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A free-volume interpretation of the decoupling parameter in bioactive-compound diffusion from a glassy polymer

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ABSTRACT

Delivery of techno- and biofunctionality in all-natural processed foods is an area of steadily increasing fundamental and technological interest. We prepared a range of condensed biopolymer-vitamin systems and monitored the kinetics of bioactive compound release as a function of environmental temperature. Distinct patterns of structural relaxation were noted for the polymer matrix and microconstituent above the glass transition temperature of the high-solid sample. Then, there was a qualitative agreement between fractional free-volume of polymer and effective diffusion coefficient of vitamin within the glass transition region. These observations encouraged us to develop for the first time a mathematical expression that argues for linearity in the relationship between diffusion coefficient and inverse of fractional free volume yielding the so-called decoupling parameter of polymeric motion and small-molecule diffusion. Quantifying the cooperativity of vitamin and biopolymer interaction allows informed manipulation of bioactivity release, and the generic nature of the fundamental treatise invites validation in systems beyond the current range.

The concept of shifting a range of data, in relation to a reference temperature, obtained with physical techniques that include mechanical and visible spectroscopy for biopolymers and microconstituents, respectively, has been used widely to advance the technological functionality of systems based on amorphous synthetic polymers and high-solid biopolymers. Shifting data obtained for several high hydrostatic pressures, oscillatory frequencies or temperatures to a common experimental parameter allows making informed decisions on the usage of many biopolymer composites that are now available for the design of innovative condensed preparations (Dissanayake et al., 2012). The important physicochemical event of glass transition can thus be thoroughly identified and effectively utilised in molecular processes that govern multifaceted material processing, quality control or long-time safety and stability.

Industrial based research and development employs this approach to achieve accelerated testing that avoids the necessity of collecting a large population of data or imposing severe test conditions. The overriding assumption is of time-temperance equivalence where elevated temperature accelerates molecular phenomena thus reducing assessment time. Matching individually a list of experimental values against that of the reference temperature, T_o, generates a set of the so-called horizontal shift factors, a_T. In effect, the temperature dependent shift factor multiplies a frequency, ω, or divides a time, t, to yield a reduced parameter of ωa_T or t/a_T. Horizontal superposition of experimental data around T_o and plotting against the reduced parameter generates a master or composite curve (Lorenz, Pyckhout-Hintzen, & Persson, 2014). In terms of mechanical spectroscopy, the time-temperature superposition principle (*TTS*) generates master curves of the relaxation modulus, $G(t)$, or creep compliance, $J(t)$, that clearly disentangle the relative contribution of time and temperature functions to the overall viscoelastic response of a material.

The above discussion of thermorheological simplicity leads naturally to a plot of logarithmic shift factor as a function of experimental temperature that allows modelling of the kinetics of molecular mobility in the vicinity of the glass transition temperature, T_g. The approach is relevant to hydrophilic carrier materials in the glassy state, using at least in part a biopolymer matrix to hold and deliver a naturally found bioactive compound, which are of increasing interest in nutraceuticals and added value food formulations (Walker, Perkins, Kratz, & Raucher, 2012). Such design of control delivery vehicles that are able to provide specific and desirable release properties requires knowledge of the effect of

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polymeric structural relaxation on the diffusional mobility of entrapped bioactive molecules. That would then allow prediction of the exact mass transport mechanism and kinetic rate involved in the release profile of a bioactive agent.

To identify the relationship between structural relaxation of polymeric matrix and bioactive compound diffusion, we implemented the aforementioned approach, with some outcomes being reproduced in Fig. 1. Work included preparation of aqueous 9.5% (w/w) whey protein isolate suspensions, with about 92% (w/w) protein content, in the presence of 0.5% (w/w) nicotinic acid (also known as niacin or vitamin B3) at neutral pH. The whey protein-nicotinic acid suspension was spray dried at a flow rate of 8.5 mL/min, controlled air pressure of 250 kPa, and inlet and outlet temperatures of 120 and 75 °C, respectively. Creamy-white whey protein capsules have a narrow particle size distribution (diameter = 4.9 ± 0.2 μm), moisture content (%) on a wet basis of 9.4 ± 0.1, and an excellent encapsulation efficiency (%) of nicotinic acid (95.2 ± 0.7).

Small-deformation mechanical properties of whey protein microcapsules were examined in-tension using a Dynamic Mechanical Analyser. Work was performed in a single cantilever mode at a heating rate of 2 °C/min from −100 °C to 140 °C, with liquid nitrogen as the coolant, at a frequency of 1 Hz and a strain of 0.5 micrometer (or about 0.02%). Tensile storage modulus (E'), loss modulus (E'') and the damping factor ($tan\ \delta = E''/E'$) were thus evaluated. The mechanical glass transition temperature was pinpointed from the maximum point in the loss tangent and midpoint of the storage modulus trace, and it was found to be 30 ± 1 °C.

Results from the rheological analysis were fed into a Williams-Landel-Ferry (WLF) type of equation, which brings together the shift factor of horizontally superposed mechanical traces with the experimental temperature range (Kasapis, 2008):

$$-\log a_T = \frac{C'_{1g}(T - T_g)}{C'_{2g} + T - T_g} \tag{1}$$

For polymeric matrices and temperatures above the glass transition temperature, i.e. within the glass transition region, the following applies:

$$-\log a_T = \log[E'(T)/E'(Tg)] \tag{2}$$

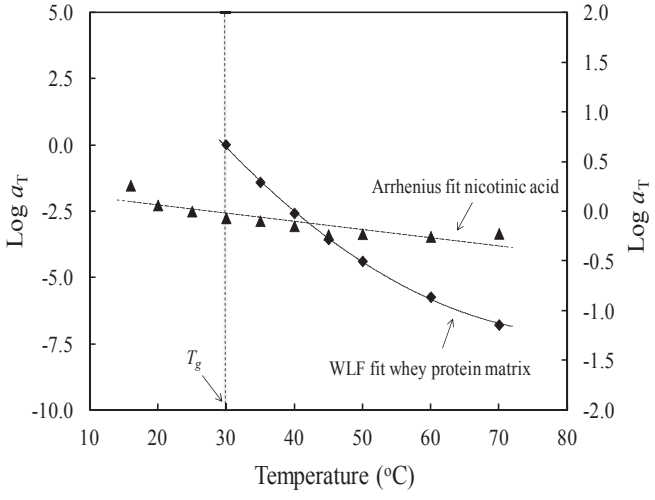

Fig. 1. Logarithmic shift factor, a_T, as a function of temperature for whey protein-nicotinic acid microcapsules (left y-axis, ◆), and nicotinic acid being diffused from the protein matrix to DMSO (right y-axis, ▲), with the arrow indicating the mechanical T_g.

$$C'_{1g} = C_{1g} \tag{3a}$$

$$C'_{2g} = C_{2g} \tag{3b}$$

where, C_{1g} and C_{2g} are known as the WLF parameters that relate to the fractional free volume at the glass transition temperature, f_g, as follows (Ferry, 1991):

$$C_{1g} = B/2.303f_g \tag{4a}$$

$$C_{2g} = f_g/\alpha_f \tag{4b}$$

where, α_f is the difference in the thermal expansion coefficients of the material above and below the glass transition temperature, and B is commonly set for simplicity to 1. For whey protein at $T \geq T_g$, this school of thought generates a non-exponential progression of viscoelastic functions as a function of experimental temperature, as shown in Fig. 1. It makes free volume the overriding molecular mechanism of structural relaxation in the polymeric matrix, which is characterised by $f_g = 0.029$ and $\alpha_f = 6 \times 10^{-4}\ deg^{-1}$; these values are according to experience from studies on the vitrification of amorphous synthetic polymers (Wang et al., 2004).

Once the polymeric part of the composite was studied, we turned our attention to the vitamin diffusion. That was monitored by transferring to the sample a solution of dimethyl sulfoxide (DMSO), which does not mix with whey protein but supports the solubility of nicotinic acid diffusing from the proteinaceous matrix. For each experimental temperature, aliquots of DMSO-niconic acid were obtained at regular time intervals and a colorimetric method based on the reaction amongst nicotinic acid, cyanogen bromide and sulfanilic acid was used to obtain absorbance values that reflected the vitamin release. A very acceptable linear relationship for the readings of absorbance *versus* time allows treating spectra as a zero-order kinetic reaction with the gradient being constant at $k = dx/dt$. A spectroscopic shift factor, $\log(k_o/k)$, was then advanced, where k_o is the rate constant at the reference temperature of 30°C (Kasapis & Shrinivas, 2010).

Spectroscopic shift factors for the molecular transport of nicotinic acid as a function of experimental temperature are also plotted in Fig. 1, and modelled using a modified expression of the Arrhenius equation, which utilises a set of two experimental temperatures (Mano & Viana, 2006):

$$a_T(T) = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{5}$$

where, E_a is the activation energy of molecular reorientation from one conformational state to another and R is the universal gas constant. Evidently, a highly linear correlation ($r^2 = 0.920$) is obtained for the progress in the spectroscopic shift factor with temperature. Activation energy for the diffusional mobility of the vitamin was thus estimated to be 10.2 kJ/mol, with the corresponding parameter for the whey protein matrix at the glass transition temperature of 30 °C being 256.9 kJ/mol. Results in Fig. 1 argue that although the glassy consistency of the proteinaceous matrix controls transport patterns of the vitamin, structural relaxation of the two constituents leading to molecular mobility in the composite follows distinct kinetic rates.

The above work dealt with the interplay between free volume theory and the predictions of the reaction rate theory in shaping up the vitrification properties of a high-solid biomaterial, which allowed the design of a composite incorporating a bioactive