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Effect of copper and iron fortifications on rheological properties of water-in-oil spreads containing κ -carrageenan

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Work was undertaken to investigate the effect of copper and Iron fortification (up to 15 mM) on the rheology and firmness of water-in-oil spreads (60 % fat) produced using 0.25 % κ -carrageenan. The apparent viscosity of the aqueous phase (10.9 mPa s) was significantly reduced by fortification with 15mM copper (4 mPa s) or iron (3.2 mPa s) at 60 °C. However, inclusion of minerals resulted in gelation of the aqueous phase at 6°C and increased the melting temperature on reheating. Copper addition at 7.5mM levels formed the strongest gel (storage modulus of 7.6 kPa) and increased the melting temperature of the aqueous phase from 21°C (control) to 49°C. At the higher levels of addition (7.5-15 mM), the minerals impaired the firmness at 6°C and rheology of the spreads on heating with copper inclusion resulting in the greatest reductions. The rheological and textural effects observed on fortification were attributed to the pro-oxidant effects of the metallic cations on the oil-phase of the spreads.

Zum Einfluss eines Zusatzes von Kupfer und Eisen auf die rheologischen Eigenschaften von Wasser in Öl-Brottaufstrichen mit κ -Karrageenan

Die Studie wurde durchgeführt, um den Einfluss eines Zusatzes von Kupfer und Eisen (bis zu 15mM) auf die Rheologie und die Festigkeit von Wasser in Öl-Brottaufstrichen mit 80% Fett und bei Verwendung von 0,25% κ -Karrageenan zu untersuchen. Die apparente Viskosität der wässrigen Phase (10,9 mPa s) wurde durch die Zusätze von 15 mM Kupfer oder Eisen signifikant reduziert (4 mPa s bzw. 3,2 mPa s bei 60°C). Die Einbeziehung der Mineralstoffe führte jedoch zu einer Gerinnung der wässrigen Phase bei 6°C und erhöhte die Schmelztemperatur bei der Erhitzung. Ein Kupferzusatz von 7,5 mM bildete das festeste Gel (Lagerungsmodulus von 7,5 kPa) und erhöhte die Schmelztemperatur der wässrigen Phase von 21°C (Kontrolle) auf 49°C. Bei höheren Zusatzkonzentrationen (7,5-15 mM) beeinträchtigten die Mineralien die Gelfestigkeit bei 6°C sowie die Rheologie der Aufstriche bei der Erhitzung, wobei der Kupferzusatz zu den deutlichsten Reduktionen führte. Die bei den Zusätzen beobachteten rheologischen und Textur bezogenen Effekte werden auf den pro-oxidativen Effekt der Metallkationen in der Ölphase der Aufstriche zurückgeführt.

42 Spreads, water-in-oil (copper / iron fortification, rheology)

42 Brotaufstrich, Wasser in Öl (Kupfer-/Eisenzusatz, Rheologie)

1. Introduction

In recent decades, due to economic and health considerations, spreads have been produced with reduced levels of fat while attempting to retain the texture and flavour of butter (1-4). Properties required of reduced-fat spreads (water-in-oil emulsions) include having a relatively firm consistency and a plastic rheology so that the product does not become much thinner during spreading (2). A number of different biopolymers such as protein (from egg, milk, gelatin), intact and modified starch, and/or polysaccharides (e.g. carrageenan, alginate, pectin) are used to provide structure to the aqueous phase of these food systems (5).

Deficiencies in micronutrient such as iron and copper afflict an appreciable fraction of the worlds population

(6). In an attempt to address this problem, fortification of spreads has been proposed and attempted (7). Carrageenans such as κ -carrageenan are high-molecular weight linear sulphated polysaccharides extracted from red seaweed (8). κ -carrageenan exists as random coils at high temperatures, a coil-to-helix transition occurs on cooling below a certain temperature, which is dependant on the ionic environment [8]. Cations such as Ca^{2+} contribute to the formation of electrostatic bonds between the negatively charged double-helices, thereby causing aggregation and gelation (9). Previous work was undertaken in an attempt to utilise the properties of κ -carrageenan to contribute to structure as well as electrostatically bind added zinc (10). The resultant spreads had acceptable texture and microstructure although the

melting properties on heating were impaired. Studies on the effect of minerals on the oxidative stability of reduced-fat spreads revealed that copper and iron addition was detrimental by promoting and accelerating lipid oxidation (11).

The objective of this study was to investigate the effects of copper and iron fortification on the rheology of the aqueous phase as well as the rheology and texture of the final reduced fat spread.

2. Materials and methods

2.1 Production of water-in-oil spreads

A ten kg water-in-oil spread (60% fat) was manufactured with the following commercial-type formulation: an oil phase containing 5860 g vegetable oil blend (code BDG:WPGLTC, Cargill, France) and 60 g mono-glyceride emulsifier (Paalgaard 0291, Grinstead A/S, Braband, Denmark); and an aqueous phase containing 5975 g water and 25 g κ -carrageenan (Deltagel P379; Kerry Biosciences, Carragiline, Co. Cork, Ireland). The κ -carrageenan contained 5.8% potassium, 0.4% sodium, 0.4% calcium and 0.4% magnesium. A series of fortified water-in-oil spreads were also prepared by including copper or iron at levels of 0.3–15 mM (ion concentration in final product). The copper (CuCl_2) and iron (FeCl_3) were reagent grade and obtained from BDH Chemicals (Poole, England). The levels of addition were such as to cover 0–100 % of the Recommend Daily Allowance (12, 13). The pilot scale processing was carried out using a Perfector scraped surface cooler (Gerstenberg and Agger, Copenhagen, Denmark) with a 25-litre jacketed tank connected to a 3-piston pump which fed the Perfector unit.

2.2 Dynamic oscillatory rheology of the aqueous phase

A controlled stress Bohlin CVO rheometer (Bohlin, Cirencester, UK) was used in the dynamic mode for small-scale deformation measurements. A concentric cylinder (C25) measurement system was used. The diameter of the bob was 25 mm and the internal diameter of the cup was 27.5 mm. Measurements were taken at a frequency of 1 Hz and a strain of 0.5%. Samples were loaded at 60°C before n-Tetradecane (Sigma Chemical Co., St. Louis, MO, USA) was added to the surface of the rheometer cup to avoid evaporation. The change in storage modulus (G') was measured during cooling from 60 to 6°C at a rate of 1°C/min followed immediately by re-heating to 60°C at the same rate. The melting temperature was taken as the temperatures at which $G' = 1$ Pa on reheating.

2.3 Dynamic oscillatory rheology of the water-in-oil spreads

The Bohlin CVO rheometer was used in the dynamic mode with a 25mm diameter serrated-plate geometry. Measurements were taken at a frequency of 1 Hz and a strain of 0.5%. Samples were loaded at 6°C before n-Tetradecane was added to the surface of the sample. The change in G' and the T_m were measured during heating from 6 to 60°C at a rate of 1°C/min.

2.4 Viscosity measurements

Viscosity was measured using the concentric cylinder (C25) measurement system as above. All measurements were taken at 60°C. Sufficient stress was applied to the sample to attain a pre-shear rate of 200 s^{-1} , which was applied for 30 s. A shear rate sweep from 10 to 200 s^{-1} was applied over 4 min. The apparent viscosity (mPa s) was determined at a shear rate of 100 s^{-1} .

The spreading behaviour was characterised rheologically by compression testing using a TA-XT2 Texture Analyser from Stable Microsystems Ltd. (Godalming, UK). Cylindrical samples, measuring 26 mm in length and 26 mm in diameter, were compressed to 10% of their initial height (i.e. 90% compression) at 0.8mm/s between the flat parallel plates of the instrument (6°C).

2.5 Textural analysis of water-in-oil spreads

The spreading behaviour was characterised rheologically by compression testing using a TA-XT2 Texture Analyser from Stable Microsystems Ltd. (Godalming, UK). Cylindrical samples, measuring 26 mm in length and 26 mm in diameter, were compressed to 10% of their initial height (i.e. 90% compression) at 0.8mm/s between the flat parallel plates of the instrument (6°C).

2.6 Statistical analysis

The water-in-oil spreads were manufactured in triplicate. All tests were replicated 4 times. Dynamic rheological analysis and viscosity determination of the aqueous phase was undertaken on the day of manufacture of spreads. Dynamic rheological analysis and textural analysis of the spreads was undertaken one day after spread manufacture. Analysis of variance (ANOVA) was carried out using SigmaStat (version 3.0; Jandel Scientific, Corte Madera, CA, USA). Student-Newman-Keuls pairwise-comparison test was used to determine differences between treatment means. Treatment means were considered significantly different at $P \leq 0.05$.

3. Results and discussion

The effect of copper and iron on the viscosity, gelation properties and thermoreversibility of the aqueous phase of the water-in-oil spreads was examined to give information on the behaviour of the aqueous phase during manufacture and cooling of the water-in-oil spreads.

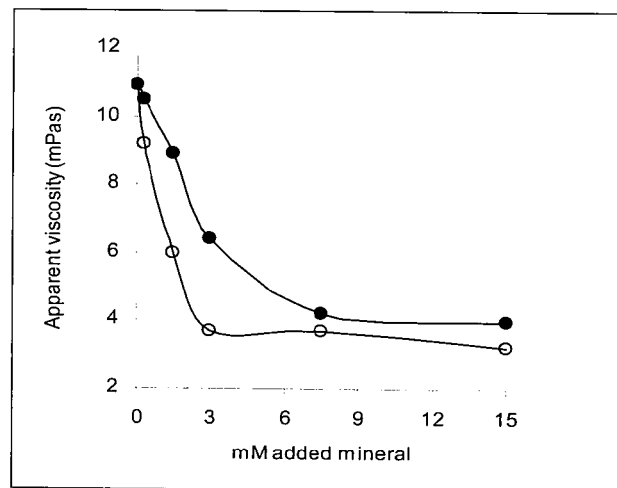


Fig. 1: The effect of increasing copper (●) or iron (○) content on the apparent viscosity of the aqueous phase of water-in-oil spreads at 60°C.

Fig. 1 shows the effect of increasing zinc content on the apparent viscosity of the aqueous phase of water-in-oil spread at 60°C. The aqueous phase had an apparent viscosity of 10.9 mPa s and flow properties very close to Newtonian. Addition of increasing levels of copper or

iron at 60°C caused a significant ($P \leq 0.05$) reduction in the apparent viscosity of the aqueous phase to 4.0 or 3.2 mPa s with 15 mM copper or iron, respectively. These findings are in agreement with previous work of MOUNSEY *et al.* (10), which showed a reduction in viscosity at 60°C on addition of zinc to κ -carrageenan. The reduction in viscosity on addition of minerals is caused by a reduction in the electrostatic repulsion between the negatively charged sulphate groups (14).

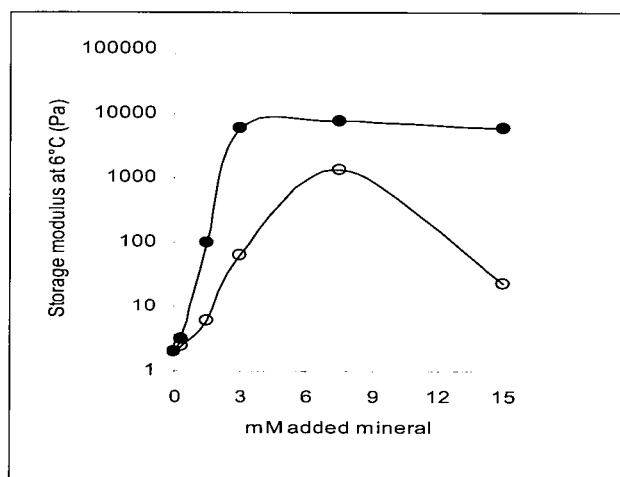


Fig. 2: Effect of increasing copper (●) or iron (○) content on the storage modulus (G') at 6°C of the aqueous phase of water-in-oil spreads.

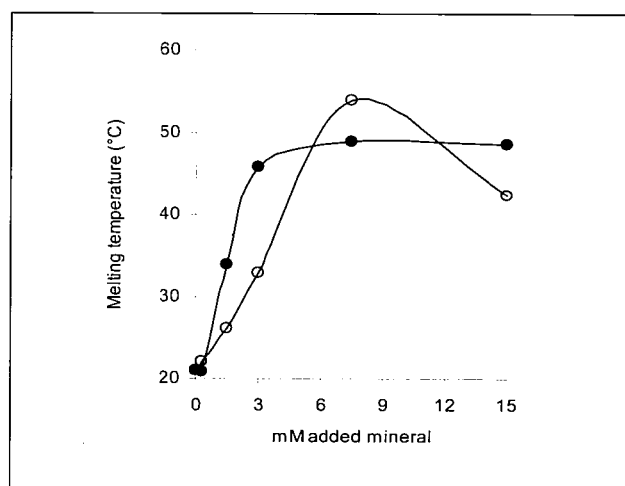


Fig. 3: Effect of increasing copper (●) or iron (○) content on the melting temperature (°C) of the aqueous phase of water-in-oil spreads on heating from 6 to 60°C.

The effect of increasing copper or iron concentration on the storage modulus (G') of the aqueous phase of the water-in-oil spread on cooling to 6°C is illustrated in Fig. 2. It can be seen that G' of the aqueous phase increased dramatically to 7.6 kPa with increasing concentration of copper (0–7.5 mM) and then decreased to 6.0 kPa at 15 mM Copper. Previous work has shown that increasing quantities of calcium (15) and zinc (10) had a similar effect on the gel strength of κ -carrageenan gels. The G' of the aqueous phase increased to a lesser degree with increasing concentrations of iron (to 1.3 kPa with 7.5 mM iron) and then decreased markedly to 24

Pa at 15 mM Iron. Results showed that up to a maximum concentration of 7.5 mM, the inclusion of either metal resulting in increased network formation in the aqueous phase on cooling.

Fig. 3 shows the effect of increasing copper or iron on the melting temperature (temperature where $G' < 1$ on heating above 6°C) of the aqueous phase of reduced-fat spread. It can be seen that the melting temperature increased with increasing copper or iron concentration. On heating the carrageenan molecules undergo a helix-to-coil transition, passing from an ordered (gelled in the present work) to a disordered (melted) state. In the present investigation it can be clearly seen that at higher concentrations of copper and zinc there is an increase in the melting and gelation temperature and a corresponding increase in the hysteresis which reflects the presence of a stronger gel network. The slight decrease in the melting temperatures and subsequent hysteresis at the highest level of iron indicates reduced chain association and network formation which is consistent with the gel strength (G') observations.

The texture of spreads is mostly determined by the properties of the fat phase which is made up of agglomerated fat crystals dispersed in liquid oil (2).

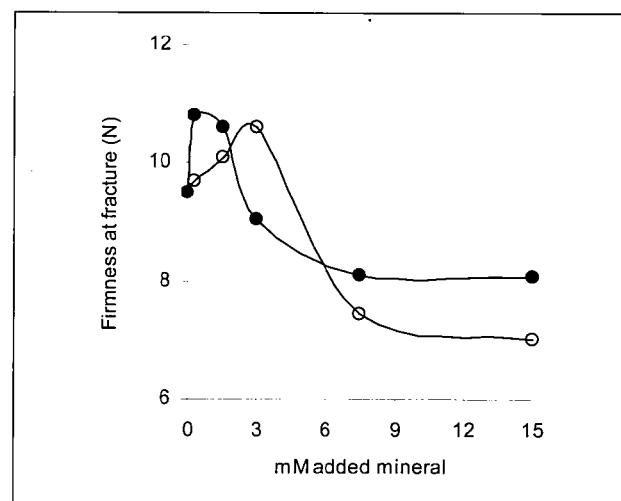


Fig. 4: The effect of increasing copper (●) or iron (○) content on the firmness (N) at fracture of water-in-oil spreads at 6°C.

The firmness (peak force in Newtons, N) at 6°C of the water-in-oil spreads was monitored (Fig. 4). The control spread containing κ -carrageenan had a firmness of 9.5 N at fracture. It can be seen from the figure that the textural firmness of water-in-oil spreads was increased with metallic cation addition to levels of 1.5 mM for copper and to levels of 3 mM for iron. At higher a level of each cation, the firmness of the spreads was reduced compared to the control. Despite the fact that mineral addition increased the gel strength of the aqueous phase the textural firmness of the spreads was less affected, which is in agreement with previous work (1, 10).

Work was undertaken to characterise the non-destructive rheological properties of water-in-oil spreads on heating/melting. The effect of copper or iron at 0.3 mM or 15 mM levels on the storage modulus (G') of the water-in-oil spread on heating from 6 to 60°C is illustrated in Fig. 5.

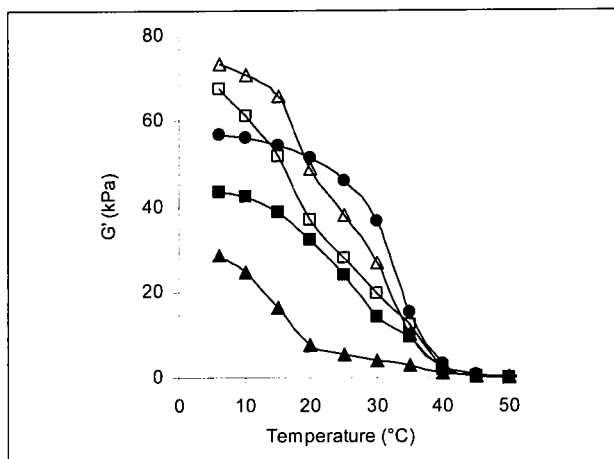


Fig. 5: The effect of increasing levels of copper (Δ ; 0.3 mM, \blacktriangle ; 15 mM) or iron (\square ; 0.3 mM, \blacksquare ; 15 mM) on the storage modulus (G') of water-in-oil spreads (\bullet ; control) on heating from 6 to 60°C.

The control water-in-oil spread had a G' of 57 kPa at 6°C, which was consistent with very gel-like behaviour at this temperature. On heating, the G' of the control was reduced with the greatest decreases occurring between 30 and 40°C, corresponding with the melting of the crystalline continuous fat phase. The G' at 6°C of the water-in-oil spreads was increased to 67.8 and 73.6 kPa, respectively with iron and copper addition at levels of 0.3 mM zinc. In accordance with the destructive firmness analysis results, at higher levels of mineral addition, the G' at 6°C of the water-in-oil spreads were significantly ($P \leq 0.05$) reduced compared to the control. The temperature-dependent changes in the mineral-containing samples showed the same trend as the control though were generally lower. The reduction in the G' and firmness values of the water-in-oil spreads brought about by copper and iron inclusion was probably due to the effect of the minerals in having a pro-oxidant effect in promoting and accelerating oxidation of the fat phase of the spreads (11).

4. Conclusions

The findings of the present work showed that fortification of κ -carrageenan-based oil-in-water spreads with copper and iron resulted in reduced viscosity of the aqueous phase at 60°C yet resulted in gelation of the aqueous phase at 6°C and increased the melting tem-

perature on reheating. At higher levels of addition, the minerals impaired the firmness at 6°C and rheology of the spreads on heating. These effects were attributed to the pro-oxidant effects of the metallic cations on the oil-phase of the spreads.

Acknowledgements

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