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PHYSICOCHEMICAL, SENSORIAL AND RHEOLOGICAL PROPERTIES OF *DOCE DE LEITE* WITH XANTHAN GUM AND WHEY PROTEIN CONCENTRATE

PROPRIEDADES FÍSICO-QUÍMICAS, SENSORAIS E REOLÓGICAS DE *DOCE DE LEITE* COM GOMA XANTANA E CONCENTRADO PROTÉICO DE SORO

João Vitor Zimmermann[1], Eliana Fortes Gris[1], Eduardo Sidinei Chaves[1], Elane Schwinden Prudêncio[1], Pedro Luiz Manique Barreto[1], Renata Dias de Mello Castanho Amboni[1], Marilde Bordignon-Luiz[1]*

[1*] Autor para contato: Universidade Federal de Santa Catarina - UFSC, Centro de Ciências Agrárias, Departamento de Ciência e Tecnologia de Alimentos, Itacorubi, Florianópolis, SC, Brasil; (48) 3721 5376; Fax: (48) 3721 9943; e-mail: marildebordignon@gmail.com

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RESUMO

O objetivo deste estudo foi avaliar as características físico-químicas, a aceitabilidade sensorial e as propriedades reológicas de doce de leite elaborado com a adição de concentrado protéico de soro (CPS), goma xantana. Variou-se a concentração de sacarose. Na amostra A utilizou-se 10,0 % de sacarose, enquanto que na amostra B 8,0 % de sacarose. Menor valor calórico (284,00 ± 1,02 Kcal/100g) foi obtido para a amostra B, que apresentou menor teor de carboidratos (45,57 ± 0,54 % p/p) e maior teor de umidade (35,89 ± 0,44 % p/p). Os modelos lei da potência e Herschel-Buckley foram aplicados para descrever as propriedades reológicas das duas amostras (A e B) de doce de leite. As amostras exibiram um comportamento pseudoplástico, caracterizado pelo índice de comportamento de fluxo ($\eta < 1$), confirmando assim um comportamento não-Newtoniano. A amostra A apresentou um aumento na viscosidade aparente e no índice de consistência. A utilização de goma xantana e CPS na elaboração de doce de leite resultou em produtos com reduzido teor de sacarose, comparado ao *doce de leite* tradicional, apresentando boa aceitabilidade sensorial com índices superiores a 7,0.

Palavras-chave: doce de leite, concentrado protéico de soro, goma xantana, reologia.

ABSTRACT

The purpose of this research work was to evaluate the physicochemical characteristics, sensorial acceptability and rheological properties of *doce de leite* with whey protein concentrate (WPC) and xanthan gum. The sucrose concentration varied. In Sample A, 10.0 % sucrose was used, while in Sample B, 8.0 % sucrose was used. A lower caloric value (284.00 ± 1.02 Kcal/100g) was obtained for sample B, which presented lower carbohydrate (45.57 ± 0.54 % w/w) and greater humidity contents (35.89 ± 0.44 % w/w). The *power law* and the *Herschel-Buckley* models were applied to describe the rheological properties of both *doce de leite* samples. The samples exhibited a shear-thinning behavior, characterized by a flow behavior index ($\eta < 1$), thus confirming a non-Newtonian behavior. Sample A presented an average increase in the apparent viscosity and in the consistency index. The use of xanthan gum and WPC in the elaboration of *doce de leite* resulted in products with a reduced sucrose content, as compared with the traditional *doce de leite*, presenting a good acceptability, with indices above 7.0.

Key words: *doce de leite*; xanthan gum; whey protein concentrate, rheology.

1 Introduction

Doce de leite is an important regional food produced and consumed in large scale in Brazil and Argentina. Traditionally *doce de leite* is obtained by heating and evaporating a mixture of fluid milk, sucrose, glucose syrup and sodium bicarbonate (MARTINS and LOPES, 1980). During evaporation extensive nonenzymatic browning occurs, resulting in a brown-colored, soft, creamy product. Dairy industries of southern Latin American countries also use Whey Protein Concentrate (WPC) in the elaboration of *doce de leite* (HEIMLICH et al., 1994) due to its gelation, one of its most important functional properties (LI et al., 2006).

Gums are a widely used food ingredient, mainly for their thickening and stabilizing properties, in order to avoid syneresis (KATZBAUER, 1998). Milk products have been developed with a variety of gums, including xanthan, Arabic, locust bean and guar gums (BACHMANN, 2001). The important properties of xanthan gum are its ability to form high viscosity solutions at low shear forces, its high pseudoplasticity and the fact that it may also display a viscosity yield value, as well as being stable over a wide range of salt concentrations (up to 150 g L^{-1} NaCl), temperatures (up to 90 °C) and pH values (2 – 11) (ROSALAM and ENGLAND, 2006).

Rheological properties are important for foods, such as *doce de leite*, in the design of flow processes, quality control, storage and processing and in predicting food textures (HEIMLICH et al., 1994; HOUGH *et al*., 1991). More importantly, rheological properties determine product texture, thereby affecting sensory perception and, ultimately, consumer acceptance of a product (KONKEL et al., 2004; DEMIATE et al., 2001; GARITTA et al., 2004). To describe the rheological behavior of *doce de leite*, the following models were very helpful: (a) the power law model $\sigma = k\dot{\gamma}^{\eta}$ and (b) the Herschel-Buckley model $\sigma - \sigma_0 = k\dot{\gamma}^{\eta}$, where s is the shear stress, k is the consistency index, $\dot{\gamma}$ is the shear rate, η is the flow behavior index and σ_0 is the yield stress.

The purpose of this research work was to evaluate the physicochemical characteristics, sensorial acceptability and rheological properties of *doce de leite* produced with low sucrose content, added of xanthan gum and WPC.

2 Material and methods

2.1 Material

For the elaboration of *doce de leite*, pasteurized cows milk (3.0 % lipids), sucrose, glucose syrup, sodium bicarbonate (Vetec Química Fina LTDA, Rio de Janeiro, RJ), xanthan gum (Kelko, CA, USA), WPC (AMP-8000, Praliant Inc., Ankeny, USA) and caramel coloring were used. For the chemical analyses, all the reagents were of analytical grade.

2.2 Methods

2.2.1 Preparation of *doce de leite* formulations

Preliminary trials had shown that it was possible to obtain a *doce de leite* presenting a smooth texture and glossy appearance. The cooking time, on a direct low fire and with constant stirring, was standardized at 80 min in order to provide similar yields. Each sample was prepared in triplicate. The yields of *doce de leite* samples were measured gravimetrically as the ratio between the final weight of the product and the initial weight of the mixture of ingredients before cooking.

Doce de leite, sample A, was elaborated according to the following formulation: 10.0 % sucrose, 2.0 % glucose syrup, 2.0 % WPC and 0.1 % xanthan gum; values calculated over the total mass of milk at the onset of cooking. For sample B, the same formulation was used with a 20 % reduction in sucrose concentration. Samples A and B were added sodium bicarbonate and caramel coloring.

2.2.2 Physicochemical characteristics

The samples were submitted to the following physicochemical analyses: moisture [% (w/w)]; ash [% (w/w)]; lipids [% (w/w)]; proteins [% (w/w)]; and total solids [% (w/w)] (AOAC, 1999). Carbohydrate values [% (w/w)] were obtained by weight difference (BRASIL, 2001). The pH measurements were realized with a pH meter (MP 220 Metler Toledo, Greinfensee, Switzerland). All the analyses were carried out in triplicate. The caloric value was calculated by the Atwater factors, i.e., 4.0 for proteins, 4.0 for carbohydrates and 9.0 for fats (DE ANGELIS, 1977).

2.2.3 Sensory assessment

The acceptability of the *doce de leite* samples A and B was evaluated by 55 untrained judges using a structured numeric scale of nine points (1 = dislike extremely, 9 = like extremely). The samples of approximately 20 g were served at room temperature (24 ± 2 ºC) in disposable cups codified with 3 digit algorithms. Both water and bread were served to clear the palate between sample evaluations. Sensory evaluation was conducted in individual booths under controlled conditions of light, temperature and humidity (MEILGAARD *et al.*, 1999).

2.2.4 Rheological measurement

Rheological measurements of the samples were realized using a Brookfield rotational rheometer (Brookfield Engineering Laboratories, model DV III, Stoughton, MA, USA), with a RV-SC4 – 28 spindle. Samples were loaded into the sample cup and were subjected to a programmed shear rate (γ) linearly increased from 0.336 to 0.532 s^{-1}, measurements of apparent viscosity (η) were realized every 5 min for 40 min. The data were registered via a personal computer using Rheocalc software (Brookfield Engineering Laboratories). A controlled temperature bath circulated water through the jacket surrounding the rotor and cup assembly to maintain the temperature at 23 ± 0.5 ºC. The flow curves were described by the power law and Herschel-Bulkley models, as used by Vélez-Ruiz and Barboza-Cánovas (1998) for dairy products and Heimlich et al. (1994) for *doce de leite*, respectively.

2.2.5 Statistical analysis

The experimental data were analyzed with Statsoft software, Statistica version 6.0 (STATSOFT INC., 2001). The Tukey test was applied whenever a difference was detected at a 5 % level of significance.

3 Results and discussion

3.1 Physicochemical characteristics

Table 1 shows the results of the physicochemical characteristics, which verify that moisture, carbohydrates and caloric value differed between samples A and B ($p < 0.05$).

Table 1 - Physicochemical characteristics - average values (standard deviation) of *doce de leite* formulation with added xanthan gum and whey protein concentrate.

PHYSICOCHEMICAL CHARACTERISTICS	SAMPLE A	SAMPLE B
Moisture (% w/w)	28.22 (0.42)[a]	35.89 (0.44)[b]
Carbohydrates (% w/w)	54.09 (0.52)[a]	45.57 (0.54)[b]
Lipids (% w/w)	6.88 (0.39)[a]	7.26 (0.38)[a]
Ashes (% w/w)	1.94 (0.10)[a]	2.05 (0.07)[a]
Proteins (% w/w)	8.78 (0.16)[a]	9.23 (0.15)[a]
Caloric value (kcal $100g^{-1}$)	313.34 (1.39)[a]	284.00 (1.02)[b]
Yield (%)	29.43 (0.96)[a]	28.91 (0.89)[a]

a, b = different letters in a specific characteristic show a statistical difference between samples ($p< 0.05$). Sample A, 10.0 % sucrose, 2.0 % WPC and 0.1 % xanthan gum; Sample B, 8.0 % sucrose, 2.0 % WPC and 0.1 % xanthan gum.

In a study realized by Demiate et al. (2001), where 42 commercial *doce de leite* samples elaborated with full fat or fat-free milk were analyzed, the mean chemical composition results observed were: moisture (% w/w) 26.50, sucrose (% w/w) 57.15, protein (% w/w) 7.07, lipids (% w/w) 3.90, ashes (% w/w) 1.41 and starch (% w/w) 2.78, with a mean caloric value of 330.0 kcal $100g^{-1}$.

Thus the chemical composition obtained in our study was different that found in the commercial samples, because was elaborated using xanthan gum for to substitute the sucrose and starch traditionally used in commercial *doce de leite*.

Comparing the results obtained in samples A and B, observation showed that sample A presented lower moisture content as a result of the higher sucrose content used in the *doce de leite* formulation. Carbohydrates are the principal components of total solids in *doce de leite* and present a correlation inversely proportional to moisture content, a relation observed between samples A and B. The higher carbohydrate content used in sample A also contributed to a greater caloric value. Martins and Lopes (1980) affirmed that *doce de leite* is a food with high nutritional value, since it contains proteins and minerals, as well as a high energetic content. The lipid content of *doce de leite* elaborated with full fat milk was 8.0 % on average.

The energetic value observed could be attributed to the use of xanthan gum and WPC, which provide stability, increased water retention and act as emulsifiers in foods (SUDHAKAR et al., 1996). According to Lizarraga et al. (2006) the protein-polysaccharide interactions offer the opportunity for sensitive control of stability and texture in multicomponent structured food systems.

Besides contributing to a functional property of *doce de leite*, WPC is responsible for the increase in protein content that was observed in this work. In a study realized by Demiate et al. (2004), analyzing *doce de leite* samples elaborated with different concentrations of starch, the mean protein content was 4.63 % w/w; less than the minimum 5% demanded by Brazilian legislation.

Even when using different sucrose concentrations, the yields of samples A and B showed no statistical difference between each other ($p> 0.05$).

3.2 Sensory assessment

The test results regarding overall acceptability are presented in Table 2, where observation reveals that the samples presented no differences ($p> 0.05$) between the mean notes obtained. The samples presented notes above 7.0 (like moderately), indicating that xanthan gum and WPC can be used in *doce de leite* formulations with reduced sucrose content. Best (1992) affirmed that xanthan gum conferred viscosity, thus doubling the effect of food flavor permanence in the mouth, contributing to the acceptability of the same. This behavior was similar to that found by Franco et al. (2005), who used xanthan gum and WPC in *requeijão*, a creamy cheese spread, with reduced fat content and products with notes higher than 7.0. The results obtained for the *doce de leite* samples A and B were better than those presented by Konkel et al. (2004) for commercial *doce de leite* samples of Brazil, for which notes between 4.9 and 6.7 were given

Table 2 - Results of the overall acceptability tests of the *doce de leite* samples (A and B).

SAMPLES	A	B
Number of Judges	55	55
Mean notes (Standard deviation)*	7.35 (1.02)[a]	7.69 (1.03)[a]

* Means with different letters in a specific characteristic show statistical difference between samples ($p< 0.05$). Sample A, 10.0 % sucrose, 2.0 % WPC and 0.1 % xanthan gum; Sample B, 8.0 % sucrose, 2.0 % WPC and 0.1% xanthan gum.

3.3 Rheological properties

The apparent viscosity of *doce de leite* samples A and B decreased with increasing shear rate, indicating a non-Newtonian fluid and showed shear-thinning behavior (Figure 1). These findings are in agreement with those reported by Marcotte et al. (2001) and Lizarraga *et al*. (2006), who evaluated the rheological behavior of xanthan gum at 20 ºC and WPC with carrageen gum in aqueous mixtures, respectively. Increasing the sucrose concentration from 8 to 10 % (w/v) led to an average increase in the apparent viscosity. Similar qualitative behavior was observed by Abu-Jdayil *et al*. (2004) using sucrose in wheat starch milk sugar paste.

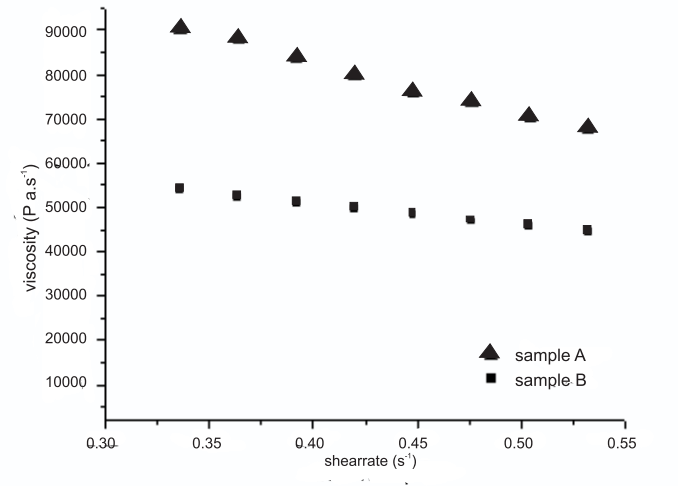

Figure 1 - Apparent viscosity x shear rate relationship of *doce de leite* A (2 % WPC, 0.1 % xanthan gum and 10 % sucrose) and B (2 % WPC, 0.1 % xanthan gum and 8% sucrose) at 23 ± 2 °C.

The rheological properties of *doce de leite* samples A and B described by the power law and Herschel-Bulkley models, at 23 ± 2 °C, are presented in Table 3. Determination coefficients (R^2) for the models ranged from 0.9761 to 0.9944, showing an adequate fit of the flow curves.

Doce de leite samples A and B exhibited shear-thinning behavior, characterized by flow behavior index (η) values of less than 1, thus confirming non-Newtonian behavior. Similar results were observed by Heimlich et al. (1994), who evaluated commercial *doce de leite* samples and samples with added WPC. The consistency index (K) calculated by both models increased with the sucrose concentration (10 and 8 %) used. Abu-Jdayil et al. (2004) and Cancela et al. (2005) also observed that η decreased and that K increased with sucrose concentration.

A higher yield stress value was observed at higher sucrose concentrations. Szczesniak (1985) affirmed that the appearance of yield stress followed by shear-thinning is a typical behavior for xanthan gum. It has been recognized that the yield stress is a useful property of gums when they are used as binders, because it helps keep various components of the food formulation in place (RAO and KENNY, 1975; SZCZESNIAK, 1985). Christianson and Bagely (1984) discussed the concept of yield stress in detail and affirmed that it depends on the evaluation method and the experimental conditions.

Table 3 - Rheological parameters of *doce de leite* samples A and B obtained by the power law ($\sigma = k\,g^{\varsigma}$) and Herschel-Buckley models ($\sigma_0 = kg^{\varsigma}$) at 23 ± 2 °C.

		* SAMPLES	
		A	**B**
POWER LAW	R^2	0.9761	0.9944
	Flow behavior index (η)	0.3572	0.5751
	Consistency index (K) (Pa.s$^{\eta}$)	453.63	341.15
HERSCHEL-BULKLEY	R^2	0.9669	0.9914
	Flow behavior index (η)	0.7795	0.8620
	Consistency index (K) (Pa.s$^{\eta}$)	300.75	291.96
	Yield stress value (σ_0) (Pa)	179.20	68.32

* Sample A, 2 % WPC, 0.1 % xanthan gum and 10 % sucrose; Sample B, 2 % WPC, 0.1 % xanthan gum and 8 % sucrose.

Conclusions

The elaboration of *doce de leite* using xanthan gum and whey protein concentrate resulted in products with reduced sucrose content, compared with the traditional *doce de leite*, and good acceptability.

Both samples of *doce de leite* presented shear-thinning behavior ($\eta < 1$), thus confirming non-Newtonian behavior. Increasing the sucrose concentration led to an average increase in the apparent viscosity and consistency index. The power law and Herschel-Buckley models were applied successfully to describe the rheological properties of *doce de leite*.

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REFERENCES

1. ABU-JDAYIL, B.; MOHAMEED, H. A.; EASSA, A. **Rheology of wheat starch–milk–sugar systems: effect of starch concentration, sugar type and concentration, and milk fat content**. **Journal of Food Engineering**, **v. 64,** n. 2, p. 207-212, 2004.

2. ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (AOAC). Official methods of analysis of the Association Analytical Chemists, Washington, DC: AOAC, 1999, v II.

3. BACHMANN, H – P. Cheese analogues: a review. **International Dairy Journal,** v.11, p. 505–515, 2001.

4. BEST, D. New dimensions in fat substitution. **Prepared Foods**, v. 161, n.3, p.59–62, 1992.

5. BRASIL. Ministério da Saúde. ANVISA (Agência Nacional de Vigilância Sanitária). Aprova a Rotulagem Nutricional Obrigatória de Alimentos e Bebidas Embalados. Resolução RDC nº 40 de 21/03/2001. Diário Oficial da República Federativa do Brasil. Brasília, 1998.

6. CANCELA, M. A.; ÁLVAREZ, E.; MACEIRAS, R. Effects of temperature and concentration on carboxymethylcellulose with sucrose rheology. **Journal of Food Engineering**, v. 71, p. 419–424, 2005.

7. CHRISTIANSON, D. D.,; BAGLEY, E. B. Yield stresses in dispersions of swollen, deformable cornstarch granules. **Cereal Chemistry**, v. 61, p. 500–503, 1984.

8. DE ANGELIS, R. C. **Fisiologia da nutrição: fundamentos para nutrição e desnutrição.** São Paulo: EDART/EDUSP, 1977, v. 1.

9. DEMIATE, I. M.; KONKEL, F. E.; PEDROSO, R. A. Avaliação da qualidade de amostras comerciais de *doce de leite* pastoso - composição química. **Ciência e Tecnologia de Alimentos**, v. 21, n. 1, p. 108-114, 2001.

10. FRANCO, J.; ZIMMERMANN, J. V.; POSSIK, P.; TAHA, P.; TEIXEIRA. E.; BORDIGNON LUIZ, M. T. Características físico-químicas e sensoriais de requeijão culinário adicionado de goma xantana com aplicação em produtos prontos para o consumo. **Revista do Instituto Cândido Tostes**, v. 60, n. 342, p. 13-19, 2005.

11. GARITTA, L.; HOUGH, G.; SÁNCHEZ, R. Sensory shelf life of dulce de leche. **Journal of Dairy Science**, v. 87, p. 1601-1607, 2004.

12. HEIMLICH, W.; BÓRQUEZ, R.; CÉSPEDES, I. Effects of milk replacement by whey protein concentrates on the rheological properties of dulce de leche. **Wiss Technology**, v. 27, p. 289-291, 1994.

13. HOUGH, G.; BUERA, M.P.; MARTINEZ, E.; RESNIK, S. Effect of composition on non-enzymatic browning rate in dulce de leche-like systems. **Anales de la Associación Química Argentina**, Buenos Aires, v. 79, n.1, p.31-40, 1991.

14. KATZBAUER, B. Properties and applications of xanthan gum. **Polymer Degradation and Stability**, n. 59, p. 81-84, 1998.

15. KONKEL, F. E.; OLIVEIRA, S. M. A.; SIMÕES, D. R. S.; DEMIATE, I. M. Avaliação sensorial de *doce de leite* pastoso com diferentes concentrações de amido. **Ciência e Tecnologia de Alimentos**, v. 24, n. 2, p. 249-254, 2004.

16. LI, J.; OULD ELEYA, M. M.; GUNASEKARAN, S. Gelation of whey protein and xanthan mixture: Effect of heating rate on rheological properties. **Food Hydrocolloids**, v. 20, p. 678–686, 2006.

17. LIZARRAGA, M.S.; DE PIANTE VICIN, D.; GONZÁLEZ, R.; RUBIOLO, A.; SANTIAGO, L.G. Rheological behaviour of whey protein concentrate and g-carrageenan aqueous mixtures. **Food Hydrocolloids**, v. 20, p. 740–748, 2006.

18. MARCOTTE, M.; HASHAHILI, A. R. T.; ROMASWAMY, H. S. Rheological properties of selected hydrocolloids as a function of concentration and temperature. **Food Research International,** v. 34, p. 695–703, 2001.

19. MARTINS, J. F. P.; LOPES, C. N. ***Doce de leite*: aspectos da tecnologia de fabricação. Instruções Técnicas**, n. 18. Campinas: ITAL, 1980. 37p.

20. MEILGAARD, M.; CIVILLE, G. V.; CARR, B. T. **Sensory Evaluation Techniques,** 3 ed., CRC Press, INC., Boca Raton, FL, 1999. 387p.

21. RAO, M. A.; KENNY, J. F. Flow properties of selected food gums. **Canadian Institute of Food Science and Technology Journal**, v. 8, p. 142–148, 1975.

22. ROSALAM, S.; ENGLAND, R. **Review of xanthan gum production from unmodified starches by** *Xanthomonas comprestris* **sp. Enzyme and Microbial Technology**, v. 39, n. 2, p. 197-207, 2006.

23. SUDHAKAR, V.; SINGHAL, R. S.; KULKARNI, P. R. Starch–galactomannan interactions: functionality and rheological aspects. **Food Chemistry**, v. 55, p. 259–264, 1996.

24. SZCZESNIAK, A.S. Rheological basis for selecting hydrocolloids for specific application. In: PHILLIPS, G. O., WEDLOCK, D. J., WILLIAMS, P.A. 3 ed. **Gums and stabilisers for the food industry**. London: Elsevier, 331-323, 1985.

25. VÉLEZ-RUIZ, J. F; BARBOSA-CÁNOVAS, G. V. Rheological Properties of Concentrated Milk as a Function of Concentration, Temperature and Storage Time. **JournaI of Food Enginerring**, v. 35, p. 177-190, 1998.