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Release mechanism of omega-3 fatty acid in κ-carrageenan/polydextrose undergoing glass transition

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ABSTRACT

A high-solid matrix of κ-carrageenan with polydextrose was developed to entrap α-linolenic acid, which is an omega-3 bioactive compound. Physicochemical analysis of this system utilised modulated DSC, dynamic oscillation in shear, ESEM, FTIR and WAX diffraction. The carbohydrate matrix was conditioned through an extensive temperature range to induce changes in molecular morphology and identify the network glass transition temperature. Thermally induced variation in phase morphology was employed to rationalise transportation patterns of the bioactive compound within the high-solid preparation. Thus, experimental observations using UV–vis spectroscopy modelled diffusion kinetics to document the mobility arresting effect of the vitrifying matrix on the micro-constituent. Within the glass transition region, results argue that free volume theory is the molecular process governing structural relaxation. Further, Less Fickian diffusion follows well the rate of molecular transport of α-linolenic acid as a function of time and temperature of observation in the condensed matrix.

1. Introduction

α-Linolenic (ALA, C18:3, $n-3$) is a long chain polyunsaturated fatty acid with double bonds at 9, 12 and 15-carbon from the carboxylic acid end. This fatty acid is known as a precursor of longer chain omega-3 fatty acids including the eicosapentaenoic (EPA, C20:5, $n-3$) and docosahexaenoic (DHA, C22:6, $n-3$) acids. These lipids are considered to be essential to wellbeing, since they impart many health benefits and can only be acquired through the diet (Jacobsen, 2011). Consequently, attempts have been made to increase the level of α-linolenic acid in the diet by incorporating it in processed foods. The challenge remains, however, to efficiently design protective matrices in order to prolong bioavailability by limiting oxidation, due to the polyunsaturated nature of the fatty acid, in novel formulations (Ma, Floros, & Zieger, 2011).

Oxidation of omega-3 fatty acids leads to undesirable changes in sensory perception and nutritional profile. Thus, protective and controlled delivery of these essential fatty acids in processed foods attempts to significantly improve preservation status. Commonly, efforts focus on protocols of empirical utility that protect fatty acids against oxidative substances through encapsulation in biopolymer shells or physicochemical binding with antioxidants (Karmas, Buera, & Karel, 1992). Entrapment of essential fatty acid in condensed systems, i.e. above seventy percent solids in formulations, is increasingly of considerable interest (Karel et al., 1994). The novelty behind this approach lies in the phenomenon of glassy consistency that is common in dehydrated preparations being able to curb physicochemical, biological and enzymatic reactions (Le Meste, Champion, Roudaut, Blond, & Simatos, 2002).

Informed manipulation of structural functionality based on type and concentration of biopolymer, physicochemical environment, e.g. pH and/or ionic strength, and the addition of co-solute in the form of maltodextrins, sugar and their substitutes, engineers a temperature range of interest where molecular rearrangements are retarded (Farhat, Mousia, & Mitchell, 2003). Thus, the concept of glass transition temperature, T_g, has been evolved from an empirical index of convenience to a fundamental parameter that rationalises the preservation of bio- and technofunctionality in systems on the basis of an amorphous vitreous transition (Rieger, 2001). This has been used in following the glass-to-rubber transformation in a plethora of biomaterials (Gunning, Parker, & Ring, 2000) and, more recently, in the elucidation of diffusional kinetics of bioactive compounds in high-solid matrices; the examples of caffeine and vitamin B1 among others are cited here (Jiang & Kasapis, 2011; Panyoyai, Bannikova, Small, & Kasapis, 2015).

The current investigation aims to extend fundamental understanding on the physics and kinetic rates of molecular mobility in condensed carbohydrate matrices. It takes advantage of earlier work on structure formation based on associations between potassium ions and κ-carrageenan helices according to the domain

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model (Watase & Nishinari, 1982). It also utilises knowledge of the interactions between the polysaccharide and small molecule co-solute in high-solid preparations that can serve as the protecting matrix (Kasapis, 2001). Identification of the molecular processes and rates of α-linolenic acid diffusional mobility in a glassy matrix is of fundamental and technological consequence for potential applications in added value food and pharmaceutical industries.

2. Materials and methods

2.1. Materials

κ-Carrageenan was purchased from Sigma–Aldrich Co. (Sydney, Australia). The polysaccharide is extracted from *Euchema cottonii* type III and used as the basic material for further purification prior to our experimentation.

Polydextrose, as the co-solute, was Sta-Lite III powder, supplied by Tate & Lyle ANZ, Pvt. Limited (Decatur, IL). Based on the specification provided by the manufacturer, the powder is 90% pure with 4% moisture. Polydextrose comprises repeating glucose residues linked with 1,6-glycosidic linkage of approximately twelve molecules in the backbone to form a bulky amorphous structure.

α-Linolenic acid is a polyunsaturated fatty acid of *cis*, *cis*, *cis*, 9, 12, 15-octadecatrienoic conformation. It was the main constituent (70%) of the material obtained from Sigma–Aldrich Co. (Sydney, Australia), with the remaining being 20% linoleic acid and 10% oleic acid.

Potassium chloride was supplied by Sigma–Aldrich Co (Sydney, Australia) and Milli-Q water was used for ingredient hydration.

2.2. κ-Carrageenan purification

To better control the gelation process of the polysaccharide, ion exchange in the potassium form was implemented, as follows (Chen, Liao, & Dunstan, 2002; Evageliou, Kasapis, & Hember, 1998): Amberlite IR-120 was regenerated by eluting 200 g of the resin in 0.1 M HCl to the required pH 1. Remaining HCl was washed away and the resin was submerged to 2 M KCl solution to convert it from H^+ to K^+ form. Excess amounts of salt were removed by continuously rinsing with water and the filtrate was titrated with $AgNO_3$ until a colourless solution was obtained. Temperature of the resin was then increased to 90 °C to match that of 0.5% κ-carrageenan solution, and an ion exchanging step was carried out by mixing them for 30 min. The solution was collected, filled in 40 mm cellulose based semi-permeable tubes and dialysed by submerging in Milli-Q water overnight at room temperature. Preparations were freeze dried to obtain the material for subsequent experimentation.

κ-Carrageenan in the potassium form was subjected to atomic absorption spectrometry (Varian Inc., Palo Alto, USA). Ionisation of cations was performed in an air-acetylene flame, except for calcium that was determined using nitrous oxide–acetylene flame. Standard curves of cation concentration from 0.1 to 6.0 μg/ml were utilised for corresponding estimations in the experimental material. Sulphate content was determined following the method of Dodgson and Price (1962), with modification. In doing so, 0.5 g of the polysaccharide was hydrolysed with 1 M HCl for 30 min with boiling. Ten ml $BaCl_2$ (0.25 M) was added drop wise within 5 min of boiling, and the solution was cooled eventually to ambient temperature. It was then filtrated, with the precipitate being $BaSO_4$. That was rinsed several times and burned overnight in a furnace at 700 °C to obtain white ash. The initial weight of κ-carrageenan and remained ash were marked as W1 and W2, respectively, and their ratio was calculated using a conversion factor of 0.4116 for sulphate (Table 1).

Table 1
Composition of major cations and sulphate in unpurified and purified κ-carrageenan in the potassium form.

Cations	Unpurified κ-carrageenan (%, w/w)	Purified κ-carrageenan (%, w/w)
Potassium	6.275	7.455
Magnesium	0.092	0.043
Sodium	0.483	0.181
Calcium	1.132	0.211
Sulphate	17.834	18.088

2.3. Sample preparation

Various samples were prepared on a weight per weight basis including 2% κ-carrageenan, 85% polydextrose, 2% κ-carrageenan with 83% polydextrose, and 2% κ-carrageenan with 82% polydextrose and 1% linolenic acid following the same procedure. In the latter, for example, purified κ-carrageenan in the potassium form was used by dispersing appropriate amounts in Milli-Q water with constant stirring on a magnetic plate at 90 °C to form a clear solution within 10 min. Temperature was reduced to 80 °C and polydextrose was added to make up the required concentration in the mixture. Solutions were removed from the hotplate and linolenic acid, with 50 mM KCl, was added at 40 °C to the liquid phase. Besides the single polydextrose system, 50 mM KCl was incorporated to all other samples.

2.4. Oscillatory measurements

These were implemented using the Advanced Rheometer Generation 2 equipped with magnetic thrust bearing technology (TA Instruments, New Castle, DE). Samples were loaded onto the preheated Peltier plate at 80 °C with a 10 mm parallel plate measuring geometry and edges were covered with silicone oil (BDH, 50 cS) to minimise moisture loss. Cooling (followed by heating runs) was performed at 1 °C/min to −50 °C in controlled strain of 0.01% and constant oscillatory frequency of 1 rad/s (normal force was maintained at 0.05 ± 0.01 N). In addition, a series of mechanical spectra were taken within 0.1–100 rad/s every four degrees centigrade within the above temperature range. Thus, the transformation from glassy consistency to a melt was covered for implementation of the time–temperature superposition principle that generates the master curve of viscoelasticity. Isochronal and isothermal routines were carried out in duplicate returning consistent results.

2.5. Calorimetric analysis

Heating and cooling thermograms of high-solid preparations were performed on Q2000 (TA instruments, New Castle, DE) with a refrigerated cooling system (RCS90) and constant purging of nitrogen gas at a rate of 50 ml/min. T_{zero} aluminium pans were used to contain 10 mg sample and sealed hermetically, with empty pans being the reference. Enthalpic relaxation in relation to vitrification was monitored by heating or cooling the samples between 90 and −80 °C at 1 °C/min to follow the rheological protocol. Heat flow signals were calibrated using traceable indium standards (ΔH_f = 28.3 J/g) and the heat capacity response was measured with a sapphire standard. Modulation was 0.53 °C for every 40 s, and all measurements were performed in triplicate to yield effectively overlapping results.

2.6. Fourier transform infrared spectroscopy

FTIR spectra were recorded on a Perkin Elmer Spectrum 100 using MIRacle TMZnSe single reflection ATR plate system (Perkin Elmer, Norwalk, CT). Samples of κ-carrageenan, polydextrose,