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# Thermal gelation of mixed egg yolk/kappa-carrageenan dispersions

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ABSTRACT

This study aims to evaluate the effect of gum content and pH on the thermal gelation of mixed egg yolk/κ-carrageenan (EY/κC) dispersions, monitored by linear viscoelastic measurements.

Heat processing induces dramatic changes in the microstructure and viscoelastic properties of EY/κC systems, which may be attributed to a multistage mechanism that yields an interparticle gel network. An increase in κC content generally induces an enhancement in viscoelasticity. A reduction in pH hinders this enhancement and causes an anticipation of the multistage process, which confirms the importance of the electrostatic interactions of EY/κC dispersions.

The viscoelastic properties of EY/κC gels generally fit a master mechanical spectrum, which suggests that the protein matrix generally dominates the microstructure of EY/κC gels. However, SEM images reveal formation of a κC network at low pH, at which some κC autohydrolysis may also play a role. Electrostatic attractions seem to favour interactions among EY aggregates and κC into the carrageenan network.

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## 1. Introduction

Hen egg yolk is a multifunctional ingredient widely used in the manufacture of food products, since it provides an inexpensive and low calorie source of high-quality protein that possesses much appreciated organoleptic characteristics, distinctive colour and well-known functional properties (emulsifying, coagulating, and gelling properties).

In terms of composition, egg yolk is a complex association of lipids (33 wt%), proteins (17 wt%) and water (50 wt%) in which several types of solids are suspended in a protein solution or plasma (Pisuchpen, Chaim-ngoen, Intasanta, Supaphol, & Hoven, 2011). Plasma (about 78% of yolk dry matter) is composed of 85% low-density lipoproteins (LDLs) and 15% livetins. More specifically, LDL consists of spherical particles (17–60 nm in diameter) with a liquid core formed by 61–66% neutral lipids (triglycerides, cholesterol esters) surrounded by a layer of 21–23% phospholipids and 11–17% apoprotein (Cook & Martin, 1969). It is generally accepted that the structure of LDL is fairly stable and basically remains unaltered even after protein gelation (Kiosseoglou, 2003). Granules (about 22% of yolk dry matter) are non-soluble protein aggregates suspended in the plasma which are mainly constituted by high-density lipoproteins (HDLs) and phosvitin (70% and 16%, respectively) linked by phosphocalcic bridges (Li, Guo, Wei, MacDiarmid, & Lelkes, 2006; Yu, Fridrikh, & Rutledge, 2006; Zhang, Reagan, & Kaplan, 2009).

Polysaccharides are also available natural macromolecules which are commonly used as functional ingredients, aiming for contributing to the structure, texture and stability of food systems through their thickening or gelling behaviour. Carrageenan is a sulphated anionic polysaccharide obtained from red seaweeds that consists of a galactose backbone with different proportions and locations of ester sulphate groups. The main carrageenan types -kappa, iota and lambda- exhibit a wide spectrum of rheological profiles and interactions with other biopolymers (Dzenis, 2004).

As is well known, κ-Carrageenan forms thermo-reversible gels in aqueous solution and in presence of cations. Although the gelation mechanism is not fully understood, the model originally proposed by (Anderson, Dolan, & Rees, 1965) and subsequently modified by (Morris, Rees, & Robinson, 1980) is commonly accepted. At high temperature, κ-Carrageenan is presented as a random coil. On cooling, two-step gelation occurs and is characterised by a coil (disordered)-helix (ordered) transition followed by aggregation and network formation (Fernandez-Saiz, Lagaron, & Ocio, 2009). Conformational ordering of κ-carrageenan is promoted through lowering the electrostatic repulsion between the sulphate groups and by specific incorporation in the ordered struc-

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ture of large Group I cations such as $K^+$, $Rb^+$, and $Cs^+$, in preference to both smaller ($Li^+$ and $Na^+$) ions (Luo et al., 2010). However, divalent cations such as $Ca^{2+}$, and $Ba^{2+}$ can also lead to gelation (Morris, 1986), which suggests that gel formation depends to a great extent on the counterions size.

On the other hand, κ-Carrageenan solutions lose viscosity and gel strength when subjected to pH values below 5.5, but this effect is not significant for heat-set systems until pH lower than 4.3. This is caused by an autohydrolysis effect, occurring at low pH values as carrageenan in the acid form cleaves at the 3,6-anhydrogalactose linkage in the molecule (Hoffmann, Russell, & Gidley, 1996). The rate of autohydrolysis increases at elevated temperature and low cation levels. However, once the solution is cooled below the gelling temperature, potassium ions associate with the sulphate groups on the carrageenan, which has been found to prevent autohydrolysis (Imeson, 2009).

(Tolstoguzov, 2003) stressed out the importance of thermodynamic considerations in protein-polysaccharide interactions to design food formulations with novel or improved properties. (Ma, Kotaki, Yong, He, & Ramakrishna, 2005) reviewed the relative importance of non-covalent interactions, such as electrostatic interactions, steric exclusion, hydrophobic interactions and hydrogen bonding, between the particular molecules involved. A relatively strong electrostatic attraction between the two polymers could either result in soluble complexes evenly distributed throughout the entire system or in a two-phase system with an enriched phase in both associated polymers, which may be a coacervate or a precipitate. In contrast, if the environmental conditions led to repulsive interactions between polymers another two scenarios could be possible. Thermodynamic incompatibility has been reported by some authors in mixed system consisting of κ-Carrageean and different proteins, such as pea protein (Nunes, Raymundo, & Sousa, 2006), soybean isolate (Molina Ortiz, Puppo, & Wagner, 2004), fish gelatine (Haug, Draget, & Smidsrod, 2004), or β-lactoglobulin (Dumay, Laligant, Zasypkin, & Cheftel, 2011; Roesch, Cox, Compton, Happek, & Corredig, 2004). But, probably, the best known synergy is exhibited between carrageenan and positively charged amino acids of κ-casein micelles of milk proteins (Sambaer, Zatloukal, & Kimmer, 2012). On the other side, thermal stability of egg proteins have been investigated in presence of pectin or guar gum (Hernandez-Munoz, Kanavouras, Lagaron, & Gavara, 2005), modified starch (Grevellec, Marquie, Ferry, Crespy, & Vialettes, 2001), or different hydrocolloids gums including κ-carrageenan (Georgopoulos, Larsson, & Eliasson, 2004).

Furthermore, the effect of pH and protein-polysaccharide ratio on the linear viscoelastic behaviour of egg yolk/κ-carrageenan mixtures in aqueous solution and their heat-set gels was previously studied (Aguilar et al., 2011). And, recently, (Navidghasemizad, Temelli, & Wu, 2015) studied the types of interactions after mixing egg yolk components with some polysaccharides including ι-carrageenan. These authors evaluate their behaviour in selective phase separation of egg yolk proteins. Despite all the above developments, the complex interactions between egg yolk proteins and/or lipoproteins and polysaccharides have not been sufficiently studied, particularly when mixed systems are subjected to thermal processing.

The main objective of this work was the analysis of the effect of the progressive addition of kC on the behaviour of technical egg yolk over heat-induced gelation, at different pH values. To accomplish this objective, zeta-potential measurements of EY/κC dispersions were previously determined, whereas the thermal gelation process were continuously monitored by using linear viscoelastic measurements. Likewise, linear viscoelastic properties and microstructure of the heat-set gels obtained were also evaluated.

## 2. Experimental

### 2.1. Materials

κ-Carrageenan (κC) was kindly provided by Degussa (France) under Satiagel AMP45 trademark, containing 94.86 wt% kappa-carrageenan and 5.14 wt% iota-carrageenan. Egg Yolk (EY) was obtained from fresh chicken eggs purchased in a local market according to grade A and type L (63–73 g) commercial specifications, being discarded all damaged or cracked eggs. Hydrochloric acid (analytical grade) was purchased from Merck (Germany).

### 2.2. Methods

Chicken eggs were hand broken and the white was carefully separated from the yolk using the preparation method proposed by (Harrison & Cunningham, 1986). Afterwards, EY solid content wt% was quantified by loss of mass after drying some aliquots at 105 °C (±2 °C) in a temperature-controlled oven at atmospheric pressure for 24 h (Miranda, Partal, Cordobes, & Guerrero, 2002).

Native EY pH (close to 6.0) was determined for each sample using a digit 501 pH-meter (Crison, Spain) and EY/κC mixtures were prepared by dispersing different amounts of κC (0–0.5 wt%) in native EY containing $50.43 \pm 0.8$ wt% solids. Mixing was performed by using a mechanical stirring (300 rpm, 1 h) at room temperature. The initial pH of the system was modified by using hydrochloric acid (1 M and 2 M solutions) as acidulant up to the desired pH value (i.e. 3.5, 4.5, 5 or 6), and adding later the amount of demineralised water required to raise a 45 wt% solids content. It is worth mentioning that κC is not fully hydrated under the experimental mixing conditions. In fact, given the reduced amount of water required to prepare EY dispersions (from 50 to 45 wt%) it is not possible to use any pre-hydrated κC solution. Moreover, κC is added as late as possible, particularly at low pH, in order to minimize autohydrolysis.

Small-amplitude oscillatory shear (SAOS) measurements, including either stress sweep, frequency sweep or temperature ramp tests, were performed by means of controlled-stress rheometer Haake RS-300 (Thermo Scientific, Germany). A 20 mm plate–plate serrated geometry with 1 mm gap was selected for all measurements, except for kC solutions where a 60 mm hard anodized aluminium plate–plate geometry was used. All the samples were maintained in the sensor system for 20 min before running any rheological test, in order to reach temperature and structure equilibrium. To ensure a correct stress control, temperature ramp experiments, performed from 20 to 90 °C, were carried out into three zones using dynamic viscoelasticity monitoring (Cordobes, Partal, & Guerrero, 2004) at 1.5 °C/min heating rate and constant frequency ($2\pi$ rad/s). A shear stress sweep test was previously performed at a frequency of $2\pi$ rad/s for each region and sample to keep measurements within the linear response regime. Similarly, all the dynamic viscoelasticity frequency sweep measurements were carried out using a shear stress clearly lower than the critical value for linear viscoelasticity. At least two replicates were performed on each rheological measurement.

Zeta potential measurements of all the systems under study were performed using a Zetasizer Nano ZS (Malvern Instruments, U.K.). Aliquots of 0.5 g were diluted in deionised water up to 100 ml of total volume, keeping adjusted the pH value of the dispersion with 0.1 N HCl. Prior to analysis, the samples were tempered at 20 °C and stirred in order to keep the suspension homogeneous, avoiding segregation. The samples were measured in triplicate and each measurement was an average of twelve determinations. During the experiments, no flocculation was observed and each measurement was conducted at 20 °C. Zeta potential values were calculated from the electrophoretic mobility using the Henry equation and the Smoluchowski approximation (Aydt, Weller, & Testin, 1991)

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