# EFFECT OF ADDITION OF CARRAGEENAN ON RHEOLOGICAL BEHAVIOUR OF YOGURT

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**Abstract:** The purpose of this work is to study the effect of addition of  $\kappa$ -kappa carrageenan and  $\iota$ iota carrageenan on the rheological behaviour of different types of yogurts. The role of concentration as well as the type of carrageenan used ( $\kappa$ -kappa carrageenan and 1-iota carrageenan) has been analysed. The most common technique used for rheological liquids is Viscometers, measuring shear strength, described by the coefficient of viscosity. The most common technique used for rheological liquids is Viscometers, measuring shear strength, described by the coefficient of viscosity. For this study, the yogurt samples were obtained in the laboratory using the cultures starter DIPROX YBA 986. The effect of addition of carrageenan in yoghurt was investigated by a rotational viscometer, Brookfield viscometer (Brookfield Engineering Inc, Model RV – DV I Prime) with RV spindles. The Brookfield viscometer DV I Prime with disk spindles represents an easy and cheap method for the rheological characterization of non-Newtonian fluids, in this case of yoghurt. The cluster analysis was performed using Unsrambler X version 10.1 (CAMO Process As, Oslo, Norway, 2005), all the rheological and physicochemical parameters were weighed and normalized for performing the cluster analysis. In the case of yogurt samples obtained in the laboratory, the addition of carrageenan increases the viscosity. 1-iota carrageenan has been evaluated as more effective for increasing the viscosity of yogurt in comparison with  $\kappa$ -kappa carrageenan (with the same concentration).

**Keywords:** *yogurt, viscosity, viscometer* 

# 1. Introduction

Rheology is the deformation and flow of matter [1].

Polysaccharides are widely used in food systems as, e. g. thickeners [2].

Polysaccharides (pectin, modified starch, xanthan gum, locust bean gum, guar gum, alginate, etc.) are often added to dairy products to stabilise their structure, enhance viscosity and alter textural characteristics [3].

Carrageenans are anionic linear polysaccarides extracted from the red seaweed (*Rhodophyceae*), consisting of alternating  $\alpha$ -1,4 and  $\beta$ -1,3 linked anhydrogalactose residues. There are three major fractions ( $\kappa$ -kappa,  $\iota$ -iota and  $\lambda$ -lambda) with varying number and position

of sulphate groups on the galactose dimer.  $\kappa$ -Carrageenan and *i*-carrageenan undergo a temperature-dependent coil (disordered state) to helix (ordered state) transition in aqueous solution. Both of these carrageenans are able to form gels (the process of gelation is closely associated with helix formation). κ-Carrageenan usually forms firm, britlle gels and tcarrageenan usually generates soft, elastic gels. The strength of the gels formed by both polysaccarides is strongly influenced by the presence of cations.  $\kappa$ -Carrageenan is especially sensitive to potassium and *t*carrageenan to calcium ions. On the other hand,  $\lambda$ -lambda carrageenan is not able to build up stable gels [4].

Yogurts are dairy products obtained by fermentation with lactic acid bacteria

during which a weak protein gel develops due to a decrease in the pH of the milk. Following the fermentation of lactose lactic acid is formed causing the coagulation of milk proteins (casein) to form a gel-like structure, in which fat globules and the aqueous phase are embedded [5]. In the liquid milk, casein micelles are presented as individual units. As the pH reaches pH 5.0, the casein micelles are partially broken down and become linked to each other under the form of aggregated and chains forming part of a three-dimensional protein matrix in which the liquid phase of the milk is immobilized. This gel structure contributes substantially due to the overall texture and organoleptic properties of yoghurt and gives rise to shear and time dependent viscosity [6].

The gel strength of yogurt is related to the cumulative effects of the chemical interactions [7].

The most frequent defects related to yogurt texture that may lead to consumer rejection are apparent viscosity variations and the occurrence of syneresis [8].

Yogurt rheological characterization is required for product and process acceptability [9]. This characterization can be made using either instrumental or sensory measurements.

The firmness of yogurt and the viscosity of just-stirred gel are greatly influenced by the amount of heat treatment the yogurt mix receives. Heating unfolds the globular whey proteins and exposes sulphydryl groups, which react with other sulphydryl groups and disulfides and induce linkages and protein-casein aggregates [10, 11].

The gel strength of yogurt is related to the cumulative effects of the chemical interactions. The binding of  $\delta$ -lacto globulin to the casein micelle seems to be responsible for the increase of gel strength [12, 13, 14].

# 2. Materials and methods

#### 1.1. Materials

UHT milk, Lactobacillus bulgaricus Streptococcus thermophilus and pure culture DIPROX YBA 986 starter provided by Enzymes & Derivates, Piatra Neamt, România; κ-kappa carrageenan and 1-iota carrageenan provided by Enzymes & Derivates, Piatra Neamt, România: orbital shaker; thermostat; Brookfield viscometer Model RV- DV II Pro, with disk spindle, RV3, RV4, RV5, RV6 type.

#### 1.2. Sample preparation

The yogurt samples were made using UHT milk, having the physical and chemical parameters in Tabel 1.

Table 1. Milk properties

Fat, g/100g	3
Protein, g/100 g	3
Sugar, g/100g	4.5
Ash, %	0.72
Acidity, <sup>0</sup> T	18

Table 2.pH of yogurt samples

Sample	pH
S 1	4.0
S 2	4.5
S 3	4.2
S 4	4.0
S 5	4.5

300 mL milk was inoculated using 0.015 g starter culture. After inoculation with starter culture, the samples were homogenised with an orbital shaker for 15 min. at 100 rpm. After shaking the samples were thermostated at  $42^{\circ}$ C for 6 hours. Carrageenans were added in the next concentration to the yogurt sample: 0.9 g  $\kappa$ -kappa carrageenan (S1), 0.9 g  $\iota$ -iota carrageenan and 0.3 g  $\iota$ -iota carrageenan

(S3), 0.45 g  $\kappa$ -kappa carrageenan and 0.45 g  $\iota$ -iota carrageenan (S4) and 0.3 g  $\kappa$ -kappa carrageenan and 0.6 g  $\iota$ -iota carrageenan (S5). The pH of the yogurt samples is presented in table 2.

# 2.3. Determination of rheological properties

Viscosity measurements were carried out on the yogurt samples at ambient temperature (25<sup>o</sup>C), with a Brookfield viscometer (Brookfield Engineering Inc, Model RV- DV II Pro+) at 0.5, 1, 2, 2.5, 4, 5 and 10 rpm with RV spindle (RV3, RV4, RV5, RV6 type). The spindle no was used in accordance with the sample nature to get all readings within the scale [15].

The samples in 300 mL of beaker with a 8.56 cm diameter (according to the Brookfield requests) were kept in a thermostatically controlled water bath for about 10 min before measurements in order to attain desirable temperature of  $25^{\circ}$ C.

First measurements were taken 2 min. after the spindle was immersed in each sample, so as to allow thermal equilibrium in the sample, and to eliminate the effect of immediate time dependence.

All data were then taken after 40 s in each sample. Each measurement was duplicated on the sample.

The obtained empirical data were converted using the Mitschka relationships to shear rate and shear stress. The shear rate versus shear stress data were interpreted using the power law expression

where:

 $\sigma$  – shear stress (N/m<sup>2</sup>),

 $\sigma = \mathbf{k} \cdot \gamma^n$ 

 $\gamma$  is the shear rate (s<sup>-1</sup>),

n is the flow behaviour index, k is the consistency index  $(Ns^{n}/m^{2})$ .

The values for the flow behaviour index n, were obtained from plots of log shear stress versus log rotational speed; the slope of the line (if the dependence is sufficiently close to a linear one) is simply equal to the flow index of the fluid, n.

The shear stress is calculated using the next equation:

 $\tau_i = k_\tau \cdot \alpha_i \cdot C \tag{2}$ 

where:

 $\tau_i$  – shear stress, (dyne/cm<sup>2</sup>)

 $k_{\tau} = 0.119$ , this constant is for the spindle nos 2

 $\alpha_i$  – torque dial, (%)

C – 7.187 dyne/cm for RV viscometer

The shear rate is calculated using the next equation:

$$\gamma_i = k_{\gamma}(n) \cdot N_i \tag{3}$$

where:

n

 $\gamma_i$  – shear rate, (s<sup>-1</sup>)  $k_v(n)$  – constant, depends by the value of

N<sub>i</sub> – rotational speed, (rpm).

**Statistical analysis** The cluster analysis was performed using Unsrambler X version 10.1 (CAMO Process As, Oslo, Norway, 2005), all the rheological and physico-che mical parameters were weighed and normalized for performing the cluster analysis.

# 3. Results and discussion

The yogurt samples exhibited a non-Newtonian behaviour. The power law model is a suitable one for predicting the rheological parameters.

Sample	Viscosity* [cP]
S1	60947
S2	107000
<b>S</b> 3	213000
S4	106000
S5	144000

Table 3.Viscosity for yogurt samples

\*Viscosity was measured at 0.5 1/s

In general, addition of carrageenan increases the viscosity of yogurt, as shown in table 3. It achieved a stabilization of

(1)

aqueous dispersions whose continuous phase is the water and the dispersed one is solid or liquid and tends to separate. Through the addition of carrageenan, the viscosity is increased and the tendency of destabilization by separation of components is reduced.

Upon cooling and in the presence of appropriate cations, kappa and iota carrageenan polymers align themselves to form individual helices. These helices can further associate with divalent cations that are present, e.g. calcium, to form a gel matrix. Figure schematic 1 is a representation of the gelling mechanism for carrageenan.



Figure 1. Gelation mechanism [16]

The gel texture of the basic carrageenans can be modified by blending carrageenans to meet specified gel texture parameters. Figure 2 illustrates the penetration or elasticity of carrageenan gels before the gels are fractured. The gels can be made more elastic or less elastic by combining kappa and iota carrageenans until the desired texture is achieved.



Gels prepared with carrageenan are thermally-reversible. These gels will become fluid when heated above the

melting point of gels and will reset into a gel when cooled, with minimal loss of the original gel strength.

In food systems, one of the most important properties that truly differentiate carrageenan from other hydrocolloids is its ability to complex or interacts with proteins. In milk protein systems, at peripheral locations on the casein micelle there is a concentration of positive charges. This positive electrostatic charge attracts the negatively-charged sulfate groups of the carrageenan molecule to form linkages among the dispersed casein micelles as illustrated in figure 3.

This reaction, in combination with the normal water gelling capabilities of carrageenan, can increase the gel strength about 10-fold.

The ability of carrageenan to complex with milk proteins, combined with its water gelling properties enhances the functionality of carrageenan, e.g. increased gel potential.



Figure 3. Interaction of milk protein with carrageenan

Figure 4 shows the evolution of viscosity with the two hidrocolloid with its concentration and shear rate. It can be observed that the viscosity of the yogurt sample with t-iota carrageenan (S2) is higher than that of the yogurt that contains the same amount of  $\kappa$ -kappa carrageenan added (S1). Carrageenan mixtures have a

different rheological behavior on the samples of yogurt. Thus, the sample with a mixture of both types of echimolecular carrageenan has the lowest viscosity, followed by the sample with a smaller amount of  $\kappa$ -kappa carrageenan. Sample S5 has the highest viscosity and also a higher content of t-iota carrageenan.





The results of cluster analysis shows that the samples with  $\kappa$ -kappa carrageenan and  $\iota$ -iota carrageenan added are in the same group, while the samples with the mixture of the two types of carrageenans make a different group – see figure 5.



Figure 5. Diagram of yogurt samples clustered according to rheological and physicochemical properties

#### 4. Conclusion

Due to large molecular sizes, to the specific configuration, the charge and possible formation of intra- and intermolecular links, gums are able to reduce water mobility. This reduction in water mobility increases the viscosity of gum solutions in water.

In the case of yogurt samples obtained in the laboratory, the addition of carrageenan increases the viscosity. By means of carrageenan addition, yogurt viscosity is increased and reduces the tendency to destabilize the separation of components.

t-iota carrageenan has been evaluated as more effective for increasing the viscosity of yogurt in comparison with  $\kappa$ kappa carrageenan (with the same concentration).

The results of cluster analysis shows that the samples with  $\kappa$ -kappa carrageenan and  $\iota$ -iota carrageenan added are in the same group, while the samples with the mixture of the two types of carrageenans make a different group.

# 5. References

1. OROIAN M. A., GUTT G., Influence of total soluble content, starter culture and time period on rheological behaviour of cultured buttermilk, *Food and Environment Safety – Journal of Faculty of Food Engineering*, Stefan cel Mare University – Suceava, Year IX, No 2, 73 p, (2010) 2 KLEIN C. VENEMA P. SAGIS I. VAN

2. KLEIN, C., VENEMA, P., SAGIS, L., VAN DER LINDEN, E., Rheological discrimination and characterization of carrageenans and starches by Fourier transform-rheology in the non-linear viscous regime, *J. Non-Newtonian Fluid Mech.*, 151, 145-150, (2008)

3. ČERNIKOVÁ, M., BUŇKA, F., PAVLÍNEK, V., BŘEZINA, P., HRABĚ, J., VALÁŠEK, P., Effect of carrageenan type on viscoelastic properties of processed cheese, *Food Hydrocolloids*, 22, 1054-1061, (2008)

4. Imeson, A. P., Carrageenan, In G. O. Philips, & P. A. Williams (Eds.), *Handbook of hydrocolloids* (p. 87-102), Boca Raton, FL: Woodhead Publishing Limited, CRC Press. 5. BANU, C. (coordinator), Aditivs and ingredients in food industry (in romanian: *Aditivi şi ingrediente pentru industria alimentară*), Editura tehnică, București, (2000) 6. OROIAN M. A., ESCRICHE I., GUTT G., Rheological, textural color and physicochemical properties of some yoghurt products from the Spanish market, *Food and Environment Safety – Journal of Faculty of Food Engineering*, Stefan cel Mare University – Suceava, Year X, No 2, 24 p, (2011)

7. DAMIAN, C., OROIAN, M.A., ŞMADICI, A., Effect of addition of corn flakes on rheological behaviour of some yogurt, *Food and Environment Safety – Journal of Faculty of Food Engineering*, Stefan cel Mare University – Suceava, Volume X, Issue 4, 84 p, (2011)

8. KROGER, M. Quality of yogurt. *Journal of Dairy Science* 59(2): 344-350. (1975)

9. BENEZECH, T., MAINGONNAT, J.F. Characterization of the Rheological Properties of Yogurt-A Review. *Journal of Food Engineering*. 21, 447-472. (1994)

10. SAWYER WH. Complex between -lacto globulin and  $\gamma$ -casein. A review. *Journal of Dairy Science* 52:1347–55. (1969)

11. KINSELLA H. Milk proteins: physiochemical and functional properties. *CRC Crit Rev Food Sci Nutr* 21(3):197. (1994)

12. BONOMI F, IAMETTI S, PALGLIARINI E, PERI C. A spectrofluorometric approach to estimation of the surface hydrophobicity modifications in milk proteins upon thermal treatment. *Milchwissenschaft* 43:281–5, (1998)

13. MOTTAR J, BASSIER A, JONIAU M, BAERT J. Effect of heat-induced association of whey proteins and casein micelles on yogurt texture. *Journal of Dairy Science* 72(9):2247–56, (1989)

14. BONOMI F, IAMETTI S. Real-time monitoring of the surface hydrophobicity changes associated with isothermal treatment of milk and milk protein fractions. *Milchwissenschaft* 46:71–4, (1991)

15.http://www.brookfieldengineering.com/products /accessories/spindles/rv\_ha\_hb\_spindles.asp (7.09.2011)

16.http://www.fmcbiopolymer.com/Food/Ingredien ts/Carrageenan/FunctionalityandRheology.aspx

17.http://www.fmcbiopolymer.com/Food/Ingredien ts/Carrageenan/GelTexture.aspx

18.http://www.fmcbiopolymer.com/Food/Ingredien ts/Carrageenan/MilkProteinInteraction.aspx