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THE EFFECT OF ADDITION OF SELECTED CARRAGEENANS ON VISCOELASTIC PROPERTIES OF MODEL PROCESSED CHEESE SPREADS

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Abstract

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The effect of 0.25% w/w κ-carrageenan and ι-carrageenan on viscoelastic properties of processed cheese were studied using model samples containing 40% w/w dry matter and 45 and 50% w/w fat in dry matter. Experimental samples of processed cheese were evaluated after 14 days of storage at the temperature of 6 ± 2 °C. Basic parameters of processed cheese samples under study (i.e. their dry matter content and pH) were not different ($P \geq 0.05$). There were no statistically significant differences in values of storage modulus G´ [Pa], loss modulus G´´ [Pa] and tangent of phase shift angle tan δ [-] for the reference frequency of 1 Hz between processed cheese with κ-carrageenan applied in the form of powder and in the form of aqueous dispersion ($P \geq 0.05$). The addition of 0.25% w/w κ-carrageenan and ι-carrageenan (in the powder form) resulted in an increase in storage (G´) and loss (G´´) moduli and a decrease in values of tan δ ($P < 0.05$). As compared with control (i.e. without added carrageenans), samples of processed cheese became firmer. Iota-carrageenan added in the powder form in concentration of 0.25% w/w showed a more intensive effect on the increase in firmness of processed cheese under study than κ-carrageenan ($P < 0.05$).

processed cheese, fat in dry matter, kappa-carrageenan, iota-carrageenan, rheology

Hydrocolloids (carrageenan, pectin, modified starch, gums, etc.) are used as stabilizing and thickening agents in the processed cheese production. Processed cheese is cheese-base food produced by comminuting, melting and emulsifying into a smooth homogeneous molten blend, one or more natural cheeses and optional ingredients using heat, mechanical shear and emulsifying salts (Guinee *et al.*, 2004).

Carrageenans are anionic linear polysaccharides extracted from red seaweed (*Rhodophyceae*), consisting of alternating α-1,4 and β-1,3 linked anhydrogalactose residues. There are three major fractions (κ-kappa, ι-iota and λ-lambda) with varying number and position of sulphate groups. Kappa-carrageenan and ι-carrageenan undergo a temperature-dependent coil (disordered state) to helix (ordered state) transition (in aqueous solution). Kappa-carrageenan usually forms firm, brittle gels and ι-carrageenan usually generates soft elastic gels. Gel strength of both polysaccharides strongly depends on cations present – κ-carrageenan is especially sensitive to potassium and ι-carrageenan to calcium. Lambda-carrageenan is not able to build up stable gels (Syrbe *et al.*, 1998; Tziboula and Horne, 1999; Imeson, 2000; Singh *et al.*, 2003; Ribeiro *et al.*, 2004; Spagnuolo *et al.*, 2005).

Casein micelles are complex of individual casein fractions: α_{S1}, α_{S2}, β and κ-casein. Kappa-casein is located on the periphery of micelle, providing an electrostatic stabilising outer layer (Bourriot *et al.*, 1999; de Kruif and Tuinier, 2001). Interactions κ-carrageenan and ι-carrageenan with milk proteins, especially with casein micelles, have been widely studied (Thaiudom and Goff, 2003). "Milk reactivity" of κ-carrageenan and ι-carrageenan is mostly attributed to interactions between the negative sulphated groups of the carrageenans and a positively charged region situated between residues 97 and 112 of κ-casein at the surface of the casein micelle (Garnier *et al.*, 2003; Vega *et al.*, 2005). Behaviour of milk protein-carrageenan systems depends on a many parameters, such as hydrocolloid, protein and dispersed particle concentration, pH, ionic environment (e.g. potassium and calcium concentration), sugar content, temperature, molecular weight, milk protein processing, thermal history (Syrbe *et al.*, 1998).

In nature cheese (raw material for processed cheese production) there is neither casein in micellar form nor κ-casein ("natural" with full 169 residues). In the processed cheese there is no significant amount of micellar casein (excluding of situation when skim milk powder or other materials containing casein micelles are added). Only a few studies have dealt with interactions of κ-carrageenan and ι-carrageenan with non-micellar casein systems or individual casein fractions except κ-casein (e.g. α_S and β). Lynch and Mulvihill (1996) proposed that ability of α_S and β-caseins to interact with carrageenans requires the presence of calcium ions and ester-bound phosphorus on seryl residues of casein fractions.

The object of this paper was to use κ-carrageenan and ι-carrageenan in processed cheese production (products with 45% w/w and 50% w/w fat in dry matter) and find out differences in viscoelastic properties of both of applied carrageenans in model concentration.

MATERIAL AND METHODS

Model samples of processed cheese spreads containing 40% w/w dry matter (DM) and 45% w/w or 50% w/w fat in dry matter (FDM) were manufactured from a mixture of natural cheese (Edam block cheese with 30% w/w FDM and Edam block cheese with 45% w/w FDM), butter, deionized water (to assure a constant concentration of ions) and commercially supplied emulsifying salts.

In the first part of this experiment (Group I), the effect of the form of added κ-carrageenan on viscoelastic properties of model processed cheeses containing 45% w/w and 50% w/w FDM was studied. Kappa-carrageenan was applied into both types of cheese (i.e. with 45% w/w and 50% w/w FDM) in concentration of 0.25% w/w, partly in the form of powder and partly in the form of aqueous dispersion (in deionized water, which was used in such amount that did not influenced the DM content in the final products). Two control samples (for both FDM contents under study) were prepared as well.

In the second part of this experiment, four groups of model processed cheese samples were used (i = II, III, IV, V). All of them were manufactured using the same technology (see below), and carrageenans in powder form were applied to each of them. In particular, each of these four groups consisted of six types of samples (batches): (1) product with 0.25% w/w of κ-carrageenan (KC) and with 45% w/w FDM; (2) product with 0.25% w/w of ι-carrageenan (IC) and with 45% w/w FDM; (3) product with 0.25% w/w KC and 50% w/w FDM; (4) product with 0.25% w/w IC and 50% w/w FDM; (5) control sample without carrageenan and with 45% w/w FDM; (6) control sample without carrageenan and with 50% w/w FDM. In the second part of this experiment, samples of natural cheese with a different degree of maturity were used (Group II – 6 weeks; Group III – 8 weeks; Group IV – 10 weeks and Group V – 16 weeks). In individual test groups, the initial firmness of control samples was different (see values of storage (G´) and loss (G´´) moduli in Tabs II and III). For that reason the conclusions concerning effects of KC and IC addition were related to the control sample of each group. This experimental layout was used to reach a higher information capability and representativeness of results for industrial practice where it is sometimes difficult to assure a constant degree of maturity of the basic raw material (i.e. natural cheese).

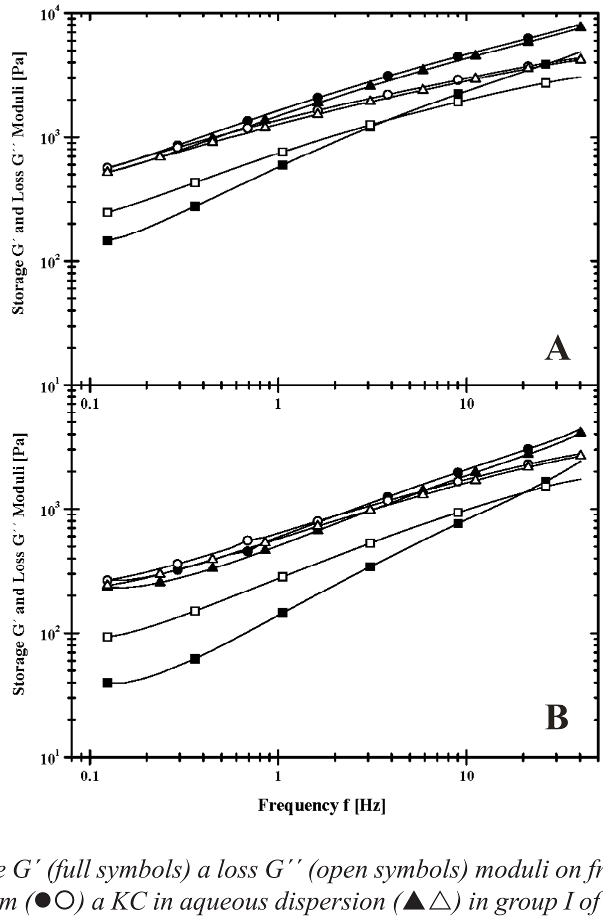
Processed cheese spreads were manufactured using the equipment Vorwerk Thermomix TM 21 blender cooker (Vorwerk & Co. Thermomix; GmbH, Wuppertal, Germany); the melting temperature was 92 °C (the time interval necessary to reach the melting temperature was 9–10 min. and the melting temperature was maintained for 1 min.). Thereafter the processed cheese was cooled down to 6 ± 2 °C and stored for 14 days at the same temperature. Carrageenans (KC and IC) used in this experiment were supplied by the company Sigma Aldrich, Inc., St. Louis, USA.

The content of DM was determined at the temperature of 102 ± 1 °C, which was maintained till the loss of weight remained to be constant (Berger *et al.*, 2002). Values of pH were measured with the pH-meter Gryf 209 S with a combined glass electrode at 22 ± 1 °C. Viscoelastic properties of processed cheese samples were measured by Bohlin Gemini (Malvern Instruments, UK) rheometer with parallel plate geometry (diameter of 40 mm, gap 1 mm) at the temperature of 20 °C. All the experiments were performed in the control shear stress mode at frequency ranging from 0.1 to 50 Hz. The amplitude of shear stress 50 Pa was chosen in the region of linear viscoelasticity. The exposed edge of parallel plates geometry was covered with a thin layer of silicone oil to prevent the samples from dehydration. Values of storage modulus G´, loss modulus G´´ and tangents of phase shift angle (tan δ = G´´/G´) were chosen for comparison of cheese properties.

Treatments were statistically evaluated by Wilcoxon test for comparison of mean values. Non-parametrical procedures were chosen due to a low amount of available data (Agresti, 1984). To show the significance, differences among comparisons had to achieve $P < 0.05$.

RESULTS AND DISCUSSION

At first, the rheological analysis of model processed cheese from Group I containing 40% w/w DM and 45% w/w or 50% w/w FDM was performed with the aim to evaluate the effect of a dosing procedure of 0.25% w/w KC (in the form of powder and aqueous suspension) on viscoelastic properties of the final product. The basic analysis revealed that all samples had practically the same content of DM (i.e. ranging from 40.62 to 41.15% w/w; $P \geq 0.05$) and that also their pH was very similar (i.e. ranging from 5.86 to 5.92; $P \geq 0.05$). These similar characteristics enabled to compare the effect of KC application because both showed a high effect on the consistency of processed cheese (Marchesseau *et al.*, 1997; Lee *et al.*, 2004). As shown in Tab. I and Fig. 1 the form, in which the κ-carrageenan is applied (i.e. either as a powder or as dispersed in water prior to the application into the raw material), did not show any significant effect on storage (G´) and loss (G´´) moduli ($P \geq 0.05$). The efficiency of KC applied in concentration of 0.25% w/w was not dependent on its physical form and for that reason it was decided to use it as a powder. From the economic point of view this method of application is easier and thus also cheaper.



1: *Dependence of storage G´ (full symbols) a loss G´´ (open symbols) moduli on frequency f for control sample (■□), KC in powder form (●○) a KC in aqueous dispersion (▲△) in group I of processed cheeses with 45% w/w (A) and 50% w/w (B) FDM.*

I: *Values of storage (G´) and loss (G´´) moduli and tan δ for reference frequency 1 Hz in processed cheese group I with addition of 0.25% w/w κ-carrageenan applied in powder form and dispersed in water **

The fat in dry matter content of processed cheeses (% w/w)	Form of applied κ-carrageenan	G´ [Pa]	G´´ [Pa]	tan δ [-]
45	none	596 ± 89.2 [a]	760 ± 54.6 [a]	1.275
	powder form	1682 ± 167.7 [b]	1397 ± 132.7 [b]	0.831
	dispersed in water	1525 ± 159.1 [b]	1296 ± 116.3 [b]	0.850
50	none	145 ± 21.6 [a]	284 ± 19.1 [a]	1.959
	powder form	612 ± 66.3 [b]	653 ± 53.5 [b]	1.067
	dispersed in water	522 ± 58.2 [b]	590 ± 37.4 [b]	1.130

* Storage G´ and loss G´´ moduli are presented by mean ± S.D.; tan δ = G´´/G´. Means (*n* = 4) within a column followed by no common superscript letter differ (P < 0.05); samples with 45% w/w and 50% w/w FDM were evaluated separately.

Thereafter, the rheological analysis of model processed cheese samples from Groups II to V with 40% w/w DM and 45% w/w or 50% w/w FDM was performed. Both KC and IC were applied in the target concentration of 0.25% w/w in the final product. The results of a basic analysis indicated that samples from all four groups under study showed a practically identical content of DM (ranging from 40.20–41.13% w/w; P ≥ 0.05) and also pH values (ranging from 5.85–5.93; P ≥ 0.05).

As shown in Tabs II and III and Figs 2 and 3, in which results of a dynamic oscillation rheometry of Groups II–V with the contents of 45% w/w and 50% w/w FDM are presented, the applied concentration of carrageenans (0.25% w/w) increased significantly the values of both storage (G´) and loss (G´´) moduli (P < 0.05) within the whole range of tested frequencies (0.1–50Hz) as compared with corresponding controls. This effect was observed in all tested Groups (II–V) irrespective of degree of maturity. These changes indicate that the presence of 0.25% w/w of both KC and IC in processed cheese can change the character of its gel: as compared with control, the firmness of test samples was higher. This can be explained by the fact that interactions of both KC and IC chains contribute to the formation of a more complex matrix in samples of processed cheese (Langendorff *et al.*, 1999; Langendorff *et al.*, 2000).

II: *Values of storage (G´) and loss (G´´) moduli and tan δ for reference frequency 1 Hz in processed cheese groups II and III with addition of 0.25% w/w κ-carrageenan (KC) and ι-carrageenan (IC) applied in powder form **

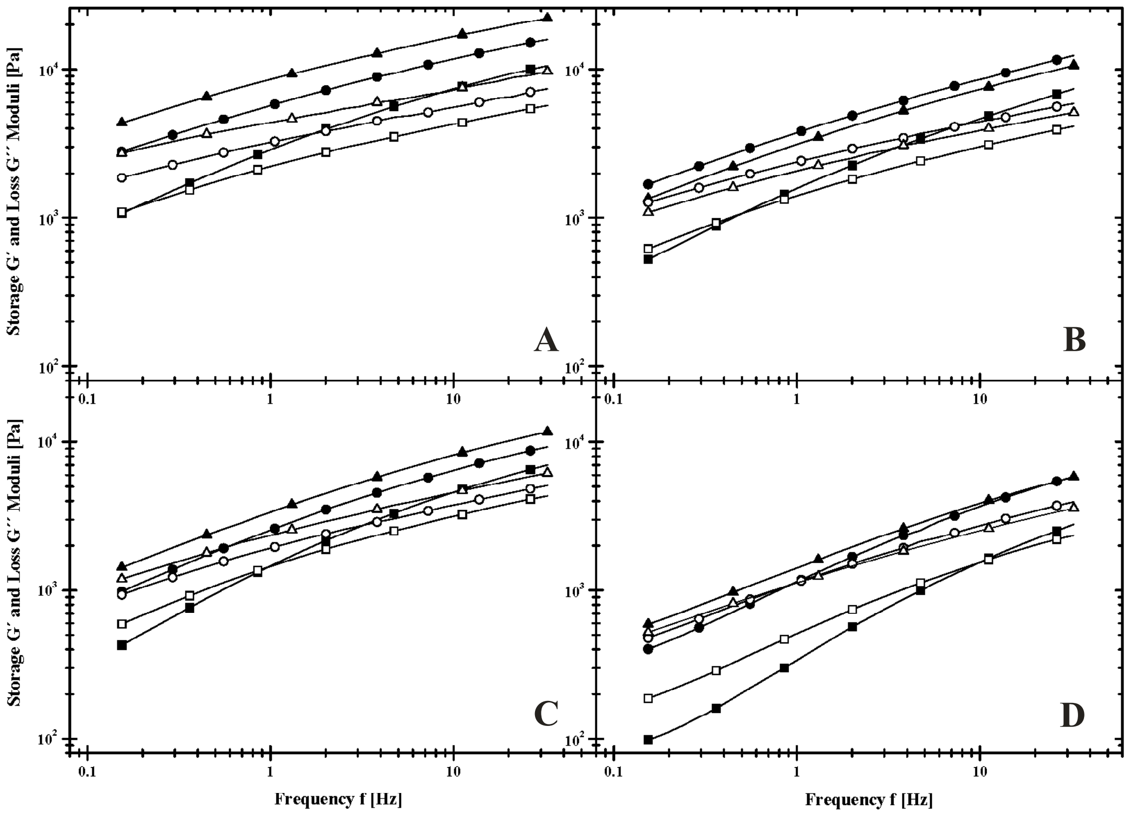
The fat in dry matter content of processed cheeses (% w/w)	Type of added carrageenan	Group of processed cheese					
		II			III		
		G´ [Pa]	G´´ [Pa]	tan δ [-]	G´ [Pa]	G´´ [Pa]	tan δ [-]
45	none	2952 ± 153.5 [a]	2267 ± 82.3 [a]	0.767	1627 ± 76.6 [a]	1436 ± 57.3 [a]	0.882
	KC	5835 ± 121.9 [b]	3270 ± 127.1 [b]	0.561	3826 ± 112.9 [b]	2424 ± 287.4 [b]	0.635
	IC	8714 ± 404.8 [c]	4445 ± 295.7 [c]	0.510	3197 ± 156.2 [c]	2107 ± 268.5 [b]	0.659
50	none	1275 ± 102.2 [a]	1329 ± 97.5 [a]	1.043	352 ± 32.3 [a]	563 ± 62.4 [a]	1.600
	KC	4098 ± 99.7 [b]	2719 ± 132.0 [b]	0.664	641 ± 45.2 [b]	721 ± 104.1 [b]	1.126
	IC	5288 ± 275.3 [c]	2969 ± 186.4 [c]	0.561	2750 ± 154.6 [c]	1722 ± 243.4 [c]	0.627

* Storage G´ and loss G´´ moduli are presented by mean ± S.D.; tan δ = G´´/G´. Means (*n* = 4) within a column followed by no common superscript letter differ (P < 0.05); samples with 45% w/w and 50% w/w FDM were evaluated separately.

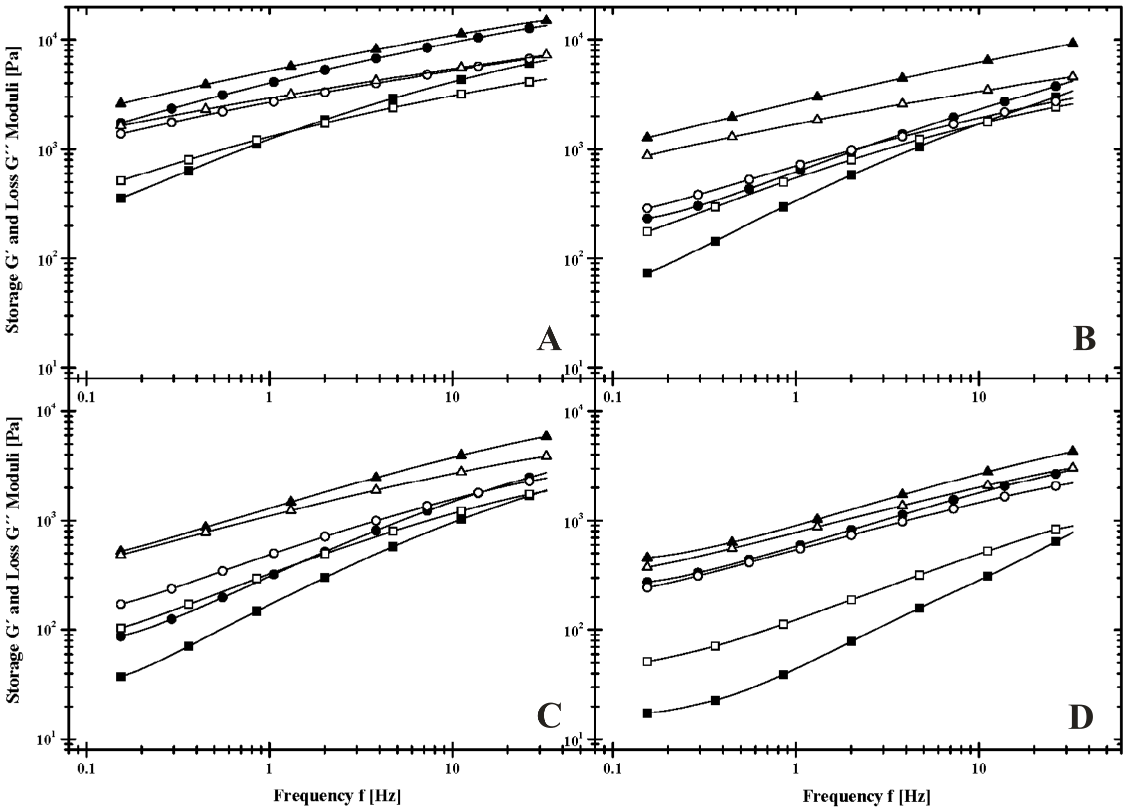
III: *Values of storage (G´) and loss (G´´) moduli and tan δ for reference frequency 1 Hz in processed cheese groups IV and V with addition of 0.25% w/w κ-carrageenan (KC) and ι-carrageenan (IC) applied in powder form **

The fat in dry matter content of processed cheeses (% w/w)	Type of added carrageenan	Group of processed cheese					
		IV			V		
		G´ [Pa]	G´´ [Pa]	tan δ [-]	G´ [Pa]	G´´ [Pa]	tan δ [-]
45	none	1509 ± 87.4 [a]	1483 ± 91.8 [a]	0.983	352 ± 10.1 [a]	525 ± 16.8 [a]	1.488
	KC	2616 ± 48.6 [b]	1958 ± 142.7 [b]	0.748	1179 ± 132.4 [b]	1155 ± 23.5 [b]	0.979
	IC	3450 ± 122.9 [c]	2387 ± 159.0 [c]	0.692	1452 ± 60.0 [c]	1143 ± 16.1 [b]	0.787
50	none	178 ± 28.9 [a]	337 ± 26.6 [a]	1.889	46 ± 3.6 [a]	128 ± 11.2 [a]	2.762
	KC	322 ± 76.0 [b]	500 ± 37.1 [b]	1.552	597 ± 14.3 [b]	552 ± 18.7 [b]	0.926
	IC	1335 ± 129.5 [c]	1133 ± 82.8 [c]	0.848	924 ± 69.2 [c]	796 ± 25.6 [c]	0.863

* Storage G´ and loss G´´ moduli are presented by mean ± S.D.; tan δ = G´´/G´. Means (*n* = 4) within a column followed by no common superscript letter differ (P < 0.05); samples with 45% w/w and 50% w/w FDM were evaluated separately.



2: *Dependence of storage G´ (full symbols) a loss G´´ (open symbols) moduli on frequency f for control sample (■□), KC in powder form (●○) a IC in powder form (▲△) for processed cheeses with 45% w/w FDM (A – group II, B – group III, C – group IV and D – group V).*



3: *Dependence of storage G′ (full symbols) a loss G′′ (open symbols) moduli on frequency f for control sample (■□), KC in powder form (●○) a IC in powder form (▲△) for processed cheeses with 50% w/w FDM (A – group II, B – group III, C – group IV and D – group V).*

Tabs II and III and Figs 2 and 3 also indicate that application of IC in concentration of 0.25 % w/w resulted in the formation of a firmer gel than that of KC ($P < 0.05$). An explanation of a better efficiency of IC is not simple, especially with regard to the findings published by Imeson (2000) that KC formed firm gels and IC soft elastic gels. The answer can be looked for e.g. in the ionic environment (especially in the presence of ions), which shows a significant effect on the strength of carrageenan network (Nickerson *et al.*, 2004). In natural cheese, which is the basic raw material for production of processed cheese, the content of calcium ions is approximately ten-times higher than that of potassium ions (Fox *et al.*, 2000). It is known that IC is more sensitive to potassium while KC is more susceptible to calcium ions (Imeson, 2000). As mentioned by Spagnuolo *et al.* (2005) not only absolute amounts of calcium and potassium ions but also the ratio between these ions may be important. Hence, dominance in concentration of Ca^{++} ions over K^{+} ions may play a key role in the firmness of KC and IC gels, respectively. In this context it is also appropriate to take into account results published by MacArtain *et al.* (2003) who mention that in case of KC there is an optimal concentration of calcium ions in the medium and that within the range of suboptimal concentrations their increasing content results in a higher firmness of KC gel. However, if the concentration of calcium ions surpassed its optimum within a given system, any further increase resulted in a decrease in values of storage (G′) modulus (i.e. in the firmness) of the produced gel.

CONCLUSION

In this paper the effect of addition of 0.25% w/w of κ-carrageenan and ι-carrageenan on viscoelastic properties of model samples of processed cheese containing 45% w/w and 50% w/w fat in dry matter was evaluated. It was found out that at a target concentration of 0.25% w/w of carrageenans their effect on the consistency of processed cheese was not dependent on the form of applied additive (tested were its powder form and its aqueous dispersion). The addition of 0.25% w/w of both carrageenan under study resulted in the formation of firmer and less spreadable products in compare to control samples without carrageenan addition. The effect of ι-carrageenan was higher than that of κ-carrageenan.

SOUHRN

Vliv přídavku vybraných karagenanů na viskoelastické vlastnosti modelových tavených sýrů

Vliv přídavku 0,25 % w/w κ-karagenanu a ι-karagenanu na viskoelastické vlastnosti tavených sýrů byl sledován u modelových vzorků s 40 % w/w sušiny a 45 % w/w, resp. 50 % w/w tuku v sušině. Tavené sýry byly hodnoceny po 14 dnech skladování při teplotě 6 ± 2 °C. Sledované tavené sýry se nelišily v základních parametrech – sušině a pH (P ≥ 0,05). Nebyly zjištěny statisticky významné rozdíly hodnot elastického modulu pružnosti G´ [Pa], ztrátového modulu pružnosti G´´ [Pa] a tangentu úhlu fázového posunu tan δ [-] pro referenční frekvenci 1 Hz mezi tavenými sýry s aplikací κ-karagenanu v práškové formě a ve formě disperze ve vodě (P ≥ 0,05). V důsledku přídavku 0,25 % w/w κ-karagenanu i ι-karagenanu (v práškové formě) byl zaznamenán nárůst elastického G´ a ztrátového G´´ modulu pružnosti a pokles hodnot tan δ (P < 0,05). Tavené sýry se staly tužšími ve srovnání s kontrolními vzorky bez přídavku karagenanů. Iota-karagenan přidaný v práškové formě byl pro koncentraci 0,25 % w/w při zvyšování tuhosti sledovaných tavených sýrů účinnější než κ-karagenan (P < 0,05).

tavený sýr, tuk v sušině, kappa-karagenan, iota-karagenan, reologie

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