



Controlled release of thiamin in a glassy κ -carrageenan/glucose syrup matrix



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ABSTRACT

The work dealt with the diffusional mobility of thiamin embedded in a high-solid matrix of κ -carrageenan with glucose syrup. It utilized thermomechanical analysis in the form of modulated differential scanning calorimetry and small-deformation dynamic oscillation in shear, Fourier transform infrared spectroscopy, wide angle X-ray diffraction, scanning electron microscopy and UV-vis spectrophotometry. The structural properties of the matrix were assessed in a temperature induced rubber-to-glass transformation. A thiamin-dye binding assay was employed to monitor the diffusion process of the vitamin from the high-solid preparation to ethylene glycol. The relationship between mechanical properties of the carbohydrate matrix and vitamin mobility was assessed *via* the application of the combined framework of the free volume theory and the predictions of the reaction rate theory. Results argue that the transport of the micronutrient is governed by the structural relaxation of the high-solid matrix. These were further treated with the concept of Fickian diffusion coefficient to provide the rate of the bioactive compound mobility within the present experimental settings.

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1. Introduction

Thiamin (vitamin B1) is the first member of a wide group of B complex vitamins. Staple foods like cereals, grains and rice as well as the various forms of dietary supplements (capsules, tablets, powder and gels) are vehicles for thiamin fortification (Bui, Small, & Coad, 2013). The consistency and retention of thiamin in these materials have been evaluated in relation to temperature, pH, water activity and added counterion (Bell & White, 2000; Bui & Small, 2007; Zhou & Roos, 2012). A recent approach in examining the stability of micronutrients in systems of industrial interest has been focusing on the phenomenon of glass transition that allows modeling of the time-temperature function during processing and subsequent storage (Lešková et al., 2006; Rahman, 2006). This is based on the expectation that in the glassy state various diffusion processes, and rates of physicochemical, enzymatic and biological reactions become extremely slow thus facilitating the preservation of nutrients in foodstuffs (Roos, 1995, 2003, 2010).

Thermoanalytical methods including modulated differential scanning calorimetry (MDSC) and dynamic mechanical analysis

(DMA) have become useful techniques in the determination of the glass transition temperature of condensed systems (Gunasekaran & Ak, 2000). Further work using small-deformation dynamic oscillation in shear offered an avenue to define a mechanical or network glass transition temperature with physical significance in biopolymer/co-solute preparations (Kasapis, 2006). It utilized the concept of free volume to follow the relaxation kinetics within the glass transition region as a function of solids content, polymer molecular weight and extent of counterion or thermally induced network formation in biomaterials (Kasapis, 2001, 2008; Kasapis, Mitchell, Abeysekera, & MacNaughtan, 2004).

κ -Carrageenan is the collective name of a family of sulphated galactans comprising an alternating $\alpha(1-3)$ -D-galactose-4-sulphate and $\beta(1-4)$ -3,6-anhydro-D-galactose (Morris & Chivers, 1983; Michel, Mestdagh & Axelos, 1997). The marine-based polysaccharide is extracted from red algae (*Eucheuma cottonii*) and is used extensively in the food industry as a gelling, thickening, stabilizing and water holding agent, diffusion controller, and texture enhancer (Campo, Kawano, da Silva & Carvalho, 2009; Michel et al., 1997). The rapid gelation of κ -carrageenan involves coil-to-helix transformation and aggregation of the ordered molecules with alkali metal ions (particularly those of potassium), sugars and polyols (Hermansson, Eriksson & Jordansson, 1991; Nishinari & Watase, 1992; Nishinari, Watase, Williams & Phillips, 1990). Recently, the effect of network formation in a high-solid system of κ -carrageenan

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and glucose syrup on the preservation and diffusion of caffeine as a typical psychoactive stimulant and diuretic in humans has been examined (Jiang & Kasapis, 2011).

Various micronutrients and antioxidants have been widely incorporated in delivery vehicles in the form of capsules, tablets or colloidal gels, which has generated great interest in fundamental approaches that build a foundation for the design and fabrication of food-grade systems targeting specific applications (Fisher & Windhab, 2011; Lesmes & McClements, 2009; Pothakamury & Barbosa-Cánovas, 1995). The current investigation aims to provide basic understanding on the physical mechanisms and transport rates of thiamin entrapped in a condensed matrix of κ -carrageenan/glucose syrup undergoing thermally induced vitrification.

2. Materials and methods

2.1. Materials

Glucose syrup, as the co-solute of this investigation, is a product of Edlyn Foods Pty Ltd (Sydney, Australia) with a dextrose equivalent (DE) value of about 42. The total level of solids in the stock solution is 81% (w/w), and percentages in the preparations of this investigation refer to dry solids. This is a non-crystalline material that converts from a viscous solution at ambient temperature to a rigid and transparent glass at subzero temperatures.

κ -Carrageenan, as the structuring agent of this investigation, is supplied by Sigma-Aldrich Pty Ltd (Sydney, Australia). The polysaccharide is extracted from *E. cottonii* type III and used as the basic material for further purification prior to our experimentation.

Thiamin. The vitamin in its hydrochloride form ($C_{12}H_{17}ClN_4OS \cdot HCl$ with a molecular weight of 337.27 g/mol) was obtained from Sigma-Aldrich Pty Ltd (Sydney, Australia). The material was in the form of small white crystals with an analytical grade of more than 99% purity.

Ethylene glycol was purchased at a spectrophotometric grade (purity of about 99.9%) from Sigma-Aldrich Pty Ltd (Sydney, Australia). It is commonly used as an antifreeze fluid for the preservation of biological tissues and organs. Our eye observations and calorimetric analysis at a scan rate of 0.1 °C/min showed that the freezing point of ethylene glycol was below -30 °C. This property facilitates its utilization as a stable liquid phase in the current experimental temperature range of -22 to 26 °C.

Thiamin hydrochloride analytical reagents. The acid dye, Alizarin Brilliant Violet R, was purchased from Jacquard (Healdsburg, USA) in the form of a violet powder. Chloroform was obtained from Sigma-Aldrich Pty Ltd (Sydney, Australia) and potassium dihydrogen phosphate, for the preparation of the phosphate buffer at pH 4.5, was purchased from BDH Chemicals Pty Ltd (Poole, England). Reagents were used without further purification and Millipore type II water was the diluent in all experiments.

2.2. The potassium form of κ -carrageenan

The material of this investigation was converted in the potassium form by ion exchange, as described by Evageliou, Kasapis, and Hember (1998). In doing so, an Amberlite IR-120 exchanging resin from Supelco (Bellefonte, Pennsylvania, USA) was used. Two hundred grams of the resin was first eluted with 0.1 M HCl to bring it to the hydrogen form until the eluent was at pH 1, and then with a solution of 2 M KCl to bring it to the potassium form. The resin was rinsed with millipore water to remove the excess of salt until there was no precipitation in the washings with 0.1 M silver nitrate, and was heated up to 90 °C with Millipore water.

Table 1

Cation and sulphate contents of the potassium κ -carrageenan, as compared to its commercial counterpart.

Ions	Commercial κ -carrageenan (% w/w)	Potassium κ -carrageenan (% w/w)
Potassium	6.5	7.8
Calcium	2.8	0.3
Sodium	0.7	0.1
Magnesium	0.2	0.02
Sulphate	17.8	17.5

Five grams of κ -carrageenan were transferred in a conical flask and dissolved with 1 L of Millipore water followed by heating to 90 °C on a hot plate with stirring. The hot resin was introduced into the polysaccharide flask and stirred for 30 min. κ -Carrageenan in the potassium form was separated from the resin, dialyzed against Millipore water for 24 h at 25 °C and freeze-dried using an Operon freeze dryer (Gimpo, Seoul, Korea).

The purity of the ion exchanged material was analyzed with an atomic absorption spectrometer (Agilent, Santa Clara, California, USA). K^+ , Na^+ and Mg^{2+} were identified using an air-acetylene flame whereas Ca^{2+} was determined with a nitrous oxide-acetylene flame. Calibration curves were constructed for each cation, with the absorbance readings versus cation concentration in ppm being expressed finally in percentages (w/w). The amount of sulfate was evaluated gravimetrically (Chan, Mirhosseini, Taip, Ling, & Tan, 2013). The method is based on sulfate hydrolysis with 1 M HCl and reaction of the sulfate groups with barium chloride leading to the formation of a white precipitate of barium sulfate. The sulfate content was calculated by multiplying the weight of barium sulfate with a conversion factor (0.4116) and expressing in percentages (w/w). All measurements were performed in triplicate and results are presented in Table 1.

2.3. Sample preparation

In general, samples were prepared at 85% (w/w) total solids. In doing so, κ -carrageenan in the potassium form was dispersed in Millipore water at 90 °C with constant stirring for 10 min and then the temperature was reduced to 70 °C. Appropriate amounts of glucose syrup were dissolved separately and added carefully to the polymer solution at the same temperature. The total level of solids was higher than the required final concentration but that was adjusted with the addition of thiamin hydrochloride, in a potassium dihydrogen phosphate buffer (50 mM, pH 4.5), to the viscous carbohydrate preparation at 30 °C to yield the experimental concentration of 1% thiamin with 2% κ -carrageenan and 82% glucose syrup (w/w).

The above conditions encourage smooth network formation and prevention of thiamin degradation (Imeson, 2000; Pachapurkar & Bell, 2005). Care was taken to dissolve the thiamin in the potassium dihydrogen phosphate buffer using an amber glass bottle. Beakers with final preparations were wrapped in aluminum foil and the top was sealed with a stretchable film to prevent exposure to light. Samples were kept overnight at 4 °C to allow sample equilibration and used subsequently to study the controlled release of thiamin in the polymeric matrix. Other samples without thiamin were made in a similar manner to analyze the structural properties of the matrix including single systems of 85% glucose syrup, and 83% glucose syrup with 2% κ -carrageenan (w/w).

2.4. Structural studies

2.4.1. Modulated differential scanning calorimetry

Measurements were performed using Q 2000 (TA Instruments, New Castle, DE). The instrument interfaced a refrigerated

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