Influence of Composition of Emulsifier Blends on the Rheological Properties of Salad Dressing-type Emulsions

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This paper deals with the influence that composition of emulsifier blends exerts on the rheological properties of low-in-fat salad dressing-type emulsions. Binary blends of egg yolk and different types of amphiphilic molecules (low-molecular weight and macromolecules) were used in several proportions to stabilize emulsions by keeping constant the total amount of emulsifier. The different emulsifiers added to egg yolk were pea protein, sodium caseinate, polyoxyethylene(20)-sorbitan monolaurate (Tween 20) and sucrose distearate. Steady state flow tests and small-amplitude oscillatory measurements within the linear viscoelasticity region were carried out. Rheological tests were complemented with droplet size distribution measurements and observation of physical stability against creaming of these emulsions. It was pointed out that rheological properties, droplet size and physical stability of the emulsions studied depended on the weight ratio of emulsifiers in the binary blends, although the emulsifier total concentration remained constant, as well as the nature of the substance blended with egg yolk. These results have been explained on the basis of the relationship among rheological properties, droplet size distribution, continuous phase characteristics and interactions among different emulsifier molecules.

Key Words: emulsifiers, emulsions, rheology, salad dressings

INTRODUCTION

Traditionally, egg yolk has been the most common emulsifying agent in foodstuffs like mayonnaise or salad dressings due to its favourable organoleptic and functional properties (Rao, 1992). It has been reported by several authors that the combination of lipoproteins and phospholipids (lecithin) in egg yolk provides the appropriate mixture or complexes for excellent emulsifying properties (Kilgore, 1935; Kiosseoglou and Sherman, 1983a,b; Mine, 1998). However, the use of another emulsifier in addition to egg yolk provides several advantages, like a decrease in cholesterol content and, in general, in fat content, an increase in microbiological stability and, in some cases, lower costs of manufacture. In this sense, several authors have intensively investigated in recent years the substitution, total or partial, of egg yolk by other surface-active materials and related physical mechanism of stabilization. Some of these substances are vegetable proteins, like soybean (Rivas and Sherman, 1982), faba bean (Sosulski and McCurdy, 1987), lupin (Raymundo et al., 1998, 1999, 2001) or pea proteins (Bower et al., 1999; Franco et al., 2000); proteins obtained from animal sources, like milk (Dickinson and Casanova, 1999; Stephen and Robyn, 1999; Mine and Keeratiurai, 2000; Hogan et al., 2001), meat proteins (Hogan et al., 2001; Imm and Regenstein, 1997) or low-molecular weight surfactants (Franco et al., 1995, 1997; Guerrero et al., 1998; Partal et al., 1999; Söderman and Johansson, 2000). However, little research has been conducted on the optimisation of different blends of emulsifier.

The use of vegetable proteins to stabilize foodstuffs has some additional advantages. They do not contribute to the cholesterol increase, and are technologically easier to handle as coagulation occurs at higher temperatures. They are also agricultural-strategically more interesting than animal proteins in order to revalorise some vegetable cultures. For instance, pea protein isolate is a natural vegetable extract with some nutritional qualities like the absence of lipids, but appropriate physical and functional properties such as good solubility in water (Sosulski and McCurdy, 1987), high oil in water emulsifying power (Naczk et al., 1986; Koyoro and Powers, 1987; Sosulski and McCurdy, 1987) and stability to high temperatures or good foaming capacity (Fernández-Quintela et al., 1997). Pea seed proteins: are composed of two families of proteins, globulins (80–90% w/w) and albumins (10–20% w/w), (Gwiazda et al., 1980).
Globulins are made of two major proteins, legumin and vicilin, being approximately its average ratio 1:1. Beside these, a third globulin, convicilin, is also present in small quantities (Gueguen et al., 1984).

In addition to egg yolk, the most interesting animal protein from a functional point of view is sodium caseinate, the commercial form of caseins. This protein is widely used as ingredient in food processing to provide properties such as water holding, thickening, gelation, fat binding and, specially, emulsification (Dickinson and Casanova, 1999; Dickinson et al., 1999; Hogan et al., 2001). Around 3/4 of the total protein in sodium caseinate is a mixture of \( \alpha_{s1} \)-casein and \( \beta \)-casein in similar proportions.

The effect of using a mixture of different types of proteins in the properties of oil-in-water emulsions is open to discussion. Several authors reported that it might lead to a synergistic interaction, providing an improvement in the quality of the final product (Clark et al., 1992; Carrera, 2000) whereas other authors showed that it might lead to some deterioration in performance. The origin of this deterioration may be due to more disorganisation of both kind of proteins at the interface (Dagorn-Seaviner et al., 1987; Castle et al., 1988; Dickinson et al., 1989) and either thermodynamic incompatibility between them (Polyakov et al., 1997) or competitive adsorption of these protein molecules at the interface (Dickinson et al., 1990; Mine and Keeratiurai, 2000).

Sucrose esters are being increasingly used in the food industry. Its low toxicity allows its use in cosmetic, pharmaceutical or food applications. These substances can be synthesized from agricultural subproducts and sucrose (Megahed, 2000). From a functional point of view, the main advantages are their high surface-activity and the possibility of getting a wide range of hydrophilic–lipophilic balance (HLB) values by combining different lengths of fatty acid chains or different esterification degrees (Gallegos and Berjano, 1991). On the other hand, the tweens family are considered to be classical emulsifiers in the food industry with a great number of applications since their hydrophilic character can be selectively enhanced substituting different numbers of polyoxyethylene chains of different length in hydroxy groups, which results in several kinds of Tweens, like Tween 20, Tween 60 or Tween 80.

The behaviour of oil-in-water emulsions stabilized by proteins and low-molecular surfactants blends is controlled by the nature of the interactions between proteins and surfactants at the oil–water interface as well as the phase behaviour of the low-molecular weight emulsifier/water system (Raymundo et al., 1999). As a general rule, simple non-ionic surfactants at high concentrations displace proteins from the interface because they lower the interface tension (Dickinson et al., 1999; Carrera, 2000). However, several cases of coexistence of proteins and surfactants at the interface, in which surfactant molecules may fill the gaps in the adsorbed protein layers or interact with protein molecules, have also been reported, leading to a stronger and more viscoelastic interfacial layer (Coke et al., 1990; Clark et al., 1992; Carrera, 2000; Fillery-Travis et al., 2000). In addition to this, these different mechanisms of interaction may also depend on the ratio of both kinds of emulsifiers in the mixture as previously shown for vegetable protein and several surfactants (Raymundo et al., 1999).

Taking into account these considerations, the overall objective of this research was to study the influence of composition of several binary blends on some physical properties such as droplet size distribution and rheological behaviour of o/w emulsions with a formulation similar to those commercialised as salad dressings, being the emulsifier blends composed by egg yolk in every case and another surface-active component of different nature.

**MATERIAL AND METHODS**

**Materials**

Pea protein isolate (purity > 88%) and sodium caseinate (purity > 90%) were purchased from Cosucre, S.A. (Belgium) and Pronanda, S.L. (Spain) respectively. Tween 20 (sorbitan polyoxyethylene(20) monolaurate) and the sucrose distearate, chemically consisting in a sucrose ester from palmitic and stearic acid (commercially SP40), were used as received from Sigma-Aldrich (Germany) and Sisterna, C.V. (Holland) respectively. Egg yolk was kindly supplied by Hijos de Ybarra S.A. (Spain) after the application of a pasteurisation treatment. The rest of ingredients below indicated were also supplied by Hijos de Ybarra S.A. (Spain).

**Methods**

**Emulsion Preparation**

Food emulsions with a composition similar to commercial salad dressings were prepared. Sunflower oil concentration was set at 35% and total emulsifier content was fixed at 8% (all concentrations expressed by weight). Egg yolk and the second emulsifier weight ratios were 8:0, 7:1, 6:2, 4:4, 2:6, 1:7, 0:8. The different emulsions manufactured are denoted by 8Y-0E, 7Y-1E, 6Y-2E, 4Y-4E, 2Y-6E, 1Y-7E, 0Y-8E, where ‘Y’ indicates egg yolk, and ‘E’, must be substituted by ‘P’, in emulsions containing pea protein, ‘C’, in emulsions containing sodium caseinate, ‘T’, in those with Tween 20 and, finally, ‘S’, in emulsions containing sucrose distearate. Other ingredients added to the emulsions were 4% commercial sugar, 4% wine vinegar (acidity: 10.3% w/v in acetic acid), 0.4% salt, 1–2.5% modified
maize starch and the corresponding amount of distilled water to complete the formulation. As a preliminary step to emulsification, mixtures of starch, sugar and water were heated under gentle mechanical stirring until the gelation temperature of these mixtures (≈80°C) was achieved. Pea protein was also dispersed in water, heating to 70°C in order to favour a certain degree of denaturation (Franco et al., 2000). Dispersions of sucrose distearate in water were kept 24 h at 60°C for a better solubilization, whereas Tween 20 and sodium caseinate were easily dispersed at room temperature. Emulsions were manufactured using a pilot-plant colloidal mill, model “Delmix MZM/VK-7”, from Fryma (Germany). It worked at a constant rotational speed of 2830 rpm and the residence time was 5 min in all cases. Emulsions prepared were stored in a refrigerator at 4°C.

Rheological Tests

Rheological measurements were carried out in a controlled-stress rheometer, RS100 from Haake (Germany). A plate-plate geometry (PPR35; 35 mm diameter) with rough surfaces (roughness: 0.4 mm) was used in order to avoid wall-slip phenomena in steady-state flow measurements (Sánchez et al., 2001). Steady-state flow measurements were sometimes completed using a controlled-shear rate viscosimeter CV100 (Haake, Germany) using a rough surfaces plate–plate sensor system as well (PPR20; 20 mm diameter). Oscillatory tests were performed in a controlled-stress rheometer, RS100 from Haake (Germany) using a cone–plate sensor system (60 mm diameter, 4° angle). Rheological tests were made at 25°C.

Droplet Size Distribution (DSD) Measurements and Physical Stability

Ageing stability was visually determined by observing the bottom of the samples located in a 100 mL glass (30 mm diameter) cylinder. The appearance of a layer of water was chosen as a criterion of instability. DSD were determined in a range of droplet size between 0.2 and 150 μm by laser light scattering using a Malvern Mastersizer-X analyser (Malvern, UK) in the Fourier conformation (focus: 100 mm). Values of the Sauter mean diameter, which is inversely proportional to the specific surface area of droplets, were obtained as follows:

\[ d_{3,2} = \frac{\sum n_id_i^3}{\sum n_id_i} \]  

(1)

where \( n_i \) is the number of droplets with a diameter \( d_i \).

All measurements were carried out 6 days after emulsions manufacture, so that the properties of emulsions with a lower stability period are not reported in this paper. Measurements were replicated at least three times. Statistical analysis (ANOVA) was performed in order to establish the influence of the different variables. The significance level was set at 95%.

RESULTS

Viscous Flow

All the emulsions studied showed the same qualitative steady-state flow behaviour in which a shear-thinning behaviour, with a tendency to a zero-shear rate-limiting viscosity, \( \eta_0 \), at low shear rates and a slight tendency to a high-shear rate-limiting viscosity, \( \eta_\infty \), may be observed. This behaviour can be related with a mechanism of oil droplet deflocculation, as previously pointed out (Gallegos and Franco, 1999). The Carreau model fit fairly well the foregoing behaviour:

\[ \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[ 1 + (\dot{\gamma}/\dot{\gamma}_c)^2 \right]^{\gamma} \]  

(2)

where \( \dot{\gamma}_c \) is the critical shear rate for the onset of the shear thinning region, and \( \gamma \) is a parameter related to the slope of this intermediate region (Figure 1). The values of the steady-state viscosity clearly depended on the weight ratio of emulsifiers blended (i.e. egg yolk/other emulsifier weight ratio). In the case of using egg yolk/pea protein or egg yolk/caseinate blends, viscosity values were maximum for emulsions stabilized only by one of these components and passed through a minimum for emulsions stabilized by blends of both types of macro-molecular emulsifiers. In emulsions containing pea protein, small quantities of egg yolk yielded a decrease in viscosity up to a minimum value found when both emulsifiers were present at the same concentration (4:4). Nevertheless, emulsions stabilized by egg yolk and sodium caseinate reached the lowest value of viscosity at a 1:7 egg yolk/caseinate ratio. On the contrary, emulsion viscosity continuously increased with egg yolk/Tween-20 weight ratio or decreases with egg yolk/sucrose ester weight ratio in the emulsifier blend.

Dynamic Viscoelastic Measurements

All emulsions showed a predominantly elastic response, showed most of them an apparent plateau region in the experimental frequency range studied (Figures 2–5). This plateau region is characterized by the appearance of a minimum in \( G'' \) at intermediate frequencies and a plateau region in \( G' \) (i.e. slope values around 0.1). The appearance of this plateau region has been related to an extensively flocculated microstructure which occurs as a result of different interactions among the emulsifier molecules located at the oil–water
interface of adjacent droplets and non-adsorbed molecules present in the continuous medium (Gallegos and Franco, 1999; Franco et al., 2000). Although this behaviour is typically found in highly concentrated emulsions, such as commercial or model mayonnaises (Bower et al., 1999, Moros et al., 2002) it has been also found in relatively low-in-oil salad dressing-type emulsions (Franco et al., 1995).

Composition of the emulsifier blends used to stabilize the emulsions affected the viscoelastic properties of emulsions, although total emulsifier content remained constant, leading to both a quantitative change in the absolute values of the linear viscoelastic functions and a qualitative change in the evolution of these functions with frequency. It was also found that the influence of the weight ratio in emulsifier blends depended on the kind of emulsifier blended with egg yolk. Thus, different behaviours were found for emulsions stabilized by protein blends (egg yolk and pea protein or sodium caseinate), mixtures composed by egg yolk and a low-molecular weight surfactant with a high value of HLB (Tween 20) or by egg yolk and a low-molecular weight surfactant with a medium value of HLB (sucrose distearate). The absolute values of the linear viscoelastic functions obtained in dynamic measurements, $G'$ and $G''$ (Figures 2–5), presented a similar evolution with the composition of emulsifier blends to that found in the viscosity values. In addition to this, the appearance or the extension of the plateau region highly influenced by this composition. The modification of the weight ratio

**Figure 1.** Influence of composition of emulsifier blends on steady-state viscosity and zero-shear rate-limiting viscosity. (a): (□) 0Y-8P, (○) 1Y-7P, (△) 2Y-6P, (▽) 4Y-4P, (◇) 6Y-2P, (+) 7Y-1P (×) 8Y-0P; (b): (□) 0Y-8C, (○) 1Y-7C, (△) 2Y-6C, (▽) 4Y-4C, (◇) 6Y-2C, (+) 7Y-1C, (×) 8Y-0C; (c): (□) 2Y-6T, (○) 4Y-4T, (△) 6Y-2T, (▽) 7Y-1T, (◇) 8Y-0T; (d): (□) 0Y-8S, (○) 1Y-7S, (△) 2Y-6S, (▽) 4Y-4S, (◇) 6Y-2S, (+) 7Y-1S, (×) 8Y-0S. (—) Carreau’s model fittings.
The blending of both types of emulsifiers yielded a qualitative change in the evolution of both viscoelastic functions with frequency. Thus, for instance, the mechanical spectra of emulsions stabilized mainly by one type of macromolecular emulsifier showed a well-extended plateau region but, on the contrary, there was a tendency to a crossover of both viscoelastic functions, at low frequencies, when both type of emulsifiers are blended. This tendency was more noticeable in emulsions stabilized by 4Y:4P and 1Y:7C blends. This fact suggested the existence of a more developed three-dimensional internal structure when one of them is used alone. In addition to this, qualitative changes in viscoelastic properties are related to the evolution of loss tangent. The evolution of the loss tangent for most of the emulsions showed a minimum in the frequency range studied, which is related to the appearance of the plateau region. From the observation of these curves, it is possible to conclude that emulsions with a higher relative elastic response are those stabilized mainly by pea protein, sodium caseinate or egg yolk. On the contrary, mixing both kinds of emulsifiers in similar proportions yields emulsions with higher values of loss tangent and, consequently, higher relative

**Figure 2.** Viscoelastic properties of emulsions stabilized by egg yolk and pea protein blends, and 1% starch. (a) Evolution of $G'$: (■) 0Y-8P, (●) 1Y-7P, (▲) 2Y-6P, (▼) 4Y-4P, (◆) 6Y-2P, (+) 7Y-1P, (▲) 8Y-0P; and $G''$: (□) 0Y-8P, (○) 1Y-7P, (△) 2Y-6P, (▼) 4Y-4P, (◇) 6Y-2P, (×) 7Y-1P, (−) 8Y-0P; (b) Evolution of $\tan \delta$: (□) 0Y-8P, (○) 1Y-7P, (▲) 2Y-6P, (▼) 4Y-4P, (◇) 6Y-2P, (+) 7Y-1P, (×) 8Y-0P.

**Figure 3.** Viscoelastic properties of emulsions stabilized by egg yolk and sodium caseinate blends and 1% starch. (a) Evolution of $G'$: (■) 0Y-8C, (●) 1Y-7C, (▲) 2Y-6C, (▼) 4Y-4C, (◆) 6Y-2C, (+) 7Y-1C, (▲) 8Y-0C; and $G''$: (□) 0Y-8C, (○) 1Y-7C, (△) 2Y-6C, (▼) 4Y-4C, (◇) 6Y-2C, (×) 7Y-1C, (−) 8Y-0C; (b) Evolution of $\tan \delta$: (□) 0Y-8C, (○) 1Y-7C, (▲) 2Y-6C, (▼) 4Y-4C, (◇) 6Y-2C, (+) 7Y-1C, (×) 8Y-0C.
viscous character. Nevertheless, when egg yolk and a low-molecular weight surfactant are blended, high values of egg yolk/low-molecular weight surfactant weight ratios lead to a decrease in the values of the loss tangent (i.e., higher elastic response) especially at low frequencies.

**DISCUSSION**

As several authors have previously reported, the above-mentioned results may be explained according to changes in several structural parameters, which affect the bulk rheology of emulsions, such as droplet size distribution (Sánchez et al., 2000; Moros et al., 2002), rheology of the continuous phase (Barnes, 1994; Gallegos et al., 1996), interparticle interactions (Kiosseoglou and Sherman, 1983a; Dickinson and Casanova, 1999; McClements, 1999) and interactions of molecules at the interface, related to the interfacial viscoelasticity (Graham and Phillips, 1980; Kiosseoglou and Sherman, 1983b,c). Concerning droplet size distribution (Figure 6) emulsions generally tended to smaller sizes and narrower distributions as egg yolk concentration increases, except

**Figure 4.** Viscoelastic properties of emulsions stabilized by egg yolk and Tween 20 blends and 2.5% starch: (a) Evolution of $G'$: (■) 2Y-6T, (●) 4Y-4T, (▲) 6Y-2T, (▼) 7Y-1T, (◆) 8Y-0T; and $G''$: (□) 2Y-6T, (○) 1Y-7P, (△) 6Y-2T, (▼) 7Y-1T, (○) 8Y-0T; (b) Evolution of $\tan \delta$: (□) 2Y-6T, (●) 4Y-4T, (▲) 6Y-2T, (▼) 7Y-1T, (○) 8Y-0T.

**Figure 5.** Viscoelastic properties of emulsions stabilized by egg yolk and sucrose distearate blends and 2% starch: (a) Evolution of $G'$: (■) 0Y-8S, (●) 1Y-7S, (▲) 2Y-6S, (▼) 4Y-4S, (◆) 6Y-2S, (+) 7Y-1S, (△) 8Y-0S; and $G''$: (□) 0Y-8S, (○) 1Y-7S, (△) 2Y-6S, (▼) 4Y-4S, (◆) 6Y-2S, (∗) 7Y-1S, (–) 8Y-0S; (b) Evolution of $\tan \delta$: (□) 0Y-8S, (○) 1Y-7S, (△) 2Y-6S, (▼) 4Y-4S, (◆) 6Y-2S, (+) 7Y-1S, (∗) 8Y-0S.
for emulsions containing egg yolk and Tween 20, that showed the opposite tendency. Values of the Sauter mean diameter showed the same trend. This fact could be explained by the smaller size of Tween 20 molecules, which favoured the diffusionalong the continuous phase, reaching the oil–water interface faster than macromolecules. Moreover, low-molecular weight surfactants did not require a molecular rearrangement as they locate at the interface (Fillery-Travis et al., 2000). Consequently, they can stabilise just-formed interface during the emulsification process faster than protein molecules. This hypothesis failed in the case of emulsions stabilized by egg yolk and sucrose distearate. The reason of the different behaviour shown by these emulsions can be related with the HLB value. Thus, like other surfactants with medium or low HLB values, due to its lower solubility in water, sucrose distearate was able to form a highly viscous gel-like structure in aqueous medium, which acts as a hydrodynamic barrier to the disruption of oil droplets (Gallegos et al., 1996; Raymundo et al., 1999; 2001). On the other hand, the high concentration of surface-active components of egg yolk, including low-molecular weight emulsifier like phospholipids, provides excellent emulsifier properties, better than other protein isolates. This fact could explain the lower droplet sizes and narrower distributions reached when egg yolk

Figure 6. Influence of composition of emulsifier blends on droplet size distributions and Sauter diameter: (a): (□) 0Y-8P, (○) 1Y-7P, (△) 2Y-6P, (▽) 4Y-4P, (◇) 6Y-2P, (+) 7Y-1P, (×) 8Y-0P; (b): (□) 0Y-8C, (○) 1Y-7C, (△) 2Y-6C, (▽) 4Y-4C, (◇) 6Y-2C, (+) 7Y-1C, (×) 8Y-0C; (c): (□) 2Y-6T, (○) 4Y-4T, (△) 6Y-2T, (▽) 7Y-1T, (◇) 8Y-0T; (d): (□) 0Y-8S, (○) 1Y-7S, (△) 2Y-6S, (▽) 4Y-4S, (◇) 6Y-2S, (+) 7Y-1S, (×) 8Y-0S.
concentration increases in relation to pea protein or sodium caseinate concentrations.

It is a well-known fact that fine emulsions with narrow distributions yield higher values of most rheological parameters and more elastic features than coarse emulsions with broad distributions (Guerrero et al., 1998; Rahalkar, 1992; Sánchez et al., 2000). Then, it could be expected that an increase in egg yolk content when it is blended with other proteins or sucrose distearate yields an increasing emulsion viscosity and linear viscoelastic properties. Nevertheless, as previously shown, some rheological parameters of emulsions containing egg yolk/pea protein or egg yolk/caseinate blends presented an intermediate minimum value whereas viscous and viscoelastic functions of emulsions containing sucrose distearate continuously decrease with egg yolk concentration. Consequently, it seems clear that droplet size distribution cannot be the only variable which justifies the obtained rheological results. Other structural parameters, like the continuous phase rheology and interparticle interactions seemed to develop a crucial role.

Droplet size distribution and rheological properties are interrelated as expected in emulsions stabilized by mixtures of both egg yolk and pea protein and sodium caseinate, when egg yolk was the main emulsifier. Nevertheless, an increasing pea protein concentration led to higher viscosity values, probably produced by the high viscosity of the continuous phase, promoted by an important amount of unabsorbed pea protein. The rather high temperatures at which pea protein was dispersed, provoked a significant denaturation process, which improved the rheological characteristics of these emulsions (Franco et al., 2000). The same explanation could be used for egg yolk/caseinate-stabilized emulsions. However, a different mechanism seems to govern these systems. The extremely high values of viscosity and viscoelasticity of the emulsion stabilized exclusively by sodium caseinate and the following dramatic decrease in the rheological parameters observed, when formulation had contained small amounts of egg yolk, could be attributed to a depletion flocculation mechanism. The high proportion of hydrophobic amino acid side chains throughout the casein primary structure caused the formation of sodium caseinate aggregates in aqueous media (Dickinson and Golding, 1997), which favours this particular flocculation mechanism, extensively described by several authors (Sperry, 1982; McClements, 2000), and enhances an extensive flocculated microstructure with a higher density of entanglements among droplets called a particulate network (Cao et al., 1990; Dickinson and Golding, 1997). The replacement of a very small fraction of milk protein by egg yolk proteins caused a displacement of caseinate from the interface by egg yolk components, since these were more surface active than sodium caseinate (Mine and Keeratiurai, 2000). If more sodium caseinate is replaced by egg yolk, the rheological parameters of emulsions continuously increased with egg yolk concentration, since droplet sizes reached lower values. This behaviour was very similar to that observed by Mine and Keeratiurai (2000), in oil-in-water emulsions stabilized by mixtures of sodium caseinate and LDL or egg yolk granules.

The increase in the rheological parameters of emulsions containing a mixture of egg yolk and sucrose distearate, when egg yolk is partially replaced by the low-molecular surfactant, must be explained taking into account the high viscosity that this surfactant confers to the continuous medium (7000 Pa s at 3×10⁻⁵/s) (Gallegos et al., 1996; Raymundo et al., 1999, 2001) and not by an enhancement of particle interactions. However, in spite of the high steady-state viscosity, dynamic viscoelastic response of emulsions containing higher levels of sucrose distearate were characterized by a clear tendency to a crossover of both viscoelastic functions in frequency sweep tests, showing a lower relative elastic character in almost all the frequency range studied (Figure 5b). On the contrary, emulsions containing a higher proportion of egg yolk displayed a plateau region, which corresponds to a highly flocculated state, as a result of the formation of physical entanglements among protein molecules adsorbed or non-adsorbed at the interface. This fact was also favoured by the lower droplet diameters observed. On the other hand, an increase in egg yolk concentration always produced higher values of viscosity and viscoelastic functions in emulsions stabilized by egg yolk and Tween 20 blends, in spite of the higher droplet sizes observed. In this case, it must be noticed that Tween 20 is highly soluble in water yielding a much less viscous continuous medium (≈3000 Pa s at 3×10⁻⁵/s, in spite of a higher content in starch).

As previously summarized (Gallegos and Franco, 1999) the relationship between structural parameters and rheology affect significantly physical stability of emulsions. Creaming stability periods were longer as egg yolk content increased respect to the second emulsifier, except for those emulsions containing pea protein (Table 1). This evolution did not only depend on droplet size and bulk rheological properties of emulsions. As previously mentioned, bridging flocculation is favoured by egg yolk components. Although droplets flocculation usually acts like a destabilization process, since droplets aggregates can move along the continuous phase at higher speed than individual droplets, it may constitute a stabilization process when the flocculation is extensive enough to induce droplets to form a structural network which disables droplets movement (Cao et al., 1990; Franco et al., 1997). Hence, this could be the most relevant factor which affects the stability of emulsions containing egg yolk and sodium caseinate, Tween 20 or sucrose distearate blends, and not the reduction in droplet sizes produced by an increase in
Tween 20 concentration nor the enhancement in viscosity produced by an increase in sucrose distearate concentration, although this latter effect may be considered an additional stabilizing effect as shown in Table 1. It must be noticed again that emulsions exclusively stabilized by sodium caseinate were able to flocculate by a depletion mechanism. Since this kind of flocculation was weak and reversible, this emulsion is extremely unstable (Cao et al., 1990; Dickinson and Golding, 1997; Sperry, 1982). On the other hand, creaming stability period for emulsions stabilized by egg yolk and pea protein blends pass through a minimum when both kinds of emulsifiers were blended at similar concentrations. In this sense, several authors have found that the use of a mixture of proteins as emulsifier can lead to a decrease in the emulsifier activity and emulsion stability, rather an improvement, due to the formation of weaker and more disordered mixed interfacial layers (Dagorn-Scaviner et al., 1987; Castle et al., 1988; Imm and Regenstein, 1997). Moreover, different proteins can show thermodynamic instability, due to their different conformational states, favouring the self-association of molecules of the same kind and leading to the instability of emulsions (Polyakov et al., 1997). This hypothesis is also confirmed by the experimental rheological results shown in this work.

Finally, taking into account the rheological results, the stability periods and some structural considerations previously discussed, the convenience of replacing egg yolk, totally or partially, by pea protein must be emphasized. Thus, the use of blends, with high weight ratios of pea protein/egg yolk, leads to emulsions with similar or improved rheological characteristics and better physical stability than egg yolk-stabilized emulsions. The manufacture of emulsions stabilized only by pea protein may interestingly result in free-cholesterol products. In addition to this, the replacement of small quantities of egg yolk by sucrose distearate may be considered in order to increase some rheological parameters without loss of stability.

### REFERENCES


