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Modeling rheological properties of low-in-fat o/w emulsions stabilized with xanthan/guar mixtures

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ABSTRACT

The incorporation of hydrocolloids is a suitable alternative to stabilize low-in-fat o/w emulsions against creaming. The effect of composition on rheological properties and stability of low-in-fat o/w emulsions formulated using xanthan/guar gum mixtures in an acidic aqueous solution containing 2% NaCl was studied. A central composite design involving oil fraction and gum content was used. Frequency sweeps showed that both G' and G'' increased with oil content. However, the viscoelastic behavior was mainly governed by the hydrocolloid content. The shear-thinning behavior of both aqueous dispersions (continuous phases) and emulsions was successfully modeled with Ellis equation. Mooney equation was used to obtain the shape factor and maximum packaging volume fraction. Zero shear viscosity was also predicted based on emulsion composition by response surface methodology. Droplet size distribution was measured by light scattering; microscopic observations revealed a flocculated system. Visual inspections of the formulated emulsions showed that they remained stable after eight months.

1. Introduction

Oil-in-water emulsions have attracted considerable attention in the food industry due to their physicochemical properties and physical attributes. These systems have a significant potential for the solubilization of active water-insoluble materials (food additives such as nutraceuticals and antioxidants) at concentrations much above the solubility power of the oil or the oil/surfactant mixtures (De Campo et al., 2004). However, they are thermodynamically unstable systems, especially those with reduced oil content, usually splitting into two distinct phases. The presence of salts and an acidic medium, usually found in food emulsions used as salad dressing, enhances the instability of these systems (Kokini & Fischbach, 1988; Quintana, Califano, Zaritzky, & Partal, 2002a).

Several kinds of physicochemical mechanisms contribute to the instability of an emulsion, such as creaming (or sedimentation), flocculation, coalescence, Ostwald ripening or phase inversion (McClements, 1999; Robins & Hibberd, 1998; Walstra, 1996). The addition of salt to an emulsion alters the colloidal interactions in a number of ways: (i) it reduces the electrostatic repulsion (which promotes flocculation), (ii) it reduces van der Waals attraction (which opposes flocculation), and (iii) it reduces depletion attraction, which opposes flocculation (Demetriades & McClements, 1998).

Polysaccharides are usually added to the aqueous phase of low-in-fat o/w food emulsions to improve their creaming stability (Quintana, Califano, Zaritzky, Partal, & Franco, 2002b; Tabilo-Munizaga & Barbosa-Cánovas, 2005). Their efficiency depends on polymer concentration in the aqueous phase as well as on the structural features of the aqueous polymer system. Indeed, the formation of a weak-gel-like polymer network in the continuous phase leads to very high viscosities in the low stress range and imparts additional elastic properties to the whole system so that emulsion creaming is strongly inhibited (McClements, 1999). The effectiveness of polysaccharides for enhancing the viscosity of aqueous solutions depends on the size and shape of its molecules, as well as the conformation they adopt in the solvent (BeMiller & Whistler 1996).

The flow properties of an emulsion are among the most important features. These properties need to be understood to meet technical requests (mixing efficiency, power consumption, etc.) encountered during emulsions manufacturing process, such as mixing, pumping, filling, etc. The consumer-perceived attributes, such as pouring or extrusion of emulsions from packs, are also related to their flow properties and must be also explained (Barnes, 1994). Depending on the field of application of these emulsions, their stability and rheology vary widely. The most significant factors which influence the emulsions characteristics are the rheological behavior of the continuous phase, the nature of the particles, their concentration, their size distribution and the particle-particle

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interactions (Masmoudi, Piccerelle, Le Dréau, & Kister, 2006; McClements, 2000; Tadros, 1996).

The objectives of the present work are:

(a) To study the effect of oil and hydrocolloid concentrations on the droplet size distribution, stability and rheological properties of low-in-fat o/w emulsions containing sodium chloride and acetic acid.
(b) To analyze the steady-state flow curves and comment on the viscoelastic behavior of both, the continuous phase (mixture of xanthan and guar gums) and the emulsions, and model the obtained results.
(c) To determine the relationship among rheological characteristics of either gum suspensions (continuous phases) or food emulsions and microstructural parameters such as shape of the particles and interactions between them.
(d) To apply response surface methodology to predict the necessary hydrocolloid concentration for developing an emulsion with predetermined oil concentration and rheological properties.

2. Materials and methods

2.1. Materials

Commercial 100% sunflower oil (Molinos Río de La Plata SACIFI, Buenos Aires) was purchased from a local supermarket and used without any further treatment. Polyoxyethylene sorbitan monooleate (Tween® 80) emulsifier, xanthan and guar gums used were of food-grade commercial type purchased from Sigma Chemical Co. (St. Louis, MO). Analytical grade NaCl and acetic acid were added to emulsions (Anedra, Argentina). Distilled and deionized water was used in all solutions and emulsions.

2.2. Emulsion preparation

Oil-in-water emulsions were prepared using commercial sunflower oil (10–30 wt.%) and stabilized with Tween® 80 (1 wt.%). Continuous phases were prepared with xanthan gum and guar gum in a synergistic ratio, 7:3 (BeMiller & Daniels, 2002; Dea et al., 1977). Hydrocolloids were added to an aqueous solution containing NaCl (2 wt.%) and acetic acid (2 wt.%). The solution was gently stirred for 3 h at 60 °C. This temperature, above the order-disorder temperature of xanthan (51 °C) in water, ensured a strong synergistic interaction between both hydrocolloids (Khouryieh, Herald, Aramouni, & Alavi, 2006). Solutions were weighed and aqueous solution (2 wt.% acetic acid + 2 wt.% NaCl) was added to make up any weight lost in evaporation. All emulsions prepared also contained sodium azide (0.01 wt.%) as an antimicrobial agent.

Lab-scale manufacture of emulsions (300 g) was carried out using an Ultra Turrax T-25 homogenizer (Ika, Steufen, Germany). Sunflower oil was added slowly to the aqueous phase containing the remaining ingredients at room temperature. Emulsions were homogenized at 11,500 rpm for 4 min without thermal control during homogenization; they were stored at room temperature for 24 h before testing.

A central composite design (Box & Draper, 1987) involving oil fraction (10–30 wt.%) and gum content (0.5–2 wt.%) was used. Thus, nine formulations were tested replicating the central point three times (Table 1).

Table 1
Emulsion formulations and their respective coded variables

Formulation	O	G	Oil (wt%)	Gum (wt%)
1	−1.41	0	10.00	1.25
2	−1	−1	12.91	0.72
3	−1	1	12.91	1.78
4	0	−1.41	20.00	0.50
5	0	0	20.00	1.25
6	0	1.41	20.00	2.00
7	1	−1	27.09	0.72
8	1	1	27.09	1.78
9	1.41	0	30.00	1.25

O = oil; G = gums.

2.3. Droplet size distribution (DSD)

Mean droplet size and droplet size distribution of emulsions were determined by static light scattering using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcester, UK). The fundamental size distribution derived by this technique is volume based, which uses the Mie theory. The refractive index was 1.449 for emulsion particle and 1.33 for dispersant medium. The absorbance value of emulsion particle was 0.001.

Sauter average diameter ($D[3,2]$) was calculated for each sample as follows:

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

where d_i is the droplet diameter, N is the total number of droplets and n_i is the number of droplets having a diameter d_i.

Microscopic observations of all the emulsions were carried out after a 1:20 dilution with distilled water on a microscope coupled to a DC 100 camera (Leica Microscopy Systems Ltd., Heerbrugg, Switzerland).

2.4. Visual assessment of 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 determined the stability period.

2.5. Density measurements

The densities of the continuous phases were determined with a standardized 25-ml pycnometer. The mass of the solution was calculated from the weight difference between the empty and the filled pycnometer. The pycnometer filled with each gum solution was incubated at 20 °C for 1 h in order to equilibrate the sample before density determinations. These measurements were used to calculate volumetric fractions from weight percentages.

2.6. Rheological tests

All rheological measurements were performed on the continuous phases and on the emulsions using a Controlled Stress Rheometer Haake RS 600 (Thermoelectron, Karlsruhe, Germany). After positioning the sample on the sensor system, it was allowed to rest for 10 min before starting the corresponding measurement. In all cases samples were covered with a thin film of silicone oil to avoid evaporation during the measurements and temperature was maintained at 25 °C throughout the experiment. Three replicates of each test were performed.

2.6.1. Oscillatory shear tests

Dynamic rheological measurements (storage modulus (G'), loss modulus (G'') vs. frequency (ω)) were done using a smooth plate-and-plate geometry (60 mm diameter, 1 mm gap). Frequency ranged from 0.0428 to 92.32 rad/s. Linear viscoelasticity region was determined through stress sweep tests at a fixed frequency (6.28 rad/s – 1 Hz).

2.6.2. Steady-state flow measurements

The steady flow behavior (viscosity (η) vs. shear stress (σ)) was studied using a serrated plate-and-plate geometry (35 mm diameter, 1 mm gap), in order to avoid wall slip phenomena (Sanchez, Valencia, Franco, & Gallegos, 2001). The flow measurements were obtained by imposing a ramp of shear stresses in a range between 0.1 and 70 Pa and waiting until the slope of the resulting shear rate versus time was less than 0.001% at each point, so that it could be assumed that steady-state was almost attained. The maximum measuring time per point was set at 300 s, but all the measurements were obtained before the cut off time.

2.7. Statistical analysis

Nonlinear regression analyses were carried out using the SYSTAT software (SYSTAT Inc., Evenston, IL, USA). The following second order polynomial model was fitted to the data:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \qquad (2)$$

where Y is the response variable, X_i are the coded process variables and β_{ij} are the regression coefficients. A stepwise methodology was followed to determine the significant terms in Eq. (2). Differences in the computed parameters were considered significant when the computed probabilities were less than 0.05 ($P < 0.05$). After model fitting was performed, residual analysis was conducted to validate the assumptions used in the ANOVA (results are not shown). This analysis included calculating case statistics to identify outliers and examining diagnostic plots such as normal and residual plots (Eren & Kaymak-Ertekin, 2007).

3. Results and discussion

3.1. Droplet size distribution and visual stability of emulsions

Droplet size distribution was not modified by hydrocolloid content. A bimodal distribution was observed on a Malvern MasterSizer 2000 equipment for all emulsions analyzed (Fig. 1). Average Sauter diameters ($D[3,2]$) are given in Table 2; they were not significantly modified by gum content. In all cases $D[3,2]$ values between 1.7 and 1.8 μm were obtained.

Microscopic observations showed that all emulsions studied could be considered as highly flocculated systems. Fig. 2 shows two different emulsions where the presence of cluster of droplets is noticeable. These aggregations could be explained in terms of depletion flocculation caused by the presence of individual non-adsorbing molecules. As the droplets come closer together due to Brownian motion, the region between emulsion droplets is depleted of polysaccharides leaving only the solvent. This induces a hydrocolloid concentration gradient between the inner-particle region and the bulk solution and hence an osmotic pressure exists. The solvent between the droplets tends to diffuse out to reduce the concentration gradient, causing the droplets to aggregate (McClements, 2000; Radford & Dickinson, 2004; Sun, Gunasekaran, & Richards, 2007).

Visual assessment showed that all emulsions studied remained stable for over eight months, even those with lowest thickening agent content. Thus, the addition of xanthan and guar mixture stabilizes the emulsion against creaming either by increasing the viscosity of the continuous phase as a consequence of the formation of a gel network (Dickinson, Ma, & Povey, 1994; McClements, 2000; Quintana et al., 2002a, 2002b) or by promoting the formation of a three-dimensional network of aggregated droplets (Dickinson, 2003; Dickinson et al., 1994; Parker, Gunning, Ng, & Robins, 1995).

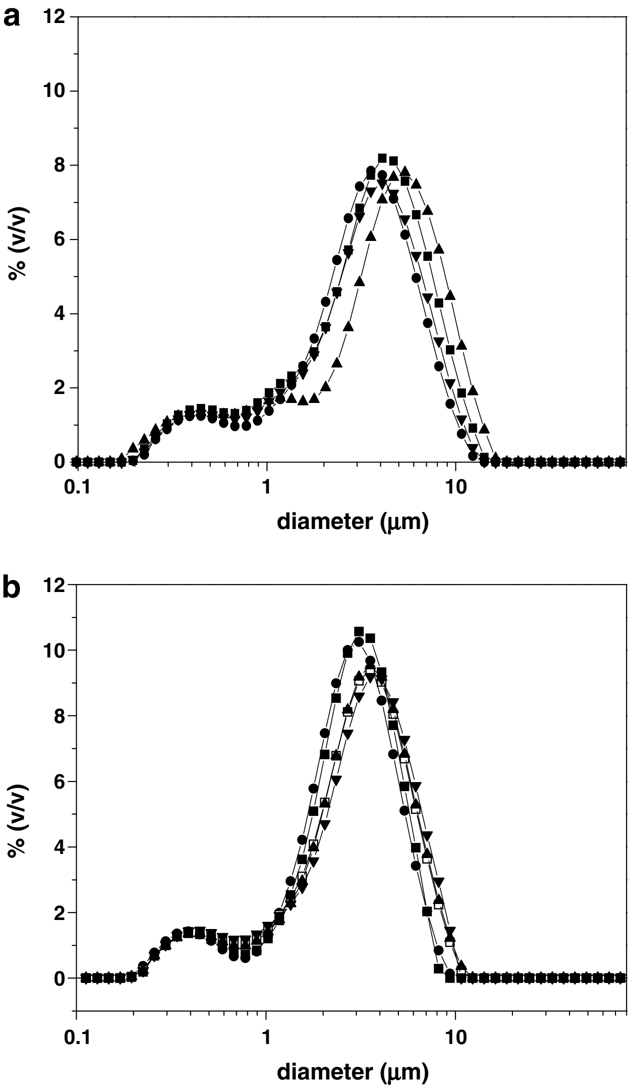

Fig. 1. Droplet size distribution of the studied emulsions. (a) Formulations 1 (▼), 2 (▲), 3 (●), 4 (■), (b) formulations 5 (□), 6 (▲), 7 (▼), 8 (●), 9 (■). Keys for the formulations are in Table 1.

Table 2
Sauter diameter, $D[3,2]$, and corresponding variance (Var $D[3,2]$) for all the modeled emulsions

Formulation	$D[3,2]$ (μm)	Var ($D[3,2]$) (μm)
1	1.74	0.020
2	1.75	0.015
3	1.78	0.020
4	1.78	0.026
5	1.74	0.014
6	1.79	0.016
7	1.77	0.016
8	1.68	0.007
9	1.76	0.009

3.2. Frequency sweep tests of continuous phases and emulsions

Aqueous suspensions (continuous phases) showed a rubber-fluid like to weak-gel-like transition as the hydrocolloid concentra-

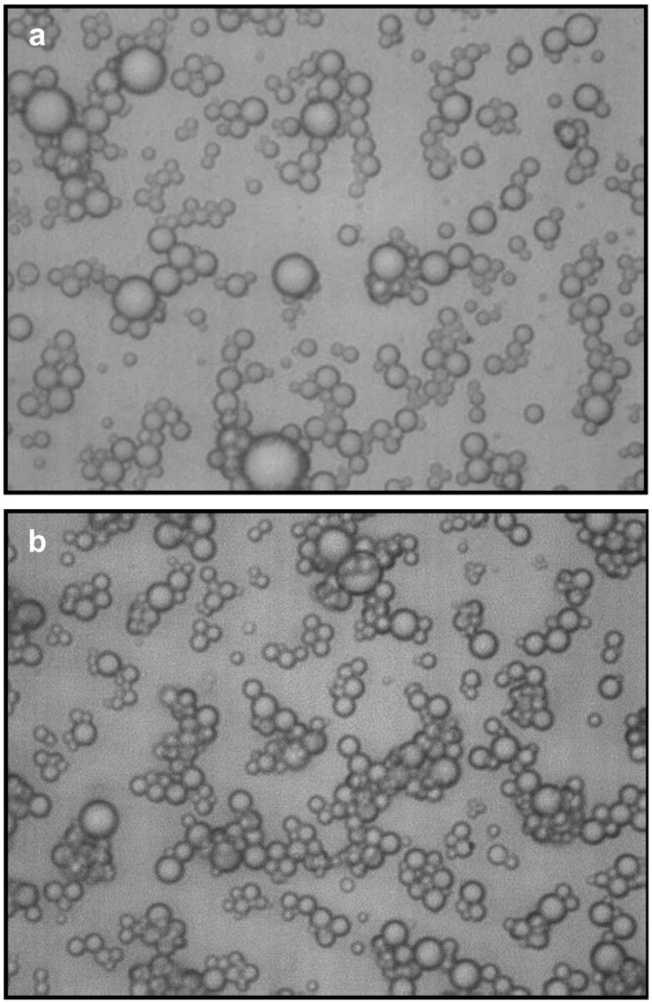

Fig. 2. Photomicrographs of o/w emulsions with: (a) 20 wt.% oil content and a continuous phase containing 0.5 wt.% of xanthan–guar mixture and (b) 30 wt.% oil content and a continuous phase containing 1.25 wt.% of xanthan–guar mixture.

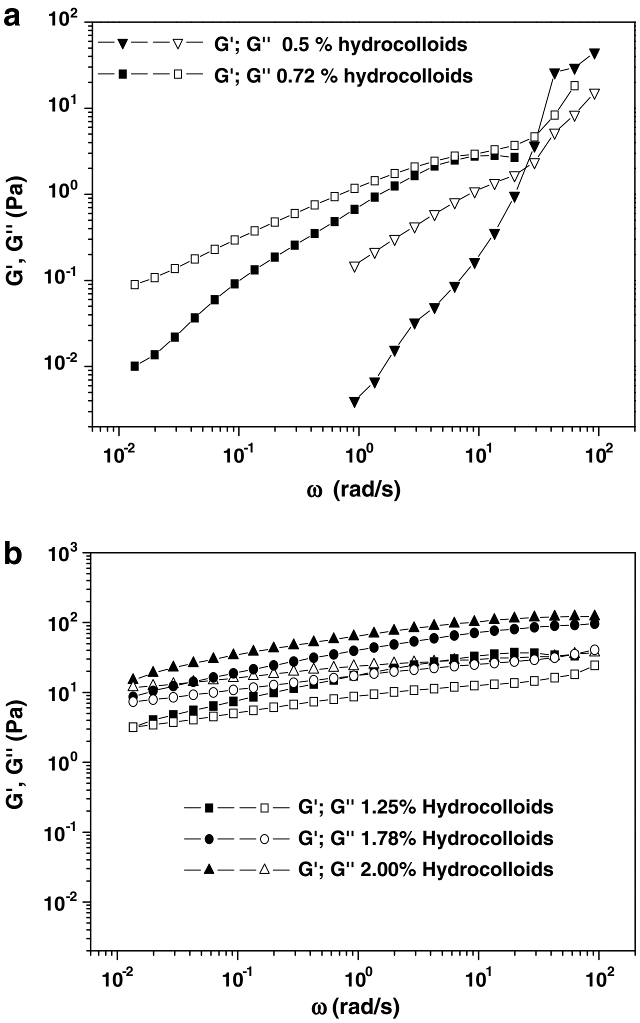

Fig. 3. Oscillatory sweep (storage (G') and loss (G'') moduli vs. frequency (ω)) for the aqueous continuous phases containing different concentrations (wt.%) of xanthan–guar mixture (a) 0.50%, 072% (b) 1.25%, 1.78%, 2.00%.

tion increases. A markedly viscous behavior was observed in continuous phases with 0.5% and 0.72% gum content, exhibiting very low values of storage and loss moduli and a pronounced frequency dependence in the whole studied range. The first points of the spectrum obtained for 0.5% hydrocolloids were omitted because it was considered that those extremely low values presented high relative errors related to sensitivity of the sensor used. G'' was higher than G' until a certain characteristic frequency ω_c where a crossover of the G' and G'' vs. frequency curves occurred ($G'(\omega_c) = G''(\omega_c)$) (Ferry, 1980; Steffe, 1996). This is a useful parameter to make a rough estimation of the relaxation time ($\tau = 1/\omega_c$), which is employed to describe the tendency of the flow properties of the material (Tadros, 1996). Fig. 3a showed that ω_c decreased from 20 rad/s to 10 rad/s when gum content increased from 0.5% to 0.72%. In both cases, τ was not higher than 0.1 s which was an indication of low elasticity. A major increase in relaxation time was observed when gum concentration reached 1.25% ($\tau \sim 100$ s), which is related with a marked increment in the elastic behavior and the strength of the structure (Fig. 3b). Particularly, aqueous solutions with 2% of hydrocolloids showed a gel-like behavior, with a slightly dependence of G' and G'' on frequency. In polymeric systems, a plateau region for G' or a minimum in the loss modulus (G'' curves) was attributed to a tridimensional gel structure caused by physical entanglements among polymeric chains. Synergistic interaction between both hydrocolloids favored the development of the crosslinked network (BeMiller & Whistler, 1996; Casas, Mohedano, & García-Ochoa, 2000). The nature of the intermolecular binding between xanthan and guar gums is still undetermined. Dea et al. (1977) and Morris, Rees, Young, Walkinshaw, and Darke (1977) suggested that intermolecular binding occurs between the ordered (helix) xanthan chains and unsubstituted or poorly substituted regions of the galactomannan backbone. An alternative model for gelation was proposed by Cairns, Miles, Morris, and Brownsey (1987) where the xanthan helical structure needs to be disrupted in order to allow intermolecular binding with galactomannans. They proposed that xanthan has a disordered, extended, twofold, cellulose-like conformation, rather than a fivefold helix, when interacting with galactomannan (Khouryieh et al., 2006).

In the case of the tested emulsions, mechanical spectra obtained from small-amplitude oscillatory shear tests, reveal a characteristic dependence on the oil concentration and continuous phase composition. However, the percentage of hydrocolloids influenced mostly the rheological behavior of the emulsions (Fig. 4a–c). When gum concentration was 1.25% or higher, emulsions showed a weak-gel-like behavior with G' higher than G'' in the frequency range analyzed. In particular, formulation 9 (i.e. 30% oil content) exhibited an ordered structure, with elastic modulus nearly flat, independent of the frequency while the viscous modulus falls below G' with a similar trend (Fig. 4a). This behavior corresponds to a

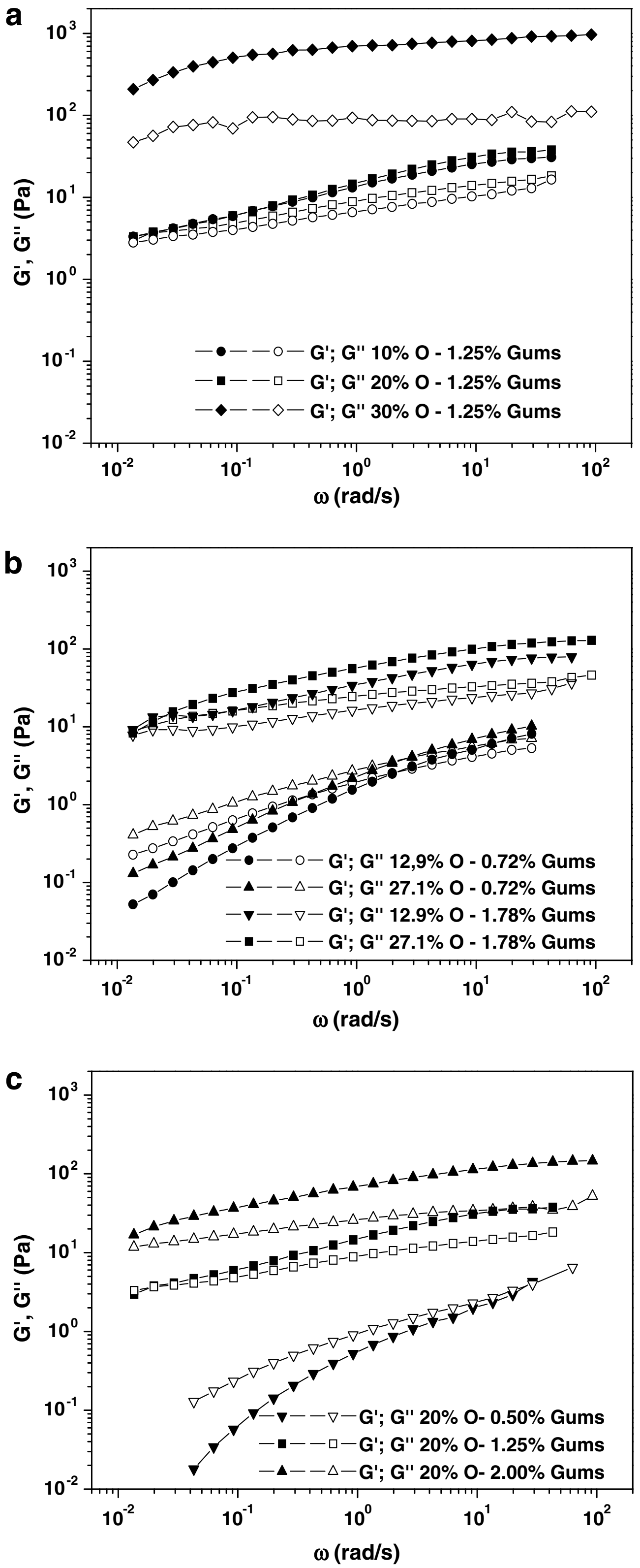

Fig. 4. Frequency sweep tests (G', G'' vs. frequency) for all the studied emulsions. (a) Formulations 1, 5 & 9, (b) formulations 2, 3, 7 & 8 and (c) formulations 4, 5 & 6. Keys for the formulations are in Table 1.

Viscoelastic behavior of the emulsions with 0.72% and 0.5% hydrocolloids corresponds to polymeric solutions where G' and G'' curves intersected within the range of tested frequencies ($\tau \sim 0.1$ s), showing a clear fluid like behavior (Fig. 4b and c).

3.3. Steady-state flow curves of continuous phases and emulsions

Flow curves have been plotted as a function of shear stress instead of the traditionally one versus shear rate because it was previously found that such curves are more discriminating and with a better quality of the results (Roberts, Barnes, & Carew, 2001). Aqueous gum dispersions (continuous phase) showed high viscosity at low shear stresses and a notorious shear-thinning behavior in a wide range of shear stresses (Fig. 5a). Additionally, it was observed that not only the viscosity increased with hydrocolloids content but that the aqueous dispersions were less susceptible to break down by shear since more crosslinked sites were formed.

Emulsions also presented a shear-thinning behavior which is shown in Fig. 5b for formulations at +1 and −1 levels of both factors. Flow curves correspond to a structured fluid, with three well defined regions (Fig. 5b); at low shear stresses (σ), viscosity reaches a limiting value namely zero shear viscosity (η_0); as the shear stress increases an abrupt decay in the viscosity was observed until a new flocculated system where droplets form a structural network (Guerrero, Partal, & Gallegos, 1998; Partal, Guerrero, Berjano, & Gallegos, 1999; Quintana et al., 2002a; Quintana et al., 2002b).

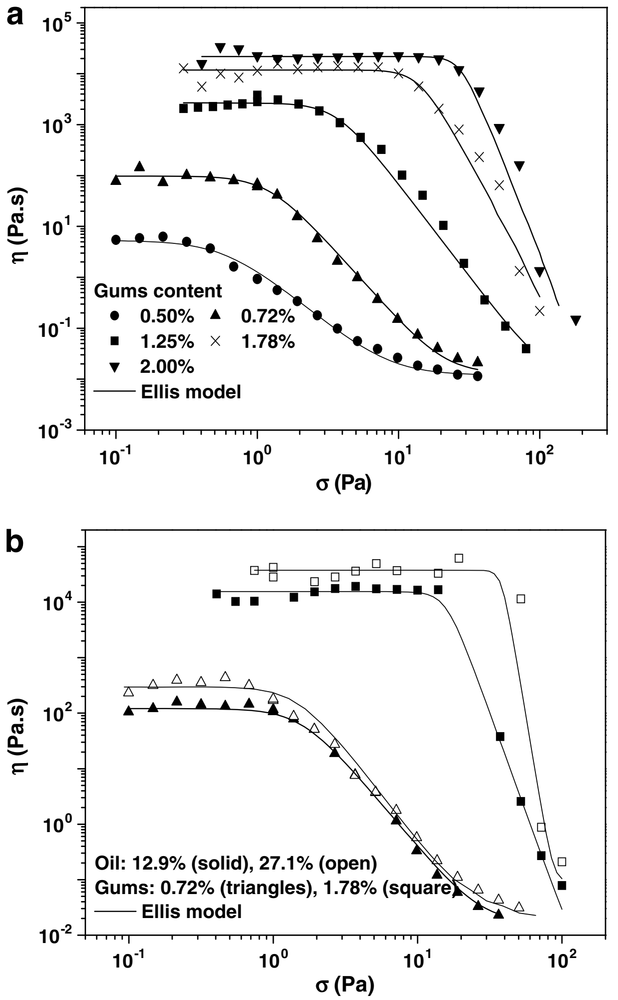

Fig. 5. Steady-state flow curves: variation of viscosity (η) with shear stress (σ). (a) Continuous aqueous systems formulated with different gum mixture concentrations: ● 0.50%; ▲ 0.72%; ■ 1.25%; × 1.78%; ▼ 2.00% and (b) emulsions formulated with: □ 27.1% oil, 1.78% gums; ■ 12.9% oil, 1.78% gums; △ 27.1% oil, 0.72% gums; ▲ 12.9% oil, 0.72% gums. Lines correspond to Ellis equation.

plateau region (η_∞), which is the high shear limiting viscosity (Tadros, 2004). Shear-thinning behavior of emulsions was related not only to droplet deflocculation on the disperse phase, but also to the non-Newtonian behavior of the continuous phase. This pronounced transition between second and third region may be attributed to two different processes: one reversible and the other one irreversible. In the first one, high shear stresses disrupt the flocs decreasing their effective volume fraction and therefore lowering the viscosity. Besides, high shear stresses also induce coalescence (Franco, Berjano, Guerrero, Muñoz, & Gallegos, 1995). Increasing droplet size produces weaker interparticle interactions, thus lowering the emulsion viscosity (Rao & Steffe, 1992).

Flow curves were modeled by Ellis equation (Ellis, 1927), which correlates fluid viscosity with applied shear stress (σ):

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\sigma/\sigma_c)^n} \tag{3}$$

where η_0 and η_∞ are first and second Newtonian viscosity, respectively; n is the exponent and σ_c is a critical stress denoted as "true yield stress". σ_c could be defined as the stress above which the structure of the system is broken down (Tadros, 2004). Parameters like zero shear viscosity (η_0) were obtained with this model for both, food emulsions and continuous aqueous phases. Tables 3 and 4 show the parameters obtained with Ellis model for the continuous phases and the emulsions, respectively. Fig. 5b and Table 4 also show that gums content dominates the viscosity of the assayed emulsions. Changing gums concentration in the aqueous phase from 0.72% (−1) to 1.78% (+1) raised significantly the first Newtonian viscosity (η_0) in about two orders of magnitude. Higher hydrocolloids concentration increased the junction zones between polymer chains, which was reflected in the higher true yield stresses and the sharp decay observed (Launay, Doublier, & Cuvelier, 1986). On the other hand when the oil content was raised from 12.9% (−1) to 27.1% (+1) produced a threefold increase on η_0 (Fig. 5b). There were no marked changes in the shape of the flow curves even when oil concentration was doubled; this confirms that the oil effect was not as pronounced as the effect of gum content in the range of studied composition.

Besides, Mooney model (Eq. (4)) was used to determine the relationship among rheological characteristics of either food emulsion or gum suspensions (continuous phases) and microstructural parameters such as shape of the particles and interactions between them (Launay et al., 1986; Lee, Kim, & Yang, 1983; Rha & Pradipasena, 1986).

$$\eta_{r0} = \exp\left[\frac{B\phi}{1 - (\phi/\phi_{max})}\right] \tag{4}$$

where

- $\eta_{r0} = (\eta_0/\eta_{s0})$, is the relative zero shear viscosity, referred to the continuous phase viscosity (η_{s0}) at the same conditions.
- B = shape factor, depending on the asymmetry of the molecule expressed as the axial ratio (major axis/minor axis).
- ϕ = volume fraction of the dispersed phase.
- ϕ_{max} = maximum packaging volume fraction.

Table 3
Ellis model parameters of the continuous phases flow curves

Hydrocolloids content (%)	η_0 (Pa s)	η_∞ (Pa s)	n	σ_c (Pa)
0.50	5.30	0.01	2.3	0.61
0.72	47.7	0.02	2.5	0.94
1.25	3.59×10^3	0.02	4.8	5.8
1.78	15.6×10^3	0.04	6.1	17
2.00	21.9×10^3	0.09	7.1	28

Table 4
Ellis model parameters of the emulsion flow curves

Emulsion formulation	η_0 (Pa s)	η_∞ (Pa s)	n	σ_c (Pa)
1	3.70×10^3	2.1×10^{-2}	4.7	5.4
2	1.21×10^2	1.7×10^{-2}	3.1	1.6
3	1.55×10^4	3.0×10^{-3}	7.2	16
4	4.10×10^1	9.7×10^{-3}	2.4	0.5
5	3.66×10^3	1.9×10^{-2}	4.9	4.4
6	1.85×10^4	1.9×10^{-2}	6.2	20
7	2.98×10^2	1.8×10^{-2}	3.4	1.5
8	3.79×10^4	9.2×10^{-2}	15.6	38
9	2.01×10^5	2.1×10^{-2}	25.7	39

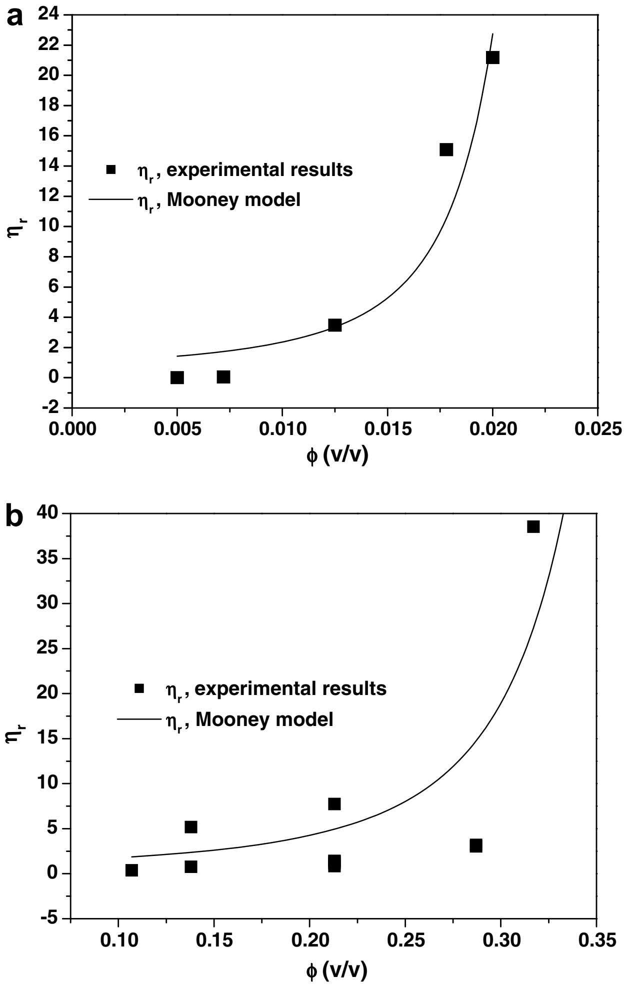

Fig. 6. Relative viscosity at zero shear rate (η_r) as a function of the volume fraction of the dispersed phase (ϕ): (a) results corresponding to the continuous system in which the dispersed phase is constituted by the hydrocolloids mixture and (b) results corresponding to the emulsions where oil is the dispersed phase. Lines represent Mooney model.

Table 5
Parameters of Mooney model for both continuous phases and emulsions

	B	ϕ_{max}
Continuous phases	59 (±2)	0.032 (±0.009)
Emulsions	4.8 (±0.8)	0.58 (±0.06)

B: shape factor; ϕ_{max}: maximum volume fraction. 95% confidence limits are given between parentheses.

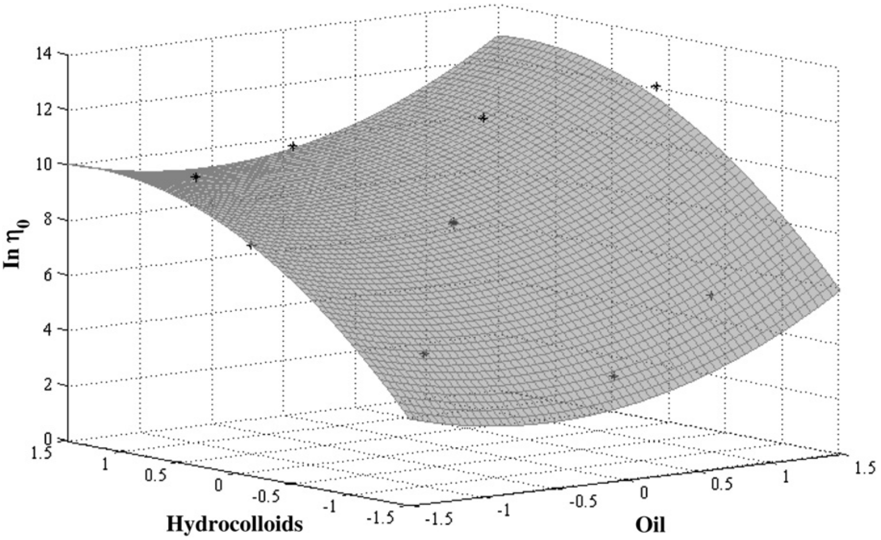

Fig. 7. Response surface plot of zero shear viscosity of the emulsions (η_0) as a function of hydrocolloid and oil levels.

The viscosities of the hydrocolloid dispersions were analyzed considering that η_{s0} was the viscosity of the aqueous solution containing NaCl and acetic acid. Afterwards, in the case of the o/w emulsions (dispersed phase: sunflower oil), η_{s0} was referred to the viscosities of the continuous phases with different gums content.

Experimental results, fitted with Mooney model are presented in Fig. 6a and b for both hydrocolloid dispersions (continuous phases) and food emulsions. Parameters which led to these fittings are listed in Table 5.

The structure of the systems could be predicted from Mooney equation parameters. ϕ_{max} value obtained for gum solutions was extremely low ($\phi_{max} = 0.03$). It is related to rod-like particles of great length in a three-dimensional random packaging (Rha & Pradipasena, 1986). This is in agreement with the weak gel structure expected for xanthan/guar gum mixture dispersions, where physical entanglements occur among xanthan side chains and mannose backbone of galactomannan (Casas et al., 2000). A macromolecule with a non-spherical conformation may be considered as an ellipsoid with axial ratio (major axis/minor axis) or a rod. The high value of the shape factor ($B = 59$) indicates that the axial ratio of the cross-linked macromolecules ranges between 20 and 30 (Scheraga, 1961).

For food emulsions, $\phi_{max} = 0.58$ and shape factor $B = 4.8$ may be associated with rods with a length/diameter ratio of about 5 rather than to a system constituted by spherical particles (Rha & Pradipasena, 1986). This could be explained because the oil droplets form rod-shaped aggregates as it was shown previously in the micrographs (Fig. 2). When flocculation takes place, the effective volume fraction of the disperse phase is larger than the actual volume fraction (ϕ), since it includes not only the volume occupied by the particles, but also the volume of the solvent immobilized hydrodynamically in the flocs. At low ϕ, the clusters move freely through the medium and the suspension remains fluid. As ϕ increases, the clusters overlap and these systems display a solid-like behavior (Berli, 2005).

Zero shear viscosity (η_0) values of the tested emulsions were also analyzed with a stepwise regression model (SYSTAT, USA), to find the response surface that fitted the experimental data (Box & Draper, 1987). The obtained predictive equation correlates the zero shear viscosity (η_0) with concentration of both oil (O) and hydrocolloids (G) according to Eq. (2)

$$\ln(\eta_0) = 8.152 + (0.931)\mathrm{O} + (0.83)\mathrm{O}^2 + (2.296)\mathrm{G} - (0.903)\mathrm{G}^2 \qquad (5)$$

where oil (O) and gum (G) content are coded according to Table 1. Fig. 7 shows experimental η_0 values together with the response surface obtained from Eq. (5) (correlation coefficient $r = 0.974$).

4. Conclusions

Low-in-fat o/w emulsions formulated with NaCl and containing acetic acid were stabilized using xanthan–guar mixtures as thickening agents; the creaming process was avoided and emulsion stability was ensured for over eight months.

Frequency sweeps of the emulsions showed that both G' and G'' increased with oil content. However, the viscoelastic behavior was mainly governed by the hydrocolloid concentration. At 1.25 wt.% gum concentration or over, a weak gel structural network was observed ($G' > G''$) due to droplet flocculation. Below 1.25 wt.%, the viscoelastic behavior corresponded to polymeric dispersion where G' and G'' curves intersected within the range of tested frequencies.

Steady-state flow curves of both, aqueous dispersions (continuous phases) and emulsions showed a shear-thinning behavior, and were successfully modeled with Ellis equation.

Mooney model was used to determine the relationship among rheological characteristics of either gum suspensions (continuous phases) or food emulsions and microstructural parameters such as shape of the particles and interactions between them. The equation which relates relative viscosity with oil fraction was used to obtain the shape factor and maximum packaging volume fraction.

Response surface methodology led to a phenomenological equation which allows to predict the necessary hydrocolloid concentration to develop an emulsion where oil concentration and zero shear viscosity (η_0) are predetermined.

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