



Rheological characterization of O/W emulsions incorporated with neutral and charged polysaccharides

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ABSTRACT

The effects of polysaccharides, including xyloglucan from *Hymenaea courbaril* (XG), galactomannans from *Schizolobium parahybae* (GMSP) and *Mimosa scabrella* (GMMS), xanthan gum (XT), sodium hyaluronate (HNa) and Fucogel® (FG), on the rheological behavior of cosmetic emulsions were evaluated. These incorporations gave rise to six emulsified systems, denoted XGE, GMSPE, GMMSE, XTE, HNaE and FGE, respectively. The emulsion consistency was found to follow the trend GMSPE > XGE > HNaE > FGE > XTE > GMMSE. In general, the addition of polysaccharides increased the viscoelastic properties of the emulsions and decreased the creep compliance. The neutral polysaccharides (GMSPE, GMMSE) led to better stability of the emulsions after storing for 20 days relative to charged polymers. It was found that polysaccharides XG, GMSP and GMMS, which come from the seeds of native Brazilian plant species, might be used to modify the flow properties and stabilities of oil–water emulsions.

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1. Introduction

Emulsions play a fundamental role in many fields, including the pharmaceutical, cosmetics and food industries, and their properties have been reviewed in several articles (Chappat, 1994; Dickinson, 2010; Tadros, 1992). An emulsion is a dispersion of droplets of liquids that are not completely miscible and may exhibit structural changes in various ways depending on the characteristics of the system and conditions it is under. Several breakdown processes of emulsions may occur, including creaming or sedimentation, which occurs when two or more droplets merge to form a droplet of larger volume and smaller area; flocculation caused by van der Waals attraction, which is when there is not sufficient repulsion between the droplets; Ostwald ripening caused by differences in chemical potentials of the materials within the small and large droplets; coalescence, induced by the thinning and disruption of the liquid film between the droplets; and phase inversion, whereby the dispersion phase and medium interchange (Tadros, 2004).

Rheological measurements provide information on the physical stability of emulsions. The factors that control the rheology of emulsions are (I) a continuous phase rheology; (II) the nature of the particles, such as their size distribution, deformability, internal

viscosity, and concentration; and (III) the nature of particle–particle interactions (Barnes, 1994).

Polysaccharide dispersions in water result in different rheological behaviors due to their unique molecular structures and conformations and are incorporated in the continuous phase of oil-in-water (O/W) emulsions (Bais, Trevisan, Lapasin, Partal, & Gallegos, 2005). These rheology modifiers can control the consistency of emulsions (Tadros, 2004) and can adsorb on interfaces at multiple sites, creating an electrostatic or steric barrier that acts between the droplets. The formation of extended hydrogel networks and their solvation properties serve to increase the effective adsorbed layer thickness, increase the interfacial viscosity, and thus slow down the droplet motion (Myers, 1999). Neutral polysaccharides, such as galactomannans, or some polyelectrolytes, such as arabic gum and pectin, can stabilize emulsions by reducing the interfacial tension as they display surface active properties (Dickinson, 2003).

The galactomannan source and its mannose to galactose ratio (M/G) can affect the emulsion capacity and stability (Hayati, Man, Tan, & Aini, 2009; Wu, Cui, Eskin, & Goff, 2009). Galactomannans with different M/G ratios extracted from seeds of *Mimosa scabrella* (GMMS, M/G ~ 1.1) and *Schizolobium parahybae* (GMSP, M/G ~ 3.0), sources found in plant species of the Brazilian biodiversity, were characterized structurally (Ganter, Zawadzki-Baggio, Leitner, Sierakowski, & Reicher, 1993) and rheologically (Bresolin, Milas, Rinaudo, Reicher, & Ganter, 1999), with GMMS studied in hydrogel

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matrix systems to stabilize the ascorbic acid (Koop, Praes, Reicher, Petkowicz, & Silveira, 2009). Xyloglucan (XG) found in *Hymenaea courbaril* Brazilian seeds is another nonionic polysaccharide whose gel properties have also been studied (Freitas, Busato, Mitchell, & Silveira, 2011; Lima-Nishimura, Quoirin, Naddaf, Wilhelm, Ribas, & Sierakowski, 2003) and that can therefore be tested in other complex systems such as emulsions.

Some anionic polysaccharides, such as sodium hyaluronate (HNa), xanthan gum (XT) and Fucogel® (FG) (Solabia BioEurope, Paris), are often added to cosmetics as moisturizing agents (Balazs & Band, 1984), viscosity controllers (Renaud, Belgacem, & Rinaudo, 2005) or psychosensorial agents (Guetta, Mazeau, Auzely, Milas, & Rinaudo, 2003).

In the present study, the rheological effect of incorporating XG, GMMs, GMSP, HNa, XT and FG into a cosmetic emulsion was investigated. This assessment was carried out by analyzing the steady state shear flow, creep–recovery and dynamic mechanical analysis of each formulation.

2. Materials and methods

2.1. Materials

The *S. parahybae* and *H. courbaril* seeds, collected in Piracicaba and Itatiba (São Paulo, Brazil), respectively, were purchased from Mata Atlântica Viveiro Florestal (Itatiba, São Paulo, Brazil). The *M. scabrella* seeds collected on natural stands of Bocaiúva do Sul (Paraná, Brazil) were provided by Instituto Ambiental do Paraná – IAP (Curitiba, Paraná, Brazil). Xanthan gum was obtained from CPKelco, Atlanta, USA. Sodium hyaluronate was obtained from HTL. Fucogel® was purchased from Solabia. Pemulen™ TR1 and TR2 were obtained from Noveon. Potassium cetyl phosphate was purchased from Sino Lion. Ethylenediaminetetraacetic acid (EDTA), triethanolamine and ethylhexyl methoxycinnamate were obtained from BASF. Glycerin, dibutyl adipate, dicaprylyl ether, 1-octadecanol and tocopheryl acetate were purchased from Cognis. Maleated soybean oil was obtained from ISP. Cetearyl wheat bran glycosides™ were obtained from Soliance. Butylhydroxytoluene (BHT) was purchased from Shell Chemicals. Cyclopentasiloxane was obtained from Dow Corning. Propylene glycol was obtained from Jeen. Benzyl alcohol was purchased from Clariant. Ethylhexylglycerin was purchased from Nikko.

2.2. Extraction and characterization of polysaccharides from Brazilian seeds

Galactomannans from *S. parahybae* (GMSP) and *M. scabrella* (GMMs) were extracted and identified according to Bresolin et al. (1999). The xyloglucan from *H. courbaril* (XG) was extracted and identified according to Freitas et al. (2005). The molar masses (M_w) of the polysaccharides were determined according to Freitas et al. (2011).

2.3. Preparation of emulsions

The O/W emulsions were manufactured as follows: the aqueous phase was prepared by the dispersion of a polysaccharide (0.15%, w/w) and other ingredients (4.0%, w/w, glycerin; 0.15%, w/w, Pemulen TR2; 0.1%, w/w, Pemulen TR1; 0.05%, w/w, disodium EDTA) in water (70.50%, w/w) under mechanical stirring (500 rpm, RW20, IKA, Germany) at 25 °C for 5 h and then heated to 75 °C. The oil phase was prepared by blending the ingredients (7.5%, w/w, ethylhexyl methoxycinnamate; 5.0%, w/w, dibutyl adipate; 3.0%, w/w, dicaprylyl ether; 1.0%, w/w, tocopheryl acetate; 1.0%, w/w, maleated soybean oil; 0.3, w/w, cetearyl glycosides; 0.25%, w/w, 1-octadecanol; 0.05%, w/w, BHT) and heating to 75 °C. The

oil phase (75 °C) and potassium cetyl phosphate (1.0%, w/w) were added to the continuous phase (75 °C), and the system was emulsified under mechanical stirring (1000 rpm) for 3 min. The remaining ingredients (3.0, w/w, cyclopentasiloxane; 1.5, w/w, propylene glycol; 0.6, w/w, benzyl alcohol; 0.5, w/w, ethylhexylglycerin; 0.35, w/w, triethanolamine) were mixed (35 °C) in with this system (500 rpm) during cooling to room temperature (25 °C) until thermal equilibrium was reached. Six types of emulsions were prepared, including a xyloglucan *H. courbaril* emulsion (XGE), a galactomannan *S. parahybae* emulsion (GMSPe), a galactomannan *M. scabrella* emulsion (GMMSE), a xanthan gum emulsion (XTE), a Fucogel (FGE) emulsion and a sodium hyaluronate emulsion (HNaE). A control emulsion (CE) was prepared without the addition of any polysaccharide. Each emulsion was prepared in three independent replications. The emulsions were stored in PVC recipients with screw caps in a dry place at a controlled temperature of 25 °C. The pH of all emulsions was not significantly affected by the presence of the polysaccharide dispersions and did not differ significantly among them (pH 6.5). There was neither an observable phase separation nor syneresis for any fresh sample with the storage time of 20 days.

2.4. Rheological analysis

The rheological properties of the emulsions were determined using cone and plate geometries (60 mm diameter; 2° cone angle; 0.105 mm gap) on a RheoStress 75 (Haake, Germany) rheometer with a controlled temperature maintained by a circulating water bath (DC5, Haake) and a Peltier (TC 81, Haake) and kept at 25 °C. Measurements were performed at 24 h, 15 days and 20 days after the sample preparation. Data collection, treatment and regression were performed on RheoWin 3 (Haake) software. After loading into the rheometer, the emulsion remained undisturbed for 10 min before the following tests were performed: (1) flow curve ($\dot{\gamma} = 0.1 - 100 \text{ s}^{-1}$; $t = 200 \text{ s}$), where the coefficient of determination R^2 was used as a parameter for the choice of the rheological model adopted; (2) stress ramp ($\sigma = 0.01 - 70 \text{ Pa}$; 10^3 s), where the yield stress value was established at a breakpoint in the slope of two power law regressions in a deformation, γ , versus stress, σ , double logarithmic plot. The intercept of the two curve fits was calculated by software (Kutschmann, 2003); (3) dynamic stress sweep ($\sigma = 0.01 - 100 \text{ Pa}$; $f = 1 \text{ Hz}$); (4) dynamic frequency sweep ($f = 0.01 - 10 \text{ Hz}$; $\sigma = 1.0 \text{ Pa}$); and (5) creep–recovery test ($\sigma = 2.5 \text{ Pa}$; 300 s ; $\sigma = 0 \text{ Pa}$; 300 s) and ($\sigma = 5.0 \text{ Pa}$; 300 s ; $\sigma = 0 \text{ Pa}$; 300 s) for emulsions and ($\sigma = 0.05 \text{ Pa}$; 300 s ; $\sigma = 0 \text{ Pa}$; 300 s) for polysaccharide solutions (3.5%, w/w) in which the compliance, J , versus time were plotted and the recovery, γ_E/γ_{MAX} , of deformation, γ , was determined (γ_E is the elastic deformation and γ_{MAX} is the maximum deformation).

3. Results and discussion

The rheological behavior of the six types of emulsions (XGE, GMSPe, GMMSE, XTE, FGE, and HNaE) was evaluated as a function of the type of polysaccharide added and the emulsion aging time at 25 °C.

3.1. Steady state rheology

Flow curves were obtained for oil-in-water emulsions with the addition of polysaccharides at 24 h, 15 days and 20 days after sample preparation. Flow curves representing the shear rate, $\dot{\gamma}$, and dependence of the shear stress, σ , recorded at 25 °C for oil-in-water emulsions with the addition of polysaccharides after 20 days of aging are shown in Fig. 1. None of the emulsions exhibited a linear relationship between the shear stress and shear strains (Fig. 1), thus

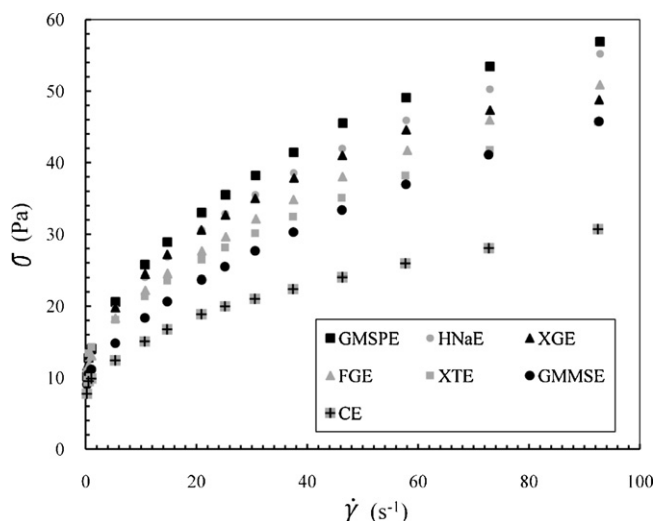


Fig. 1. Flow curves representing the shear rate, $\dot{\gamma}$, dependence of the shear stress, σ , recorded at 25 °C after aging (20 days) of oil-in-water emulsions. Samples containing polysaccharides, 0.15% (w/w), as: XGE, xyloglucan from *H. courbaril*; GMSPE, galactomannan from *S. parahybae*; GMMSE, galactomannan from *M. scabrella*; XTE, xanthan gum; HNaE, sodium hyaluronate; FGE, Fucogel; CE, control emulsion (without polysaccharide).

demonstrating non-Newtonian behavior. This occurs when chains detangle the spherical coils and the droplets in the emulsions are deformed into ellipsoidal shapes, while aggregates are broken into their elements and start to form layers coincident with the plane of shear, therefore offering less resistance to flow (Brummer, 2006; Tadros, 2011). The yield stress (σ_0) at the beginning of the flow curve is another feature observed for all emulsions; this threshold stress must be applied to breakdown the van der Waals interactions among the dispersed particles in order to initiate flow. Therefore, for shear stresses under the yield stress, the emulsion acts like an elastic solid. The attraction forces between the particles will be stronger with higher σ_0 because the system flows when the shear stress applied has a sufficient capacity to collapse these interactions (Hayati, Man, Tan, & Aini, 2007). From the flow curves, where CE had the lowest apparent viscosity, it is possible to observe that the resistance to flow was greater for emulsions containing polysaccharides. Similar flow profiles were obtained for oil-in-water emulsions with the addition of polysaccharides after 24 h and 15 days of storage (data not shown).

The flow curves for emulsions obtained at 20 days, 15 days and 24 h after sample preparation were fitted according to the Herschel–Bulkley model. The rheological parameters n and K of the samples (Table 1) changed from 24 h to 20 days storage time, especially in the presence of polysaccharides. The GMMSE had the

Table 1
Rheological parameters for oil-in-water emulsions with an addition of different types of polysaccharides (0.15%, w/w) and without polysaccharides obtained after storage times from flow curves ($\dot{\gamma} = 0.1 - 100 \text{ s}^{-1}$, 25 °C).

Sample	K^a (Pa s n)			n^a		
	24 h	15 days	20 days	24 h	15 days	20 days
CE	1.63	2.03	2.06	0.64	0.54	0.53
FGE	3.50	3.49	3.78	0.54	0.54	0.53
HNaE	5.40	5.40	4.39	0.49	0.48	0.51
XTE	4.57	3.85	2.72	0.47	0.51	0.56
GMMSE	1.60	2.44	2.34	0.67	0.60	0.60
GMSPE	4.60	4.61	5.59	0.53	0.51	0.48
XGE	4.78	5.17	5.20	0.49	0.50	0.51

^a Flow behavior index, n , and consistency coefficient, K , obtained by the fit ($R^2 = 0.99-1.00$) to the Herschel–Bulkley model: $\sigma = \sigma_0 + K\dot{\gamma}^n$.

Table 2

Yield stress (25 °C) for oil-in-water emulsions with an addition of different types of polysaccharides (0.15%, w/w) and without polysaccharides obtained after storage times.

Sample	Yield stress ^a σ_0 (Pa)		
	24 h	15 days	20 days
CE	5.2 ± 0.2	4.5 ± 0.3	4.6 ± 0.2
FGE	4.9 ± 0.5	4.2 ± 0.6	5.6 ± 0.4
HNaE	6.4 ± 0.3	6.6 ± 0.2	6.7 ± 0.3
XTE	8.2 ± 0.2	8.0 ± 0.1	8.0 ± 0.2
GMMSE	4.0 ± 0.4	4.5 ± 1.0	5.7 ± 0.3
GMSPE	5.2 ± 0.3	5.5 ± 0.5	6.0 ± 0.2
XGE	7.5 ± 0.6	8.3 ± 0.2	8.3 ± 0.1

^a The yield point, σ_0 , was established by the tangent method in a stress ramp.

highest flow behavior index, n , whereas XTE had the lowest n after 24 h. This parameter showed an increase with time, and after 20 days, the GMSPE was found to be the most shear-thinning, showing the lowest flow behavior index ($n = 0.48$).

Table 1 shows an increase in the emulsion consistency coefficient (K) when the polysaccharides GMMSE, XT, FG, HNa, XG and GMSP were added to the systems between 24 h and 20 days, with an intensity increase for GMSPE and XGE after 20 days, with values of $K = 5.59 \text{ Pa s}^n$ and $K = 5.20 \text{ Pa s}^n$, respectively. The consistency coefficient of the systems showed a slight increase from 24 h to 20 days except for the cases of XTE and HNaE. Mostefa, Sadok, Sabri, and Hadji, (2006) supposed that this increase in consistency with xanthan gum (1.61%, w/w) added to an oil in water emulsion was caused by a reorganization of the suspension in which oil droplet aggregates are trapped by the polymers in a continuous phase forming a three-dimensional network that is more resistant to flow.

Yield stress values, found overtime, for all samples are given in Table 2. At 20 days, only XGE, XTE and HNaE were within the range ($6.5 \text{ Pa} < \sigma_0 < 13 \text{ Pa}$) of a lotion considered to have a good primary skin feel (Brummer & Godersky, 1999). In general, the addition of polysaccharides led to increased σ_0 when held over the storage time. The σ_0 of the CE decreased with time, reflecting the weaker interactions of the enlarged oil droplets as a result of their greater mobility and collision frequency (Pal, 1997). These results are in agreement with Hayati et al. (2009), where the influence of xanthan (non-surface active), gum arabic (non-thickening), carboxymethyl cellulose (CMC) and commercial galactomannans (guar gum and locust bean gum) on the rheology of O/W emulsions were investigated. They reported an increase in the consistency coefficient and in the yield stress, followed by a gain in the emulsion stability for emulsions containing the galactomannans and CMC due to their surface activity at the oil–water interface and their thickening capacities.

3.2. Dynamic mechanical analysis

The effect of the O/W emulsion on the mechanical response with the addition of different types of polysaccharides was investigated by oscillatory tests. These assessments are sensitive to changes in chemical composition and in the physical structure of the samples due to allow a nearly non-destructive measuring method. Stress sweep experiments (0.01 Hz, 1.0 Hz, and 10.0 Hz) were carried out to ensure that the frequency sweep measurements were performed within the linear viscoelastic region. Fig. 2 shows the mechanical spectra of the O/W emulsions with different polysaccharides (0.15%, w/w) after storage times of 24 h, 15 days and 20 days. For all emulsions, $G' > G''$ throughout the entire frequency range and a linear reduction in $\log \eta^*$ was observed, featuring viscoelastic solid behavior with a gel-like structure. According to Brummer (2006), a mechanical spectrum of a stable emulsion with greater internal

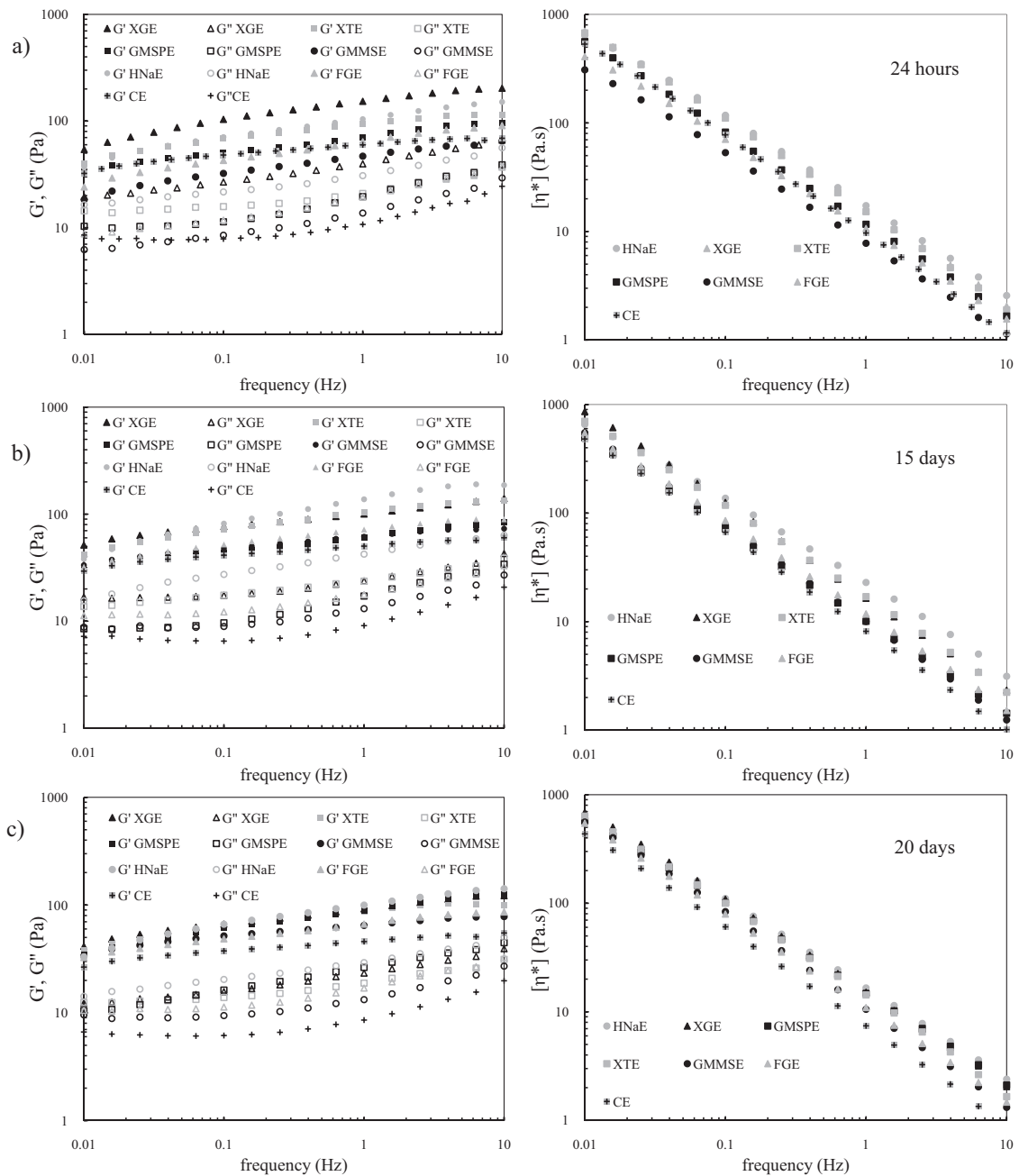


Fig. 2. Mechanical spectra (25 °C, $\sigma = 1.0$ Pa) showing the frequency dependence of G' , G'' , and η^* for the samples with 0.15% (w/w) and without polysaccharides at different storage times. (a) spectra recorded at 24 h; (b) spectra recorded at 15 days; and (c) spectra recorded at 20 days. Samples containing polysaccharides, 0.15% (w/w), as: XGE, xyloglucan from *H. courbaril*; GMSPE, galactomannan from *S. parahybae*; GMMSE, galactomannan from *M. scabrella*; XTE, xanthan gum; HNaE, sodium hyaluronate; FGE, Fucogel; CE, control emulsion (without polysaccharide).

strength shows a storage modulus, G' , higher than its loss modulus, G'' , and both moduli should be almost parallel throughout the observed frequencies, with a slight increase in the slope at high frequencies.

Frequency dependences of G' and G'' were evaluated by a power law regression (Valdez et al., 2006), and the exponents of the frequencies obtained were compared with the intention of observing the parallelism between the moduli and their changes with time. The gradient increases of G' and G'' at 24 h (Fig. 2a) for the samples were CE (0.23 and 0.40), FGE (0.27 and 0.38), GMMSE (0.27 and 0.41), GMSPE (0.22 and 0.42), XTE (0.24 and 0.35), HNaE (0.32 and 0.45) and XGE (0.19 and 0.34). Compared to a storage time of 24 h,

the rate of increase of G' and G'' with frequency did not change after 15 days of aging (Fig. 2b) for all samples tested, except for HNaE (0.29 and 0.33). After 20 days (Fig. 2c), the frequency dependence of G' and G'' showed a change in the gradient variation power: CE (0.18 and 0.46), FGE (0.13 and 0.35), GMMSE (0.13 and 0.40), GMSPE (0.30 and 0.41), XTE (0.17 and 0.35) and HNaE (0.24 and 0.38), whereas for XGE (0.28 and 0.30), both moduli varied in an almost parallel manner. The differences in the spectra from 24 h to 20 days could reflect some changes in the internal network structure during maturation of the emulsions. Fig. 2c shows higher G' and G'' values over the entire frequency range for polysaccharide added emulsions than for the control emulsion after 20 days. The

Table 3

Storage, G' , and loss, G'' , moduli recorded at 1.0 Hz for oil-in-water emulsions with an addition of different types of polysaccharides (0.15%, w/w) and without polysaccharides obtained after storage times.

Sample	G' (Pa)			G'' (Pa)		
	24 h	15 days	20 days	24 h	15 days	20 days
CE	59.9	50.3	45.9	10.8	9.1	8.6
FGE	63.9	71.9	66.5	19.4	17.7	17.0
HNaE	104.2	115.1	99.8	30.8	33.9	29.3
XTE	93.4	87.6	87.8	20.9	18.9	18.9
GMMSE	46.9	61.6	64.8	13.7	13.1	13.3
GMSPE	70.5	60.9	89.0	19.6	17.2	26.4
XGE	94.3	93.3	92.2	24.1	23.9	23.4

storage modulus (1.0 Hz) of the HNaE, XGE, GMSPE and XTE were approximately twice as high as the CE after 20 days (Table 3). CE had the highest G' decrease over time (Table 3).

The differences found in the mechanical properties of the emulsions studied were related to the nature of the polysaccharide added. In general, according to Table 3, the G' of the emulsions containing galactomannan (GMSPE and GMMSE) showed an increase between 24 h and 20 days, whereas G' showed a decrease over this same time period for the charged polymers.

These observations may reflect the singular structure of each natural polymer that can interact with other components of the system in its peculiar mechanism. The neutral polysaccharide (GMSP and GMMS) interactions with surfactants could be favored or not favored due to the peculiar hydrophobic domains among their structures; these can somehow interact better for one type of polymer than another. Interactions between polyelectrolytes and the anionic surfactant (potassium cetyl phosphate) may not be occurring due to electrostatic repulsions from their negative charges. The presence of glucuronic acid in HNa, XT and FG and also the pyruvate groups on the terminal mannose units of XT make these materials polyelectrolytes. Because the pK_a 's of XT (~ 3.2), HNa (~ 3.0) and FG (~ 3.5) are below the system pH (6.5), the carboxyl groups distributed along the polymer chains become almost entirely ionized (Cooper et al., 2006; Garna, Emaga, Robert, & Paquot, 2011; Young & Torres, 1989).

According to Myers (1999), besides the thickening of the continuous phase, there are also others factors that can change the rheology of emulsified systems. Interactions between surfactants and polysaccharides can affect the macroscopic properties of the systems. These interactions may occur by distinct mechanisms that depend on the chemical composition of the polymer chain, the nature of the surfactant and on the electrical charges involved.

3.3. Creep–recovery tests

Creep–recovery analysis depicts the transient behavior of the viscoelastic properties of a material. This method can provide information for short time periods to very long periods, allowing a more complete evaluation of these properties; with oscillatory tests, one can evaluate the properties on a smaller time scale (Scborsch, Gamier, & Doublier, 1997).

Fig. 3 shows the creep–recovery curves recorded for emulsions after 24 h (Fig. 3a), 15 days (Fig. 3b) and 20 days (Fig. 3c). The curves of compliance versus time exhibited the strain response pattern of viscoelastic materials. During the creep period, there is a sudden increase in strain (and consequently in compliance) when stress (2.5 Pa) is applied, in which the linkages between the structural units are elastically stretched. After this occurs, the strain increases slowly with time due to structural re-arrangements (Rao, 1999). During the recovery period, when stress is removed, the elastic response of the structure causes a quick drop in strain (hence, in compliance) releasing stored energy. This is followed by

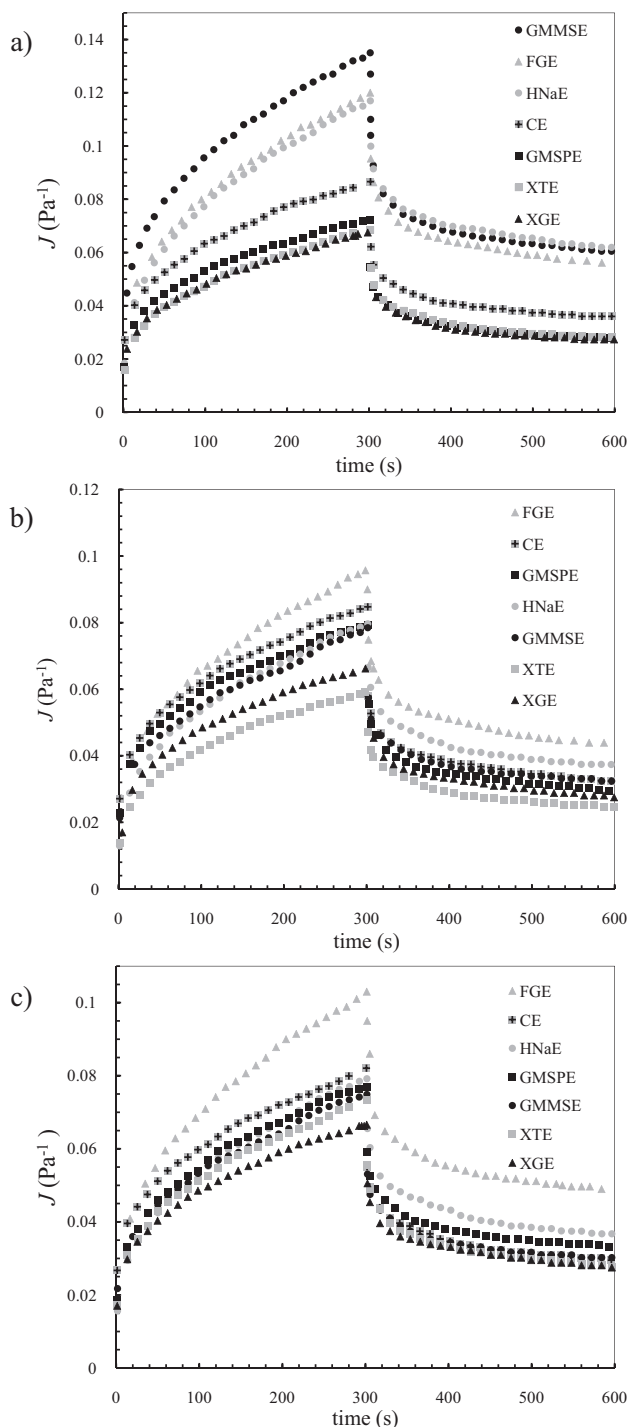


Fig. 3. Creep compliance, $J(t)$, plotted against time at 25 °C for the samples with 0.15% (w/w) and without polysaccharides at different storage times. The curves show the variation of J , in response to applied stress of 2.5 Pa. (a) Creep–recovery curves recorded at 24 h; (b) creep–recovery curves recorded at 15 days; and (c) creep–recovery curves recorded at 20 days. Samples containing polysaccharides, 0.15% (w/w), as: XGE, xyloglucan from *H. courbaril*; GMSPE, galactomannan from *S. paratybae*; GMMSE, galactomannan from *M. scabrella*; XTE xanthan gum; HNaE sodium hyaluronate; FGE, Fucogel; CE, control emulsion (without polysaccharide).

a progressive decrease in this response over time until permanent deformation is achieved, where a part of the structure is not recovered due to the development of a viscous component in the system (Steffe, 1996).

The compliance, $J(t) = \gamma(t)/\sigma_{\text{constant}}$, is the strain–stress ratio in which the higher the value of J , the lower the resistance

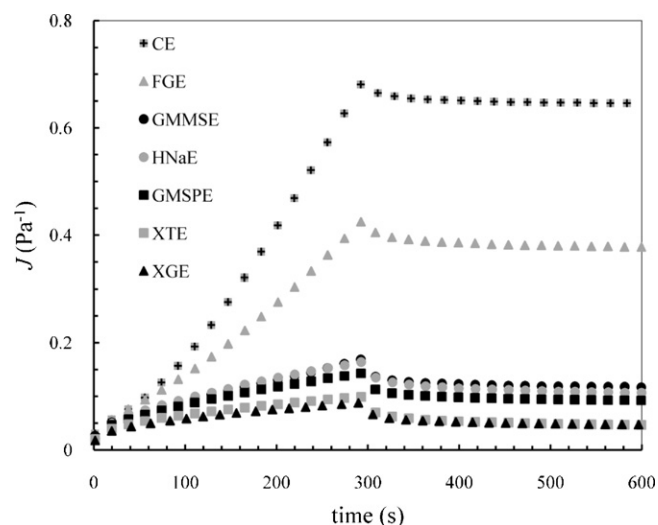


Fig. 4. Creep compliance, $J(t)$, plotted against time at 25 °C for the samples with 0.15% (w/w) and without polysaccharides after aging (20 days). The curves show the variation of J , in response to applied stress of 5.0 Pa. Samples containing polysaccharides, 0.15% (w/w), as: XGE, xyloglucan from *H. courbaril*; GMSPE, galactomannan from *S. parahybae*; GMMSE, galactomannan from *M. scabrella*; XTE xanthan gum; HNaE sodium hyaluronate; FGE, Fucogel; CE, control emulsion (without polysaccharide).

of the material to deformation. As shown in Fig. 3a–c, for an applied stress of 2.5 Pa in the interval between 0 and 300 s, the maximum creep compliance value, J_{MAX} , for XGE and CE showed a small fluctuation over the studied aging time (maintained at ~ 6.6 and ~ 8.4 cPa^{-1} , respectively), whereas for GMMSE (13.5 – 7.4 cPa^{-1}), HNaE (11.6 – 7.8 cPa^{-1}) and FGE (12.1 – 10.2 cPa^{-1}), a decrease was observed. For GMSPE (7.2 – 7.9 cPa^{-1}), a slight increase was observed. Sample XTE had a J_{MAX} value that was reduced from 24 h (6.9 cPa^{-1}) to 15 days (5.9 cPa^{-1}) and then increased after 20 days (7.3 cPa^{-1}). The recovery, γ_E/γ_{MAX} , of the structure was calculated by dividing the elastic recoverable strain by the maximum strain and multiplying by one hundred. There were no great differences in the recovery responses ($\sim 55\%$) among all samples tested for an applied stress of 2.5 Pa.

Further testing was carried out under greater deformation conditions, with an applied stress of 5.0 Pa. As shown in Fig. 4, while other systems maintained viscoelastic profiles, CE and FGE showed dramatic, almost linear increases in compliance in the creep period, with a small recovery when the stress was suspended. These characteristics were interpreted by Fitzsimons, Tobin, and Morris (2008) as the network fracture and flow of the system.

The differences in the maximum compliance and recovery capacity of the samples described in Table 4 show that the presence of XG, GMSP, GMMS, XT and HNa in low concentrations promotes

Table 4

The maximum compliance, J_{MAX} , and the recoverable strain, γ_E/γ_{MAX} , for oil-in-water emulsions with an addition of different types of polysaccharides (0.15%, w/w) and without polysaccharides obtained after storage times from creep–recovery curves ($\sigma = 2.5$ Pa; 300 s; $\sigma = 0$ Pa; 300 s).

Sample	J_{MAX} (cPa^{-1})			γ_E/γ_{MAX} (%)		
	24 h	15 days	20 days	24 h	15 days	20 days
CE	68.0	67.7	69.9	10.3	11.0	7.6
FGE	54.7	51.2	44.2	13.7	9.6	14.5
HNaE	21.3	23.2	16.6	23.5	25.1	35.9
XTE	8.4	7.5	10.1	51.4	54.1	53.4
GMMSE	98.8	17.1	17.3	7.9	33.3	32.4
GMSPE	13.4	15.4	14.5	41.5	38.0	36.4
XGE	10.8	9.6	9.0	43.6	45.9	47.0

a dramatic increase in the resistance to deformation (J_{MAX}) and on the recovery capacity of the system, highlighting the reinforcement of its structure. The aging time has a great influence on the behavior of the GMMSE, as it seems that the GMMS needs more time to form a network relative to the other polysaccharides. The gain in elastic properties may arise from a system with an enhanced structure where droplets are trapped by the formation of a network of carbohydrate molecules.

Creep and recovery tests ($\sigma = 0.05$ Pa) were also performed on isolated polysaccharide solutions (0.35%, w/w). The maximum compliances attained increased in solutions as XT (3.8×10^3 cPa^{-1}), HNa (4.8×10^4 cPa^{-1}), FG (3.8×10^5 cPa^{-1}), XG (8.4×10^5 cPa^{-1}), GMSP (1.0×10^6 cPa^{-1}) and GMMS (2.5×10^6 cPa^{-1}). Among the polyelectrolytes and the neutral polysaccharides, this order was maintained in the emulsified systems. Contrary to this trend, neutral and charged polysaccharide emulsions do not follow this order, as discussed above. It was found that the neutral polymers promoted a particular stability of the studied system. The great rheological influence on the emulsion with XG could be due to its interaction properties that promote the formation of gels with many substances, including alcohols, polyphenols and dyes (Nitta, Fang, Takemasa, & Nishinari, 2004).

Lower M_w 's for XT (9.0×10^5 g/mol), HNa (8.9×10^5 g/mol) and FG (1.1×10^6 g/mol) were found than for XG (1.8×10^6 g/mol), GMSP (1.5×10^6 g/mol) and GMMS (2.2×10^6 g/mol). Further, the higher molar mass of the neutral polysaccharides might be one of the factors that results in the positive effects observed for the rheology and stability of the emulsions studied. Among the neutral polysaccharides, GMSP (M/G ~ 3.0) has greater thickening properties than GMMS (M/G ~ 1.0) (Bresolin et al., 1997). Due to its higher M/G, GMSP displays better interaction abilities with other components relative to GMMS (Dea, Clark, & McCleary, 1986), resulting in a more structured system that can contribute to the stability of the emulsion by reducing the mobility of oil droplets.

From the present set of results, it was possible to observe that the initial stability promoted by XT to the emulsions decreased along storage time. However, galactomannans from seeds of *Mimosa scabrella* (GMMS, M/G ~ 1.1) and *Schizolobium parahybae* (GMSP, M/G ~ 3.0) were able to maintain their stabilities over time, probably because these polysaccharides display thickening and surface activity properties, while XT almost do not have a surface activity (Hayati et al., 2009).

4. Conclusions

This study confirmed that the rheological response of an oil-in-water emulsion depends on the type of polysaccharide added into the aqueous phase, even at low concentrations (0.15%, w/w). From the rheological analyses, the long term stability of the emulsions was favored by neutral polysaccharides (XGE, GMSPE, GMMSE) rather than by charged polysaccharides (XTE, HNa, FGE), as shown by the decrease in rheological parameters with storage time. In contrast to their behaviors in solution, emulsions of GMMS (M/G ~ 1.1) and GMSP (M/G ~ 3.0) were able to maintain their stabilities over time, probably because these polysaccharides display thickening and surface activity properties. The macromolecular characteristics, singular chemical structure and interactive properties determined the effects on emulsion rheology. In this way, the behavior in solution was not the only trend to be considered to select a polysaccharide for emulsion applications. Taken together, these results suggest that the rheological features of an emulsion can be modulated by choosing the right polysaccharide, thus allowing the preparation of emulsions for specific intended uses. Further, this work shows that biopolymers extracted from seeds of the native Brazilian species *S. parahybae*, *M. scabrella* and *H. courbaril* have the potential for applications in industry.

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