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Formulation and characterisation of kappa-carrageenan gels with non-ionic surfactant for melting-triggered controlled release

Thomas Fenton*, Kelsey Kanyuck, Tom Mills, Eddie Pelan

Department of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, United Kingdom

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ABSTRACT

Kappa carrageenan was identified as a possible gel for melting-triggered release at 30–40 °C with the inclusion of a non-ionic surfactant for use in detergency or food-related applications. The gel formulation was kappa carrageenan (0.6–3% w/w) and either Tween 20 or Dehypon LS 36: two different non-ionic surfactants (0–5% w/w). Rheology and micro differential scanning calorimetry (μ DSC) found that the addition of either non-ionic surfactant had a significant increase in the gelling and melting temperatures, however the gelling and melting enthalpies remained unchanged with additional surfactant. Additionally, the elastic modulus, increased by up to an order of magnitude upon addition of the surfactant. Surface tension measurements showed that the critical micelle concentration of both non-ionic surfactants did not change with the addition of carrageenan, indicating no electrostatic interactions. The mechanism of interaction between carrageenan and non-ionic surfactants is suggested to be hydrophobic interactions leading to electrostatic shielding, which enhances carrageenan aggregation. Melting measurements of kappa-carrageenan gels with non-ionic surfactant proved that temperature-mediated release at 40 °C was achieved.

1. Introduction

The gelling capacity of hydrocolloids has been exploited for decades as a texture modifier in foodstuffs (Saha & Bhattacharya, 2010), however, attention has since been given to hydrocolloids for their controlled release properties (Burey, Bhandari, Howes, & Gidley, 2008; Gulrez, Saphwan, & Phillips, 2011; Patil & Speaker, 1998). Hydrocolloids can make ideal controlled release vehicles by helping to solubilise insoluble or volatile species (Chakraborty, 2017) and controlled release can be obtained by formulating biopolymers to have burst release in response to an external stimuli such as a change in temperature, pH, or salt concentration, or a more steady, diffusion/erosion-mediated release (Pal, Paulson, & Rousseau, 2009).

Carrageenan, an algae-derived polysaccharide originating from *Rhodophyta* seaweed, is one such hydrocolloid that has been highlighted for its potential as a controlled release agent. It is a negatively-charged polyelectrolyte consisting of a sulphated polysaccharide chain, hence its structure is sensitive to its ionic environment, most notably, the pH and cation concentrations (Imeson, 2000). The degree of chain substitution with sulphate groups, and hence the physical properties of the resultant gels, is used to classify common carrageenans into three types: kappa-carrageenan (κ C), iota-carrageenan (ι C) and lambda-carrageenan (λ C), which have one, two and three sulphate groups per idealised re-

peat unit respectively. Under suitable cation conditions, gelation in carrageenans is possible and is attributed to the formation and subsequent aggregation of double helices. The degree of carrageenan aggregation, and hence the resulting gel structure, is strongly salt dependent, particularly potassium salts for kappa carrageenan and calcium salts for iota carrageenan (Imeson, 2000). Cations interact with the anionic carrageenan helices and screen the negative charges on the chain, reducing interchain repulsion and encouraging aggregation. The process of gelation in carrageenans is fully thermally-reversible, therefore release can be theoretically triggered through melting of gelled structures upon the application of heat (Liu, Huang, & Li, 2016).

Surfactants, or surface-active agents, are amphiphilic molecules which adsorb at interfaces, lowering the interfacial tension. Surfactant molecules have a hydrophobic and a hydrophilic region, which gives them the ability to adsorb across interfaces formed when mixing two phases of differing polarities. They are known to form ordered structures called micelles once the concentration of surfactant reaches or exceeds the critical micelle concentration (CMC). Once the CMC is reached, it is characteristic that the surface tension does not decrease further with additional surfactant. The presence of a surfactant makes the two phases more compatible with each other and results in wetting or emulsification due to a decrease in interfacial tension. It is this principle that allows cleaning of soiled clothes and crockery in detergency applications.

* Corresponding author.

E-mail addresses: TFF710@student.bham.ac.uk (T. Fenton), KXK720@student.bham.ac.uk (K. Kanyuck), t.b.mills@bham.ac.uk (T. Mills), e.pelan@bham.ac.uk (E. Pelan).

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Non-ionic surfactants, produce little foam, are tolerant of a range of water hardnesses, and are generally safer to handle and consume in edible formulations (Blagojević, & Pejić, 2016), hence they are the preferred choice in automatic dishwashing detergent (ADD) and food-grade formulations.

The combination of gelling hydrocolloids with surfactants has been featured widely in literature for the past several decades (Piculell and Lindman, 1992; Griffiths and Cheung, 2003; Wang et al., 2006; Moonprasith et al., 2008; Pepić, Filipović-Grčić and Jalšenjak, 2009; Bonnaud, Weiss and McClements, 2010b; Vinceković et al., 2010; Sreejith, Nair and George, 2010; Vinceković et al., 2011; Rosas-Durazo et al., 2011; Fasolin et al., 2013; Picone and Cunha, 2013; Yin et al., 2014; Grządka, 2015). The majority of this literature is concerned with structures formed between a polyelectrolyte and a surfactant, often with each species having opposing electrical charges - termed polyelectrolyte-surfactant complexes - which interact through electrostatic interactions. Upon complexation, the critical micelle concentration of a surfactant can decrease in the presence of a polymer due to complexation of the polymer and the surfactant, sometimes by several orders of magnitude (Jain et al., 2004). This new concentration can be denoted the critical aggregation concentration (CAC) and is a useful indicator of polyelectrolyte-surfactant binding. For polymers and surfactants without opposing charges, hydrophobic interactions can occur between the two species also resulting in some level of complexation, however, if this interaction is weak then the CMC and CAC of the surfactant are very similar (Yang & Pal, 2020).

Understanding the mechanical and thermal properties of a sample is central to predicting how that material will perform as a controlled release product, and also how easily the product can be handled and can withstand shear before irreversibly breaking. Oscillatory rheology is a powerful tool for elucidating these properties, since it can determine gelling (T_g) and melting (T_m) temperatures by the cross-over of G' and G'' (Warner, Norton, & Mills, 2019), and a frequency sweep can predict if the sample is solid-like or liquid-like by examining the values of G' and G'' , and their dependence on frequency. Micro differential scanning calorimetry (μ DSC) also examines thermal transitions by measuring the heat produced or absorbed upon bond formation or breakage. μ DSC is more sensitive than conventional differential scanning calorimetry, as well as being able to perform scans at much slower heating and cooling rates.

The purpose of this work was to quantify and understand the change in mechanical and thermal properties of kappa-carrageenan when formulated in combination with non-ionic surfactant, and to determine whether the resulting formulation is suitable for temperature-triggered release at temperatures of 30–40 °C. This temperature was chosen to provide melt-in-the-mouth release in food formulations, or early release in a dishwasher cycle, which would avoid deactivation by surfactant-deactivating species, such as bleaches, if formulated in tandem with a higher melting point species (50–60 °C). Kappa carrageenan was chosen due to its desirable thermal, mechanical and environmental properties; it forms thermoreversible firm gels, derived from renewable natural resources. The surfactants used were Tween 20, a common, edible non-ionic surfactant, and Dehypon LS 36 (D36), a fatty alcohol-type non-ionic surfactant used in detergent formulations. The gelling and melting temperatures were determined using rheology and micro-differential scanning calorimetry (μ DSC), which also provided mechanical properties and thermal transition enthalpies respectively. Turbidity measurements were performed to investigate any change to the size and number of carrageenan aggregates. The CMC (only surfactant and water) and CAC (surfactant, water and carrageenan) of the non-ionic surfactants were determined using tensiometry. The melting performance of the gels were elucidated using conductivity in a custom, temperature-controlled setup by detecting the release of ions in water from the carrageenan gels.

Hypotheses:

- Kappa carrageenan gels that melt at 30–40 °C can be formulated for controlled release.
- Non-ionic surfactant does not cause adverse consequences to the gel strength or melting temperature.

2. Experimental

2.1. Materials

Genugel® CG-130 (batch no. SK30005409), a commercially available carrageenan was kindly gifted by CP Kelco (USA) – from this point on, Genugel® CG-130 shall be referred to as Genugel®, κ C or kappa-carrageenan. The ^{13}C NMR spectrum of Genugel® is given in Figure S1 shows that Genugel® can be treated as 'pure' G4S-DA kappa carrageenan (Lahaye, 2001) as there is only one peak at ca. 95 ppm, corresponding to the α -anomeric carbon of κ C (Villanueva, Mendoza, Rodriguez, Romero, & Montañó, 2004). The ion content of Genugel® was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (PerkinElmer Optima 8000) as (% w/w): $\text{Na}^+ = 0.332$, $\text{K}^+ = 2.20$, $\text{Mg}^{2+} = 0.0191$, $\text{Ca}^{2+} = 1.15$. Tween 20 was purchased from Merck (Germany). Dehypon LS 36 was purchased from BASF (Germany). All water used was purified using a reverse-osmosis Millipore® unit. All materials were used without any further purification.

2.2. Methods

2.2.1. Preparation of carrageenan and carrageenan-surfactant solutions

An appropriate mass of Genugel® was added to hot distilled water (ca. 80 °C), covered to prevent evaporation and was allowed to fully disperse and hydrate under agitation from a magnetic stirrer bar for 2 hours. If required, an appropriate mass of surfactant (0.1–5% w/w) was added to the hot carrageenan solution, and this was stirred at a reduced speed for a further 30 min at ca. 80 °C to minimise foam formation. Solutions were removed from heat and kept at room temperature overnight. Prior to measurement, samples were re-heated to ca. 80 °C under agitation until isothermal. Solutions were formulated at 0.6%, 1%, 2%, and 3% w/w carrageenan with 0%, 1%, 2%, 3%, 4% and 5% w/w surfactant.

2.2.2. Rheological measurements

An MCR 302 rheometer (Anton Paar, Austria) equipped with a PP50-TG roughened parallel plate geometry ($D = 50.0$ mm) and a P-PTD200/62/TG roughened lower plate geometry ($D = 62$ mm) was used to characterise the rheology of the samples. In all measurements, samples were loaded in sol form (80 °C) and trimmed to a gap of 1 mm, with the geometry pre-heated to 70 °C. A thin layer of silicone oil was immediately added to the outer edge of the samples to prevent evaporation and a Peltier hood (H-PTD-200) was lowered. For samples with a gelling temperature of below 20 °C, for the frequency and amplitude sweeps, after loading samples were initially cooled to 5 °C for 10 min, before heating back to 20 °C to ensure gelation had taken place.

Amplitude sweep to determine the linear viscoelastic region (LVR): An amplitude sweep was performed from 0.01% to 100% strain, at a frequency of 6.28 rad s^{-1} (1 Hz) and a temperature of 20 °C. The linear viscoelastic region was determined as the range of strain values which showed no significant degradation ($\pm 1\%$) in the value of the storage (G') modulus. This data was only used to determine strain values in proceeding oscillatory rheology and is not presented in this manuscript.

Temperature sweep to determine the gelling and melting temperatures: A temperature sweep was performed from 70 °C to 10 °C and from 10 °C back to 70 °C to record gelling and melting temperatures respectively, and this was performed in triplicate for each sample. Strain values were chosen to be within the LVR of the samples, and all sweeps were per-

formed at a frequency of 6.28 rad s^{-1} (1 Hz). The rate of temperature change was $1 \text{ }^\circ\text{C}$ per minute. T_g and T_m were determined by the crossover point of the elastic modulus (G') and viscous modulus (G'') (Warner et al., 2019).

Frequency sweep to determine the mechanical spectra: A frequency sweep was performed in triplicate, with the frequency varying between 10 rad s^{-1} to 0.1 rad s^{-1} (1.59 Hz to 0.0159 Hz), at strain within the LVR of the samples. The measurements were performed at $20 \text{ }^\circ\text{C}$.

2.2.3. μ DSC measurements

A Setaram evo3 differential scanning calorimeter was used to record the thermal transitions of the prepared samples. An appropriate mass (0.6–0.8 g) of melted sample was loaded into a screw-top, stainless steel cell using a pipette, and this was mass-balanced to within $\pm 0.005 \text{ g}$ with deionised water in the reference cell. Both cells were sealed with a new o-ring gasket. After an initial hold at $20 \text{ }^\circ\text{C}$ for 30 min to allow for sample equilibration, samples were cooled down to $-5 \text{ }^\circ\text{C}$, followed by a heating step to $90 \text{ }^\circ\text{C}$ before cooling back to $-5 \text{ }^\circ\text{C}$. In all cases, the rate of change of temperature was kept constant at $1 \text{ }^\circ\text{C}$ per minute. Each heating and cooling cycle was performed a total of 3 times per sample, with a 5 min isothermal hold between each cycle.

2.2.4. Tensiometry measurements - Critical Micelle Concentration (CMC) and Critical Aggregation Concentration (CAC) determination

A Sinterface PAT1M Droplet-Shape Tensiometer was used to measure CMC and CAC aqueous solutions of non-ionic surfactant without and with additional carrageenan respectively. Sample preparation involved performing serial dilutions of a surfactant with deionised water or a solution of 0.6% w/w Genugel®, to achieve final concentrations of surfactant of 0.001–0.01% w/w (10 to 100 mg L^{-1}). Measurements were performed at room temperature ($22 \text{ }^\circ\text{C}$). The samples containing carrageenan were not gelled, which was necessary for the measurements. The tensiometric measurement was continued until the surface tension reached a steady value ($\pm 1\%$), with each experiment being performed in triplicate. The droplets were formed as pendant drops, and were kept at a constant area of 25 mm^2 , extruded from a capillary with a 3 mm diameter. Density values were previously obtained as 0.997 g cm^{-3} and 1.002 g cm^{-3} for the surfactant-water and surfactant-water-carrageenan samples respectively. The density of air was assumed as 0.0012 g cm^{-3} .

2.2.5. Turbidity measurements

A Thermo Scientific Orion AquaMate 8000 UV–vis spectrometer was used to determine turbidity by measuring absorbance at a wavelength of 600 nm. Hot melted samples were poured in to 10 mm disposable plastic cuvettes, cooled to below their gelling temperature and subsequently stored overnight at room temperature until measurement. Measurements were performed in triplicate at room temperature and distilled water was used as a blank.

2.2.6. Melting of gels in water using conductivity

A Mettler Toledo SevenEasy conductivity meter was used monitor conductivity. The gel formulations were 0.6% w/w Genugel® with 3% w/w Tween 20 or Dehypon LS 36, and 10 g of this hot solution was added to a silicone ice tray (dimensions $27 \text{ mm} \times 27 \text{ mm} \times 21 \text{ mm}$) in order to form duplicate cubes. The gel cubes were covered and stored at $5 \text{ }^\circ\text{C}$ overnight. Prior to measurement, the gels were weighed to ensure no evaporative losses had taken place and were allowed to come to room temperature. A conductivity probe was inserted in to a 1 dm^3 beaker containing 900 g of distilled water through a hole in a custom 3D-printed lid: this ensured that the relative position of the probe to the sample was fixed. The gel cubes were placed in a porous net attached to the lid and the endpoint of the release measurement was determined once the conductivity value was steady ($\pm 0.01 \text{ mS cm}^{-1}$) for a period of 5 min. The water was kept isothermal at either 20, 30 or $40 \text{ }^\circ\text{C}$ using a thermostatic probe connected to a stirrer hotplate, and the solution was agitated at a constant rate of 200 rpm with a magnetic stirrer bar.

Conductivity was logged via Mettler Toldedo LabX Direct-pH software, which recorded the conductivity once per second until it was manually stopped.

2.2.7. Statistical analysis

Gelling and melting temperatures and enthalpies, and turbidity measurements were analysed by calculating the Pearson correlation coefficient (ρ): a positive correlation is indicated if $0 < \rho \leq 1$, and a negative correlation if $-1 \leq \rho < 0$, whereby the strength of the correlation increases as ρ moves away from 0. The CMC and CAC values were compared using the two-sample T-test in the Analysis ToolPak for Microsoft Excel, and the two populations were considered to have equal means if $t \text{ Stat} < t \text{ Critical two-tail}$.

3. Results

3.1. Rheological characterisation of Genugel® with non-ionic surfactant

3.1.1. Determination of the gelling and melting temperatures

A temperature sweep was used to determine the gelling and melting temperatures of samples by noting the temperature at which the elastic and viscous moduli are equal: an example of this is given in Figure S2. This data was gathered for Genugel® samples at the aforementioned concentrations, formulated in tandem with non-ionic surfactants, and this data is plotted in Fig. 1. There are three variables in these temperature sweep data: the concentration of carrageenan (and hence the concentration of gelling cations), the concentration of non-ionic surfactant and the type of the non-ionic surfactant, and each will be examined in turn for its influence on the gelling and melting temperatures of the carrageenan gels.

As the concentration of carrageenan was increased, the gelling and the melting temperatures both increased, with gelling temperatures increasing from ca. $10 \text{ }^\circ\text{C}$ to $35 \text{ }^\circ\text{C}$, and melting temperatures increasing from ca. $30 \text{ }^\circ\text{C}$ to $55 \text{ }^\circ\text{C}$ as the concentration of carrageenan increased from 0.6% to 3% w/w. The increase in gelling and melting temperatures of carrageenan can be attributed to more effective screening of negative charges on the polysaccharide chain of carrageenan reducing the intermolecular repulsion between chains and encouraging aggregation of double helices Norton et al. (1983). The magnitude of the thermal hysteresis – the numerical difference between the gelling and the melting temperatures – also increased slightly from ca. $20 \text{ }^\circ\text{C}$ for 0.6% w/w carrageenan, to ca. $25 \text{ }^\circ\text{C}$ for 2 and 3% w/w carrageenan. This rise in thermal hysteresis with increasing carrageenan concentration suggests that the gel structure became more thermally stable – and therefore more aggregated (Liu et al., 2016). Thermal hysteresis is a well-known phenomenon for κC (Díaz et al., 2019), and the magnitude of the measured thermal hysteresis agreed closely with previously published literature by Lai, Wong and Lii (2000), who reported an average thermal hysteresis of $22.5 \text{ }^\circ\text{C}$ of $1.5 \text{ g} / \text{dL } \kappa\text{C}$ in water.

The introduction of non-ionic surfactant led to an increase in gelling and melting temperatures across all tested carrageenan concentrations. As surfactant concentration was increased from 0% to 5% w/w, the gelling and melting temperatures increased by approximately $5 \text{ }^\circ\text{C}$, regardless of the concentration of carrageenan. Furthermore, the Pearson correlation coefficient values, shown in Table 1, were $0.77 \leq \rho \leq 0.93$, indicating a statistically strong positive relationship between gelling & melting temperatures and the concentration of surfactant. There was very little difference between the phase transition temperatures measured between the Tween 20 and Dehypon LS 36-containing formulations, which provides evidence that similar changes may be seen with many other non-ionic surfactants in similar formulations.

With regards to the most effaceable concentration for controlled release, the measured melting temperatures of the carrageenan-non-ionic surfactant gels suggest that 0.6% w/w Genugel® would be ideal for release at $30\text{--}40 \text{ }^\circ\text{C}$ since it was the only formulation that melted in this temperature range, regardless of the presence of any surfactant.

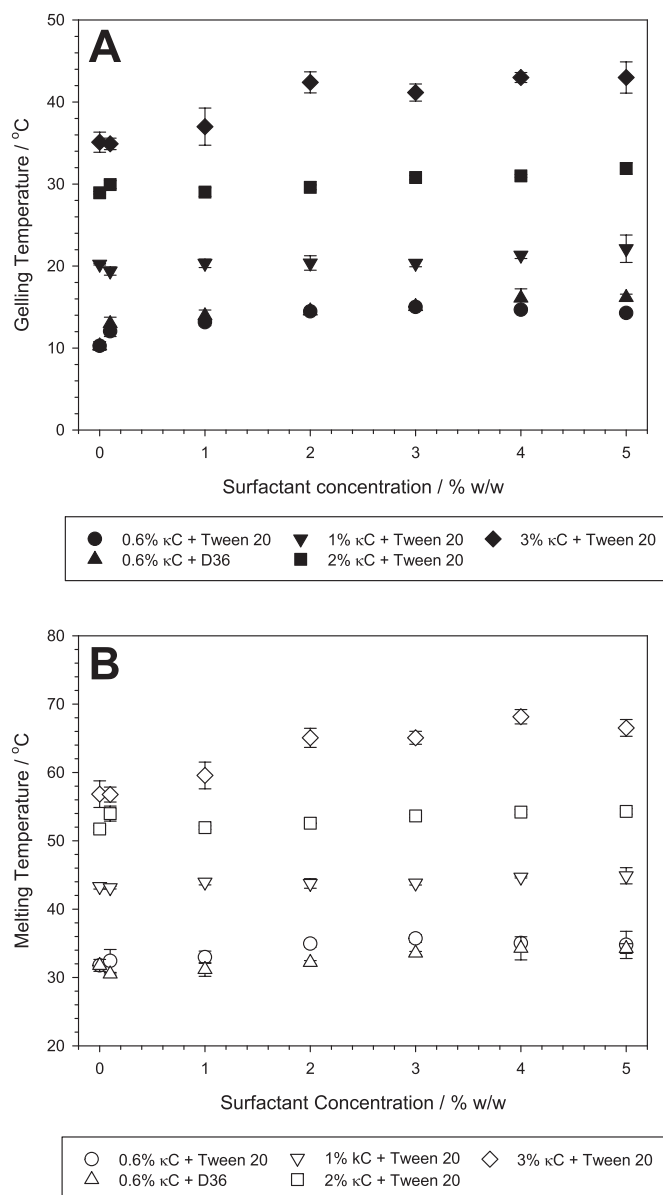


Fig. 1. Temperature sweep data for Genugel® solutions at with different concentrations of added surfactants. (A) shows data for the gelling temperature, (B) shows data for the melting temperature, both of which were obtained by the crossover of G' and G'' .

3.1.2. Determination of the mechanical spectra

A frequency sweep was performed to examine the frequency dependence and the magnitude of the viscoelastic moduli of the carrageenan-non-ionic surfactant gels: this data is shown in Fig. 2. For clarity only frequency sweep data at surfactant concentrations of 0%, 1%, 3% and 5% w/w are plotted. The remaining frequency sweep data at surfactant concentrations of 0.1%, 2% and 4% w/w are plotted in Figure S3.

The first observation is that as the concentration of carrageenan was increased, the values of G' increased markedly: the difference between 0.6% and 3% w/w carrageenan was approximately 3 orders of magnitude, increasing from ca. 10 Pa, to 10^4 Pa. Furthermore, at concentrations of 2% w/w carrageenan and above, the samples shifted from being frequency dependent to almost frequency independent, which indicated that the samples became more solid-like in nature. The value of G' at 0% w/w surfactant did not change between 2% and 3% w/w carrageenan, which suggests that a maximum in aggregation without any additional species was reached.

Interestingly the addition of non-ionic surfactant to the carrageenan also resulted in a greater measured value of G' , in some cases by up to an order of magnitude. Similar increases in G' were seen for both Tween 20 and D36-containing formulations. As the concentration of carrageenan was increased from 0.6% to 2% w/w the influence that the surfactant had on the carrageenan gel strength decreased. At 0.6% w/w carrageenan G' increased by 2 orders of magnitude across the range of surfactant concentrations tested, decreasing to 1 order of magnitude at 1% w/w carrageenan, then less than an order of magnitude at 2% and 3% w/w carrageenan. This is likely because at lower carrageenan concentrations – and therefore lower gelling cation concentrations – the gel structure is less aggregated and hence there is more potential for aggregation to increase. The storage modulus values aligned well with those measured during the temperature sweeps, as shown in Table S2.

Material properties are not only dictated by G' , but also G'' , or more specifically the phase angle. The difference between G' and G'' defines the phase angle (δ), as shown in Eq. 1.

$$\tan(\delta) = G''/G' \quad (1)$$

The phase angle can predict if the gel is self-supporting, as this is essential for many applications. Work by Gholamipour-Shirazi, Norton and Mills (2019) outline the following rules: phase angles of below 3° are very firm, stiff materials; 3 – 15° gives semi-solid, self-supporting materials; 15 – 45° gives semi-solid but non-self-supporting materials and any material with a phase angle above 45° is a liquid by definition. Phase angle values were calculated at each based on frequency sweep data, and averaged, as shown in Fig. 3.

It was found that only 0.6% w/w carrageenan gels at surfactant concentrations of 1% w/w or below can be classed as non-self-supporting, soft gels, and would therefore be unsuitable for many applications. As the surfactant concentration was increased past 1% w/w, the phase angle of 0.6% w/w carrageenan samples decreased such that all subsequent samples can be classed as self-supporting. For carrageenan at concentrations of 1% w/w or less, the addition of surfactant had a strong influence on the phase angle, whereas at carrageenan concentrations of 2% w/w and above, there was no influence on the phase angle.

3.2. Micro-differential scanning calorimetry of Genugel® with non-ionic surfactant

Micro differential scanning calorimetry (μ DSC) was performed on Genugel® samples in combination with Tween 20 at the aforementioned concentrations. Dehypon LS 36 could not be tested due to the fact that its cloud point occurred in the temperature range tested, which masked any signal from the gelling or melting of the carrageenan: a characteristic of ethoxylated polyol surfactants. The phase transition temperatures were taken as the maximum or minimum in the heat flow for both cooling and heating cycles respectively (Núñez-Santiago & Tecante, 2007), and enthalpies were calculated from integration of the thermograms: these data are discussed separately in 3.2.1 and 3.2.2 respectively.

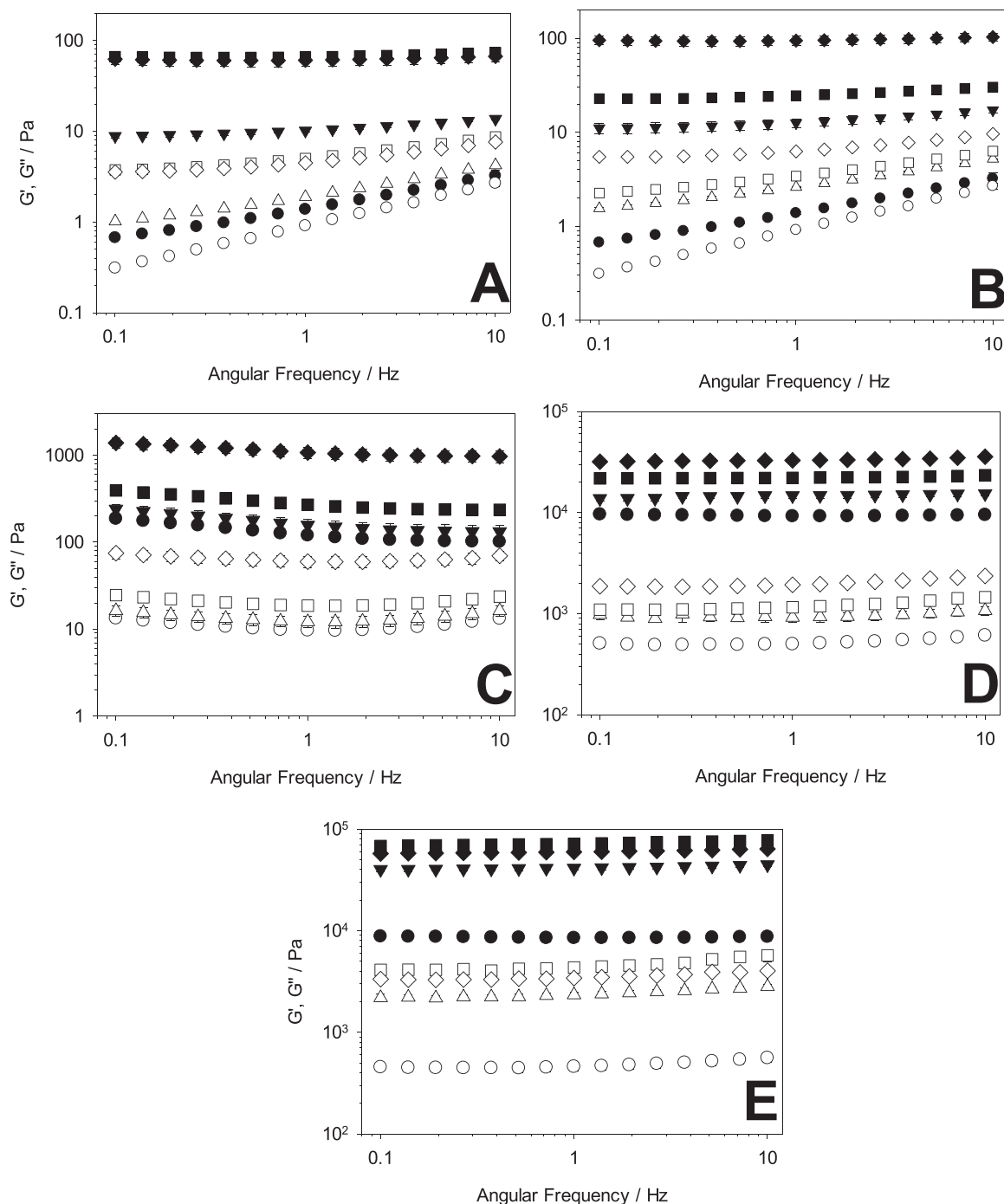


Fig. 2. Frequency sweep data for Genugel and surfactant solutions. (A) – 0.6% Genugel with Tween 20, (B) – 0.6% Genugel with D36, (C) – 1% Genugel with Tween 20, (D) – 2% Genugel with Tween 20 and (E) – 3% Genugel with Tween 20. Filled black symbols indicates values of G' , and filled white symbols indicates values for G'' . Different concentrations of surfactant are denoted by the symbol shape – ● - no surfactant, ▼ - 1% surfactant, ■ - 3% surfactant, ◆ - 5% surfactant).

3.2.1. Determination of phase transition temperatures

The phase transition temperatures were plotted as a function of increasing Tween 20 concentration, as shown in Fig. 4, and as previously, Pearson correlation coefficients were calculated to examine if there was a statistical trend, shown in Table 2.

When examining the phase transition temperatures, it is apparent that the values obtained using μ DSC were 5–10 °C lower than those measured with rheology, as shown in 3.1.1, apart from 0.6% w/w Genugel® which showed good parity. Gelling values ranged from ca. 10–30 °C and melting values from ca. 25–50 °C, compared to ca. 10–40 °C and ca. 30–65 °C measured by rheology. A very strong positive correlation be-

tween surfactant concentration and phase transition temperature was measured across all carrageenan and surfactant concentrations tested ($\rho \geq 0.90$). The Pearson correlation coefficient values were generally larger than those previously calculated in the rheological data, likely because the measurements made in the μ DSC were more repeatable, hence giving less measurement variability.

Upon addition of Tween 20, measured phase transition temperatures increased in the order of 2–5 °C across the surfactant concentrations tested: very similar to the behaviour measured using rheology. Additionally, the value of the thermal hysteresis increased with increasing carrageenan concentration, from ca. 15 °C for 0.6% and 1% w/w car-

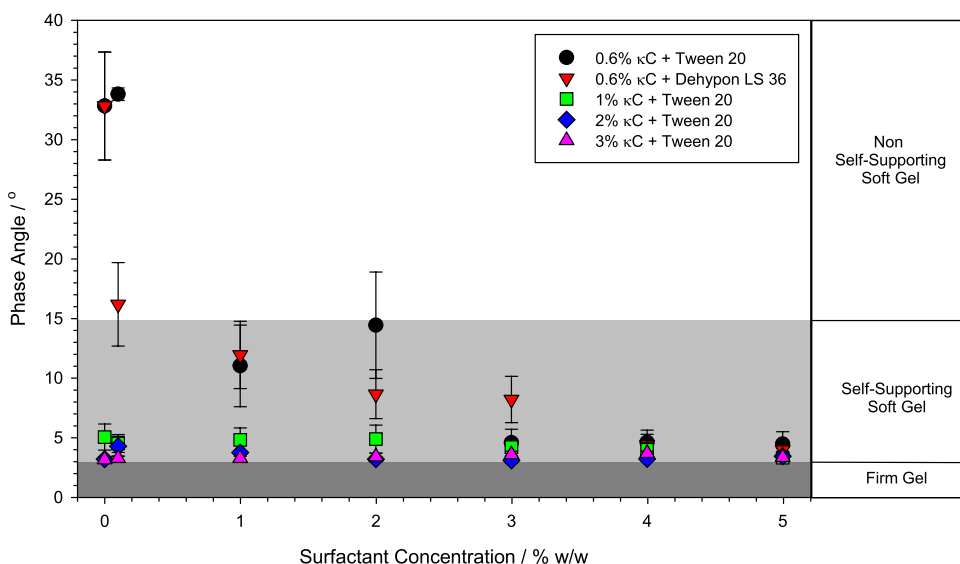


Fig. 3. Phase diagram for Genugel®-non-ionic surfactant systems, showing how the material properties change with carrageenan and surfactant concentration, and surfactant type. The shading of the graph background indicates the material behaviour shown (white – non-self-supporting soft gels, light grey – self-supporting soft gel, dark grey – firm gel).

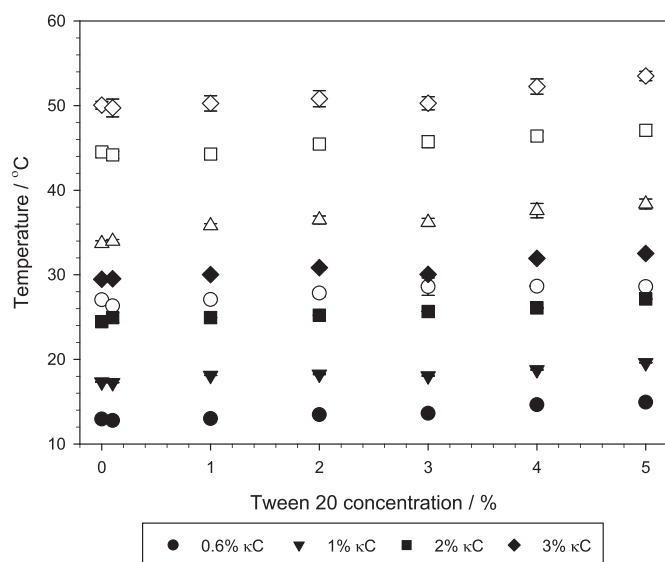


Fig. 4. Data for the phase transition temperatures of Genugel® samples at different concentrations of Tween 20, obtained by μ DSC. Filled markers (●) indicate coil-helix temperatures, whereas unfilled markers (○) indicate helix-coil temperatures.

Table 2

Statistical analysis for the μ DSC phase transition temperature data presented in Fig. 4.

Formulation	$\rho(T_{\text{coil-helix}})$	$\rho(T_{\text{helix-coil}})$
0.6% κ C + Tween 20	0.97	0.92
1% κ C + Tween 20	0.94	0.95
2% κ C + Tween 20	0.96	0.99
3% κ C + Tween 20	0.92	0.90

rageenan, to 20 °C for 2% and 3% w/w carrageenan: once again, very similar to that measured with rheology. The shapes of the profiles are given in the appendix Figure S4A-H, and can be seen to have a single peak in each exotherm and endotherm, indicating a single transition. If strong polyelectrolyte-surfactant complexes were formed, one would expect to see an associated enthalpy upon formation or breakage of these complexes, which was not seen. Tween 20 itself, without carrageenan, did not produce any detectable signal in the temperature range tested,

hence all contributions must be due to carrageenan-associated interactions.

3.3. Determination of phase transition enthalpies

Phase transition enthalpies can be measured by integration of the heat flow-temperature curve: these data are given in Fig. 5.

It is apparent that 0.6% w/w Genugel® had the smallest phase transition enthalpy values, which is indicative of a weaker gel network, which aligns with rheological data obtained during frequency sweeps. As the concentration of carrageenan was increased, the phase transition enthalpies increased, and this trend holds for the entire range of concentrations tested. Previous literature has reported that phase transition enthalpies and κ C concentration share a linear relationship (Iijima, Hatakeyama, Takahashi, & Hatakeyama, 2007; Liu et al., 2016), which appears to agree with the reported data for Genugel®. The range of enthalpy values obtained for the gelling and melting processes is ca. 0.1–1 J g⁻¹, which also agrees closely with previously reported data for κ C (Iijima et al., 2007).

In contrast, it is apparent that the addition of non-ionic surfactant to the carrageenan gels had no measurable influence on the gelling or melting enthalpies at all concentrations tested. The Pearson correlation coefficient values were $\rho < 0.7$ (data not given) across all carrageenan concentrations tested which further evidences the lack of any strong correlation between surfactant concentration and phase transition enthalpy.

3.4. Determination of the critical micelle and aggregation concentrations of Genugel® with non-ionic surfactants

Determining the CMC and CAC of both surfactant systems serves two purposes: firstly, it will determine a useful-dose of surfactant required in a detergent formulation, since detergency does not improve past the CMC (Poce-Fatou, 2006). Secondly, if the CAC and the CMC are very different (an order of magnitude or more), this suggests that carrageenan and non-ionic surfactants electrostatically interact. Whereas is the CAC and CMC are very similar, this indicates no interaction or weak, hydrophobic-driven interactions (Yang & Pal, 2020). Hence, the CAC and CMC was determined for Tween 20 and Dehypon LS 36 with and without Genugel® present respectively, as shown in Fig. 6.

As can be seen from the data, the CMC values for Tween 20 and Dehypon LS 36 were both close to 60 mg / L. For Tween 20, this agrees well with previously reported values (Mittal, 1972), however for Dehypon LS 36, no literature value for the CMC could be found. Low CMC

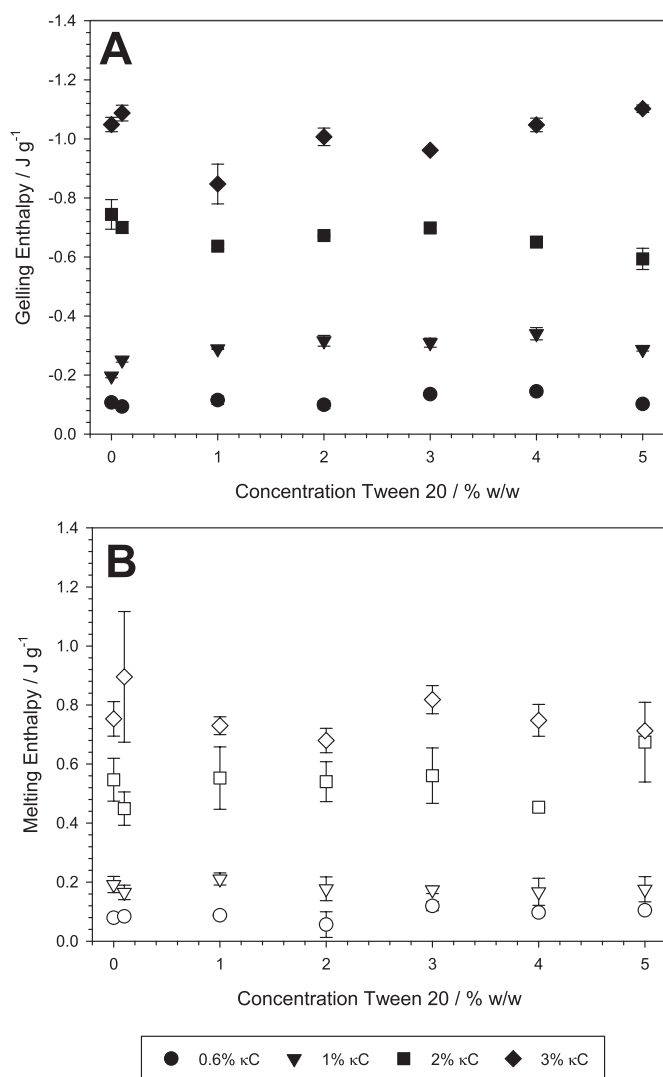


Fig. 5. Phase transition enthalpies measured by μ DSC for Genugel®-Tween 20 gels. (A) – gelling enthalpies, (B) – melting enthalpies. Filled markers (●) indicate gelling enthalpies, whereas unfilled markers (○) indicate melting enthalpies.

values such as these are characteristic of non-ionic surfactants. For a dishwasher of a 10 L capacity (Bengtsson, Berghel, & Renström, 2015), this would mean that the ideal surfactant concentration would be ca. 3–6% w/w for 10–20 g of gel, hence the previous formulations of up to 5% w/w surfactant are industrially-relevant. The relatively large error bars seen at low concentrations of Tween 20 are attributed to the heterogeneity of its formulation, which is amplified at very low concentrations, resulting in variability in the measurements. Additionally, at very low surfactant concentrations, the mobility of the surfactant to arrive at the interface can be extremely slow, resulting in a long time to reach an equilibrium surface tension, making it difficult to determine the exact endpoint. As the concentration of Tween 20 was increased, the inhomogeneities in the Tween 20 solutions became less apparent, and the time taken to reach apparent equilibrium decreased dramatically: both of these made the surface tension measurements more repeatable.

The introduction of Genugel® to either surfactant mixtures had no measurable impact ($p > 0.05$) on the value of the CMC with all critical concentration values measuring as approximately 60 mg / L. If the carrageenan and non-ionic surfactant were electrostatically interacting, then one would expect to see a large difference between the CMC and CAC values, due to stabilisation of the micelles by the carrageenan chains (Griffiths & Cheung, 2003). Overall these surface tension data

indicates two possibilities: weak non-ionic surfactant-carrageenan interactions, or no attractive interactions at all between the two species, which agrees with the previous μ DSC data showing only one peak in the thermograms.

3.5. Turbidity of Genugel®-non-ionic surfactant gels

A change in turbidity of a gel suggests that a microstructural change has taken place, and so turbidity measurements were performed in order to evaluate if the addition of non-ionic surfactant to κ C resulted in such a microstructural change – these results are shown in Fig. 7. Turbidity is caused by the formation of structures that are large enough to scatter light (Bonnaud et al., 2010), and therefore an increase in turbidity can be seen as an increase in the number these structures, in this case, aggregates of carrageenan helices. A UV-vis spectrometer can be used to determine the turbidity of gels by measuring the absorbance at 600 nm. Absorbance values (A) can be converted to turbidity values (τ / cm^{-1}) by using the path length (L / cm), as shown in Eq. 2 (Sow et al., 2017).

$$\tau = \left(\frac{1}{L}\right)A \quad (2)$$

Firstly, it was ensured that surfactant micelles were not interfering with scattering, hence Tween 20 in water was investigated without any carrageenan. As can be seen, no absorbance was detected at 600 nm, due to the fact that the small surfactant micelles are not large enough to scatter light. Hence, it was known that any change in the turbidity of carrageenan gels, in the concentration range tested, was not simply due to an increase in the number or size of surfactant micelles, and therefore it was assumed that the carrageenan aggregates must have been responsible.

Secondly, it can be noted that upon increasing the concentration of carrageenan from 0.6% to 3% w/w gave a large, steady increase in the turbidity of the gels: increasing from ca. 0.1 to ca. 0.9 cm^{-1} . It is taken that this is simply due to additional carrageenan aggregates scattering more light. Interestingly, there was a small statistical decrease in the turbidity upon the addition of non-ionic surfactant across every concentration of carrageenan tested, as shown by the negative Pearson correlation coefficient values in Fig. 7. This indicates that the introduction of surfactant actually decreased the number of carrageenan aggregates, which seems to contradict the earlier rheological data.

There did not appear to be any trend in the Pearson correlation coefficient values with concentration of carrageenan, indicating that the introduction of surfactant affected each concentration of carrageenan equally, which does agree with the previously reported rheological data.

3.6. Measuring the melting of Genugel®-non-ionic surfactant gels in water

To estimate the release of non-ionic surfactant from κ C-surfactant gels, ca. 10 cm^3 cuboid gels were placed in to water and the conductivity of the water was logged over time. The solutions were stirred slowly as to homogenise the vessel, yet not so fast as to significantly shear and break the gel. The release experiments were performed at 20, 30 and 40 $^{\circ}\text{C}$, and the corresponding release profiles are given in Fig. 8. Carrageenan at concentrations of 0.6% and 1% w/w were initially tested due to having melting temperatures either side of 40 $^{\circ}\text{C}$, as measured by rheology. If the release was melting-mediated (rapid at 40 $^{\circ}\text{C}$ yet much slower at 20 and 30 $^{\circ}\text{C}$), then successful controlled release was achieved. Any successful carrageenan-Tween 20 formulations were then verified at that carrageenan concentration with Dehypon LS 36. Release was calculated as a percentage based on the difference in final conductivity of the water once melted (σ_{final}), and conductivity of the water at time t (σ_t), using the initial conductivity ($\sigma_{initial}$) to normalise the results as shown in Eq. 3.

$$\text{Release (\%)} = \frac{(\sigma_t - \sigma_{initial})}{(\sigma_{final} - \sigma_{initial})} \times 100\% \quad (3)$$

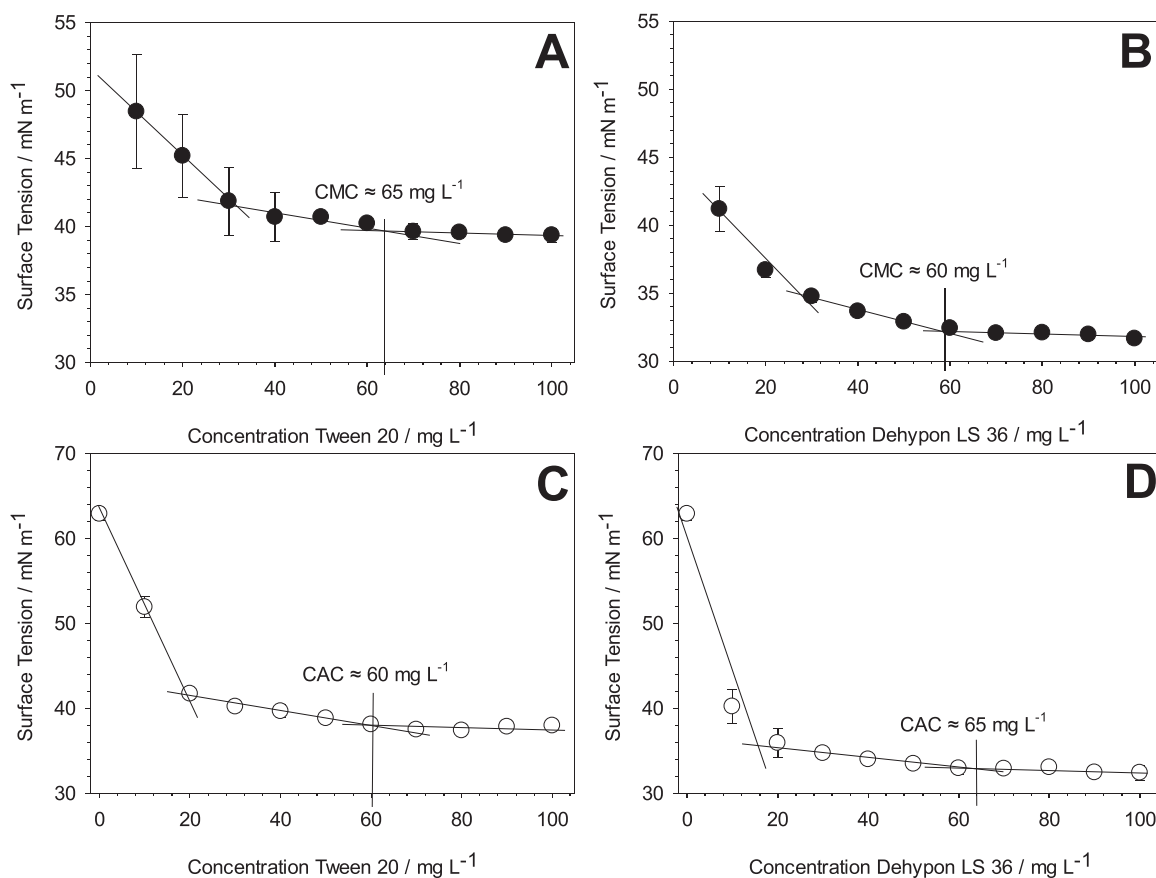


Fig. 6. Surface tension measurements for Tween 20 in water (A), Dehypon LS 36 in water (B), Tween 20 in 0.6% Genugel® (C) and Dehypon LS 36 in 0.6% Genugel® (D). Filled markers (●) indicate surfactant-water solutions, whereas unfilled markers (○) indicate surfactant-carrageenan solutions. The concentration at which the surface tension did not change – the CMC or CAC – is indicated on each graph. The CMC/CAC was estimated by the intersection point between a horizontal and a diagonal trendline.

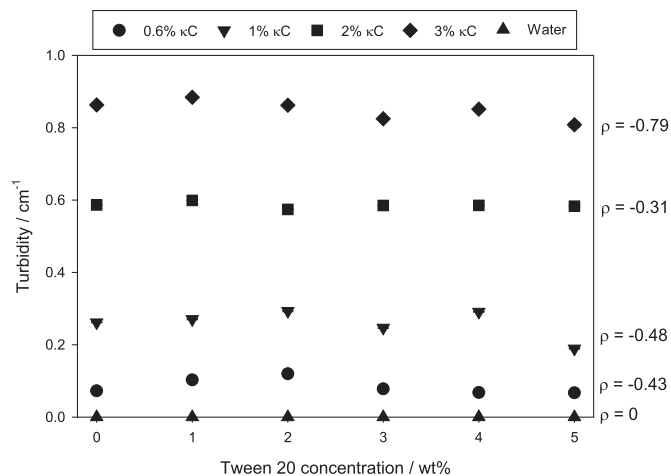


Fig. 7. Turbidity data obtained for κ C gels at different combinations as a function of increasing Tween 20 concentration. Water was also tested as a control. Pearson correlation coefficient (ρ) values are given alongside the data.

The release data at a range of temperatures was measured, as shown in Fig. 8. For both 0.6% w/w carrageenan-surfactant formulations, release of salt was rapid at 40 °C (ca. 5 min), taking considerably longer at 30 °C (ca. 30 min) and longer still at 20 °C (ca. 1–2 h). These data indicates that melting of the biopolymer took place. Similar release behaviour upon melting has also been reported by Mills et al. (2011). For 1% w/w Genugel®, even at 40 °C the release took over 30 min, with release at 30 °C taking ca. 100 min and at 20 °C, nearly 3 h, indicat-

ing that melting behaviour was not observed. In all release experiments there was no solid material left in the vessel, regardless of temperature or carrageenan concentration.

For non-melting scenarios an increase in temperature still resulted in faster release rates. This can be attributed to faster diffusion of gelling cations out of the gel, faster swelling of the carrageenan and perhaps some breakage of weaker helical aggregates: both leading to faster erosion. The melting thermograms shown in Figures S4E-H are relatively broad, which indicates that there is a corresponding broad distribution of aggregate strengths. Mills et al. (2011) found that salt release from non-swelling gels – gelatin, gellan and alginate – at a temperature well below their melting temperatures (25 °C) all occurred at nearly the same rate: this is indicative of a pure-diffusion controlled process. However, in these data there was a significant difference between the release profile for 0.6% and 1% w/w Genugel® at 20 and 30 °C, despite the fact that both of these temperatures are below the melting temperatures of both gels, which further evidences that swelling and/or erosive release was taking place.

4. Discussion

Upon the addition of surfactant to the carrageenan, the major changes measured by rheology were an increase in the gelling and melting temperatures, and an increase in gel strength. Explaining this behaviour could take one of several mechanisms. Firstly, one must consider the influence of concentration: the addition of surfactant meant (a) removal of water from the formulation, and (b) the introduction of a species (surfactant) that to must be hydrated, potentially leading to competition with carrageenan for water. Both of these factors would reduce

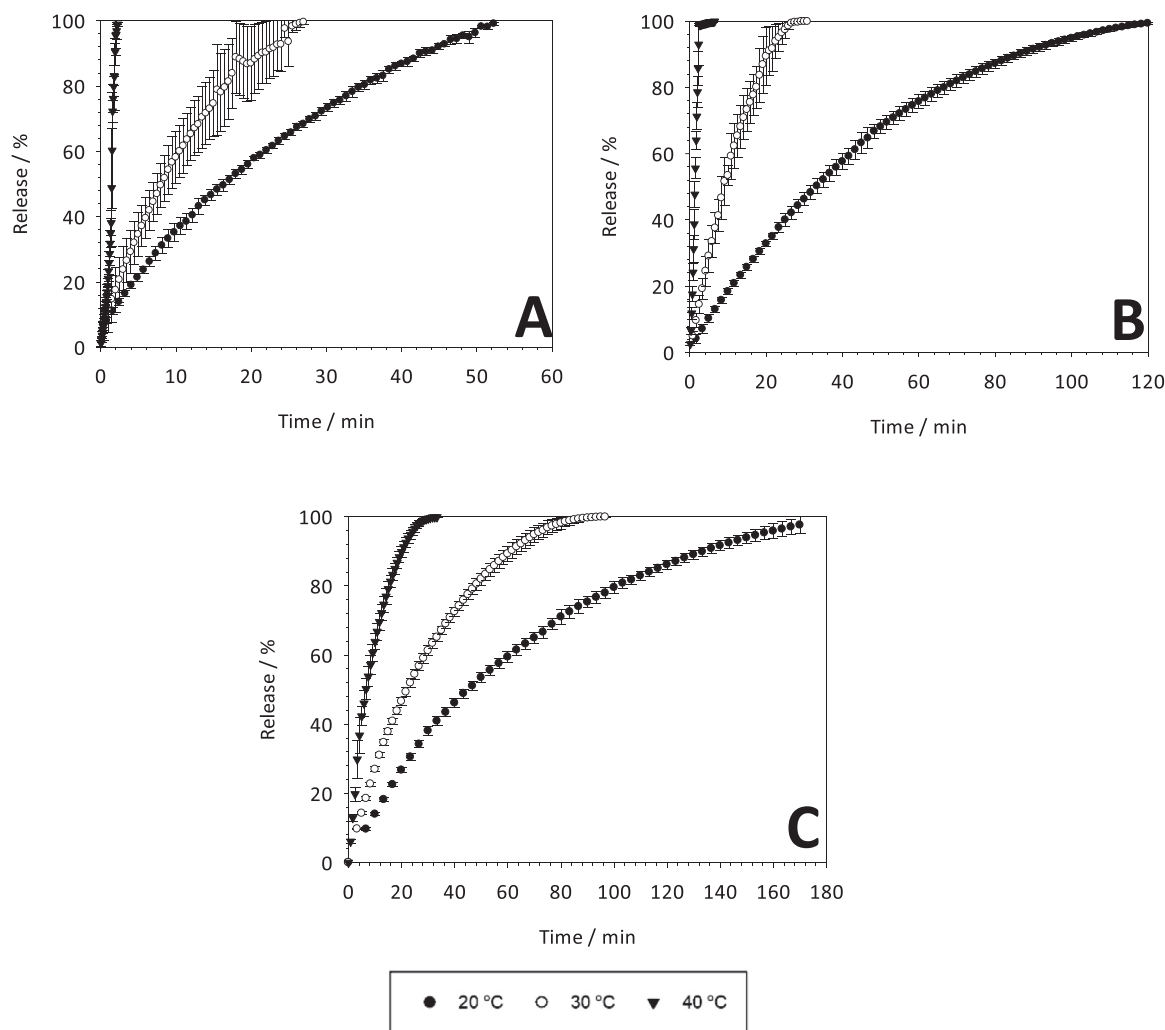


Fig. 8. Release profiles resulting from the melting of carrageenan-non-ionic surfactant cubes. (A) – 0.6% w/w Genugel® + 3% w/w Tween 20. (B) – 0.6% w/w Genugel® + 3% w/w D36. (C) – 1% Genugel® + 3% w/w Tween 20.

the volume of water available to the carrageenan, therefore increasing the effective concentration of carrageenan and gelling cations, and hence potentially resulting in the observed increase in gelling and melting temperatures. To investigate this further, samples of carrageenan containing 5 g less of water to match the water content of the 5% w/w surfactant formulations were made and analysed in the same manner as the previous samples – data given in Table S2. In almost all cases there was a small increase between the regular samples and the samples with reduced water content, owed to concentration effects. However, in a large number of samples the increase did not extend to match those of the surfactant-containing samples, indicating that concentration effects were not the only driving force behind the changes measured. Additionally, one would expect to see much smaller changes in the gelling and melting temperatures at lower concentrations of carrageenan if altering the effective concentration was the sole contributor, which was not observed.

The combination of a charged polyelectrolyte, such as κ C, with a non-ionic surfactant, such as Tween 20 or Dehypon LS 36, would theoretically result in no electrostatic attraction between the two species, and therefore no binding or adsorption of micelles: this is evidenced by μ DSC (there were only single peaks in the thermograms) and surface tension measurements (no change in the CMC upon addition of carrageenan). The microstructure of such gels would therefore be either a phase-separated or a bicontinuous morphology. Phase separation between the carrageenan and surfactant could explain the increase in

gelling and melting temperatures due to exclusion effects leading to an increase in the effective concentration of carrageenan and salts. However the lack of an increase in turbidity on mixing – a characteristic of phase separated mixtures (Vinceković et al., 2011), was observed for all tested formulations, making phase separation unlikely. The exception to this were formulations with Dehypon LS 36 that were cloudy at room temperature due to the surfactant reaching its cloud point, which according to previously obtained μ DSC data, was 15–16 °C (data not given). Phase separation was made unlikely due to the small size of the non-ionic surfactant micelles which had a consequently small enthalpy for segregation, compared to the relatively larger entropy of mixing (Morris, 2009). Therefore in this carrageenan-surfactant system, surfactant micelles were likely to have been dispersed throughout the carrageenan network forming a bicontinuous system.

Previous work by Johansson, Skantze and Löfroth (1993) has shown that there is a slight repulsive interaction between non-ionic surfactant micelles and kappa carrageenan chains, which may have made chain aggregation more thermodynamically favourable by reducing the number of carrageenan-micelle interactions. However, if the repulsion was not significant enough to trigger phase separation, it is unlikely that repulsion of the same magnitude would lead to significant differences in carrageenan chain aggregation.

The final mechanistic explanation for these carrageenan-surfactant interactions is electrostatic shielding through hydrophobic interactions. Aggregation of helical chains in carrageenan is driven by electrostatic

shielding, and so an increase in gelling and melting temperatures upon addition of surfactant indicates that the surfactant assisted the shielding of the carrageenan in some capacity beyond increasing the effective concentration of cations (as water was removed). Therefore, the authors believe that the only reasonable explanation for the change in properties must be shielding of the carrageenan chains by the non-ionic surfactant micelles since it is the only mechanism by which a similar increase in gelling and melting temperature would occur for each carrageenan concentration, and would explain why there the reduced-water samples did not match with the 5%-surfactant-carrageenan samples. In this mechanism, the surfactant micelles aggregate on the carrageenan chain through hydrophobic interactions, adding additional screening effects and therefore encouraging aggregation. Such mechanisms have been recently reported for other anionic polymer-non-ionic surfactant systems in water (Yang & Pal, 2020). It should be stated that variations in the structure of different carrageenan samples could potentially lead to alterations in the manner that the surfactant micelles and carrageenan helices interact, hence these results may not be applicable to other carrageenan samples.

Disparities between the gelling and melting temperatures measured by rheology and μ DSC were clear throughout the presented data, with μ DSC being consistently 5–10 °C lower than rheology. Such discrepancies can arise to differences in heating/cooling rate (Liu et al., 2016), hence this was kept constant at 1 °C per minute for both rheology and μ DSC. μ DSC measured the energy (heat) produced or absorbed from the formation or breakage of carrageenan double helices, rather than the formation and breakage of aggregates, and the phase transition temperatures were taken as maxima and minima in the thermograms: these can be termed $T_{\text{coil-helix}}$ and $T_{\text{helix-coil}}$ to avoid confusion with T_g and T_m , measured by rheology. This is evidenced by the fact that the addition of non-ionic surfactant had no measurable change on the value of the phase transition enthalpies of carrageenan, despite the fact that the rheological data showed that surfactant increased gel strength, which indicates increased aggregation. In short, the μ DSC could not measure the increase in aggregation as instead it was measuring the number of coil-helix and helix-coil transition, which did not change with surfactant concentration. In contrast, rheology measured the change in bulk material properties, which is associated with progressive aggregation of carrageenan helices, and the gelling and melting temperatures were taken at the point at which the samples changed from solid to liquid ($\delta = 45^\circ$, $G' = G''$) (Miyoshi & Nishinari, 1999). Therefore, one would expect that $T_{\text{coil-helix}} \geq T_g$ and $T_{\text{helix-coil}} \geq T_m$ since during gelation, the coil-helix transition must occur *before* aggregation, and the inverse is true for the melting process. Yet this is the exact opposite of what was observed: the data collected suggests $T_{\text{coil-helix}} < T_g$ and $T_{\text{helix-coil}} < T_m$. Identical behaviour has been reported previously in carrageenan (Liu et al., 2016), however a satisfactory explanation behind its origins was not included. For formulations of carrageenan past a critical concentration the temperature difference between the formation ($T_{\text{coil-helix}}$) and aggregation (T_g) of helices becomes so close to 0 that it is indistinguishable (Miyoshi & Nishinari, 1999). Hence this indicates an issue with either one of the measuring systems.

Slip due to syneresis can lead to poor rheological measurements of carrageenan (Thrimawithana, Young, Dunstan, & Alany, 2010), however no degradation in the viscoelastic moduli was detected during the LVR of the amplitude sweeps (data not given). Alternatively, the shrinkage of samples during gelation can cause issues with rheological measurements by reducing contact with the top rheometer geometry and migration of silicone oil (applied to prevent evaporation) in to the rheometer gap. It was shown by Mao, Divoux, & Snabre (2016) that conventional measurements using a fixed gap can lead to lower overall measurements of elastic modulus combined with a slow increase in elastic modulus after gelation termed 'strain hardening', by where contraction results in a large negative normal force. The example temperature sweep data given in Figure S2 indicates that such strain hardening was seen, and hence in future the zero normal force protocol should be used for

such gelation measurements. Mao et al. (2016) also have reported that issues can also arise due to thermal contraction by the rheometer geometries, however the TruGap™ feature was enabled which accounts for this. Despite these potential pitfalls, the rheological data was more accurate in predicting the onset of melting in the carrageenan samples, as proved in the release experiments.

The turbidity data indicated that the number of carrageenan aggregates decreased upon addition of non-ionic surfactant, which perhaps is the opposite of what one might expect. This information, coupled with the rheological data suggests that aggregation was enhanced by forming larger carrageenan aggregates. The turbidity decreased due to a small number of larger carrageenan aggregates forming from a smaller number of larger carrageenan aggregates, hence explaining both the rheological and turbidity data.

The release data for the carrageenan samples showed that the 0.6% w/w carrageenan-surfactant formulations could operate as temperature-mediated controlled release vehicles in dishwashing or food-related applications. Selective rapid release was measured at 40 °C compared to much slower release at decreased temperatures. In terms of the mechanism of the release of salt there are three possible mechanisms: Fickian diffusion, swelling and erosion (melting) (Lin & Metters, 2006). For diffusion, there is no change in the matrix of the material and the release is governed simply by diffusion from the porous gel network. For swelling, gelling cations diffuse and out water penetrates the outer layer of the gel and expands to become much more porous and open, which leads to much quicker diffusion of subsequent cations via non-Fickian diffusion. And thirdly, for erosive (melting) release, the carrageenan aggregates are directly broken with heat leading to dismantling of the gel network and dispersal almost instantly in to the bulk. In this mechanism, the release rate is governed by macroscopic stirring effects and is much faster than the other two mechanisms. The erosive release model can also occur in swollen gels by where the swollen layer is sufficiently weakened that it can be eroded, however the mechanisms by which the gel is weakened are different. In swelling-mediated erosion, the release rate is governed by how fast the gelling cations diffuse out whereas in the melting scenario, heat breaks the carrageenan aggregates resulting in much quicker erosion. The fact that no sample remained in any of the experiments indicates that at temperatures below the melting temperature, swelling followed by surface erosion took place.

5. Conclusions

The properties of κ C-non-ionic surfactant gels were probed using rheology, μ DSC, turbidity and tensiometry. These measurements showed an increase in phase transition temperatures and gel strength, a loss in turbidity whilst no measurable change in phase transition enthalpies, critical micelle concentrations. Overall there is significant evidence that kappa-carrageenan and non-ionic surfactants have a mechanism of interaction between the two species that allows for more effective shielding of the carrageenan helices during the aggregation step.

The ideal concentration of this κ C for release at 30–40 °C was identified as 0.6% w/w, due to its relevant melting temperature and self-supporting mechanical properties. This was verified in the melting experiments where it was found that rapid melting could be achieved at 40 °C, compared to much slower degradation at 20 and 30 °C. Therefore, this gel system is appropriate for applications such as food, pharmaceuticals and automatic dishwashing detergent formulations where release at 40 °C via a rapid melting mechanism is desirable.

Future formulations could involve inclusion of an oil phase to the carrageenan gels, which would be stabilised by the presence of a non-ionic surfactant, and would allow for temperature-triggered delivery of hydrophobic actives such as food flavourings or pharmaceutical ingredients. More work is needed in order to understand the reported discrepancies between phase transition temperatures measured by rheology and μ DSC.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.carpta.2021.100060.

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