Influence of Semicontinuous Processing on the Rheology and Droplet Size Distribution of Mayonnaise-like Emulsions

C. Bengoechea, M.L. López, F. Cordobés and A. Guerrero*

Departamento de Ingeniería Química, Universidad de Sevilla
Facultad de Química. Profesor García González 1, 41012 Sevilla Spain

Oil-in-water (o/w) emulsions stabilized by egg yolk, with a composition similar to those found in commercial mayonnaises or salad dressings, were processed in a semicontinuous device. This specially designed emulsification device consists of, basically, a vessel provided with an anchor impeller, where the continuous phase was initially placed; a pumping system that controls the addition of the oily phase; a rotor-stator unit, where the major breaking of the oily droplets takes place, and a recirculation system. The design allowed the introduction of a rotational rheometer to obtain viscosity data along the emulsification process. The most important advantages of this in-line emulsification device, when compared to discontinuous emulsification equipment, are the possibilities of recording viscosity data along the process and the higher values for the storage, G', and loss moduli, G'', of the resulting emulsions. The influence of egg yolk concentration, agitation speed, and flow rate over the rheological properties (G', G'') as well as droplet size distribution were investigated. Higher protein concentration, agitation speed and flow rate generally produce emulsions with higher G' and G'' values.

Key Words: emulsion, emulsification, particle size distribution, linear viscoelasticity, flow properties

INTRODUCTION

Commercial food emulsions (mayonnaise, salad dressings, and creams) are complex systems in which one phase (i.e. oil phase for oil-in-water (o/w) emulsions) is dispersed in the form of small droplets into a continuous phase. Such systems must exhibit high long-term stability in order to find a suitable applicability. Processing conditions such as energy input, temperature, mixing time, impeller geometry, etc., are extremely important due to their decisive influence on both microstructure and rheological properties of the final emulsions, and as a consequence, on their stability. The presence of proteins or low molecular weight emulsifying agents in the formulation of the emulsion is a key factor to ensure the required long-term stability (Rahalkar, 1992; McClements, 2004). In this work egg yolk proteins have been used as emulsifying agents of concentrated o/w food emulsions (60–80 wt%), as they are exceptionally good emulsifying agents, being traditionally used in the food industry. Low-density lipoproteins (LDL) are their main constituent and they provide a greater emulsifying activity and emulsion stability than egg lecithin (Mizutany and Nakamura, 1984; Martinet et al., 2005). LDL are spherical particles of about 35 nm in diameter, consisting of a core of triglycerides, cholesterol and cholesteryl esters, surrounded by a monolayer of phospholipids in which apoproteins are embedded. Proteins and phospholipids result from the break down of LDL micelles. They are adsorbed at the oil-water interface, forming a film that allows the stability of emulsions (Martin et al., 1964; Garland, 1973; Kiosseoglou, 1989).

There are different emulsification systems, though the most frequent ones are the rotor-stator systems (toothed disc dispersing machine, colloid mill) and high-pressure homogenizers. The choice of one emulsification system or another depends on several factors, such as oil volume fraction, or desired droplet diameters, (Walstra, 1983). In the present study, a lab-scale semicontinuous emulsification device, provided with a rotor-stator unit has been used. This device allows for a good mixing of the emulsion, as well as for the application of a high energy density during the emulsification process. It also provides an interesting tool for the study of different parameters along the emulsification process by means of an in-line rheometer, which permits us to monitor the viscosity of the forming emulsion. Some of the variables that may be controlled in the emulsification process are: emulsion composition, oil phase flow rate, temperature, residence time, and energy input in the emulsification chamber.

**To whom correspondence should be sent (e-mail: aguerrero@us.es).*
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Emulsion rheology has been widely described in the literature (Martin et al., 1964; Garland, 1973; Franco et al., 1995; Bengoechea et al., 2006). The plateau modulus (G_N^0), which may be approximated to the value of G', corresponding to a minimum in the loss tangent (Wu, 1989), has been previously related to emulsion stability (Franco et al., 1995). A higher value of this parameter is associated with a greater stability of the emulsion product.

The main objective of this work has been to study the linear viscoelastic properties and droplet size distribution (DSD) of o/w emulsions processed in the lab-scale semicontinuous emulsification device and studying the influence of some parameters, like protein or oil concentration as well as the rotor agitation speed. A comparison between semicontinuous and discontinuous emulsification has also been included.

MATERIALS AND METHODS

Materials

The composition of the o/w emulsions studied were: sunflower vegetable oil, 75 wt%; commercial native egg yolk, 2–5 wt%; vinegar, 3 wt%; salt, 0.4 wt%; and distilled water, 16.6–19.6 wt%. All the ingredients were purchased in a local supermarket.

Semicontinuous Emulsification Device

A diagram of the emulsification device used is shown in Figure 1. It consists of the following elements: (1) A 26 mL emulsification chamber (UTL-25 Basic Inline, IKAVISC, Staufen, Germany) with a rotor-stator turbine inside, which may operate at different agitation speed values; (2) A 1000 mL disperse phase tank connected to the emulsification chamber through a four channel peristaltic pump (P1) from Ismatec, (Switzerland); (3) A recirculating system that consists of a jacketed 1000 mL mixing tank, fitted with an anchor impeller, which initially contains only the continuous phase. The continuous phase is pumped from this tank to the emulsification chamber by means of a one channel peristaltic pump (P2) from Heidolph (Germany) and from there back to the mixing tank that is gradually being filled with the forming emulsion. Water at 20 °C was circulated through the jacket by means of a Heto cryostat bath circulator (Denmark) in order to compensate for the mechanical energy dissipation produced during emulsification; this refrigeration system allowed us to maintain the temperature of the obtained emulsion always under 40 °C approximately. There is also a bypass placed between the emulsification chamber and the mixing tank, which operates at alternate pumping/resting periods, through an in-line rotational rheometer; (4) Rotational viscosity measurements are made with a coaxial cylinder (Rotovisco RV20, Haake M5-OSC, Haake, Karlsruhe, Germany) at a steady shear rate of $100\,s^{-1}$ with an M10 measuring system and a couette sensor HS1 system operating at room temperature. This in-line rheometer is used to monitor the steady state apparent viscosity of the system at constant shear rate as the emulsification process takes place. However, rheological monitoring has to be performed when the pump is turned off to avoid instabilities due to cross-flow of the emulsion sample. The circulation time for the emulsion through the rheometer chamber was set at 2 min, which allows a complete refreshing of the sample along the by-pass circuit. A 2-channel peristaltic pump (P3) from Ismatec (Switzerland) was used for this circuit to ensure the same flow rate for both upstream and downstream along the in-line rheometer.

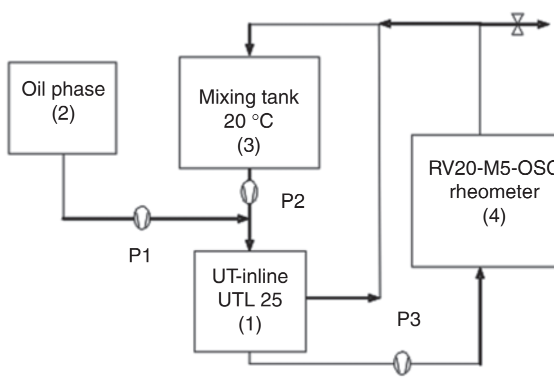

Figure 1. Flow diagram for the emulsifying device.

Methods

Rheological Measurements

Samples from emulsions processed in the semicontinuous device were submitted to oscillatory shear measurements in a Haake RS100 RheoStress rheometer (Karlsruhe, Germany), using a rough plate-plate sensor system PP35R to avoid the presence of slip effects. The stress range for linear viscoelasticity was determined through a dynamic stress sweep at a fixed frequency (6.28 rad/s). All samples were previously stored at 4 °C for 24 h before their characterization. Rheological tests were carried out at 20 °C, after 2 h at room temperature for temperature equilibration.

Droplet Size Distribution (DSD) Measurements

DSD results were determined using a Mastersizer X analyser (Malvern Instrument Ltd, UK). Values of the Sauter mean diameter, $d_{3,2}$, inversely proportional to the specific surface area of droplets, were obtained as follows:

$$d_{3,2} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{1}$$

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

Statistical Analysis

Three replicates of all rheological and DSD measurements were conducted and reported as means ±95% confidence limits. Statistical analyses were performed using *t*-test and one-way analysis of variance (ANOVA, $p < 0.05$).

RESULTS AND DISCUSSION

Evolution of the Emulsification Process

Figure 2 shows a typical evolution of viscosity for an o/w emulsion recorded by the in-line RV20 rheometer as it is being formed in the emulsification device previously described at an oil flow rate of 0.215 mL/s. The evolution of oil volume fraction, φ, along the semicontinuous operation is also shown in Figure 2 for the system containing 75% wt% of oil and 3 wt% of egg yolk, as an example. The viscosity profile obtained at each oil volume fraction (at one time/volume point) and at a fixed shear rate ($100\,s^{-1}$) is similar for all the emulsions studied, being characteristic of a structured o/w emulsion that shows a thixotropic behavior (Partal et al., 1999; Quintana et al., 2002; Riscardo et al., 2003; Bengoechea et al., 2008). In-line rheological measurements were taken along the resting periods. After each resting period, pumping through the in-line rheometer was carried out. At each resting period, after application of a constant shear rate, a sudden stress growth showing a well pronounced overshoot was registered, followed by an exponential decrease to a steady state viscosity value. The overshoot of the stress growth function is related to an elastic behavior, while the decay region is related to the viscous behavior of the sample (Kokini and Dickie, 1981). Steady state viscosity increased as the oil volume fraction increased, eventually leading to a plateau value once the addition of oil was completed (Figure 2).

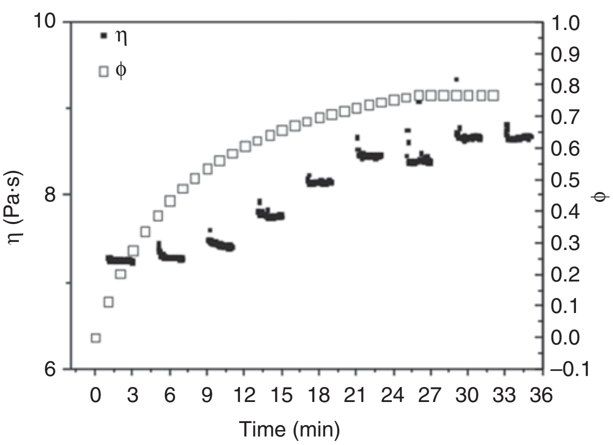

Figure 2. Evolution of oil volume fraction and viscosity at $100\,s^{-1}$ along the emulsification process at 20,500 rpm for a system containing 75 wt% oil (0,215 mL/s) and 3 wt% yolk.

Sampling of the evolving emulsion was carried out at different times along the emulsification process. This made it possible to study how the mechanical spectra and the DSD develop as the final emulsion is being produced. The estimated values for oil volume fraction, φ, protein content and oil concentration are shown in Table 1 as a function of emulsification time (13, 17, 21, and 26 min). The latter sample corresponds to the final emulsion containing 3 wt% yolk. Prior samples could not be analyzed since they undergo an early phase separation. In fact, even the samples measured at the shortest time did not show long-term stability. Table 1 also shows the values obtained for some parameters calculated from the DSD curves (Sauter diameter, $d_{3,2}$) or from linear dynamic viscoelasticity measurements (critical strain, γ_c; G' and tan δ at 1 rad/s, G'_1 and tan δ_1). It is possible to observe how droplet diameters tend to reach lower values as the emulsification process takes place. The final emulsion was obtained about 10 min after all of the oil phase was added, when properties registered with the in-line rheometer reached the plateau value. A minimum in droplet size was found after 21 min (sample 3). Although this minimum is hardly significant, it reflected the occurrence of coalescence induced by a rise in the temperature of the rotor-stator unit, as a consequence of energy dissipation during processing. Initially, an increase in temperature is believed to produce a decrease in the typical droplet size, as a consequence of favorable variations in the viscosity ratio ($\eta_{Disperse}/\eta_{Continuous}$) and/or a slight reduction in the interfacial tension between the oil and water phases. A further increase in temperature results in coalescence, which may be explained by unfolding and aggregation of the protein molecules on the interface (McClements, 2004). An increase in the linear viscoelastic range was observed as oil was being added to the system, as the highest value of the critical strain corresponds to the final emulsion.

Table 1. Composition, DSD, and rheological parameters at different emulsification times for an o/w emulsion processed in a semicontinuous device.

	Sample 1	Sample 2	Sample 3	Final emulsion
t (min)	13	17	21	26
φ (%)	62.50	68.50	72.90	76.90
Vegetable oil (wt%)	60.00	66.23	70.79	75.00
Egg yolk (wt%)	5.41	4.63	4.04	3.00
$d_{3,2}$ (μm)	4.57	3.73	2.30	2.79
γ_c	0.053	0.074	0.084	0.102
G'_1 (Pa)	161	174	214	355
tan δ_1	0.208	0.163	0.142	0.114

Values shown in Table 1 for G'_1 indicate how linear viscoelastic properties tend toward higher values as the emulsion is processed, the values in tan δ_1 reflecting an increase in the elastic character. As oil is added, the number of droplets present in the system increases, since the rotor-stator device breaks the larger droplets into smaller ones. When these droplets are covered with a convenient amount of protein, an enhancement of the network structure takes place. This effect manifests itself in higher values of G' and G'' and lower values of tan δ. It is worth mentioning that the evolution of linear viscoelastic parameters along the emulsification process is consistent with the effect of an increase in oil volume fraction that typically produces an enhancement in the interactions among oil droplets (Bengoechea et al., 2006).

Batch Versus Semicontinuous Emulsification

Emulsions with identical composition (3 wt% egg yolk, 75 wt% oil phase) were processed at 13,500 rpm in two emulsification devices that use the same rotor–stator turbine as the homogenization element. The process lasted 7 min, which corresponds to an oil flow rate of 0.98 mL/s. The first of the devices used was the previously described semicontinuous device (UTL25), and the second was an open vessel for batch operations (UT25).

Figure 3 shows DSD profiles (3a) and mechanical spectra (3b) obtained for emulsions prepared using either of the two devices. As can be observed, both emulsions show very similar DSD profiles, displaying a typical bimodal distribution. The linear viscoelastic parameters of the emulsion processed in the UTL25 are higher than those values for the emulsion produced by means of the batch process (UT25), both showing a gel-like behavior with a well developed plateau region typical of highly concentrated emulsions (Franco et al., 1995; Guerrero et al., 1998; Sánchez et al., 2001). A possible explanation of the differences found in DSD, and to a larger extent in rheological properties, may lay on the different amount of energy density applied due to the different volume of the emulsification chambers used in each case. Thus, the energy density for the UTL25 semicontinuous process is about six times the value -of the UT25 batch operation, although the total amount of energy input is the same. Moreover, the presence of a pre-emulsification mixing tank in the semicontinuous device also facilitates the homogenization process and contributes to improve DSD and linear viscoelastic properties of the emulsion.

Concentration of Egg Yolk

To study the effect of the concentration of egg yolk on the rheology and droplet size distribution of the emulsions processed in the semicontinuous device, emulsions containing 2–5 wt% egg yolk were prepared at 13,500 rpm for 7 min (0.98 mL/s). An increase in egg yolk content produces emulsions with DSD profiles displaced towards lower diameters and higher values for the storage and loss moduli, as can be observed in Figure 4.

Table 2 shows values of parameters obtained from DSD profiles and linear viscoelastic properties for emulsions stabilized with different egg yolk content. A decrease in the Sauter diameter and an increase in the viscoelastic properties (i.e., the plateau modulus) as the protein content is increased, is evident from these data. An increase of the protein concentration leads to lower values of critical strain, though a slight minimum appears at 4 wt%.

All these results indicate that higher egg yolk content allows stabilizing a greater interfacial area, which would lead to lower droplet sizes, and as a result, to a higher

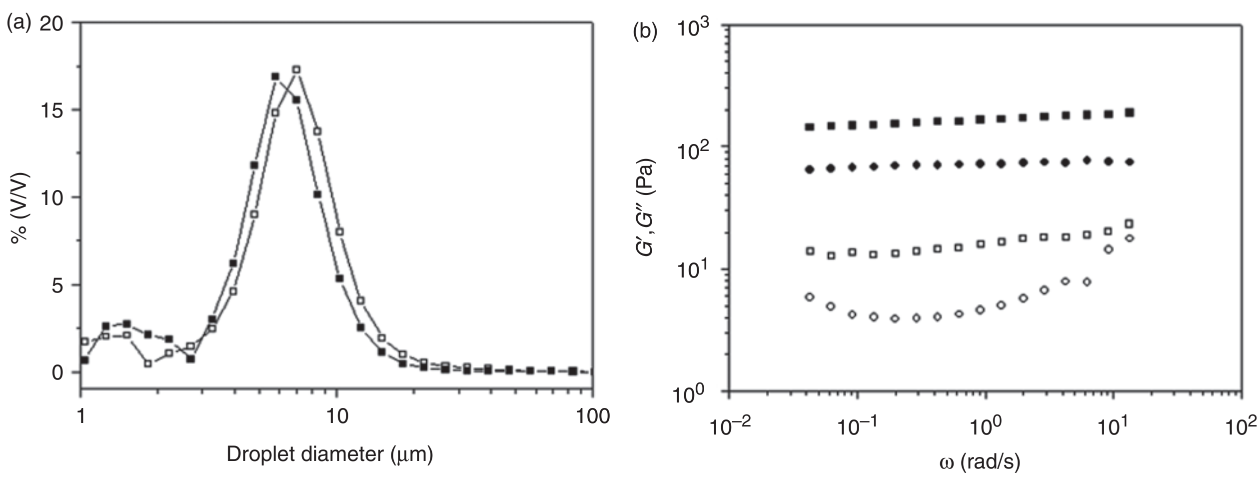

Figure 3. (a) DSD and (b) mechanical spectra for an emulsion processed at 13,500 rpm in a semicontinuous device (UTL25) and in a discontinuous batch (UT25). (a) (■) UTL 25; (□) UT 25. (b) UTL25, (■) G' (□) G'' UT25, (•) G', (○) G'' UT25.

number of interactions, leading to an increase in viscoelastic properties.

Influence of Agitation Speed

DSD profiles (Figure 5) were very similar except for the emulsification process carried out at the lowest agitation speed, which show much higher droplet sizes and polidispersity. Linear viscoelastic properties show maximum values for G' and G'' at intermediate values of the agitation speed (13,500 rpm) as may be observed in Figure 5. Table 3 shows the values for the Sauter mean diameter, the critical strain for linear viscoelasticity and the plateau modulus. As may be seen, the emulsion prepared at 13,500 rpm also showed a maximum in G_N^0, and a minimum in γ_c and $d_{3,2}$, and significant difference can be observed of the latter parameter for emulsions prepared at 13,500 and 24,000 rpm.

Table 2. Influence of egg yolk (EY) content on droplet diameter and rheological parameters for o/w emulsions (75% oil) processed at 20,500 rpm.

EY content (wt%)	$d_{3,2}$ (μm)	γ_c (%)	G_N^0 (Pa)
2	2.48 ± 0.04	13.4 ± 1.4	212.1 ± 4.2
3	1.80 ± 0.04	10.2 ± 1.1	271.1 ± 2.8
4	1.61 ± 0.02	9.9 ± 1.2	315.0 ± 5.5
5	1.51 ± 0.03	10.9 ± 1.2	337.0 ± 13.2

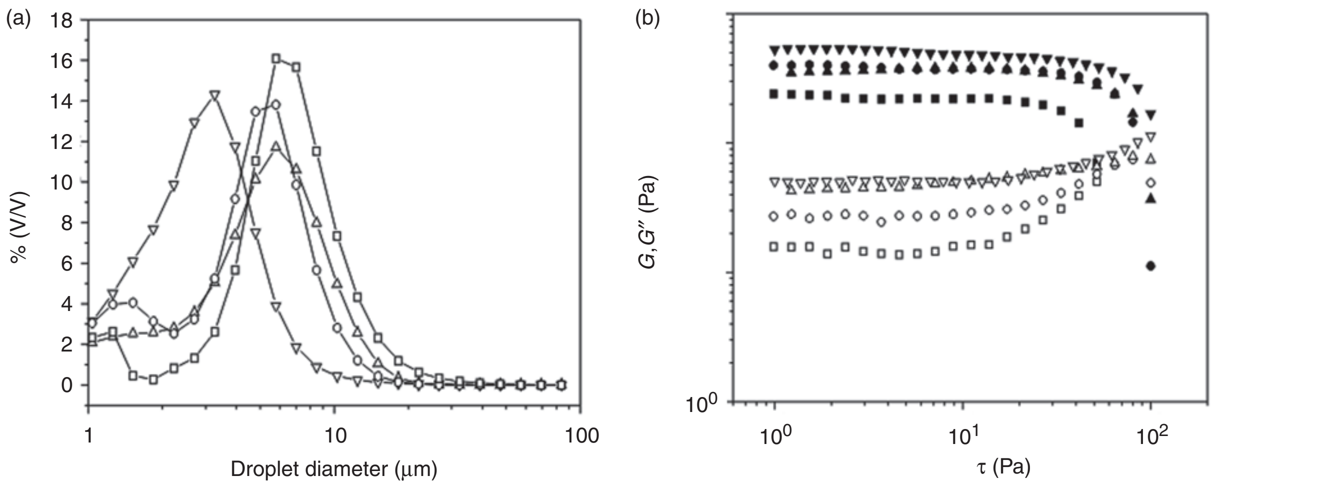

Figure 4. (a) DSD and (b) stress sweep (at ω = 6.28 rad/s) for emulsions processed at 20,500 rpm containing different egg yolk concentrations (2, 3, 4, 5 wt%). (a) (□) 2%; (○) 3%; (△) 4%; (▽) 5%. (b) (■) G' (□) G'' 2%; (•) G' (○) G'' 3%; (▲) G' (△) G'' 4%; (▼) G' (▽) G'' 5%.

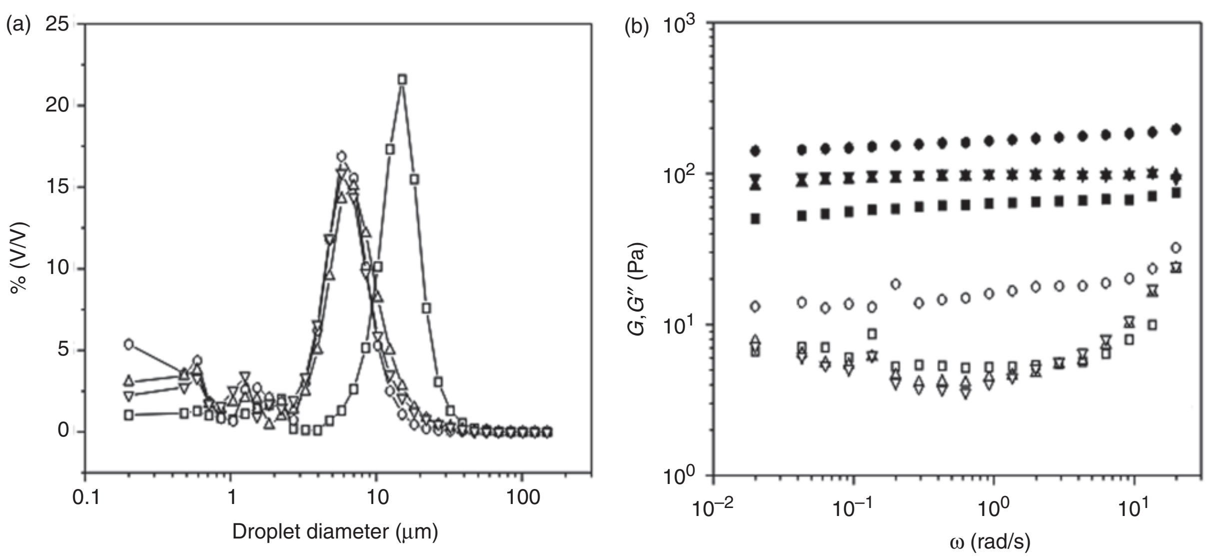

Figure 5. (a) DSD and (b) mechanical spectra for emulsions stabilized by 3 wt% egg yolk at different rotation velocities (□) 8,000 (◇) 13,500, (△) 20,500; (▽) 24,000. (b) (■) G' (□) G'' 8,000 rpm, (•) G'; (○) G'' 13,500 rpm, (▲) G'; (△) G'' 20,500 rpm (▼) G'; (▽) G'' 24,000 rpm.

Table 3. Influence of agitation speed on droplet diameter and rheological parameters for o/w emulsions (3 wt% EY; 75 wt% oil).

N (rpm)	$d_{3,2}$ (μm)	γ_c (%)	G_N^0 (Pa)
8 000	4.32 ± 0.03	13.6 ± 1.5	62.2 ± 3.2
13 500	2.23 ± 0.02	9.4 ± 2.0	151 ± 6.2
20 500	2.40 ± 0.10	10.4 ± 1.6	95.8 ± 3.5
24 000	2.51 ± 0.03	13.0 ± 2.0	98.9 ± 0.7

The influence of energy input on DSD and linear viscoelasticity of these emulsions can be explained in terms of a balance between shear induced coalescence and disruption of droplets (Sánchez et al., 2001). The higher the energy input the greater extension of both effects. Moreover, the temperature at the end of the process is higher for those emulsions processed at the higher velocity, which may predominantly promote shear-induced coalescence. These events would explain the appearance of the above mentioned minimum in droplet size and maximum in linear viscoelastic properties.

Influence of Flow Rate

Figure 6 shows the influence of oil phase volumetric flow rate on DSD profiles (Figure 6(a)), mechanical espectra (Figure 6(b)) and their corresponding parameters $d_{3,2}$ and G_N^0 (Figure 6(c)) for an o/w concentrated emulsion containing 3% w/wt egg yolk. An increase in flow rate produces a decrease in droplet size and polydispersity as well as an increase in both the storage (G') and loss (G'') moduli. An increase in flow rate produces a continuous increase in the plateau modulus showing a tendency toward higher values at high flow rate (Figure 6(c)). Correspondingly, the Sauter mean diameter undergoes a continuous decrease that also seems to tend to an asymptotic value. These results suggested that the elastic network formed for the final emulsion might undergo a remarkable enhancement with increasing flow rate, which may be related to an increase in emulsion stability (Franco et al., 1995).

The effect of flow rate may be explained by shear-induced coalescence enhanced by thermal effects as a consequence of energy dissipation. An increase in flow rate implies a reduction in emulsion processing time. As a consequence, higher final temperatures correspond to longer processes achieved at lower flow rates, which eventually would lead to higher extents of droplet coalescence.

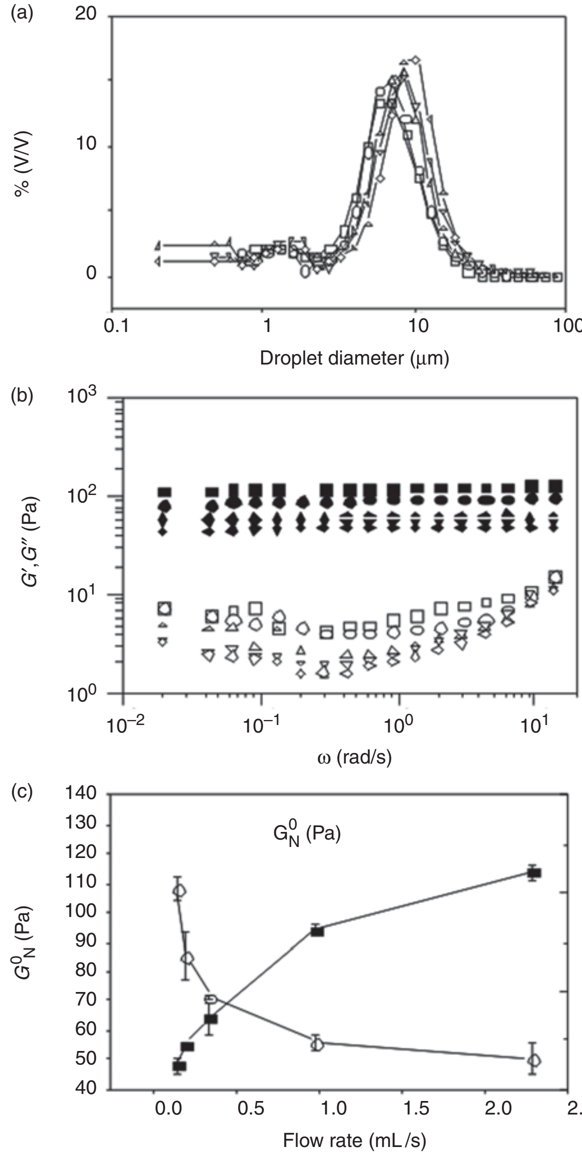

Figure 6. (a) DSD and (b) mechanical spectra of o/w emulsions with 75 wt% oil and 3 wt% egg yolk processed at 20,500 rpm at different oil phase volumetric flow rates. (c) Evolution of the sauter diameter, $d_{3,2}$ (open symbols) and the plateau modulus, G_N^0 (closed symbols) with the oil phase volumetric flow rate. (a) (□) 2.29 mL/s; (○) 0.98 mL/s; (△) 0.34 mL/s; (▽) 0.19 mL/s; (◇) 0.14 mL/s. (b) (■) G' (□) G'' 2.29 mL/s; (●) G' (○) G'' 0.98 mL/s; (▲) G' (△) G'' 0.34 mL/s; (▼) G' (▽) G'' 0.19 mL/s; (♦) G' (◇) G'' 0.14 mL/s. (c) (■) G_N^0, (○) $d_{3,2}$.

Concluding Remarks

The higher rheological properties (both storage G', and loss modulus G'') obtained for an emulsion stabilized by egg yolk using the semicontinuous device compared to the results from the batch, and the possibility of recording the viscosity data along the process, indicate the suitability of using this device instead of the batch.

An increase in the egg yolk content in the emulsion favors the formation of presumably more stable emulsions, with lower droplet diameters and higher plateau modulus. This effect may be attributed to stabilization of a greater interfacial surface area, leading to an increase in interactions among droplets.

Emulsions with optimum properties were obtained at intermediate agitation speeds (i.e., 13,500 rpm) and at higher oil flow rate values. This fact can be explained in terms of the balance between droplet disruption and shear-induced coalescence, modulated by a rise in temperature as a result of mechanical energy dissipation.

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