

PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION OF “DULCE DE LECHE”

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ABSTRACT

Physicochemical and rheological characterization of “dulce de leche,” a milk-based sauce especially popular in South America, was carried out on different types of commercial products (traditional, confectionery, reduced calories or reduced fat). Proximal composition, solid content, water activity, pH and color (Minolta Co., Ramsey, NJ) were evaluated. A controlled stress rheometer (Haake RS600; ThermoGap, Karlsruhe, Germany) was used to perform flow curves, dynamic oscillatory test in the linear viscoelastic range and creep-recovery experiments. Although in all samples, η decreased with increasing γ' , corresponding to shear-thinning behavior, clear differences were found in the rheological characteristics of different types of products. Experimental dynamic data were successfully modeled using the Baumgärtel–Schausberger–Winter equation to predict the mechanical relaxation spectrum. Satisfactory prediction of other mechanical properties was validated using creep experiments.

PRACTICAL APPLICATIONS

In spite of the differences in composition and rheological behavior of the several types of “dulce de leche” studied, it was possible to analyze the rheological characteristics of all systems and model the obtained results using the broadened Baumgärtel–Schausberger–Winter (BSW) model as a representation of the relaxation spectra to convert dynamic data into time domain. The parameters of the BSW model were used to explain structural characteristics of the systems; thus, the overall microstructural pattern of “dulce de leche” might be similar, and the differences observed would be mainly explained by the level of interactions among macromolecular components. Using the discrete spectrum obtained from the BSW model, it was possible to calculate other viscoelastic properties of interest; thus, the proposed methodology is a useful tool, especially for establishing a rheological data bank and analyzing viscoelastic experiments of this type of product.

INTRODUCTION

“Dulce de leche” (DL) is a milk-based sauce especially popular in South American countries. Primarily consumed as a sweet or spread as a jam, it is vaguely similar in taste to caramel. It is also the basis for the elaboration of many sweets and desserts which form part of the classics of the Latin American cuisine (“dulce de leche” in Argentina and Uruguay, “arequipe” in Colombia, “manjar blanco” in Peru

and “doce de leite” in Brazil). The consumption in Argentina is about 3 kg/caput per annum, with a stable production of 125,000 tons/year (Anon 2010).

It is prepared by boiling whole milk with added sucrose until 70% (w/w) total solids is reached. Usually, sucrose is replaced partially by glucose syrup to avoid crystallization (Martinez *et al.* 1990; Código Alimentario Argentino and Anexo Mercosur 1996; Hynes and Zalazar 2008). Another ingredient is sodium bicarbonate (about 1%), which

increases browning reactions and prevents protein coagulation by increasing the pH of the mixture above the isoelectric point of the protein. Sometimes, vanilla extract is added for flavoring. During evaporation, extensive nonenzymatic browning occurs, leading to a brown-colored product that has a characteristic and pleasant flavor. The product used in confectionery usually has a higher viscosity than the one used as a spread. The type of sugar and the stage at which it is added can strongly affect the characteristics of the final product (Corradini and Peleg 2000). The whole process takes 2–3 h. It ends when the total soluble solid content reaches 65–70°Brix. The resulting mixture of carbohydrates, proteins, and fats in this type of product generally determines its rheological, thermal and structural properties, thus affecting its functional characteristics. DL is a mixed disperse system; as the dispersant medium might contain several types of dispersed particles, the product might be, simultaneously, an emulsion, a suspension and a gel. It is mainly an aqueous nonequilibrium system with structures based on biopolymers. The two main construction materials of DL are proteins and polysaccharides. They are multifunctional and simultaneously fulfill several structural function systems (Tolstoguzov 2000).

DL has a typical texture that is important for consumers when evaluating its overall acceptability (Hough *et al.* 1986). Therefore, texture characterization is required for product standardization, process development, quality control and consumer acceptability. The kinetics of color and texture development has been discussed by Buera *et al.* (1990) and Pauletti *et al.* (1990, 1996). The texture of DL was studied earlier by coaxial shear viscometry (Moro and Hough 1985; Hough and Moro 1988; Rovedo *et al.* 1991; Heimlich *et al.* 1994). These authors reported that the pseudoplastic behavior of DL could be described by either Casson's or the Herschel–Bulkley models. When the latter was used, the flow index was on the order of 0.75, and the consistency coefficient was between 4 and 78 Pa·s. Those instrumental parameters that were related to the firmness of DL (yield stress, extrusion force, hardness, modulus and adhesiveness) were highly correlated with sensory hardness. No instrumental parameter was able to reflect the sensory ropiness of the samples (Ares *et al.* 2006). Using oscillatory dynamic tests, Pauletti *et al.* (1990), Navarro *et al.* (1999) and Pedrero *et al.* (2001) found that the rheological behavior of DL is intermediate between a concentrated solution and a gel, depending on the type and the solid content. Corradini and Peleg (2000) evaluated lubricated squeezing flow as an alternative method to assess the consistency of this product.

Rheological measurements are appropriate tools for obtaining information about the organization of macromolecules in the medium; thus, the correlation of the microstructural information with rheology is useful in understanding the macroscopic behavior in terms of the microstructural organization. The relaxation of polymeric materials reveals

the existence of a broad distribution of relaxation times. A particularly effective way of examining this experimentally is to determine the dynamic moduli G' and G'' (Tschoegl 1997).

DL is commercialized in four types of products in Argentina to be used in different applications: traditional, reduced calories, reduced fat and confectionery. They differ in their composition, caloric and lipid contents, and flow characteristics; under the common name of "dulce de leche," different products are available to consumers.

The objectives of the present work were to analyze the physicochemical properties of the four types of typical commercial DL (traditional, reduced calories, reduced fat and confectionery) and to develop a comprehensive study on the viscoelastic behavior of these products. This rheological characterization included the estimation of the relaxation mechanical spectra of the systems from dynamic oscillatory experiments performed within the linear viscoelastic range; the developed models were validated by comparing experimental creep-recovery results with the predictions calculated from the mechanical spectra.

MATERIALS AND METHODS

Materials

Samples of seven brands of DL were purchased in local retailers. Two brands corresponded to the traditional DL (M1, which is a premium brand, and M2); M3 was a confectionery DL; M4 is a reduced calorie type; and M5 and M6 corresponded to reduced fat. Except for M3, the rest of the products were supposed to be used as spreads. According to the specifications of the manufacturers, formulations also contained the following additives: M1 and M2 (glucose syrup, NaHCO₃), M3 (glucose, carrageenan, agar and pectin), M4 (fructose, sorbitol, polydextrose and microcrystalline cellulose), M5 (corn syrup, NaHCO₃) and M6 (glucose syrup, maltodextrin, carrageenan, corn starch and NaHCO₃).

Physicochemical Analyses

Proteins and lipids were determined according to AOAC (1984) methods 16.206 and 16.205, respectively, in triplicate. Moisture content was analyzed according to Moro and Hough (1985). The pH values of the homogenized samples were determined with a spear tip glass electrode (Cole-Palmer, Vernon Hills, IL, Catalog No. U-05998–20) on a pH meter (model EC30; Hach, Loveland, CO) previously calibrated with appropriate buffer solutions. The water activity (a_w) of the DL samples was determined in duplicate using an AquaLab Series 3 equipment (Decagon Devices, Inc., Pullman, WA) at 25°C. A Digit-080 refractometer (CETI Optical Instruments, Brussels, Belgium) was used to evaluate the solid content according to

Moro and Hough (1985). The instrument was calibrated prior to use with a standard refractive index glass.

Color

Color was measured at room temperature using a Chroma Meter CR-400 colorimeter (Minolta Co.) and Commission internationale de l'éclairage $L^*a^*b^*$ parameters (L^* , a^* and b^*) were determined. Averages of the three samples were considered for the analysis of color data.

Rheological Characterization

Rheological measurements were carried out using a controlled stress rheometer (Haake RS600; ThermoGap) with a serrated parallel plate fixture (diameter of 35 mm with a gap of 1 mm) at $20\text{C} \pm 0.1\text{C}$ controlled by means of a controlled fluid bath unit and an external thermostatic bath. After positioning the sample on the sensor system, it was allowed to rest for 10 min before starting the corresponding measurement. To minimize dehydration, samples were covered with a thin layer of silicone oil and a solvent trap was used. At least three measurement replicates were performed for each sample.

Steady Shear Flow

To obtain steady-state flow curves (viscosity η versus shear rate $\dot{\gamma}'$) of the DL samples, shear stress was measured by increasing the shear rate in steps between 0 and 100/s. The maximum measuring time per point was set at 300 s, but all measurements were obtained before the cut-off time, so it could be assumed that steady state was almost attained.

Oscillatory Shear Tests

Dependence of storage modulus (G') and loss modulus (G'') on angular frequency (ω) was determined at a small stress magnitude in the linear viscoelastic region (LVR). In the experiments, stress (σ) is applied as a sinusoidal time function at a fixed small amplitude. Stress frequency is stepwise increased, and at any frequency step, the resulting signal is transformed into the elastic and viscous components. The range of frequency used was from 0.01 to 300/s. G' is a measure of the energy stored and recovered per cycle, whereas G'' is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation (Ferry 1980).

Previously, oscillatory tests were conducted at a constant frequency of 6.28/s (1 Hz), varying the amplitude of the stress applied on the samples in order to search for the LRV. The criterion followed to its determination was the linear relationship between strain and stress. When materials are tested in the linear range, material functions such as G' and G'' do not depend on the magnitude of the applied stress, the magnitude

of the deforming strain or the rate of application of the strain. If linear, an applied stress will produce a proportional strain response.

Creep-recovery Experiments

Creep compliance as a function of time was determined in creep-recovery tests where the undeformed samples were suddenly subjected to a constant shear stress of 1 Pa within the LVR. All experiments were performed under a shear stress for 420 s and then released to allow sample recovery for 420 s.

Statistical Analysis

One-way analysis of variance (ANOVA) was performed by using the ANOVA procedures of the SYSTAT software (SYSTAT Inc., Evenston, IL). Least significant difference test was chosen for simultaneous pairwise comparisons. Differences in means and F -tests were considered statistically significant when $P < 0.05$.

RESULTS AND DISCUSSION

Physicochemical Characterization

Table 1 shows average protein, lipid, moisture and solid contents of the analyzed products, as well as the average water activity and pH of the samples. Moisture contents of traditional brands of DL (M1 and M2) were similar to those found by Castañeda *et al.* (2004) for eight samples of commercial DL, while protein contents of the same samples were equal or slightly higher than the values reported by these authors. DL of reduced calorie (M4 brand) presented the highest moisture content and a_w values (Table 1), with the lowest value for carbohydrates estimated by difference. M5 and M6 samples, with moisture levels in the range of 33–35%, presented the lowest fat content as advertised.

Ferramondo *et al.* (1984) found that the average values of a_w were in the range of 0.812–0.847 and pH values were in the range of 5.57–5.97 for six brands of traditional DL. The average a_w values for the two brands of confectionery-type DL were 0.802 and 0.831 and their pH was 5.79–6.17.

Table 1 also shows the average values of color parameters for lightness (L^*), redness (a^*) and yellowness (b^*) for the brands analyzed. Reduced calorie DL (M4) presented the highest lightness (L^*) and yellowness (b^*) values, while M1 (traditional) showed the lowest. Color parameters varied between types of DL and within one type, between brands, according to the formulations and different ingredients that were included. Luminosity (L^*) was the color parameter that presented more variability. Castañeda *et al.* (2004) reported the same conclusions when they analyzed eight traditional commercial DL brands. According to Pauletti *et al.* (1992), L^*

TABLE 1. PROXIMATE COMPOSITION, SOLID CONTENT, WATER ACTIVITY (a_w), pH AND COLOR PARAMETERS OF COMMERCIAL SAMPLES OF "DULCE DE LECHE"*

Type	M1 Traditional	M2 Traditional	M3 Confectionery	M4 Reduced calories	M5 Reduced fat	M6 Reduced fat
% Proteins	6.4 ^c	7.1 ^{bc}	7.5 ^{ab}	7.7 ^{ab}	6.5 ^c	8.2 ^a
% Lipids	7.2 ^a	7.9 ^a	3.3 ^b	5.8 ^a	1.3 ^b	1.4 ^b
% Moisture	31.5 ^e	32.4 ^d	33.7 ^c	48.8 ^a	35.3 ^b	33.7 ^c
% Solids	76 ^a	70 ^b	78 ^a	59 ^c	70 ^b	70 ^b
a_w	0.764 ^d	0.830 ^c	0.843 ^b	0.882 ^a	0.838 ^{bc}	0.833 ^c
pH	5.70 ^a	6.04 ^b	5.79 ^a	6.15 ^b	5.88 ^a	5.73 ^a
Color						
L^*	36.4 ^f	44.4 ^b	42.1 ^c	50.4 ^a	40.9 ^d	37.9 ^e
a^*	6.56 ^e	8.15 ^c	8.58 ^b	8.15 ^c	7.95 ^d	9.07 ^a
b^*	16.9 ^f	25.4 ^b	23.5 ^c	26.1 ^a	21.6 ^d	20.1 ^e

* Different superscripts within the same row indicate significant differences ($P < 0.05$).

explained 92% of the color variability sensorially detected on nine commercial sample representative of the Argentinean market; L^* ranged between 31.2 and 42.5. In the present work, the L^* values are somewhat higher (36.4–50.4).

Rheological Characterization

All experimental tests used to evaluate the rheological properties of the products showed marked dissimilarities between the different types of products.

Steady-state flow curves of all samples corresponded to a structured fluid with a clear shear-thinning behavior, also known as pseudoplastic behavior, over a wide range of shear rates, where two well-defined regions could be noticed; at low shear rates ($\dot{\gamma}'$), viscosity reaches a limiting value, namely zero-shear viscosity (η_0); as the shear rate increases, an abrupt power-law decay in the viscosity was observed (Fig. 1).

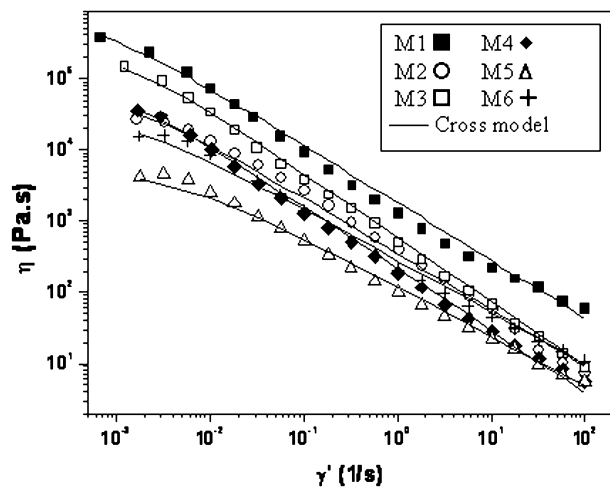


FIG. 1. STEADY-STATE FLOW CURVES OF COMMERCIAL "DULCE DE LECHE"

The flow behavior of the DL systems was fitted to the Cross model without the second Newtonian viscosity, η_∞ (Launay *et al.* 1986). The modified Cross model has been previously applied to other hydrocolloids with some deviations at low shear rate (Rao 1999):

$$\eta = \frac{\eta_0}{(1 + [\tau\dot{\gamma}']^m)} \tag{1}$$

where η_0 is the zero-shear-rate viscosity, m is a nondimensional exponent and τ is a characteristic relaxation time of the system. When $\eta < \eta_0$, Eq. (1) predicts a power-law behavior, where $(1 - m)$ is close to the flow index n . Figure 1 shows that the modified Cross model satisfactorily fitted the experimental data. The fitted η_0 , τ and m parameters of the model of each of the formulations are shown in Table 2. It can be seen that the M1 product (premium) showed the highest η_0 , being even more viscous than the confectionery DL (M3), while M2 had flow characteristics similar to that of both "light" products, M4 and M6. The lowest η_0 corresponded to M5.

The development of the storage and loss moduli with frequency was always qualitatively similar, but there were some fine structural differences in the mechanical spectrum.

TABLE 2. STEADY-STATE FLOW: ESTIMATED PARAMETERS OBTAINED BY CROSS MODEL, ZERO-SHEAR-RATE VISCOSITY, η_0 , NONDIMENSIONAL EXPONENT "m", AND CHARACTERISTIC RELAXATION TIME, τ , FOR THE DIFFERENT BRANDS STUDIED*

Brand	η_0 (Pa·s)	τ (s)	m
M1	$(9.7 \pm 0.2)10^5$	$(2.4 \pm 0.1)10^3$	0.81 ± 0.02
M2	$(7.3 \pm 0.1)10^4$	$(8.7 \pm 0.1)10^2$	0.79 ± 0.02
M3	$(3.2 \pm 0.2)10^5$	$(1.1 \pm 0.1)10^3$	0.91 ± 0.02
M4	$(1.1 \pm 0.1)10^5$	$(1.3 \pm 0.1)10^3$	0.87 ± 0.02
M5	$(6.5 \pm 0.2)10^3$	$(3.0 \pm 0.1)10^2$	0.70 ± 0.02
M6	$(4.0 \pm 0.2)10^4$	$(9.0 \pm 0.1)10^2$	0.73 ± 0.02

* Values are means \pm standard error of the mean.

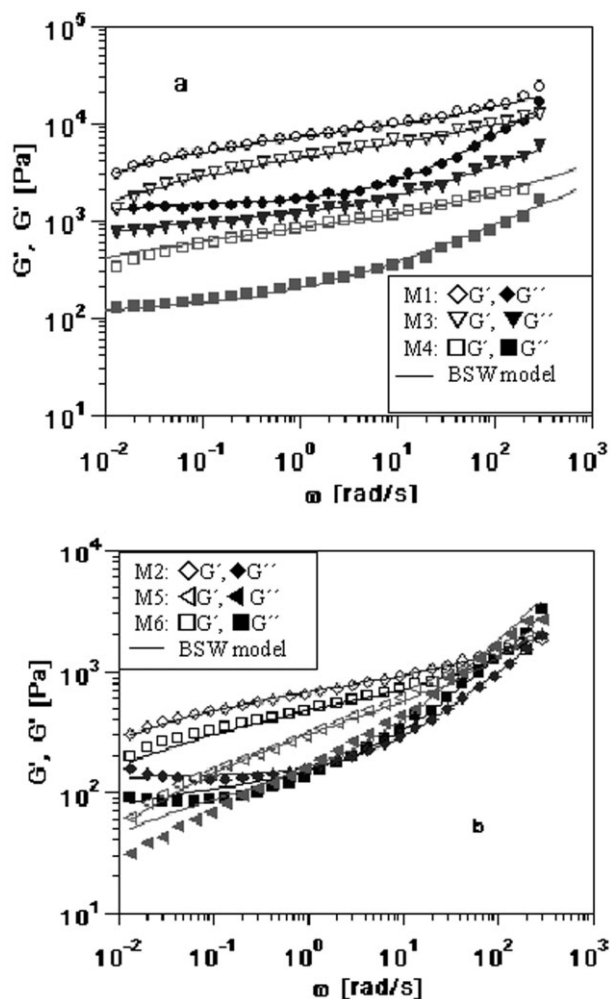


FIG. 2. FREQUENCY DEPENDENCE OF STORAGE (G') AND LOSS (G'') MODULI FOR THE DIFFERENT COMMERCIAL BRANDS OF "DULCE DE LECHE"

Dynamic oscillatory tests showed that storage moduli (G') were higher than loss moduli (G'') for nearly three decades, and a minimum in G'' at low frequencies, for all the assayed brands except M5 (Fig. 2a,b), was found. At intermediate frequencies of the mechanical spectra, a "plateau" region was observed; it is an intermediate zone between the "terminal" and the "transition" zones characterized by a decrease in the slope of both moduli and a possible minimum in the loss modulus G'' . This region has been attributed to the existence of a highly structured system caused by physical entanglements among polymeric chains (Ferry 1980). A similar behavior has been previously reported by Navarro *et al.* (1999). Loss tangent ($\text{tg}[\delta] = G''/G'$) in the plateau zone presented values between 0.2 and 0.3 that corresponded to amorphous polymer solutions for all products except M5 (Steffe 1996). In the case of M5, $\text{tg}(\delta)$ was higher, ranging between

0.4 and 0.6. The confectionery DL (M3) presented higher values of both moduli than traditional (M2) DL because the addition of cornstarch to the formulation increases elastic characteristic of the system.

For "light" DL, the curves were qualitatively similar, except for M5, where G'' was slightly lower than G' , without showing a minimum, with a greater dependency of both moduli with frequency, typical of weak gel-like less concentrated systems, with a smaller degree of entanglements (Schorsch *et al.* 1997). M5 and M6 had similar moisture and fat contents; however, it is evident that the addition of gums and starch gave a more solid-like behavior to M6.

The mechanical properties of a given material might be described by certain response functions of the material, also known as constitutive equations or rheological equations of state. These properties are related to consumer perceived attributes (oral texture, pouring or extrusion from packs) and they are required to be understood to design or select equipment (pumps, pipelines, extruders, mixers and heat exchangers) (Hough *et al.* 1986). These response functions can be evaluated experimentally and the results fitted with a mathematical model. A classical approach to describe the mechanical response of materials that exhibit viscous and elastic properties is based on the analogy with the response of certain mechanical elements. This implies building viscoelastic models by combining mechanical elements that simulate pure viscous or elastic properties, thus describing behaviors in the linear viscoelastic range. As real materials show no linear responses when subjected to large strains, these models are appropriate only for describing material behavior under small strains.

If a system of Maxwell with infinite elements (spring and dashpot in series) is available in an infinite time scale, a situation practically unreachable, it is possible to define a continuous relaxation spectrum of the material as a function of time $H(\lambda)$, where $H(\lambda)$ expresses the distribution of the relaxation stresses as a function of the relaxation time λ . It is a positive-valued function that is finite in the range $0 < \lambda < \lambda_{\max}$ and zero above the longest relaxation time λ_{\max} . In the range of small deformations, polymeric materials are expected to be characterized by a unique relaxation time spectrum, $H(\lambda)$. This spectrum cannot be measured directly but has to be calculated from stress/strain data of linear viscoelastic experiments. Several theories have been developed to predict $H(\lambda)$ from observable material functions (Tschoegl 1989; Mours and Winter 2000). However, from the experimental data, the spectrum is necessarily obtained as an approximation to the unknown "true" spectrum whose existence is but assumed. The expressions that relate the storage modulus and loss modulus to $H(\lambda)$ are as follows (Ferry 1980):

$$G'(\omega) = \int_0^{\lambda_{\max}} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \frac{d\lambda}{\lambda} \quad (2)$$

	M1	M2	M3	M4	M5	M6
From broadened BSW spectrum (Eq. 4)	12 × 10 ³	11 × 10 ³	7.9 × 10 ³	3.8 × 10 ³	2.8 × 10 ³	195
From frequency sweep data (Eq. 5)	8.7 × 10 ³	9 × 10 ³	7.1 × 10 ³	0.8 × 10 ³	–	410

TABLE 3. PLATEAU MODULI G_N^0 (Pa) FOR COMMERCIAL “DULCE DE LECHE” ESTIMATED USING THE BROADENED BAUMGÄRTEL–SCHAUSBERGER–WINTER (BSW) SPECTRUM AND DIRECTLY FROM THE EXPERIMENTAL FREQUENCY SWEEP DATA

$$G''(\omega) = \int_0^{\lambda_{max}} H(\lambda) \frac{\omega\lambda}{1 + \omega^2\lambda^2} \frac{d\lambda}{\lambda} \quad (3)$$

Thus, using an appropriate representation of the relaxation time spectrum, it is possible to model the dynamic moduli. The broadened Baumgärtel–Schausberger–Winter (BSW) spectrum (Eq. 4) describes the experimental frequency sweep data (G' , G'') corresponding to linear, long, flexible molecules, with a broad distribution of molecular weights (Baumgaertel *et al.* 1990). The validity of the BSW spectrum in polymeric systems was studied extensively elsewhere (Jackson *et al.* 1994). The BSW model was used previously to describe the experimental regions that appear in the linear relaxation spectra, $H(\lambda)$, of oil-in-water emulsions (Franco *et al.* 1995a,b; Quintana *et al.* 2002a,b). The spectrum has the following form:

$$H(\lambda) = G_N^0 \left(A \left[\frac{\lambda}{\lambda_0} \right]^{-n_0} + n_c \left[\frac{\lambda}{\lambda_c} \right]^{n_c} \right) \exp \left(- \left[\frac{\lambda}{\lambda_{max}} \right]^\beta \right) \quad (4)$$

for $\lambda \leq \lambda_c$
 $H(\lambda) = 0$ for $\lambda > \lambda_c$

where G_N^0 is the plateau modulus, n_c and n_0 are the slopes of the spectrum in the entanglement and high-frequency glass-transition regime, respectively, A is the glass-transition front factor and λ_c is the relaxation time corresponding to the beginning of the pseudoterminal region. The exponent β controls the sharpness of the cutoff of the spectrum, λ_{max} is the longest relaxation time and λ_0 is the cross-over time to the glass transition.

The plateau modulus G_N^0 reflects the molecular architecture of the polymers and it is proportional to the number of entanglements per unit volume and inversely proportional to the average molecular weight of the molecular segment between entanglements. It is a measure of the contribution of the entanglements between polymeric molecules to the elastic or storage modulus (Flory 1953).

	M1	M2	M3	M4	M5	M6
G_g (Pa)	8.2 × 10 ⁴	1.7 × 10 ⁴	2.4 × 10 ⁴	2.1 × 10 ⁴	2.8 × 10 ³	1.8 × 10 ⁴
η_0 (Pa·s)	6.5 × 10 ⁶	3.1 × 10 ⁵	2.6 × 10 ⁶	9.4 × 10 ⁵	1.7 × 10 ⁵	4.0 × 10 ⁵
J_e^0 (Pa ⁻¹)	4 × 10 ⁻⁴	6.5 × 10 ⁻³	7.7 × 10 ⁻⁴	3.2 × 10 ⁻³	1.4 × 10 ⁻²	6.2 × 10 ⁻³
λ_t (s)	2,609	2,008	2,030	3,054	2,300	2,507

TABLE 4. MATERIAL FUNCTIONS (GLASSY SHEAR MODULUS, G_g , ZERO-SHEAR-RATE VISCOSITY, η_0 , STEADY-STATE COMPLIANCE, J_e^0 , AND TERMINAL RELAXATION TIMES, λ_t) CALCULATED FROM THE RELAXATION SPECTRA FOR THE DIFFERENT “DULCE DE LECHE” SAMPLES STUDIED

The inversion of a single integral equation such as Eq. (2) for G' (or Eq. 3 for G'') is known to be an ill-posed problem. However, the typical characteristics of ill-posedness completely vanished when simultaneously performing the above inversion on both integrals for G' and G'' . This lack of ill-posedness is most valuable for the purposes of finding the spectrum. In the present work, a nonlinear method, proposed by Baumgärtel and Winter (1989, 1992) and Winter (1997) – the so-called IRIS method developed by Winter and Mours (2006) – was used (Iris Rheo-Hub software; Iris Development LLC, Amherst, MA). The linear relaxation spectrum ($H[\lambda]$) was obtained from the linear viscoelasticity functions by inverting Eqs. (2) and (3), where the broadened BSW model was chosen to mathematically describe ($H[\lambda]$).

The application of the BSW model to DL systems satisfactorily fitted the dynamic data, as shown in Fig. 2. Although this methodology is mathematically complex, according to Baumgaertel *et al.* (1990), when mechanical properties are evaluated directly from relaxation or creep experiments, it is lost in accuracy what is gained in simplicity.

Table 3 shows the plateau moduli predicted by the broadened BSW model for the different DL assayed.

Once the continuous relaxation spectra were known, it was possible to calculate other material functions such as glassy

(or instantaneous) shear modulus ($G_g = \int_{-\infty}^{\infty} H[\lambda] d \ln \lambda$), zero-shear-rate viscosity ($\eta_0 = \int_{-\infty}^{\infty} H[\lambda] \lambda d \ln \lambda$), steady-state compliance $[J_e^0 = \int_{-\infty}^{\infty} H[\lambda] \lambda^2 d \ln \lambda / \left(\int_{-\infty}^{\infty} H[\lambda] \lambda d \ln \lambda \right)^2]$

and terminal relaxation time λ_t ($\lambda_t = \eta_0 \cdot J_e^0$) (Ferry 1980). J_e^0 is a measure of the stored energy in steady flow under small stresses and can be attributed to the elastic components of the DL. Table 4 shows the calculated values of the above mentioned material functions. It can be observed that terminal relaxation times are on the order of 10³ s, which corresponds to frequencies of 10⁻³ 1/s from the zone where

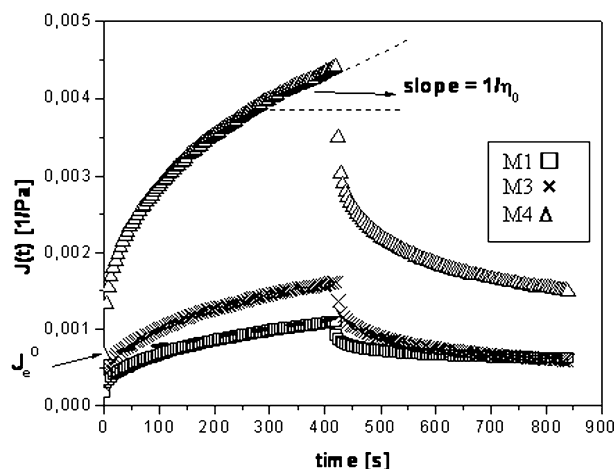


FIG. 3. CREEP-RECOVERY DATA. TO ILLUSTRATE, J_e^0 CORRESPONDS TO THE STEADY-STATE COMPLIANCE OF SAMPLE M1 AND η_0 TO THE ZERO-SHEAR-RATE VISCOSITY OF SAMPLE M4

$G' \cong G''$. Again, the highest η_0 values corresponded to brands M1 and M3, while M5 resulted in the less-viscous product.

Creep behavior is usually described by the generalized Voigt model (Steffe 1996). A group of Voigt elements in series represent a discrete spectrum of retardation times, each time λ_i is associated with a spectral compliance magnitude (J_i). Thus, creep compliance ($J(t)$) can be calculated as

$$J(t) = J_0 + \sum_{i=1}^N J_i \left(1 - e^{-\frac{t}{\lambda_i}} \right) + \frac{t}{\eta_0} \quad (5)$$

where J_0 is the instantaneous compliance and η_0 is the zero-shear viscosity.

As an example, Fig. 3 shows the experimental creep-recovery data corresponding to DL brands M1, M3 and M4. Table 5 presents the parameters η_0 , J_e^0 , and λ_c (characteristic time of the system) calculated by fitting a four-parameter Voigt model to experimental curves. As it can be seen, the predicted η_0 agree with those parameters predicted from steady-state flow curves using the Cross model and with the viscosities at zero-shear rate evaluated with the viscosities at

TABLE 5. VISCOELASTIC FUNCTIONS CALCULATED FROM THE CREEP-RECOVERY TEST: η_0 (ZERO-SHEAR-RATE VISCOSITY), J_e^0 (STEADY-STATE COMPLIANCE) AND λ_c (CHARACTERISTIC TIME OF THE SYSTEM)

Brand	η_0 (Pa·s)	J_e^0 (1/Pa)	λ_c (s)
M1	9.0×10^5	6.3×10^{-4}	580
M2	1.4×10^5	5.2×10^{-3}	630
M3	1.1×10^6	7.6×10^{-4}	720
M4	2.6×10^5	3.7×10^{-3}	950
M5	3.0×10^4	3.1×10^{-2}	940
M6	1.3×10^5	7.4×10^{-3}	970

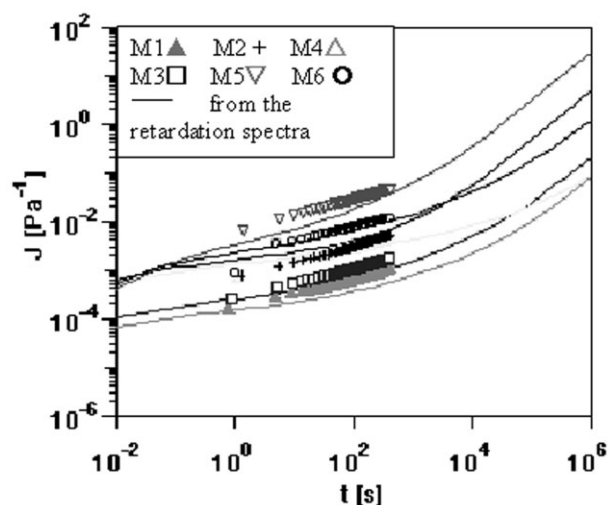


FIG. 4. COMPARISON BETWEEN TRANSIENT EXPERIMENTAL DATA (CREEP) AND THE CURVES PREDICTED FROM THE RETARDATION SPECTRA

zero-shear rate evaluated from the relaxation spectra (Tables 2 and 4).

As there is a one-to-one relationship between relaxation ($H[\lambda]$) and retardation ($L[\lambda]$) spectra (Ferry 1980), $L(\lambda)$ was derived from the corresponding relaxation spectrum for each of the samples using IRIS Rheo-Hub software (Winter and Mours 2006) using Eq. (6):

$$L(\lambda) = \frac{H(\lambda)}{\left(\int_{-\infty}^{\infty} \frac{H[u]}{\lambda} d \ln u \right)^2 + \pi^2 H^2(\lambda)} \quad (6)$$

For an infinite number of elements and infinitesimal retardation times, the continuous retardation spectrum, $L(\lambda)$, is defined as the sum of infinitesimal contributions to the material behavior; it represents the contribution to the compliance of the viscoelastic mechanism with retardation times. Thus, the compliance or retardation function $J(t)$ may be defined from the continuous retardation spectrum of the material (Mours and Winter 2000; Riande *et al.* 2000):

$$J(t) = J_0 + \int_{-\infty}^{\infty} L \left(1 - e^{-\frac{t}{\lambda}} \right) d \ln \lambda + \frac{t}{\eta_0}. \quad (7)$$

After obtaining $L(\lambda)$ for each type of product, creep-compliance results were simulated using Eq. (7). The satisfactory agreement between experimental creep data and predictions is shown in Fig. 4

G_N^0 may also be estimated directly from the experimental frequency sweep curves as

$$G_N^0 = G'_{\text{tg}(\delta) \rightarrow \text{min}} \quad (8)$$

The calculated values of G_N^0 for the tested commercial samples are also shown in Table 3, except for M5, where the minimum of the loss tangent lies outside the experimental range. It can be observed that both sets of predicted plateau moduli agree within the expected errors, showing the highest values for M1 and M3 in accordance with the experimental viscosity observed.

It was observed that the traditional and confectionery DL presented the highest storage moduli (G'), zero-shear-rate viscosity (η_0) and plateau moduli (G_N^0), reflecting a structure with more solid characteristics that correlates with a higher concentration of components (e.g., dairy proteins) that form the entanglements. A higher number of entanglements leads to a firmer matrix, with a higher resistance to flow. Besides, the confectionery DL had thickening and gelling agents in its formulation (carrageenan, agar and pectins), which reinforced the network. Conversely, reduced fat systems showed stronger fluid characteristics with the lowest rheological parameters. The differences in composition and rheological behavior of the brands reflects the needs and preferences of the consumers, but in spite of these differences, it was possible to analyze the rheological characteristics of all systems and model the obtained results using the broadened BSW model as a representation of the relaxation spectra to convert dynamic data into time domain; thus, the overall microstructural pattern of DL might be similar, and the differences observed would be mainly explained by the level of interactions among macromolecular components.

CONCLUSIONS

Water activity of the analyzed DL ranged between 0.764 and 0.882, while water content varied from 31.5 to 48.9%, depending on the type of DL. The largest and smallest solid contents corresponded to the traditional premium DL (76°Brix) and the "reduced calories" product (59°Brix), respectively. Color presented differences between and within brands, reflecting the differences in formulations and production conditions.

All commercial DL showed a pseudoplastic behavior. Flow curves were modeled using Cross' equation; from the regressed parameters, the traditional premium DL was even more viscous than the confectionery-type DL (largest η_0). Viscoelastic behavior of DL was satisfactory modeled using the BSW equation to predict the mechanical relaxation spectrum in the linear viscoelastic range. Creep compliance was predicted from this spectrum and compared with the experimental data to confirm the correct fitting of the mechanical spectrum. Any dynamic data measured in this work have been successfully converted into time domain by the application of the BSW model, and satisfactory prediction of other

mechanical properties was validated using creep and flow experiments. It is a useful tool, especially for establishing a rheological data bank and analyzing viscoelastic experiments of this type of product.

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