

# Paper B11

*by* Vilia Paramita

---

**Submission date:** 22-Apr-2023 02:38AM (UTC-0400)

**Submission ID:** 2072010556

**File name:** B11\_FH\_Journal.pdf (1.41M)

**Word count:** 7945

**Character count:** 41873



## Effect of co-solute concentration on the diffusion of linoleic acid from whey protein matrices



Vilia Darma Paramita, Jordan Domenic Lo Piccolo, Stefan Kasapis\*

<sup>12</sup> School of Science, RMIT University, Bundoora West Campus, Plenty Road, Melbourne, VIC 3083, Australia

### ARTICLE INFO

#### Article history:

Received 10 February 2017

Received in revised form

14 March 2017

Accepted 1 April 2017

Available online 5 April 2017

#### Keywords:

Whey protein

Glucose syrup

Linoleic acid

Glass transition region

Effective diffusion coefficient

### ABSTRACT

<sup>3</sup> Structural relaxation of a delivery vehicle has been identified in the literature as a limiting parameter for the controlled diffusion of a bioactive compound. To further examine the kinetics of controlled release, this study designed a system of homogeneously dispersed linoleic acid in a high-solid whey protein matrix. Amorphous glucose-syrup liquid was added systematically up to about 48% (w/w), with the total solids level in the formulation being kept constant at 80% (w/w), and experimental observations were obtained over a broad timeframe and temperature range. Structural and physicochemical properties of the blend were monitored using dynamic oscillation in-shear, WAXD, FTIR and confocal laser scanning microscopy. A specific chromogenic reaction with UV–vis spectroscopy was employed to follow the release of linoleic acid under perfect sink conditions. Variation in the amount of glucose syrup <sup>15</sup> the co-solute, within the high-solid whey protein network affected profoundly the values of the mechanical glass transition temperature. That was reflected in the kinetics of fatty acid diffusion from the glass transition region of our composite materials. Transport phenomena were quantified via the concept of effective diffusion coefficient, which increases with higher levels of glucose syrup leading to structural relaxation of the delivery vehicle.

© 2017 Published by Elsevier Ltd.

### 1. Introduction

In the last century, a plethora of studies documented that quenching of organic liquids may lead to a change in consistency, which is known as a vitreous solid or glass. Hardening takes place over a broad temperature range and without a maximum in the variation of heat capacity (Vreeswijk, Gossink, & <sup>1</sup>Levels, 1974). Experimental observations led us to understand that glass is a supercooled liquid whose therm <sup>1</sup> conversion is entirely distinct from the crystalline state, but in the nature of a second-order thermodynamic transition (Ngai, 2000). It is well known from differential scanning calorimetry, for example, that the supercooled thermogram of glycerol is characterised by a step-change in heat capacity with temperature at 190 K (Sou, Nishikawa, Koga, & Tozaki, 2011). In the case of hydrocolloids, which are quite poly-disperse, softening of matrices during the process of <sup>4</sup> vitrification occurs over a large temperature interval centred on a mean value called the glass transition temperature,  $T_g$  (Binder, Baschnagel, &

Paul, 2003). In the glassy state, which is the temperature range below  $T_g$ , materials exhibit high strength, brittleness and ultimately low molecular mobility that slows down dramatically physico-chemical and biological processes (Slade & Franks, 2002).

In view of the nature of this work, it is appropriate to mention concisely the approach used extensively by synthetic polymer scientists, with expertise in thermomechanical measurements, <sup>7</sup> acquire a mechanistic understanding of glass transition phenomena. This is based on the concept of free volume ( $v_f$ ) referring to the space between packing irregularities of macromolecules, which <sup>8</sup> is required for their string-like vibrations (Mansilla et al., 2013). Free volume is about thirty percent of the total (free plus occupied) volume in polymer melts, and the theory predicts that it collapses <sup>10</sup> to between two and four percent at the glass transition temperature depending on the rate of cooling and the density of the polymeric glass (Cangialosi, Schut, van <sup>11</sup> Leeen, & Picken, 2003). At this point, there is a discontinuity in the linear dependence of total volume with temperature leading to a reduction in the value (obtained from the linear gradient) of the thermal expansion coefficient, <sup>11</sup> Campbell & Vogt, 2007).

The free volume theory in the form of the Williams, Landel and Ferry (WLF) equation found widespread application not only in

<sup>12</sup>

\* Corresponding author.

E-mail address: [stefan.kasapis@rmit.edu.au](mailto:stefan.kasapis@rmit.edu.au) (S. Kasapis).

synthetic polymers but also in inorganic materials and low molecular weight organic liquids (Wang et al., 2003). This has prompted calls for utilisation of the equation in hydrocolloids where the process of vitrification might also be governed by free volume, i.e. being independent of chemical features (Dlubek, Fretwell, & Alam, 2000). In the case of whey protein, which is the subject matter of this investigation (and BSA), it was found that high-solid preparations undergo a rubber-to-glass transformation upon cooling following thermal denaturation. Values of  $T_g$  were pinpointed in the viscoelastic spectrum using the combined WLF/free volume approach that were affected considerably by the extent of thermal treatment, i.e. the density of intermolecular associations in the protein network (George, Lundin, & Kasapis, 2014). Introduction of small polyhydroxy compounds, e.g. glucose syrup or lactose, to concentrated whey protein systems reduces the glass transition temperature of the polymer due to the plasticizing effect of co-solute (Dissanayake et al., 2013).

Experimentation partnered with theoretical modeling of structural properties has been used as a useful avenue of developing technofunctionality for further explorations in biomaterials of added value. These include the design of a delivery vehicle for biofunctionality, which is a subject of steadily increasing scientific and technical importance in food and nutraceutical industries. Future research and development in these materials will deal with the optimisation of formulations for novel dosage forms of bioactivity. Within this broad area of high future potential, the present communication aims to study the kinetics of diffusional mobility of an essential fatty acid, linoleic acid, in relation to the content of plasticizing glucose syrup in a high-solid matrix of whey protein.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Whey protein isolate

The powder was obtained from Fonterra Co-operative Group Ltd (Palmerston North, New Zealand). It contained 90.4% protein (N x 6.38) and 4.7% moisture with the minor addition of carbohydrate, fat and minerals at 0.9, 0 and 3.0% (w/w), respectively. As a standard whey protein, it is mainly a mixture of  $\beta$ -lactoglobulin (~65%),  $\alpha$ -lactalbumin (~25%), bovine serum albumin (~8%) and immunoglobulins. It passed microbial tests, with the estimated amounts of yeast and mould being less than 10 cfu/g and 10,000 cfu/g, respectively. Physical tests showed a bulk density of 0.34 g/ml for the powder and pH 6.9 of 5% (w/w) solution at 20 °C.

#### 2.1.2. Glucose syrup

It was purchased in a viscous liquid form at ambient temperature from Edlyn Foods Pty Ltd (Melbourne, Australia). The total level of solids is 81% (w/w) and concentrations in this investigation refer to dry solids. About forty-five percent glucose residues is present as reducing end groups contributing to an overall dextrose equivalent, DE, of 42 for the sample. A trace of sodium is detected at about 0.005% (w/w).

#### 2.1.3. Linoleic acid (cis-9,cis-12-octadecadienoic acid)

It was purchased from Sigma Aldrich Co (Sydney, Australia). This fatty acid is a high purity product of  $\geq 98.5\%$ , as confirmed by GC analysis with an average molecular weight of 280.45 g/mol and density of 0.902 g/ml at 25 °C.

#### 2.1.4. Other reagents

Sulfo-phospho-vanillin (SPV) chemicals, i.e. a mixture of vanillin (99.0%), ethyl acetate ( $\geq 99.0\%$ ), phosphoric acid (85.0%), and sulphuric acid ( $\geq 98.0\%$ ) met AR standards for use in the chromogenic

assay of this work, and were obtained from Sigma Aldrich Co (Sydney, Australia). The same supplier also provided Nile red and acetone ( $\geq 99.5\%$ ) for lipid staining.

### 2.2. Sample preparation

High solid mixtures of whey protein/glucose syrup/linoleic acid were formulated using a systematic variation in the ratio of protein to co-solute: 100:0, 80:20, 70:30, 60:40, 40:60 and 0:100 (w/w) to make up 79% (w/w) total solids plus 1.0% (w/w) linoleic acid. In doing so, Milli-Q water was added to glucose syrup at ambient temperature and stirred thoroughly on a magnetic plate until a clear and homogeneous solution was obtained. An appropriate amount of whey protein was included to make up a dispersion of 30% (w/w) solids. That was stirred for 2 h and stored overnight at 4 °C to facilitate hydration and removal of air bubbles. Samples were collected and stirred for 15 min at ambient temperature before adding 1.0% linoleic acid. Tertiary preparations were mixed for another 30 min to enhance homogeneity and subjected to a homogenisation step for 3 min at 3000 rpm with a laboratory homogeniser (Ultra-Turrax T25, IKA-Labortechnik, Staufen, Germany). Finally, they were transferred to the evaporation flask of a rotary evaporator and concentrated up at 40 °C to achieve a level of 80% (w/w) solids. Concentrated matrices of 80% solids without linoleic acid were also prepared as the reference material.

### 2.3. Experimental analysis

#### 2.3.1. Rheological measurements

These were performed on a controlled strain rheometer (AR-G2 from TA Instruments, New Castle, DE) equipped with a magnetic thrust bearing technology. The instrument was connected to 60 L liquid nitrogen tank provide purging nitrogen gas for efficient subzero cooling. All samples were loaded onto the parallel plate geometry (10 mm diameter) of a Peltier device at 25 °C. Measuring gap of the two stainless-steel plates was 1000  $\mu$ m and silicone oil (BDH, 50 cS) was added at the edges to minimize sample moisture loss. Constant cooling rate of 1 °C/min, strain of 0.01% (within the linear viscoelastic region of the material; LVR), normal force at 0.08 N and oscillatory frequency of 1 rad/s during a temperature ramp from 25 to -55 °C were carried out to record the storage ( $G'$ ) and loss ( $G''$ ) modulus values in-shear. Mechanical spectra were also obtained at regular temperature intervals of 6 °C within the angular frequency range of 0.1–100 rad/s. Experimental work includes triplicate runs that yield effectively overlapping mechanical spectra.

#### 2.3.2. Fourier transform infrared spectroscopy (FTIR)

Spectra were recorded using Perkin Elmer Spectrum 100 FTIR Spectrometer (Norwalk, CT). Condensed samples of 79% whey protein/glucose syrup with 1% linoleic acid at the compositions described earlier, and single whey protein or glucose syrup at 80% solids (reference systems) were examined. They were placed on the surface of MTEC ZnSe single reflection ATR plate, scanned from 4000 to 600  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and averaged over thirty two scans. Each measurement was performed in triplicate.

#### 2.3.3. Wide angle X-ray diffraction (WAXD)

Freeze-dried tertiary mixtures and single globular protein or co-solute systems at a total solid level of 80% were examined for X-ray diffraction with Bruker D4 Endeavour (Karlsruhe, Germany). Diffraction patterns of bulk samples were subjected to accelerating voltage of 40 kV and current of 40 mA using a position sensitive detector (PSD) within the  $2\theta$  range of 5–90° in measuring intervals of 0.1°. Data were converted using DIFFRACplus Evaluation (Eva),

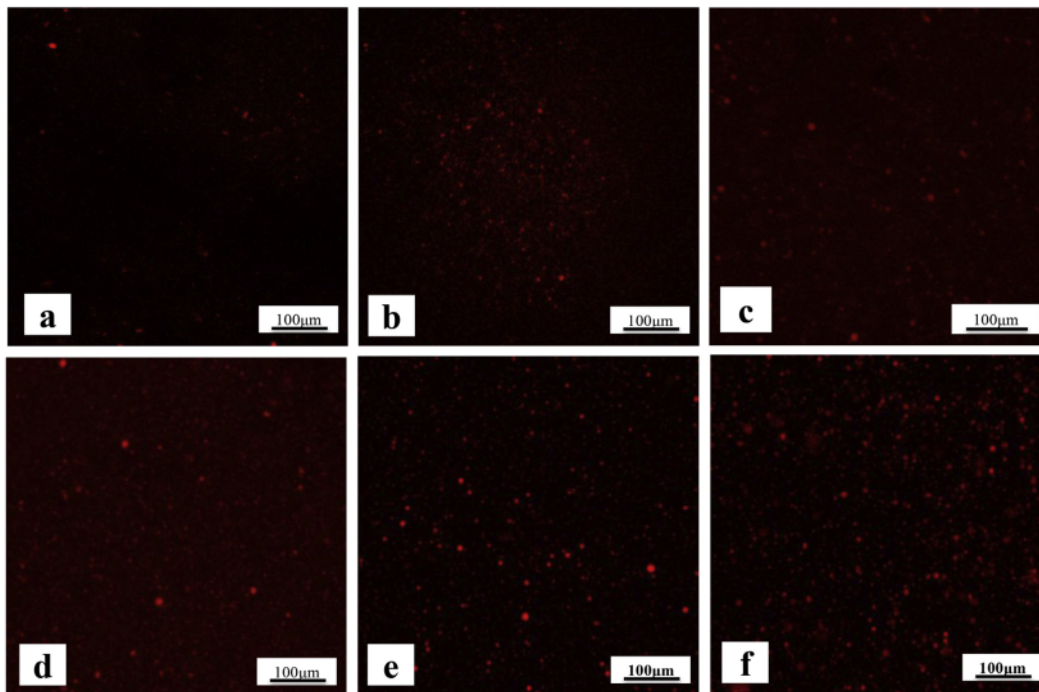


Fig. 6. CLSM images of 1% fatty acid entrapped in 79% total solids of whey protein/glucose syrup at (a) 100:0, (b) 80:20, (c) 70:30, (d) 60:40, (e) 40:60, (f) 0:100.

intervals corresponding to diffusion data of a wide temperature range (6 to  $-30^{\circ}\text{C}$ ) obtained for the six systems of whey protein and/or glucose syrup following 9 h of observation. At the high temperature end, describing conditions of the glass transition region, transport phenomena are at their highest level. The importance of the glassy state is documented at  $-30^{\circ}\text{C}$ , which lies below or above the  $T_g$  estimate in Table 1 for 100:0 and 0:100 whey protein/glucose syrup preparations, leading to contrasting low and high levels of fatty acid release.

Plasticisers like glucose syrup, water molecules, etc. are able to increase free volume by occupying space between polymeric chains and disturbing intermolecular hydrogen bonding that retard reformation of a rigid structure (Bocque, Voirin, Lapinte, Cailol, & Robin, 2016). This accelerates the diffusional mobility of small-molecules including the linoleic acid of this study. The effect of free volume in promoting microconstituent transport has been demonstrated by Maeda and Paul (1987) who recorded a six-order increment in oxygen diffusion as a result of free-volume increase in various polymeric matrices from about 0.03 to 0.21.

Plotting all diffusion data of linoleic acid against time of observation for each experimental temperature and whey protein/glucose syrup sample, subsets of which are shown in Fig. 7(a and b), generates good linear fits ( $r^2 = 0.97 \pm 0.01$ ), which indicate zero order release kinetics with the gradient being the rate constant ( $k = dx/dt$ ). This allows estimation of the so-called spectroscopic shift factor ( $\log a_T = \log k_0/k$ ), where  $k_0$  is the gradient of a reference temperature chosen arbitrarily within the experimental range of interest (Kasapis & Shrinivas, 2010). Fig. 8a illustrates an example of this approach for 40:60 wp/gS having a reference temperature of  $-34^{\circ}\text{C}$ . Good linear relationships were taken for  $\log a_T$  versus temperature plots ( $r^2 = 0.95 \pm 0.02$ ), which allow estimation of activation energy ( $E_{a, LA}$ ) for the diffusion of linoleic acid in all

samples shown in Table 1. These vary consistently, i.e. reduced, from 55 to 41 kJ/mol with increasing addition of glucose syrup in the system.

Fig. 8a also reproduces the corresponding mechanical shift factors obtained from the horizontal superposition of frequency sweeps in the glass transition region and glassy state of the 40:60 wp/gS composite; these were obtained from equations (1) and (2), and some outcomes of this type of modeling are also depicted in Fig. 3b. The modified Arrhenius fit yields an activation energy ( $E_{a, M}$ ) of 206 kJ/mol, which is considerably higher than for linoleic acid ( $E_{a, LA} = 42$  kJ/mol). Similar comparisons for all preparations in Table 1 underline the difficulty to structural relaxation in the polymer based matrix, as compared to the diffusional mobility of fatty acid. Theory of motion identifies the importance of segmental mobility in polymeric networks in allowing the diffusion of small molecules entrapped within the delivery vehicle at temperatures above  $T_g$  (Chan, Pathmanathan, & Johari, 1986; Roudaut, Simatos, Champion, COUNTERERAS-LOPEZ, & Le Meste, 2004; Tiemblo, Guzman, Riande, Mijangos, & Reinecke, 2001).

Once the physics of molecular diffusion and structural relaxation in the whey protein/glucose syrup/linoleic acid sample have been discussed, there is a need to advance the treatise in relation to the rate of mass transport (Crank, 1975, pp. 44–103; Roudaut, Van Dusschoten, Van As, Hemminga, & Le Meste, 1998; Siepmann & Siepmann, 2008). In doing so, we selected the generalised Fickian diffusion model, which has found widespread utility in model drug release for slabs:

$$\frac{M_{\infty} - M_t}{M_{\infty} - M_i} = 4 \left( \frac{D_{eff}}{\pi L^2} \right)^{1/2} \quad (3)$$

where,  $M_i$ ,  $M_t$  and  $M_{\infty}$  are the cumulative amounts of fatty acid

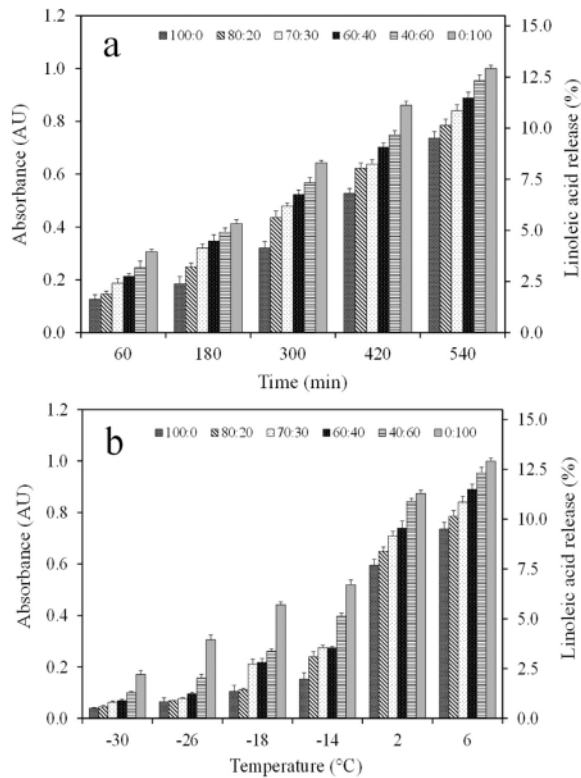


Fig. 7. Absorbance and percentage release of linoleic acid to ethyl acetate as a function of (a) time for mixtures comprising whey protein/glucose syrup at 6 °C as indicated and (b) temperature for the same mixtures after 9 h diffusion.

released at initial,  $t$  and infinite time, respectively;  $D_{eff}$  is the effective or apparent diffusion coefficient of the bioactive material that travels only in the  $L$  direction (Choi et al., 2005; Peppas & Peppas, 1994; Tutuncu & Labuza, 1996; Wang, Wu, & Lin, 2008).

Fig. 8b illustrates the values of diffusion coefficient as a function of temperature difference from the  $T_g$  estimates, i.e.  $T-T_g$ , for all samples of this investigation from equation (3). Gratifyingly, a smooth polynomial progression is obtained, especially for temperatures within the glass transition region, i.e.  $T > T_g$ , leading to higher molecular mobility. This is confirmed in Table 1 where  $D_{eff}$  increases from  $1.63$  to  $2.50 \times 10^{-10} \text{ m}^2/\text{s}$  with increasing addition of glucose syrup at  $-16$  °C, which is the highest recorded glass transition temperature and corresponds to the condensed whey protein matrix.

Our results add to the work by Champion, Hervet, Blond, Le Meste, and Simatos (1997) who reported higher fluorescein diffusion in sucrose-whey solutions with increasing temperature and moisture content. Contreras-Lopez, Champion, Hervet, Blond, and Le Meste (2000) argued that at least 10% polysaccharide (dextran, gum arabic or pullulan) is needed to have a significant effect on retarding the diffusion of sucrose in aqueous systems depending on the type of polymer. Diffusion of oxygen and various aroma compounds was also examined in relation to the physical ageing and glass transition temperature of natural polymers and edible films (Miller & Krochta, 1997; Tiemblo et al., 2001).

#### 4. Conclusions

The diffusion of linoleic acid molecules from the whey protein/

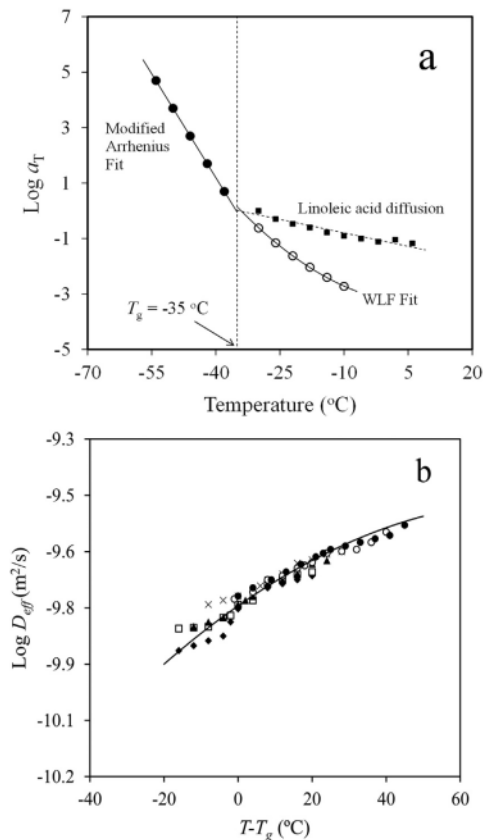


Fig. 8. (a) Spectroscopic shift factors of fatty acid diffusion in comparison to the mechanical shift factors of the whey protein/glucose syrup matrix at 40:60 (w/w) as a function of temperature and (b) Diffusion coefficients of linoleic acid in whey protein/glucose syrup matrices at 100:0 (●), 80:20 (□), 70:30 (▲), 60:40 (×), 40:60 (○) and 0:100 (●) as a function of  $T-T_g$ .

glucose syrup matrix was examined during vitrification of the condensed preparations. Results unveil the effect of rising molecular mobility in composite structures by increasing the level of small-molecule co-solute. It was documented that addition of distinct amounts of glucose syrup plasticised effectively the whey protein network, an outcome which was reflected in reduced values of the glass transition temperature. Generalised Fickian Law was utilised to generate effective diffusion coefficients, which increased smoothly with higher temperatures within the glass transition region of experimental preparations. It appears that the combined framework of glass transition and diffusion theory is robust enough to predict the lipid-matrix mobility for a broad temperature range above  $T_g$ . Thus, the effect of different levels of plasticiser on the diffusional kinetics of linoleic acid through condensed whey-protein networks was quantified.

#### References

- Angell, C. A. (2002). Liquid fragility and the glass transition in water and aqueous solutions. *Chemical Reviews*, 102, 2627–2650.
- Barth, A. (2007). Infrared spectroscopy of proteins. *Biochimica et Biophysica Acta (BBA) – Bioenergetics*, 1767, 1073–1101.
- Binder, K., Baschnagel, J., & Paul, W. (2003). Glass transition of polymer melts: Test of theoretical concepts by computer simulation. *Progress in Polymer Science*, 28, 115–172.

- Bocque, M., Voirin, C., Lapinte, V., Cailol, S., & Robin, J. J. (2016). Petro-based and bio-based plasticizers: Chemical structures to plasticizer properties. *Journal of Polymer Science, A: Polymer Chemistry*, 54, 11–33.
- Cakmak, G., Miller, L. M., Zorlu, F., & Severcan, F. (2012). Amifostine, a radio-protectant agent, protects rat brain tissue lipids against ionizing radiation induced damage: An FTIR microspectroscopic imaging study. *Archives of Biochemistry and Biophysics*, 520, 67–73.
- Campbell, C. G., & Vogt, B. D. (2007). Examination of the influence of cooperative segmental dynamics on the glass transition and coefficient of thermal expansion in thin films probed using poly(n-alkyl methacrylate)s. *Polymer*, 48, 7169–7175.
- Cangialosi, D., Schut, H., van Veen, A., & Picken, S. J. (2003). Positron annihilation lifetime spectroscopy for measuring free volume during physical aging of polycarbonate. *Macromolecules*, 36, 142–147.
- Champion, D., Hervet, H., Blond, G., Le Meste, M., & Simatos, D. (1997). Translational diffusion in sucrose solutions in the vicinity of their glass transition temperature. *The Journal of Physical Chemistry B*, 101, 10674–10679.
- Chan, R. K., Pathmanathan, K., & Johari, G. P. (1986). Dielectric relaxation in the liquid and glassy state of glucose and its water mixtures. *Journal of Physical Chemistry*, 90(63), 6358–6362.
- Choi, J. H., Choi, W. Y., Cha, D. S., Chinnan, M. J., Park, H. J., Lee, D. S., et al. (2005). Diffusivity of potassium sorbate in  $\kappa$ -carrageenan based antimicrobial film. *LWT*, 38, 417–423.
- Contreras-Lopez, E., Champion, D., Hervet, H., Blond, G., & Le Meste, M. (2000). Rotational and translational mobility of small molecules in sucrose plus polysaccharide solutions. *Journal of Agricultural Food Chemistry*, 48, 1009–1015.
- Crank, J. (1975). *The mathematics of diffusion*. Bristol: Clarendon Press.
- Dissanayake, M., Kasapis, S., George, P., Adhikari, B., Palmer, M., & Meurer, B. (2013). Hydrostatic pressure effects on the structural properties of condensed whey protein/lactose systems. *Food Hydrocolloids*, 30, 632–640.
- Dlubek, G., Fretwell, H. M., & Alam, M. A. (2000). Positron/positronium annihilation as a probe for the chemical environment of free volume holes in polymers. *Macromolecules*, 33, 187–192.
- Ferry, J. D. (1991). Some reflections on the early development of polymer dynamics: Viscoelasticity, dielectric dispersion, and self-diffusion. *Macromolecules*, 24, 5237–5245.
- George, P., Lundin, L., & Kasapis, S. (2013). Fundamental studies on the structural functionality of whey protein isolate in the presence of small polyhydroxyl compounds as co-solute. *Food Chemistry*, 139, 420–425.
- George, P., Lundin, L., & Kasapis, S. (2014). Effect of thermal denaturation on the mechanical glass transition temperature of globular protein/co-solute systems. *Food Hydrocolloids*, 41, 156–163.
- Grattard, N., Salaun, F., Champion, D., Roudaut, G., & Le Meste, M. (2002). Influence of physical state and molecular mobility of freeze-dried maltodextrin matrices on the oxidation rate of encapsulated lipids. *Journal of Food Science*, 67(8), 3002–3010.
- 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.
- Huang, Y., Szleifer, I., & Peppas, N. A. (2002). A molecular theory of polymer gels. *Macromolecules*, 35, 1373–1380.
- Kasapis, S., & Mitchell, J. R. (2001). Definition of the rheological glass transition temperature in association with the concept of iso-free-volume. *International Journal of Biological Macromolecules*, 29, 315–321.
- 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.
- Kavanagh, G. M., Clark, A. H., & Ross-Murphy, S. B. (2000). Heat-induced gelation of globular protein: Part 3. Molecular studies on low pH  $\beta$ -lactoglobulin gels. *International Journal of Biological Macromolecules*, 28, 41–50.
- Kilburn, D., Claude, J., Schweizer, T., Alam, A., & Ubbink, J. (2005). Carbohydrate polymers in amorphous states: An integrated thermodynamic and nano-structural investigation. *Biomacromolecules*, 6, 864–879.
- Kulmyrzaev, A., Bryant, C., & McClements, D. J. (2000). Influence of sucrose on the thermal denaturation, gelation, and emulsion stabilization of whey proteins. *Journal of Agricultural Food Chemistry*, 48, 1593–1597.
- Maeda, Y., & Paul, D. R. (1987). Effect of antiplasticizing on gas sorption and transport. III. Free volume interpretation. *Journal of Polymer Science: B: Polymer Physics*, 25, 1005–1016.
- Mansilla, M. A., Rodriguez Garraza, A. L., Silva, L., Salgueiro, W., Macchi, C., et al. (2013). Evolution of the free volume and glass transition temperature with the degree of cure of polybutadiene rubbers. *Polymer Testing*, 32, 686–690.
- Miller, K. S., & Krochta, J. M. (1997). Oxygen and aroma barrier properties of edible films: A review. *Trends in Food Science & Technology*, 8, 228–237.
- Mulvihill, D. M., & Donovan, M. (1987). Whey protein and their thermal denaturation – a review. *Irish Journal of Food Science and Technology*, 11, 43–75.
- Ngai, K. L. (2000). Dynamic and thermodynamic properties of glass-forming substances. *Journal of Non-crystalline Solids*, 275, 7–51.
- Peleg, M. (1992). On the use of the WLF model in polymers and foods. *Critical Reviews in Food Science and Nutrition*, 32, 59–66.
- Peppas, N. A., & Peppas, L. B. (1994). Water diffusion and sorption in amorphous macromolecular systems and foods. *Journal of Food Engineering*, 22, 189–210.
- Roudaut, G., Simatos, D., Champion, D., Contreras-Lopez, E., & Le Meste, M. (2004). Molecular mobility around the glass transition temperature: A mini review. *Innovative Food Science and Emerging Technologies*, 5, 127–134.
- Roudaut, G., Van Dusschoten, D., Van As, H., Hemminga, M. A., & Le Meste, M. (1998). Mobility of lipids in low moisture bread as studied by NMR. *Journal of Cereal Science*, 28(2), 147–155.
- Siepmann, J., & Siepmann, F. (2008). Mathematical modeling of drug delivery. *International Journal of Pharmaceutics*, 364(2), 328–343.
- Slade, L., & Franks, F. (2002). Appendix I: Summary report of the discussion symposium on chemistry and application technology of amorphous carbohydrates. In H. Levine (Ed.), *Amorphous food and pharmaceutical systems* (pp. x–xxvi). Cambridge: The Royal Society of Chemistry.
- Sou, K., Nishikawa, K., Koga, Y., & Tozaki, K. (2011). High-resolution calorimetry on thermal behavior of glycerol (l): Glass transition, crystallization and melting, and discovery of a solid–solid transition. *Chemical Physics Letters*, 506, 217–220.
- Tiemblo, P., Guzman, J., Riande, E., Mijangos, C., & Reinecke, H. (2001). Effect of physical aging on the gas transport properties of PVC and PVC modified with pyridine groups. *Polymer*, 42, 4817–4823.
- Tipson, R. S. (1968). *Infrared spectroscopy of carbohydrate*. Monograph 10. Washington: National Bureau of Standards.
- Tsui, N. T., Paraskos, A. J., Torun, L., Swager, T. M., & Thomas, E. L. (2006). Minimization of internal molecular free volume: A mechanism for the simultaneous enhancement of polymer stiffness, strength, and ductility. *Macromolecules*, 39, 3350–3358.
- Tutuncu, M. A., & Labuza, T. P. (1996). Effect of geometry on the effective moisture transfer diffusion coefficient. *Journal of Food Engineering*, 30, 433–447.
- Vreeswijk, J. C. A., Gossink, R. G., & Stevels, J. M. (1974). Nucleation kinetics and critical cooling rate of glass-forming liquids. *Journal of Non-crystalline Solids*, 16, 15–26.
- Wang, B., Gong, W., Liu, W. H., Wang, Z. F., Qi, N., Li, X. W., et al. (2003). Influence of physical aging and side group on the free volume of epoxy resins probed by positron. *Polymer*, 44, 4047–4052.
- Wang, J., Wu, W., & Lin, Z. (2008). Kinetic and thermodynamic of water sorption of 2-hydroxyethyl methacrylate/styrene copolymer hydrogels. *Journal of Applied Polymer Science*, 109, 3018–3023.

# Paper B11

---

## ORIGINALITY REPORT

---

12%

SIMILARITY INDEX

9%

INTERNET SOURCES

11%

PUBLICATIONS

1%

STUDENT PAPERS

---

## PRIMARY SOURCES

---

1

[tr.scribd.com](https://tr.scribd.com)

Internet Source

1%

---

2

[docksci.com](https://docksci.com)

Internet Source

1%

---

3

[www.researchgate.net](https://www.researchgate.net)

Internet Source

1%

---

4

Diah Ikasari, Vilia Darma Paramita, Stefan Kasapis. "Glass transition effects on the molecular transport of caffeine from condensed  $\kappa$ -carrageenan/ polydextrose systems", Food Hydrocolloids, 2021

Publication

1%

---

5

Paul George, Leif Lundin, Stefan Kasapis. "Fundamental studies on the structural functionality of whey protein isolate in the presence of small polyhydroxyl compounds as co-solute", Food Chemistry, 2013

Publication

1%

---

6

[bio-protocol.org](https://bio-protocol.org)

Internet Source

1%

---

7	<p>Paul George, Leif Lundin, Stefan Kasapis.        "Effect of thermal denaturation on the mechanical glass transition temperature of globular protein/co-solute systems", Food Hydrocolloids, 2014</p>	1 %
Publication		
8	<p>"Glass Transition and Phase Transitions in Food and Biological Materials", Wiley, 2017</p>	1 %
Publication		
9	<p>Naksit Panyoyai, Anna Bannikova, Darryl M. Small, Robert A. Shanks, Stefan Kasapis.        "Diffusion of nicotinic acid in spray-dried capsules of whey protein isolate", Food Hydrocolloids, 2016</p>	1 %
Publication		
10	<p>Vilia Darma Paramita, Stefan Kasapis.        "Molecular dynamics of the diffusion of natural bioactive compounds from high-solid biopolymer matrices for the design of functional foods", Food Hydrocolloids, 2018</p>	1 %
Publication		
11	<p>core.ac.uk</p>	1 %
Internet Source		
12	<p>isiarticles.com</p>	1 %
Internet Source		
13	<p>Omar Almrhag, Paul George, Anna Bannikova, Lita Katopo, Deeptangshu Chaudhary, Stefan</p>	1 %



Kasapis. "Analysis on the effectiveness of co-solute on the network integrity of high methoxy pectin", Food Chemistry, 2012

Publication

---

14

P.J. Torley, J. de Boer, B.R. Bhandari, S. Kasapis, P. Shrinivas, B. Jiang. "Application of the synthetic polymer approach to the glass transition of fruit leathers", Journal of Food Engineering, 2008

Publication

---

1 %

15

vdoc.pub

Internet Source

---

1 %

---

Exclude quotes      On

Exclude matches      < 1%

Exclude bibliography      On