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

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ABSTRACT

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

1. Introduction

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

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

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

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

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

The objectives of the present work are:

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

2. Materials and methods

2.1. Materials

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

2.2. Emulsion preparation

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

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

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

Table 1
Emulsion formulations and their respective coded variables

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

O = oil; G = gums.

2.3. Droplet size distribution (DSD)

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

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

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

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

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

2.4. Visual assessment of stability

Two (100 ml) aliquots of each emulsion were carefully poured in 100 ml glass graduated cylinders and stored at 20 °C in a temperature-controlled room. These samples were periodically observed and the time at which an oil-water interface appeared determined the stability period.

2.5. Density measurements

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

2.6. Rheological tests

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

2.6.1. Oscillatory shear tests

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