while a maximum stress amplitude of 0.2 Pa was determined for emulsions stabilised with PS. The range of stresses over which emulsions such as mayonnaise and salad creams exhibit linear viscoelastic behaviour may be indicative of the nature of intermolecular forces between lipoprotein molecules which are adsorbed around neighbouring oil droplets (Muñoz and Sherman, 1990). Thus the smaller viscoelastic range found for PS and PS + salt emulsions showed that the intermolecular forces between amylose molecules of PS are more sensitive to shear than hydrocolloid interactions that occurs when XG is present. For high molecular weight polymers rheological behaviour is controlled by the formation of entanglements, which are caused because chains are unable to pass through each other (Kokini et al., 1995).

The results of small amplitude oscillatory shear tests are expressed in terms of the elastic modulus (G') and loss modulus (G''). It is known that if $G' \gg G''$, the material will exhibit a solid behaviour (i.e., deformation in the linear range will be essentially elastic or recoverable) however, if $G'' \gg G'$, the material will behave like a liquid (i.e., the energy used to deform the material will be viscously dissipated). In general, a viscoelastic material behaves in a solid-like manner at low frequencies when the viscoelastic moduli are considered as a function of frequency (Ferry, 1980).

The development of the storage and loss moduli with frequency was always qualitatively similar but there were some fine structural differences in the mechanical spectrum (Figures 4 a-c). According to the

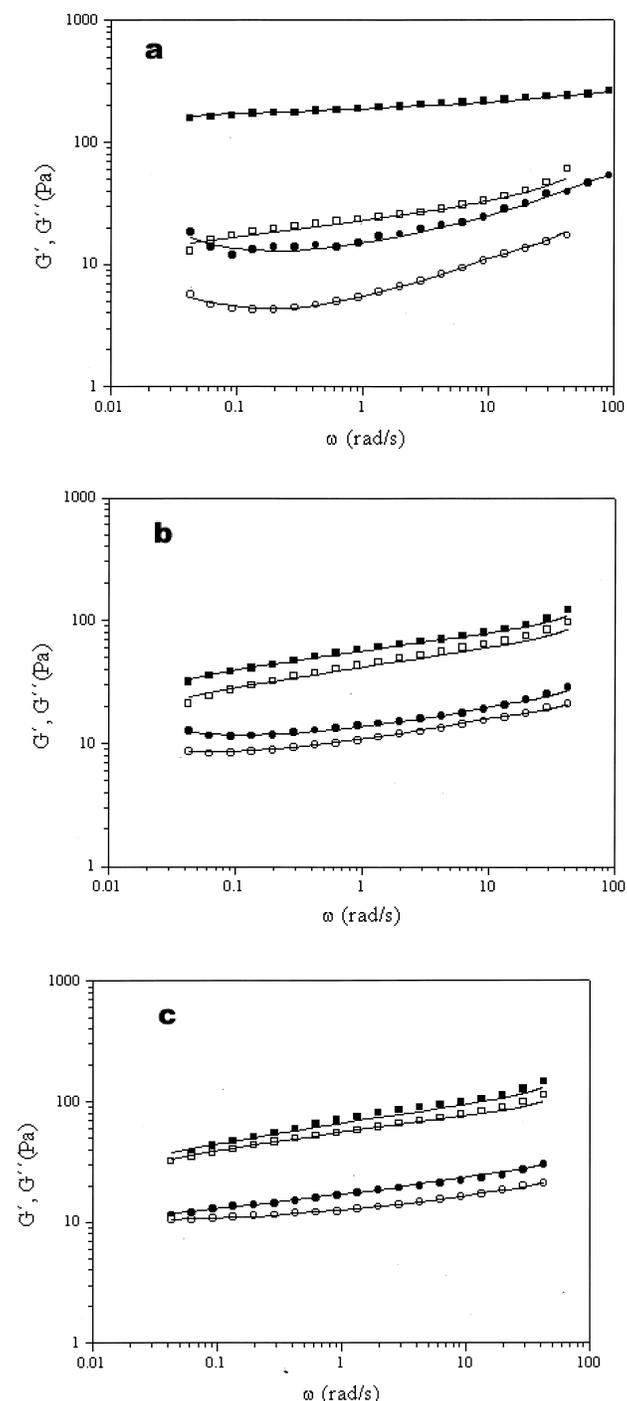


Figure 4. Storage (G' , ■, □) and loss (G'' , ●, ○) moduli as a function of frequency (ω) for 35% w/w oil-in-water emulsions stabilised with 1% Tween 60, with thickeners added. Solid line corresponds to Maxwell model. (a) ■, ● 5% PS; □, ○ 5% PS + 0.05 M NaCl; (b) ■, ● 5% PS + 0.5% XG; □, ○ 5% PS + 0.5% XG + 0.05 M NaCl; (c) ■, ● 1% XG; □, ○ 1% XG + 0.05 M NaCl.

phenomenological definition of gel by Almdal et al. (1993): "... solid-like gels are characterised by a storage modulus, $G'(\omega)$, which exhibits a pronounced plateau extending to time at least of the order of seconds, and by a loss modulus, $G''(\omega)$, which is considerably smaller than the storage modulus in the plateau region". Frequency sweeps showed that in all cases the G' (storage modulus) and G'' (loss modulus) corresponded to a weak gel structural network, where G' was always greater than G'' in the range of frequencies studied. Emulsions with 5% PS presented the highest values of elastic modulus, exhibiting a well-pronounced plateau in G' with $G' \gg G''$ for over three sequence decades and a minimum in G'' at low frequencies (Figure 4 a). A similar behaviour has been previously reported for salad-dressing type of emulsions stabilised with ionic and non-ionic surfactants (Muñoz and Sherman, 1990; Ma and Barbosa-Canovas, 1995; Franco et al., 1995b; Guerrero et al., 1998; Partal et al., 1999; Quintana et al., 2001b). The appearance of a minimum, or a plateau region in the frequency dependence of G'' has been previously related to the formation of physical entanglements among polymeric molecules (Ferry, 1980). In the emulsions studied, there existed a three-dimensional network of interacting or entangled carbohydrate molecules that traps the droplets and the structure of the systems is further enhanced by the reversible depletion attraction between adjacent emulsion droplets arising from the exclusion of polymer molecules from the narrow gap between the surfaces (Dickinson, 1997). The addition of salt decreased the values of both moduli, although the storage modulus was much more affected, the plateau region became narrower, a pseudo-terminal region at low frequencies that showed a tendency to a crossover of both viscoelastic functions appeared, and the beginning of the transition region at high frequencies became noticeable (Figure 4 a).

Frequency sweeps of emulsions containing PS + XG (Figure 4 b) or XG (Figure 4 c) presented similar characteristics. Conde-Petit et al. (1997) reported that the gels formed by starch complexation with a non-ionic emulsifier were softer when xanthan was added, suggesting that xanthan interferes with the formation of an intergranular amylose-emulsifier network. The systems including XG were only slightly affected by NaCl.

Loss tangent, $\tan(\delta) = G''/G'$, is a dimensionless value that compares the amount of energy lost during a test cycle to the amount of energy stored during this time (Ferry, 1980). The loss tangent indicates whether viscous or elastic properties predominate in a sample. There was little change of the loss tangent within the applied frequency for XG and PS + XG emulsions; these systems were not affected when salt was incorporated (Figure 5). However, PS systems showed a marked increase in their viscous properties when NaCl was added.

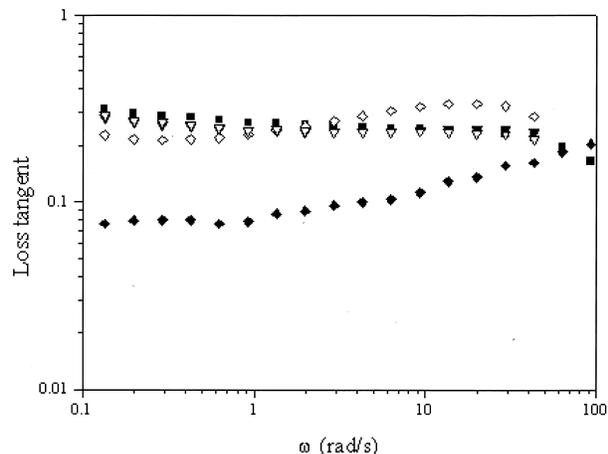


Figure 5. Effect of hydrocolloids and salt on the loss factor. ▼ 5% PS + 0.5% XG, ▽ 5% PS + 0.5% XG + 0.05 M NaCl (coincident); ■ 1% XG, □ 1% XG + 0.05 M NaCl (coincident); ◆ 5% PS, ◇ 5% PS + 0.05 M NaCl.

Loss tangent ranged between 0.08 and 0.3 (which corresponds to phase angles, δ , between 4.6° and 16.7°) for most of the experimental frequency range. This phase shift indicated a structure with a considerable 'sol-fraction', in contrast to biopolymer gels where the high elastic component drove at least a tenfold reduction in values (Paraskevopoulou et al., 1997). Similar values of phase angle have been reported for the linear viscoelastic region of commercial mayonnaises and salad creams (Muñoz and Sherman, 1990), for low-cholesterol salad dressings (Paraskevopoulou et al., 1997), and for mayonnaise prepared with different oil and XG concentrations (Ma and Barbosa-Cánovas, 1994).

Dynamic viscosities (Figure 3) were always higher than the corresponding steady shear viscosities (η) when PS was added to the system; PS and PS + salt emulsions did not obey Cox-Merz rule (Figure 3 a). The decrease in steady-state viscosity of flocculated emulsions when shear rate increases is frequently attributed to the structural damage caused by stationary shear. On the other hand, dynamic viscosity is measured within the linear viscoelastic range where no structural disruption is produced, thus achieving higher values. A similar behaviour was observed for weak gels (Clegg, 1995), for oil-in-water emulsions stabilised with egg yolk and sucrose stearate (Franco et al., 1995a), and for emulsions stabilised by a sucrose palmitate of high HLB (Partal et al., 1994). For XG and XG + salt emulsions the difference between dynamic and steady shear viscosities was minimal, and dynamic viscosities measured with or without NaCl coincided (Figure 3 c). The behaviour of the dynamic viscosity of PS + XG emulsions again resembled that of the XG emulsions, although salt addition did produce a slight decrease in the observed values (Figure 3 b).

The viscoelastic linear behaviour was described according to Maxwell generalised model (Ferry, 1980). The following equations were obtained for the storage and loss modulus when the generalised Maxwell model is used to represent the relaxation modulus:

$$G' = \sum_{i=1}^N G_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \quad (4)$$

$$G'' = \sum_{i=1}^N G_i \frac{\omega\lambda_i}{1 + (\omega\lambda_i)^2} \quad (5)$$

where G_i is the i th contribution to the modulus and λ_i are the relaxation times of the i -Maxwell element. G_i and λ_i of the emulsions studied were estimated from the experimental values of $G'(\omega)$ and $G''(\omega)$ by an iterative process using simultaneously Equations (4) and (5) and minimising the sum of the square differences (Figure 6). The computed G_i and λ_i values were used to predict the storage and loss moduli (Figures 4 a–c). As can be observed in Figure 4, there was an excellent agreement between both sets of values, confirming the accuracy of the calculations.

An empirical model (BSW-CW) for polymer melts, given by De Rosa and Winter (1994) has been successfully used (Franco et al., 1995b; Franco et al., 1997) to describe the experimental regions that appear in the linear relaxation spectra, $H(\lambda)$, of oil-in-water emulsions. This model was derived from BSW-spectrum (Baumgaertel et al., 1990) and CW-spectrum (Chambon and Winter, 1985):

$$H(\lambda) = A \left[\left(\frac{\lambda}{\lambda_c} \right)^m + \left(\frac{\lambda}{\lambda_p} \right)^n \right] \quad \text{for } \lambda_{\min} < \lambda < \lambda_p \quad (6)$$

$$H(\lambda) = A \left[\left(\frac{\lambda}{\lambda_p} \right)^c \right] \quad \text{for } \lambda_p < \lambda < \lambda_{\max} \quad (7)$$

where λ_c and λ_p are the characteristic relaxation times for the onset of the plateau and pseudo-terminal regions, respectively; λ_{\max} and λ_{\min} are the reciprocal of the minimum and maximum experimental frequencies attained; m , n , and c are the power law exponents for the three different regions, and A is an empirical constant. Equations (6) and (7) can also be used to fit the discrete relaxation spectra of the emulsions studied by replacing $H(\lambda)$ for G_i , and λ for the corresponding λ_i (Figures 6 a–c). The parameters of the BSW-CW could be used to explain structural characteristics of the systems. The slope of the plateau region was higher for emulsions prepared with PS (Table 1). The high value of the slope (n) in the plateau region may be related to the development of an entanglement network (Franco

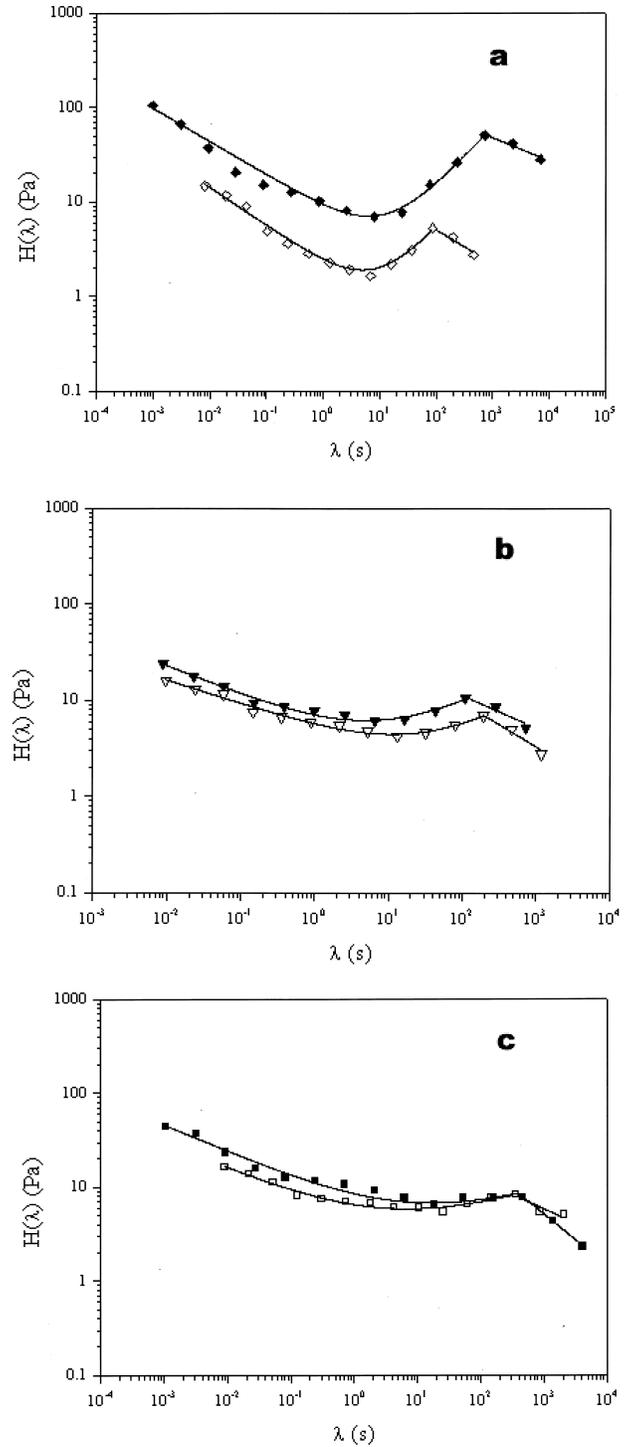


Figure 6. Relaxation spectra corresponding to 35% w/w oil-in-water emulsions stabilised with 1% Tween 60. Solid line corresponds to BSW-CW model. (a) \blacklozenge 5% PS, \diamond 5% PS + 0.05 M NaCl; (b) \blacktriangledown 5% PS + 0.5% XG, \triangledown 5% PS + 0.5% XG + 0.05 M NaCl; (c) \blacksquare 1% XG, \square 1% XG + 0.05 M NaCl.

et al., 1997). Emulsions prepared with 5% PS showed the highest n values (Figure 6 a) and also the highest η_o and elastic modulus (G') due to the formation of a gel upon cooling (Zobel, 1984). When PS was gelatinised in

Table 1. Influence of hydrocolloids and starch on the slope of the plateau region (n) for 35% oil-in-water emulsions.

Composition of the Aqueous Phase	Slope of the Plateau Region* n
5% potato starch	0.63 ^c
5% potato starch + 0.5 M NaCl	0.65 ^c
0.5% xanthan gum + 5% potato starch	0.38 ^b
0.5% xanthan gum + 5% potato starch + 0.5 M NaCl	0.44 ^b
1% xanthan gum	0.2 ^a
1% xanthan gum + 0.5 M NaCl	0.2 ^a

*Values followed by different superscripts differ significantly ($P < 0.05$).

the presence of xanthan gum (PS+XG; Figure 6 b) the slope of the plateau region n decreased, as well as the storage modulus (G') of the emulsion (Figures 4 a and b, Table 1) with respect to the system containing only PS. Thus the presence of XG interfered with the formation of junction zones between starch chains. The lowest n value was obtained for emulsions prepared with XG alone. The presence of 0.5 M NaCl in emulsions prepared with XG or PS+XG did not modify significantly ($P < 0.05$) the slope of the plateau region and thus the degree of entanglements was not affected, showing the stabilising properties of XG. The structural rigidity and extended nature of XG molecules, resulted from its linear cellulosic backbone, which is stiffened and shielded by the anionic trisaccharide side chains, could explain the small effect of NaCl on the rheological properties of the systems stabilised with XG (BeMiller and Whistler, 1996).

In conclusion, emulsions including XG were only slightly affected by NaCl. The presence of 0.5 M NaCl in emulsions prepared with XG or PS+XG did not modify the degree of entanglements which confirmed the stabilizing properties of XG.

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