

The effect of selected phosphate emulsifying salts on viscoelastic properties of processed cheese

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ABSTRACT

The aim of this study was to investigate the effect of selected phosphate emulsifying salts (Na_3PO_4 , Na_2HPO_4 , $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$, sodium polyphosphate) and their selected mixtures (sodium polyphosphate + Na_2HPO_4 ; sodium polyphosphate + $\text{Na}_4\text{P}_2\text{O}_7$) on the viscoelastic properties of model processed cheese (dry matter — 40 g/100 g; fat in dry matter — 50 g/100 g). Viscoelastic properties of model samples stored at 6 ± 2 °C were investigated by dynamic oscillation rheometry (plate—plate geometry; frequency range 0.1—50.0 Hz; temperature 20 °C). Processed cheese manufactured with different phosphates showed various pH values and different viscoelastic properties. The firmness of samples increased due to use of particular types of tested phosphates. Their influence on cheese firmness increased in the following order: orthophosphate < polyphosphate < diphosphate < triphosphate. The increasing content of polyphosphate (up to 50%) in the binary mixture of polyphosphate and orthophosphate or polyphosphate and diphosphate caused the increase of firmness of model samples. The content of polyphosphates above 50% in the binary mixture led to decrease of firmness of model processed cheese.

1. Introduction

Processed cheese is a dairy product manufactured from natural cheese and suitable emulsifying salts (e.g. sodium salts of phosphates, polyphosphates and citrates). Its matrix is formed under a partial vacuum, constant agitation and upon heating. Other optional dairy (butter, skim milk powder, whey powder, coprecipitates, caseinates, etc.) and non-dairy ingredients (water, vegetables, spices, flavourings, colourings, salt, hydrocolloids, etc.) can be added into the blend (Guinee, Carič, & Kaláb, 2004; Lee, Anema, & Klostermeyer, 2004). The consistency of processed cheese can be influenced by many factors such as type and maturity of natural cheese, pH of cheese melt, type and concentration of emulsifying salt, processing conditions, dry matter content, fat content, presence and concentration of ions (especially calcium), use of hydrocolloids, etc. (Bowland & Foegeding, 2001; Černíková et al., 2008; Dimitreli & Thomareis, 2007; Guinee et al., 2004; Gustaw &

Mleko, 2007; Lee et al., 2004; Lu, Shirashoji, & Lucey, 2007; Marchesseau, Gastaldi, Lagaude, & Cuq, 1997; Piska & Štětina, 2004; Shirashoji, Jaeggi, & Lucey, 2006).

Emulsifying salts are essential in the formation of uniform structure of processed cheese. Sodium phosphates, polyphosphates and citrates represent the most commonly used ones. Their important role is to enhance the emulsifying capability of cheese proteins by removing calcium from caseins and by peptizing, hydrating and dispersing the protein. Additional effects the above salts show are pH increase (in the majority of cases) and buffering, stabilisation of oil-in-water emulsion and structure formation (Guinee et al., 2004; Mulsow, Jaros, & Rohm, 2007). However, only limited information about the effect of individual phosphate emulsifying salts and the effect of binary mixtures of individual phosphates on viscoelastic properties of processed cheese has been found in available literature.

The objective of this research was to investigate the influence of selected phosphate emulsifying salts (Na_3PO_4 , Na_2HPO_4 , $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$, sodium polyphosphate) and their binary mixtures (sodium polyphosphate + Na_2HPO_4 ; sodium polyphosphate + $\text{Na}_4\text{P}_2\text{O}_7$) on viscoelastic properties of model

processed cheese (dry matter — 40 g/100 g; fat in dry matter — 50 g/100 g).

2. Materials and methods

2.2. Sample preparation

Edam block cheese (dry matter — 50 g/100 g, fat in dry matter — 30 g/100 g; 8–10 weeks old), deionised water (for keeping of constant ion-conditions), butter (dry matter - 84 g/100 g, fat - 82 g/100 g) and sodium salts of orthophosphates, diphosphates, triphosphates and polyphosphates (3 g/100 g of processed cheese; Na₃PO₄, Na₂HPO₄, Na₄P₂O₇, Na₂H₂P₂O₇, Na₅P₃O₁₀, sodium polyphosphate; Fosfa a.s. Břeclav-Postorna, Czech Republic) were used for preparation of model processed cheese (dry matter — 40 g/100 g; fat in dry matter - 50 g/100 g). All samples were manufactured using a 2-L capacity Vorwerk Thermomix TM 31 blender cooker (Vorwerk & Co. Thermomix; GmbH, Wuppertal, Germany). Edam block cheese, butter and a mixture of phosphates (or an individual phosphate) were premixed in the cooker at high agitation followed by water addition. Under constant agitation, the mixture was heated in the cooker to 90 °C and then heated for 1 min at the same temperature. Packed samples (100 g doses) were cooled and stored in a refrigerator at 6 ± 2 °C. The total amount of one batch was approximately 700 g and each batch was manufactured in duplicate.

At the beginning of the experiment (first stage of work), two groups of model processed cheeses (Group I and II) with addition of various phosphates (3.0 g/100 g of cheese; Na₃PO₄, Na₂HPC>4, Na₄P₂O₇, Na₂H₂P₂O₇, Na₅P₃O₁₀, sodium polyphosphate — PoP) were prepared. Each of these two groups included 6 batches that differed only in emulsifying salt applied (see Table 1). In addition, pH of model samples in Group II were adjusted by hydrochloric acid or sodium hydroxide to practically similar level (approximately to 5.5—6.0). The above chemicals were added when the melt was heated to 85 ± 1 °C.

The second part of this study explored the influence of mixture of two different phosphates on viscoelastic properties of model processed cheese. Four groups of samples (Groups III–VI; see Table 1) were manufactured and each group included 5 batches differing only in the ratio of phosphates in the mixture. Manufacturing samples in Groups III and IV, a binary mixture of polyphosphate and orthophosphate (PoP:Na₂HPO₄) was folded in and processed

cheeses in Groups V and VI were prepared with mixture of polyphosphate and diphosphate (PoP:Na₄P₂O₇). The ratio of sodium phosphates in the mixture was gradually changed in the following order; 100:0,75:25,50:50,25:75 and 0:100 (the first number refers to polyphosphate and the second one represents quantity of ortho- or diphosphate in the mixture). The values of pH of processed cheeses in Groups IV and VI were adjusted by hydrochloric acid or sodium hydroxide to practically similar level (approximately to 5.5–6.0).

All groups of model processed cheese (i = I–VI) were manufactured according to the same technology separately on different days. Model samples were produced from Edam block cheese of different batches obtained from one producer. The different batches of Edam block cheese were chosen to simulate the real industrial practice because there are processed Edam cheeses of different degree of maturity and different batches.

2.2. Chemical analysis

After 14 days of storage at 6 ± 2 °C, pH, dry matter and fat content in model processed cheeses were analysed. Dry matter was determined by drying at 102 ± 2 °C according to ISO 5534:2004. Fat content was measured by the method of van Gulik according to ISO 3433:2008. Values of pH were determined by a Gryf 208 L pH- meter with THETA 90 HC 113 glass electrode (Gryf, Havlíčkův Brod, Czech Republic) at 20 ± 2 °C. Chemical analyses were conducted in triplicate.

2.3. Rheological analysis

Viscoelastic properties of processed cheese were investigated using a controlled stress Bohlin rheometer (Bohlin GEMINI, Malvern Instruments Ltd., Malvern, UK) with parallel plates geometry (40 mm diameter, 1 mm gap) at 20.0 ± 0.1 °C. Linear viscoelastic region was determined by amplitude sweep test while frequency sweep mode was used to evaluate viscoelastic properties of model samples. The storage (G') and loss (G'') moduli were measured in the 0.1–50.0 Hz frequency range. The loss tangent (tan δ) and complex modulus (G*) for the reference frequency 1 Hz were calculated according to Eq. (1) and (2) (Gabriele, de Cindio, & D'Antona, 2001; Gunasekaran & Ak, 2000):

$$\tan\delta = G''/G'$$

$$G^*(\omega) = \sqrt{G'(\omega)^2 + G''(\omega)^2}$$

The value of reference frequency 1 Hz was recommended in available literature (Bennett et al, 2006; Lu et al., 2007; Piska & Štětina, 2004). Dynamic rheological measurements of samples were carried out after 14 days of storage at 6 ± 2 °C.

The viscoelastic properties of processed cheese were also evaluated by application of Winter's critical gel theory (Winter & Chambon, 1986), which was recommended for food samples by Gabriele et al. (2001). The complex modulus (G*) can be expressed by:

$$G^*(\omega) = A_g \omega^{1/z}$$

where ω is the frequency, (A_g) is the gel strength and (z) is the interaction factor, i.e. the number of structure units interacting with one another in a three-dimensional network. The higher is the interaction factor, the more interactions occur in sample matrix (Gabriele et al., 2001; Martinez-Ruvalcaba, Chornet, & Rodrigue, 2007).

Table 1

Groups of processed cheese manufactured with different sodium phosphates or their mixtures (PoP:Na₂HPO₄; PoP:Na₄P₂O₇)^a.

Stage of work	Group of samples	Emulsifying salt (3.0 g/100 g of cheese)
The first	I and II	Na ₃ PO ₄ Na ₂ HPO ₄ Na ₄ P ₂ O ₇ Na ₂ H ₂ P ₂ O ₇ Na ₅ P ₃ O ₁₀ PoP
The second	III and IV	PoP:Na ₂ HPO ₄ (100:0) PoP:Na ₂ HPO ₄ (75:25) PoP:Na ₂ HPO ₄ (50:50) PoP:Na ₂ HPO ₄ (25:75) PoP:Na ₂ HPO ₄ (0:100)
	V and VI	PoP:Na ₄ P ₂ O ₇ (100:0) PoP:Na ₄ P ₂ O ₇ (75:25) PoP:Na ₄ P ₂ O ₇ (50:50) PoP:Na ₄ P ₂ O ₇ (25:75) PoP:Na ₄ P ₂ O ₇ (0:100)

^a PoP – sodium polyphosphate.

2.4. Statistical analysis

Results obtained from chemical and Theological analyses were statistically evaluated by parametric *t*-test using the Unistat 5.5 statistical programme. Results were evaluated as significantly different when $P < 0.05$.

3. Results and discussion

3A. Chemical analysis

The following values illustrate dry matter content (g/100 g) in analysed samples: 42.10–42.85 (Group I), 41.90–42.98 (Group II), 41.82–42.61 (Group III), 42.06–43.67 (Group IV), 42.07–43.88 (Group V) and 42.38–42.99 (Group VI). Fat content (g/100 g) ranged between the following values: 21.0–22.0 (Group I), 21.0–22.5 (Group II), 21.0–21.5 (Group III), 22.0–22.5 (Group IV), 22.0–23.0 (Group V) and 21.5–22.5 (Group VI). Viscoelastic properties of processed cheese are substantially affected by chemical composition of the product (Lee et al., 2004; Marchesseau et al., 1997; Piska & Štětina, 2004). Similar contents of the above cheese constituents allowed the comparison of the effect of various sodium phosphates (or their mixtures) on the viscoelastic properties of processed cheese.

3.2. Processed cheese containing individual sodium phosphates

3.2.1. Assessment of pH — processed cheese without pH adjustment The values of pH of model processed cheese in Group I manufactured with addition of different sodium phosphates are given in Table 2. These values varied significantly from 4.67 to 6.93. According to scientific literature, the pH optimum for obtaining suitable structural and sensory properties of processed cheese should oscillate between 5.5 and 6.0 (Guinee et al., 2004; Lee & Klostermeyer, 2001; Lu et al., 2007; Marchesseau et al., 1997). Optimal pH was found only in samples with PoP. Compared to natural cheese (raw material for processed cheese production, its pH ~ 5.6–5.8), the usage of other phosphates caused mostly the increase of pH values of the processed cheese. The application of disodium dihydrogen diphosphate ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$) was the only exception (pH * 4.67). The values of pH of model processed cheese increased due to various phosphates usage in the following order: $\text{PoP} < \text{Na}_2\text{HPC}>_4 < \text{Na}_5\text{PaOlo} < \text{Na}_4\text{P}_2\text{C}>_7 < \text{Na}_3\text{PCU}$. Generally, it can be said that sodium salts of phosphates change the pH of the cheese blend (they usually cause increase of blend pH) and contribute to pH stabilisation due to their buffering capacity (Guinee et al., 2004; Molins, 1991; Mulsow et al., 2007).

3.2.2. Rheology — processed cheese without pH adjustment

The results for model processed cheese in Group I obtained by rheological measurement are given in Table 3. The addition of

various phosphate emulsifying salts caused formation of products with different viscoelastic properties. The lowest values of storage and loss moduli were found in samples made with orthophosphates ($\text{Na}_3\text{PC}>_4$ or Na_2HPo_4). Moreover, loss modulus value was always higher than that of storage modulus. It means that viscoelastic properties of processed cheese with orthophosphates differed from typical qualities of spreadable type of processed cheese. These samples behaved rather like a fluid than like processed cheese spreads with three-dimensional network. Model samples manufactured with tetrasodium diphosphate ($\text{Na}_4\text{P}_{207}$) had higher values of moduli compared to processed cheese with orthophosphates (Na_3PCU or Na_2HPo_4). The diphosphate gave processed cheese desirable characteristics. Model processed cheese containing sodium tripolyphosphate (Na_3PsOio) possessed the highest values of both moduli; this sample proved to be the most rigid one among all the others ($P < 0.05$). The application of sodium polyphosphate (PoP) caused the formation of products less rigid than the samples with sodium tripolyphosphate but substantially firmer than the processed cheese with ortho- or diphosphates ($P < 0.05$). Table 3 also shows the values of loss tangent. The smaller is the value of loss tangent, the more elastic is the tested material. The above mentioned results were also confirmed by data obtained by application of Winter's critical gel theory. The higher number of phosphate groups contained the emulsifying salt molecule, the higher increase of interaction factor and gel strength was observed. This can be explained by the ability of phosphates to attach to the protein molecules (especially via calcium bridges), i.e. the more phosphate groups were present, the more groups could interact. According to Lucey, Johnson, and Horne (2003), phosphates that are associated with casein might act as cross-linking agents by bridging (e. g. via calcium) within or between casein molecules. The higher gel strength can be explained by more interactions occurring in samples.

The above mentioned rheological results obtained by analyses of samples in Group I are presented in Fig. 1 as a graph which shows the dependence of the complex modulus G^* on frequency. As apparent, the complex modulus increased in the whole tested frequency range. This figure also illustrates that orthophosphate was the least effective phosphate in the formation of processed cheese network. Diphosphate and triphosphate followed the orthophosphate values.

The effectiveness of various phosphates in formation of rigid structure increased in the following order: orthophosphate < polyphosphate < diphosphate < triphosphate. Hence, samples manufactured with di- and triphosphates proved to be the most rigid ones. This fact can be explained by their ability to support the formation of three-dimensional network (Guinee et al., 2004). Mizuno and Lucey (2005) claim that some types of phosphates, especially diphosphates, can induce gelation or aggregation by the formation of caseinate-Ca phosphate complexes under specific conditions, even in dilute protein solutions. Diphosphates and triphosphates can also strongly support fat emulsification (Awad, Abdel-Hamid, El-Shabrawy, & Singh 2002). According to Rayan, Kaláb, and Ernstrom (1980), poor emulsification results in soft processed cheese, whereas well emulsified cheese shows the highest firmness.

Furthermore, processed cheese with disodium dihydrogen diphosphate ($\text{Na}_2\text{H}_2\text{P}_{207}$) was prepared. However, this product could not be subjected to rheological analyses because of crumble consistency. Moreover, this emulsifying salt (alone) failed to give stable emulsion; this sample exhibited water separation and oiling-off. According to Marchesseau et al. (1997) and Mulsow et al. (2007), low pH (4.8–5.2) usually yields short, crumbly and granular cheeses with high susceptibility to fat separation. The above mentioned phenomena can be probably elucidated by very low pH

Table 2

The values of pH of model processed cheese manufactured with different sodium phosphates (Groups I and II)^a.

Phosphate	Processed cheese group	
	I	II ^a
Na_3PCO_4	6.93 ± 0.03	5.62 ± 0.02
Na_2HPD_4	6.64 ± 0.02	5.57 ± 0.01
$\text{Na}_4\text{P}_2\text{O}_7$	6.84 ± 0.02	5.56 ± 0.03
$\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$	4.67 ± 0.02	5.62 ± 0.01
$\text{Na}_5\text{P}_3\text{O}_{10}$	6.74 ± 0.01	5.55 ± 0.03
PoP	5.79 ± 0.02	5.61 ± 0.02

^a Values of pH are expressed as mean ± standard deviation. The values of pH of processed cheeses in Group II were adjusted practically to similar level by using an acid (HCl) or a base (NaOH).

Table 3

The values of storage modulus, loss modulus, loss tangent, gel strength and interaction factor for the reference frequency 1 Hz in tested processed cheese prepared with various sodium salts of phosphates (Groups I and III).

Group of cheese	Phosphate	G' [Pa]	G'' [Pa]	$\tan \delta$ [-]	A_g [Pa·s ^{1/2}]	z
I	Na ₃ PO ₄	11 ± 6 ^a	42 ± 13 ^a	3.792	41 ± 12 ^a	1.22 ± 0.02 ^f
	Na ₂ HPO ₄	482 ± 32 ^b	558 ± 22 ^b	1.157	751 ± 36 ^b	1.99 ± 0.01 ^l
	Na ₄ P ₂ O ₇	955 ± 6 ^c	980 ± 13 ^c	1.026	1383 ± 3 ^c	2.14 ± 0.01 ^l
	Na ₂ H ₂ P ₂ O ₇	n ^b	n	n	n	n
	Na ₅ P ₃ O ₁₀	1121 ± 8 ^d	1232 ± 2 ^d	1.099	1682 ± 7 ^d	2.22 ± 0.01 ^l
	PoP	886 ± 22 ^c	695 ± 17 ^c	0.784	1105 ± 28 ^c	2.40 ± 0.02 ^l
II	Na ₃ PO ₄	479 ± 38 ^a	391 ± 6 ^a	0.816	616 ± 44 ^a	2.05 ± 0.10 ^f
	Na ₂ HPO ₄	203 ± 60 ^b	159 ± 40 ^b	0.783	231 ± 74 ^b	1.91 ± 0.09 ^l
	Na ₄ P ₂ O ₇	657 ± 19 ^c	618 ± 10 ^c	0.942	898 ± 17 ^c	2.30 ± 0.01 ^l
	Na ₂ H ₂ P ₂ O ₇	657 ± 39 ^c	685 ± 32 ^d	1.043	963 ± 48 ^c	2.16 ± 0.01 ^l
	Na ₅ P ₃ O ₁₀	1650 ± 163 ^d	1097 ± 54 ^c	0.665	1955 ± 159 ^d	2.48 ± 0.11 ^l
	PoP	1435 ± 53 ^c	1012 ± 1 ^f	0.705	1720 ± 46 ^c	2.64 ± 0.05 ^l

^a Storage modulus (G'), loss modulus (G''), gel strength (A_g) and interaction factor (z) are expressed as mean ± standard deviation; $\tan \delta = C/G$. Mean values within the group having the same superscript letter in each column are not significantly different ($P > 0.05$). PoP — sodium polyphosphate; pH of model processed cheeses in Group II was adjusted by using an acid (HCl) or a base (NaOH). ^b n — sample could not be measured.

value which is very close to isoelectric point of caseins and thus attractions between proteins can lead to the increase of casein aggregation. Hence, fat is not effectively emulsified and continuous protein matrix is not formed in such processed cheese (Gupta, Karahadian, & Lindsay, 1984).

3.2.3. Assessment of pH — processed cheese with pH adjustment

It is well known that pH value affects viscoelastic properties of processed cheese (Lee & Klostermeyer, 2001). So, an experiment with pH adjustment of cheese was realized. Just as in a study by Shirashoji et al. (2006), pH was adjusted to 5.5–6.0 with respect to common manufacturing conditions. The wide range of pH of model samples prepared in Group II was narrowed to 5.55–5.62 (see Table 2).

3.2.4. Rheology — processed cheese with pH adjustment

Results for processed cheese in Group II obtained by rheological measurement and by application of Winter's critical gel theory are given in Table 3. Similar trends like in the previous group of cheese were observed even when pH (factor affecting consistency of processed cheese) was adjusted. Model samples with orthophosphate showed the least firmness, processed cheese with diphosphates

had higher values of storage and loss moduli and the most rigid products were prepared with triphosphate.

Processed cheese manufactured with disodium dihydrogen diphosphate (Na₂H₂P₂O₇) could be analysed after pH adjustment. The increase of pH (to ~ 5.6) resulted in the formation of a homogeneous three-dimensional network where water and fat separation as well as protein aggregation were not observed sensorially. As pH increased, protein molecules (carboxyl groups) became negatively charged and attractions between protein chains decreased. These changes resulted in increase of casein hydration and in formation of a more open reactive structure with higher water-binding capability and better emulsifying properties (Guinee et al., 2004; Marchesseau et al., 1997; Molins, 1991: p. 261). The usage of both diphosphates (Na₄P₂O₇ and Na₂H₂P₂O₇) caused the formation of model processed cheese with similar viscoelastic properties (see Table 3). Generally, both diphosphates demonstrated almost the same efficiency in the formation of the processed cheese structure.

3.3. Processed cheese containing the mixture of two sodium phosphates

3.3.1. Assessment of pH — processed cheese without pH adjustment The values of pH of samples manufactured with the addition of two phosphates (PoP: Na₂HPO₄ - Groups III, IV; PoP:Na₄P₂O₇ - Groups V, VI) are given in Table 4. The pH of processed cheese increased gradually with the decrease of polyphosphate content and with the rise of orthophosphate or diphosphate amount in the blend. Abdel-Hamid, El-Shabrawy, Awad, and Singh (2000) report the same trend of pH changes in processed cheese made with the

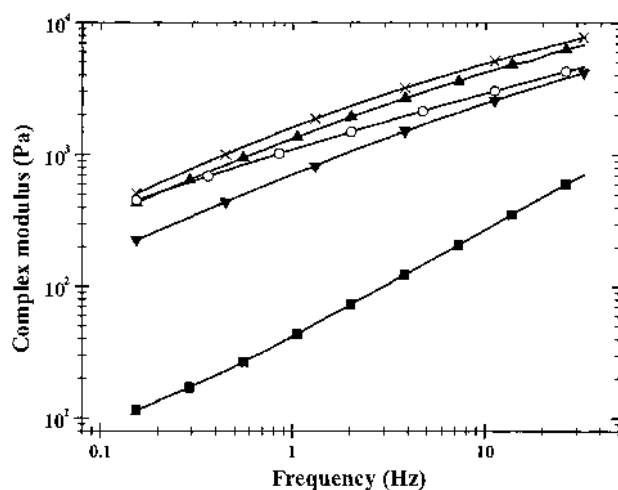


Fig. 1. Dependence of the complex modulus (G^*) on frequency (f) for products in Group I containing various sodium salts of phosphates - Na₃PO₄ (■), Na₂HPO₄ (▼), Na₄P₂O₇ (▲), Na₂H₂P₂O₇ (○), Na₅P₃O₁₀ (x), PoP(O).

Table 4

The values of pH of model processed cheese manufactured with mixtures of two sodium phosphates (PoP:Na₂HPO₄ - Groups III and IV; PoP:Na₄P₂O₇ - Groups V and VI)^a.

Ratio of sodium phosphates	Processed cheese group			
	PoP:Na ₂ HPO ₄		PoP:Na ₄ P ₂ O ₇	
	III	IV	V	VI
0:100	6.35 ± 0.01	5.78 ± 0.01	6.70 ± 0.01	5.78 ± 0.01
25:75	6.33 ± 0.01	5.69 ± 0.01	6.62 ± 0.01	5.72 ± 0.01
50:50	5.97 ± 0.01	5.80 ± 0.01	6.20 ± 0.01	5.49 ± 0.02
75:25	5.73 ± 0.01	5.79 ± 0.01	5.85 ± 0.01	5.28 ± 0.01
100:0	5.54 ± 0.01	5.74 ± 0.01	5.51 ± 0.01	5.43 ± 0.01

^a Values of pH are expressed as mean ± standard deviation. PoP — sodium polyphosphate. Values of pH of model processed cheeses in Groups IV and VI were adjusted by using an acid (HCl) or a base (NaOH).

mixture of emulsifying salts composed of sodium polyphosphate and sodium diphosphate ($\text{Na}_4\text{P}_2\text{O}_7$) in various ratios.

3.3.2. Rheology — processed cheese without pH adjustment

Results from rheological analysis of model cheeses in Groups III and V are given in Table 5. The growing polyphosphate amount in the blends of two phosphates caused firstly increase of elastic and loss moduli ($P < 0.05$) and decrease of loss tangent values. It reflects the increase of processed cheese elasticity. When the content of polyphosphate in the blend achieved a specific level (usually $\approx 50\%$ of polyphosphate in the blend), the values of both moduli started to drop and the loss tangent began to increase. The dependence of complex modulus on frequency applied to samples of processed cheese in Group V containing the mixture of PoP and $\text{Na}_4\text{P}_2\text{O}_7$ in five different ratios are presented in Fig. 2. It shows the initial increase of rigidity, which is followed by the decline of firmness caused by gradual increase of polyphosphate amount in the mixture of two phosphates.

The initial increase of firmness and elasticity of samples could be caused by the gradual hydrolysis of polyphosphate whose amount increased in the mixture subsequently. Linear condensed phosphates undergo hydrolysis to various extents during processing (melting) and storage of processed cheese (Guinee et al., 2004). Hydrolysis of polyphosphates proceeds rapidly to give triphosphates and diphosphates, and then, more slowly, to form monophosphates and it causes a significant hardening of processed cheese (Guinee et al., 2004; Kapoor & Metzger, 2008; Mulsow et al., 2007; Schär & Bosset, 2002). Products of hydrolysis, mainly triphosphates, possess high ability to aggregate casein, which leads to formation of a more rigid and elastic product (Guinee et al., 2004; Mizuno & Lucy, 2005). Hence, the more polyphosphates in the binary mixture, the higher number of triphosphates supporting the cross-linking in processed cheese. Once the polyphosphate amount in the mixture of two phosphates reaches a specific level, the quantity of unhydrolysed polyphosphates or their longer hydrolysed products can prevail over the triphosphate or diphosphate levels. These unhydrolysed polyphosphates or their longer hydrolysed products can bind calcium cations, which were

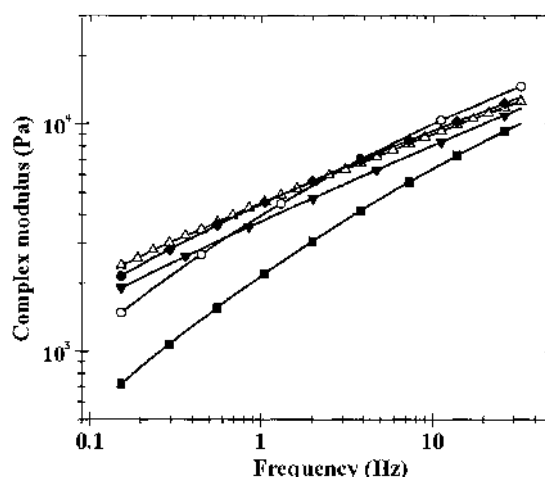


Fig. 2. Dependence of the complex modulus (G^*) on frequency (f) for products in Group V containing the mixture of two sodium salts of phosphates ($\text{PoP}:\text{Na}_4\text{P}_2\text{O}_7$) in five different ratios - 0:100 (■); 25:75 (○); 50:50 (△); 75:25 (●); 100:0 (▼).

previously sequestered by emulsifying salts too strongly. Ca^{2+} ions play important role in the formation of stable products. A part of these ions is released from emulsifying salts during cooling and they can participate in formation of three-dimensional network. The more calcium ions occur in melt, the more interactions in three-dimensional network of processed cheese can take place (Acharya & Mistry, 2007). However, polyphosphates exhibit very high ability to sequester calcium (Guinee et al., 2004; Kapoor & Metzger, 2008; Mulsow et al., 2007). These cations are bound very tightly to polyphosphates, which prevents them from cross-linking, i.e. a product with lower number of interactions is formed (Mulsow et al., 2007). This conclusion is supported by values of the interaction factor in Table 5, which are lower in mixtures with the prevalence of polyphosphates than in the mixtures containing the same ratio of polyphosphate and orthophosphate or diphosphate.

Table 5

The values of storage modulus, loss modulus, loss tangent, gel strength and interaction factor for the reference frequency 1 Hz in tested processed cheese with the mixture of sodium salts of phosphates in various ratios ($\text{PoP}:\text{Na}_2\text{HPO}_4$ — Groups III and IV; $\text{PoP}:\text{Na}_4\text{P}_2\text{O}_7$ — Groups V and VI)^a.

Group of cheese	Ratio of sodium phosphates	G' [Pa]	G'' [Pa]	$\tan \delta$ [-]	A_g [$\text{Pa} \cdot \text{s}^{1/2}$]	z
III	0:100	302 ± 62^a	404 ± 34^a	1.339	522 ± 61^a	1.84 ± 0.06^a
	25:75	2888 ± 316^b	2065 ± 117^b	0.715	3483 ± 324^b	2.81 ± 0.09^b
	50:50	2185 ± 55^c	1484 ± 14^c	0.679	2595 ± 57^c	2.79 ± 0.01^b
	75:25	1544 ± 105^d	1093 ± 71^c	0.708	1850 ± 126^d	2.67 ± 0.01^c
	100:0	860 ± 14^e	716 ± 21^c	0.832	1101 ± 24^e	2.39 ± 0.01^d
IV	0:100	61 ± 3^a	116 ± 10^a	1.900	126 ± 14^a	1.46 ± 0.06^a
	25:75	1560 ± 127^b	1105 ± 86^b	0.708	1871 ± 147^b	2.71 ± 0.02^b
	50:50	2228 ± 47^c	1507 ± 23^c	0.677	2639 ± 58^c	2.83 ± 0.01^c
	75:25	1394 ± 7^d	981 ± 6^d	0.704	1671 ± 10^d	2.63 ± 0.01^d
	100:0	809 ± 2^e	671 ± 9^e	0.829	1041 ± 3^e	2.31 ± 0.06^e
V	0:100	1553 ± 54^a	1571 ± 19^a	1.011	2231 ± 56^d	2.27 ± 0.01^a
	25:75	3153 ± 69^b	2563 ± 89^b	0.813	4019 ± 107^b	2.62 ± 0.01^b
	50:50	4061 ± 218^c	2084 ± 56^c	0.513	4474 ± 225^c	3.32 ± 0.05^c
	75:25	3932 ± 291^c	2254 ± 132^d	0.573	4424 ± 304^c	3.14 ± 0.07^d
	100:0	3302 ± 158^b	1889 ± 90^e	0.572	3737 ± 169^b	3.03 ± 0.03^e
VI	0:100	3072 ± 103^a	1741 ± 45^a	0.567	3432 ± 116^a	3.23 ± 0.01^a
	25:75	3553 ± 52^b	1940 ± 27^b	0.546	3981 ± 113^b	$3.27 \pm 0.06^{a,b}$
	50:50	3868 ± 127^c	2068 ± 76^c	0.535	4276 ± 160^c	3.31 ± 0.03^b
	75:25	4532 ± 281^d	2283 ± 79^d	0.504	4947 ± 286^d	3.46 ± 0.08^c
	100:0	2939 ± 170^a	1702 ± 73^a	0.579	3314 ± 186^a	3.10 ± 0.05^d

Values of pH of model processed cheeses in Group II were adjusted by using an acid (HCl) or a base (NaOH).

^a Storage modulus (G'), loss modulus (G''), gel strength (A_g) and interaction factor (z) are expressed as mean \pm standard deviation; $\tan \delta = G''/G'$. Mean values within the group having the same superscript letter in each column are not significantly different ($P > 0.05$). PoP — sodium polyphosphate.

3.3.3. Processed cheese with pH adjustment

The pH values of samples ranged from 5.69 to 5.80 in Group IV and from 5.49 to 5.78 in Group VI after pH adjustment (see Table 4).

Rheological properties of processed cheese in Groups IV and VI are given in Table 5. The dependence of viscoelastic properties of processed cheese on the sodium polyphosphate content in the mixture of two emulsifying salts showed a trend similar to the tendency revealed in the model samples without pH adjustment.

It can be assumed that pH is not the most important factor affecting viscoelastic properties of studied processed cheese. Hence, these properties are influenced also by other aspects, for example by the type of used emulsifying salt, the ratio of various phosphates in phosphate blend, the degree of phosphate hydrolysis, the sequestering ability of different phosphates, etc. Moreover, various factors can mutually influence each other. All these aspects should be considered while evaluating the processed cheese consistency (Guinee et al., 2004; Kapoor & Metzger, 2008; Mulsow et al., 2007).

4. Conclusion

The effect of different sodium phosphate emulsifying salts or their mixtures on pH and viscoelastic properties of processed cheese was investigated. Various phosphates affected the pH value of samples and their viscoelastic properties significantly. Optimal pH was found only in samples manufactured with sodium polyphosphate. Model processed cheese with disodium dihydrogen diphosphate had very low pH values. The pH of processed cheese increased due to the presence of various phosphates in the following order: PoP < Na₂HPo₄ < NasPsOio < Na₄P₂o₇ < Na₃Po₄. The softest processed cheeses were manufactured using orthophosphates; the application of polyphosphates caused the formation of firmer processed cheese and the samples with diphosphate and triphosphate proved to be the most rigid ones due to their highest ability to support gelation in processed cheese matrix. The initial increase of sample firmness and elasticity followed by their decrease was related to increasing amount of sodium polyphosphate in tested blends of two phosphates. Regarding viscoelastic properties of model samples with individual phosphates or their blends, similar trends were also demonstrated when pH of products was adjusted to values optimal for processed cheese. It can be concluded that this chemical parameter is not the only and the most important factor affecting processed cheese consistency. The consequent research should be aimed more complexly at interactions of caseins with phosphates in processed cheese matrix and on the phosphate hydrolysis and its influence on processed cheese quality.

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References

Abdel-Hamid, L. B., El-Shabrawy, S. A., Awad, R. A., & Singh, R. K. (2000). Chemical properties of processed ras cheese spreads as affected by emulsifying salt mixtures. *Journal of Food Processing and Preservation*, 24, 191–208.

Acharya, M. R., & Mistry, V. V. (2007). Influence of processing condition on cheddar cheese meltability. *Milchwissenschaft*, 62, 170–174.

Awad, R. A., Abdel-Hamid, L. B., El-Shabrawy, S. A., & Singh, R. K. (2002). Texture and microstructure of block type processed cheese with formulated emulsifying salt mixtures. *LWT-Food Science and Technology*, 35, 54–61.

Bennett, R. J., Trivedi, D., Hemar, Y., Reid, D. C. W., Illingworth, D., & Lee, S. K. (2006). The effect of starch addition on the rheological and microstructural properties of model processed cheese. *Australian Journal of Dairy Technology*, 61, 157–159.

Bowland, E. L., & Foegeding, E. A. (2001). Small strain oscillatory shear and microstructural analyses of a model processed cheese. *Journal of Dairy Science*, 84, 2372–2380.

Černíková, M., Buňka, F., Pavlínek, V., Březina, P., Hrabě, J., & Valášek, P. (2008). Effect of carrageenan type on viscoelastic properties of processed cheese. *Food Hydrocolloids*, 22, 1054–1061.

Dimitreli, G., & Thomareis, A. S. (2007). Texture evaluation of block-type processed cheese as a function of chemical composition and in relation to its apparent viscosity. *Journal of Food Engineering*, 79, 1364–1373.

Gabriele, D., de Cindio, B., & D'Antona, P. (2001). A weak gel model for foods. *Rheologica Acta*, 40, 120–127.

Guinee, T. P., Carić, M., & Kaláb, M. (2004). Pasteurized processed cheese and substitute/imitation cheese products. In P. F. Fox, P. L. H. McSweeney, & T. P. Cogan (Eds.), *Cheese: Chemistry, physics and microbiology. Major cheese groups, Vol. 2* (pp. 349–394). London, New York: Elsevier Applied Science.

Gunasekaran, S., & Ak, M. M. (2000). Oscillatory shear testing of foods—selected applications. *Trends in Food Science & Technology*, 11, 115–127.

Gupta, S. K., Karahadian, C., & Lindsay, R. C. (1984). Effect of emulsifier salts on textural and flavor properties of processed cheeses. *Journal of Dairy Science*, 67, 764–778.

Gustaw, W., & Miéko, S. (2007). The effect of polysaccharides and sodium chloride on physical properties of processed cheese analogs containing whey proteins. *Milchwissenschaft*, 62, 59–62.

ISO Standard No. 5534. (2004). *Cheese and processed cheese — Determination of the total solids content (reference method)*. Geneva: International Organization for Standardization.

ISO Standard No. 3433. (2008). *Cheese — Determination of fat content — Van Gulik method*. Geneva: International Organization for Standardization.

Kapoor, R., & Metzger, L. E. (2008). Process cheese: scientific and technological aspects — a review. *Comprehensive Reviews in Food Science and Food Safety*, 7, 194–214.

Lee, S. K., Anema, S., & Klostermeyer, H. (2004). The influence of moisture content on the rheological properties of processed cheese spreads. *International Journal of Food Science and Technology*, 39, 763–771.

Lee, S. K., & Klostermeyer, H. (2001). The effect of pH on the rheological properties of reduced-fat model processed cheese spreads. *LWT-Food Science and Technology*, 34, 288–292.

Lu, Y., Shirashoji, N., & Lucey, J. A. (2007). Rheological, textural and melting properties of commercial samples of some of the different types of pasteurized processed cheese. *International Journal of Dairy Technology*, 60, 74–80.

Lucey, J. A., Johnson, M. E., & Horne, D. S. (2003). Invited review: perspectives on the basis of the rheology and texture properties of cheese. *Journal of Dairy Science*, 86, 2725–2743.

Marchesseau, S., Gastaldi, E., Lagaude, A., & Cuq, J. L. (1997). Influence of pH on protein interactions and microstructure of process cheese. *Journal of Dairy Science*, 80, 1483–1489.

Martinez-Ruvalcaba, A., Chornet, E., & Rodrigue, D. (2007). Viscoelastic properties of dispersed chitosan/xanthan hydrogels. *Carbohydrate Polymers*, 67, 586–595.

Mizuno, R., & Lucey, J. A. (2005). Effects of emulsifying salts on the turbidity and calcium–phosphate–protein interactions in casein micelles. *Journal of Dairy Science*, 88, 3070–3078.

Molins, R. A. (1991). *Phosphates in food*. Boca Raton: CRC Press.

Mulsow, B. B., Jaros, D., & Rohm, H. (2007). Processed cheese and cheese analogues. In A. Y. Tamime (Ed.), *Structure of dairy products* (1st ed.). (pp. 210–235) Oxford: Blackwell Publishing Ltd.

Piska, I., & Štětina, J. (2004). Influence of cheese ripening and rate of cooling of the processed cheese mixture on rheological properties of processed cheese. *Journal of Food Engineering*, 61, 551–555.

Rayan, A. A., Kaláb, M., & Ernstrom, C. A. (1980). Microstructure and rheology of process cheese. *Scanning Electron Microscopy*, 3, 635–644.

Schär, W., & Bosset, J. O. (2002). Chemical and physicochemical changes in processed cheese and ready-made fondue during storage. A review. *LWT-Food Science and Technology*, 35, 15–20.

Shirashoji, N., Jaeggi, J. J., & Lucey, J. A. (2006). Effect of trisodium citrate concentration and cooking time on the physicochemical properties of pasteurized process cheese. *Journal of Dairy Science*, 89, 15–28.

Winter, H. H., & Chambon, F. (1986). Analysis of linear viscoelasticity of a cross-linking polymer at the gel point. *Journal of Rheology*, 30, 367–382.