

Linear Viscoelasticity of Salad Dressing Emulsions

Jose M^a Franco,[†] Manuel Berjano,[‡] and Crispulo Gallegos^{*,‡}

Departamento de Ingeniería Química, Universidad de Huelva, Escuela Politécnica Superior, 21189, La Rábida, Palos de la Frontera, Huelva, Spain, and Departamento de Ingeniería Química, Universidad de Sevilla, c/ Prof. García González s/n, 41012, Sevilla, Spain

The effects of oil, emulsifier, and starch concentrations on the linear viscoelasticity of oil/water salad dressing emulsions were studied. Oil concentration ranged between 35 and 55 wt %. Emulsions were prepared using a mixture of egg yolk (0–6 wt %) and a highly hydrophilic sucrose ester (0–10 wt %) as emulsifier. Starch (0–2 wt %) was included in the formulation to study the influence of increasing continuous phase viscosity. The influence of the concentration of these components on the linear viscoelasticity functions was generalized by using the plateau modulus as a normalization factor. An increase in oil concentration did not qualitatively modify the linear viscoelastic behavior. A frequency displacement of the plateau region took place when egg yolk and sucrose ester concentrations were changed. Results were analyzed by calculating the relaxation time spectra of these emulsions. The BSW-CW model was used to fit these spectra. The pseudo-terminal relaxation time increases with egg yolk concentration and decreases with sucrose ester concentration. The slope of the plateau region generally increases as oil or emulsifier concentration does but decreases with starch concentration. These results have been related to the formation of an extensive structural network in the emulsions.

Keywords: *Emulsifier; emulsion; linear viscoelasticity; relaxation time spectrum; starch*

INTRODUCTION

Many food colloids that contain oil or fat exist in the form of oil-in-water emulsions (Dickinson and Stainsby, 1987; Dickinson, 1992). They are typically stabilized by an adsorbed layer of protein at the oil/water (o/w) interface, which forms a protective steric barrier around the droplets. Further stabilization may arise from the presence of low concentrations of water soluble hydrocolloids which act as thickening or structuring agents in the continuous phase (Dickinson, 1988; Cao et al., 1991).

However, mixtures of macromolecular and low-molecular weight emulsifiers are being increasingly used in the food industry (Clark et al., 1992). The inclusion of another emulsifier, i.e., a sucrose ester, in addition to the traditional egg yolk, increases the stability of the emulsions to which other stabilizers, i.e., hydrocolloids, have not been added (Franco et al., 1995a). Nevertheless, aging of those emulsions always produced creaming, a low-viscosity aqueous phase separated.

Of course, stability is the most important factor to be considered in emulsion technology. Emulsion stability depends on droplet size distribution, rheology of the continuous phase, and interparticle interactions (Melik and Fogler, 1988). The flocculation of oil droplets may frequently be an intermediate step to the rupture of the emulsion and is also closely related to the creaming process since the aggregates of oil droplets have a settling velocity higher than that of the individual droplets. However, in concentrated emulsions, an extensive flocculation process may favor emulsion stability by forming a weak gel-like particulate network (Dick-

inson, 1989). Moreover, the type and the concentration of emulsifiers play a key role in the extension of the flocculated state. The strength and the nature of the interactions between emulsifier molecules in different droplets determines if the flocculation is reversible or irreversible. This aggregation process influences the bulk rheology of emulsions. Thus, the frequency dependence of the storage and loss moduli for flocculated dispersions is clearly different than that shown by nonflocculated ones (Tadros, 1990, 1993).

Furthermore, the above-mentioned entanglement network is highly influenced by processing. Previous work studied the effect that several processing variables exerted on the viscous flow, linear viscoelastic behavior, and stability of emulsions containing a mixture of egg yolk and a hydrophilic sucrose ester as emulsifier, without using other emulsion stabilizers or thickeners (Franco et al., 1995b). It was concluded that an increase in energy input and temperature of processing produced an extended linear viscoelasticity range and favored the appearance of a plateau region in the linear relaxation spectrum of the emulsions, due to the enhanced formation of an entanglement network, which led to a decrease in creaming rate. In any case, a comparison between dynamic and steady-state viscosities (Franco et al., 1995a) demonstrated that a dramatic structural breakdown took place when these emulsions were submitted to steady-state shear.

The creaming rate of emulsions stabilized by a mixture of egg yolk and sucrose ester may also be reduced by using thickening agents, which increase the continuous phase viscosity (Cavallo et al., 1990; Castelain et al., 1990). These substances would also probably lessen the dramatic decrease in viscosity produced by steady shear.

The main objective of this work was to investigate the rheological properties and stability of the unperturbed flocculated structure of food emulsions containing a mixture of egg yolk and a highly hydrophilic (HLB =

[†] Universidad de Huelva. Phone: 34-59-530245. FAX: 34-59-350311. E-mail: franco@uhu.es.

[‡] Universidad de Sevilla. Phone: 34-5-4557179. FAX: 34-5-4557134. E-mail: cgallego@cica.es.

* To whom correspondence should be addressed.

Table 1. Values of Stability and Sauter Diameter for Emulsions Having Different Compositions (0% Starch)

oil concn (wt %)	sucrose stearate concn (wt %)	egg yolk concn (wt %)	stability (days)	d_s (μm)
45	5	6	30	4.3
50	3	6	10	3.9
50	5	6	35	3.6
50	7	6	>180	4.0
50	10	6	>180	5.4
55	5	0	55	5.2
55	5	2	58	4.2
55	5	4	50	4.1
55	5	6	55	3.6

15) sucrose stearate as emulsifier and starch as thickening agent. With this aim, the influences that the oil weight fraction and emulsifiers and thickener concentrations exerted on droplet size distribution and linear viscoelasticity of these foodstuffs were studied.

EXPERIMENTAL PROCEDURES

Different o/w emulsions having a sunflower oil concentration of between 35 and 55 wt % were prepared. A mixture of sucrose stearate of high hydrophilic-lipophilic balance (HLB = 15) from Mitsubishi Food Corp. (Japan) and egg yolk from Hijos de Ybarra (Spain) was used as emulsifier. Detailed information about the sucrose stearate used has been given elsewhere (Calahorra et al., 1992). Sucrose ester and egg yolk concentrations were varied between 0 and 10 wt % and 0–6 wt %, respectively, and starch concentration was 0, 1, or 2 wt %. Other ingredients were 4% vinegar, 4% sugar, and 0.4% salt. The formulation was completed with the corresponding amount of distilled water (22.6–45.6%).

Lab-scale manufacture of starch-free emulsions was carried out using an "Ultra-Turrax T-50" homogenizer from Ika (Stauf, Germany). Emulsions were prepared for 5 min at 8000 rpm. In contrast, emulsions containing starch were prepared in a pilot plant colloidal mill, model "Delmix MZM/VK-7" from Fryma (Rheinfelden, Germany), with an emulsification time of 10 min. The emulsification temperature was fixed at 50 °C. Optimum processing parameters were previously determined (Franco et al., 1995b). Emulsions were always stored at 5 °C.

Droplet size distributions were determined with a Coulter-Counter model Z_B apparatus from Coulter Electronics Limited (Luton, England) with an orifice size of 100 μm and NaCl (10 g/L) and sodium azide (1 g/L) as electrolyte. Values of the Sauter mean diameter (Spraw, 1967), which is inversely proportional to the specific surface area of droplets, were obtained as follows:

$$d_s = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

Dynamic shear tests were carried out in a Bohlin CS-50 rheometer (Lund, Sweden) using a cone-plate sensor system (4°, 40 mm).

Rheological and droplet size distribution measurements were done 6 days after emulsion manufacture. At least two replicates of each test were performed. A statistical analysis (ANOVA) was done in order to establish the influence of the different variables. The significance level was set at 95%.

RESULTS AND DISCUSSION

Stability and Droplet Size Distribution. Tables 1–3 show the maximum stability, in days, for the different emulsions studied. The appearance of two phases, due to a creaming process, was chosen as a criterion of instability. Taking into account the sampling errors, differences of less than 2 days are not significant. As can be observed, an increase in oil, sucrose ester, or starch concentration produces longer

Table 2. Values of Stability and Sauter Diameter for Emulsions Having Different Compositions (1% Starch)

oil concn (wt %)	sucrose stearate concn (wt %)	egg yolk concn (wt %)	stability (days)	d_s (μm)
55	0	6	7	7.4
55	3	6	53	4.8
55	5	6	>180	3.2
55	7	6	>180	3.8
55	5	0	63	5.4
55	5	2	130	5.2
55	5	4	>180	3.7
55	5	6	>180	3.2

Table 3. Values of Stability and Sauter Diameter for Emulsions Having Different Oil Contents (5% Sucrose Ester, 6% Egg Yolk, 2% Starch)

oil concn (wt %)	stability (days)	d_s (μm)
35	>180	3.9
40	>180	3.7
45	>180	3.8
50	>180	3.6
55	>180	3.3

resistance to creaming. An increase in egg yolk concentration only improves stability if the emulsions contain starch.

The above-mentioned tables also show the values of Sauter's diameter as a function of the emulsion composition. Differences of less than $\pm 0.5 \mu\text{m}$ in Sauter's diameter are not significant. Droplet size is significantly influenced by egg yolk concentration (Tables 1 and 2), showing lower values of Sauter's diameter with increased concentration. Nevertheless, emulsions that only contain egg yolk as emulsifier are very unstable and exhibit a dramatic increase in droplet diameter. An increase in sucrose ester concentration generally produces lower values of Sauter's diameter, although the most concentrated emulsions (7–10 wt % in sucrose stearate) show an opposite tendency, due to the formation of a highly viscous continuous phase during processing at 50 °C. As has been previously reported (Calahorra et al., 1992), a micellar-lamellar phase transition occurs as sucrose stearate concentration increases at temperatures above 43 °C. On the other hand, there is a slight tendency to lower values of the Sauter diameter as oil concentration increases.

Linear Viscoelasticity. The evolution of the storage (G') and loss (G'') moduli with frequency is always qualitatively similar. The storage modulus is always higher than the loss modulus in the frequency range studied. In general, three characteristic regions may be observed: (i) a pseudo-terminal region at low frequencies that shows a tendency to a crossover of both viscoelastic functions, (ii) an intermediate plateau region in which G'' becomes nearly constant and the slope of G' decreases with frequency, and (iii) the beginning of the transition region at high frequencies.

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 proteins and sucrose stearate molecules adsorbed at the oil/water interface of the oil droplets which leads to the formation of an structural network (Franco et al., 1995b). However, this behavior is characteristic of emulsions stabilized not only by macromolecular emulsifiers but also by low molecular weight emulsifiers, such as CTAB (Ebert et al., 1988) or an high HLB sucrose ester (Guerrero et al., 1996) as the only emulsifiers used. The plateau modulus, G_N° , is defined as the extrapolation of the entanglement contribution to G' at high frequencies (Baumgaertel et al., 1992) and may be

calculated from the loss tangent ($\tan \delta$) as follows (Wu, 1989):

$$G_N^\circ = [G']_{\tan \delta \rightarrow \text{minimum}}$$

where $\tan \delta = G''(\omega)/G'(\omega)$. The confidence limit of G_N° is $\pm 4.3\%$. Although there are more accurate methods to calculate the plateau modulus, this method does not supply very different values despite its simplicity (Wu, 1989).

The influence of emulsion composition on the above-mentioned region may be easily characterized by calculating the linear relaxation spectra of these foodstuffs. Thus, the first-order approximation of Tschoegl (1989) was used, although the Tikhonov regularization method (Groetsch, 1984), calculated by using the software "Rheolab 2.0" (Madiedo, 1996), gives similar results (Franco, 1995).

An empirical model, given by De Rosa and Winter (1994) for polymer melts, has been used by Franco et al. (1995b) to successfully describe the experimental regions that appear in the linear relaxation spectra of this kind of emulsion as a function of processing variables:

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

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

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. This equation has also been used to fit the values of the relaxation spectra of the emulsions studied as a function of oil, emulsifier, and thickener concentrations ($r \geq 0.990$).

(i) *Influence of Oil Concentration.* Taking into account that the linear viscoelasticity functions always show a qualitatively similar frequency dependence, an empirical time-concentration superposition method has been applied, using the plateau modulus, G_N° , as normalization factor. Figure 1 shows the normalized dynamic master curves of the storage (G'/G_N°) and the loss (G''/G_N°) moduli for emulsions having different oil concentrations, as well as the corresponding linear relaxation spectra including the fitting to the BSW-CW model predictions. As may be observed in Figure 1a, the only significant influence of the oil concentration focuses on the values of the linear viscoelasticity functions, since G_N° increases with oil concentration. Nevertheless, Table 4 shows that there is an increase in the value of the slope of the plateau region, " n ", as oil concentration increases, which may be related to the development of an entanglement network. Thus, narrower droplet size and lower mean diameter (Table 1), in addition to a higher disperse volume fraction, yield stronger interparticle interactions (Rahalkar, 1992) which enhance the formation of a structural network and stability against creaming.

Figure 2 shows the normalized master curves of the storage and loss moduli, as well as the linear relaxation spectra, of emulsions containing different oil concentrations and 2 wt % starch. The influence of oil concentration on the linear viscoelasticity functions of emulsions containing starch is not very pronounced, showing a

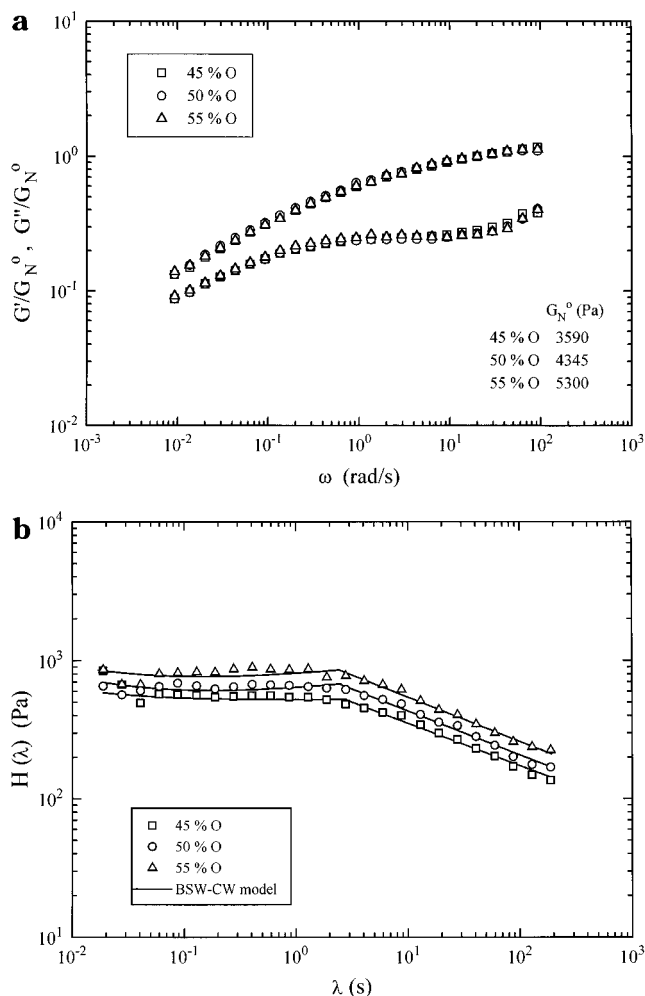


Figure 1. Influence of oil concentration on (a) the normalized viscoelasticity functions and (b) the relaxation time spectra, for free-starch emulsions (5% SE, 6% egg yolk).

Table 4. Some Parameters of Eq 2 for Emulsions Having Different Compositions (0% Starch)

oil concn (wt %)	sucrose stearate concn (wt %)	egg yolk concn (wt %)	λ_p (s)	n
45	5	6	2.76	0.009
50	3	6	4.05	-0.088
50	5	6	2.76	0.024
50	7	6	1.87	0.013
50	10	6	1.87	0.002
55	5	0	2.76	0.034
55	5	2	1.87	0.074
55	5	4	1.87	0.071
55	5	6	2.76	0.095

slight linear increase in the plateau modulus (Figure 2a). Likewise, the values of $H(\lambda)$ are very similar (Table 5) except for the less concentrated systems at the highest relaxation times because there is a sharp increase in the slope of their spectra. This increase in the slope is related to the beginning of the terminal region, where the BSW-CW model fails to describe the behavior of these emulsions. The dramatic change in the slope of this terminal region should be associated with the poorer elastic characteristics of the less concentrated emulsions (35 and 40 wt %).

In any case, there is no significant influence of the oil concentration on the relaxation time that defines the onset of the pseudo-terminal region of the relaxation spectra ($\lambda_p \approx 2.76$ s), as can be observed in Tables 4 and 5. This pseudo-terminal region always occurs for relaxation times inferior to the reciprocal of the crossover

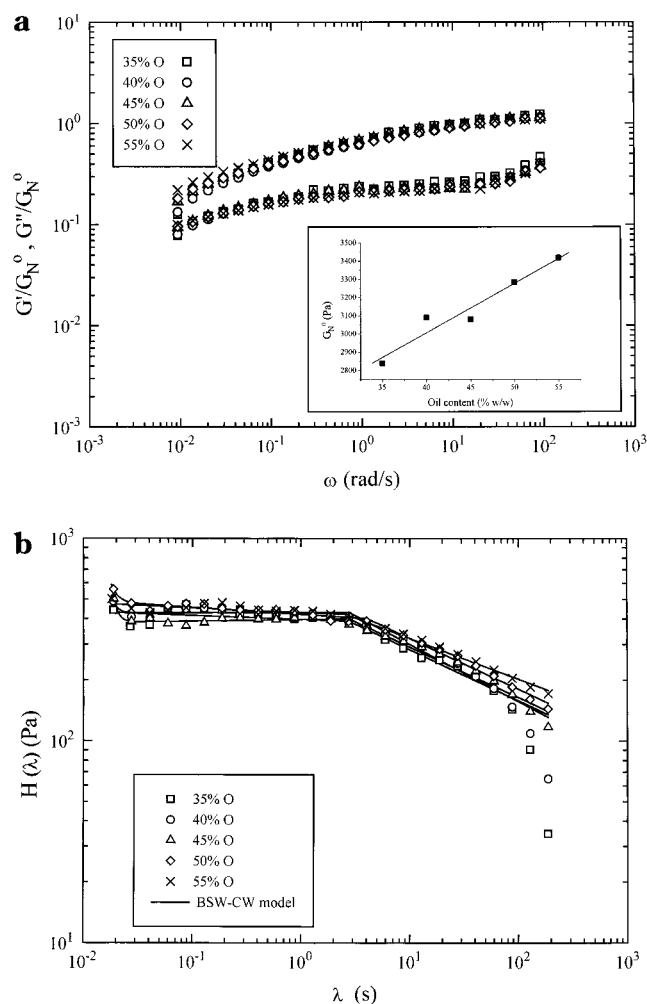


Figure 2. Influence of oil concentration on (a) the normalized viscoelasticity functions and (b) the relaxation time spectra, for emulsions containing 2 wt % starch (5% SE, 6% egg yolk).

Table 5. Some Parameters of Eq 2 for Emulsions Having Different Oil Contents (5% Sucrose Ester, 6% Egg Yolk, 2% Starch)

oil concn (% wt)	λ_p (s)	n
35	2.76	-0.019
40	2.76	0.001
45	2.76	0.008
50	4.04	-0.034
55	2.76	-0.015

frequency at which $G' = G''$, which defines the value of the terminal relaxation time.

(ii) *Influence of Sucrose Ester Concentration.* An increase in sucrose ester concentration yields effects similar to higher oil concentration, which means higher values of the linear viscoelasticity functions, G' and G'' . Figure 3a shows the normalized values of these viscoelasticity functions for emulsions that do not contain starch. Results obtained for emulsions containing less than 5 wt % sucrose ester have not been included in the Figure 3a because they cannot be superposed to the curves of the most concentrated systems, due to a significant variation in the frequency dependence of the viscoelasticity functions, showing an almost nonexistent plateau region, as may be noticed in Figure 3b. Furthermore, the plateau modulus is not sufficient to obtain a master curve, as a horizontal shift factor, a_x , is also necessary because of a frequency displacement of the plateau region. This fact is more clearly observed in Figure 3b, where the relaxation spectra of emulsions with different sucrose ester concentration are presented.

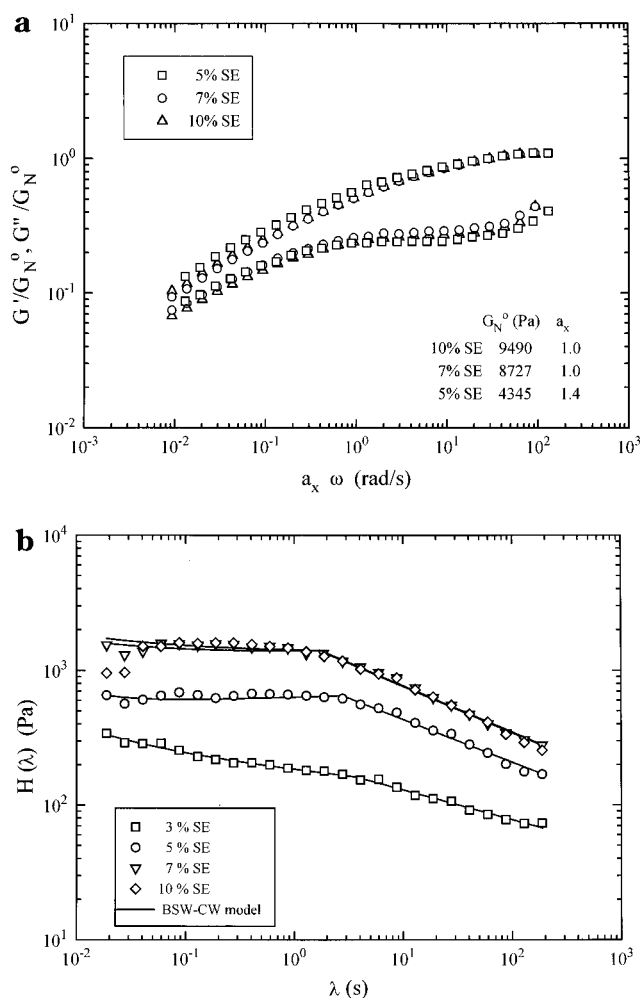


Figure 3. Influence of sucrose ester concentration on (a) the normalized viscoelasticity functions and (b) the relaxation time spectra, for free-starch emulsions (50% oil, 6% egg yolk).

It is evident that lower sucrose ester concentrations yield higher values of the relaxation time for the onset of the pseudo-terminal region (λ_p values in Table 4), which coincides with the tendency of the shift factor values, a_x , to decrease as sucrose ester concentration increases (Figure 3a). Likewise, the slope of the plateau region, " n ", changes from negative values (3 wt % sucrose ester) to positive (5 wt % sucrose ester), although a further decrease is noticed, which coincides with larger values of the Sauter diameter (7 and 10 wt % sucrose ester).

The addition of starch to these emulsions does not modify the influence of sucrose ester content on the linear viscoelasticity functions of these systems, which increase with sucrose ester concentration. Nevertheless, the superposition of the normalized viscoelasticity functions is seen to be quite good in the whole sucrose ester concentration range studied, although some scatter is observed in the plateau region (Figure 4a). Thus, the plateau region is displaced to higher frequencies as sucrose ester concentration increases, yielding lower values of λ_p and a_x and an increase in the slope of plateau region, " n " (Table 6 and Figure 4b). Consequently, for emulsions containing a mixture of both emulsifiers, an increase in sucrose ester concentration generally favors higher entanglement density, which leads to increasing positive values of the slope, " n ". Starch does not qualitatively modify this viscoelastic behavior.

However, λ_p is maximum for the emulsion that contains egg yolk as the only emulsifier (Table 5), which

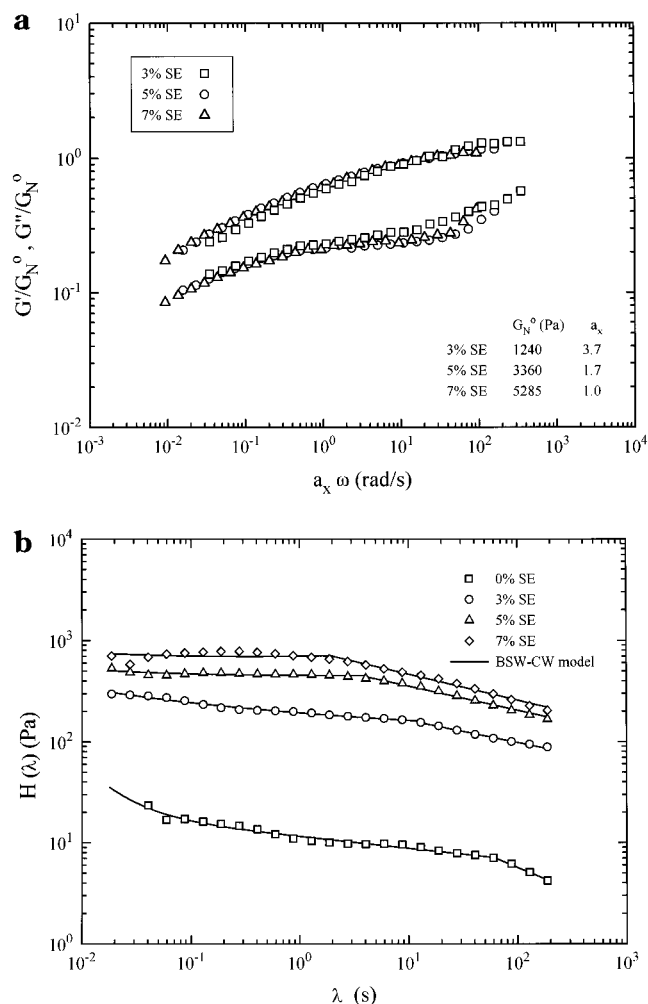


Figure 4. Influence of sucrose ester concentration on (a) the normalized viscoelasticity functions and (b) the relaxation time spectra, for emulsions containing 1 wt % starch (55% oil, 6% egg yolk).

Table 6. Some Parameters of Eq 2 for Emulsions Having Different Compositions (1% Starch)

oil concn (wt %)	sucrose stearate concn (wt %)	egg yolk concn (wt %)	λ_p (s)	n
55	0	6	59.32	-0.116
55	3	6	12.83	-0.053
55	5	6	4.04	0.011
55	7	6	2.16	0.054
55	5	0	0.19	<i>a</i>
55	5	2	2.76	-0.003
55	5	4	4.04	0.010
55	5	6	4.04	0.011

^a Not enough experimental data available in the plateau region.

implies more important elastic characteristics at high relaxation times. It is worth pointing out that the emulsifier adsorption at the oil/water interface of emulsions containing a mixture of emulsifiers having different molecular weights (sucrose stearate and egg yolk proteins and lipoproteins) results from a competition among all those types of molecules (Dickinson, 1989; Dickinson and Stainsby, 1987) which includes protein displacement from the interface to the continuous phase (Brock, 1987; Dickinson, 1994). An increase in sucrose ester concentration may favor the above-mentioned process. When protein molecules are adsorbed at the interface, they project numerous molecular segments or loops outward into the aqueous phase separating adjacent droplets. These segments may interlink oil droplets via hydrophobic bonds into a network with a weak

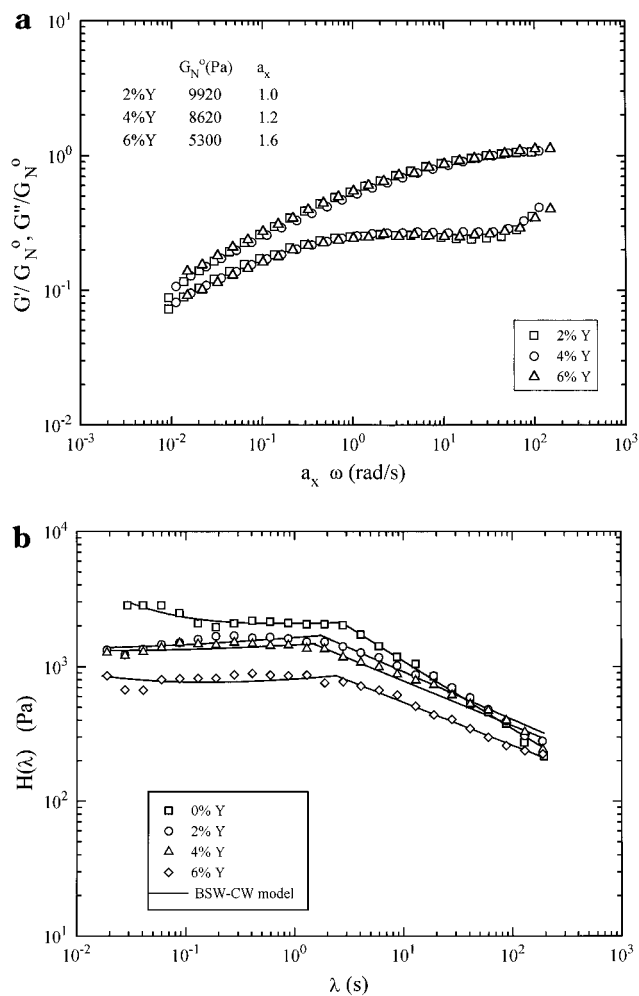


Figure 5. Influence of egg yolk concentration on (a) the normalized viscoelasticity functions and (b) the relaxation time spectra, for free-starch emulsions (55% oil, 5% SE).

gel-like structure (Van Vliet et al., 1978; Sonntang et al., 1982). However, the experimental results demonstrate that the protein displacement from the interface reduces the elastic characteristics of the emulsion but favors the development of an extensive entanglement network and the stability of the emulsion, probably due to the formation of tertiary entanglements involving nonadsorbed polymer chains, as it has been proposed for other dispersions (Aranguren et al., 1992).

(iii) *Influence of Egg Yolk Concentration.* Contrary to the above-mentioned effects of oil and sucrose ester concentration, an increase in egg yolk concentration produces a decrease in the values of the storage and loss moduli of emulsions with or without starch, as may be deduced from Figures 5a and 6a. Similar results have been obtained by other authors, analyzing the surface viscoelasticity of egg yolk films at the oil/water interface (Kiosseoglou and Sherman, 1983). Figures 5a and 6a show normalized master curves of G' and G'' as a function of egg yolk concentration. A horizontal shift factor, which increases with egg yolk concentration, has been also used to superpose the experimental curves. This means that the displacement of the plateau region is opposite to that produced by an increase in sucrose ester concentration.

For starch-free emulsions, Figure 5a, the normalized master curve, does not include the frequency dependence of the linear viscoelasticity functions corresponding to the system that contains sucrose ester as the only emulsifier. This is due to the appearance of a crossover frequency ($G' = G''$) in the experimental frequency range

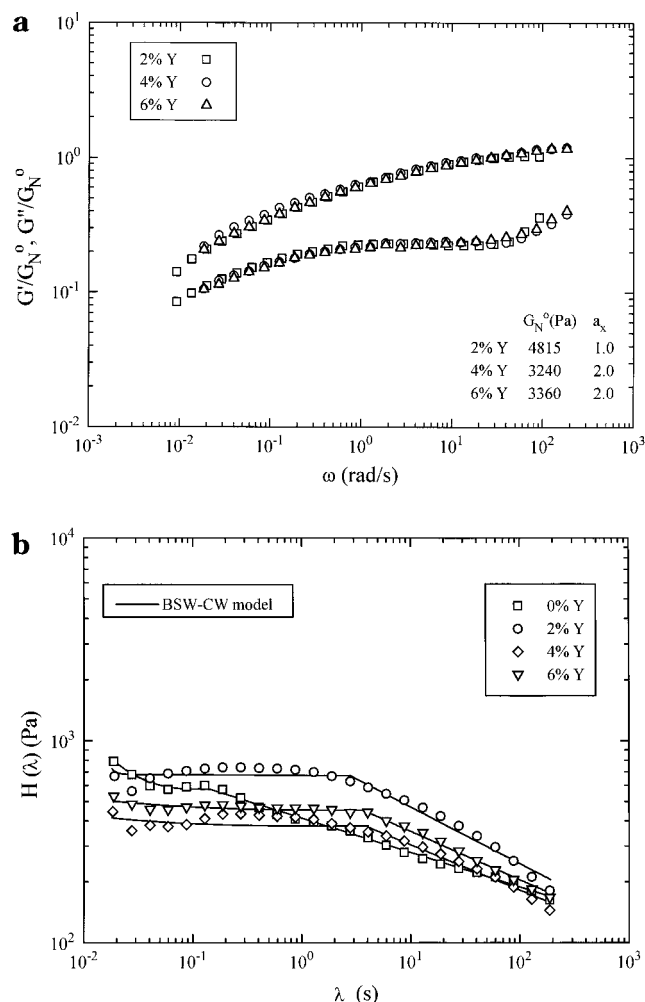


Figure 6. Influence of egg yolk concentration on (a) the normalized viscoelasticity functions and (b) the relaxation time spectra, for emulsions containing 1 wt % starch (55% oil, 5% SE).

studied, which makes the superposition less accurate. The increase in the slope of the plateau region when egg yolk is added to a starch-free emulsion (Figure 5b and Table 4) is also worth noting. On the other hand, the slope of the pseudo-terminal region for the egg yolk-free emulsion is much more pronounced due to the fact that a frequency crossover is found at low frequencies.

In the same way, Figure 6b demonstrates the singular behavior of the egg yolk-free emulsions for systems containing starch. There is a greatly reduced plateau region, and a clear transition region that does not appear in the remaining systems is noticed. It is also worth pointing out the increase in λ_p when egg yolk is added to these emulsions. Furthermore, a dramatic increase in the critical shear stress for the onset of the nonlinear viscoelasticity region is observed when egg yolk is added to the emulsion that only contains sucrose ester as emulsifier (Franco, 1995).

All of these results demonstrate that the addition of egg yolk favors the formation of an extensive structural network due to entanglements between protein molecules adsorbed at the oil/water interface of different droplets and/or among them and free protein molecules displaced to the continuous phase. It may be surprising that a higher concentration of egg yolk yields lower values of the linear viscoelasticity functions. In this sense, it has been suggested that optimum viscoelasticity was achieved at monolayer saturation. At higher protein concentrations the interfacial viscoelasticity decreases because slip planes develop at the interface

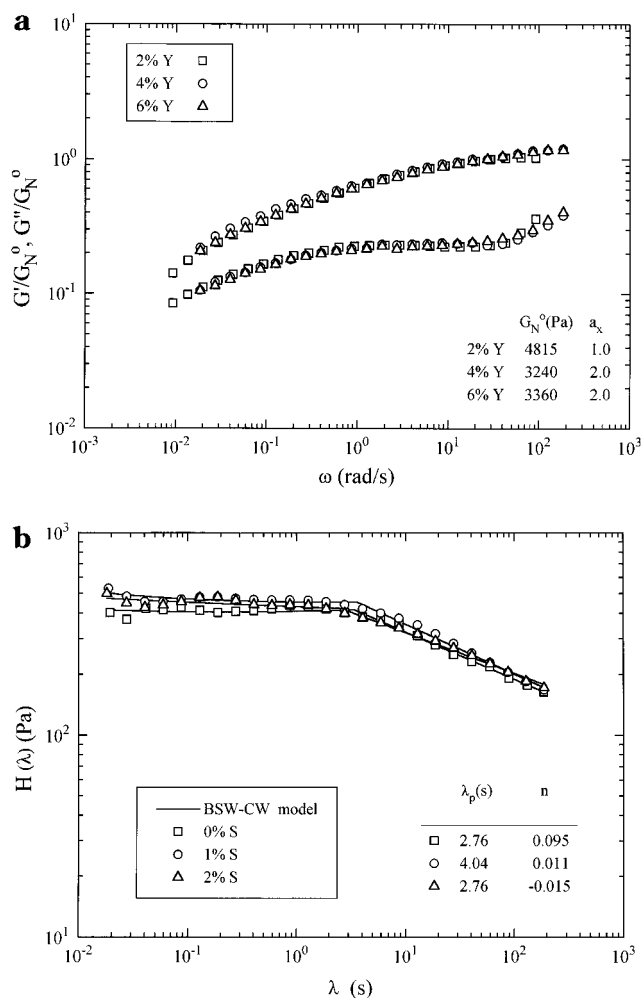


Figure 7. Influence of starch concentration on (a) the normalized viscoelasticity functions and (b) the relaxation time spectra of emulsions (55% oil, 5% SE, 6% egg yolk).

(Graham and Phillips, 1980). As has been reported by Dickinson and Hong (1995), the viscoelasticity of the emulsion structure depends on the surfactant/protein molar ratio. The crucial steps in changing the bulk rheology of the emulsions are the loss of surface viscoelasticity and the displacement of the adsorbed proteins, both effects being caused by the action of the surfactant.

(iv) *Influence of Starch Concentration.* The influence of starch concentration mainly affects the values of the linear viscoelasticity functions. There is a slight increase with starch content as may be deduced from the plateau modulus values (Figure 7a). Thus, the plateau region always occurs in the same frequency range, and the use of the plateau modulus as normalization factor is sufficient to obtain a master curve of the linear viscoelasticity functions. Consequently, the linear relaxation spectra of these systems are very similar, although the slope of the plateau region decreases continuously as starch concentration increases (Figure 7b).

The effect of a stabilizer, such as starch, on the rheological characteristics of the emulsions is to increase the viscosity of the continuous phase, reducing the creaming rate (Dickinson, 1988). Addition of starch slightly modifies emulsion droplet size and polydispersity, as can be deduced from the values of the Sauter diameter presented in Tables 1–3. Consequently, starch primarily favors the stability of the emulsion and enhances bulk steady-state viscosity due to the higher viscosity of the continuous phase (Franco, 1995). How-

ever, the decrease in the values of the slope of the plateau region may be related to a hindrance of oil droplet flocculation and, therefore, the formation of an extensive structural network. This can also explain the dramatic difference found in the relaxation spectrum of an egg-yolk-free emulsion containing starch. The presence of starch prevents the formation of a network due to interactions between sucrose ester molecules adsorbed at the oil/water interface of different droplets, and consequently, the plateau region almost vanishes. On the other hand, the above-mentioned decrease in the slope of the plateau region (Figure 7b) could also be associated to a thermodynamic incompatibility between starch and egg yolk proteins. As Dickinson (1988) stated, the formation of a phase-separated protein-polysaccharide complex around the droplets would improve the formation of a gel-like structure and, consequently, the development of the plateau region, contrary to the experimental results obtained. Nevertheless, further studies are being carried out to get experimental evidence on this matter with, much simpler, model systems.

LITERATURE CITED

- Aranguren, M. I.; Mora, E.; De Groot, J. V.; Macosko, C. V. Effect of reinforcing fillers on the rheology of polymers melts. *J. Rheol.* **1992**, *36*, 1165–1182.
- Baumgaertel, M.; De Rosa, M. E.; Machado, J.; Masse, M.; Winter, H. H. The relaxation time spectrum of nearly monodisperse polybutadiene melts. *Rheol. Acta* **1992**, *31*, 75–82.
- Brock, C. J. A model system for studying protein functionality in emulsions. In *Food Emulsions and Foams*; Dickinson, E., Ed.; Royal Society of Chemistry: London, 1987; p 277.
- Calahorra, M. C.; Muñoz, J.; Berjano, M.; Guerrero, A.; Gallegos, C. Flow behaviour of sucrose stearate/water systems. *J. Am. Oil Chem. Soc.* **1992**, *69*, 660–666.
- Cao, Y.; Dickinson, E.; Wedlock, D. J. Influence of polysaccharides on the creaming of casein-stabilized emulsions. *Food Hydrocoll.* **1991**, *5*, 443–454.
- Castelain, C.; Bronnec, I.; Genot, C.; Laroche, M. Flow behaviour and stability of concentrated oil-in-water emulsions. Effects of modified starch in aqueous phase. *Sci. Aliments* **1990**, *10*, 453, 463.
- Cavallo, J. L.; Chang, D. L.; Saleeb, F. Z. Formulation considerations in emulsion preparation and stability. *AIChE Symp. Ser.* **1990**, *86*, 16–24.
- Clark, D. C.; Wilde, P. J.; Wilson, D. R.; Wunsteck, R. C. The interaction of sucrose esters with β -casein from bovine milk. *Food Hydrocoll.* **1992**, *6*, 173–186.
- De Rosa, M. E.; Winter, H. H. The effect of entanglements on the rheological behavior of polybutadiene critical gels. *Rheol. Acta* **1994**, *33*, 220–237.
- Dickinson, E. The role of hydrocolloids in stabilising particulate dispersions and emulsions. In *Gums and Stabilisers for the Food Industry*; Wedlock, D. J., Williams, P. A., Eds.; IRL Press: Oxford, U.K., 1988; Vol. 4, pp 244–263.
- Dickinson, E. Food colloids—An overview. *Colloids Surf.* **1989**, *42*, 191–204.
- Dickinson, E. *An Introduction to Food Colloids*; Oxford University Press: Oxford, U.K., 1992.
- Dickinson, E. Interactions in protein-stabilized emulsions. In *Progress and Trends in Rheology, IV*; Gallegos, C., Ed.; Steinkopff: Darmstadt, Germany, 1994; pp 227–229.
- Dickinson, E.; Stainsby, G. Progress in the formulation of food emulsions and foams. *Food Technol.* **1987**, *41*, 75–81.
- Dickinson, E.; Hong, S. T. Influence of Water-Soluble Nonionic Emulsifier on the Rheology of Heat-Set Protein-Stabilized Emulsion Gels. *J. Agric. Food Chem.* **1995**, *43*, 2560–2566.
- Ebert, G.; Platz, G.; Rehage, H. Elastic and rheological properties of hydrocarbons gels. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1158–1164.
- Franco, J. M. Comportamiento viscoso y viscoelástico de emulsiones alimentarias del tipo salsa fina que contienen una mezcla de emulsionantes (Viscous and viscoelastic behavior of salad dressing emulsions containing a mixture of emulsifiers). Ph.D. Thesis, University of Seville, Seville, 1995.
- Franco, J. M.; Berjano, M.; Guerrero, A.; Muñoz, J.; Gallegos, C. Flow behaviour and stability of light mayonnaise containing a mixture of egg yolk and sucrose stearate as emulsifiers. *Food Hydrocoll.* **1995a**, *9*, 111–121.
- Franco, J. M.; Guerrero, A.; Gallegos, C. Rheology and processing of salad dressing emulsions. *Rheol. Acta* **1995b**, *34*, 513–524.
- Graham, D. E.; Phillips, M. C. Proteins and liquid interfaces. *V. J. Colloid Interface Sci.* **1980**, *76*, 240–250.
- Groetsch, C. W. *The theory of Tikhonov regularization for Fredholm equations of the first kind*; Pitman: London, 1984.
- Guerrero, A.; Partal, P.; Berjano, M.; Gallegos, C. Linear viscoelasticity of o/w sucrose-palmitate emulsions. *Prog. Colloid Polym. Sci.* **1996**, *100*, 246–251.
- Kiosseoglou, V. D.; Sherman, P. The influence of egg yolk lipoproteins on the rheology and stability of o/w emulsions and mayonnaise, 3. *Colloid Polym. Sci.* **1983**, *26*, 520–526.
- Madiedo, J. M. Caracterización reológica de emulsiones mediante espectros de relajación y retardación (Rheological characterization of emulsions by means of relaxation and retardation spectra). Ph.D. Thesis, University of Seville, Seville, 1996.
- Melik, D. H.; Fogler, H. S. Fundamentals of colloidal stability in quiescent media. In *Encyclopedia of Emulsion Technology, III*; Becher, P., Ed.; Marcel Dekker: New York, 1988; pp 3–78.
- Rahalkar, R. R. Viscoelastic properties of oil–water emulsions. In *Viscoelastic Properties of Food*; Rao, M. A., Steffe, J. F., Eds.; Elsevier: London, 1992; pp 317–354.
- Sonntang, H.; Ehmke, B.; Miller, R.; Knapschinsky, L. The properties of polyvinyl alcohol at the silica-water interface. In *The effects of polymers on the dispersion properties*; Tadros, Th., Ed.; Academic Press: London, 1982; pp 207–220.
- Spro, F. B. Distribution of drop sizes produced in turbulent liquid-liquid dispersion. *Chem. Eng. Sci.* **1967**, *22*, 435–442.
- Tadros, Th. F. Use of viscoelastic measurements in studying interactions in concentrated dispersions. *Langmuir* **1990**, *6*, 28–35.
- Tadros, Th. F. Fundamental principles of emulsion rheology and their applications. *Abstract of Papers*; First World Congress on Emulsions, Paris, 1993; pp 237–266.
- Tschoegl, N. W. *The Phenomenological Theory of Linear Viscoelastic Behaviour*; Springer-Verlag: Berlin and Heidelberg, 1989.
- Van Vliet; Lyklema, J.; Van den Tempel, M. Rheology of polyelectrolyte stabilized emulsions, II. Dynamic measurements. *J. Colloid Interface Sci.* **1978**, *65*, 505–508.
- Wu, S. Chain structure and entanglement. *J. Polym. Sci.* **1989**, *27*, 723–741.

Received for review July 18, 1996. Revised manuscript received November 20, 1996. Accepted November 20, 1996.® This work is part of a research project ALI 90-0503 sponsored by the CICYT (Spain) and by the Junta de Andalucía (Industrial Cooperation Program). The authors gratefully acknowledge their financial support.

JF9605355

® Abstract published in *Advance ACS Abstracts*, February 1, 1997.