Governing Dynamic Diffusion of Fatty Acids in Polysaccharide/Co-Solute Systems

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BACKGROUND

Polyunsaturated fatty acids are compounds of significance in industrial processing. Recent molecular studies are mainly interested in control delivery of these fatty acids including prevention of their oxidation during preparation, processing and storage of food products. The working protocol of this research follows the "food materials approach", which aims to characterise the capacity of biopolymers structural relaxation to control diffusion of fatty acids in high-solid systems. Structure of composite biopolymers change from rubbery to a hard solid at vicinity of their glass transition temperature (T_g) thus limiting fatty acids mobility. Therefore, understanding the patterns of matrix relaxation will draw a clear picture of the molecular mobility of fatty acids. The matter will establish foundation to control delivery of fatty acids and chemical activities related to lipid oxidation in the high-solid system.

SIGNIFICANCE

- Improving food material processing and stability for industrial formulation.
- Preservation polyunsaturated fatty acids for further application in designing functional and supplemented foods for community.

MATERIALS AND METHODS

Materials:

(1) System 1: 3% high methoxy-pectin (HMP), 81% glucose syrup as co-solute and 1% oleic acid (omega-9 fatty acid).

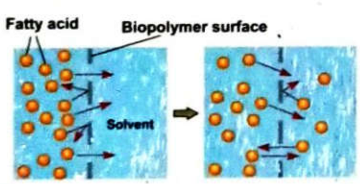
(2) System 2: 2% κ-carrageenan in its potassium form, 82% polydextrose as co-solute and 1% α-linolenic acid (omega-3 fatty acid).

Methods:

(1) Rheological characterisation: Small deformation oscillatory in shear using ARG-2

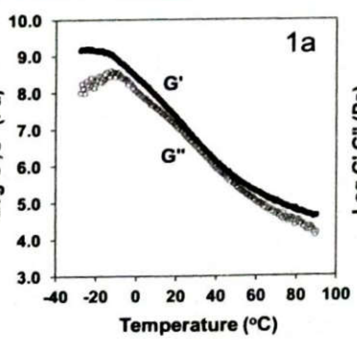
(2) Release kinetic based on difference on the gradient concentration between system and solvent using UV/VIS spectroscopy

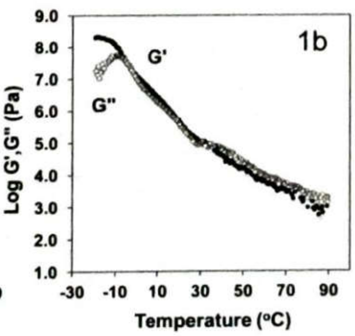
(3) Mathematical Modelling:
- Williams, Landel and Ferry equation
- Modified Arrhenius equation
- Fickian diffusion modelling



RESULTS

Rheological properties and determination glass transition temperature of the matrices





Viscoelastic history of high methoxy pectin/glucose syrup (**Fig.1a**) and κ-carrageenan/polydextrose systems (**Fig.1b**) in the presence of oleic and α-linolenic acid, respectively scanned at the rate of 1°C/min, frequency of 1 rad/s and strain 0.01%. Manifestation of shear moduli during cooling indicates glass transition state initiates by domination of storage (G') over loss (G") modulus. Further mathematical modeling was applied to the rheological data using the Williams, Landel and Ferry equation and modified Arrhenius prediction, as follows:

$$\log a_T = \log[G'(T)/G'(T_0)] = -\frac{(B/2.303f_0)(T-T_0)}{(f_0/\alpha_f)+T-T_0} \quad \& \quad \log a_T = \frac{E_a}{2.303R}\left(\frac{1}{T}-\frac{1}{T_0}\right)$$

Where a_T is shift factor, f_0 is the fractional increase in free volume at T_0, α_f is the thermal expansion coefficient, and the value of B = 1

Dynamic Diffusion of Polyunsaturated Fatty Acids in Polysaccharide/Co-solute Systems

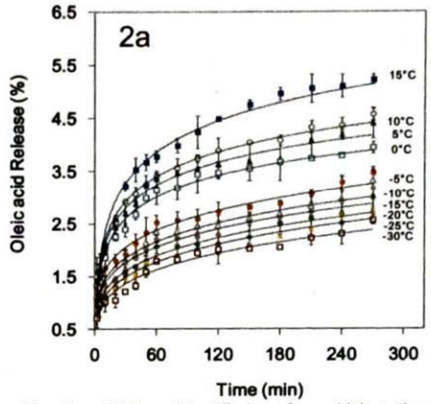


Fig 2a. Oleic acid diffusion from high-methoxy pectin/glucose syrup system.

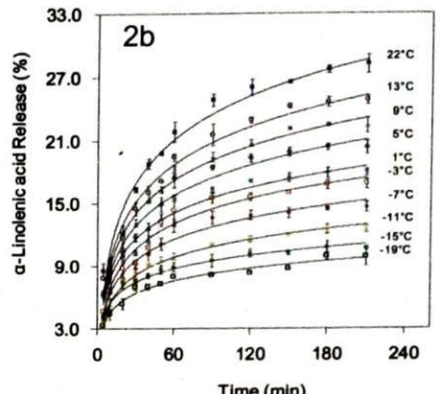
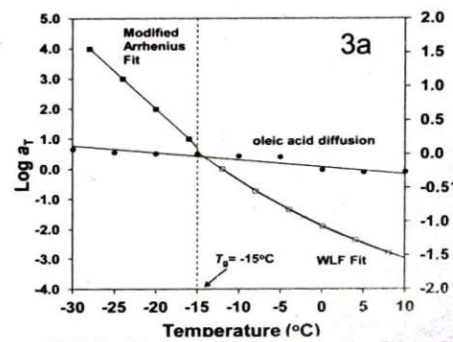


Fig.2b. α-linolenic acid diffusion from κ-carrageenan/polydextrose system.



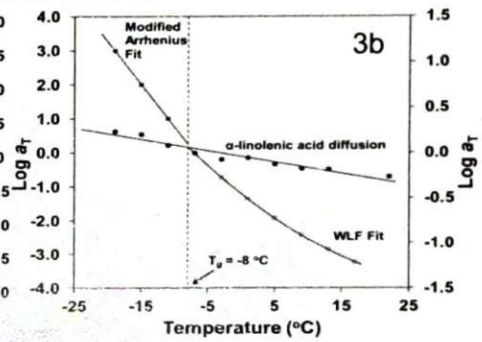
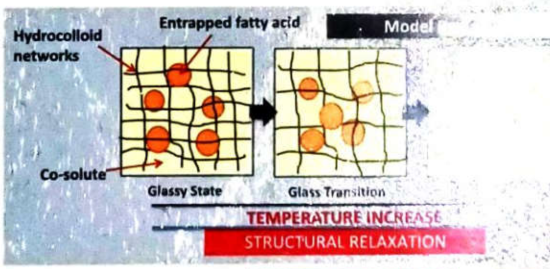


Fig 3. Predicted mechanical glass transition (T_g) for (a) high-methoxy pectin/glucose syrup and (b) κ-carrageenan/polydextrose systems.

Model



Diffusion Mechanism

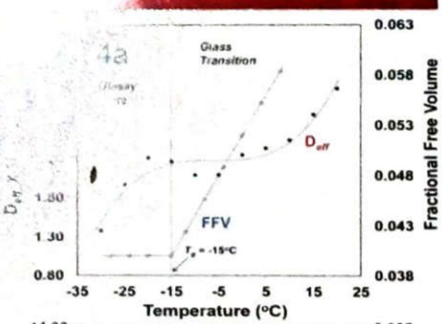
Release mechanism of fatty acids in condensed matrices of HMP/Glucose syrup (**Fig. 2a**) and κ-carrageenan/polydextrose (**Fig. 2b**) were quantified as the amount of mass diffused as a function of time and temperature. Fickian diffusion equation was used to model release mechanism, as follow:

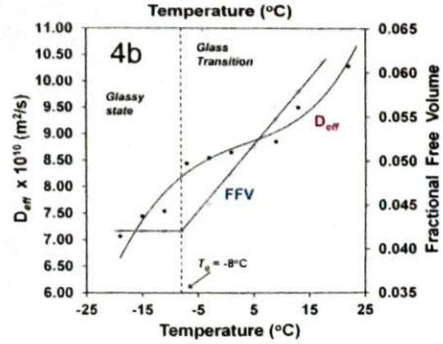
$$\frac{M_t}{M_\infty} = 4\left(\frac{D_{eff}\,t}{L^2}\right)^{1/2}\left[\left(\frac{1}{\pi^{1/2}}\right) + 2\sum_{n=1}^{\infty}(-1)^n \, ierfc\,\frac{nL}{2\sqrt{D_{eff}\,t}}\right]$$

Where D_{eff} is diffusion coefficient, M_t, M_∞ is mass release at time (t) and infinitive, L is distance.

Free volume theory in combination with the Fickian diffusion modeling indicated the structural dependency of molecular mobility of fatty acid in condensed matrix of biopolymer/co-solute following depletion in the free volume of the system (**Fig. 4a & 4b**).

Free Volume of Matrices vs ...oefficient (D_{eff}) of Polyunsaturated





CONCLUSIONS

- Experimental observations on diffusion of fatty acids suggested a limited release of fatty acids at temperatures below the recorded mechanical T_g.
- The mathematical approach affirmed the capacity of the biopolymers network relaxation to control release of fatty acids at the vicinity of glass transition phenomena.
- The Fickian diffusion modelling was brought in to quantify the rate of transport of bioactive compounds as a function of time and temperature.

Publications: *Food Hydrocolloids*, 2016, 53, 284–292. & *Carbohydrate Polymers*, 2015, 126, 141–149.

ACKNOWLEDGEMENTS

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