INVESTIGATION OF RHEOLOGICAL CHARACTERISTICS OF CONCENTRATED MILK PRODUCTS WITH A COMPLEX CARBOHYDRATE AND PROTEIN COMPOSITION

A. I. Gnezdilova*, T. Yu. Burmagina, L. A. Kurenkova

Vologda state dairy farming academy by N.V. Vereshchagin,
Schmidt Str. 2, Molochnoye, Vologda, 160555 Russian Federation

* e-mail: academy@molochnoe.ru

Received April 24, 2015; Accepted in revised form May 15, 2015; Published October 20, 2015

Abstract: When developing new types of dairy products, the formulation of which includes components of both dairy and nondairy origin, it is necessary to study the rheological characteristics of these products. The paper studies the rheological characteristics of concentrated milk products with a complex carbohydrate and protein composition. The study was conducted at the premises of FSBEI HPE "Vologda State Dairy Farming Academy named after N.V. Vereshchagin" (Russia, Vologda Region, Vologda). By using the rotary viscometer "Reotest 2.1" the dependence of shear stress (τ, Pa) and effective viscosity (ηef) on shear rate (γ, s-1) was determined. Freshly made product samples were studied, as well as product samples in the process of storage. In the course of the processing of the obtained data, it was found that freshly made concentrated milk products with sugar, as well as the same products in the process of storage during a period of up to 3 months are classified as "Newtonian" liquids, by virtue of the fact that the dependence of shear stress on shear rate for these samples has a linear character. It is recommended to use a Höppler viscometer for the measurement of viscosity in these samples. Adding starch syrup, malt, or demineralized whey powder to the products results in the deviation of their rheological characteristics from the properties of "Newtonian" liquids. The dependence of shear stress on shear rate for these product samples follows a power-law relationship. On this basis it can be concluded that these products are classified as pseudoplastic bodies. During prolonged storage, consolidation of the structure and an increasing degree of deviation from the properties of Newtonian liquids was observed in all studied samples. This behavior is attributable to the formation of filamentary bridges between the casein micelles, which takes place in the microstructure of concentrated milk products with a complex carbohydrate and protein composition after long storage. These bridges are pseudo-polymers, formed by glucose monomers, and determine the microstructure of the product, its organoleptic and rheological properties. It is recommended to measure the viscosity of the developed products using a rotary viscometer.

Keywords: Rheology, structure, shear stress, effective viscosity, shear rate, "Newtonian" liquids, pseudo-plastic food products

DOI 10.12737/13119 *Foods and Raw Materials*, 2015, vol. 3, no. 2, pp. 60–64.

INTRODUCTION

For the purpose of designing and optimization of manufacturing processes, as well as monitoring quality of food products, it is necessary to study the rheological properties of these products. It is especially important in the process of developing new types of dairy products, the formulation of which includes components of both dairy and nondairy origin [1–3].

There is a view that condensed canned milk products with sugar are classified as weakly structured products and fall in between products with crystallization and condensation structures, and in case of maximum removal of liquid dispersion medium (water) the transition to the crystallization structure is possible [4, 5]. Currently, new conceptions of the microstructure of canned dairy products with sugar emerge, according to which, the general microstructure of freshly made products is characterized by loose, unbound to each other aggregates of casein micelles [6, 10]. After long storage, micelles are bound to each other by pseudo-polymer bridges (cords, strands, filaments).

According to GOST 27709-88 "Canned condensed milk. Viscosity estimation method" [11], it is recommended to measure the viscosity of canned condensed milk products with sugar using a Höppler viscometer. However, the authors of the work [12] demonstrated that the studied samples of canned condensed milk products are classified as abnormally viscous structured liquids, so for the purpose of monitoring viscosity of canned condensed milk products with sugar, the authors recommend to use a rotary viscometer with the preliminary breakdown of structure.

Besides, currently there are widely known concentrated milk products, which are produced from dry components by recombining. To manage the quality of these products, it is necessary to evaluate their structure on the basis of the study of their rheological properties.

The purpose of this work is to study the rheological characteristics of concentrated milk products with a complex carbohydrate and protein composition and to substantiate a method of measuring viscosity of these products.

OBJECTS AND METHODS OF STUDY

The most important rheological characteristics are shear stress τ and effective viscosity ηef. These characteristics are known to depend on shear rate γ.

The object of study in this paper were concentrated dairy products with sugar, with different percentage of substitution of sugar for starch syrup, skim milk powder for dry demineralised whey powder (DWP) or malt, as well as control samples (without substitution).

The studies were conducted at 20°C using the rotary viscometer "Reotest-2.1". The obtained data were processed using Microsoft Excel.

RESULTS AND DISCUSSION

Dependences of shear stress (τ, Pa) on shear rate (γ, s^{-1}) were determined for freshly made product samples, as well as for the product samples during storage. Research results are presented in Tables 1–3.

Table 1 shows that in the control samples of concentrated milk products with the storage period of up to 3 months the determined patterns follow a linear relationship with the correlation coefficient of 0.99, which makes it possible to classify them as Newtonian liquids.

In the control samples, product solidification takes place after 3 months of storage due to the formation of pseudo-polymeric filamentary bridges, which results in the strengthening of the spatial structure. The products behave as pseudoplastic liquids and follow a power-law relationship:

$$\tau = K \cdot \gamma^{m}, \quad (1)$$

where K is the consistency coefficient; m is the flow behavior index (characterizes the degree of "non-Newtonian" nature of liquids).

For pseudoplastic food products m < 1, for dilatant products m > 1.

The situation is somewhat different in the products with substitution of sugar for starch syrup (Table 2).

As can be seen from Table 2, in freshly made samples with substitution of 30% and 40% of sugar for starch syrup and in the sample with substitution of 30% of sugar, stored during 3 months, the dependence of shear stress on shear rate is linear with the coefficient of correlation of 0.99, that makes it possible to classify these products as "Newtonian" liquids. Based on the data of Table 2, it can be concluded that the product samples with substitution of 50% or more of sugar for starch syrup are classified as pseudoplastic bodies and are described by the equation (1).

It was determined [9, 10], that after long storage, filamentary bridges are formed between casein micelles in the microstructure of concentrated milk products with the substitution of sugar for starch syrup. These bridges are pseudo-polymers, formed by glucose mono-mers, and determine the microstructure of the product, its organoleptic and rheological properties.

The conducted studies showed that there is a critical concentration of starch syrup in condensed milk, which limits its applicability in the manufacturing of the product. The percentage of substitution of sugar for starch syrup should not exceed 40%.

The present work also explores the rheological characteristics of the developed concentrated milk product with sugar, in which skim milk powder is partly substituted for fermented malt [3]. Adding malt makes it possible to increase the content of vitamins and mineral substances in the product.

The equations of the dependence of shear stress on shear rate of the developed product are shown in Table 3.

Table 3 that shows that all the samples follow a power-law relationship and therefore are classified as pseudoplastic food products, which is confirmed by a rather high correlation coefficient equal to 0.99. The analysis of the equations shows that the increase in the percentage of substitution of skim milk powder for malt results in the increase in the consistency coefficient and the decrease in the flow behavior index. It gives evidence of the consolidation of the structure and the increase of non-Newtonian properties of the product.

We also developed a concentrated milk product in which skim milk powder is partially substituted for demineralized whey powder (DWP) [1] and studied its structure. The data on the impact of shear rate on shear stress in the product samples are shown in Table 4.

Table 1. The equations of the dependence of shear stress on shear rate in the control samples of concentrated milk products with sugar at various storage durations

Storage duration	Type of dependence	Correlation coefficient
Freshly made product samples	$\tau = 3.2476\ \gamma$	0.996
3 months	$\tau = 6.0942\ \gamma$	0.992
6 months	$\tau = 7.62 \cdot \gamma 0.8252$	0.991
14 months	$\tau = 10.834 \times \gamma\ 0.8659$	0.999

Table 2. The equations of the dependence of shear stress on shear rate in the samples of concentrated milk products with sugar with different percentage of substitution of sugar for starch syrup during storage

Storage duration	30%	40%	50%	100%
Freshly made product samples	$\tau = 3.49\ \gamma$	$\tau = 3.83\ \gamma$	$\tau = 14.32\ \gamma^{0.7064}$	$\tau = 44.19\gamma^{0.5856}$
3 months	$\tau = 6.06\ \gamma$	$\tau = 21.30\ \gamma^{0.6984}$	$\tau = 33.33\ \gamma^{0.5982}$	$\tau = 44.71\ \gamma^{0.5541}$
14 months	$\tau = 16.78\ \gamma^{0.7299}$	$\tau = 25.29\ \gamma^{0.7521}$	$\tau = 30.82\ \gamma^{0.7172}$	$\tau = 39.51\ \gamma^{0.6579}$

Table 3. The equations of the dependence of shear stress on shear rate in the samples of concentrated milk product with sugar on the percentage of substitution of skim milk powder for fermented malt at various storage durations

Storage duration	5%	10%	15%
Freshly made product samples	$\tau = 4.84\times\gamma^{0.9215}$	$\tau = 6.44\times\gamma^{0.8776}$	$\tau = 9.13\times\gamma^{0.8324}$
3 months	$\tau = 40.11\times\gamma^{0.6034}$	$\tau = 55.17\times\gamma^{0.5311}$	$\tau = 59.47\times\gamma^{0.5246}$
14 months	$\tau = 43.21\times\gamma^{0.6139}$	$\tau = 59.58\times\gamma^{0.5456}$	$\tau = 81.34\times\gamma^{0.4647}$

Table 4. The equations of the dependence of shear stress on shear rate in the samples of concentrated milk product with sugar with different percentage of substitution of skim milk powder for demineralized whey powder at various storage durations

Storage duration	10%	20%	25%
Freshly made product samples	$\tau = 6.74\times\gamma^{0.8521}$	$\tau = 7.7954\times\gamma^{0.8254}$	$\tau = 11.796\times\gamma^{0.7758}$
3 months	$\tau = 9.73\times\gamma^{0.7982}$	$\tau = 10.674\times\gamma^{0.7867}$	$\tau = 12.849\times\gamma^{0.7612}$
14 months	$\tau = 13.21\times\gamma^{0.7139}$	$\tau = 26.3\ \gamma^{0.5762}$	$\tau = 29.3\ \gamma^{0.4962}$

The determined patterns indicate that the product samples are classified as pseudoplastic fluids, which is confirmed by a rather high correlation coefficient of 0.99. It follows from the equations that the increase in the percentage of substitution of skim milk powder for demineralized whey powder results in the increase in the consistency coefficient (*k*) and the decrease in the flow behavior index (*m*). It gives evidence of the consolidation of the structure, an increase of its viscosity and of non-Newtonian properties in the presence of whey proteins, which constitute the major fraction of demineralized whey powder.

To describe the dependence of effective viscosity of shear rate in the studied samples, a well-known equation was used [13]:

$$\eta_{ef} = K\cdot\gamma^{-m}, \quad (2)$$

where η_{ef} is the effective viscosity Pa·s; γ is the deformation frequency, s^{-1}; *K* is the consistency coefficient; *m* is the rate of structure breakdown.

The equations of the dependence of efficient viscosity on shear rate of the developed product are shown in Table 5.

The data of Tables 5–6 confirm that control samples of concentrated milk products and the products with substitution of 30% of sugar for starch syrup during storage for up to three months are classified as Newtonian liquids. Other dependencies follow a power-law relationship, which confirms that the samples are classified as pseudoplastic fluids (Tables 7–8).

The exponent in the equations, presented in Tables 5–8, describes the rate of structure breakdown. For a more complete description of the behavior of the products, the rate of structure breakdown was analyzed and presented in Fig. 1 and 2.

As can be seen from Fig. 1, a dramatic increase in the rate of structure breakdown is observed in all product samples in case of the substitution of 40% or more of sucrose for starch syrup.

More intense structure breakdown was observed in the products in which a part of skim milk powder was substituted by malt (Fig. 2). In freshly made product with the proportion of substitution of 5% the value of m remains almost unchanged, after which slightly increases. After three months of storage, the rate of structure breakdown in the control samples slightly increases, as compared to the freshly made product. Intense structure breakdown is observed in the samples after 3 months of storage in case of the substitution of 5% or more of skim milk powder for malt.

Table 5. The equations of the dependence of effective viscosity on shear rate in the control samples of concentrated milk product with sugar at various storage durations

Storage duration	Type of dependence	Correlation coefficient
Freshly made product samples	$\eta_{ef} = 2.6239\ \gamma$	0.995
3 months	$\eta_{ef} = 6.561\ \gamma$	0.993
6 months	$\eta_{ef} = 7.623\ \gamma^{-0.175}$	0.991
14 months	$\eta_{ef} = 11.102\ \gamma^{-0.157}$	0.959

Table 6. The equations of the dependence of effective viscosity on shear rate in the samples of concentrated milk product with sugar and starch syrup at various storage durations

Storage duration	30%	40%	50%	100%
Freshly made product	$\eta_{ef} = 3.29\ \gamma$	$\eta_{ef} = 10.309\gamma^{-0.234}$	$\eta_{ef} = 14.63\gamma^{-0.311}$	$\eta_{ef} = 46.223\gamma^{-0.412}$
3 months	$\eta_{ef} = 7.8768\ \gamma$	$\eta_{ef} = 21.304\gamma^{-0.289}$	$\eta_{ef} = 32.189\gamma^{-0.325}$	$\eta_{ef} = 42.557\gamma^{-0.423}$
14 months	$\eta_{ef} = 16.097\ \gamma^{-0.25}$	$\eta_{ef} = 23.65\ \gamma^{-0.321}$	$\eta_{ef} = 29.063\gamma^{-0.333}$	$\eta_{ef} = 0.378\gamma^{-0.444}$

Table 7. The equations of the dependence of effective viscosity on shear rate in the samples of concentrated milk product with sugar, depending on the percentage of substitution of skim milk powder for fermented malt, at various storage durations

Storage duration	5%	10%	15%
Freshly made product samples	$\eta_{ef} = 4.835\ \gamma^{-0.079}$	$\eta_{ef} = 6.436\gamma^{-0.122}$	$\eta_{ef} = 9.130\gamma^{-0.168}$
3 months	$\eta_{ef} = 40.114\gamma^{-0.386}$	$\eta_{ef} = 55.171\gamma^{-0.454}$	$\eta_{ef} = 59.474\gamma^{-0.475}$
14 months	$\eta_{ef} = 43.210\gamma^{-0.397}$	$\eta_{ef} = 59.580\gamma^{-0.469}$	$\eta_{ef} = 81.344\gamma^{-0.535}$

Table 8. The equations of the dependence of effective viscosity on shear rate in the samples of concentrated milk product with sugar, depending on the percentage of substitution of skim milk powder for demineralized whey powder, at various storage durations

Storage duration	10%	20%	25%
Freshly made product samples	$\eta_{ef} = 6.774\ \gamma^{-0.151}$	$\eta_{ef} = 7.868\ \gamma^{-0.181}$	$\eta_{ef} = 11.796\ \gamma^{-0.224}$
3 months	$\eta_{ef} = 9.725\gamma^{-0.202}$	$\eta_{ef} = 10.674\ \gamma^{-0.213}$	$\eta_{ef} = 12.849\gamma^{-0.240}$
14 months	$\eta_{ef} = 23.210\gamma^{-0.322}$	$\eta_{ef} = 26.325\gamma^{-0.424}$	$\eta_{ef} = 31.344\gamma^{-0.475}$

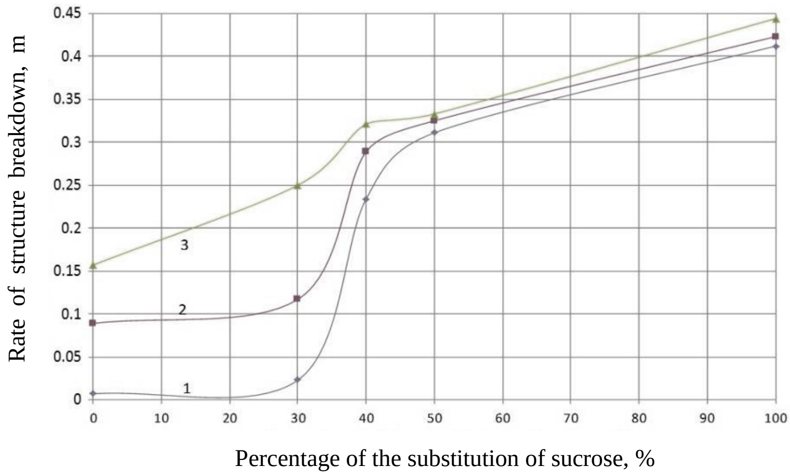

Fig. 1. The dependence of the rate of structure breakdown on the mass fraction of starch syrup: (1) freshly made product; (2) after 3 months of storage; (3) after 14 months of storage.

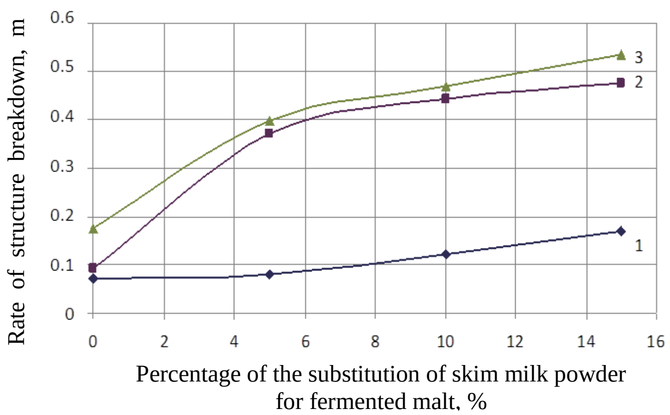

Fig. 2. The dependence of the rate of structure breakdown on the percentage of substitution of skim milk powder for fermented malt: 1 – freshly made product; 2 – after 3 months of storage; 3 – after 14 months of storage.

CONCLUSIONS

1. Freshly made concentrated milk products with sugar, and the same products in the process of storage during a period of up to 3 months, are classified as "Newtonian" liquids. It is recommended to use a Höppler viscometer for the measurement of viscosity in these samples.

2. Changing the composition of the developed products results in the deviation of their parameters from the properties of Newtonian liquids. These products are classified as pseudoplastic bodies.

3. During prolonged storage, consolidation of the structure and increased deviation from the properties of Newtonian liquids was observed in all studied samples.

4. It is recommended to measure the viscosity of the developed products using a rotary viscometer.

5. The obtained results were used to estimate the duration of storage of the developed products.

REFERENCES

1. Gnezdilova A.I., Kulenko V.G. and Glushkova A.V. *Sposob proizvodstva molokosoderzhashchego kontsentrirovannogo produkta s sakharom* [Method for production of concentrated milk-containing product with sugar]. Patent RF, no. 2407347, 2009.
2. Gnezdilova A.I., Kulenko V.G., Vinogradova Yu.V., Kurenkova L.A. and Burdeynaya O.S. *Sposob proizvodstva sgushchennogo molochnogo produkta s sakharom* [Method for production of condensed milk product with sugar]. Patent RF, no. 2490920, 2012.
3. Gnezdilova A.I., Sharova T.Yu. and Kulenko, V.G. *Sposob proizvodstva molokosoderzhashchego kontsentrirovannogo produkta s sakharom* [Method for production of concentrated milk-containing product with sugar]. Patent RF, no. 2525666, 2012.
4. Zavarin Yu.A. and Chekulaeva L.V. Structure formation in the production of condensed milk with sugar. *Dairy Industry*, 1977, no. 9, pp. 11–13. (In Russian).
5. Dobriyan E.I. and Chekulaeva L.V. Changing of the colloid-dispersed properties of milk proteins in the process of the production of condensed milk with sugar using a flow process. *Dairy Industry*, 1985, no. 4, pp. 27–29. (In Russian).
6. Araki K., Takasawa R. and Yoshikawa I. Design, fabrication, and properties of macroscale supramolecular fibers consisted of fully hydrogen-bonded pseudo-polymer chains. *Chemical Communications*, 2001, no. 18, pp. 1826–1827.
7. Roy N., Saha N., Kitano T. and Saha P. Novel hydrogels of PVP-CMC and their swelling effect on viscoelastic properties. *J. of Applied Polymer Science*, 2010, vol. 117, no. 3, pp. 1703–1710.
8. Jones O.G. *Fabrication of protein-polysaccharide particulates through thermal treatment of associative complexes*. PhD dissertation. University of Massachusetts-Amherst, 2009. 287 p.
9. Smykov I.T., Gnezdilova A.I., Vinogradova Yu.V. and Kurenkova L.A. The impact of long-term storage on the structure of condensed milk. *Storage and Processing of Farm Products*, 2014, no. 4, pp. 9–14. (In Russian).
10. Smykov I.T., Gnezdilova A.I., Vinogradova Yu.V. and Kurenkova L.A. The impact of temperature on the rheological properties of condensed milk with starch syrup. *Bulletin of the Russian Academy of Agricultural Sciences*, 2014, no. 3, pp. 68–71. (In Russian).
11. *GOST 27709-88. Konservy molochnye sgushchennye. Metod izmereniya vyazkosti* [State Standard 27709-88. Canned condensed milk. Viscosity estimation method]. Moscow: Standartinform Publ., 2009. 5 p.
12. Pirogov A.N., Pirogova N.A. and Shilov A.V. Method for determining the viscosity of canned milk products using a rotary viscometer. *Storage and Processing of Farm Products*, 2006, no. 4, pp. 46–48. (In Russian).
13. Machikhin Yu.A (Ed.). *Rheometry of food raw materials and products: a reference guide*. Moscow: Agropromizdat Publ., 1990. 271 p. (In Russian).

Please cite this article in press as: Gnezdilova A.I., Burmagina T.Yu. and Kurenkova L.A. Investigation of rheological characteristics of concentrated milk products with a complex carbohydrate and protein composition. *Foods and Raw Materials*, 2015, vol. 3, no. 2, pp. 60–64. doi: 10.12737/13119.