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TEXTURING CAPACITY OF VARIOUS STARCHES IN WHEY PROTEINS / POLYSACCHARIDES BASED MILK DESSERTS

Abstract

Experimental milk desserts were composed of reconstituted skimmed milk powder and whey protein isolate as a source of proteins, normal and waxy maize starch, potato starch and hydroxy propyl distarch phosphate (HPDP) as thickeners and ι-carrageenan (ι-C) as gelling agent. The protein and starch concentration varied between 0 and 6%, sugar between 0 and 20% and that of ι-C between 0 and 0.4%. The desserts were heat treated at 100, 110 or 120°C for 10, 20 or 30 minutes. The firmness of the desserts after 24 hours of storage at 20°C, was determined by a cone penetrometric method and expressed as stress in Pa.

The logarithm of the stress was a linear function of protein and starch content and of the logarithm of the ι-C concentration (g/100 g). To multiply the firmness of the experimental desserts by a factor of ten, it was necessary to increase the whey protein concentration by 11 to 15 g/100 g depending on the type of starch used. The same effect could be obtained with 5 to 9 g/100 g of starch. When the ι-C concentration increased tenfold the stress level was multiplied by a factor of 2.6 to 4. The desserts' firmness also depended on the heating time and temperature, even if this effect was small.

Introduction

Milk desserts are important industrial food products. A typical milk dessert is composed of 84 to 89% of liquid milk, 6.5 to 10% of sugar, 2 to 3.5% of starch 0.15 to 0.25% of carrageenan and 0 to 2% of chocolate in powder [7, 21]. Vanillin, carotenoids or xanthophylls are also added in small quantities <0.02% to improve the taste and modify the colour [21]. The gel-like texture of milk desserts is obtained by using starches and their derivatives as thickeners and some other polysaccharides as gelling agents. An important quality factor of milk desserts is their in-mouth perceived thickness. For many gel like products, including milk desserts, the relationship between the in-mouth perceived thickness and the objective viscosity follows a power law type

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equation [20, 29] i.e. the logarithm of the viscosity established by the sensory analysis is a linear function of the logarithm of the physically measured viscosity (Fig. 1).

For the starch pastes and gels, the viscosity and swelling capacity (Fig. 2 and 3) depend on the temperature, heating time and the shear rate [3].

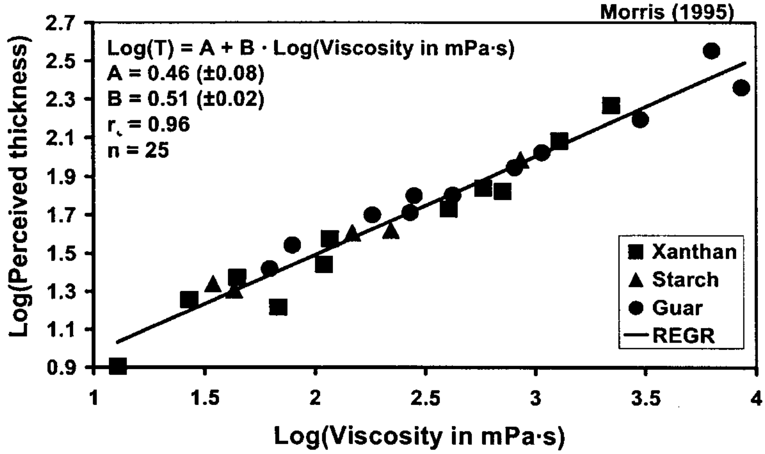

Fig. 1. Relationship between the logarithm of the in-mouth perceived thickness (T) and the logarithm of the apparent viscosity measured at shear rate = 50 s^{-1}, for the gels prepared from starch, xanthan and guar gums (based on the results published by Morris, 1995).

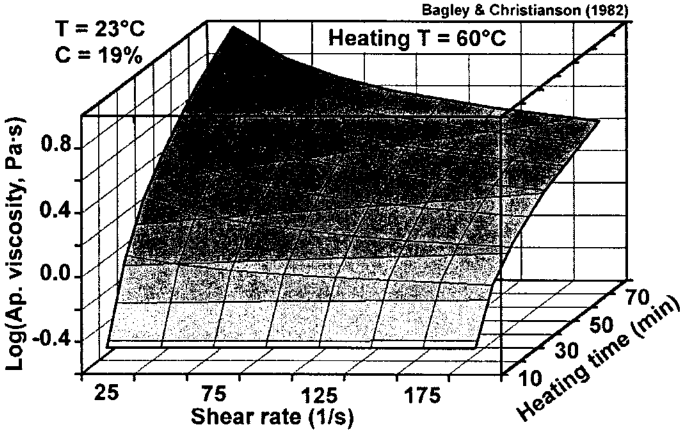

Fig. 2. Logarithm of the apparent viscosity of 19% wheat starch pastes at 23°C, as a function of the shear rate and the cooking time at 60°C (based on the results of Bagley and Christianson, 1982).

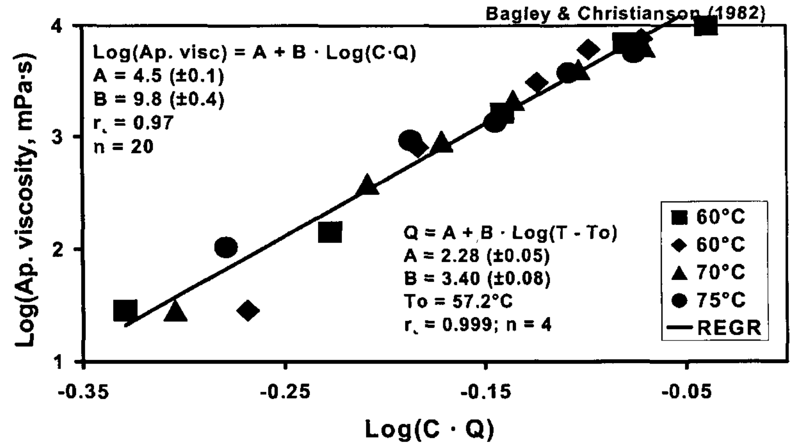

Fig. 3. Logarithm of the apparent viscosity of the wheat starch pastes at 60°C, as a function of the logarithm of the starch concentration (C in g/g) multiplied by the swelling capacity (Q in g/g), with Q being a function of the heating temperature (T in °C), for a constatnt heating time = 75 min (based on the results of Bagley and Christianson, 1982).

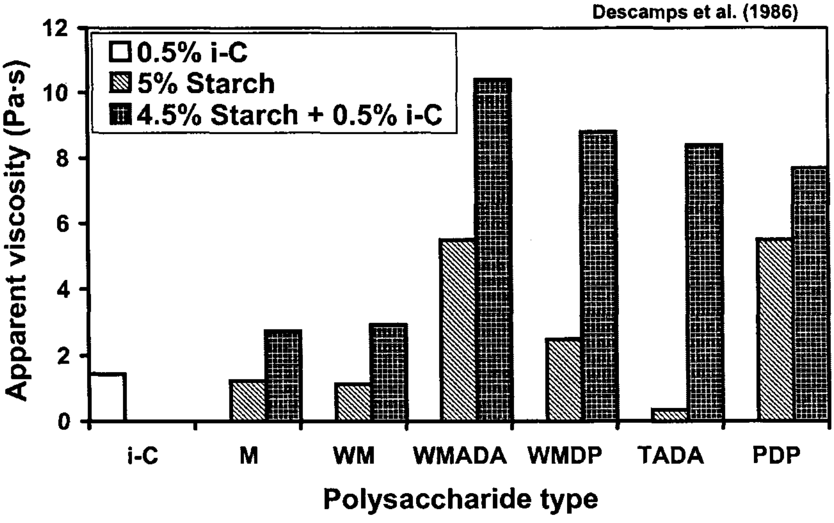

Fig. 4. Apparent viscosity at 20°C of gels prepared from different starches (4.5%) and 0.5% of i-carrageenan (ι-C). Starch type: M = maize, WM = waxy maize, WMADA = waxy maize acetylated distarch adipate, WMDP = waxy maize distarch phosphate, TADA = tapioca acetylated distarch adipate, PDP = potato distarch phosphate (based on the results of Descamps et al., 1986).

Due to the interactions between the starches and other polysaccharides, the observed viscosity of the mixtures is much higher (Fig. 4) than that which could be anticipated for non-interacting mixtures.

Owing to their high nutritional quality and gelling properties, whey proteins can be used as gelling agents in many food products including milk desserts [1, 2, 8, 9, 13-15, 17-19, 23, 31, 32]. The gel firmness of the whey proteins and starch gels increases exponentially (Fig. 5) with the dry matter content, i.e. the logarithm of the elastic modulus is a linear function of the protein or starch concentration [1].

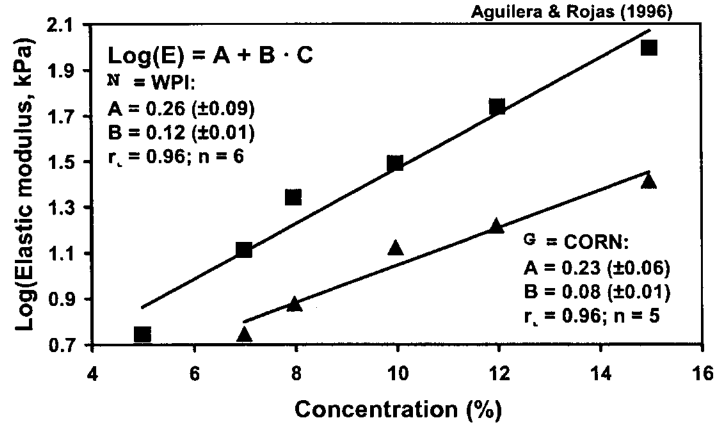

Fig. 5. Logarithm of the elastic modulus (E) of gels prepared by heating for 30 min at 85°C and cooling, as a function of the whey protein isolate (N) and corn starch (G) concentration (in % w/w) (based on the results of Aguilera and Rojas (1996).

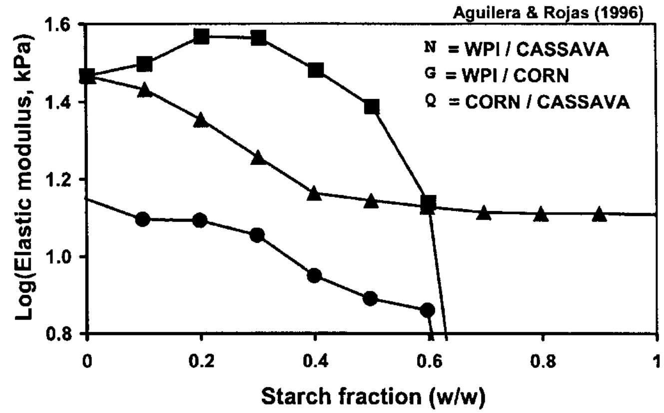

Fig. 6. Logarithm of the elastic modulus of mixed gels, prepared by heating for 30 min at 85°C and cooling, as a function of the starch fraction in the mixtures of: (N) = whey protein isolate (WPI) / cassava starch (CS), (G) = WPI / corn starch (CORN) and (Q) = CORN / CS. Total solids in all gels is 10% and the pH is 5.75 (based on the results of Aguilera and Rojas, 1996).

The firmness of mixed gels also depends, in some cases, on the protein to starch ratio (Fig. 6). Cassava starch pastes do not form gels below a 16% concentration, but when 2–3% cassava starch is mixed with 7–8% whey protein isolate, the resulting gels are stronger than either the pure protein or pure starch gels. No such interaction is observed for the corn starch mixed with whey proteins or with cassava starch.

Milk proteins interact and are precipitated by certain polysaccharides [6, 10, 11, 24, 30, 31]. Because of the interactions, the viscosity of milk protein / polysaccharide gels is multiplied by a factor of 2 to 10 (Fig. 7) in comparison with pure polysaccharides in water gels [26]. The viscosity multiplication factor depends not only on the polysaccharide and protein type but also on the heat treatment applied to the mixture. It is much higher for strongly acidic carrageenans than for neutral guar or slightly acidic xanthan gums.

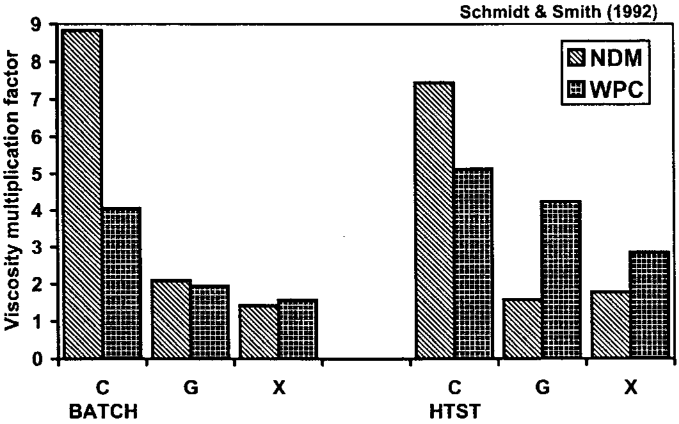

Fig. 7. Viscosity multiplication factor for the gels containing 0.1% C = carrageenan, G = guar, or X = xanthan gums and 11% (w/w) of (NDM) = non fat dry milk or (WPC) = whey protein concentrate, heated at 69°C for 30 min (BATCH) or at 80°C for 25 s (HTST) in comparison with the gels composed of 0.1% of C, G or X gums in water. Viscosity was measured at 4°C and at the shear rate 250 s^{-1} (based on the results of Schmidt and Smith, 1992).

The literature data suggest that the gel strength of milk desserts depends on several parameters: protein and starch type and their concentration, the presence of other polysaccharides and the heat treatment applied. Taking into account the existing power law type relationship between the sensory and the physical properties of milk desserts, we have chosen to use the logarithm of the gel stress measured by a penetrometric method as an indicator of the gel strength and of the texturing capacity of native and modified starches in the presence of ι-carrageenan and whey proteins, in relation to the heat treatment applied during the cooking of the desserts.

Materials and methods

The following raw materials were used in this study: normal and waxy maize starch, potato starch, hydroxy propyl waxy distarch phosphate (HPDP) from Roquette Frères, (Lestrem, France), ι-carrageenan from Sanofi Bio-Industries, (Carentan, France), wheat flour (WF) type 55%, sugar and chocolate powder (Van Houten) from the local supermarket, whey protein isolate 85% proteins in dry matter from Eurial, (Herbignac, France), low heat skimmed milk powder from NIZO, (Netherlands). Three samples of gel type market milk desserts, covering the large scale of gel firmness: Danette and Dany (Danone, France) and Crème Brulée (Triballat, France).

Two hundred grams of water suspensions containing: 0 to 6% (w/w) whey proteins, 0 to 4% milk proteins (low heat skimmed milk powder), 2 to 6% starch, modified starch or wheat flour, 0 to 0.3% ι-carrageenan and 0 to 20% sugar, were heated for 10, 20 or 30 minutes at 100, 110 or 120°C in a small (250 ml) reactor vessel with magnetic stirring. The pastes were then cooled to 90°C, poured into small (25 ml), screw sealed, plastic boxes and left overnight in a 20°C set water bath.

The texture of the desserts obtained was measured at 20°C, with a constant speed (2 mm/s), cone (20 degrees) penetrometric method [16] with a DY-30 (Adamel Lhomargy, France) traction - compression machine. The penetration depth was 20 mm and the full scale load of the force transducer was 1 N. The results of penetrometric tests are expressed as stress in Pa. The gel firmness of a part of experimental and market milk desserts was also measured by a dynamic rheological method with an AR1000 type rheometer (TA Instruments, England). A General Linear Models [25] method was used for the statistical analysis of the results.

Results and discussion

For market and experimental milk desserts gels, the logarithm of the stress level evaluated by the penetrometric method is linearly related to the logarithm of the complex modulus measured by the dynamic rheometric method (Fig. 8). It means that the simple to use, rapid and inexpensive penetrometric method gives results comparable to those obtained by a non-destructive, but time consuming rheometric method, and requiring expensive equipment. The gel firmness of milk desserts was evaluated by the viscometric method [3, 7, 14, 15, 17, 21, 26, 27, 31], by the compression method [1, 17] or by the rheometric method [12, 18, 22]. For rapid evaluation of the gel firmness of the large quantities of dessert samples, the penetrometric method could be a good choice.

For over 300 experimental desserts gels prepared and for all starches analysed in this work, the logarithm of the stress level was increasing linearly with the concentration of whey proteins and starch and with the logarithm of ι-carrageenan content (Fig. 9, 10 and 11):

$$\mathrm{Log(S)} = \mathrm{A} + \mathrm{WP} / \mathrm{B} + \mathrm{St} / \mathrm{C} + \mathrm{D \cdot Log(\iota\text{-}C)} \qquad (1)$$

where: S = stress in Pa measured by the penetrometric method, A = intercept or the hypothetical value of the logarithm of the stress for WP = 0, St = 0 and ι-C = 1. WP, St and ι-C are respectively the whey protein, starch and ι-carrageenan concentration in g/100g of solution. B and C are the coefficients indicating respectively the increase in protein and starch concentration (in g/100g) provoking ten fold increase in the stress. D is the increase in the log(S) for tenfold increase in ι-C concentration.

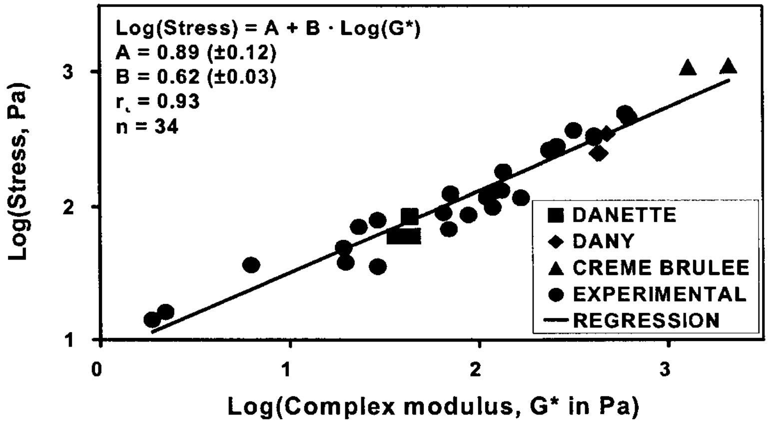

Fig. 8. Relationship between the logarithm of the stress evaluated by the penetrometric method and the logarithm of the complex modulus (G*) measured by the dynamic rheometric method.

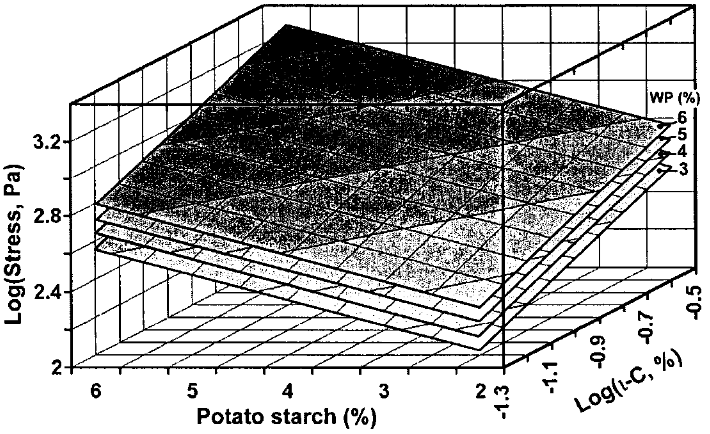

Fig. 9. Logarithm of the stress as a function of the potato starch, whey proteins (WP) and ι-carrageenan (i-C) concentration (in % w/w).

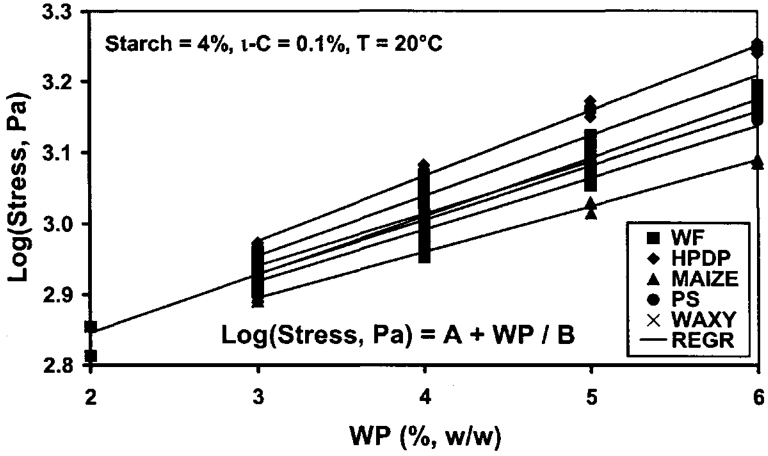

Fig. 10. Logarithm of the desserts' gels stress as a function of the whey proteins (WP) concentration for different starches: WF = wheat flour, HPDP = hydroxy propyl distarch phosphate, MAIZE = normal maize starch, PS = potato starch, WAXY = waxy maize starch, in presence of 0.1% of ι-carrageenan.

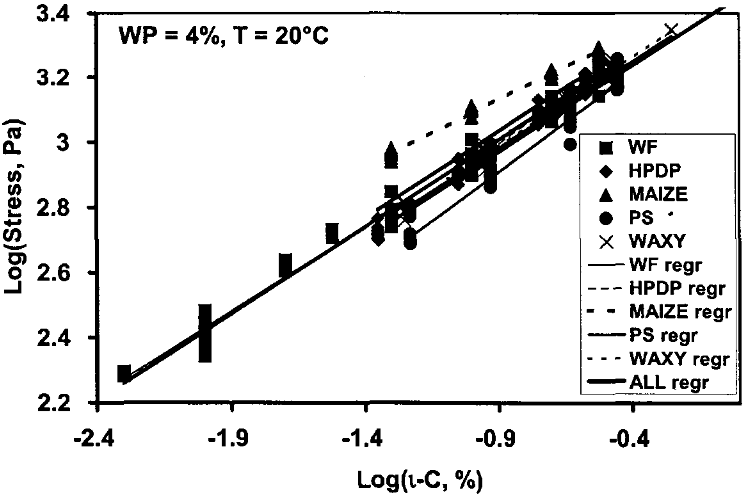

Fig. 11. Logarithm of the desserts' gels stress as a function of the logarithm of ι-carrageenan concentration for different starches: WF = wheat flour, HPDP = hydroxy propyl distarch phosphate, MAIZE = normal maize starch, PS = potato starch, WAXY = waxy maize starch, in presence of 4% whey proteins.

The coefficient A depends also on the starch, whey proteins and ι-carrageenan concentration. The value of coefficient B varied between 11 and 15 g/100 g for different starches (Tab. 1). Some of the differences were statistically significant. The highest B level (>15) was found for the maize starch, which gelatinises at a slightly higher temperature than whey proteins and on cooling, forms its own amylose and amylopectin gel structures independent of protein. This structure probably disturbs the weak protein gel that has already formed at high temperatures (>70°C) [1, 2, 14]. A similar effect was also found by Muhrbeck and Elliasson [22] for bovine serum albumin / starch gels. The lowest B value (<11) was found for the most heat resistant, and the most hydrophobic hydroxy propyl waxy distarch phosphate. This slightly acidic starch was, more hydrophobic than the others analysed and may interact with whey proteins as do other acidic polysaccharides such as carrageenans and CM-cellulose [4, 5, 10, 11, 24, 26, 28].

Table 1

Coefficients B, C and D from the equation (1) for different starches. SD = standard deviation.

Starch type	B	±SD	C	±SD	D	±SD	n
Wheat flour	12,20	0,45	5,40	0,81	0,52	0,03	76,00
HPDP	10,90	0,12	5,40	0,63	0,59	0,04	52,00
Maize	15,40	0,24	5,90	0,12	0,41	0,03	27,00
Potato	13,20	0,22	8,00	0,42	0,65	0,02	136,00
Waxy	13,60	0,55	8,90	0,88	0,55	0,02	42,00

Taking into account the coefficient C from the equation (1), two groups of starches could be distinguished (Tab. 1): one including hydroxy propyl distarch phosphate, maize starch and wheat flour which needed on average 5 to 6 % and the other group which includes potato and waxy maize starches, which needed 7 to 9% starch addition in order to multiply by ten the desserts' firmness expressed in stress units. Whey protein addition required to achieve the same effect was on average 13%. From the results of Aguilera and Rojas [1], presented in fig. 5 the coefficients B and C are 8.3% and 12.5%. respectively.

The value of the coefficient D varied between 0.4 and 0.6. Its lowest level (0.41±0.034) was observed for the maize starch gels. It was the only one of the starches analysed to form firm gels.

By using the parameters A to D from the equations (1), it is possible to calculate the stress level for a given dessert composition. Figure 12 shows the results of such a comparison for the milk desserts containing potato starch as thickeners and ι-carrageenan as gelling agent. The agreement between the experimental and calculated results is quite close for all the starches analysed in this work. Other models including starch - protein, starch - ι-C, protein - ι-C and starch - protein - ι-C interaction coefficients could be applied to describe the texture dependence on the gel composition. We tried several of these more complicated models, but the results were not better than for the simple one described by the equation (1).

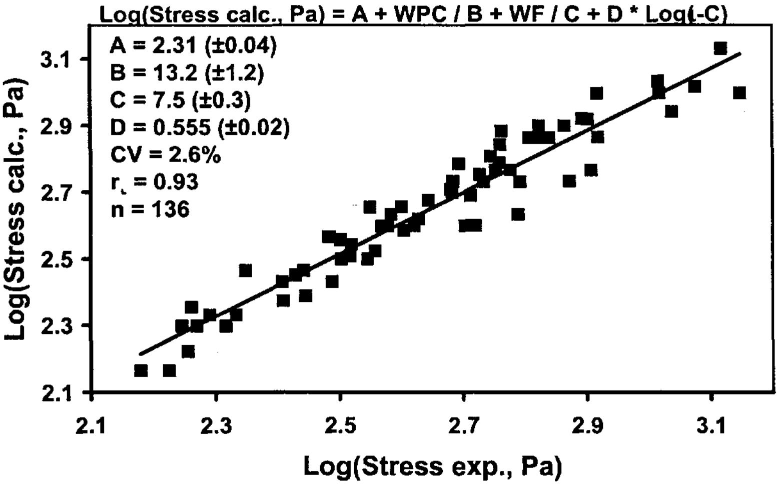

Fig. 12. Relationship between the logarithm of the stress calculated by the equation (1) and the experimental values, for the desserts gels containing whey proteins (2 - 6%), potato starch (2 - 6%), ι-carrageenan (0–0.3%), sugar 10% and chocolate powder 3%.

Cooking time and temperature are important technological parameters, influencing the firmness of pastes and gels of pure starch [3, 4, 15], of the mixtures of starch with proteins [14] and of other polysaccharides with proteins [26]. In this work we analysed the effect of the heating time (10–30 min) and temperature (100–130°C) on the desserts' gel firmness after 24 hours of storage at 20°C, for the desserts composed of whey proteins (0 or 4%), milk proteins (4 or 0%), wheat flour (4%), milk fat (3%), chocolate powder (3%), sugar (10%) and ι-carrageenan (0.1%). We used the same type of mathematical model as given in the equation (1) to evaluate the effect of the heating temperature (T in °C) and of the heating time (HT in minutes):

$$\mathrm{Log}(S) = I + T / E + HT / F \qquad (2)$$

where: I = the point of interception or the hypothetical value of the stress (S) logarithm for T = 0 and HT = 0, E = the coefficient indicating the temperature increase provoking ten fold stress increase (if +) or decrease (if -), F = the coefficient indicating the heating time increase provoking ten fold stress increase (if +) or decrease (if -).

The results obtained show that the effect of the heating time and temperature are relatively small (fig. 13 and 14), and much smaller than those observed for the pure starch pastes and gels [3, 4, 15] and for the milk proteins/starch mixtures [14]. This is probably because of multiple interactions between proteins, polysaccharides, fat and minerals which impair the formation of the three dimensional networks of whey proteins, amylose, amylopectin and ι-carrageenan.

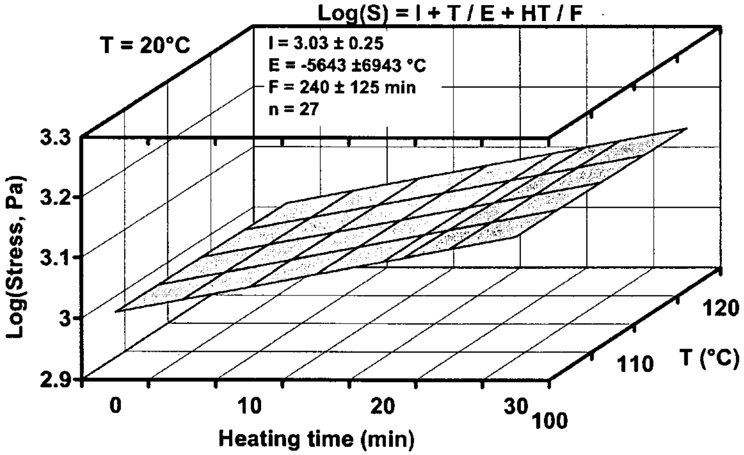

Fig. 13: Effect of the heating time (HT) and temperature (T°C) on the gel firmness at 20°C, of the dessert composed of the whey proteins (4%), wheat flour 4%, milk fat 3%, chocolate 3%, sugar 10% and ι-carrageenan 0.1%.

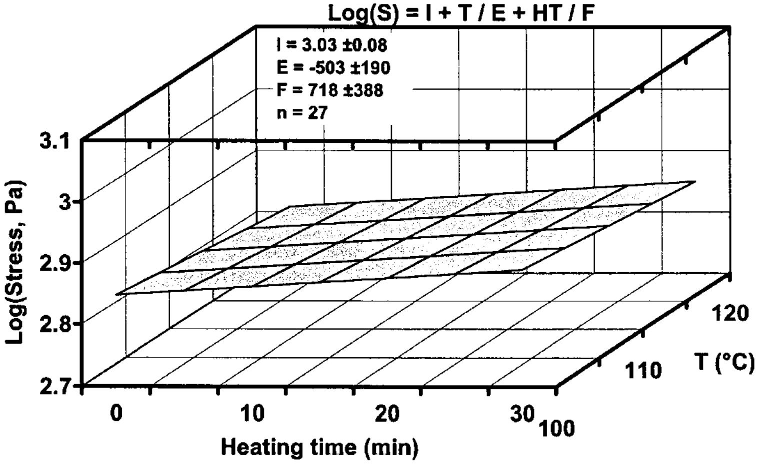

Fig. 14: Effect of the heating temperature (T°C) and the heating time on the gel firmness at 20°C, of the dessert composed of the milk proteins (4%), wheat flour 4%, milk fat 3%, chocolate 3%, sugar 10% and ι-carrageenan 0.1%.

Conclusions

1. The penetrometric method appears to be a useful tool for a rapid evaluation of the desserts' gel firmness.
2. Gel firmness expressed as the logarithm of the stress is a linear function of the whey proteins and starch and of the logarithm of the ι-carrageenan concentrations.
3. The effect of the cooking times within the analysed range (10–30 min) and temperatures (100–130°C) on the gel firmness was small.

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WŁASNOŚCI ŻELUJĄCE RÓŻNYCH SKROBI W DESERACH Z BIAŁEK SERWATKOWYCH I POLISACHARYDÓW

Streszczenie

Doświadczalne desery mleczne składały się z odtłuszczonego mleka w proszku i izolatu białek serwatkowych jako źródła białka, skrobi jako substancji zagęszczającej (normalnej i woskowej skrobi kukurydzianej, skrobi ziemniaczanej, hydroksypropylowanego fosforanu dwuskrobiowego) i ι-karagenu jako substancji żelującej. Stężenie białek i skrobi zmieniano w zakresie od 0 do 6%, cukru od 0 do 20%, i-karagenu od 0 do 0.4%. Desery były ogrzewane przy ciągłym mieszaniu w temperaturze 100, 110 lub 120°C w ciągu 10, 20 lub 30 min. Konsystencję deserów oznaczano metodą penetrometryczną po 24 godz. przechowywaniu w temperaturze 20°C.

Logarytm naprężeń ścinających był liniową funkcją stężenia białka i skrobi oraz logarytmu stężenia ι-karagenu. Aby naprężenia ścinające wzrosły 10 krotnie, stężenie białek serwatkowych powinno wzro-

snąć o 11–15% (g/100 g) zależnie od rodzaju stosowanej skrobi. Identyczny efekt uzyskuje się przy dodatku 5–9% skrobi. Kiedy stężenie ι-karagenu wzrastało 10 krotnie, naprężenia ścinające zwiększały się 2.6 do 4 krotnie.

Konsystencja deserów zależała też od czasu i temperatury ogrzewania, ale wpływ ten był stosunkowo mały. ◆