Paper 3

by Vilia Paramita

Part 3

Encapsulation and Controlled Release

RELEASE MECHANISM OF ESSENTIAL FATTY ACIDS IN POLYSACCHARIDE MATRICES UNDERGOING GLASS TRANSITION

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ABSTRACT

Identification of theoretical mechanisms governing molecular diffusion of essential fatty acids (oleic and α-linolenic acid) in high solid matrices was carried out on two polysaccharide matrices of high-methoxy pectin and κ-carrageenan in the presence of co-solute glucose syrup and polydextrose, respectively. Physicochemical analysis of this system utilised modulated DSC, dynamic oscillation in shear, ESEM, FTIR and WAX diffraction. The carbohydrate matrices were 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 the fatty acids as a function of time and temperature of observation in the condensed matrices.

1 INTRODUCTION

Oxidation of essential fatty acids leads to undesirable changes in sensory perception and nutritional profile. Thus, protective and controlled delivery of essential fatty acids in processed foods attempts to significantly improve preservation status. Strategy for lipid preservation has been focused on controlling water and oxygen transports in biopolymer shells[1-3], however, limited information is available on the lipid diffusion in high solid system (>70% total solid).

The novelty behind the current approach elucidates the importance of glass transition temperature to control physicochemical, biological and enzymatic reactions[4]. Structural consistency during glassy state of biopolymers is taken as a limitation parameter on molecular rearrangements thus allows entrapment of small and large molecules[3,7]. Transformation of structural properties within the glass-to-rubber transformation of polymeric biomaterials was suggested to allow a controlled release of bioactive substances, i.e. caffeine and vitamin C[5-6]. The current investigation aims to extend fundamental understanding on the physics and kinetic rates of molecular mobility of essential fatty acids in condensed carbohydrate matrices for further potential applications in added value food and pharmaceutical products.

2 MATERIALS AND METHODS

2.1 Materials

Experiments were conducted in two systems, the first system consisted of 3% high methoxyl pectin and 81% glucose syrup with 1% oleic acid; the second system was 2% κ-carrageenan and 82% polydextrose with 1% α-linolenic acid.

High-methoxy pectin from citrus peel was purchased from Sigma Aldrich Co (Sydney, Australia) with a degree of methyl esterification (DE) of about 65%. Glucose syrup, the co-solute, was a product of Edlyn Foods Pty Ltd (Victoria, Australia). The total level of solids was 81% with 40-45% of glucose residues present as reducing end groups (dextrose equivalent, DE is about 42). 1-Oleoyl-*rac*-glycerol, as a source of oleic acid (OA) in its glyceride form, was obtained from Sigma Aldrich Co (Sydney, Australia). It contained 40% monoglyceride and 60% di- and triglyceride mixture (TLC).

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[8].

Polydextrose, as the co-solute, was Sta-Lite III powder, supplied by Tate & Lyle ANZ, Pvt. Limited (Decatur, IL). α-Linolenic acid is obtained from Sigma Aldrich Co (Sydney, Australia) with 70% purity with the remaining being 20% linoleic acid and 10% oleic acid.

2.2 Methods

2.2.1 Sample preparation. Polysaccharide solutions (high-methoxy pectin and purified κ-carrageenan) were dispersed in appropriate amounts in Milli-Q water with constant stirring on a magnetic plate at 90°C to form a clear solution within 10-20 min. Temperature was reduced to about 80°C upon mixing of co-solutes but further reduced to 50 and 40 °C, respectively, prior to oleic and linoleic acid, addition. To promote gelation, 2 M HCl was added dropwise to meet pH 3 to high-methoxy pectin/glucose syrup system and 50 mM KCl to κ-carrageenan/polydextrose system.
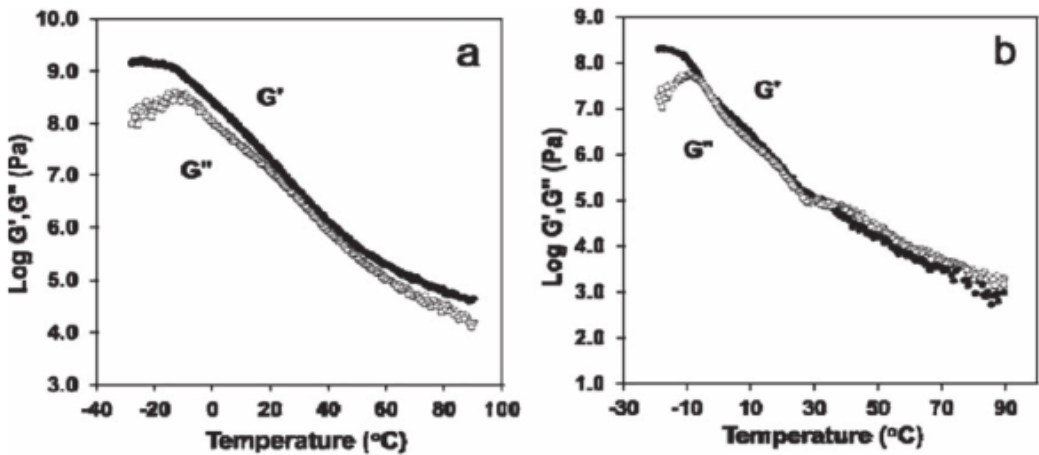
Figure 1 *Cooling profile of storage (G', •) and loss (G", ○) modulus for (a) the 3% high-methoxy pectin with 81% glucose syrup and 1% oleic acid, and (b)2% κ-carrageenan with 82% polydextrose and 1% α-linolenic acid (50 mM added KCl) at the rate of 1°C/min, frequency of 1 rad/s and strain 0.01%.*
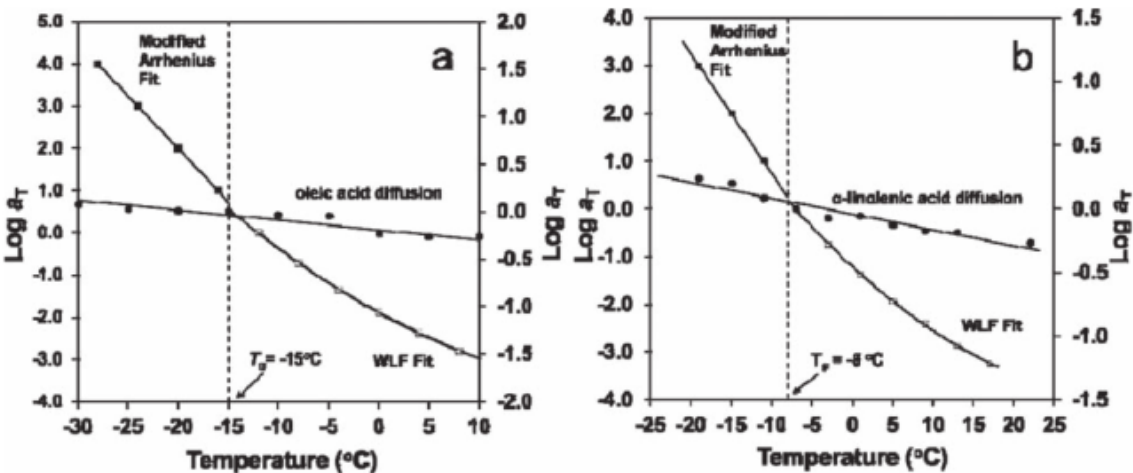

Figure 2 *Logarithmic shift factor (a_T) as a function of temperature within the glassy state (closed symbols) and glass transition region (open symbols) for (a) 3% high-methoxy pectin with 81% glucose syrup and 1% oleic acid (left y-axis), and for the oleic acid diffusion from the carbohydrate matrix at the reference temperature of -15°C (right y-axis), (b) 2% κ-carrageenan with 82% polydextrose and 1% α-linolenic acid (50 mM added KCl)(left y-axis), and for the α-linolenic acid diffusion from the carbohydrate matrix at the reference temperature of -7°C (right y-axis).*

Oscillation frequencies were taken within the whole range of experimental temperatures every 4 °C thus obtaining sequential trends of storage and loss moduli as a function of reduced frequency of oscillation (data not shown). The time-temperature superposition (TTS) principle was applied to construct a master

alongside the viscoelastic relaxation of the condensed matrix. The oleic acid mobility produces a good quality linear relationship that allows utilisation of the modified Arrhenius equation to estimate the energy of activation (E_a = 24 kJ/mol). This is contrasted with the corresponding value for the high-methoxy pectin/ glucose syrup system within the glassy state yielding an E_a value of 251 kJ/mol. Similarly, E_a = 20 kJ/mol was recorded for α-linolenic acid and 233 kJ/mol for κ-carrageenan/ polydextrose. Clearly, the energy barrier for structural relaxation of the carbohydrate molecules is much higher than for the diffusional mobility of the fatty acid.

Next, looking deeper into the mobility of the fatty acid by considering a Power Law equation that was first developed from Fick's Law to monitor the sorption/desorption of water molecules in breakfast cereals[13]:

$$\frac{M_t}{M_\infty} = kt^n \tag{5}$$

where, n is the kinetic diffusion exponent, M_t/M_∞ is the extent of fatty acids release at experimental and equilibrium time, k is a constant characteristic of the bioactive compound-polymer system and t is given in seconds.

Plotting the natural logarithms of M_t/M_∞ *versus* time from data in the first sixty minutes of experimental data in Figure 3, produces the required values of n and k for the various experimental temperatures range. The kinetic diffusion exponents (n) were calculated in this investigations to be from 0.20 to 0.34 for the high-methoxy pectin/ glucose syrup matrix and from 0.26 to 0.35 for κ-carrageenan/polydextrose system. Based on the Fick's Law, the ideal transport mechanism has an n-value equal to 0.5, whereas the rapid Case II transport is characterised by an n-value of 1.0. This makes the range of n-values between 0.5 and 1.0 a Non-Fickian or anomalous diffusion[14]. The low diffusion exponent of these investigations, i.e. Less Fickian with values below 0.5, reflects a low mobility due to the dense state of the vitrified polymeric matrix and the amphiphilic nature of α-linolenic acid that may interact in part with κ-carrageenan and/or polydextrose whilst oleic acid may undergo hydrophobic association with high-methoxy pectin/glucose syrup matrix.

Fick's second law can be further utilised to estimate the diffusion coefficient, D_{eff}, of a small molecule within solid-like macromolecular systems[14]. Simplification of Siepmann & Peppas (2011) equation for samples of slab shape where diffusion occurs through the slab's surface without any edge effects produces the following model[15-16]:

$$\frac{M_\infty - M_t}{M_\infty - M_i} = 4 \left(\frac{D_{eff}\, t}{\pi L^2}\right)^{1/2} \tag{6}$$

where, M_i, M_t and M_∞ denote the absolute amounts of the diffusant compound released at times zero, during experimentation and infinity/equilibrium, respectively, and L is the thickness of the slab.
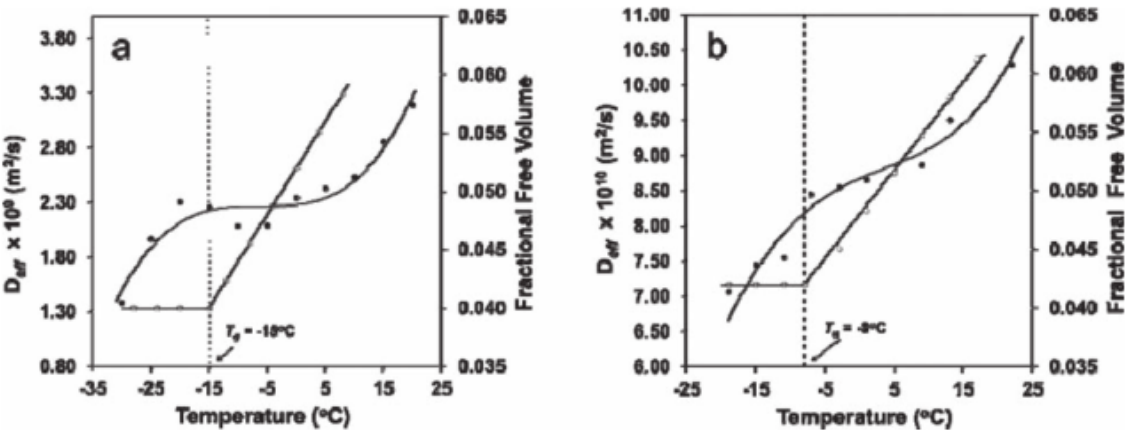
Figure 4 *Fractional free volume (○, trace on the right y-axis) of (a) 2% κ-carrageenan with 82% polydextrose and (b) 3 % high-methoxy pectin with 81% glucose syrup and relative diffusion coefficient of the fatty acids (oleic and linolenic acid, respectively) from these carbohydrate matrices within 60 min of observation (●, trace on the left y-axis).*

Figure 4 reproduces values of the diffusion coefficient over the temperature range that leads to carbohydrate vitrification. This is further compared with the fractional free volume of the matrix producing a discontinuity at the mechanical glass transition temperature. Clearly, vacant spaces amongst the adjacent macromolecules of carbohydrate matrices govern the nature and mobility rate of fatty acid in the vitrified matrix. Phenomenological estimations of the diffusion coefficient follow an approach that has proved to be a mainstay of utility in recording and then modeling experimental data to unveil the kinetics of drug delivery[15,16] Furthermore, interest in this work lies in proposing a relationship between free volume of the polymeric matrix and diffusion kinetics of the bioactive compound in the vitrified mixture.

3 CONCLUSIONS

Diffusion processes in manufactured food products are largely dominated by small molecules including oxygen, water and bioactive compounds. The present study examines the transportation mechanism of fatty acids within a carbohydrate matrix that undergoes a thermally induced glass transition. Informed manipulation of thermomechanical parameters and spectroscopic data documented the physics and kinetic rates of the release mechanism. The carbohydrate matrices are of an amorphous nature and exhibit a mechanical glass transition temperature that dictates the diffusional mobility of fatty acid. This is at its lowest within the glassy state where the free volume of the polymeric sample has collapsed to insignificant levels. The kinetic diffusion exponent and diffusion coefficient obtained from Fick's second law document a

controlled release process that is affected by the macromolecular system and the amphipathic nature of the micro-constituents.

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