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# Effect of κ-carrageenan on rheological properties, microstructure, texture and oxidative stability of water-in-oil spreads

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ABSTRACT

The effect of κ-carrageenan concentration (0-7.5 g kg$^{-1}$) on the rheology, microstructure, texture and oxidative stability of water-in-oil (W/O) spreads (600 g fat kg$^{-1}$ emulsion) was examined over 60 days storage time. Results showed that increasing the κ-carrageenan concentration to 7.5 g kg$^{-1}$ significantly increased the viscosity of the aqueous phase (to 42.7 mPa s at 60 °C) resulting in gelation of the aqueous phase on cooling. The microstructure of the spreads was disrupted by higher levels of κ-carrageenan, resulting in a less homogeneous distribution of the aqueous phase. Melt temperature (where $\tan\delta > 1$) decreased significantly from 62 to 56.2 °C with increasing κ-carrageenan concentration from 0 to 7.5 g kg$^{-1}$. The firmness and the G′ at 6 °C for all samples were significantly increased after 60 days storage with only small effects due to κ-carrageenan levels. Oxidation of the fat phase was evident by the significant increases in peroxide values of all spreads on storage, with κ-carrageenan exhibiting no antioxidant behaviour. While increased κ-carrageenan levels modified the microstructure of W/O spreads in terms of the droplet size of the aqueous phase and its distribution few changes were evident in the continuous fat phase.

## 1. Introduction

Spreadable fats are emulsions of the W/O type and were introduced as an economical, functional and low calorie alternative of butter (Caponio & Gomes, 2004; Laia, Ghazalia, Cho & Chong, 2000). Replacement of the fat with water alters the rheological properties and structural characteristics of spreads, which are mainly given by the shape and the size of the fat crystals (Kasapis, 2000). A number of biopolymers are used in low-fat formulations as fat mimics and as stabilisers of the aqueous phase (Chronakis & Kasapis, 1995a; Chronakis, 1997) through network stabilisation as well as stabilisation via interfacial action (Benichou, Aserin & Garti, 2002; Dickinson, 2003).

Polysaccharides such as κ-carrageenan have been shown to enhance the sensorial properties of reduced-fat spreads (Clegg, Moore & Jones, 1996). κ-Carrageenan has the capacity to gel on cooling through a disordered-ordered transition forming intermolecular double helices and subsequent aggregation and gelation under specific conditions (Oakenfull & Scott, 1990; Heyraud, Rinaudo, & Rochas, 1990). In a previous study by Mounsey, Stathopoulos, Chockchaisawasdee, O'Kennedy, Gee and Doyle (2008) on the fortification of W/O spreads containing κ-carrageenan, authors found that the increase in the gel strength of the aqueous phase upon addition of transition metals altered the microstructure of the W/O spreads.

The purpose of the present study was to assess the effect of κ-carrageenan on the rheology of the aqueous phase and on the microstructure, texture, and rheology of the experimental W/O spreads. Studies with reference to the antioxidant activities of sulphated polysaccharides extracted from brown and red seaweeds have been published in the literature (Sirendi, Gohtani, & Yamano, 1998; de Souza, Marques, Dore, da Silva, Rocha, & Leite, 2007; Wang, Liu, Zhang, Zhang, Qi, & Li, 2009). *In-vitro* studies showed that sulphated polysaccharides presented activity in inhibiting free radicals. The degree of sulphation was found to be directly related to the radical scavenging activity, with κ-carrageenan exhibiting mild antioxidant properties (de Souza et al., 2007). The effect of κ-carrageenan on the oxidative degradation of the W/O spreads was also investigated in the present work.

## 2. Materials and methods

### 2.1. Materials

A commercial source of κ-carrageenan (Grindsted Carrageenan CL 107, Danisco, Denmark) was used without further purification.

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The vegetable oil blend was obtained from DairyGold (Mitchelstown, Ireland). The fatty acid composition of the oil blend was 480 g $kg^{-1}$ monounsaturated, 320 g $kg^{-1}$ saturated, 190 g $kg^{-1}$ polyunsaturated and 10 g $kg^{-1}$ *trans* fatty acids. The monoglyceride emulsifier (Paalsgaard 0291) was supplied by Grinstead A/S, Braband, Denmark. All other solvents and chemicals used were of analytical grade and purchased from Sigma–Aldrich, St. Louis, MO 63103, USA. Deionised water was used for the aqueous phase.

### 2.2. Manufacture of W/O spreads

Water-in-oil spreads (batches of 10 kg) were prepared in duplicate following margarine production technology using a Perfector scraped surface heat exchanger (Gerstenberg and Agger, Copenhagen, Denmark) as described previously (Mounsey et al., 2008). A control spread was prepared by mixing an aqueous phase (water; 400 g $kg^{-1}$ of the final product) and the fat (or oil) phase contained the oil blend and the emulsifier (600 g $kg^{-1}$ of the final product) at approximately 55 °C. The preliminary mixing of the oil and aqueous phase was performed for 1 min at 1500 rpm using a Silverson mixer (model AX3, Silverson Machines Ltd., Waterside, Chesham, Bucks, UK). The formed W/O emulsion was transferred to the jacketed tank connected to the Perfector and pasteurized at 75 °C for 15–20 s and immediately cooled down to 65 °C. The emulsion (~55 °C) was pumped through two scraped-surface coolers (at 432 rpm) bringing the temperature to 12 °C before the spread was filled into 454 g plastic tubs and stored at 4.5 °C prior to testing. The spreads containing κ-carrageenan (1.56, 3.12, 6.25, 12.5 or 18.8 g $L^{-1}$ in the aqueous phase) were produced in order to give a final κ-carrageenan concentration of 0.625, 1.25, 2.5, 5, and 7.5 g $kg^{-1}$ reported to the total quantity.

### 2.3. Rheology of the aqueous phase

Small-scale deformation measurements were carried out on the aqueous phase of the spreads using cup and bob systems in an AR 2000 Rheometer (TA Instruments, UK). All measurements were made at a frequency of 1 Hz and a maximum strain of 0.500%. Parameters such as the storage modulus ($G'$), loss modulus ($G''$) and tan $\delta$ ($G'/G'$) were monitored during cooling from 60 °C to 6 °C at a rate of 1 °C $min^{-1}$ using a Peltier heating element, followed by reheating to 60 °C at the same ramp rate. The samples (15 g) were loaded at 60 °C and covered with n-Tetradecane (Sigma Chemica, Co., St. Louis, MO, USA) to minimise evaporation.

Viscosity of the aqueous phase of the spreads was measured using the same geometry of the AR 2000 Rheometer as above. A shear rate sweep from 0.1 to 500 $s^{-1}$ was applied for 5 min. The apparent viscosity (mPa s) was taken at 60 °C and a shear rate of 100 $s^{-1}$.

### 2.4. Rheology of W/O spreads

A controlled strain AR-2000 rheometer (TA Instruments, New Castle, Delaware) was used in the dynamic mode for small-scale deformation measurements. Disc-shaped samples of spread (25 mm diameter, 2.5 mm in thickness) were prepared using a 25 mm diameter cork borer. A 25 mm diameter serrated parallel plate geometry was used with a serrated lower plate. Samples were placed on the lower plate and compressed with a normal force of 0.5 N to prevent slippage, with 3 min for temperature equilibration and stress relaxation prior to testing. Measurements were taken at a frequency of 1 Hz and a strain of 0.2 %. Samples were loaded at 6 °C before n-Tetradecane (Sigma Chemical Co., St. Louis, MO, USA) was added to the side in order to avoid evaporation. The change in $G'$, $G''$ and tan $\delta$ were measured during heating from 6 to 60 °C at a rate of 1 °C $min^{-1}$. Tests were carried out in triplicate.

### 2.5. Texture Profile Analysis (TPA)

Compression tests were performed using a TA-XT2 Texture Analyser from Stable Microsystems (UK). Cylinders of spreads of 25 × 25 mm were cut and allowed to equilibrate at 4.5 °C for 4 h. Samples were compressed to 50% of their initial height (12.5 mm) at a crosshead speed of 1 mm $s^{-1}$ using a 5 kg load cell and a 75 mm diameter plate. Six samples were analysed from each spread tub. The hardness values, expressed in Newtons (N) were measured at the point of fracture.

### 2.6. Scanning Electron Microscopy (SEM)

Samples were prepared for cryo-SEM by mounting them into copper rivets and plunged into nitrogen slush (−207 °C). Samples were then transferred under vacuum into the preparation chamber, freeze fractured with a cold blade, etched at −88 °C for 5 min and then sputtered coated with gold (10 mA for 60 s). Samples were then transferred under vacuum onto the cold stage which was maintained at −125 °C and imaged using FE-SEM (Zeiss Supra Gemini, Darmstadt, Germany). Images were acquired at 2.00 kV with 2000–20,000× magnification.

### 2.7. Determination of the peroxide values (PV)

The PV test of melted fat (mEq $O_2$.$kg^{-1}$) was derived from the International Dairy Federation (IDF) Standard 74:1974. The W/O spread sample was melted at 62°C and 0.1 mL of melted fat was dissolved into 10 mL of chloroform/methanol (70:30) mixture, followed by addition of ammonium thiocyanate and ferrous chloride, respectively. Using glass stoppers, the tubes were inverted and placed in dark cupboard for 10 min. Simultaneously, a blank test with only reagents and no sample was carried out. The absorbance of the samples was read at 505 nm on a Varian Cary Scan 1 instrument. After calibration, the blank value was subtracted from the sample values (1) and the PVs were calculated.

$$\mathrm{OD} = \mathrm{Abs}_{\mathrm{sample}} - \mathrm{Abs}_{\mathrm{standard}} \tag{1}$$

where OD is the optical density.

Samples were analysed after 1, 5, 7, 15, and 31 days of storage.

### 2.8. Statistical analysis

The rheology, texture and oxidative stability data of W/O spreads containing κ-carrageenan were statistically tested by analysis of variance (ANOVA) using SigmaStat (version 3.0; Jandel Scientific, Corte Madera, CA, USA). Differences among treatments were determined by Student–Newman–Keuls pairwise-comparison test. Treatment means were considered significantly different at $^*P < 0.05$.

## 3. Results and discussion

### 3.1. Rheology of the aqueous phase of W/O spreads

#### 3.1.1. Viscosity at 60 °C

The effect of κ-carrageenan concentration on the apparent viscosity of the aqueous phase of W/O spreads is presented in Fig. 1. The sample containing 1.56 g $kg^{-1}$ κ-carrageenan (in the aqueous phase) had a low viscosity (4.31 mPa s) whereas the apparent