

Stability and rheology properties of oil-in-water emulsions prepared with mucilage extracted from *Opuntia ficus-indica* (L). Miller



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ABSTRACT

The droplet size distributions, microstructure, rheological properties, and stability of oil-in-water emulsions prepared with mucilage (PM) were studied in comparison to guar gum (GG), xanthan gum (XG), and carboxymethyl cellulose (CMC).

The results showed that the emulsions with PM had a particle size distribution and droplet diameters on the same order as the emulsions stabilized with GG and XG, and a lower polydispersity index.

All emulsions exhibited shear-thinning behavior in the range of the shear rates applied and the concentrations evaluated. Emulsions prepared with PM at 4.5% (w/v) exhibited a k value on the same order as for the emulsion with GG at 1% (w/v). The mechanical spectra of the emulsions with PM showed a viscoelastic behavior similar to that of the emulsions prepared with GG. The emulsion containing mucilage at 4.5% (w/v) presented the highest relaxation time (λ). This means that this emulsion had a more elastic behavior and greater resistance of its structure.

The stability of the emulsions prepared with PM depends on the test conditions. Under static conditions, the emulsion prepared with 4.5% (w/v) mucilage showed similar stability to the emulsion prepared with GX and GG. On the other hand, the PM emulsion stability was higher than that of GX when it was evaluated under stress conditions.

1. Introduction

Oil-in-water (O/W) emulsions are heterogeneous systems composed of a mixture of two immiscible phases, a continuous and a dispersed one, as micro- or nanodroplets. From a physicochemical point of view, emulsions are a lyophobic colloidal dispersion and due to their high interfacial area are thermodynamically unstable (McClements, 1999, 2015).

The term “stable emulsion” refers to the system's ability to resist changes in its properties over time (Dickinson, 2003). The greater the stability of an emulsion, the greater the ability to withstand process conditions such as pumping, extraction, filtration, extrusion, etc. (Marcotte, Taherian Hoshahili, & Ramaswamy, 2001).

The stability of an O/W emulsion depends on many variables, such as distribution and particle size of the dispersed phase, concentration and viscosity of the continuous phase, temperature, phase density difference, and volume ratio (Dickinson & Golding, 1997).

The stabilization of O/W emulsions starts in the continuous phase or

at the droplet surface, depending on the chemical nature of components. Dickinson (2003) divided the components responsible for the emulsion stability into two categories: emulsifying agents (emulsifiers) and stabilizers. Emulsifiers are surface-active molecules capable of fast emulsion stabilization. They adsorb at the oil-water interface, reduce interfacial tension, and create a protecting film (McClements, 2005). Stabilizers are commonly used to provide long-term emulsion stability. They are usually biopolymers: proteins or polysaccharides. The mechanism of stabilization depends on their adsorption ability, some of them adsorb at the oil-water interface, while others only modify the viscosity of the aqueous phase due to their nonadsorbing nature (Bais, Trevisan, Lapasin, Partal, & Gallegos, 2005; Dickinson, 2003; Jafari, Beheshti, & Assadpoor, 2012; Prochaska, Kedziora, Thanh, & Lewandowicz, 2007).

In addition to studying the stability of an O/W emulsion, it is important to know its rheological properties, since they are required for the calculations in any process involving fluid flow and play an important role in the analysis of the flow conditions in food processes

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(Derkach, 2009; Marcotte et al., 2001; McClements, 2005; Pal, 2011).

Numerous methods are available to investigate emulsion flow properties. It is possible to perform flow, creep, and oscillatory experiments. In oscillatory measurements, a viscoelastic material is subjected to a sinusoidally varying strain (or stress). The response to stress (and strain) is then monitored. From these measurements, it is possible to determine emulsion viscoelastic parameters such as storage (G') and loss (G'') moduli. The G' modulus represents the elastically stored energy in the emulsion, and the G'' modulus the energy dissipated in viscous flow (Tadros, 2004). Depending on their properties, emulsions can either maintain the necessary fluidity for their transport and distribution or exhibit a yield behavior inhibiting flow under small shear stress. The shear-thinning behavior is probably the most encountered rheological behavior in the field of emulsions: the apparent viscosity decreases when increasing the shear rate. From the variation of the different rheological parameters, it is possible to infer the stability of emulsions, their texture, and conditioning possibilities for future applications (Tadros, 2004).

Polysaccharides have been widely used in food products to provide viscosity to the continuous phase, modify textural attributes and rheological properties, stabilize emulsions and suspensions, and enhance or standardize the eating quality of a product due to their odorless, colorless, tasteless, low energy value, and digestibility properties.

In emulsion products, polysaccharides such as xanthan gum, guar gum, modified starch, as well as carboxymethyl cellulose, are the most commonly used (Hayati, Ching, & Rozaini, 2016).

Xanthan gum is an anionic gum that is frequently used in O/W emulsion products in order to impart a gel-like textural property. It is highly pseudoplastic and stable towards acid, temperature and enzymes. It gives a high viscosity solution at low concentration.

Guar gum is a neutral galactomannan and does not affect the pH when added to food products (Laaman, 2010). It gives high viscosity to products when used in low concentration.

Carboxymethyl cellulose, a water-soluble cellulose derivative, has been proven to provide a good uniformity of droplet size in O/W emulsions. A high water-binding capacity of the carboxymethyl functional groups enables the CMC to provide excellent stability to the emulsion with no phase separation (Hayati, Che Man, Tan, & Aini, 2009).

While the functionality of the above polysaccharides is wide, there is a constant search for new hydrocolloids, which are obtained from natural sources. Consumers are increasingly demanding label-friendly products fabricated from natural and sustainable ingredients (De, Malik, Ghosh, Saha, & Saha, 2015; McClements & Gumus, 2016; Ozturk & McClements, 2016).

One of the hydrocolloids obtained from natural sources being studied is brea gum, a natural hydrocolloid exudate from the bark of *Cercidium praecox* tree (Bertuzzi, Slavutsky, & Armada, 2012). Brea gum consists of 83.7% of polysaccharide and 7.52% of protein. The polysaccharide protein complex present in brea gum molecular structure gives it high interfacial activity and good emulsifying properties (Castel et al., 2016). Mesquite gum is another exudate gum obtained from the trees of *Prosopis* spp. that is being studied. The functionality of mesquite gum is comparable to that of arabic gum (Beristain, Azuara, & Vernon-Carter, 2002; Dickinson, 2003).

The physicochemical properties of mucilage extracted from *Opuntia ficus-indica* were studied by Cárdenas, Higuera-Ciagara, and Goycoolea (1997) and Trachtenberg and Mayer (1982).

However, the potential uses of mucilage as emulsifier and/or stabilizer (Garti & Reichman, 1993) have not been exhaustively studied.

The mucilage is a polysaccharide present in the cladodes (stems) of the prickly pear plant (*Opuntia ficus-indica* L. Mill) (Cárdenas et al., 1997). This is a complex high molecular weight polyelectrolyte (Ting, 1997) whose chemical structure contains residues of arabinose, galactose, galacturonic acid, rhamnose, and xylose (McGarvie & Parolis,

1979). It is soluble in water and its configuration in solution corresponds to a random coil (Cárdenas et al., 1997). Medina-Torres, Brito-De La Fuente, Torrestiana-Sánchez, & Katthain (2000) suggest, a mucilage solutions exhibits pseudoplastic behavior similar other commercial polysaccharides. A previous study conducted by our research group showed that mucilage presented high intrinsic viscosity, with similar properties to guar gum and xanthan gum. The pH and ionic strength did not affect the viscosity (Quinzio, Ayunta, Alancay, Lopez de Mishima, & Iturriaga, 2017).

The aim of this work was to evaluate the stability and rheological properties of an O/W emulsion prepared with mucilage extracted from the cladodes of *Opuntia ficus-indica* (L.) Mill and to compare it with an emulsion containing commercial hydrocolloids such as guar gum, xanthan gum, and carboxymethyl cellulose.

2. Materials and methods

2.1. Materials

Two-year old cladodes of *Opuntia ficus-indica* (L.) Mill, from the El Zanjón cultivar belonging to the School of Agronomy and Agribusiness of the National University of Santiago del Estero, Argentina, were used. Food-grade gums such as guar gum (GG), xanthan gum (XG) and carboxymethyl cellulose (CMC) supplied by Gelfix S.A. were used as well. To prepare the emulsions commercial sunflower oil (Natura[®]) was used as dispersed phase.

2.2. Mucilage extraction and purification

The natural exudate of diced parenchymatic tissue from cladodes was extracted using a stainless steel extruder and centrifuged at 10,000 rpm for 1 h. The supernatant was precipitated using five volumes of ethyl alcohol. Afterwards, the precipitate was dried in an oven at 60 °C up to constant weight (precipitated mucilage, PM) (Iturriaga, Quinzio, Corvalán, & Lopez, 2009).

2.3. Solution preparation

Aqueous solutions of PM, GG, XG, and CMC at 0.5%, 1.0% and 1.5% (w/v) were prepared by dissolving the appropriate amount of the biopolymer in distilled water. The solutions were stirred using a magnetic stirring for 6 h at room temperature and allowed to stand for 24 h at 4 °C in order for the polysaccharides to dissolve completely. A solution of PM at 4.5% (w/v) was also prepared because at this concentration the PM viscosity is similar to that of the solution of GG and XG at 1.5% (w/v) (Quinzio, Ayunta, Alancay, Lopez de Mishima, & Iturriaga, 2017).

2.3.1. Intrinsic viscosity

The viscosity of dilute solutions was measured at 25 °C, using a Micro-Ubbelohde viscometer (DIN 55 350), suspended in a thermostatic water bath.

The intrinsic viscosity [??] was determined from the extrapolation of the reduced (η_{red})_{c→0} and inherent (η_{inh})_{c→0} viscosity at zero concentration in accordance with the empirical expressions of the Huggins and Kraemer equations (1) and (2), respectively.

$$\eta_{red} = \eta_{sp}/c = [\eta]_H + K_H[\eta]^2_H c \quad (1)$$

$$\eta_{inh} = \ln \eta_{rel}/c = [\eta]_K + K_K [\eta]^2_K c \quad (2)$$

The solutions were prepared in distilled water to give a relative viscosity ranging from 1.2 to 2.0, in order to assure good accuracy and linearity of extrapolation to zero concentration (Da Silva & Rao, 1992).

The intrinsic viscosity can also be calculated by measuring the slope of relative viscosity or specific viscosity vs. concentration.

Therefore, the following equations were also used to determine the

intrinsic viscosity:

Tanglerpaibul-Rao's equation (Tanglerpaibul & Rao, 1987).

$$\eta_{rel} = 1 + [\eta]C \quad (3)$$

Higiro's equation (Higiro, Herald, & Alavi, 2006):

$$\eta_{rel} = e^{[\eta]C} \quad (4)$$

2.3.2. Viscosity average molecular weight

The viscosity average molecular weight (\overline{M}_v) was determined using the Mark-Houwink Sakurada equation,

$$[\eta] = K[\overline{M}_v]^\alpha \quad (5)$$

where $[\eta]$ is the intrinsic viscosity (dl/g), \overline{M}_v is the viscosimetric average molecular weight, K and α are constants for a given solute-solvent system and for a given temperature.

2.4. Emulsion preparation

The O/W emulsions were prepared with commercial sunflower oil (Natura[®]) and aqueous solutions of PM, GG, XG, and CMC at all concentrations at a ratio of 1:5 (v:v; oil:solution). The emulsification was carried out for 4 min at high speed (25,000 rpm) using an OMNI International Tissue Master 125 homogenizer (rotor-stator system).

2.5. Characterization of emulsions

2.5.1. Droplet size distribution

The mean droplet diameters and droplet size distribution (DSD) of emulsions were determined by laser light scattering using a Micro Particle Analyzer (Malvern Mastersizer 2S, Malvern Instruments Ltd, UK). The droplet size distribution determination was based on the best fit between the experimental measurements and the Mie theory. The software used a refractive index of 1.47 (sunflower oil) and 1.33 for the dispersant medium (water). All measurements were done on freshly prepared samples, and the results are reported as average values. The mean droplet diameter was expressed as the volume mean diameter (De Brouckere, $D_{[4,3]}$) and the cumulative distribution at 50% ($D_{[0,5]}$).

$$D_{[4,3]} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (6)$$

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

To determine the distribution width of droplet sizes (polydispersity index, PI), the following formula was used:

$$PI = \frac{[d(0,9) - d(0,1)]}{d(0,5)} \quad (7)$$

In the formula, $d(0,1)$, $d(0,5)$, and $d(0,9)$ are diameters at 10%, 50% and 90% cumulative volume, respectively.

2.5.2. Emulsion microstructure

The microstructure of the emulsions was observed by optical microscopy (CME Leica optical microscope) at room temperature (25 °C) for fresh emulsions. A small drop of emulsion was placed onto the microscope slide and carefully covered. The photomicrographs (100x magnifications) were taken using Sony digital camera (8 megapixels).

2.5.3. Rheological behavior

All the rheological determinations were done in an AR1000 TA Instruments rheometer (New Castle, DE 19720), at 25 °C, using stainless-steel cone-plate geometry (60 mm diameter and 2° angle). The equipment was driven through the TA Instruments-Waters LLC. Data were collected running the 5.2.18 release of the Rheology Advantage Data Analysis software.

2.5.3.1. Steady-shear flow measurements. The flow behavior of all the samples at different concentrations was studied. The viscosity curves were obtained using a one-step program (0 s⁻¹ to 100 s⁻¹) applied for 2 min. The experimental flow curves were modeled using the Ostwald-de Waele model (Brito de la Fuente, Leuliet, Choplin, & Tanguy, 1992) as expressed in the following equation:

$$\eta = k \dot{\gamma}^{n-1} \quad (8)$$

where k is the consistency coefficient (Pa sⁿ), $\dot{\gamma}$ is the shear rate (s⁻¹), and n is the flow behavior index (dimensionless).

2.5.3.2. Steady oscillatory flow measurements. The dynamic moduli, G' (storage modulus) and G'' (loss modulus), were determined through small amplitude oscillatory shear flow at frequencies ranging from 0.01 to 10 Hz, and a constant stress of 0.4 Pa, within the linear viscoelastic range (LVR). The relaxation time λ ($\lambda = 1/\omega_c$) can be estimated from the ω_c frequency value at the crossover point between G' and G'' and represents the tendency of the material to flow (Tadros, 1996).

2.5.4. Creaming stability (static method)

Creaming stability was investigated to evaluate the relative stability of the emulsions prepared with PM and hydrocolloid solutions whose concentrations were 0.5%, 1% and 1.5% (w/v). In addition, the PM emulsion at 4.5% (w/v) was evaluated. Sodium azide (0.04% w/w) was added to the continuous phase to prevent microbial growth. The emulsion samples were poured into 10-cm high glass test tubes, that were sealed to prevent evaporation. They were kept at ambient temperature, and the movement of any creaming boundary was tracked visually for 90 days. The emulsions were separated into a top cream layer and a bottom serum layer. The total emulsion height (H_T) and serum layer height (H_S) were measured. A creaming index (CI %) was calculated as reported by Keowmaneechai and McClements (2002).

$$CI(\%) = 100 \frac{H_s}{H_t} \quad (9)$$

CI (%) can provide indirect information about the extent of droplet aggregation in an emulsion; the greater the aggregation, the larger the flocs and the faster the creaming.

2.5.5. Emulsion extensibility (rheology method)

From a stress sweep test (0.01 and 100 Pa) at a constant frequency of 1 Hz and at 25 °C, the upper limit of the LVR and the values of γ_c and τ_c were determined. Critical strain (γ_c) and critical stress (τ_c) values were identified as the maximum strain and stress amplitude at which both moduli (G' and G'') were independent of the perturbation applied. The parameter γ_c is regarded as an index of emulsion extensibility (Mancini, Montanari, Peressini, & Fantozzi, 2002). After γ_c or τ_c the structure of the emulsion started to break down, which might involve the breakdown of flocs into a smaller unit and/or breakdown of the structuring agent (Tadros, 2004).

2.6. Statistical analysis

In order to find significant differences, a one-way analysis of variance (ANOVA) as well as tests of mean differences for a significance level of $\alpha = 0.05$ using Tukey's test were carried out. The tests were done in triplicate using the Info Stat software.

3. Results and discussion

3.1. Intrinsic viscosity

Table 1 shows the values of intrinsic viscosity and viscosity average molecular weight of PM, GG, XG and CMC. The intrinsic viscosity was estimated from the slope of the Higiro's equation (4) because it showed a better linear fit with higher correlation (R^2) compared to those

Table 1

Intrinsic viscosity values and viscosimetric average molecular weight for mucilage (PM), guar gum (GG), xanthan gum (XG) and carboxymethyl cellulose (CMC).

Hydrocolloid	$[\eta]$ (dl/g)	α	K (dl/g)	MV (Da)	Reference
PM	10.94	0.723 ^a	3.810 ^{-4a}	1.48 10 ⁶	Current research
GG	9.80	0.723 ^a	3.810 ^{-4a}	1.26 10 ⁶	Current research
	10.30			1.45 10 ⁶	Azéro & Andrade, 2002.
				1.8 10 ⁶	Robinson, Ross-Murphy, & Morris, 1982.
XG	49.47	1.27 ^b	2.79 10 ^{-5b}	8.2 10 ⁴	Current research
	44.93			1.67 10 ³	Launay et al., 1997.
	155.7				Khouryieh, Herald, Aramouni, & Alavi, 2007.
CMC	5.13	0.63 ^c	5.37 10 ^{-4c}	5.3 10 ⁵	Current research
				1.56 10 ⁵	Funami et al., 2007.
				3.77 10 ⁵	

The determinations were made at 25 °C using distilled water as solvent.

a (Robinson et al., 1982), b (Masuelli, 2014); c (Donges, 1990).

obtained by extrapolation from the Huggins and Kraemer's equations (1) and (2). The methods for determining the intrinsic viscosity based on slopes of plots have larger correlation coefficients and smaller standard errors than those based on intercepts of plots (McMillan, 1974; Razavi, Mohammadi Moghddam, Emadzadeh, & Salehi, 2012).

The intrinsic viscosity value of mucilage was similar to that of guar gum. The xanthan gum showed the highest value and carboxymethyl cellulose the lowest (Table 1).

The intrinsic viscosity is a characteristic property of individual molecules in a given polymer–solvent pair. It is related to the conformation of the molecules in a way that a higher value of intrinsic viscosity represents a more extended structure at a given chain length. In this way, the intrinsic viscosity of GG has a characteristic value of an open, flexible, disordered random coil molecule. The intrinsic viscosity of XG was the highest, in agreement with helix-like conformation and can be regarded as relatively stiff or semirigid. As a result, the hydrodynamic volume adopted by such rigid macromolecule in aqueous medium is much higher than a random coil. In this sense, the PM viscosity value would indicate a flexible molecule, similar to GG. Consistent with this, the PM showed an viscosity average molecular weight in the same order of magnitude as GG and higher than XG and CMC (Table 1).

The specific viscosity (η_{sp}) was calculated from the intrinsic viscosity values obtained from the technique of capillary viscosimetry in the dilute regime and from the viscosity at zero shear rate (η_0) obtained from the rheometry technique. The dependence of the specific viscosity (η_{sp}) on the overlay parameter ($C[\eta]$) for hydrocolloids systems is shown in Fig. 1. The plot of $\log(\eta_{sp})$ vs $\log C[\eta]$ is used to determine the coil overlap parameter (critical concentration) and the dilute Newtonian domain (Launay, Cuvelier, & Martinez-Reyes, 1997; Morris, Cutler, Ross-Murphy, Ress, & Price, 1981).

The specific viscosity increases with the polymer concentration, presenting two types of dependence that also define two concentration intervals (Fig. 1). The slope is lower in the range of low concentrations of polymer and therefore changes in viscosity with the concentration are lower. The second slope shows a greater dependence of the viscosity on the concentration. The dependences in the dilute concentration range (slope 1) for PM, GG, CMC and XG were similar to each other and were in agreement with the results obtained for other natural and synthetic polymers. On the other hand, at higher concentration (slope 2) the dependence was greater for GG, in accordance with the results obtained by other researchers for this and other galactomannans, which characterizes it as a randomly arranged polymer that presents hyperentanglements (Morris et al., 1981). The slope 2 of the PM curve

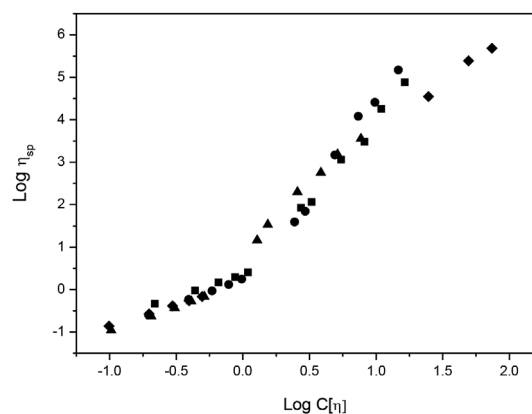


Fig. 1. Variation in the 'zero shear' viscosity of polysaccharide solutions with the degree of occupancy of space by the polymer coils (characterized by the coil-overlap parameter $c[\eta]$). The results shown are for: (■) mucilage; (●) guar gum; (▲) carboxymethyl cellulose; (◆) xanthan gum. The determinations were made at 25 °C using distilled water as solvent.

approached that of GG, therefore a behavior similar to that of this gum can be assumed.

In the dilute regime, $\log(\eta_{sp})$ vs $\log C[\eta]$ obtained with XG was superimposed with the master curve corresponding GG, PM and CMC, but at concentrations higher than C^* , when polymer coils begin to shrink, the curve of XG presents discrepancies regarding the GG, PM and CMC curves. They are no longer attributable to strong interactions between two chains and now their progressive osmotic compression has to be taken in account (Launay et al., 1997).

The values of the slope obtained for the gum systems were in the range of 1.05–1.20 and 2.44–4.74, in the dilute and semidilute concentration ranges, respectively (Table 2). The results obtained, as well as the type of dependence are, in accordance with previous studies (Morris et al., 1981; Rayment, Ross-Murphy, & Ellis, 1995) in which the concentration was found to depend on $c^{1.4}$ and $c^{3.3}$ for dilute and semidilute, solutions respectively, as occurs in polysaccharides with random organization such as guar gum.

Furthermore, in dilute regimes, slope values greater than unit have been reported to be associated with a random coil conformation (Lapasin & Pricl, 1995) or entanglement (Morris, 1995) and slope less than unity have been reported to be associated with a rod-like conformation (Lai & Chiang, 2002). In this study, the slope value for the PM was 1.05, which could indicate that the molecular conformation of PM is between random coil and rod-like.

The transition from the diluted range to the semidilute range of concentration can be evaluated at the critical concentration C^* , obtained by the following relationship: $(a/[c])$, where a is an integer that varies for different polysaccharides between 1 and 4 (Williams & Phillips, 2001).

Table 2 lists the parameters C^* and $C[\eta]$ obtained in this work, as well as the values reported by other authors for these hydrocolloids, where we can see a satisfactory correspondence between the values of different research studies. The C^* values for the PM and GG solutions were similar. In the case of XG presented the lowest value of C^* and CMC the highest.

The transition (at concentration C^*) is attributed to the initial contact between the individual coils when, in aggregate, their swept-out volume becomes equal to the total volume of the solution, which normally occurs when the degree of space-occupancy reaches $C[\eta] \sim 1$. The region of higher concentration dependence corresponds to the initial compression and subsequent interpenetration of the polymer coils in response to increasing space-occupancy. The molecular entanglement occurs when the dimensionless concentration $C[\eta]$ exceeds one (Graessley, 1974; Hager & Berry, 1982), and the semidilute regime is in the range of $C[\eta]$ of 1.0–10.0 (Graessley, 1974).

Table 2

Slopes, critical concentration (C^*) and coil overlap parameter $C[\eta]$ of the solutions of mucilage (PM), guar gum (GG), xanthan gum (XG) and carboxymethyl cellulose (CMC).

Hydrocolloid	Slope 1 (below C^*)	Slope 2 (above C^*)	C^* (g/dl)	$C[\eta]$ 0.5%	$C[\eta]$ 1%	$C[\eta]$ 1.5%	$C[\eta]$ 4.5%	Reference
PM	1.05	3.74	0.36	5.47	10.94	16.41	49.23	Current research
GG	1.20	4.74	0.41	4.90	9.80	14.70		Current research
	1.3	5.1	0.084					Robinson et al., 1982.
	1.1	4.3	0.1					Rayment, Ross-Murphy, Ellis, 2000
	1.5	4.2	0.05					Cook, Hollowood, Linforth, & Taylor, 2002.
	0.98	2.44	0.08	24.72	49.44	74.16		Current research
XG	1.25	1.98	0.025					Launay, Couvelier, & Martinez-Reyes, 1984.
	0.786		0.025					Higiro et al., 2006.
	1.14	3.07	0.78	2.56	5.13	7.7		Current research

As this parameter was in the range of 1.05–16.4 for PM and 0.98–14.7 for GG in the concentration range 0.1–1.5% (w/v), we could assume that the polymer conformation corresponds to a coil overlap or molecular entanglements (Table 2).

On the other hand, XG and CMC showed $C[\eta]$ values in the range of 0.99–74.2 and 1.28–7.7 in the concentration range 0.02–1.5% (w/v) and 0.25–1.5% (w/v) respectively, therefore a coil overlap or entanglement could occur at lower concentration for XG and higher than 0.25% (w/v) for CMC.

Table 2 also lists the $C[\eta]$ values corresponding to the solutions at concentrations 0.5%, 1% and 1.5% (w/v) of the hydrocolloids studied. For the same concentration the values of $C[\eta]$ of PM and GG were similar, while XG showed the highest values and CMC the lowest.

The lowest values of $C[\eta]$ for PM and GG would indicate that their molecules are less entangled and have more free volume to occupy than XG, which presents the highest values of $C[\eta]$. The latter would have its molecules more intertwined, with less free space to occupy and increased intermolecular interactions. The PM solution at 4.5% (w/v) showed a $C[\eta]$ value similar to GG at 1.5% (w/v) and at XG at 1% (w/v) (Table 2).

The values of intrinsic viscosity and viscosimetric molecular weight obtained in the dilute regime provide information on the type of conformation adopted by the polymer molecule. In the semidilute regime, the behavior of the solutions depends on the parameter $C[\eta]$ that determines the degree of space occupied by the polymer chains. That is, it depends not only on the concentration but also on the intrinsic viscosity and viscosimetric molecular weight.

Consequently, knowing the behavior of the polysaccharides in the dilute and semidilute regimes will be important to analyze the rheological properties and stability of the emulsions prepared with them.

3.2. Characterization of emulsions

3.2.1. Droplet size distribution

The emulsions, except those containing CMC, exhibited a bimodal character at all the concentrations tested (data not shown). The bimodal distribution is characterized by a secondary maximum at relatively high diameters, and a primary peak at smaller diameters. In the case of emulsions with CMC, populations II (droplets between 10 and 100 μm) and III (large droplets, 100 μm) concentrated almost the entire volume of the dispersed phase of the emulsions. These populations of droplets lead to destabilization processes (coalescence and creaming). A bimodal distribution could be explained by the short time of homogenization and type of homogenizer employed. The high-speed homogenizer used to prepare the emulsion is only capable of generating low energy inputs (Walstra, 1983) to disrupt and mix the oil and water phases, so small droplet sizes cannot be obtained. The emulsions were homogenized for a short time (4 min), so only a small fraction of the emulsion remained in the region where the most intensive disruptive forces were generated.

Table 3 lists mean values from De Brouckere diameter ($D_{[4,3]}$),

Table 3

Droplet mean diameters $D_{[4,3]}$, $D_{[0,5]}$ and polydispersity index of emulsions containing mucilage (PM), guar gum (GG), xanthan gum (XG), and carboxymethyl cellulose (CMC).

Emulsion	$D_{[4,3]}$ (μm)	$D_{[0,5]}$ (μm)	IP
PM 0.5%	40.16 ^{a1}	36.33 ^{a1}	1.6 ^{a1}
GG 0.5%	45.83 ^{b1}	38.61 ^{a1}	1.98 ^{b1}
GX 0.5%	43.33 ^{ab1}	39.62 ^{a1}	1.45 ^{c1}
CMC 0.5%	33.05 ^{c1}	30.40 ^{b1}	1.41 ^{c1}
PM 1%	40.47 ^{a1}	36.20 ^{a1}	1.75 ^{a1}
GG 1%	45.23 ^{b1}	37.98 ^{a1}	2.07 ^{b1}
GX 1%	51.19 ^{c1}	46.14 ^{b1}	1.54 ^{c1}
CMC 1%	33.17 ^{d1}	24.67 ^{c1}	1.68 ^{a1}
PM 1.5%	43.33 ^{a1}	37.99 ^{a1}	1.92 ^{a1}
GG 1.5%	51.64 ^{bc1}	38.89 ^{a1}	2.38 ^{b1}
GX 1.5%	62.37 ^{b1}	56.4 ^{b1}	1.6 ^{a1}
CMC 1.5%	71.9 ^{b1}	42.58 ^{a1}	3.98 ^{b1}
PM 4.5%	79.17 ^{a1}	64.85 ^{a1}	2.22 ^{a1}
Range of standard deviation	0.84–9.70	0.82–9.01	0.03–0.56

^{a1}Data are the mean of three independent replications for each sample. Values with the same letter in a row and the same number in the same column are not significantly different. Test of mean differences for a significance level $\alpha = 0.05$, using Tukey's test.

median ($D_{[0,5]}$) and the polydispersity index (PI). It was observed that at equal concentrations of continuous phase, the $D_{[4,3]}$ and $D_{[0,5]}$ of the emulsions with PM were lower than the respective values of GG and XG emulsions. In addition, the polydispersity index of the emulsions containing PM was lower than in the emulsions containing GG, indicating greater uniformity in particle size distribution. Emulsions with CMC generally had lower values of $D_{[4,3]}$ and $D_{[0,5]}$ lower than the rest of the emulsions, but with higher polydispersity. Table 3 shows that the $D_{[4,3]}$, $D_{[0,5]}$ and the polydispersity index of the emulsion containing PM at 4.5% (w/v) were higher than the respective values of the more concentrated emulsions prepared with GG and XG.

The same table also shows that the $D_{[4,3]}$ and $D_{[0,5]}$ of the emulsions with PM experienced no significant changes with increasing emulsion concentration except for PM 4.5% (w/v) sample. These parameters shifted to higher values when the concentration was increased in the case of emulsions prepared with XG and GG. This can be explained considering that as the concentration increases the viscosity increases, which may reduce the efficiency of the homogenization process, resulting in larger droplets. According to the results obtained, the increase of viscosity with the concentration would apparently be more marked in GG and GX than in PM emulsion. On the other hand, the polydispersity index of these emulsions increased with their concentration, but not significantly. Emulsions containing CMC did not show a clear trend in the values of $D_{[4,3]}$ and $D_{[0,5]}$; however, the PI increased with increasing concentration.

The stability of an emulsion is influenced, among other variables, by the size and particle size distribution. A stable emulsion generally corresponds to a distribution of sizes slightly dispersed with a

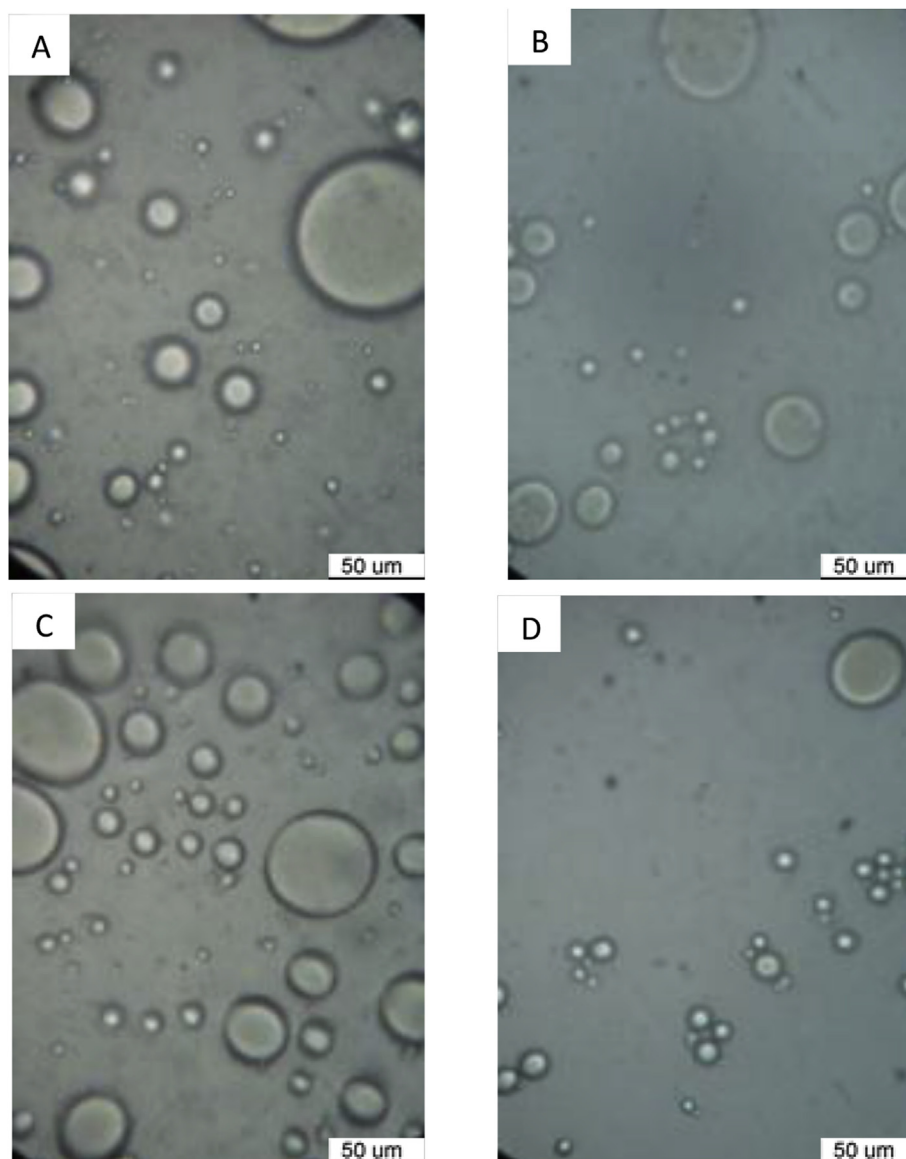


Fig. 2. Optical micrographs (100x) of emulsions of (A): mucilage, (B): guar gum, (C): xanthan gum, and (D): carboxymethyl cellulose. Concentration of the continuous phase: 1.5% (w/v).

maximum located in small diameters (Lissant, 1974). In our case, the emulsions prepared with PM presented $D_{[4,3]}$ and $D_{[0,5]}$ values usually lower than the rest of the emulsions studied and narrower size distributions; as evidenced by lower polydispersity index values, one would expect that these emulsions will be stable.

3.2.2. Microstructure of emulsions

Fig. 2 (A, B, C, and D) corresponds to 1.5% (w/v) emulsions prepared with PM, GG, XG, and CMC, respectively. This figure shows that the microstructure of fresh emulsions was similar. Furthermore, the polydispersity characteristic of the emulsions was also well demonstrated in their respective micrographs by the existence of a mixture of droplets with different sizes.

3.2.3. Rheological behavior

3.2.3.1. Steady-shear flow measurements. The emulsions studied in the present work are dilute emulsions (dispersed phase < 30%), therefore the individual droplets would not interfere with each other appreciably, and the properties of the system would be mainly determined by those of the continuous phase (Lissant, 1974; Hayati et al., 2009). Therefore,

flow curves of the solutions of the hydrocolloids studied are previously presented in Fig. 3. All of them exhibit a pseudoplastic behavior, but the onset of shear thinning for each polysaccharide was different. It depended on the degree of space-occupancy ($C[\eta]$), proportional to the number of coils present and the intrinsic viscosity (proportional to the volume occupied by each coil).

Fig. 3 shows that the PM has a behavior similar to GG at low concentrations and similar to XG at higher concentrations. XG is the most pseudoplastic and the one that presents the highest values of $C[\eta]$ (Table 2).

The flow curves (data not shown) of all emulsions exhibited a shear-thinning behavior similar to that of their hydrocolloid solutions. Their viscosity gradually dropped with increasing shear rate. Table 4 shows the parameters k and n obtained by linear regression analysis according to Ostwald-de Waele model for the flow curves of emulsions at all the concentrations studied.

It was observed that the flow behavior index shows values lower than 1 corresponding to a pseudoplastic behavior. From a macromolecular point of view, this behavior of emulsion systems can be explained by a change in the orientation and shape of the hydrocolloid

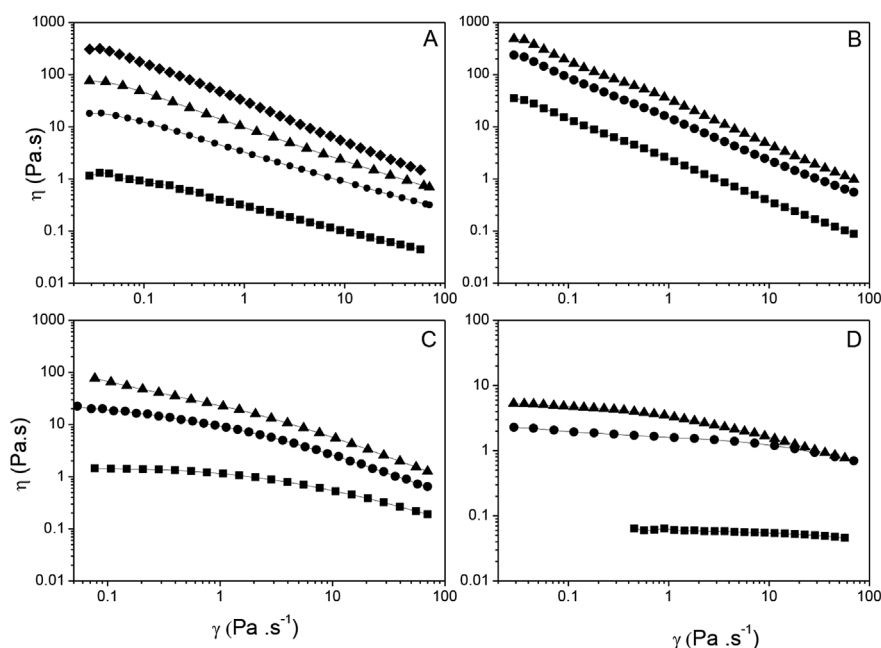


Fig. 3. Shear rate dependence of the apparent viscosity of (A) mucilage, (B) xanthan gum, (C) guar gum, and (D) carboxymethyl cellulose solutions at: ■ 0.5, ● 1, ▲ 1.5, ◆ 4.5 (%w/v).

Table 4

Rheological parameters from Ostwald-de Waele equations and the relaxation time for emulsions containing mucilage (PM), guar gum (GG), xanthan gum (XG), and carboxymethyl cellulose (CMC).

Hydrocolloid	Concentration (%w/v)	k	n	λ (s)
PM	0.5%	0.24	0.58	
	1%	2.67	0.48	1.00 ^{a1}
	1.5%	3.33	0.41	3.71 ^{b1}
	4.5%	20.92	0.22	50 ^{c1}
GG	0.5%	4.27	0.39	0.32 ^{d1}
	1%	16.89	0.31	1.86 ^{e1}
	1.5%	51.63	0.20	3.71 ^{b1}
XG	0.5%	2.54	0.28	
	1%	5.08	0.24	
	1.5%	9.85	0.18	
CMC	0.5%	0.08	0.94	
	1%	2.99	0.75	
	1.5%	6.44	0.57	

^m Average value of three replicates. Values with the same letter in a row and the same number in the same column are not significantly different ($\alpha < 0, 05$). R² (coefficient of determination) was between 0.985 and 0.996.

chain forming the continuous phase. In addition, the oil droplets having a spherical shape can be deformed by acquiring an elongated shape with the increase of the applied shear rate and consequently, the viscosity decreases.

The flow index of the emulsions prepared with PM were higher than that GG and XG, except at the concentration of 4.5% (w/v), which presented a value n similar to that of 1.5% (w/v) GG and 1% (w/v) XG. The emulsions containing XG showed the lowest values of n and the emulsion prepared with CMC, the highest. This indicated that, the emulsions with XG had a more marked pseudoplastic behavior than the emulsions containing PM, GG and CMC. This may be due to their exceptional stiffness given by their rod-like conformation, which is more sensitive to shear than a conformation of statistical ball (Urlacher & Noble, 1997). According to de Cassia da Fonseca et al. (2009), xanthan molecules form weak gels through hydrogen bonding and polymer entanglement, which are progressively disrupted under the influence of the applied shear (i.e., highly pseudoplastic behavior) (Williams & Phillips, 2001).

The less pseudoplastic behavior of emulsions with CMC ($n = 0.94$ – 0.54) may be related to the linear structure (without ramifications) of

this polysaccharide, which allows it to undergo constant changes in its shape resulting in high flexibility and withstand stresses or deformations without changes in its macromolecular organization (Elliott & Ganz, 1977).

Table 4 also shows the consistency coefficient k for all emulsions in the different concentrations.

It was observed that an increase in the hydrocolloid concentration increased the consistency coefficient values. At equal concentration of the continuous phases, in the PM emulsion the values of k were lower than in XG and GG, but higher than in CMC. However, in the emulsion containing PM at 4.5% (w/v) the value of k was comparable with that of the emulsion containing GG at 1% (w/v).

Particularly, the increase in viscosity in mucilage emulsion can be explained by the fact that at higher hydrocolloid concentration in the solution, the number of molecules increase, therefore a greater intermolecular interaction of the polymer chains were is generated (Cárdenas et al., 1997). This results in increasingly entangled and less mobile macromolecular systems (Bhattacharya, Ghil, & Vulis, 1982; Maskan & Gogus, 2000).

3.2.3.2. Steady oscillatory flow measurements. Fig. 4 shows the mechanical spectra describing the viscoelastic behavior of emulsions at different concentrations of PM. As can be observed, both the dynamic storage modulus (G') and the viscous modulus (G'') of the emulsions with PM depended on the frequency. As illustrated in Fig. 4 A, at low concentration (0.5% w/v), the emulsion had a viscous behavior, with G'' higher than G' across all the frequencies examined. In dilute solutions below C^* where intermolecular entanglement does not occur, most polymers show G'' greater than G' over much of the frequency range (Williams & Phillips, 2001).

At concentrations of 1%, 1.5% and 4.5% (w/v) (Fig. 4 B, C, D), G'' was higher than G' at the low frequency region, until a certain characteristic frequency (ω_c) where a crossover point occurred ($G'(\omega_c) = G''(\omega_c)$). After that, the behavior became rather elastic ($G' > G''$) (Ferry, 1980; Steffe, 1996). At higher concentrations, in the entanglement region above C^* , G' and G'' are still frequency dependent but G' is greater than G'' over a broader range of frequencies (Williams & Phillips, 2001). According to this, PM shows a $C^* = 0.4$ (Table 2).

The same experiments were carried out with GG, XG and CMC. The mechanical spectra of emulsions prepared with GG (Fig. 5A) revealed a viscoelastic behavior with a crossover similar to that of emulsions with

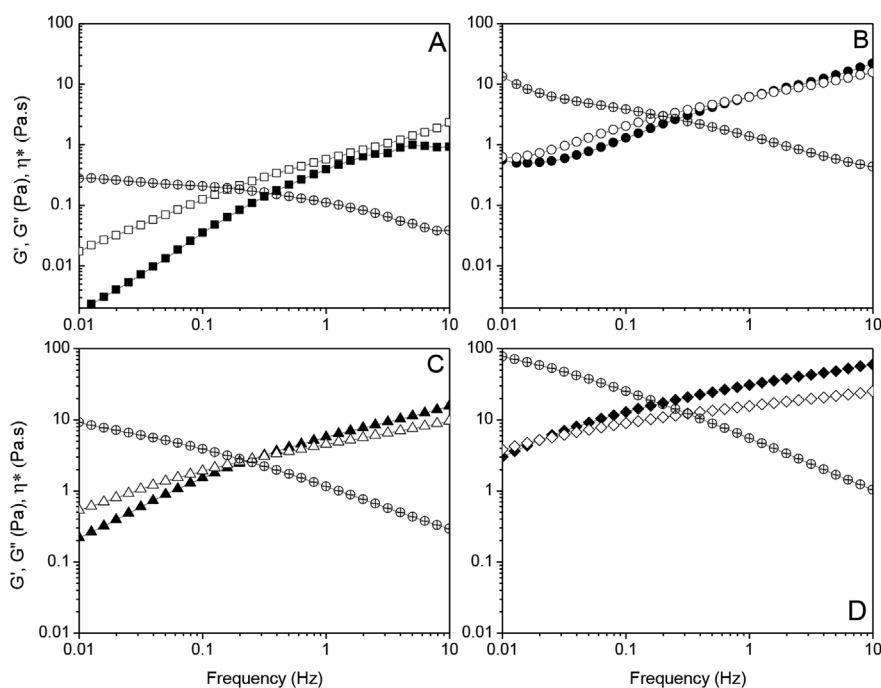


Fig. 4. Frequency dependence of the storage modulus G' , loss modulus G'' and $|\eta^*|$ of mucilage emulsions at different concentrations (% w/v): (A) ■ 0.5 (B) ● 1 (C) ▲ 1.5, and (D) ◆ 4.5. Filled symbols, G' . Blank symbols, G'' . ⊕ $|\eta^*|$. (Stress 0.4, 25 °C).

PM. This crossover suggests a conformational change in the molecule and has been explained as the transition from a random coil to an entangled conformation (Macosko, 1994).

Table 4 lists the relaxation times (λ) obtained from the frequency rheograms of emulsions prepared with PM and GG. The increase in relaxation time was observed when gum concentration increased.

At 1% (w/v) the relaxation time of the emulsion with PM was lower than that of the emulsion with GG. However, at 1.5% (w/v) the emulsions containing PM and GG showed the same relaxation times. A greater increase in relaxation time (50 s) was observed when mucilage concentration reached 4.5% (w/v). Lorenzo, Zaritzky, and Califano (2008) reported that the relaxation times on the order of 0.1 s are an indication of low elasticity and those on the order of 100 s are related to a notable increase in the elastic behavior and the strength of the structure. In this respect, the λ value of PM emulsion (4.5% (w/v)) would indicate a more elastic behavior and greater resistance of its structure, which might favor the stability of this emulsion.

However, another kind of behavior was observed for all emulsions containing different concentrations of XG (Fig. 5B), which exhibited a typical plateau region in the frequency range indicating a small frequency dependence of both moduli. The G' modulus was always higher than the G'' modulus, within the experimental frequency range. The plateau region is normally attributed to the formation of a pseudo-gel network due to polysaccharide chain entanglements.

Figs. 4 and 5 also show the dependence of complex viscosity (η^*) on the frequency of the PM, GG and XG. The complex viscosity reflects the trends observed in the dynamic moduli, decreasing with increasing the frequency. PM at 4.5% (w/v) and XG at all concentrations showed a strong dependence on the complex viscosity with the frequency, indicative of an ordered structure such as a weak gel (Wang & Cui, 2005). Furthermore, this dependence is in agreement with the viscoelastic behavior of the systems that present entanglements at $C > C^*$ (Sworn, 2007).

On the contrary, in the rheograms of emulsions with CMC (not shown) G'' was higher than G' , indicating a viscous behavior across the frequency range at all the concentrations studied. It was also noted that the G' and G'' moduli were strongly dependent on the frequency and the values were close to each other with increasing frequency, and the dynamic viscosity (η^*) was virtually independent of frequency. This is a

typical dilute solution behavior, which indicates a loss of structure at these conditions (Xiu, Zhou, Zhu, Wang, & Zhang, 2011).

3.2.4. Emulsion stability

3.2.4.1. *Creaming stability (static method)*. The plots of the creaming index (CI %) of emulsions containing PM, GG and CMC vs. storage time are shown in Fig. 6 as functions of the continuous phase concentration. This index has been used to indicate the susceptibility of the oil droplets to creaming and coalescence induced by gravitational forces (McClements, 1999; Pearce & Kinsella, 1978).

Fig. 6 shows that the CI (%) increased with the storage time, except for the emulsion containing PM at 4.5% (w/v) (Fig. 6 A) and the emulsion with GG at 1.5% (w/v) (Fig. 6 B), which were completely stable without creaming or phase separations during the test period.

At equal concentration of the continuous phase, the emulsions with CMC (Fig. 6 C) showed the highest CI (%).

In addition, increased concentration of the continuous phase reduced the rate of creaming of O/W emulsions, which may be because an increase in concentration causes an increase in viscosity in the continuous phase that slows down the movement of dispersed droplets and thus, the stability of emulsions is greater. A higher concentration increases the degree of interaction between polymer chains (Launay, Doublier, & Cavalier, 1986), giving rise to macromolecular systems increasingly entangled and with less mobility, which results in an increase in viscosity (Bhattacharya et al., 1982; Maskan & Gogus, 2000).

The emulsions prepared with XG were superior to the other emulsions in terms of stability. They were completely stable with no creaming or phase separations at any of the concentrations studied. This behavior could result from the ability of the molecules to form aggregates through hydrogen bridges and entanglement of the polymer. This highly ordered network produces a high viscosity at low shear rate (Sworn, 2000).

To corroborate this assumption, data of the apparent viscosities were taken at low shear (0.03s^{-1}) of the flow curves of the emulsions of different hydrocolloids. The viscosities were taken at this low shear rate to approximate the system to static conditions. These data were compared at the same continuous phase concentrations and are shown in Fig. 7. In all cases it was observed that an increase in the hydrocolloid concentration resulted in an increase in apparent viscosity. By

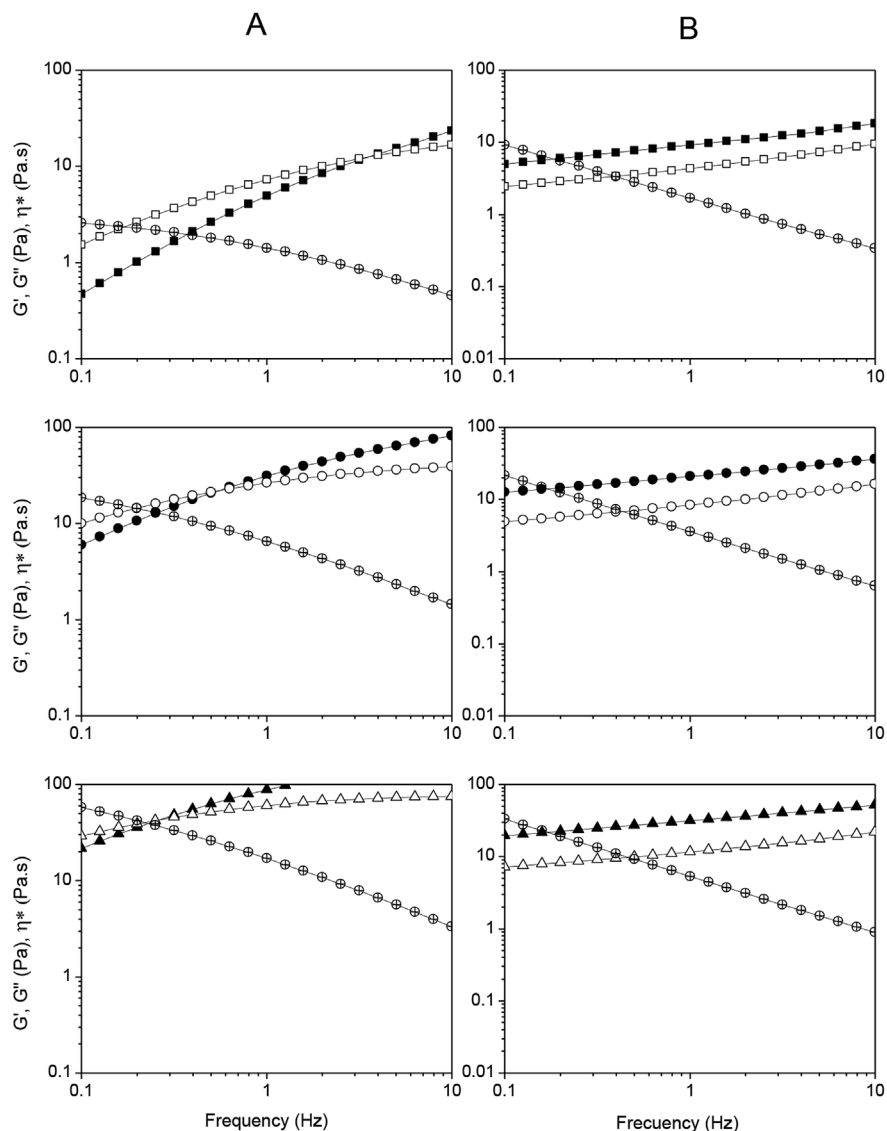


Fig. 5. Frequency dependence of the storage modulus G' , loss modulus G'' and $|\eta^*|$ of emulsions with (A) guar gum and (B) xanthan gum at different concentrations (% w/v): ■ 0.5, ● 1, ▲ 1.5. Filled symbols, G' . Blank symbols, G'' . ⊕ $|\eta^*|$. (Stress 0.4, 25 °C).

comparing these data with the values of CI (%) (Fig. 6), a correspondence between them was observed, i.e., the rate of creaming decreased with increasing viscosity. This behavior was also observed by Buscall, Goodwin, Ottewill, and Tadros (1982) for high molecular weight polysaccharides. In this sense, at equal concentration of the continuous phase, the emulsions with higher viscosities were the most stable (XG and GG). Emulsions prepared with PM showed apparent viscosities higher than those of CMC; consequently their CI (%) values were smaller. However, the emulsion with PM at 4.5% (w/v) showed similar viscosity to that of the emulsion with GG at 1.5% (w/v) and did not destabilize either during the test time. Huang, Kakuda, and Cui (2001) found that in the emulsions prepared with GG and CMC solutions, an increase in the concentration of the continuous phase from 0.5 to 1.5% (w/v) increased their stability. One of the causes to which they attributed this increase in the stability is the increase in the viscosity of the continuous phase that surrounds the oil droplets.

On the other hand, the stability is also associated with a homogeneous particle size distribution and lower $D_{[4,3]}$ values. Although the emulsions with PM showed a narrow particle size distribution and the characteristic $D_{[4,3]}$ diameter lower than those of the other emulsions (Table 3), they were more unstable than GG emulsions. Therefore, we can conclude that in this study the stability of emulsions is more related

to the viscosity of the continuous phase and to the type of hydrocolloid than to the particle size.

3.2.4.2. Emulsion extensibility (rheological methods). In Fig. 8 critical shear stress (τ_c) values of all the emulsions at the different continuous phase concentrations tested are presented. This parameter is an indicator of loss of emulsion stability (Tadros, 2004). Above this value, the structure of the emulsion starts to break down (for example, breakdown of flocs into smaller units and/or breakdown of a structuring agent). On the other hand, the higher the τ_c value the more extensible the emulsion and the greater the system ability to be dispersed without breaking (Hayati et al., 2009).

Fig. 8 also shows that τ_c values increased with the hydrocolloid concentration in the continuous phase and presented the following order GG > PM > XG > CMC for each concentration tested. The most extensible emulsion was the emulsion containing GG, although the emulsion with PM was more extensible than the emulsions prepared with XG and CMC. This behavior could be related to the conformation of the molecule; GG has a random coil that is less sensitive to the application of oscillatory stress, which could explain the higher values of τ_c . The τ_c values of XG were lower than that of GG and PM because of its exceptional stiffness and rod-like conformation, which is more sensitive

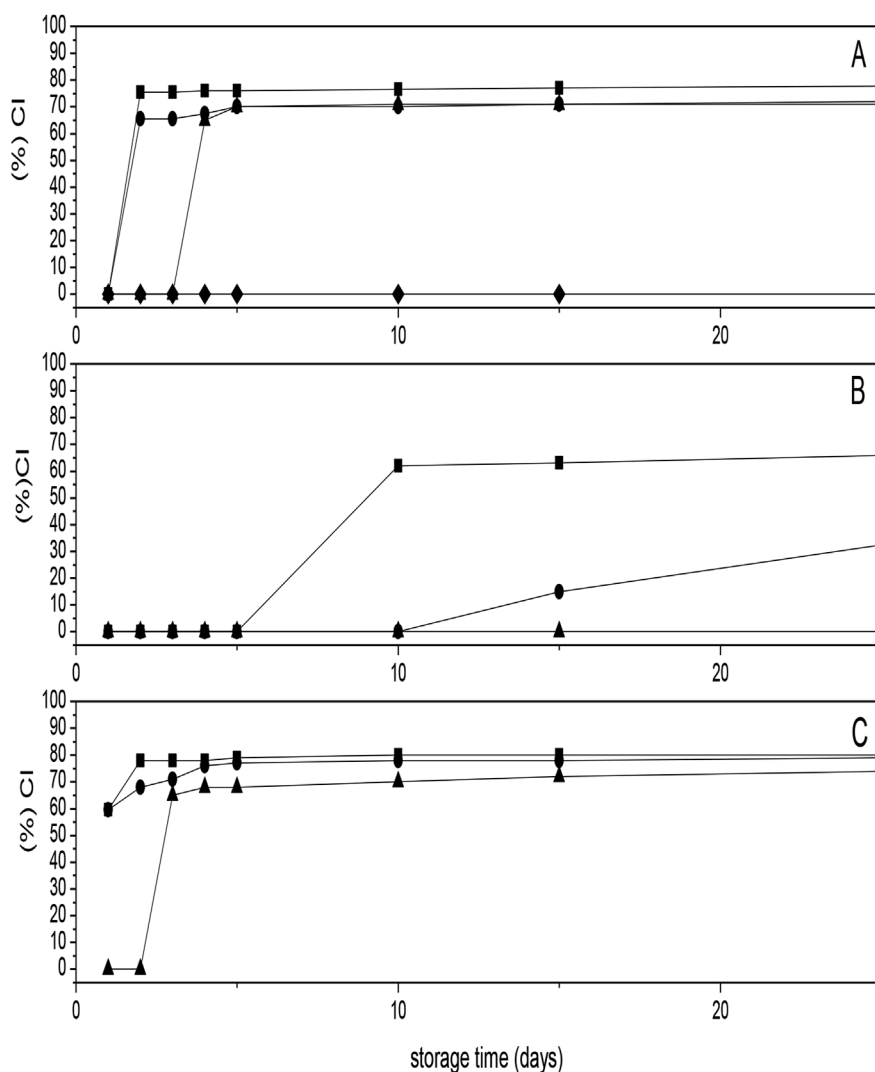


Fig. 6. Evolution of CI % vs. storage time of emulsions with (A) mucilage, (B): guar gum, and (C): carboxymethyl cellulose at ■ 0.5%, ● 1%, ▲ 1.5%, and ◆ 4.5% (w/v).

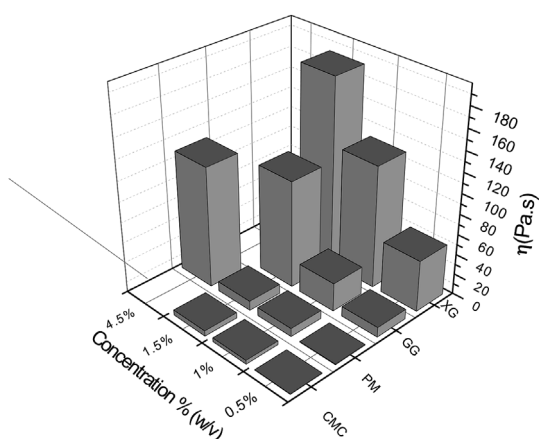


Fig. 7. Apparent viscosity of emulsions taken at $\dot{\gamma} = 0.03s^{-1}$ of mucilage (PM), guar gum (GG), xanthan gum (XG), and carboxymethyl cellulose (CMC).

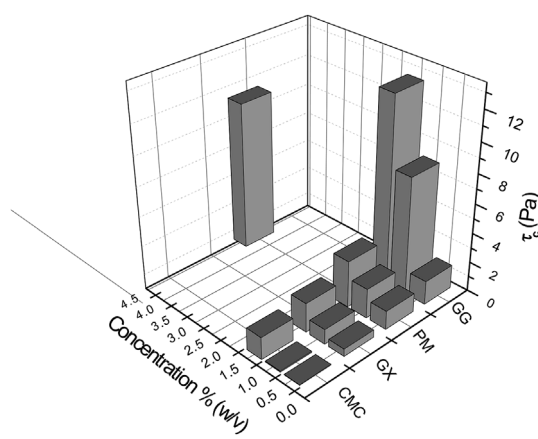


Fig. 8. Effect of concentration on the extensibility of emulsions with mucilage (PM), guar gum (GG), xanthan gum (XG), and carboxymethyl cellulose (CMC).

to oscillatory stress than a random coil conformation (Urlacher & Noble, 1997). Conversely, PM presented τ_c values lower than GG but greater than XG, which could be explained due to the presence of molecular aggregates (Cárdenas et al., 1997) that are more sensitive to the application of stress than a random coil conformation but less stiff

than a rod-like conformation. These conformations in the range of concentrations studied are supported by the values of $C[\eta]$ obtained for the solutions of the polymers used to prepare the emulsions.

An important result was found when the stability of the emulsions was evaluated under stress conditions. The emulsion at all the

concentrations of PM tested showed a τ_c value higher than that of the emulsions with XG. This indicates that emulsions with PM were more stable than the emulsions containing XG when stress was applied. This is contrary to the results obtained by the static method (Fig. 6) where the emulsions with XG were the most stable.

On the other hand, the τ_c of the emulsion containing PM at 4.5% (w/v) was higher than that of the rest of the emulsions except for the emulsion with GG at 1.5% (w/v) and therefore, it was one of the most extensible emulsions.

4. Conclusions

This study compared the stability and rheological properties of PM emulsions with food-grade hydrocolloid emulsions such as GG, XG and CMC. At equal continuous phase concentration, the emulsion with PM had a droplet mean diameter on the same order as that of the emulsions containing GG and XG, but a lower polydispersity index.

The emulsions presented pseudoplastic behavior and fitted Ostwald-de Waele model. The consistency coefficients of emulsions with PM were the lowest at equal concentration of hydrocolloid, indicating less viscosity. However, in the emulsion containing PM at 4.5% (w/v) the value of k was comparable with that of the emulsion containing GG at 1% (w/v). On the other hand, the flow behavior index of the PM emulsion showed less pseudoplastic behavior than the emulsion containing GG and greater resistance to the application of stress. The mechanical spectra of emulsions with PM revealed a viscoelastic behavior similar to that of the emulsions stabilized with GG. The rheograms of the emulsions prepared with PM and GG showed values of G'' higher than G' at the low frequency region, until a certain characteristic frequency (ω_c) where a crossover point occurred ($G'(\omega_c) = G''(\omega_c)$). After that, the behavior became rather elastic ($G' > G''$). The relaxation times (??) obtained from these rheograms showed that the emulsion containing mucilage at 4.5% (w/v) presented the highest λ . This means that this emulsion had a more elastic behavior and greater resistance of its structure than the emulsion containing GG.

The stability of the emulsions was evaluated by the static method, and it was determined that the creaming index of emulsions with PM was higher than that of GG. However, the emulsion with PM at 4.5% (w/v) did not become destabilized. The emulsions containing XG did not destabilize at any of the concentrations studied. The stability of these emulsions is related to the viscosity of the continuous phase; an increase in concentration causes an increase in viscosity, which slows down the movement of the dispersed droplets thus producing a greater stability of emulsions.

The stability of the emulsions was also evaluated by a rheological method. The emulsions prepared with GG were the most extensible presenting the highest critical shear stress (τ_c). In the emulsions containing PM, τ_c was lower than in the emulsion with GG but higher than in the emulsions containing XG.

The emulsions with XG were more stable against creaming but less stable against stress, showing the lowest τ_c . Emulsions with CMC were found to be the most unstable against creaming and stress.

The emulsion containing PM at 4.5% (w/v) exhibited a stability similar to that of the emulsion with GG under stress and static conditions. On the other hand, the stability of this emulsion was higher than that of the emulsion with XG under stress conditions.

The emulsion of PM containing 4.5% (w/v) of continuous phase ensures reaching a higher viscosity and complete retardation of destabilization by creaming in emulsions. The stability and the viscoelastic properties of these emulsions are related to the viscosity of the continuous phase. Under these conditions, the mucilage could be used in order to modify the rheological and dispersion characteristics of emulsions.

Considering that, mucilage is an abundant regional resource, easy to extract, inexpensive and with properties similar to the most widely used hydrocolloids, it would be feasible to use it in food applications.

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