AGING OF AMORPHOUS RASPBERRY POWDER: ENTHALPY RELAXATION AND FRAGILITY

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ABSTRACT

Enthalpy relaxation experiments were conducted in freeze-dried raspberry powder at 5, 10 and 15°C below its onset glass transition temperature (T_{gi}) using differential scanning calorimetry (DSC). No statistical significant differences ($p > 0.05$) in glass transition temperatures were observed for the raspberry powders aged at (T_{gi} - 5), (T_{gi} - 10), and (T_{gi} - 15) from 6 to 96 h. The non-exponential behavior of enthalpy relaxation in raspberry powder was fitted with the Kohlrausch-Williams-Watts (KWW) model. The mean relaxation time constant (τ) (1017.4 h) for raspberry powder aged at the temperature (T_{gi} - 15) was greater than the τ (147.1 h) at (T_{gi} - 5). The KWW model parameter β values for freeze-dried raspberry powders were greater than the β values of pure food constituents. The activation energy for enthalpy relaxation in the glassy state was determined as 145.4 kJ/mol by approximating with the Arrhenius equation. The dependence of mean relaxation time on temperature followed an Arrhenius behavior indicating raspberry powder is a strong system. Several approaches were used to classify raspberry powder into strong/fragile system. There is a difference among fragility parameters of raspberry powders determined using selected methods.

Keywords: Arrhenius equation, differential scanning calorimetry, glass transitions, KWW equation, VTF equation

INTRODUCTION

Constituents of many processed foods such as milk powder, instant coffee, infant formula, biscuits and cookies, extruded cereals, pasta, beverage mixes and culinary food powders exist in an amorphous state. Amorphous systems are characterized by short-range molecular arrangement but lack long-range order, while crystalline systems exhibit three dimensional long range order (Yu, 2001). Amorphous glassy materials are thermodynamically non-equilibrium systems, which tend to reach equilibrium super cooled liquid state over extended periods of time when aged below their glass transition temperatures (Gupta et al., 2004; Wungtanagorn and Schmidt, 2001a & b). This change in the thermodynamic properties of the glassy materials towards equilibrium is described as physical aging or enthalpy relaxation (Struik, 1978). The macroscopic properties of glassy materials, such as the volume, enthalpy, refractive index, electrical conductivity and viscosity, change as materials approach the equilibrium state over a long time (Yu, 2001; Hilden and Morris, 2004). The changes in macroscopic properties of low moisture amorphous foods during storage may adversely affect their nutritional and sensory qualities (Farahnaky et al., 2008). Some amount of energy is lost/relaxed in the form of enthalpy during the nonequilibrium glassy to equilibrium super cooled liquid transition in a glassy system (Gupta et al., 2004). This lost energy is recovered during the reheating of the glassy system using a DSC and the enthalpy recovered is a measure of molecular mobility of the system at the selected temperature (Gupta et al., 2004). A large number of studies are reported relating physical aging or enthalpy relaxation of synthetic polymer and pharmaceutical materials. However, the enthalpy relaxation studies in foods are

limited to pure components (Le Meste et al., 1996; Lammert et al., 1999; Wungtanagorn and Schmidt, 2001a & b; Noel, et al., 2005; Haque et al., 2006; Liu et al., 2007).

Enthalpy relaxations in foods may vary depending on the thermal history, cooling rate used to reach the amorphous glassy state, heating rate used after aging, water content, aging temperature and the type of food constituents. Enthalpy relaxation in amorphous foods increases due to increase in three main factors i.e. water/additives, temperature and time (Yu, 2001; Liu et al., 2002). Most foods consist of formulated components which may exhibit selected enthalpy relaxation characteristics and the total enthalpy relaxations may result from the cumulative effect of various components (Liu et al., 2006). The molecular interactions among various food components may also contribute to the total enthalpy relaxation of the food during physical aging.

Amorphous state of foods has high molecular mobility and free energy, and hence they are kinetically and thermodynamically unstable. Many physicochemical reactions continue to occur in the glassy state of foods i.e. below their glass transition temperature (Karmas et al., 1992; Lievonen et al., 1998). Diffusion of small molecules in glassy matrices can be rapid enough to start various diffusion-limited reactions (Hill et al., 2005). This has practical implications since many of the amorphous food matrices are in their glassy state during processing and storage. Enthalpy relaxation can be used to assess the molecular mobility, which is related to the rates of diffusion-limited physical and chemical reactions in foods (Byrn et al., 2001; Luthra et al., 2008). Enthalpy relaxation time (τ) is related with the rate (k) of undesirable physicochemical reactions in foods and pharmaceuticals (Byrn et al., 2001). Zhou et al. (2008) proposed inverse relationship between diffusivity/reaction rate and relaxation time. They observed partial correlation

between rate of crystallization and molecular mobility, explained by enthalpy relaxation. Guo et al. (2000) correlated rate of a process and diffusivity using Stokes-Einstein equation for translational molecular diffusivity as:

$$\frac{k_1}{k_2} = \left(\frac{D_1}{D_2}\right)^n \quad (1)$$

where k_1 and k_2 are the rate constants of a process at two temperatures T_1 and T_2, respectively, and D_1 and D_2 are the corresponding diffusivities. n is the correlation index with values ranging from 0 to 1. Diffusion process is rate limiting when n = 1 while diffusion of reactants and products doesn't control the rate of a reaction when n = 0. Considering free volume theory explained by Doolittle (Doolittle, 1951) and Turnbull equations (Cohen and Turnbull, 1959), rate of a process, diffusivity, and relaxation time can be correlated as (Zhou et al., 2008):

$$\frac{k_1}{k_2} = \left(\frac{D_1}{D_2}\right)^n = \left(\frac{T_1}{T_2}\right)^{\frac{n}{2}} \left(\frac{\tau_2}{\tau_1}\right)^n \quad (2)$$

where τ_1 and τ_2 are the relaxation times at T_1 and T_2 respectively.

Bansal et al. (2008) observed a decrease in time for 10% crystallization with an increase in enthalpy relaxation in amorphous valdecoxib. Gupta et al. (2004) reported inverse correlation between enthalpy relaxation and solubility of celecoxib-polyvinylpyrrolidone. So enthalpy relaxation is related with rate of various diffusion-limited physicochemical degradation reactions occurring in food and pharmaceuticals. It is essential to study the enthalpy relaxations in foods to understand the fundamental requirements for safe and extended storage in the glassy state.

112 The Kohlrausch-Williams-Watts (KWW) equation is the most extensively used for
113 describing the kinetics of enthalpy relaxation in glassy materials during aging (Hancock
114 et al., 1995; Hancock and Shamblin, 2001; Liu et al., 2007). The KWW equation (3)
115 describes the non-exponential kinetic behavior of enthalpy relaxation. Long term
116 enthalpy relaxation in glassy state of foods can be predicted by KWW equation. KWW is
117 an empirical equation with two unknown parameters, mean molecular relaxation time (τ)
118 in days and constant β. The KWW equation is

119 $$\phi_t = \exp\left(\frac{-t}{\tau}\right)^{\beta} \quad (3)$$

120 where φ(t) is the extent of enthalpy relaxation over time t. φ(t) is described as the amount
121 of unreleased enthalpy at the specific annealing temperature (Liu et al., 2007). It is
122 assumed that individual components in amorphous formulations have separate relaxation
123 times and the τ value obtained from KWW equation (3) gives the mean relaxation time of
124 the whole amorphous system (Yoshioka et al., 2001). The degree of deviation of the
125 relaxation from exponential behavior is accounted by the parameter β. To estimate the
126 extend of enthalpy relaxation in raspberry powder over time φ(t), the maximum possible
127 enthalpy recovery (ΔH_∞) in raspberry powder at an aging temperature is required.

128 $$\phi_t = 1 - \frac{\Delta H_{relax}}{\Delta H_\infty} = \exp\left(\frac{-t}{\tau}\right)^{\beta} \quad (4)$$

129 $$\Delta H_\infty = \Delta C_p \left(T_g - T_a\right) \quad (5)$$

130 Where ΔH_∞ and ΔH_{relax} are the maximum enthalpy recovery and the enthalpy relaxation
131 during the aging time (t), respectively. ΔC_p is a heat capacity change at the glass
132 transition temperature (T_g) and aging temperature (T_a).

Enthalpy relaxation in foods is strongly related to the nature of food components as well as the interactions among food components. Food systems may be divided into *strong* and *fragile* similar to pharmaceutical and other material systems (Angell, 1991). Strong and fragile classification is determined from the changes in dynamic properties and configurational structure of amorphous foods near or above their T_g. The temperature dependence of mean molecular relaxation time near or above their T_g is also related to the fragility of the system (Angell, 1991; Hilden and Morris, 2004; Wungtanagorn and Schmidt, 2001a; Hodge, 1996; Kaushal and Bansal, 2008). Strong systems show broad glass transition while fragile systems have sharp glass transition representing the rapid change from glassy to rubbery state and dynamic properties during glass transition. Dynamic properties and structure of fragile systems are more temperature sensitive than strong systems in their rubbery state. Strong systems follow a linear Arrhenius relationship of temperature dependence on mean relaxation time (Angell, 1991; Borde et al., 2002). Fragile liquids exhibit nonlinear dependence of temperature on viscosity and molecular mobility, and a strong departure from Arrhenius relationship (Kaushal and Bansal, 2008). Deviation from linear relationships define fragile systems when ln τ is plotted against $1000/T_a$ (Hancock et al., 1995). The relaxation times of fragile liquids tend to follow temperature dependence described by the Vogel-Tamman-Fulcher (VTF) equation. (Hancock et al., 1995; Shamblin and Zografi, 1998). However, the Vogel-Tamman-Fulcher equation (VTF equation) is applicable at temperature greater than T_g and used to identify the fragility of material (Hancock et al., 1995). A modified VTF model by the introduction of 'strength parameter' D may be used for better representation of the fragility concept (Angell, 1991):

$$\tau = \tau_o \exp\left(\frac{DT_0}{T - T_0}\right) \quad (6)$$

Strong materials exhibit D values greater than 30, while fragile materials exhibit smaller D values ($D < 10$). Fragility index (m) can be alternatively used to dynamic and structural behavior of amorphous components in their rubbery state. Fragility index (m) is defined as

$$m = \frac{\Delta E}{2.303RT_g} \quad (7)$$

where ΔE is the activation energy for molecular motions near T_g and R is the gas constant.

Strong food systems exhibit m value between 16 and 100, while fragile systems exhibit m value between 100 and 200 (Champion et al., 2000). The fragility parameter (m) of a food system is dependent on the water content of the food system and may be associated to change in physical and thermodynamic properties with respect to transition temperature, especially during glass to liquid transitions. Fragility of amorphous components can decide the physical or chemical stability with varying temperature near their T_g (Hancock et al., 1998)

The consumption of berry products is encouraged worldwide because of their potential health benefits. Red raspberry fruit is rich in flavonoids and phenolic acids that provide antioxidant activity. Raspberries contain large concentrations of ellagic acid, a dimeric derivative of gallic acid exhibiting anticarcinogenic and antioxidant effects. Raspberries are highly perishable fruits frequently dried to extend shelf life. Dehydrated berries are also desirable as ingredients in dairy and bakery products. However, dried raspberry powders may be subjected to physical aging/enthalpy relaxation during storage at the

178 room temperature (~25°C) which is below their glass transition temperatures (T_{gi} =
179 37.8°C). Physical aging may result in unfavorable changes in functional and nutritional
180 properties of raspberry powders. So it is critical that the changes in physicochemical
181 properties during storage should be determined to better assess the functional value of the
182 processed foods.
183 The objectives of this study were to investigate the enthalpy relaxation of freeze-dried
184 raspberry powder using differential scanning calorimetry, characterize the non-
185 exponential behavior of enthalpy relaxation using Kohlrausch-Williams-Watts (KWW)
186 model, and classify raspberry powder into strong/fragile system.
187
188 **MATERIALS AND METHODS**
189 **Sample preparation**
190 Washington grown fresh red raspberries (*Rubus idaeus*) were generously supplied by
191 Milne fruit products (Milne fruit products Inc. Prosser, WA). The fresh raspberries were
192 frozen immediately to -35°C. The frozen raspberries were freeze-dried by using a
193 laboratory freeze dryer (Virtis freeze mobile 24 with Unitop 600L, VirTis SP Industries
194 Co., New York) to decrease the water content to 0.03 kg H_2O/kg raspberry powder. The
195 shelf temperature was set at 20°C with a vacuum of 20 Pa and the condenser temperature
196 of -60°C. After 48 h of freeze drying, the raspberries were ground to a fine powder using
197 mortar and pestle. Dry raspberry powder was kept in a desiccator above P_2O_5 desiccant
198 at room temperature (298 K) for two days. The moisture content of dry raspberry powder
199 was analyzed using vacuum oven method (0.005 kg H_2O/kg raspberry powder).
200

Differential Scanning Calorimetry (DSC)

Glass transition determination and enthalpy relation experiments were performed on a differential scanning calorimeter (DSC), (Q2000, TA Instruments, New Castle, DE). Three replicates were used in all the experiments. Before conducting any aging experiments, the onset (T_{gi}), midpoint (T_{gm}) and endpoint (T_{ge}) glass transition temperatures of the raspberry powder were determined (Syamaladevi et al., 2009). For glass transition temperature determination (T_g), 10–20 mg raspberry powder was scanned from room temperature to -90°C at 5°C/min and equilibrated for 10 min. Raspberry powders were scanned from -90°C to 70°C at a rate of 5°C/min. The temperature range corresponding to the (vertical) shift in the heat flow curve of DSC thermogram is assigned as T_g (Syamaladevi et al., 2009; Syamaladevi et al., 2010). The temperature at the intersection of the tangent before the vertical shift in heat flow curve and inflection tangent of DSC thermogram is identified as T_{gi}. Similarly, the temperature at the intersection of the tangent after the vertical shift in heat flow curve and inflection tangent of DSC thermogram is identified as T_{ge}. T_{gm} is identified as the mid temperature between T_{gi} and T_{ge}. For annealing/aging experiments, the raspberry powders were heated to (T_{gi} + 50)°C and cooled to (T_{gi} - 50)°C at 5°C/min to erase the thermal history of the raspberry powder (Figure 1). The raspberry powder was reheated from (T_{gi} - 50)°C to selected aging temperatures. Three aging temperatures selected for raspberry powders were 5, 10 and 15°C below its T_{gi}. The raspberry powders were annealed/aged isothermally at the selected aging temperature ([T_{gi}-5], [T_{gi}-10], and [T_{gi}-15] °C) for selected aging times (1.0 to 96 hrs) in DSC. After aging, the raspberry powders were cooled to (T_{gi} - 60)°C at 5°C/min. The raspberry powders were reheated to (T_{gi} + 60)°C at 5°C/min and cooled to

ambient temperature (Figure 1). The enthalpy relaxation during reheating of the raspberry powders after aging at the selected temperatures and times were determined by drawing a linear baseline to the enthalpy endotherm.

RESULTS AND DISCUSSION

Glass transition temperature vs Aging conditions

The onset glass transition temperature (T_{gi}) of the freeze-dried raspberry powder was 37.8°C which agreed well with previous determinations reported in Syamaladevi et al., (2009). Glass transition temperature is kinetically governed. Experimental conditions such as heating or cooling rates and physical aging influence the assignment of glass transition temperature (Liu et al., 2007). Physical aging results in nonequilibrium glassy state to equilibrium super cooled liquid state in amorphous foods. Theoretically, glass transition temperature should decrease with increase in aging time due to the decrease in enthalpy of the amorphous component as it approaches equilibrium (Wungtanagorn and Schmidt, 2001a). However, the increase in the Universal Analysis software assigned T_{gi} with aging time may be due to the shifting of T_g overshoot peak along x axis and the steeper second tangent with increased aging time (Wungtanagorn and Schmidt 2001a & b). If T_g is measured without the interference of the physical aging peak (i.e. by the intersection of the extrapolated enthalpy-temperature for glassy and rubbery states), T_g should decrease with aging time. Physical aging often results in densification, increase in relaxation time and decrease in free volume and molecular mobility (Shi et al., 2008; Surana et al., 2005). Therefore, the glass transition temperature of a food may increase with aging time. Therefore, T_g may be greater for materials in equilibrium super cooled

liquid state than the T_g in the nonequilibrium amorphous state. Chung and Lim (2003) indicated that the conformation changes in glassy polymer during aging decreases free volume and molecular mobility, increasing the T_g. In the present study, no statistically significant difference ($p > 0.05$) in T_g values of raspberry powder was observed with increasing aging time (Table 1). Craig et al. (2000) observed no significant difference in T_g of lactose with increasing aging time. However, some studies report a small increase of 1-1.5 ^{o}C in T_g with aging time when foods were aged at temperatures less than their respective glass transition temperatures (Chung and Lim, 2003; Schmidt and Lammert, 1996; Wungtanagorn and Schmidt, 2001a).

The amount of enthalpy relaxation during aging may depend on the aging temperature as well as aging time. When foods are aged at selected temperatures below their glass transition temperatures, the maximum enthalpy relaxation occurs at temperatures near the glass transition temperatures. Molecular mobility is drastically reduced when foods are aged at temperatures far below the glass transition temperatures. The T_g of the aged foods may decrease with increasing temperature of aging because higher temperatures may result in greater structural and molecular rearrangement. However, no significant change was observed in T_g of the raspberry powder with increasing temperatures of aging (Table 1). Chung and Lim (2003) reported a decrease of 1-3^{o}C in T_g of normal and waxy starches as the aging temperature approached the T_g, attributing to the increased mobility of amorphous chain segments when the aging temperature approached T_g.

Aging time dependence of enthalpy

The enthalpy relaxation during aging increased non-linearly and non-exponentially with an increase in the aging time indicating kinetic nature (Figure 2 and Figure 3). The major components of raspberry powder are glucose and fructose. The enthalpy relaxation in raspberry powder during aging was smaller compared to the pure components such as fructose, glucose and sucrose (Wungtanagorn and Schmidt, 2001a; Liu et al., 2007). For instance, the relaxation enthalpy of raspberry powder ranged between 0.12 to 1.76 J/g for aging times of 6 to 72h at an aging temperature of (T_g-5). While the relaxation enthalpy of glucose ranged between 3 to 6.6 J/g for aging times of 6 to 72h at the aging temperature of (T_g-5) (Wungtanagorn and Schmidt, 2001a). In the case of fructose, relaxation enthalpy ranged between 2 to 5.5 J/g for aging times of 6 to 72h at the aging temperature of (T_g-5) (Figure 4). The small enthalpy relaxation may be attributed to the complex structure, interactive forces between glucose and fructose, and the presence of other components in raspberry powder. Enthalpy relaxation in large molecular weight foods such as starch and protein based foods are much smaller compared to the small molecular food components such as sugars. When the aging temperature of raspberry powder was close to the T_{gi}, the enthalpy relaxation in raspberry powder was greater than the enthalpy relaxation in raspberry powder aged at temperatures far below the T_{gi}, indicating the importance of glass transition temperature in the determination of appropriate storage temperatures for low moisture foods.

Kinetics of enthalpy relaxation

The non-exponential behavior of enthalpy relaxation is presented by plotting φ(t) against the aging time (Figure 3). The KWW equation was used to fit the non-exponential

behavior of enthalpy relaxation in raspberry powder during aging. τ and β are mean enthalpy relaxation time and non-exponential parameter, respectively. The non-exponential parameter β is related to the distribution of enthalpy relaxation times, which varies between 0 and 1 (Christensen et al., 2002; Van den Mooter et al., 1999). A value of β =1 reduces the KWW equation to an exponential expression. With small values of β (β << 1) presents the non-exponentiality of the enthalpy relaxations (Liu et al., 2006). In the KWW equation, both τ and β are adjustable parameters determined from fitting the experimental data on enthalpy relaxation and time.

A large τ value represents slow molecular movement in foods and consequently small free volume increase indicating the complex nature of foods. Nonlinear optimization of the experimental data is conducted by a Statistica® version 5 computer program and the values for the parameters τ and β in the KWW equation are determined. The values of τ and β may be used to compare molecular mobility of constituents in foods in the glassy state. The KWW equation constants for raspberry powder and selected food components are presented in Table 2.

Molecular motions are considerably reduced in glassy food systems and a drastic increase in the value of τ is observed when the storage temperatures of foods are reduced below the glass transition temperatures. For instance, the τ value of raspberry powder aged at a temperature (T_{gi} - 15)°C is 1017 h, much greater than the τ value (147.1 h) of the raspberry powder aged at (T_{gi} - 5)°C (Table 2). The larger τ value indicates reduced molecular mobility in raspberry powder aged at temperatures less than its T_g compared to the raspberry powder aged near its glass transition temperature. τ values of aged raspberry powder is greater than the τ values of glucose and fructose. For instance, the τ

315 value of glucose and fructose aged at (T_g - 5) are 3.35 and 14.3 h respectively while the τ
316 value of raspberry powder is 147.1 h (Wungtanagorn and Schmidt, 2001a). Christensen et
317 al. (2002) and Chung and Lim (2003) observed decrease in β as the aging temperature
318 decreases and moisture content increases. In the current study, β values decreased with
319 decreasing temperature of aging. The β values at (T_{gi} - 5), (T_{gi} - 10) and (T_{gi} - 15) are
320 0.967, 0.902 and 0.69 respectively. The larger β values of raspberry powder compared to
321 other food components may be attributed to complex interaction of components present
322 in raspberry powder. This interaction may result from the formation of hydrogen bonds
323 among glucose and fructose, the main components of raspberry powder. However, the
324 enthalpy relaxation distribution of multicomponent foods with complex interactions
325 between the biomolecules may not be correctly expressed by the KWW equation
326 (Shamblin and Zografi, 1998).

327 The time ($\tau_{\varphi(t)=50\%}$) required for 50% of the maximum enthalpy during the aging
328 process is determined at a specific aging temperature from τ and β values obtained from
329 the KWW equation using non-linear optimization (Liu et al., 2007). A small decrease in
330 the aging temperature exerts considerable enhancement to the value of $\tau_{\varphi(t)=50\%}$ indicating
331 the importance of consistency of the storage temperature (Table 3). For instance, the time
332 required for half completion of the relaxation process increased from 4 to 25 days when
333 the aging temperature decreased from (T_{gi} - 5) to (T_{gi} - 15). The values of $\tau_{\varphi(t)=50\%}$
334 obtained for raspberry powder are greater than the $\tau_{\varphi(t)=50\%}$ of sucrose and glucose syrup
335 solids (GSS) attributed to complex interactions of components in raspberries compared to
336 interaction among pure components (Liu et al., 2007). Also the time ($\tau_{\varphi(t)=1\%}$) required for
337 obtaining 99% of the maximum enthalpy during the aging process was determined at a

specific aging temperature (Table 3). The value of $\tau_{\varphi(t)=1\%}$ increased from 30 to 388 days when the aging temperature was decreased from (T_{gi} - 5) to (T_{gi} - 15), greater than the $\tau_{\varphi(t)=1\%}$ values for sucrose and GSS (Liu et al., 2007). $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ values may provide indications on the stability of raspberry powders during long term storage at room temperature.

Temperature dependence of molecular relaxation times

Temperature dependence of enthalpy relaxation kinetics greater and less than T_g is described by Arrhenius and Vogel-Tamman-Fulcher equations (VTF equation) (Hancock etal., 1995). The relaxation times and molecular mobility vary considerably between glassy and rubbery states. The temperature dependence of glucose, sucrose, maltose and trehalose relaxation times is described using the Arrhenius equation (Kawai et al., 2005).

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (7)$$

where E_a is the apparent activation energy (J) and R is the universal gas constant (8.314 J/K.mol).

The relaxation times of raspberry powder aged at temperatures less its T_g decreased as the aging temperature increased, indicating slower relaxation in the glassy state at lower temperatures. In the current study, the temperature dependence of relaxation times was approximated using the Arrhenius relationship by drawing a straight line between ln τ and $1000/T_a$. The calculated E_a was 145 kJ/mol for raspberry powder (Figure 5). The E_a obtained for raspberry powder was smaller than the E_a of other pure components indicating structural differences in raspberry powder compared to structural differences among individual components such as fructose or glucose (Liu et al., 2007; Hancock et

al., 1995). At small activation energies, chemical reactions require a longer time. The activation energy of β relaxations in sugar glasses is in the range of 40-70 kJ/mol. The E_a for enthalpy relaxations in glassy state is less than the E_a for temperatures at and greater than glass transition temperatures (Champion et al., 2000; Le Meste et al., 2002).

The Vogel-Tamman-Fulcher equation (VTF equation) is often used to approximate a non-Arrhenius relaxation time distribution greater than and less than the T_g in many foods, with a large increase in molecular mobility for a small temperature increase (Hancock et al., 1995; Mao et al., 2006). The VTF equation is

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \quad (8)$$

where τ_o, B, and T_o are empirical parameters to fit the experimental data. The parameter τ_o is related to the relaxation time for a free molecule in an open space (Hancock et al., 1995; Hancock and Shamblin, 2001). The constant B is also related to the fragility of a food system described as the temperature dependence of relaxation time for a material at its T_g (Kaushal and Bansal, 2008; Hancock et al., 1995). Also the third parameter T_o is the temperature at which all molecular relaxations cease or τ becomes infinite and corresponds to the theoretical Kauzman temperature (Liu et al., 2007). Kauzman temperature is described as the temperature limit where molecular mobility of amorphous food and pharmaceutical components is negligible over extended experimental time scales and thus mean relaxation time is assumed as infinite (Kaushal and Bansal, 2008; Liu et al., 2007; Hancock and Shamblin, 2001). The theoretical Kauzman temperature is approximately 50 K below T_g. When T_o = 0, the VTF equation (8) is simplified to the Arrhenius equation (Equation 7). The experimental data is fitted to the VTF equation and the VTF parameters are determined by non-linear optimization using Statistica® version

384 5 (Table 4). The initial values of the VTF parameters used in non-linear optimization to
385 fit the experimental data to the VTF equation were $\tau_o = 10^{-9}$, $B = (T_{gi}\text{-}50)\times 10$ and $T_o =$
386 $(T_{gi}$ -50) (Hancock et al., 1995). The predicted values of the constants by non-linear
387 optimization are presented in Table 4.

388 The logarithm of τ of raspberry powder was plotted against the scaled temperature (T_g
389 - T_a) (Figure. 6). Large τ values were observed for large values of (T_g - T_a) indicating
390 enthalpy relaxations are slow at low aging temperatures (Kim et al., 2003). The τ value at
391 room temperature (298 K) for raspberry powder used in the experiment was 25 days
392 (Figure. 6). This τ value may be approximated as the time required for crystallization and
393 other physicochemical occurrences in foods during aging. The τ value at room
394 temperature (298 K) for raspberry powder was smaller than the τ value at room
395 temperature of sucrose and starch at room temperature storage (Hancock et al., 1995;
396 Kim et al., 2003), attributed to the greater T_g and molecular weights of starch and
397 sucrose. Hancock et al., (1995) reported an approximate shelf life determined by this
398 method is similar to the real shelf lives of selected products implying enthalpy relaxation
399 studies may be useful in predicting the appropriate storage time of foods.
400

401 **Fragility index**

402 The fragility of food systems may be identified by determining the activation enthalpy of
403 structural relaxation analysis of the glass transition width (Crowley and Zografi, 2001).
404 Fragile glass formers normally exhibit dramatic changes in thermodynamic properties at
405 glass transition temperatures and display narrow glass transition width (Moynihan et al.,
406 1996). The following equation relates activation enthalpy to glass transition width.

$$\left(\frac{\Delta E}{R}\right)\left(\frac{1}{T_{gi}}-\frac{1}{T_{ge}}\right)=\text{Constant} \quad (9)$$

where ΔE is the activation enthalpy at the glass transition temperature and T_{gi} and T_{ge} are the onset and end point glass transition temperatures. The constant has a value of 5 ± 0.5, obtained by experimental investigations for selected glass formers. In the current study, the value used for the constant was 5. The fragility index (m) of a food is obtained from enthalpy relaxation data during aging experiments. The activation enthalpy and fragility parameter m are related by (Crowley and Zografi, 2001):

$$m=\frac{d\log\tau}{d\left(T_g/T\right)}\Big|_{T=T_g}=\frac{\Delta E}{(\ln 10)RT_g} \quad (10)$$

The strength parameter D in the modified VTF model may be obtained from the glass transition width information. The fragility parameter m and strength parameter D are related by

$$m=\frac{DT_o/T_g}{(\ln 10)\left(1-T_o/T_g\right)^2} \quad (11)$$

The values of m and D are obtained for freeze-dried raspberry powders using equations 10 and 11 with τ = 100 s at the glass transition temperature and $\tau_o=10^{-14}$ s in the VTF equation (Table 4). The fragility parameter (m) may also be approximated from the VTF parameters (B and T_o) (Angell et al., 1994).

$$m=16+\frac{590T_o}{B} \quad (11)$$

Fragile glass formers exhibit structural instability and significant changes (60-80%) in ΔC_p at T_g or $C_{p(liquid)}/C_{p(glass)}$ of strong systems is smaller than 1.1 (Angell, 1991). Strong systems display structural resistance to degradation at T_g. selected methods may be used

427 to identify the fragility of materials. The ratio of T_m/T_{gi} (both in K) may be selected as an
428 indicator of fragility. The ratio of T_m/T_{gi} of fragile systems is normally smaller than 1.5
429 (Hancock et al., 1995; Kaushal and Bansal, 2008). The small value of the non-
430 exponential parameter β of the KWW model also indicates fragility of food systems
431 (Champion et al., 2000). The relaxation time and fragility can be coupled with the
432 physico-chemical changes in foods during storage (Hancock et al., 2001). Studies on
433 temperature dependence of the relaxation time and molecular mobility are important to
434 predict acceptable storage of foods.

435 In this research, selected methods were followed to determine the fragility of raspberry
436 powder. Fragility prediction for raspberry powder by the selected methods is presented in
437 Table 5. Raspberry powder exhibited temperature dependent Arrhenius behavior in the
438 glassy state, indicating that raspberry powder is a strong system. The relaxation time for
439 free molecules (τ_o) and the parameter B obtained for raspberry powder are similar to
440 strong food and pharmaceutical systems (Table 5) (Hancock et al., 1995). However, the
441 value of the parameter T_o was much smaller than the value of (T_{gi} - 50).

442 The D value obtained for raspberry powder using the modified VTF equation (6) was
443 18.7, smaller than the D values of strong systems ($D > 30$) and larger than fragile system
444 ($D < 10$) (Wungtanagorn and Schmidt, 2001b). However, a comparison of the D values
445 with other food systems is only reasonable at equivalent preparation and experimental
446 conditions. The predicted parameters of the modified VTF equation (Table 5) indicate the
447 raspberry powder is a moderately strong food system. More data on the temperature
448 dependence of molecular mobility in raspberry powder at temperatures greater than the
449 T_g is important in analyzing fragility.

450 The activation enthalpy of raspberry powder at the glass transition temperature was
451 determined using equation 9 was 266 kJ/mol. This activation energy is greater than the
452 activation energy obtained for enthalpy relaxation of raspberry powder in glassy state.
453 The experimental T_o is smaller than the Kauzman temperature (T_K). m (45) and D (23.1)
454 values (Table 5) obtained for raspberry powders using activation enthalpy at glass
455 transition temperature indicate raspberry powders are strong food systems during glass
456 transitions. A large strength parameter and a small fragility parameter are preferred for
457 desirable storage of foods near glass transition temperatures. Raspberry powders presents
458 strong behavior similar to main components, glucose and fructose (m values 70.2 and
459 47.6, respectively) (Wungtanagorn and Schmidt, 2001b). The m value approximated
460 using the VTF parameters is 58, larger than the m value determined for raspberry powder
461 using the activation enthalpy at the glass transition temperature. However, this m value
462 represents the strong behavior raspberry powder. A larger β value (β ~1) for the raspberry
463 powder also indicates a strong behavior of raspberry powder.
464 However, based on the small ΔC_p at T_g (0.736 J/gK), raspberry powder may be
465 categorized as moderately fragile (Table 5). The $C_{p(liquid)}/C_{p(glass)}$ ratio of raspberry
466 powder was 1.39 (Table 5), greater than 1.1 (Borde et al., 2002). The ratio of T_m/T_{gi}
467 (1.38) predicts a fragile behavior of freeze-dried raspberries as the ratio is lower than 1.5.
468 The T_m/T_{gi} ratio for sucrose (1.29) is smaller than raspberry powder. Glucose and
469 fructose are the main constituents of raspberry powder, presenting a similar
470 $C_{p(liquid)}/C_{p(glass)}$ and T_m/T_{gi} ratios (Wungtanagorn and Schmidt, 2001b).
471 The fragility indices (m) of raspberry powder described by modified VTF equation
472 and glass transition width approaches predict freeze-dried raspberry powder is a strong

food system. The strength parameters (D) obtained from modified VTF equation and glass transition width approaches presents freeze-dried raspberry powder falls between strong and fragile food systems. However, $C_{p(liquid)}/C_{p(glass)}$ ratio and T_m/T_{gi} ratio predicts a fragile behavior of freeze-dried raspberries. The discrepancy among the fragility elucidations by heat capacity, T_m/T_{gi} ratios and the fragility index of materials was previously reported (Wungtanagorn and Schmidt, 2001b). More research is required for a clarification for this discrepancy.

The kinetic parameters of enthalpy relaxation of raspberry powder obtained in this study can be related to selected physico-chemical changes in raspberry powder occurring during glassy state storage. This will improve our understanding on the effect of molecular mobility and relaxation time on stability and shelf life of foods.

CONCLUSIONS

The onset glass transition temperature (T_{gi}) of the freeze-dried raspberry powder was 37.8°C. Physical aging of raspberry powder at selected temperatures 5, 10, and 15°C below the T_{gi} did not significantly change the glass transition temperatures of freeze-dried raspberry powder. Enthalpy relaxation during aging of raspberry powder was smaller than the enthalpy relaxation of glucose and fructose, two major components of raspberry powder, at equivalent experimental conditions. Enthalpy relaxation of amorphous components can be related to their structural and physicochemical degradation. Structural and physicochemical stability raspberry powder may be higher than that of individual components due to interactions among them. A non-exponential expression of enthalpy relaxation is observed for raspberry powder. A larger mean

enthalpy relaxation time for raspberry powder at lower temperatures than the T_g suggests molecular level relaxations are much slower at temperatures smaller than T_g. The physicochemical degradation rates in raspberry powder are expected to be lower at temperatures smaller than their T_g. There is a discrepancy among fragility determination, as the selected approaches predicted both fragile and strong behavior of raspberry powder.

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652

LEGENDS TO FIGURES

1. Enthalpy relaxation experimental procedure for freeze-dried raspberry powder
2. Relaxation enthalpy of freeze-dried raspberry powder at aging temperatures (T_{gi} - 5), (T_{gi} - 10), (T_{gi} - 15)°C for selected aging times.
3. Variation of $1-\frac{\Delta H_{relax}}{\Delta H_{\infty}}$ with aging time for freeze-dried raspberry powder at (T_{gi} - 5), (T_{gi} - 10), (T_{gi} - 15)°C for selected aging times.
4. Comparison of relaxation enthalpy of raspberry powder, glucose and fructose aged from 6h to 72h at (T_g - 5).
5. Plot of ln τ Vs 1000/ T_a to calculate the activation energy.
6. Variation of mean relaxation time (τ) with (T_{gi} - T_a) for freeze-dried raspberry powder compared with mean relaxation times of sucrose (Hancock et al., 1995) and starch (Kim et al., 2003).

Table 1. Onset (T_{gi}), midpoint (T_{gm}) and endpoint (T_{ge}) glass transition temperatures of freeze-dried raspberry powder aged at selected times and temperatures

	(T_{gi}-5)			(T_{gi}-10)			(T_{gi}-15)		
Time t, (h)	T_{gi} (°C)	T_{gm} (°C)	T_{ge} (°C)	T_{gi} (°C)	T_{gm} (°C)	T_{ge} (°C)	T_{gi} (°C)	T_{gm} (°C)	T_{ge} (°C)
6	39[a] (1.98)[*]	43.7[b] (0.566)	46[c] (0.141)	38.1[a] (0.849)	41.6[b] (0.282)	43.2[c] (0.212)	-	-	-
12	39.7[a] (1.67)	45.3[b] (0.681)	46.6[c] (1.21)	40[a] (2.12)	43.6[b] (2.12)	45.3[c] (1.06)	38.3[a] (0.071)	41.3[b] (0.636)	43.4[c] (0.212)
24	40[a] (0.586)	46.7[b] (0.520)	47.4[c] (0.693)	40.2[a] (1.84)	44.7[b] (0.707)	45.8[c] (0.0)	38.3[a] (0.990)	40.9[b] (1.13)	43.4[c] (0.566)

48	41.3^{a} (0.283)	47.9^{b} (1.10)	50.4^{c} (0.495)	40.2^{a} (2.12)	44.7^{b} (0.212)	45.8^{c} (0.354)	39^{a} (1.414)	43.4^{b} (0.354)	43.9^{c} (0.424)
72	40^{a} (1.56)	46.1^{b} (0.778)	47.7^{c} (1.70)	41.7^{a} (0.990)	43.8^{b} (3.61)	46.5^{c} (1.41)	41^{a} (1.344)	44.2^{b} (0.212)	45.3^{c} (0.071)
96	-	-	-	39.8^{a} (1.27)	43.4^{b} (1.06)	44.8^{c} (0.990)	38.7^{a} (0.071)	42.6^{b} (0.0)	43.6^{c} (0.283)

* Standard deviation of the glass transition temperature values

- experiments not performed

Same superscripts in rows and column indicates that there is no significant difference in the values

Table 2. Enthalpy/structural relaxation modeling by KWW model and KWW model parameter values

Product	Method	T_{gi} (°C)	Aging Temperatures (°C)	Model parameters		References
				τ (h)	β	
Raspberry powder	DSC	37.8	(T_{gi}-5)	147.1	0.967	Current study
			(T_{gi}-10)	423.5	0.902	
			(T_{gi}-15)	1017.4	0.690	
Sucrose	DSC	67.2±0.5	(T_g-10)	3.59-78.1	0.6-0.62	Liu et al. (2007)
Glucose syrup solids (GSS)		52.9±1.8	(T_g-15)	11.5-173.5	0.62-0.7	
Sucrose/GSS (75:25)		61.9±1.1	(T_g-20)	19.8-247.2	0.46-0.53	
Sucrose/GSS (50:50)		71.5±1.4		83.1-255.5	0.3-0.36	
Sucrose/GSS (25:75)		73.4±2.2		47.8-197.7	0.41-0.52	
Glucose	DSC	36	(T_g-10)	-`	0.46-0.53	Kawai et al. (2005)
Sucrose		8	(T_g-20)		0.53-0.62	
Maltose		90	(T_g-30)		0.47-0.55	

Tehalose		113			0.51-0.75	
Dry emulsions	DSC		(T_g-20)	τ = 46- 10^7	0.29-0.22	Christensen et al.
amorphous sucrose			(T_g-30)	τ = 8-10^7	0.38-0.23	(2002)
			(T_g-50)			
Lactose	MDSC	116.9±0.5	80-100	-	-	Craig et al. (2000)
Lactose	DSC	102	25	-	0.81-0.89	Haque et al. (2006)
			60			
			75			
			90			
Normal rice starch	DSC	-	25	294.9	0.68	Chung and Lim
(11% water content)						(2003)
Waxy rice starch (11% water content)				112.0	0.47	
Normal rice starch				198.3	0.34	
(15% water content)						
Waxy rice starch (15% water content)				79.7	0.37	

Sucrose-water glass (40% sucrose)	DSC	-	-55	-	0.44-0.87	Inoue and Suzuki
Sucrose-water glass (80% sucrose)			-60		0.53-0.63	(2006)
			-65			
			-70			
Potato starch (16% moisture content)	DSC	59	25	$3.12\pm0.66\times10^{5}$	0.34	Kim et al. (2003)
			33	$1.51\pm0.58\times10^{4}$	0.23	
			42	$6.37\pm1.17\times10^{5}$	0.30	
Freeze-dried sucrose	MDSC and micro	-	40	2.6×10^{3}	0.304	Liu et al. (2002)
Freeze-dried trehalose	calorimeter (Thermal		40	2.51×10^{7}	0.159	
Quenched sucrose	activity		40	1.47×10^{4}	0.155	
Quenched trehalose	monitor, TAM)		40	2.5×10^{7}	0.286	
Quenched trehalose			50	7.7×10^{6}	0.290	

Table 3. ΔH_{∞}, $\tau_{\varphi(t)=50\,\%}$, $\tau_{\varphi(t)=1\,\%}$ experimental values calculated for freeze-dried raspberry powder

T_{gi}-T_a (K)	ΔH_{∞} (J/g)	$\tau_{\varphi(t)=50\%}$ (h)	$\tau_{\varphi(t)=1\%}$ (h)
5	4.08	101	714
10	7.28	282	2299
15	10.3	598	9305

Table 4. Arrhenius, VTF and modified VTF constants derived from mean relaxation time constants

Activation energy, E_a (kJ/mol)	145.4
τ_o (from VTF equation) (hours)	10^{-9}
B (from VTF equation) (K)	2760
T_o (from VTF equation) (K)	196.5
τ_o (from modified VTF equation) (hours)	2.12×10^{-8}
D (from modified VTF equation)	18.7
T_o (from modified VTF equation) (K)	167.9

Table 5. Fragility prediction for freeze-dried raspberry powder by selected methods

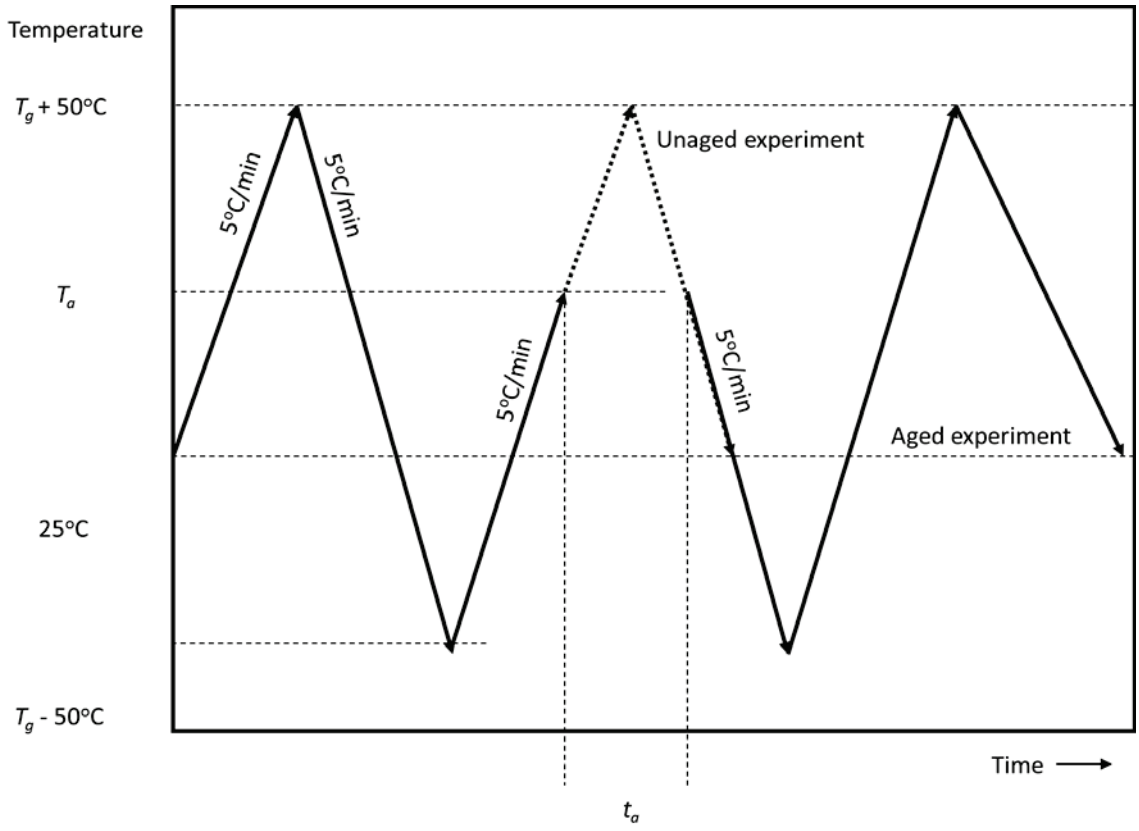
Method	Value	Fragility prediction
D value from modified VTF equation (6) using mean relaxation time (τ) and aging temperature data	18.7	Moderately Strong[1]
D value from modified VTF equation using glass transition width data	23.1	Moderately Strong[1]
Fragility parameter (*m*) using activation enthalpy at glass transition temperature data	45	Strong[2]
Fragility parameter (*m*) from VTF parameters	58	Strong[2]
$C_{p(liquid)}/C_{p(glass)}$	1.39	Fragile[3]
T_m/T_g	1.38	Fragile[4]

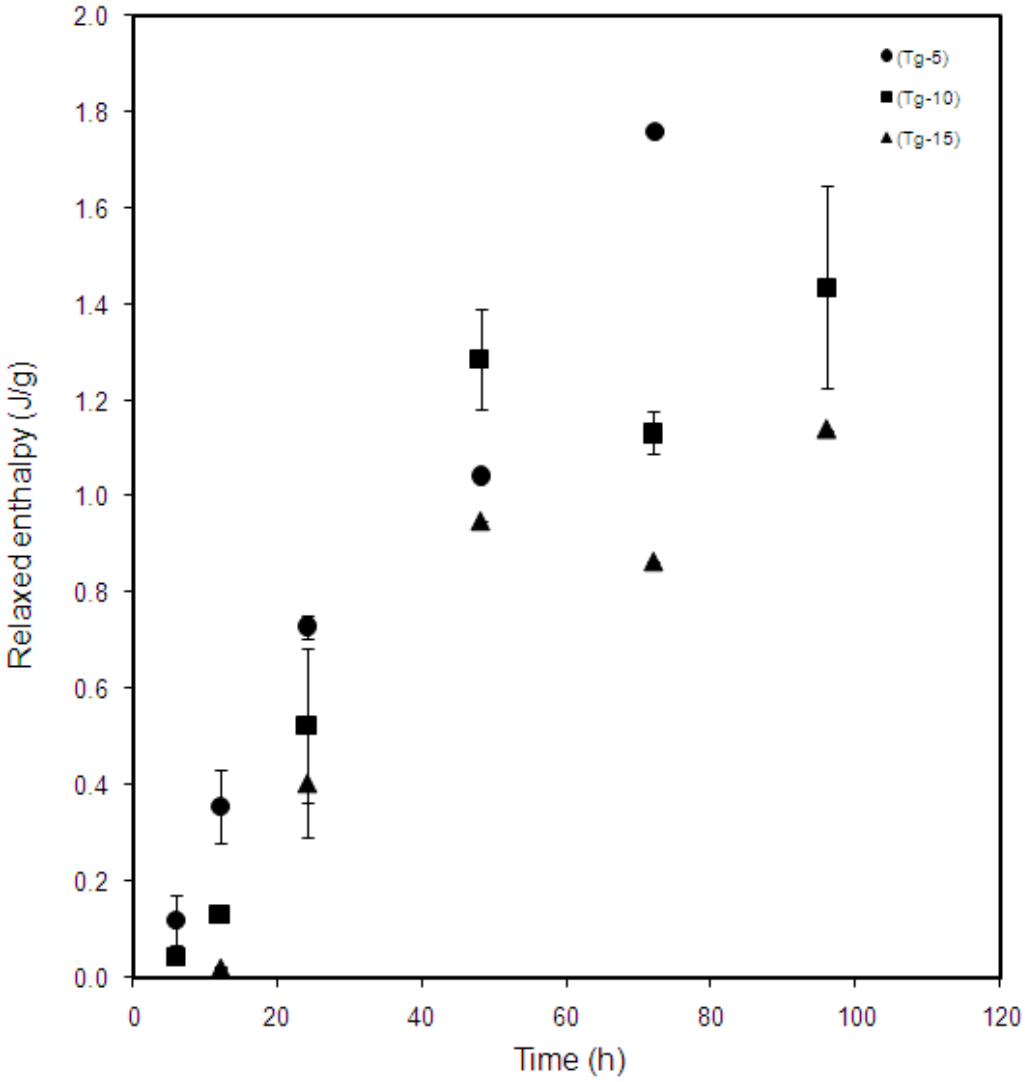
[1]Strong systems: $D>30$; Fragile systems: $D<10$

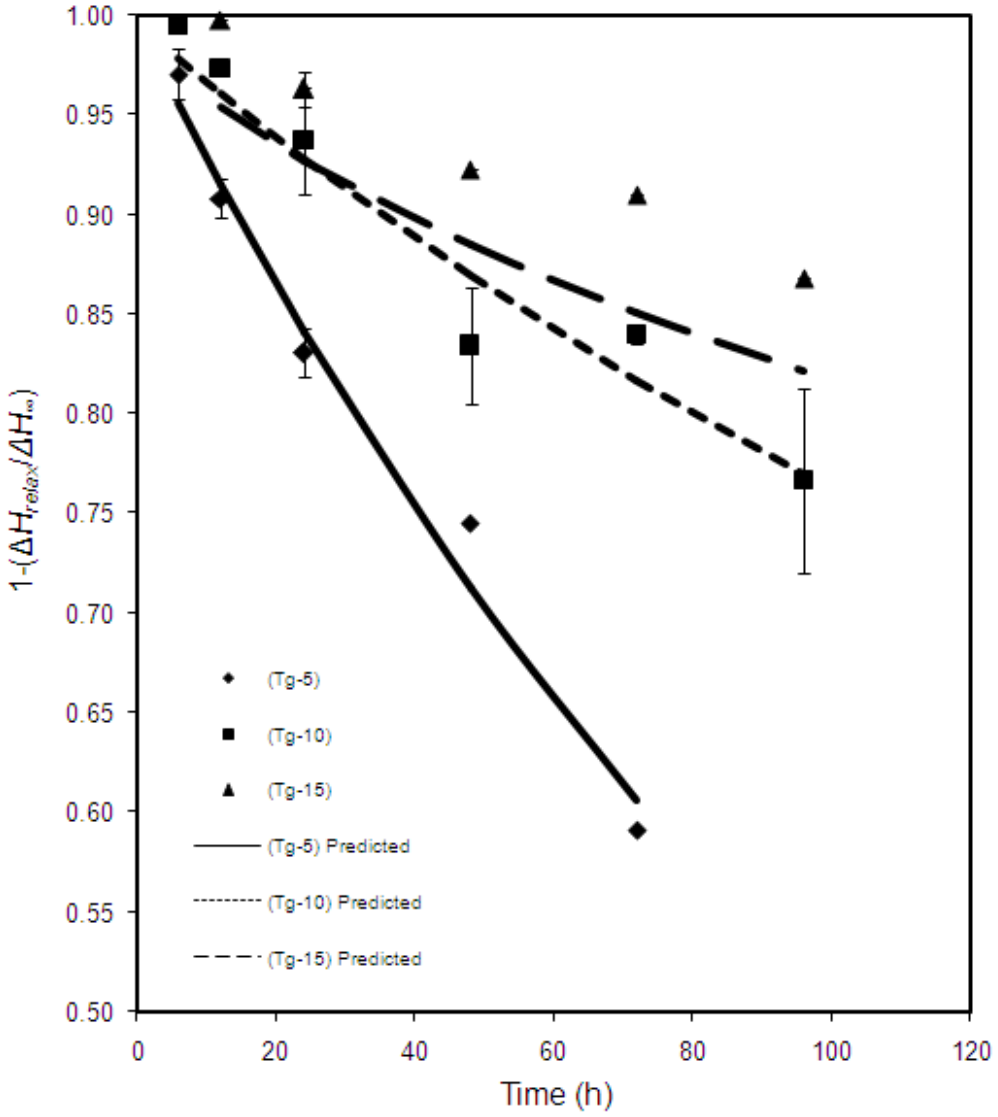
[2]Strong systems: $16<m<100$; Fragile systems: $100<m<200$

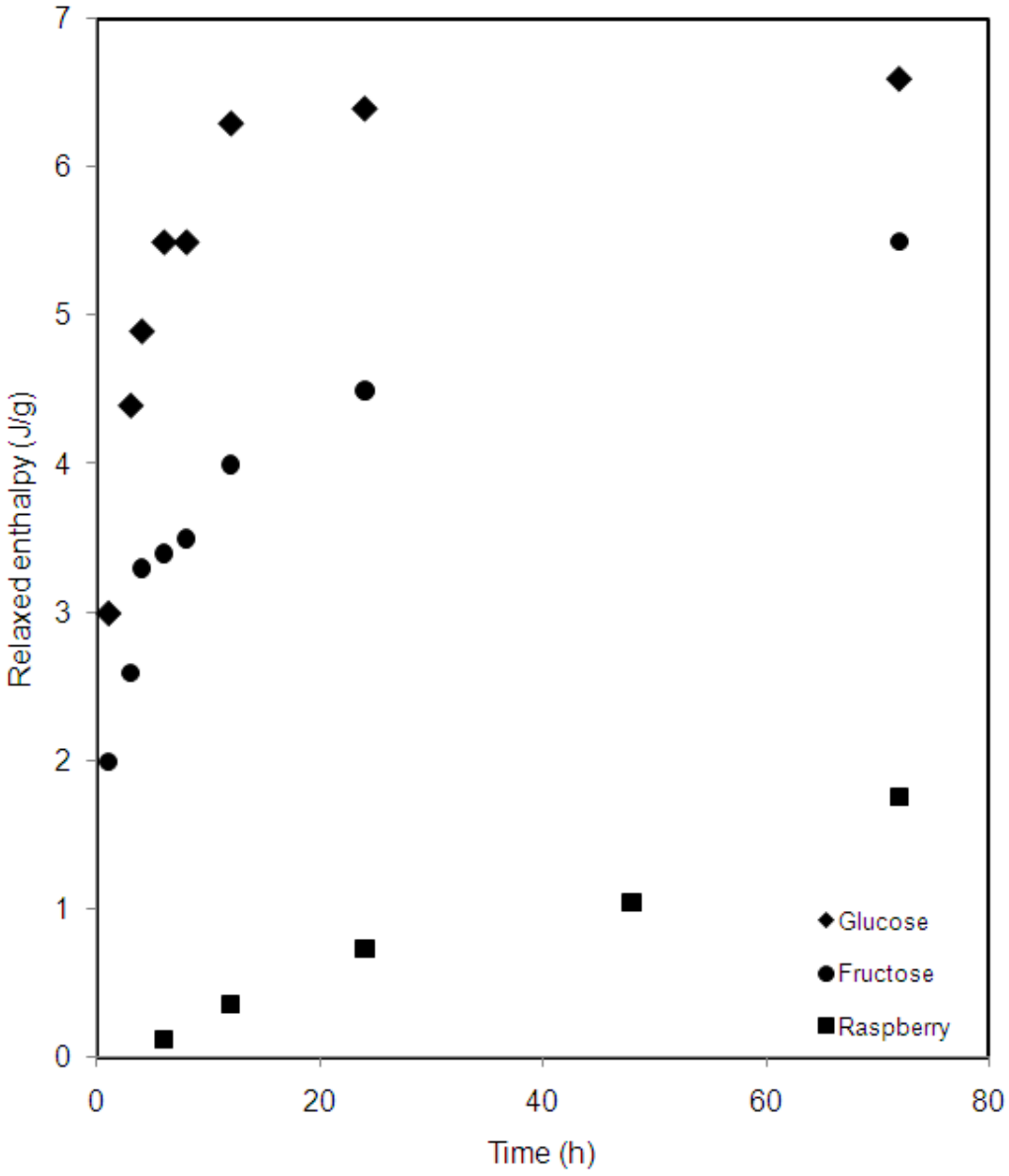
[3]Strong systems: $C_{p(liquid)}/C_{p(glass)}<1.1$; Fragile systems: $C_{p(liquid)}/C_{p(glass)}>1.1$

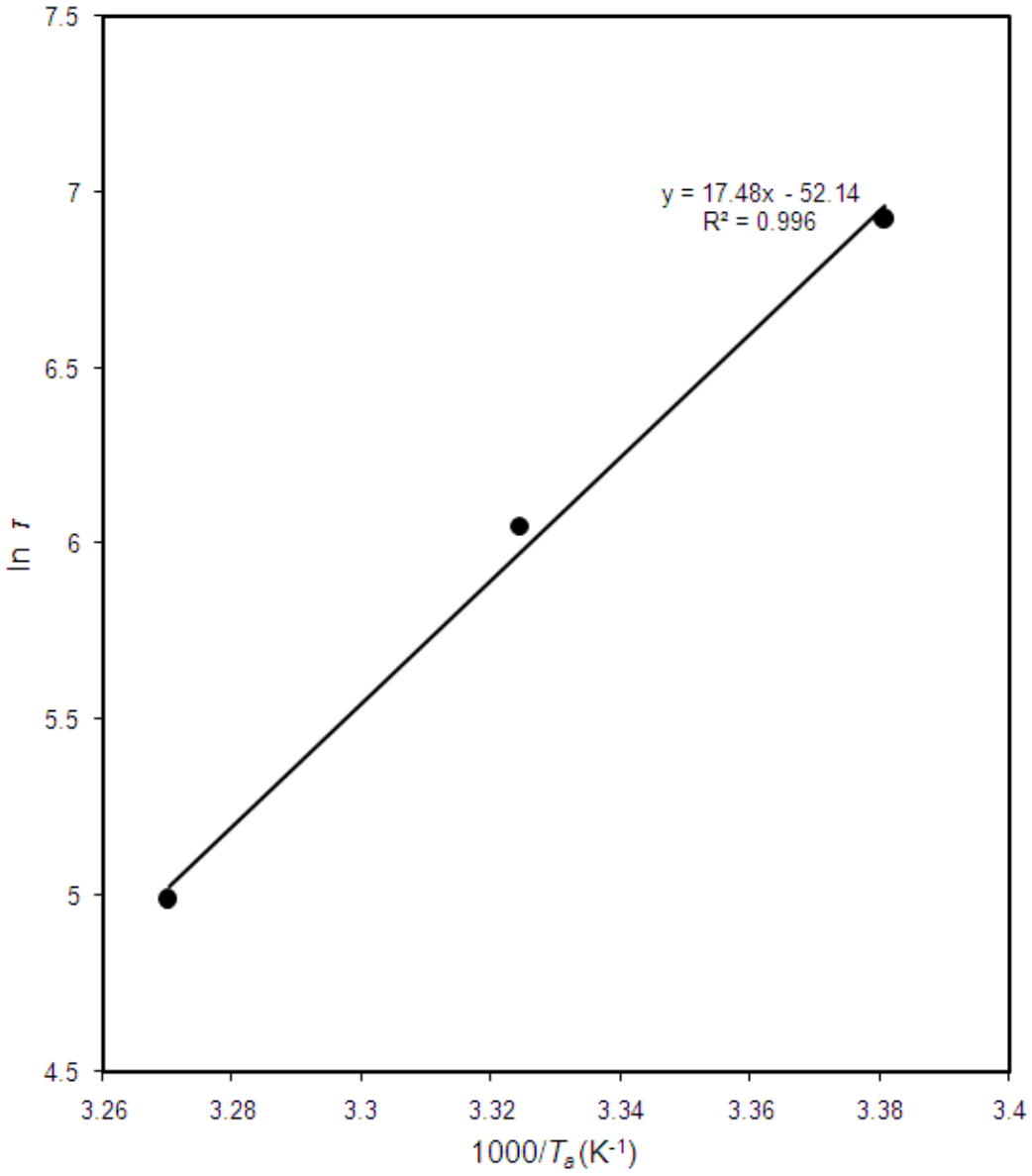
[4]Strong systems: $T_m/T_g>1.5$; Fragile systems: $T_m/T_g<1.5$

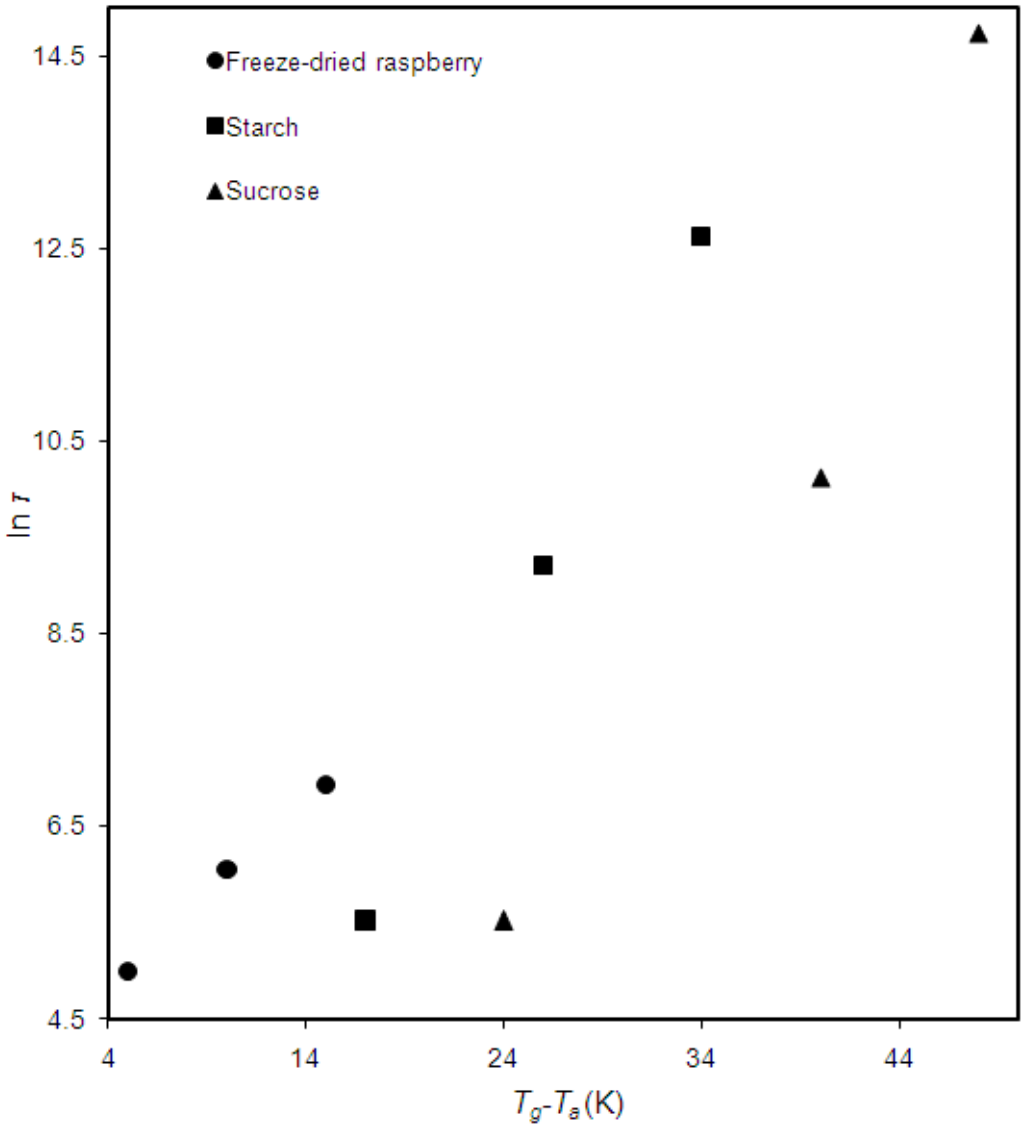

Temperature
T_g + 50°C
T_a
25°C
T_g - 50°C
5°C/min
5°C/min
5°C/min
5°C/min
Unaged experiment
Aged experiment
Time
t_a


Relaxed enthalpy (J/g)
Time (h)
(Tg-5)
(Tg-10)
(Tg-15)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
20
40
60
80
100
120


1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
1-(ΔH_relax/ΔH_∞)
0
20
40
60
80
100
120
Time (h)
(Tg-5)
(Tg-10)
(Tg-15)
(Tg-5) Predicted
(Tg-10) Predicted
(Tg-15) Predicted


Relaxed enthalpy (J/g)
Time (h)
0
1
2
3
4
5
6
7
0
20
40
60
80
Glucose
Fructose
Raspberry


y = 17.48x - 52.14
R² = 0.996
ln τ
1000/T_a(K^{-1})
7.5
7
6.5
6
5.5
5
4.5
3.26
3.28
3.3
3.32
3.34
3.36
3.38
3.4


Freeze-dried raspberry
Starch
Sucrose
14.5
12.5
10.5
8.5
6.5
4.5
ln τ
4
14
24
34
44
T_g-T_a (K)