LINEAR AND NONLINEAR VISCOELASTIC BEHAVIOR OF OIL-IN-WATER EMULSIONS STABILIZED WITH POLYSACCHARIDES

J.M. QUINTANA[1], A.N. CALIFANO[1,4], N.E. ZARITZKY[1,2], P. PARTAL[3]
and J.M. FRANCO[3]

[1]*CIDCA, CONICET*
Facultad de Ciencias Exactas
Universidad Nacional de La Plata
47 y 116, La Plata (1900), Argentina

[2]*Dep. Ingeniería Química*
Facultad de Ingeniería, UNLP
47 y 116, La Plata (1900), Argentina

[3]*Dep. Ingeniería Quimica*
Universidad de Huelva
Escuela Politécnica Superior, 21819,
La Rábida, Palos de la Frontera, Huelva, Spain

(Manuscript received November 9, 2001; in final form June 5, 2002)

ABSTRACT

The rheological behavior and stability of oil-in-water emulsions stabilized by different thickening agents were analyzed. Food emulsions were prepared with commercial sunflower oil (40% w/w oil-in-water) and stabilized with 1% emulsifier. The tested thickeners were: (1) 1% w/w xanthan gum (XG), (2) 5% w/w potato starch (PS), (3) 5% PS + 0.5% XG, (4) 1% w/w guar gum (GG), and (5) 0.5% XG + 0.5% GG. Mean droplet size and droplet size distribution (DSD) of emulsions were determined by static light scattering. Steady flow (viscosity versus shear rate), transient flow (viscosity versus time) and oscillatory shear tests (linear viscoelasticity) were performed. The addition of thickening agents improved the stability of the emulsions, the effect was less marked in systems containing only GG. DSD was not significantly modified in emulsions containing starch or hydrocolloids. Microscopic observations showed that all the tested emulsions were flocculated due to the presence of hydrocolloids. The observed shear thinning behavior was attributed to the molecular structure of the polysaccharides and to the flocculation/deflocculation process; viscosity data were satisfactorily fitted to the Cross model. Frequency sweeps showed that

---

[4] Corresponding author. TEL: +54-221-4254853; E-mail address: anc@quimica.unlp.edu.ar

Journal of Texture Studies 33 (2002) 215-236. *All Rights Reserved.*

emulsions with PS or XG have a weak gel structural network (G' > G"); those with GG correspond to a polymeric solution where G' and G" curves intersect within the range of tested frequencies. The viscoelastic linear behavior was described according to the Maxwell generalized model. The discrete relaxation spectrum and relaxation times were estimated from the experimental values of G' and G" for emulsions with PS, PS + XG, and XG. Nonlinear viscoelasticity was also studied from stress relaxation curves at different shear strains. The damping function was calculated and the Soskey-Winter parameters were determined. Transient flow viscosities at different shear rates were comparable to the values estimated from stress relaxation measurements.

INTRODUCTION

Emulsions have a tendency to breakdown over time because they are thermodynamically unstable systems (Dickinson 1992; McClements 1999). Several kinds of physicochemical mechanisms contribute to the instability of an emulsion, including gravitational separation (creaming), coalescence, flocculation, Ostwald ripening and phase inversion (Walstra 1996; Friberg 1997; McClements 1999). Polysaccharides are usually added to the aqueous phase of oil-in-water food emulsions to improve creaming stability of emulsions. Their efficiency depends on polymer concentration in the aqueous phase as well as on the structural features of the aqueous polymer system. 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 that they adopt in the solvent (BeMiller and Whistler 1996). Nonadsorbing colloidal particles, such as polysaccharides, induce flocculation in emulsions when they exceed a particular concentration because of an osmotic effect. In a narrow region surrounding each droplet, the concentration of nonadsorbing polymers is much lower than in the bulk. As a consequence, the solvent molecules move from the depletion zone into the bulk of the liquid due to the osmotic potential difference. This process is known as depletion flocculation and it can only be achieved into the bulk if droplets aggregate, thus reducing the volume of the depletion zone. Then, there is an osmotic driving force that favors droplet aggregation, which manifests itself as an attractive force between droplets (Walstra 1996; McClements 2000).

Theoretical predictions of the influence of the volume ratio and polysaccharide concentration indicate that the magnitude of the depletion attraction increases as the polysaccharide concentration and effective volume ratio of the molecule in solution increase.

According to McClements (2000), there are four regions in which the system can exist depending on its polysaccharide concentration: (1) unstable, unflocculated and relative low viscosity (low polymer concentration); the droplets move upward following Stokes' law. (2) Highly unstable, the effective size of the particles in the emulsion increases because of flocculation, but the viscosity is not high enough to prevent the flocs from creaming. (3) Stable, the droplets are not flocculated but the viscosity of the aqueous phase is so large that they cannot move. (4) Stable, the droplets are flocculated but the viscosity of the aqueous phase is so large that they cannot move. The last two systems would have significantly different rheological characteristics since one would contain nonflocculated emulsion droplets embedded in a polymer network while in the other system the polysaccharide network entraps flocculated oil droplets.

Xanthan gum, guar gum and potato starch are some of the hydrocolloids that may be added to the aqueous phase of food emulsions to increase its viscosity. The specific polysaccharide component of guar gum is guaran, a galactomannan where about one-half of the β-D-mannopyranosyl main-chain units, joined by (1→4) bonds, contain an α-D-galactopyranosyl side chain attached at 0-6. Xanthan gum is an exocellular polysaccharide produced by the bacterium *Xanthomonas campestris* and it may be considered an anionic polyelectrolyte. Its primary structure is based on a β-1,4 linked glucan backbone, as in cellulose, but every second glucose residue is attached to a charged trisaccharide side chain (β-D-mannopyranosyl-(1→4)- β-D*-glucuronopyranosyl-(1→2)-6-o-acetyl- β-D-mannopyranosyl units, about half of them have pyruvic acid attached to a 4,6-cyclic acetal) (BeMiller and Whistler 1996). 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 gelatinization temperature, and a medium to low tendency to retrograde (BeMiller and Whistler 1996).

The main objective of the present work is to fully characterize the rheological behavior and stability of low-in-fat oil-in-water emulsions stabilized by different thickening agents, such as starch, xanthan and guar gums.

MATERIALS AND METHODS

Materials

Commercial 100% sunflower oil was purchased from a local supermarket and used without further treatment. Tween 60 (T60, ethoxylated-60-sorbitan monostearate) emulsifier, and potato starch (S-4251, lot 123H0866) were purchased from Sigma Chemical Co. (St. Louis, MO). Xanthan and guar gums used were of food-grade commercial type provided by Saporiti Hermanos SACIF (Argentina). Distilled and deionized water was used in all solutions and emulsions.

Preparations of the Emulsions

Food emulsions were prepared with commercial sunflower oil (40% w/w oil-in-water) and stabilized with 1% w/w T60. The tested thickeners were: (1) 1% w/w xanthan gum (XG), (2) 5% w/w potato starch (PS), (3) 5% PS + 0.5% XG, (4) 1% w/w guar gum (GG), and (5) 0.5% XG + 0.5% GG. 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 a 0.5% XG solution and samples were heated at 90C for 30 min. All gum and starch dispersions were let stand overnight at 5C. Tween 60 was always incorporated to the aqueous phase prior homogenization at room temperature.

Lab-scale manufacture of emulsions 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 prepared at 11500 rpm for 4 min without thermal control during homogenization; they were stored at 5C for 24 h and then equilibrated at 25C for 1 h before testing. Emulsions prepared to observe stability also contained 0.01% sodium azide as an antimicrobial agent.

Droplet Size Distribution (DSD)

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;

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

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.

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 20C in a temperature-controlled room. These samples were periodically observed and the time at which an oil-water interface appeared in each case determined the stability period.

Rheological Tests

After positioning the sample on the sensor system, a resting time of 10 min was allowed 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 25C throughout the experiment. Two replicates of each test were performed.

Flow Behavior. The steady flow behavior (viscosity (η) versus shear rate (γ')) was studied on a Controlled Stress Rheometer RS 150 (Haake, Germany) using a serrated plate-and-plate geometry (35 mm diameter, 1 mm gap), in order to avoid wall slip phenomena (Sanchez *et al.* 2001). The flow measurements were obtained by imposing a ramp of shear stresses in a range between 1 and 100 Pa and waiting until the slope of the resulting shear rate versus time was less than 0.001% at each point, so that steady-state was attained.

Transient flow tests (η vs time) were performed in a Controlled Strain Rheometer ARES (Rheometrics Sci., Germany) at different shear rates (0.1, 1, and 10 s^{-1}), using a serrated plate-plate sensor system (25 mm diameter, 1 mm gap).

Oscillatory Shear Tests. Dynamic rheological measurements were performed 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. The linear viscoelasticity region was determined through stress sweep tests at a fixed frequency (6.28 rad/s).

Stress Relaxation Tests. Stress relaxation curves were obtained in a Controlled Strain Rheometer ARES (Rheometrics Sci., Germany) at different shear strains (10 to 200%) corresponding to the nonlinear viscoelastic range using a serrated plate-and-plate sensor (25 mm diameter, 1 mm gap).

Statistical Analysis

Nonlinear regression analysis were carried out using the SYSTAT software (SYSTAT, Inc., Evanston, IL). Differences in the computed parameters were considered significant when the computed probabilities were less than 0.05 ($P<0.05$).

RESULTS AND DISCUSSION

Droplet Size Distribution and Stability

Visual inspection of the emulsions containing a thickening agent showed that they remained stable after 6 months, except emulsions containing 1% guar gum, which destabilized in a three-month period. Emulsions prepared without the addition of any thickening agent showed an incipient interface after 24 h (Quintana *et al.* 2001). Thus the addition of the thickening agent clearly prolongs shelf life of low-in-fat (40% wt.) oil-in-water products.

The rheology of emulsions is influenced by several structural parameters: interparticle interactions (more important in concentrated emulsions), particle size, shape and polydispersity (Rahalkar 1992). Besides the stability of an emulsion depends, among other things, on droplet size since Stokes's law indicates that the velocity at which a droplet moves is proportional to the square of its radius (McClements 1999). DSD measurements showed a bimodal droplet size distribution (Fig. 1(a) and (b)). Average Sauter diameters (D[3,2]) are given in Fig. 1(a) and 1(b). They were not significantly modified in emulsions containing starch or hydrocolloids. In all cases D[3,2] values between 2-3 μm were obtained. Microscopic observations showed that all the emulsions were flocculated (Fig. 2) but 40% oil-in-water emulsions prepared with the same constituents without the addition of thickeners did not show the presence of flocs (Quintana *et al.* 2002). The aggregations observed in the emulsions could be explained in terms of depletion flocculation caused by the presence of individual nonadsorbing molecules (Walstra 1996; McClements 1999, 2000). It has been suggested that the formation of a weak particle network when the entire volume of the emulsion was flocculated could help to prevent creaming (Parker *et al.* 1995). Consequently, the addition of the polysaccharides stabilizes the emulsion against creaming by enhancing the viscosity of the continuous phase, as a consequence of the formation of a gel network (Dickinson *et al.* 1994; McClements 2000).

Steady-State Flow Measurements

All the emulsions formulated with polysaccharides (XG, GG, and PS) showed shear-thinning behavior. Viscosity-shear rate plots for emulsions containing XG and PS show two different regions (Fig. 3(a) and (b)). The first one, at low shear rates, indicates a tendency to a constant viscosity, η_o. At higher shear rates, the flow curves present a power-law decrease in viscosity.

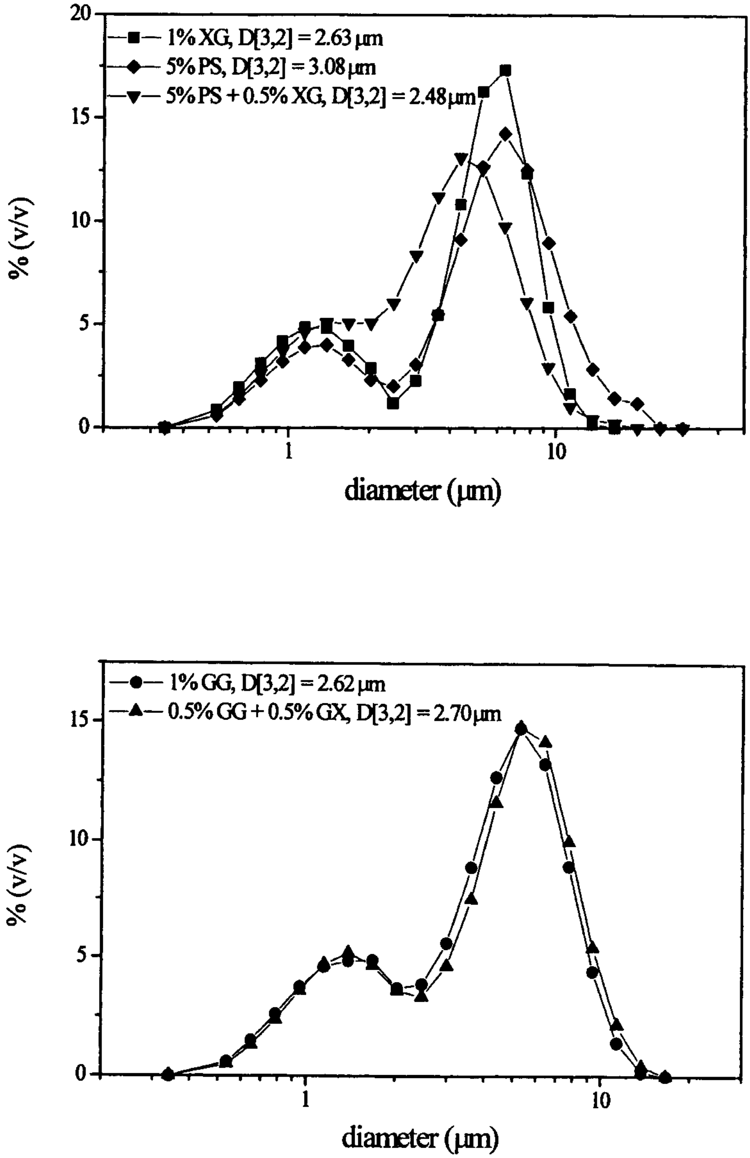


FIG. 1. DROPLET SIZE DISTRIBUTIONS FOR EMULSIONS PREPARED WITH DIFFERENT POLYSACCHARIDES

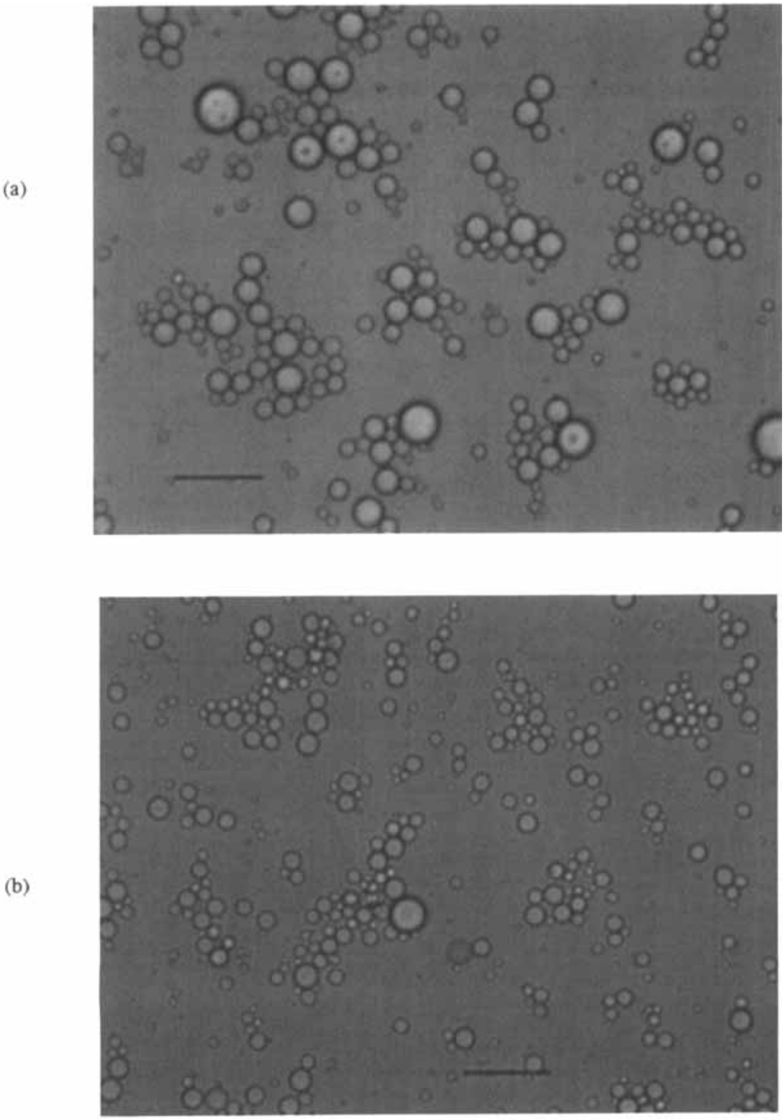
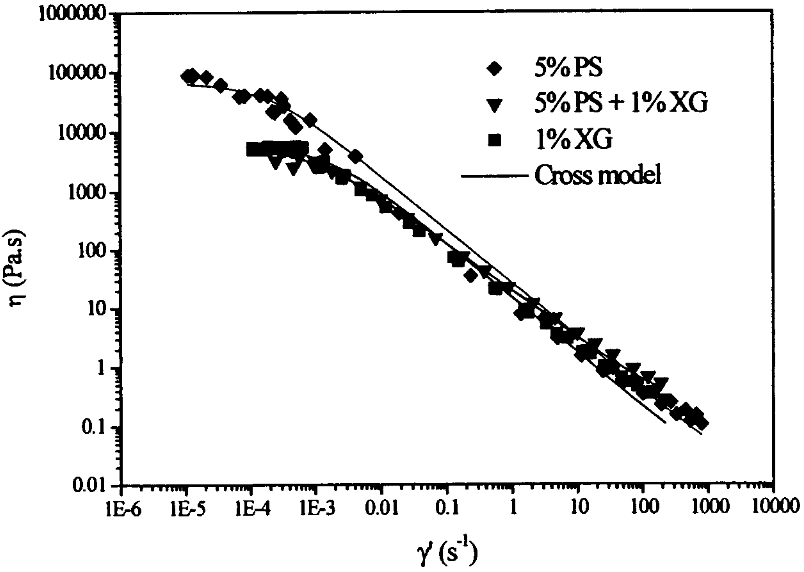


FIG. 2. FLOCCULATED OIL DROPLETS OF A 40% OIL-IN-WATER EMULSION WITH 1% TWEEN 60 CONTAINING: (a) 1% XANTHAN GUM, (b) 5% POTATO STARCH + 0.5% XANTHAN GUM
The bar represents 20 μm.



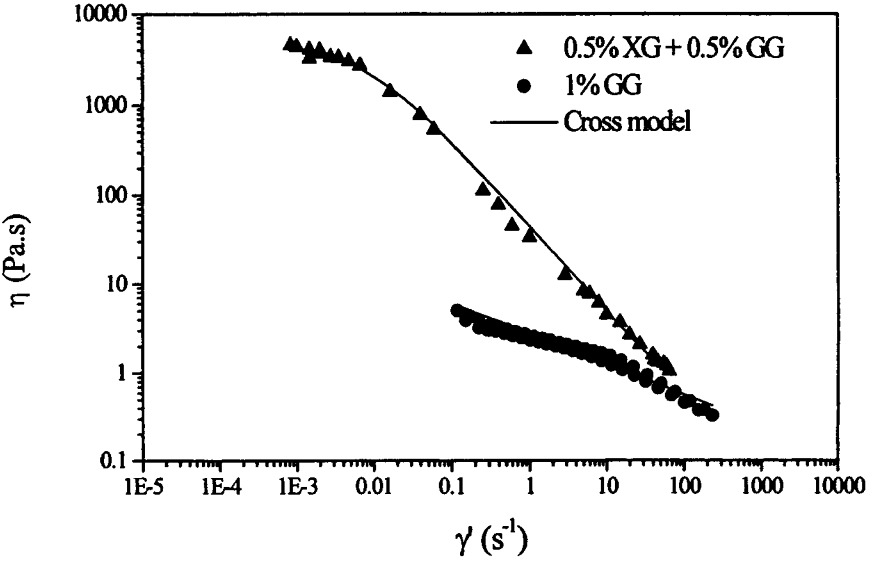


FIG. 3. STEADY-STATE FLOW CURVES FOR 40% OIL-IN-WATER EMULSIONS STABILIZED WITH 1% TWEEN 60

Oil droplets are dispersed in a continuous phase that has weak gel-like characteristics due to the presence of xanthan gum or potato starch (Clegg 1995). The high viscosities at low shear rates and extremely shear-thinning behavior of xanthan solutions are related to the semi-flexible structure of xanthan molecules (Rodd *et al.* 2000). Potato starch has weak intermolecular bonding and swell greatly to yield high viscosities pastes. Because the highly swollen starch granules break easily, the viscosity quickly decreases with moderate shear (BeMiller and Whistler 1996). Systems containing only guar gum showed lower viscosity values. In addition to this, the flocculation/deflocculation process must also be considered (Franco *et al.* 1995a). A significant shear thinning behavior in flocculated emulsions is attributed to both an irreversible process in which a shear-induced DSD change occurs, and a reversible one due to flocculation/deflocculation process.

The flow behavior of emulsion systems was satisfactorily fitted to the Cross model without the second newtonian viscosity, η_∞ (Launay *et al.* 1986):

$$\eta = \eta_0 / (1+(\tau.\gamma')^m) \tag{2}$$

where η_0 is the zero shear-rate viscosity, τ is a relaxation time and "m" is a nondimensional exponent. When $\eta << \eta_0$, Eq. (1) predicts a power-law behavior and (1-m) is close to the flow behavior index "n". The fitted parameters of the model as well as the correlation coefficients (R) are shown in Table 1.

TABLE 1.
PARAMETERS OF THE CROSS'MODEL AND CORRELATION COEFFICIENTS FOR 40% OIL-IN-WATER EMULSIONS CONTAINING HYDROCOLLOIDS

Composition of the aqueous phase	η_0 (Pa.s)	τ (s)	n	R
1% xanthan gum	6.0×10^3	6.0×10^2	0.94	0.96
5% potato starch	6.5×10^4	4.8×10^3	0.92	0.98
0.5% xanthan gum+ 5% potato starch	5.9×10^3	1.0×10^3	0.82	0.97
0.5% xanthan gum + 0.5% guar gum	4.6×10^3	1.2×10^2	0.97	0.96
1% guar gum	61.	4.	0.29	0.98

R: Correlation coefficient

Dynamic Tests (Linear Viscoelasticity)

Figures 4 (a) and (b) show data of G′ (storage moduli) and G″ as a function of frequency for the systems containing PS or XG. The differences in such moduli between replicate runs were less than 7%. The evolution of the storage and loss moduli with frequency depends on the nature and concentration of the selected thickener, so that two characteristic regions may be found: a pseudo-terminal region at low frequencies that shows a tendency to a crossover of both viscoelastic functions (beginning of the viscous region) for emulsion containing 1% GG; and the plateau region, for the other emulsions. The presence of a pseudo-terminal region at low frequencies has been previously reported for emulsions stabilized by a mixture of egg yolk and a high HLB sucrose stearate (Franco *et al.* 1995b) and also for emulsions stabilized by lupin protein and low-molecular-weight emulsifiers (Raymundo *et al.* 1999). The appearance of a plateau region in the mechanical spectrum has been previously related to the formation of physical entanglements among polymetric molecules (Ferry 1980) that form a three-dimensional network of interacting or entangled molecules that traps the droplets in oil-in-water emulsions (Dickinson 1992). Frequency sweeps showed that the G′ (storage modulus) and G″ (loss modulus) correspond to a weak gel structural network, where G′ is always greater than G″ in the range of frequencies studied (Fig. 4 (a) and (b)).

Viscoelastic behavior of the 40% oil emulsion with 1% guar gum corresponds to a polymeric solution where G′ and G″ curves intersect within the range of tested frequencies, showing a fluid like behavior (Fig. 4b). These findings support the observed low stabilizing effect of guar gum in the tested emulsions; thus guar gum alone was not adequate to prolong the shelf-life of these emulsions.

Dynamic viscosities (η^*) were always higher than the corresponding steady shear viscosities (η), and the studied emulsions did not obey Cox-Merz rule. 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, complex viscosity is measured within linear viscoelastic range where no structural disruption is produced, thus achieving higher values. A similar behavior was observed for weak gels (Clegg 1995), for oil-in-water emulsions stabilized with egg yolk and sucrose stearate (Franco *et al.* 1995a), and for emulsions stabilized by a sucrose palmitate of high HLB (Partal *et al.* 1994).

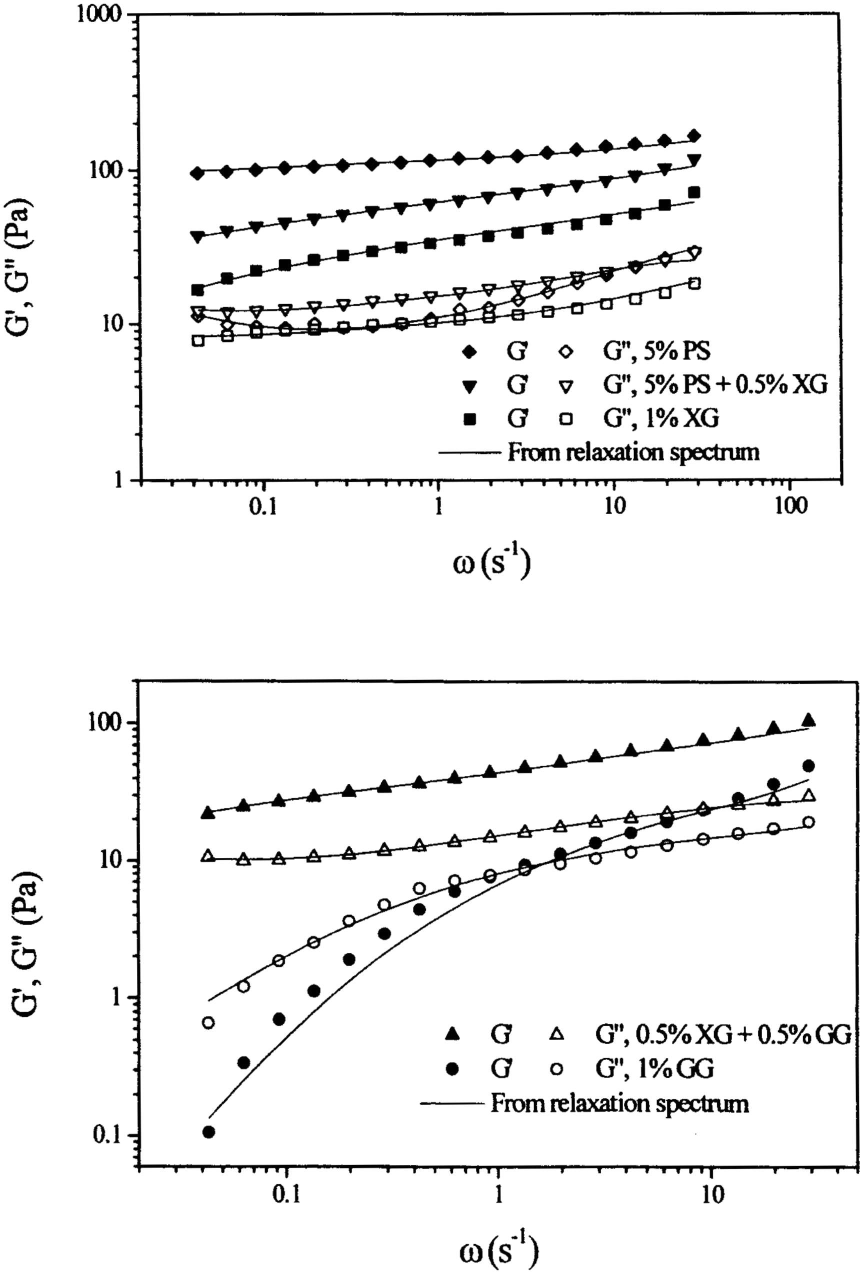


FIG. 4. STORAGE (G′) AND LOSS (G″) MODULI AS A FUNCTION OF FREQUENCY (ω) FOR 40% w/w OIL-IN-WATER EMULSIONS STABILIZED WITH 1% TWEEN 60, WITH THICKENERS ADDED

The viscoelastic behavior was described according to the Maxwell generalized model, where the linear relaxation modulus G(t) is given by:

$$G(t) = G_e + \sum_{i=1}^{N} G_i \exp(-t/\lambda_i) \tag{3}$$

where λ_i is the relaxation time of the i-Maxwell element, G_i is the ith contribution to the modulus and G_e is the equilibrium modulus, the asymptotic value at infinite relaxation time in the case of solids, being zero for viscoelastic liquids. Viscoelastic relaxation can be visualized as the overlying of elementary processes in which stress relaxes exponentially (Ferry 1980; Tschoegl 1989). Thus, the storage and loss moduli are related to the linear relaxation spectrum by means of the following equations:

$$G' = G_e + \sum_{i=1}^{N} G_i \frac{(\omega\lambda_i)^2}{1+(\omega\lambda_i)^2} \tag{3}$$

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

The discrete relaxation spectrum (G_i) and relaxation times (λ_i) of the material were estimated from the experimental values of G′ (ω) and G″ (ω) for PS, PS + XG, and XG stabilized emulsions by an iterative process (simultaneously using Eq. 3 and 4) that minimized the sum of the square differences; results are shown in Fig. 5. The computed G_i and λ_i values were used to predict the storage and loss moduli (Fig. 4 (a) and (b)). There is an excellent concordance between both sets of values, confirming the accuracy of the calculations. Table 2 presents the mean percent error (e%) between experimental and predicted values for both moduli.

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

$$\text{BSW-spectrum: } H(\lambda) = A\left[\left(\frac{\lambda}{\lambda_c}\right)^m + \left(\frac{\lambda}{\lambda_p}\right)^n\right] \text{for } \lambda_{min} < \lambda < \lambda_p \tag{5}$$

$$\text{CW-spectrum:}\quad H(\lambda)=A\left[\left(\frac{\lambda}{\lambda_p}\right)^c\right] \text{for } \lambda_p < \lambda < \lambda_{max} \qquad (6)$$

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 (5) and (6) 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. Figure 5 shows the linear relaxation spectra of oil-in-water emulsions including the prediction of the BSW-CW model. Although both equations were fitted, CW model parameters (Eq. 6) were not used for the discussion of results, since they do not correspond to the experimental range of relaxation times. Table 3 shows the value of parameters A, m, n, c, λ_c, and λ_p for the different emulsions studied. The slope of the plateau region is higher for emulsions prepared with PS and XG+GG. The increase in the value of the slope (n) in the plateau region may be related to the development of an entanglement network (Franco *et al.* 1997). It is well known that when a hot potato starch paste cools gelation of amylose occurs as the hydrated and dispersed starch molecules reassociate (Zobel 1984), which explains that emulsions prepared with 5% PS showed the highest η_0 and "n" values and high elastic moduli (G').

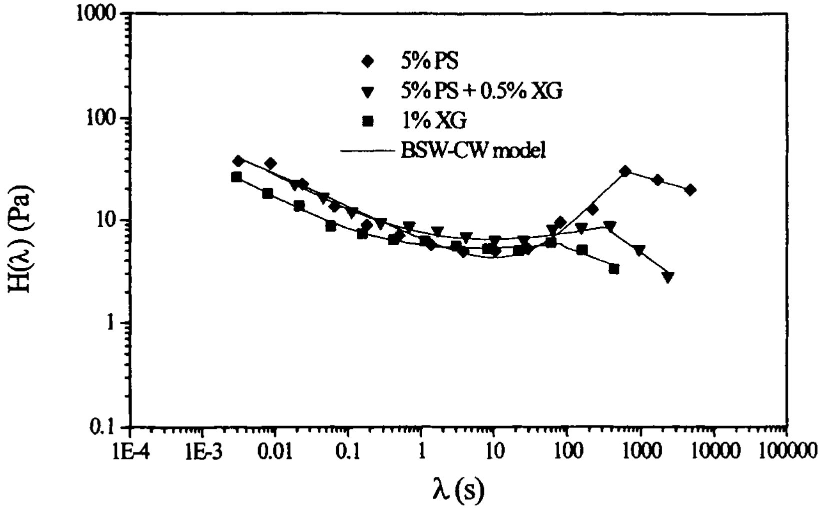
TABLE 2.
MEAN PERCENTUAL ERROR (e%) BETWEEN MEASURED MODULI AND THE VALUES PREDICTED BY MAXWELL MODEL FOR 40% OIL-IN-WATER EMULSIONS

Composition of the aqueous phase	e%(G')*	e%(G'')**
1% xanthan gum	2.7	0.9
5% potato starch	0.5	0.6
0.5% xanthan gum + 5% potato starch	0.6	2.2
0.5% xanthan gum + 0.5% guar gum	1.8	1.4
1% guar gum	13	0.5

*Mean percent error (e%) were calculated as follows:

$$e\%(G') = (\Sigma(G'_{exp}-G'_{pred})/\, G'_{pred}).100/N$$

$$e\%(G'') = (\Sigma(G''_{exp}-G''_{pred})/\, G''_{pred}).100/N$$



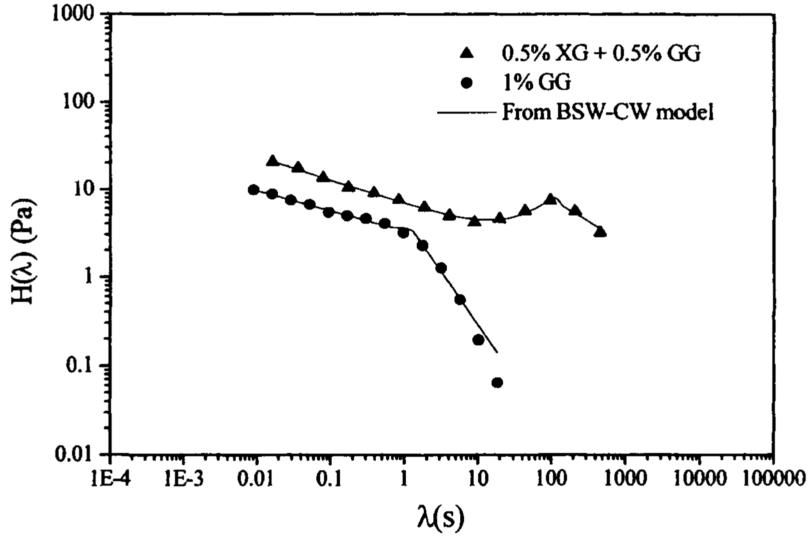


FIG. 5. RELAXATION SPECTRA CORRESPONDING TO 40% w/w OIL-IN-WATER EMULSIONS STABILIZED WITH 1% TWEEN 60

TABLE 3.
INFLUENCE OF THE AQUEOUS PHASE EMULSION COMPOSITION (HYDROCOLLOIDS AND STARCH) ON THE PARAMETERS OF THE BSW-CW MODEL

Composition of the aqueous phase	A	m	n	c	λ_c (s)	λ_p (s)	R
1% XG	5.8^{a}	-0.44^{a}	0.08^{a}	-0.44^{a}	0.07^{a}	121^{a}	0.998
5% PS	$30.^{b}$	-0.32^{a}	0.76^{b}	$-.022^{a}$	0.008^{b}	654^{b}	0.97
0.5% XG + 5% PS	8.8^{a}	-0.43^{a}	0.12^{a}	-0.67^{ab}	0.032^{a}	131^{a}	0.997
0.5% XG + 0.5% GG	7.5^{a}	-0.27^{b}	0.86^{b}	-0.72^{ab}	0.7^{c}	139^{a}	0.998
1% GG	$3.^{c}$	-0.38^{a}	-0.21^{c}	-1.2^{b}	0.003^{b}	$1.^{c}$	0.995

^{a,b,c}: different superscripts within the same column indicate that the values differ significantly ($P<0.05$). R: correlation coefficient

When potato starch was gelatinized in the presence of xanthan gum (PS+XG), η_0 and the slope of the plateau region "n" markedly decreased, as well as the storage moduli (G′) of the emulsion (Fig. 3(a), Fig. 4(a), Tables 1 and 3). It appears that the presence of the polysaccharide interfered with the formation of junction zones between starch chains; Navarro *et al.* (1997) reported that 10% corn starch pastes with 0.3% of xanthan gum added showed lower G′ values compared with those for starch without XG and proposed that XG prevented the double helix aggregation between amylose molecules. The emulsions thickened with a mixture of 0.5% of both xanthan gum and guar gum also showed high "n" values and the observed storage moduli were much higher than those corresponding to emulsions containing only xanthan gum (XG), which indicates that the presence of guar gum, due to its synergistic interaction with xanthan gum helps to develop a more entangled network than when XG is used alone (BeMiller and Whistler 1996). In emulsions containing guar gum only, the presence of the polysaccharide produced a dramatic decrease in the slope of the plateau region, which tended to disappear, which implies that an entanglement network has not been produced in the presence of guar gum. Table 3 also shows a maximum value in λ_p for the emulsion with potato starch, which implies more important elastic characteristics at higher relaxation times.

Nonlinear Viscoelasticity

In most food forming operations, deformations are generally both large and rapid (mixing, flow through pipes, etc.). Consequently linear viscoelastic properties will not be adequate for material characterization needed for quality control and process design (Kokini *et al.* 2000), so that large rapid deformation testing and the resulting nonlinear viscoelastic characterization appears to be of great importance. One of the most relevant nonlinear phenomena is the dependence of the rheological properties not only on time, but also on the magnitude of the deformation.

Nonlinear stress relaxation curves were obtained at different shear strains (γ), comprised between 10-200%. After the shear rate was removed, the values of the nonlinear relaxation modulus $G(t-t', \gamma)$ were calculated from:

$$G(t-t',\gamma) = \frac{\sigma(t-t',\gamma)}{\gamma} \tag{7}$$

where $\sigma(t-t',\gamma)$ are the experimental stress decay values and γ the total strain imposed on the sample. As an example, Fig. 6 shows the nonlinear relaxation modulus as a function of time and the previously applied strain for the emulsions stabilized with 1% xanthan gum. The shape of $G(t-t', \gamma)$ is independent of the strain previously applied on the sample. The same behavior was found for the rest of the emulsions studied. Similar findings were reported for sucrose palmitate oil-in-water emulsions (Partal *et al.* 1999) and mayonnaise (Gallegos *et al.* 1992), Consequently, the nonlinear relaxation modulus may be factorable in two terms, one depending on time, $G(t-t')$, and the other depending on strain, the so-called "damping function" $h(\gamma)$:

$$G(t-t',\gamma) = G(t-t')h(\gamma) \tag{8}$$

Figure 6 also shows the linear relaxation modulus predicted by the Maxwell model (Eq. 2). As can be seen, there is a good agreement between experimental data and the predictive model when the lowest strain was applied, indicating that the application of a 10% strain practically yields a linear viscoelastic response.

The value of the damping function $h(\gamma)$ can be obtained from the $G(t-t', \gamma)/G(t-t')$ ratio and provides information about the shear-induced structural breakdown. Figure 7 shows the evolution of $h(\gamma)$ with the applied strain, γ, for the samples studied. Damping function decreases as strain is increased but a different behavior is observed depending on the thickener used. Thus, the higher values of $h(\gamma)$ showed by XG-GG stabilized emulsions would indicate a more

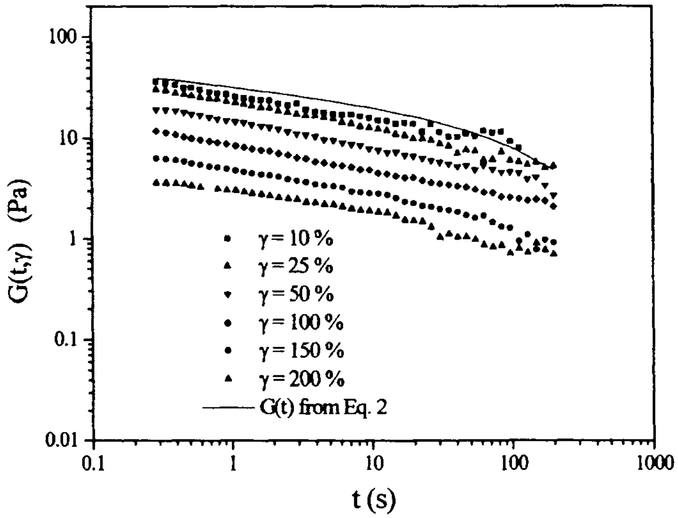


FIG. 6. EVOLUTION OF LINEAR AND NONLINEAR RELAXATION MODULI FOR A 40% w/w OIL-IN-WATER EMULSION WITH 1% XANTHAN GUM IN THE AQUEOUS PHASE

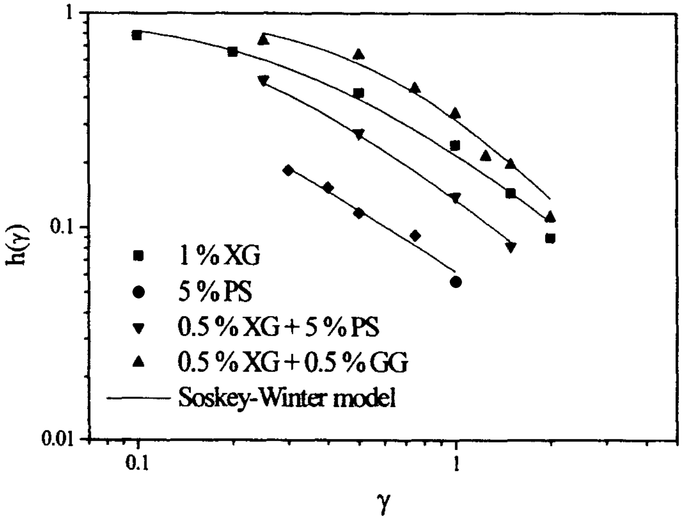


FIG. 7. DAMPING FUNCTION, h(γ), AS A FUNCTION OF STRAIN, γ, FOR EMULSIONS CONTAINING DIFFERENT THICKENERS

resistant microstructure. On the contrary, microstructure of emulsions stabilized by PS appears to be highly shear-dependent in spite of the highest values of their linear viscoelastic functions previously shown. This behavior can be explained by the Soskey-Winter model (Soskey and Winter 1999):

$$h(\gamma) = \frac{1}{1 + a\gamma^{b}} \tag{9}$$

where "a" and "b" are material parameters. The equation fits the damping function values obtained from the relaxation data fairly well (Fig. 7). Soskey-Winter parameters and the corresponding correlation coefficients of the nonlinear regressions are shown in Table 4. Transient flow viscosity may be predicted from stress relaxation measurements, using the Wagner constitutive model (Wagner 1976) with the Soskey-Winter's damping function (Madiedo *et al.* 2000):

$$\eta(t-t',\gamma') = \int_{-\infty}^{t} \sum_{i=1}^{N} \frac{G_i}{\lambda_i} \exp\left(-\frac{t-t'}{\lambda_i}\right) \frac{1}{1 + a[\gamma'(t-t')]^{b}} (t-t')dt' \tag{10}$$

where the integration is carried out over all past times t′ up to the current time t.

TABLE 4.
PARAMETERS OF THE SOSKEY-WINTER DAMPING FUNCTION FOR EMULSIONS CONTAINING DIFFERENT THICKENERS

	a	b	R
1 % xanthan gum	3.6^{a}	1.22^{a}	0.999
5 % potato starch	15.0^{b}	1.0^{a}	0.999
0.5 % xanthan gum+ 5 % potato starch	6.4^{c}	1.25^{a}	0.999
0.5 % xanthan gum + 0.5 % guar gum	2.1^{d}	1.6^{a}	0.996

a,b,c: different superscripts within the same column indicate that the values differ significantly ($P<0.05$). R: Correlation coefficient

Figure 8 shows experimental values of the transient flow viscosity, at three different shear rates, for the XG emulsion studied. The response is clearly dependent on the shear rate applied on the sample. An initial viscosity increase is noticed, reaching a constant value at the lowest shear rate applied (0.1 s^{-1}). At higher shear rates a viscosity overshoot appears, decreasing afterwards to steady-state values. The viscosity values predicted with Eq. (10) are also shown in Fig. 8. It can be seen that the model underestimates the experimental values. A similar behavior was found for the other systems studied.

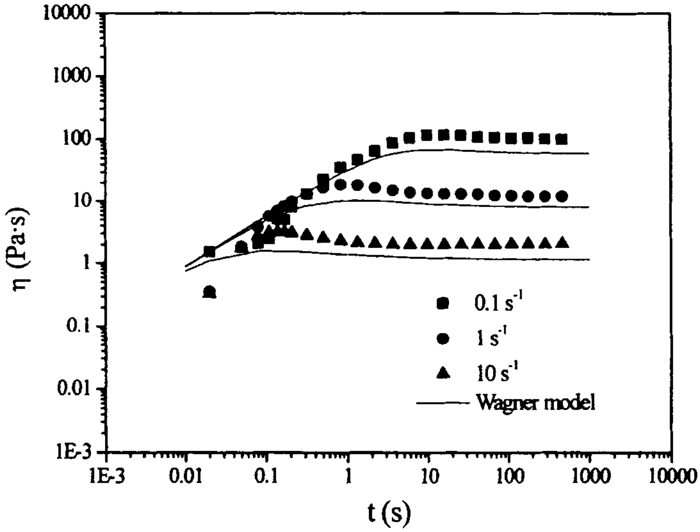


FIG. 8. TRANSIENT FLOW FOR A 40% w/w OIL-IN-WATER EMULSION WITH 1% XANTHAN GUM IN THE AQUEOUS PHASE

ACKNOWLEDGMENTS

The authors acknowledge the financial supports of the Consejo Nacional de Investigaciones Cientificas y Tecnológicas (CONICET, Argentina), Agencia Nacional de Promoción Científica y Tecnológica (Argentina), Universidad Nacional de La Plata (Argentina), University of Huelva (Spain), and Programa de Cooperación España-Iberoamérica (Project BOE 26-II.99).

REFERENCES

BARNES, H.A., HUTTON, J.F. and WALTERS, K. 1989. *An Introduction to Rheology, Rheology Series 3*, Elsevier Scientific Pub. Co., Amsterdam.

BAUMGAERTEL, M., SCHAUSBERGER, A. and WINTER, H.H. 1990. The relaxation of polymer with linear flexible chains of uniform length. Rheol. Acta *29*, 400–408.

BeMILLER, J.N. and WHISTLER, R.L. 1996. Carbohydrates. In *Food Chemistry* (3), (O.R. Fennema, ed.) Marcel Dekker, New York.

CHAMBON, F. and WINTER, H.H. 1985. Stopping of crosslinking reaction in PDMS polymer at the gel point. Polym. Bull. *13*, 499–503.

CLEGG, S.M. 1995. Thickeners, gells and gelling. In *Physico-chemical Aspects of Food Processing*, (S.T. Beckett, ed.) Blackie Academic and Professional, Glasgow.

DE ROSA, M.E. and WINTER, H.H. 1994. The effect of entanglements on the rheological behavior of polybutadiene critical gels. Rheol. Acta *33*, 220–237.

DICKINSON, E. 1992. *Introduction to Food Colloids*, Oxford University Press, Oxford.

DICKINSON, E., MA, J. and POVEY, M.J.W. 1994. Creaming of concentrated oil-in-water emulsions containing xanthan. Food Hydrocolloids *8*(5), 481–497.

FERRY, J.D. 1980. *Viscoelastic Properties of Polymers*. John Wiley & Sons, New York.

FRANCO, J.M., BERJANO, M. and GALLEGOS, C. 1997. Linear viscoelasticity of salad dressing emulsions. J. Agric. Food Chem. *45*, 713–719.

FRANCO, J.M., BERJANO, M., GUERRERO, A., MUNOZ, J. and GALLEGOS, C. 1995a. Flow behavior and stability of light mayonnaise containing a mixture of egg yolk and sucrose stearate as emulsifiers. Food Hydrocolloids *9*, 111–121.

FRANCO, J.M., GUERRERO, A. and GALLEGOS, C. 1995b. Rheology and processing of salad dressing emulsions. Rheol. Acta *34*, 513–524.

FRIBERG, S. 1997. Emulsion stability. In *Food Emulsions* (3), (S. Friberg and K. Larsson, eds.) Marcel Dekker, New York.

GALLEGOS, C., BERJANO, M., MUÑOZ, J. and FLORES, V. 1992. Transient flow of mayonnaise described by a nonlinear viscoelasticity. J. Texture Studies *23*, 153–168.

KOKINI, J.L., DHANASEKHARAN, M., WANG, C-F. and HUANG, H. 2000. Integral and differential linear and nonlinear constitutive models for the rheology of wheat flour doughs. In *Food Preservation Technology Series: Trends in Food Engineering*, (J. Lozano, M.C. Añon, E. Parada-Arias and G. Barbosa-Cánovas, eds.) Technomic Publishing Co., Lancaster, PA.

KWON, B.D., FOSS, P.A. and RHA, C.H.K. 1987. Rheological characterization of high viscosity polysaccharides. In *Industrial Polysaccharides: Genetic Engineering, Structure/Property Relations and Applications*, (M. Yalpani, ed.) Elsevier Science Publishers B.V., Amsterdam.

LAUNAY, B., DOUBLER, J.L. and CUVELIER, G. 1986. Flow properties of aqueous solutions and dispersions of polysaccharides. In *Functional Properties of Food Macromolecules*, (J.R. Mitchel and D.A. Ledward, eds.) Elsevier Applied Science Publishers, Essex.

MADIEDO, J.M., FRANCO, J.M., VALENCIA, C. and GALLEGOS, C. 2000. Modeling of the non-linear rheological behavior of a lubricating grease at low-shear rates. J. Tribology *122*, 590–596.

McCLEMENTS, D.J. 1999. *Food Emulsions: Principles, Practice and Techniques*, CRC Press, Boca Raton, Florida.

McCLEMENTS, D.J. 2000. Comments on viscosity enhancement and depletion flocculation by polysaccharides. Food Hydrocolloids *14*, 173–177.

NAVARRO, A., MARTINO, M. and ZARITZKY, N. 1997. Viscoelastic properties of frozen starch-triclycerides systems. J. Food Eng. *34*, 411–427.

PARKER, A., GUNNING, P.A., NG, K. and ROBINS, M.M. 1995. How does xanthan stabilise salad dressing? Food Hydrocolloids *9*(4), 333–342.

PARTAL, P., GUERRERO, A., BERJANO, M. and GALLEGOS, C. 1999. Transient flow of o/w sucrose palmitate emulsions. J. Food Eng. *41*, 33–41.

PARTAL, P., GUERRERO, A., BERJANO, M., MUÑOZ, J. and GALLEGOS, C. 1994. Flow behavior and stability of oil-in-water emulsions stabilized by a sucrose palmitate. J. Texture Studies *25*, 331–348.

QUINTANA, M., CALIFANO, A.N. and ZARITZKY, N.E. 2001. Influence of formulation on droplet distribution and stability of food emulsions stabilized with mixed emulsifiers. Scanning *23*(3), 221–222.

QUINTANA, M., CALIFANO, A.N. and ZARITZKY, N.E. 2002. Microstructure and stability of non protein stabilized oil-in-water food emulsions measured by optical methods. J. Food Sci. *67*(3), 1130–1135.

RAHALKAR, R.R. 1992. Viscoelastic properties of oil-water emulsions. In *Viscoelastic Properties of Food*, (M.A. Rao and J.F. Steffe, eds.) Elsevier Applied Science Publishers, London.

RAYMUNDO, A., FRANCO, J.M., PARTAL, P., SOUSA, I. and GALLEGOS, C. 1999. Effect of the lupin protein/surfactant ratio on the linear viscoelastic properties of oil-in-water emulsions. J. Surfactants Detergents *4*, 545–551.

RODD, A.B., DUNSTAN, D.E. and BOGER, D.V. 2000. Characterization of xanthan gum solutions using dynamic light scattering and rheology. Carb. Polym. *42*, 159–174.

SANCHEZ, M.C., VALENCIA, C., FRANCO, J.M. and GALLEGOS, C. 2001. Wall slip phenomena in oil-in-water emulsions: effect of some structural parameters. J. Coll. Interf. Sci. *241*, 226–232.

SOSKEY, P.R. and WINTER, H.H. 1984. Large step shear strain experiments with parallel-disk rotational rheometers. J. Rheol. *28*(5), 625–634.

TSCHOEGL, N.W. 1989. *The Phenomenological Theory of Linear Viscoelastic Behaviour*, Suringer, New York.

WAGNER, M.H. 1976. Analysis of time-dependent nonlinear stress-growth data for shear and elongational flow of a low-density branched polyethylene melt. Rheol. Acta *15*(2), 136–145.

WALSTRA, P. 1996. Dispersed systems. In *Food Chemistry* (3). (O.R. Fennema, ed.) Marcel Dekker, New York.

ZOBEL, H.F. 1984. Gelatinization of Starch and Mechanical Properties of Starch Pastes. In *Starch. Chemistry and Technology* (2), (R.L. Whistler, J.N. BeMiller and E.F. Paschall, eds.) Academic Press, Orlando, Florida.