



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

Vilia Darma Paramita, Anna Bannikova, Stefan Kasapis*

School of Applied Sciences, RMIT University, Melbourne, Victoria 3000, Australia

ARTICLE INFO

Article history:

Received 14 January 2015

Received in revised form 18 February 2015

Accepted 15 March 2015

Available online 21 March 2015

Keywords:

κ -Carrageenan

Polydextrose

α -Linolenic acid

Glass transition

Diffusion coefficient

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.

© 2015 Published by Elsevier Ltd.

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

* Corresponding author. Tel.: +61 3 992 55244; fax: +61 3 992 55241.
E-mail address: stefan.kasapis@rmit.edu.au (S. Kasapis).

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 AgNO₃ 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 μ g/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 BaCl₂ (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 BaSO₄. 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 pre-heated 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 \pm 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 ($\Delta H_f = 28.3$ 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,

large agglomerates with a relatively uneven surface (Fig. 5c), which contrast strongly with the featureless characteristics of the micrograph depicting condensed preparations at 85% solids (Fig. 5d). Composite matrices comprising the polysaccharide, the co-solute in the absence (Fig. 5e) or presence (Fig. 5f) of the fatty acid exhibit coherent structures that flow in amorphous streams, arguing for efficient entrapment of the micro-constituent within the dense carbohydrate matrix.

3.3. Release kinetics of α -linolenic acid in the κ -carrageenan/polydextrose system

The early work of Shimada, Roos, and Karel (1991) focused on oxygen permeability in an amorphous lactose matrix in relation to oxidation of methyl linoleate. The aim of the present study is to identify the physics and quantify the kinetics of fatty acid release within a glassy system. Release of the micro-constituent from the condensed κ -carrageenan/polydextrose matrix to dichloromethane was followed with the sulfo-phosphovanillin method. The assay is based on the hydrolysis of linolenic acid by sulphuric acid producing a carbonium ion that develops a pink adduct upon reacting with phospho-vanillin reagent. Colour is recorded as total fatty acid diffused to dichloromethane at $\lambda_{\max} = 525$ nm. The relationship between fatty acid concentration and absorbance returns a very acceptable fit that follows the Beer–Lambert Law from 0 to 0.998 AU (data not shown here).

Rate of fatty acid diffusion is presented in Fig. 6a extending for 3.5 h over the temperature range of -19 to 22 °C, which encompasses much of the glass transition region and the glassy state. Increasing time and temperature of observation results in higher release rates of the micro-constituent from the carbohydrate sample to dichloromethane. In particular, release is rapid in the first 60 min and approaches an asymptotic equilibrium at longer times of observation. The magnitude of increase varies from 0.30 AU at -19 °C to 0.95 AU at 22 °C over the timeframe of 3.5 h. Data is replotted as a function of temperature in Fig. 6b to demonstrate the drop in the values of absorbance within the glassy state of the κ -carrageenan/polydextrose matrix. Statistical analysis of data demonstrates that time and temperature significantly influence the rate of diffusion of the fatty acid in Fig. 6a ($p < 0.05$ from two-ways ANOVA test), and temperature intervals of four degree centigrade in Fig. 6b were also significant in changing molecular mobility ($p < 0.05$ from Tukey's post hoc analysis).

Absorbance–time data in Fig. 6a exhibited a very acceptable linearity ($r^2 = 0.962 \pm 0.020$) for all temperatures tested in the first 60 min and their gradient was employed to calculate the rate constant considering a zero-order reaction rate ($k = dx/dt$). Based on this, the concept of spectroscopic shift factor was developed for each experimental temperature, as follows (Kasapis & Shrinivas, 2010):

$$\log a_T = \log \frac{k_0}{k} \quad (4)$$

where k_0 is the rate constant at the reference temperature of -7 °C (as for the earlier studies of rheological simplicity in Fig. 3b).

Fig. 7 contrasts the molecular dynamics, as seen in shift-factor variation in relation to experimental temperature, for the polymeric sample and bioactive compound. The latter produces a good quality linear relationship that allows utilisation of the modified Arrhenius equation to estimate the energy of activation ($E_a = 20$ kJ/mol). This is contrasted with the corresponding value for the macromolecular system within the glassy state yielding an E_a value of 233 kJ/mol. Clearly, the energy barrier for structural relaxation of the carbohydrate molecules is much higher than for the diffusional mobility of the fatty acid. The two molecular processes exhibit distinct temperature profiles but it is the vitrification state

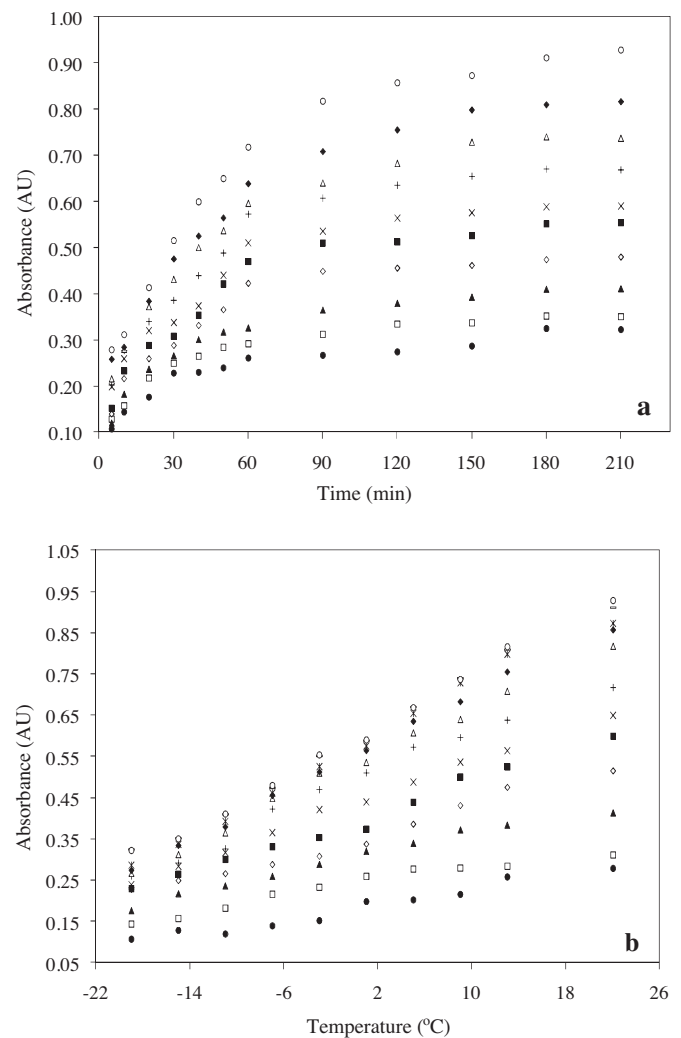


Fig. 6. (a) Absorbance of 1% α -linolenic acid diffused to dichloromethane from 2% κ -carrageenan with 82% polydextrose (50 mM added KCl) as a function of time of observation at -19 (●), -15 (□), -11 (▲), -7 (◇), -3 (■), 1 (×), 5 (+), 9 (△), 13 (◆) and 20 (○) °C obtained at 525 nm; (b) Absorbance of 1% α -linolenic acid diffused to dichloromethane from the same carbohydrate sample as a function of temperature at 5 (●), 10 (□), 20 (▲), 30 (◇), 40 (■), 50 (×), 60 (+), 90 (△), 120 (◆), 150 (°), 180 (–) and 210 (○) min obtained at the same wavelength.

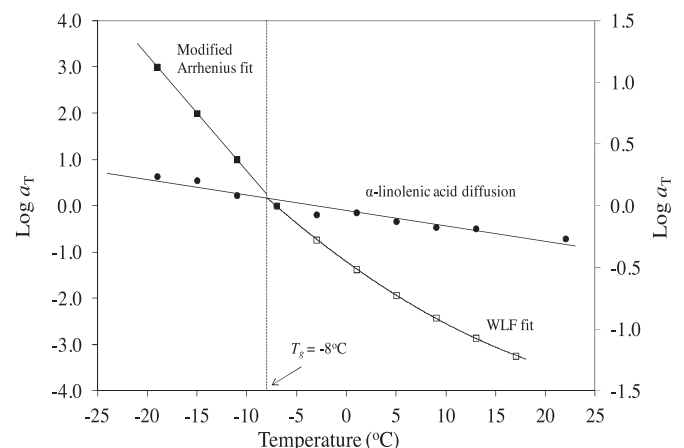


Fig. 7. Logarithmic shift factor as a function of temperature for 1% α -linolenic acid diffused to dichloromethane from the 2% κ -carrageenan with 82% polydextrose matrix at the reference temperature of -7 °C (trace on the right y-axis), with the structural relaxation of the carbohydrate matrix also shown within the glassy state and glass transition region (trace on the left y-axis).

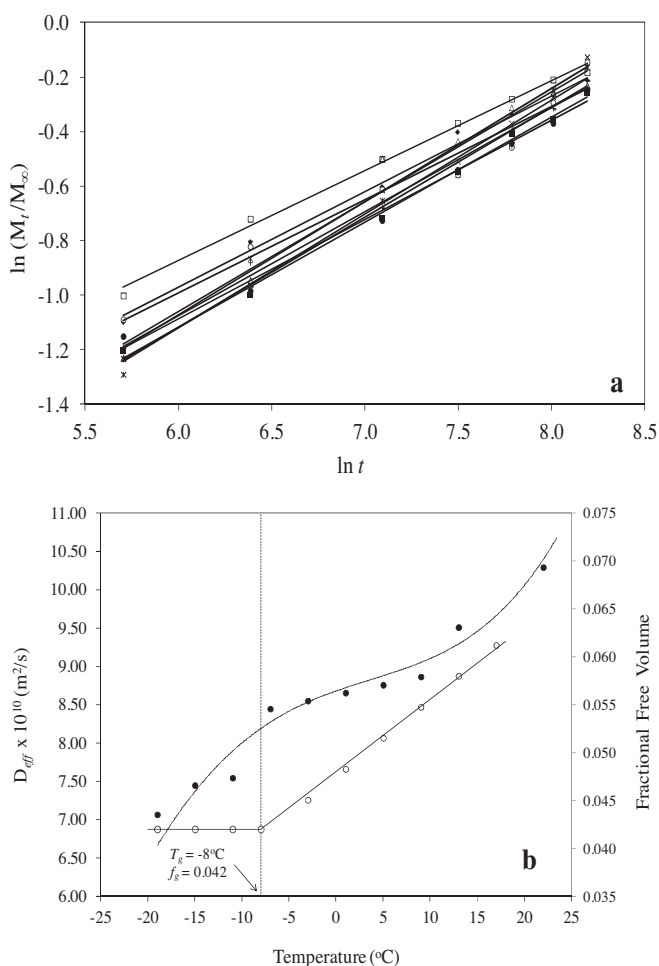


Fig. 8. (a) Variation of absorbance with different times of observation at -19 (\blacklozenge), -15 (\square), -11 (\triangle), -7 (\times), -3 ($*$), 1 (\circ), 5 ($+$), 9 ($-$), 13 (\bullet) and 22 (\blacksquare) $^{\circ}\text{C}$; (b) Fractional free volume of 2% κ -carrageenan with 82% polydextrose and 1% α -linolenic acid (\circ , trace on the right y-axis) and relative diffusion coefficient of the fatty acid from the same carbohydrate matrix within 60 min of observation (\bullet , trace on the left y-axis).

and free volume of the κ -carrageenan/polydextrose matrix that dictates the kinetic rates of α -linolenic acid transportation.

Next, we delved 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 (Ritger & Peppas, 1987; Singh & Chauhan, 2009):

$$\frac{M_t}{M_\infty} = kt^n \quad (5)$$

where n is the kinetic diffusion exponent, M_t/M_∞ is the extent of α -linolenic acid 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 60 min of Fig. 6a, produces the required values of n and k for the various experimental temperatures in Fig. 8a ($r^2 = 0.981 \pm 0.011$), which are reproduced in Table 2. The kinetic diffusion exponent in this investigation was found to vary from 0.26 to 0.35. Based on 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 (Bajpai, Bajpai, & Shukla, 2001). The low diffusion exponent of this investigation, i.e. Less Fickian with values below 0.5, reflects a low mobility due to the dense state of the vitrified polymeric matrix

Table 2

Variation of the kinetic diffusion exponent (n) and gel characteristic constant (k) for α -linolenic acid in κ -carrageenan and polydextrose.

Temperature ($^{\circ}\text{C}$)	Kinetic diffusion exponent, n	Gel characteristic constant, k	Diffusion mechanism
22	0.35	5.67E-04	Less Fickian
13	0.34	7.54E-04	Less Fickian
9	0.34	7.96E-04	Less Fickian
5	0.33	9.79E-04	Less Fickian
1	0.31	1.68E-03	Less Fickian
-3	0.34	8.31E-04	Less Fickian
-7	0.32	1.27E-03	Less Fickian
-11	0.32	1.24E-03	Less Fickian
-15	0.26	4.27E-03	Less Fickian
-19	0.28	2.73E-03	Less Fickian

and the amphiphilic nature of α -linolenic acid that may interact in part with κ -carrageenan and/or polydextrose.

Fick's second law can be further utilised to estimate the diffusion coefficient, D_{eff} , of a small molecule within a solid-like macromolecular system (Busk & Labuza, 1979; Crank, 1975):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (6)$$

where c is the concentration of the diffusant molecule, x is the relative distance travelled and t is time in seconds. Siepmann and Peppas (2011) integrated Eq. (6) for samples of slab shape, where diffusion occurs through the slab's surface without any edge effects, to produce the following error function series:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{D_{eff} t}{L^2} \right)^{1/2} \left[\left(\frac{1}{\pi^{1/2}} \right) + 2 \sum_{n=1}^{\infty} (-1)^n \text{ierfc} \frac{nL}{2\sqrt{D_{eff} t}} \right] \quad (7)$$

where the term $\text{ierfc } x$ represents the integrated complementary error function of x . Earlier work in various food systems demonstrated that only the first term in this series equation is of consequence, which yields the below relationship (Tutuncu & Labuza, 1996):

$$\frac{M_\infty - M_t}{M_\infty - M_i} = 4 \left(\frac{D_{eff} t}{\pi L^2} \right)^{1/2} \quad (8)$$

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.

Fig. 8b 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 of -8°C . As the fractional free volume increases from 0.042 in the glassy state to 0.061 at ambient temperature, values of diffusion coefficient also increase from 8.5×10^{-10} to $10.3 \times 10^{-10} \text{ m}^2/\text{s}$. A sudden drop in D_{eff} estimates down to $7.1 \times 10^{-10} \text{ m}^2/\text{s}$ is recorded at temperatures below the network T_g . Clearly, vacant spaces amongst the adjacent macromolecules of κ -carrageenan and polydextrose govern the nature and mobility rate of α -linolenic 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 modelling experimental data to unveil the kinetics of drug delivery (Siepmann & Siepmann, 2008). 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, as shown in Fig. 8b. Computer simulations have also been employed in an attempt to predict the techno-functionality of self-assembling colloidal materials (de las Heras, Tavares, & Telo da Gama, 2012).

We have shown earlier that high-solid polysaccharide/co-solute systems possess reduced level of cross-linking that allows undergoing a rubber-to-glass transformation (Kasapis, 2008). In terms of the atomic model of colloidal spheres with functional patches on the surface, this morphology could be seen as a percolated network of low-volume intermolecular associations being permanent, in supporting an amorphous state, within the timescale of observation. It has been reported in such simulation studies that a critical slow down in diffusion occurs at volume fractions accessible to spherical traces that fall below ~ 0.03 (Babu, Gimel, & Nicolai, 2008). This generic result of diffusion restriction based on accessible volume theory is consistent with the present study arguing for a rapid drop in the values of diffusion coefficient for α -linolenic acid once the fractional free volume of the κ -carrageenan/polydextrose matrix falls below ~ 0.04 .

4. 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 an omega-3 fatty acid 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 κ -carrageenan/polydextrose matrix is of amorphous nature and exhibits a mechanical glass transition temperature that dictates the diffusional mobility of α -linolenic 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 amphiphatic nature of the micro-constituent. Fig. 8b is a novel depiction of the relationship between free volume of the polymeric matrix and kinetics of diffusional mobility of the fatty acid that should determine stability and quality control in these product concepts.

References

- Al-Ruqaie, I. M., Kasapis, S., Richardson, R. K., & Gordon, M. (1997). The glass transition zone in high solids pectin and gellan preparations. *Polymer*, *38*, 5685–5694.
- Arridge, R. G. C. (1975). The glass transition. In R. G. C. Arridge (Ed.), *Mechanics of polymers* (pp. 24–50). Oxford: Clarendon Press.
- Babu, S., Gimel, J. C., & Nicolai, T. (2008). Tracer diffusion in colloidal gels. *Journal of Physical Chemistry B*, *112*, 743–748.
- Bajpai, A. K., Bajpai, J., & Shukla, S. (2001). Water sorption through a semi-interpenetrating polymer network (IPN) with hydrophilic and hydrophobic chains. *Reactive & Functional Polymers*, *50*, 9–21.
- Busk, J. R. G. C., & Labuza, T. P. (1979). A dye diffusion technique to evaluate gel properties. *Journal of Food Science*, *44*, 1369–1372.
- Chen, Y., Liao, M.-L., & Dunstan, D. E. (2002). The rheology of κ -carrageenan as a weak gel. *Carbohydrate Polymers*, *50*, 109–116.
- Crank, J. (1975). *The mathematics of diffusion*. Bristol: Clarendon Press.
- de las Heras, D., Tavares, J. M., & Telo da Gama, M. M. (2012). Bicontinuous and mixed gels in binary mixtures of patchy colloidal particles. *Soft Matter*, *8*, 1785–1794.
- Dodgson, K. S., & Price, R. G. (1962). A note on the determination of the ester sulphate content of sulphated polysaccharides. *Biochemical Journal*, *84*, 106–110.
- Evageliou, V., Kasapis, S., & Hember, M. W. N. (1998). Vitrification of κ -carrageenan in the presence of high levels of glucose syrup. *Polymer*, *39*, 3909–3917.
- Farhat, I. A., Mousia, Z., & Mitchell, J. R. (2003). Structure and thermomechanical properties of extruded amylopectin-sucrose systems. *Carbohydrate Polymers*, *52*, 29–37.
- Ferry, J. D. (1980). Dependence of viscoelastic behavior on temperature and pressure. In *Viscoelastic properties of polymers*. New York: John Wiley.
- Goff, H. D. (1992). Low-temperature stability and glassy state in frozen foods. *Food Research International*, *25*, 317–325.
- Guillén, M. D., & Cabo, N. (1997). Infrared spectroscopy in the study of edible oils and fats. *Journal of the Science of Food and Agriculture*, *75*, 1–11.
- Gunning, Y. M., Parker, R., & Ring, S. G. (2000). Diffusion of short chain alcohols from amorphous maltose-water mixtures above and below their glass transition temperature. *Carbohydrate Research*, *329*, 377–385.
- Jacobsen, C. (2011). Omega-3 polyunsaturated fatty acids (PUFAs) as food ingredients. In M. Saarela (Ed.), *Functional foods – concept to product* (2nd ed., pp. 401–424). Cambridge: Woodhead Publishing.
- Jiang, B., & Kasapis, S. (2011). Kinetics of a bioactive compound (caffeine) mobility at the vicinity of the mechanical glass transition temperature induced by gelling polysaccharide. *Journal of Agricultural and Food Chemistry*, *59*, 11825–11832.
- Karmas, R., Buera, M. P., & Karel, M. (1992). Effect of glass transition on rates of non-enzymic browning in food systems. *Journal of Agricultural and Food Chemistry*, *40*, 873–879.
- Karel, M., Anglea, S., Buera, P., Karmas, R., Levi, G., & Roos, Y. (1994). Stability-related transitions of amorphous foods. *Thermochimica Acta*, *246*, 249–269.
- Kasapis, S. (2001). The use of Arrhenius and WLF kinetics to rationalise the rubber-to-glass transition in high sugar/ κ -carrageenan systems. *Food Hydrocolloids*, *15*, 239–245.
- Kasapis, S. (2006). Definition and applications of the network glass transition temperature. *Food Hydrocolloids*, *20*, 218–228.
- Kasapis, S. (2008). Recent advances and future challenges in the explanation and exploitation of the network glass transition of high sugar/biopolymer mixtures. *Critical Reviews in Food Science and Nutrition*, *48*, 185–203.
- Kasapis, S., Al-Marhoobi, I. M., & Mitchell, J. R. (2003). Testing the validity of comparisons between the rheological and the calorimetric glass transition temperatures. *Carbohydrate Research*, *338*, 787–794.
- Kasapis, S., & Sablani, S. S. (2005). A fundamental approach for the estimation of the mechanical glass transition temperature in gelatin. *International Journal of Biological Macromolecules*, *36*, 71–78.
- Kasapis, S., & Shrinivas, P. (2010). Combined use of thermomechanics and UV spectroscopy to rationalize the kinetics of bioactive compound (caffeine) mobility in a high solids matrix. *Journal of Agricultural and Food Chemistry*, *58*, 3825–3832.
- Kibar, E. A. A., Gönenç, İ., & Us, F. (2013). Effects of fatty acid addition on the physicochemical properties of corn starch. *International Journal of Food Properties*, *17*, 204–218.
- Le Meste, M., Champion, D., Roudaut, G., Blond, G., & Simatos, D. (2002). Glass transition and food technology: A critical appraisal. *Journal of Food Science*, *67*, 2444–2458.
- Levine, H., & Slade, L. (1992). Glass transitions in foods. In H. G. Schwartzberg, & R. W. Hartel (Eds.), *Physical Chemistry of Foods* (pp. 83–222). New York: Marcel Dekker, Inc.
- Luk, E., Sandoval, A. J., Cova, A., & Muller, A. J. (2013). Anti-plasticization of cassava starch by complexing fatty acids. *Carbohydrate Polymers*, *98*, 659–664.
- Ma, U. V. L., Floros, J. D., & Zieger, G. R. (2011). Formation of inclusion complexes of starch with fatty acid esters of bioactive compounds. *Carbohydrate Polymers*, *83*, 1869–1878.
- Manoj, B., & Kunjomana, A. G. (2012). Study of stacking structure of amorphous carbon by X-ray diffraction technique. *International Journal of Electrochemical Science*, *7*, 3127–3134.
- Martins, J. T., Cerqueira, M. A., Bourbon, A. I., Pinheiro, A. C., Souza, B. W. S., & Vicente, A. A. (2012). Synergistic effects between κ -carrageenan and locust bean gum on physicochemical properties of edible films made thereof. *Food Hydrocolloids*, *29*, 280–289.
- Nishinari, K., Koide, S., Williams, P. A., & Phillips, G. O. (1990). A zipper model approach to the thermoreversible gel-sol transition. *Journal de Physique*, *51*, 1759–1768.
- Panyoyai, N., Bannikova, A., Small, D. M., & Kasapis, S. (2015). Control Release of thiamin in a glassy κ -carrageenan/glucose syrup matrix. *Carbohydrate Polymers*, *115*, 723–731.
- Probst, A. J., Holman, H. N., DeSantis, T. Z., Andersen, G. L., Birarda, G., Bechtel, H. A., et al. (2013). Tackling the minority: Sulfate-reducing bacteria in an archaea-dominated subsurface biofilm. *ISME Journal*, *7*, 635–651.
- Rieger, J. (2001). The glass transition temperature T_g of polymers – comparison of the values from differential thermal analysis (DTA, DSC) and dynamic mechanical measurements (torsion pendulum). *Polymer Testing*, *20*, 199–204.
- Ritger, P. L., & Peppas, N. A. (1987). A simple equation for description of solute release II. Fickian and anomalous release from swellable devices. *Journal of Controlled Release*, *5*, 37–42.
- Roos, Y. H. (2006). Phase transitions and transformations in food systems. In D. R. Heldman, & D. B. Lund (Eds.), *Handbook of food engineering* (2nd ed., pp. 287–352). Boca Raton: CRC Press, Taylor & Francis Group.
- Shimada, Y., Roos, Y., & Karel, M. (1991). Oxidation of methyl linoleate encapsulated in amorphous lactose-based food model. *Journal of Agricultural and Food Chemistry*, *39*, 637–641.
- Siepmann, J., & Peppas, N. A. (2011). Higuchi equation: Derivation, application, use and misuse. *International Journal of Pharmaceutics*, *418*, 6–12.
- Siepmann, J., & Siepmann, F. (2008). Mathematical modeling of drug delivery. *International Journal of Pharmaceutics*, *364*, 328–343.
- Singh, B., & Chauhan, N. (2009). Modification of psyllium polysaccharide for use in oral insulin delivery. *Food Hydrocolloids*, *23*, 928–935.
- Tipson, R. S. (1968). *Infrared spectroscopy of carbohydrate*. Washington: National Bureau of Standards, Monograph 10.
- Tutuncu, M. A., & Labuza, T. P. (1996). Effect of geometry on the effective moisture transfer diffusion coefficient. *Journal of Food Engineering*, *30*, 433–447.
- Watase, M., & Nishinari, K. (1982). The rheological study of the interaction between alkali metal ions and kappa-carrageenan gels. *Colloid & Polymer Science*, *260*, 971–975.
- Yang, L., & Paulson, A. T. (2000). Effects of lipids on mechanical and moisture barrier properties of edible gellan film. *Food Research International*, *33*, 571–578.