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Rate of fatty acid transport in glassy biopolymers: A free volume based predictive approach

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ABSTRACT

Metastable properties of biopolymer networks affect significantly the diffusion kinetics of bioactive compounds. That was shown to be the case in high solid samples of protein and polysaccharide supporting a homogeneous distribution of polyunsaturated fatty acids. Thermomechanical behaviour of these matrices was characterised in relation to their glass transition temperature (T_g). A free volume theory of diffusion was considered to treat transport phenomena of fatty acids within glassy polymers. It was found that at $T > T_g$ the effective diffusion coefficient of microconstituent transport would increase in accordance with the free volume of the polymer matrix. Fitting experimental diffusivity data in glassy polymers to a free volume based theory generates a two-parameter equation that calculates the extent of molecular interaction between macromolecule and microconstituent. Gradual substitution of polymer with small-molecule co-solute, glucose syrup in this case, induces a plasticising effect that profoundly affects the level of interaction, hence the diffusion of fatty acids in the condensed biomaterial.

This article has been written in celebration of the scientific work of Professor Glyn O. Phillips on the occasion of his 90th birthday in 2017. He is a Founding Father of research in structure-function relationships of industrial hydrocolloids and Founder of the prestigious journal *Food Hydrocolloids*. We wish him many happy returns in leading the field of hydrocolloid research.

In the area of high-solid systems, biopolymer mobility at the vicinity of the glass transition temperature is related to complex molecular phenomena. Within the glass transition region, amorphous viscoelastic materials see a dramatic reduction in free volume with rapid cooling, which can be monitored as a broad variation in heat capacity or steady shear viscosity (Perez, 1990; Roudaut & Champion, 2011). The dramatic decrease in viscosity is accompanied by reduced thermal vibration leading to limited translational mobility that promotes physicochemical stability (Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Roudaut, Maglione, van Dusschoten, & Le Meste, 1990). Devitrification can be achieved by increasing the temperature above T_g, with the frozen-in molecules starting to resonate leading to a structural relaxation of the condensed matrix (Roudaut, Simatos, Champion, Countreras-Lopez, & Le Meste, 2004).

Mechanical properties of the polymeric material within the glass transition region can be followed with the free volume theory, as quantified by the Williams-Landel-Ferry (WLF) equation (Ferry, 1991; Kasapis, 2009, pp. 225–260). The approach is followed presently for several matrices based on natural polymers, i.e. high methoxy pectin/glucose syrup, κ-carrageenan/polydextrose, and whey protein/glucose syrup at various combinations: 100:0, 80:20, 70:30, 60:40, 40:60 and 0:100 (w/w).

We prepared polysaccharide matrices that were composed of 3% (w/w) high-methoxy pectin (HMP) with 81% (w/w) glucose syrup and 2% (w/w) κ-carrageenan with 83% (w/w) polydextrose. To each formulation, 1% (w/w) of fatty acid, i.e. oleic acid and α-linolenic acid were added, respectively. Polysaccharide powder was dissolved in Milli-Q water at about 90 °C, followed by cooling to 50 °C for the addition of co-solute. Temperature was decreased even further to 40 °C prior to fatty acid addition. A 2 M HCl solution was added to the HMP/glucose syrup mixture to obtain pH 3, which is needed for gelation, and 50 mM KCl solution was utilised for gelation of the κ-carrageenan/polydextrose sample. These were concentrated under vacuum to achieve 85% (w/w) total solids.

Whey protein/glucose syrup (wp/gs) matrices were prepared by dissolving whey protein isolate at ambient temperature for 2 h in Milli-Q water, diluting the glucose syrup solution in Milli-Q water and mixing them up at appropriate levels to create a system of 30% total solids. That was stirred for 15 min prior to addition of 1% (w/

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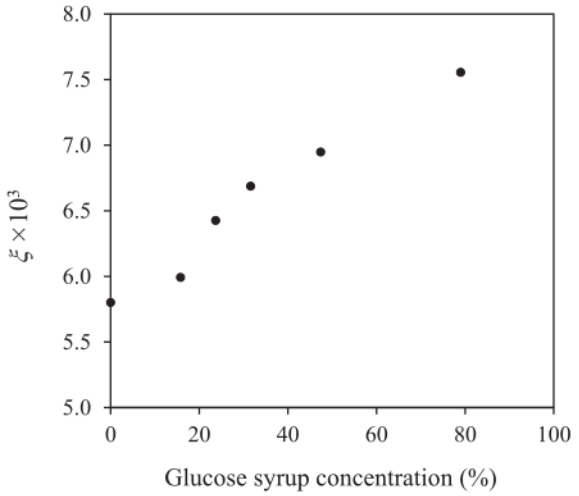

Fig. 3. Coupling parameters (ξ) of linoleic acid release from whey protein/glucose syrup matrices as a function of co-solute concentration (%).

Calculation of ξ values from Fig. 2 and equation (6) has been implemented for the polysaccharide and whey protein networks with glucose syrup or polydextrose, with outcomes being given in Table 1. These range from 4.25 to 7.55 × 10^{-3} and are in the same ballpark with earlier estimates on vitamin diffusion from condensed networks of natural polymers (Panyoyai & Kasapis, 2016). Moreover, these values have been plotted in Fig. 3 for the proteinaceous materials with increasing additions of co-solute.

In essence, they constitute evidence of the extent of interaction between the two constituents in the mixture and increase in an exponential fashion. This is due to the reduction in the critical molecular volume of the jumping unit of the polymer with the introduction of the low molecular weight co-solute (glucose syrup), with the critical molecular volume of linoleic acid remaining unaltered. Rapid redistribution of "hole-free volume" within the system facilitates jumping of fatty acids from one lattice point to another thus accelerating diffusion.

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