INFLUENCE OF MOLECULAR WEIGHT ON ENTHALPY RELAXATION AND FRAGILITY OF AMORPHOUS CARBOHYDRATES

Roopesh M. Syamaladevi[1],

Gustavo V. Barbosa-Cánovas[1], **Shelly J. Schmidt**[2], **and Shyam S. Sablani**[1]*

[1]Biological Systems Engineering Department,

Washington State University, Pullman, WA 99164-6120

[2]Food Science and Human Nutrition,

University of Illinois at Urbana Champaign, 367 Bevier Hall,

905 South Goodwin Ave., Urbana, IL 61801

***Corresponding author**

(Email: ssablani@wsu.edu; Tel: +509 335 7745; Fax: +509 335 2722)

ABSTRACT

Enthalpy relaxation and fragility of selected carbohydrates were correlated with their molecular weight. Anhydrous glucose and its oligomers (i.e., maltose and maltotriose) were selected to represent amorphous carbohydrates with increasing molecular weight. The enthalpy relaxation behavior of glucose, maltose and maltotriose was determined at 5°C below their respective glass transition temperatures using differential scanning calorimetry (DSC). The non-exponential behavior of enthalpy relaxation was fitted with the Kohlrausch-Williams-Watts (KWW) equation. The mean relaxation time constants (τ) for glucose, maltose and maltotriose at (T_g-5) were 16.9, 38.4 and 128.6 h, respectively. The greater glass transition temperature and enthalpy relaxation time of maltotriose are attributed to the decreased specific volume, segmental mobility and increased entanglements resulting from its higher molecular weight. Maltotriose may be preferred as an encapsulant or food ingredient to reduce structural relaxation in food formulations during storage. The enthalpy relaxation data of the current study might be used to predict the enthalpy relaxation behaviors of amorphous carbohydrates with molecular weights within the range of glucose and maltotriose. The fragility indices (m) of glucose, maltose and maltotriose, determined using the DSC glass transition width approach, were 105, 88.1 and 97.6, respectively. This study indicated that the glass transition temperature and mean enthalpy relaxation time increased with molecular weight for the selected carbohydrates studied herein. In general, molecular weight did not affect the fragility indices of glucose, maltose and maltotriose. Inconsistencies were observed in the prediction of the fragility indices determined by different methods.

Keywords: Glass transition temperature, modulated differential scanning calorimetry, KWW model, Physical aging, *X*-ray diffraction

INTRODUCTION

Amorphous foods and food ingredients are produced by many food processing techniques such as dehydration, concentration, extrusion and freezing[1,2]. Below the glass transition temperature (T_g), amorphous food constituents exist in a thermodynamically unstable non-equilibrium and disordered state. Isothermal aging during storage of glassy amorphous food components results in structural relaxations that achieve a more stable equilibrium state over extended time periods[1,2,3,4]. Since the equilibrium state is a low energy state, some of the energy is lost/relaxed in the non-equilibrium glassy amorphous state during the isothermal storage of food components[3]. This energy can be recovered in the form of enthalpy during the reheating of the glassy system by using a differential scanning calorimeter, since physical aging is a reversible process. The enthalpy recovered during reheating of the aged material system is a measure of the system's molecular mobility at the selected aging temperature[4]. Structural relaxation in the glassy state of amorphous food components during isothermal storage/aging is also known as enthalpy relaxation/physical aging. Many macroscopic properties of glassy materials, such as volume, enthalpy, refractive index, electrical conductivity and viscosity, change during physical aging[3]. The changes in macroscopic properties may adversely affect the physicochemical stability during the isothermal storage of low water amorphous foods and food constituents[5].

Enthalpy relaxation results in unwanted quality changes in amorphous foods stored in the glassy state, wherein quantification of the relaxed enthalpy and the speed of enthalpy relaxation during isothermal aging are significant. Due to the micro-structural heterogeneities of materials, enthalpy relaxation is more complex than expressed by a simple exponential function[6]. Non-exponential expressions, such as the Kohlrausch-Williams-Watts (KWW) equation, are used extensively to describe the kinetics of enthalpy relaxation in glassy materials during aging[7,8,9]. The KWW equation was originally developed to explain dielectric relaxation and has been used to describe structural and enthalpy relaxation[10]. The KWW equation is expressed as:

$$\phi_t = \exp\left(\frac{-t}{\tau}\right)^{\beta} \tag{1}$$

where φ(t) is the relaxation function, indicating the kinetics of non-equilibrium to equilibrium transformation of the system; φ(t) provides an estimation of unreleased enthalpy or the extent of enthalpy relaxation at the specific annealing temperature[9]. Individual components of amorphous food formulations and mixtures have separate relaxations. So, a mean relaxation time is assumed to represent the molecular mobility of amorphous mixtures. The τ (days) obtained from the KWW equation is the mean molecular relaxation time of the entire amorphous system and β is the relaxation distribution parameter[11]. The parameter β characterizes the deviation of the relaxation from exponential behavior. The value of β varies between 0 and 1[10,12]. When β =1, the KWW equation is equivalent to an exponential expression. The relaxation function φ(t) is expressed as:

$$\phi_t = 1 - \frac{\Delta H_{relax}}{\Delta H_{\infty}} = \exp\left(\frac{-t}{\tau}\right)^{\beta} \tag{2}$$

$$\Delta H_{\infty} = \Delta C_p \left(T_g - T_a\right) \tag{3}$$

where ΔH_{∞} and ΔH_{relax} are the total enthalpy available for relaxation and the enthalpy relaxation during the aging time (t), respectively; ΔC_p is a heat capacity change at the glass transition temperature (T_g) and aging temperature (T_a); ΔH_{relax} is determined by calculating the area of the enthalpy relaxation peak by drawing a linear baseline. However, it is important to accurately draw the baseline since the error in calculating the area ranges between 1 and 6%[10]. In the KWW equation, both τ and β are adjustable parameters determined from fitting the experimental data on enthalpy relaxation and time via the non-linear optimization technique.

Enthalpy relaxation occurs in many amorphous carbohydrates since they are in a glassy state at room temperature (23°C). Enthalpy relaxations may adversely affect the physicochemical stability of foods during storage[13,14]. Enthalpy relaxation is a measure of molecular mobility of amorphous systems during isothermal storage[15,16]. Rates of many diffusion-limited physicochemical degradation reactions in amorphous systems can be dependent on molecular mobility and relaxation time[15,16,17]. A relationship between process rate, diffusivity, relaxation time and temperature can be established[14]:

$$\frac{k_1}{k_2} = \left(\frac{D_1}{D_2}\right)^n = \left(\frac{T_1}{T_2}\right)^{\frac{n}{2}} \left(\frac{\tau_2}{\tau_1}\right)^n \qquad (4)$$

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. τ_1 and τ_2 are the relaxation times at temperatures T_1 and T_2, respectively. n is the correlation index with values ranging from 0 to 1. Zhou et al.[14] reported partial correlation between enthalpy relaxation and rate of crystallization. Bansal et al.[13] reported inverse correlation between time for 10% crystallization and enthalpy relaxation in amorphous valdecoxib. Gupta et al.[4] reported that enthalpy relaxation and solubility of celecoxib-polyvinylpyrrolidone are also inversely related. It is important to estimate the enthalpy relaxation rate to select adequate storage conditions of foods and pharmaceuticals in their glassy state.

The '*fragility*' concept introduced by Angell[18,19] also has practical implications in predicting the physical and chemical stability of foods. The '*fragility*' concept differentiates the amorphous systems as either '*strong*' or '*fragile*' based on their temperature dependence on dynamic properties, structural changes and relaxation behavior near or above T_g. Fragile systems exhibit sharp and narrow glass transitions, presenting rapid increases in heat capacity and dynamic properties, such as viscosity at or near T_g[20]. Strong systems generally have broad glass transitions and exhibit less temperature sensitivity, presenting a gradual change in heat capacity and viscosity at or near T_g. Fragile systems exhibit significant changes (60-80%) in heat capacity (ΔC_p) at T_g [18,19]. The ratio $C_{p(liquid)}/C_{p(glass)}$ of fragile systems is greater than 1.1[18]. Fragile systems also exhibit a small enthalpy relaxation distribution parameter (β), as demonstrated by the KWW model[21]. A fragility index (m) was introduced to better quantify the fragility concept[19]. The fragility index is defined as:

$$m = \frac{\Delta E}{2.303 R T_g} \qquad (5)$$

where ΔE is the activation energy for structural relaxations at T_g, and R is the gas constant. Fragile systems exhibit large m values between 100 and 200, while strong systems present small m values between 16 and 100[21]. The physical, chemical and structural stability of amorphous food systems is related to their fragility, as it provides information on the variation in dynamic properties and relaxation times of amorphous systems near or above T_g[22]. Above T_g, strong systems exhibit greater relaxation times, while below T_g a reversal of dynamic properties and relaxation times occurs[23]. Many physicochemical degradation reactions may be controlled by molecular mobility/relaxations in food systems where relaxation times provide useful information on the rates of these reactions. By relating fragility to the relaxation times, one can predict the temperature dependence of relaxations and thereby the rates of degradation reactions in amorphous systems[20]. For instance, the rate of molecular mobility of fragile systems is changed by one order of magnitude (approximately) for every 10°C difference in temperature; whereas in strong systems, the rate of molecular mobility changes (approximately) every 25°C[22].

Hatley[20] reported that fragile systems may be preferable in their glassy state since dynamic properties such as viscosity increase rapidly with small decreases in storage temperature, which may increase the stability of glassy systems.

A glass transition width approach was used to determine the fragility of food systems. Strong systems normally display broad glass transition, while fragile systems exhibit narrow glass transition and dramatic changes in thermodynamic properties at glass transition temperatures[24]. Fragility was determined by calculating the activation enthalpy of structural relaxation identifying the glass transition width[24,25,26]. The activation enthalpy and glass transition width are related by:

$$\left(\frac{\Delta E}{R}\right)\left(\frac{1}{T_{gi}}-\frac{1}{T_{ge}}\right)=\text{Constant} \qquad (6)$$

where ΔE is the activation energy for structural relaxations at the glass transition temperature. T_{gi} and T_{ge} are the onset and endpoint glass transition temperatures. Since the glass transition is kinetic in nature, and the assigned value of T_g is dependent on the heating (q_h) and cooling rate (q_c), equation (6) is applicable for a specific q_c/q_h[25], provided:

$$0.2 \le \left|\frac{q_c}{q_h}\right| \le 5 \qquad (7)$$

By studying several material systems, the constant in equation (6) was identified as 5 ± 0.5. In the current study, the value of the constant was selected as 5. The activation enthalpy and fragility index (m) are related in equation (5)[26].

It is well known that glass transition temperature is influenced by the heating/cooling rates used. Glass transition dependence on heating/cooling rates may be expressed as[27,28]:

$$\frac{d\ln|q_h|}{d\frac{1}{T_g}} = -\frac{\Delta E}{R} \tag{8}$$

where q_h is the heating rate and ΔE is the activation energy for structural relaxations. The fragility index (m) may be determined by using the ΔE value obtained from equation 8 in equation 5. Since T_g is dependent on the heating (q_h) and cooling rate (q_c), equation 8 should be used satisfying the conditions of equation 7.

Enthalpy relaxation in amorphous food systems is strongly dependent on aging temperature, aging time, thermal history, and properties of food components. Similar to the glass transition temperature, enthalpy relaxation may also depend on the molecular weight of the food components. The rate at which relaxations occur may vary depending on the molecular weight of the amorphous carbohydrates. Molecular weight may play an important role in the selection of amorphous carbohydrates as encapsulating agents/ingredients based on their physical and chemical stability at room temperature. Similarly, fragility may also be dependent on the molecular weight of amorphous carbohydrates. Information on the dependency of molecular weight on fragility improves our understanding of the temperature dependency of amorphous carbohydrates at T_g. Amorphous carbohydrates such as glucose, maltose, and maltotriose are often used as food ingredients or encapsulating agents due to their high T_g and viscosity[29].

Thus, the objective of this study was to investigate the effects of molecular weight on enthalpy relaxation and the fragility of amorphous carbohydrates. Anhydrous glucose, maltose and maltotriose were chosen to characterize amorphous carbohydrates with increasing molecular weight.

MATERIALS AND METHODS

Anhydrous glucose, maltose and maltotriose were purchased from Fisher Scientific (Pittsburg, PA). The maltose and maltotriose are oligomers of glucose consisting of two and three glucose molecules, respectively. Glucose, maltose and maltotriose solutions were prepared by dissolving them in distilled water (10 g carbohydrates/100 g water). The carbohydrate solutions were dried in a laboratory freeze dryer (VirTis Freeze Mobile 24 with Unitop 600L, Virtis SP Industries Co., New York). Initially the carbohydrate solutions were frozen to -35°C. The frozen carbohydrate solutions were transferred to a freeze dryer shelf maintained at -25°C. The shelf temperature was increased to 20°C with a vacuum of 20 Pa and condenser temperature at -60°C. After 48 h of freeze drying, the amorphous carbohydrates were ground to a fine powder using mortar and pestle. Glucose, maltose and maltotriose were kept in a desiccator with P_2O_5 at room temperature (298 K) for two days. The moisture content of dry amorphous carbohydrates was analyzed using the vacuum oven method and was ~0.005 kg H_2O/kg sample[30].

Differential Scanning Calorimetry (DSC)

Enthalpy relaxation experiments were conducted using a modulated differential scanning calorimeter (MDSC) (Q2000, TA Instruments, New Castle, DE) using nitrogen as the purge gas at a rate of 50 mL/min. Baseline calibration of the DSC was conducted using sapphire. MDSC was calibrated for temperature and heat flow using indium (T_m = 156.6°C) and for heat capacity, using sapphire as standards. MDSC deconvolutes total heat flow into nonreversing and reversing (heat capacity) signals[31]. In the glass transition temperature identification experiments, small amounts of freeze-dried glucose, maltose and maltotriose (10–20 mg) were scanned above their respective melting temperatures to remove their thermal history after equilibration at 25°C for 5 minutes (Figure 1). Then the carbohydrates were scanned to (T_{gi}-50) at 3°C/min to make carbohydrate glasses. After equilibrating the carbohydrates for 1 min, they were reheated to (T_{gi}+100) at a rate of 3°C/min in the second scan and then cooled back to 25°C (Figure 1). The selected modulation amplitude and modulation period were ±0.5°C and 45 seconds, respectively[32]. The onset (T_{gi}), midpoint (T_{gm}) and endpoint (T_{ge}) glass transition temperatures of the glucose, maltose and maltotriose were determined as shown in the thermograms (Figure 2). T_{gi} was identified as the temperature equivalent to the intersection of the regression line before the step change in the reversible heat flow curve and inflection tangent of MDSC thermogram in the second scan as presented in Figure 2[32]. Similarly, T_{ge} was identified as the intersection of the tangent after the step change in the reversible heat flow curve and inflection tangent of MDSC thermogram[32]. T_{gm} was assigned as the mid temperature between T_{gi} and T_{ge}, corresponding to 50% transition (Figure 2).

After identifying the glass transition temperatures, annealing/aging experiments were conducted for glucose, maltose and maltotriose in at least, duplicate. The temperature selected for aging of glucose, maltose and maltotriose was 5°C below their T_{gi} since maximum enthalpy relaxation is found near T_g (Figure 1). In the annealing experiments, carbohydrates were scanned above their respective melting temperatures (~T_{gi} +100) to remove their thermal history (Figure 1). The carbohydrates were cooled backed to (T_{gi}-50) at 3°C/min to make a carbohydrate glasses. Then the carbohydrates were annealed isothermally at (T_{gi}-5) for selected periods of time (0.5 to 48 h). After aging, samples were cooled to (T_{gi} -50) and reheated to (T_{gi}+100) at 3°C/min. The enthalpy recovered during reheating was determined by drawing a linear baseline to the enthalpy endotherm in the nonreversible heat flow curve of MDSC thermogram (Figure 2). In the nonreversible heat flow thermogram of an unaged sample, an endotherm attributable to the "frequency effect" appears. For determining the enthalpy corresponding to the "frequency effect", the unaged carbohydrates were heated to T_{gi} +100 (above their respective melting temperatures) and then cooled back to T_{gi} - 50. Further, in the second scan, the carbohydrates were heated to T_{gi} +100 and then cooled back to 25°C. The enthalpy corresponding to the "frequency effect" was determined by drawing a linear baseline to the enthalpy endotherm in the nonreversible heat flow curve of MDSC thermogram similar to the aged carbohydrates. The actual enthalpy recovered during the aging process was obtained by subtracting this "frequency effect" from the enthalpy in the nonreversible heat flow thermogram of aged sample. The analysis of the thermogram was conducted using TA Instrument's Universal Analysis software. The enthalpy relaxation data of glucose, maltose and maltotriose were fitted with the KWW equation to obtain the values of characteristic relaxation time (τ) and relaxation distribution parameter (β) using Statistica® version 5 computer program. The fragility indices (m) of glucose, maltose and maltotriose were determined by the glass transition width approach by identifying the onset (T_{gi}), end point glass transition temperatures (T_{ge}) and heat capacity change (ΔC_p) at glass transition as presented in the Figure 3. The fragility index was also determined using T_g dependence on heating rate method. The glass transition temperatures of selected amorphous carbohydrates were determined at different heating rates using a MDSC. A graph between ln $|q_h|$ and $1000/T_{gi}$ was plotted and the slope of the regression line was determined. The values of ΔE and m were determined considering equations 5 and 8.

Statistical significance of the results was analyzed using SAS 9.1 (SAS Institute, Inc., Cary, NC, USA). A value of $P < 0.05$ was selected as statistically significant using least square difference (LSD) method.

X-ray diffraction

Wide angle *X*-ray diffraction measurements were performed at 23°C using a D-500 powder *X*-ray diffractometer (Siemens, Bruker, Karlsruhe, Germany) to observe the densification of amorphous carbohydrates during storage. Amorphous maltose was stored in aluminum cells at aging temperature (T_g-5) for selected periods of time in a convection oven. The *X*-ray diffraction spectra of aged maltose were compared with the *X*-ray diffraction spectra of completely crystalline maltose. The copper target tube of the diffractometer was set at 35 kV and 30 mA, with a wavelength of 1.5 Å. XRD spectra of selected carbohydrate samples were obtained, analyzing them over a 2θ range of 2-50° at 0.05° intervals.

RESULTS

Glass transition temperature vs Aging conditions

The Glass transition temperatures of the selected amorphous carbohydrates were dependent on their molecular weight. The molecular weights of glucose, maltose and maltotriose are 180, 342 and 504 g/mol, respectively. The onset glass transition temperatures (T_{gi}) of unaged glucose, maltose and maltotriose obtained were 34.5±0.20, 78.5±1.75 and 128.8±4.13°C respectively. It is well established that increasing molecular weight results in an increase in glass transition temperature due to a reduction in specific volume[33,34]. No significant difference was observed between the T_{gi} of unaged and aged carbohydrates (Table 1). Aging/annealing at (T_{gi}-5) did not significantly alter the T_{gi} of glucose, maltose and maltotriose for selected periods of time (Table 1). Previous literature reported no significant difference in T_g of systems after aging at selected temperatures for selected period of time[35,36,37]. However, a small increase in the glass transition temperature after aging is observed in selected foods and pharmaceuticals[38,39,40]. This increase in T_g is associated with the smaller free volume and molecular mobility of the metastable equilibrium state in comparison to the non-equilibrium state after aging[40]. A slight decrease in T_g of salicin during aging was reported by Mao et al.[23]. Wungtanagorn and Schmidt[1] mentioned that the increase or decrease of T_g with aging time is dependent on the method used in the assignment of T_g. No statistically significant difference in T_{gi} was observed for glucose aged for selected aging periods (0-48 h). Significant difference in T_{gi} was observed between maltose aged for 12 and 48 h (Table 1). The T_{gi} of maltotriose aged for 48 h was significantly different from the maltotriose aged for 0.5-12 h (Table 1). During the determination of T_{gi}, the carbohydrates were heated above their melting points using MDSC, which could result in thermal decomposition, influencing the T_{gi} values[41,42]. Glass transition temperature width (T_{ge}-T_{gi}) of glucose did not change significantly during isothermal aging at (T_{gi}-5) for 0.5 to 48 h (Table 1). The (T_{ge}-T_{gi}) of unaged glucose was significantly different from aged glucose (0.5-48 h). The (T_{ge}-T_{gi}) of 2 h aged maltose was significantly different from rest (Table 1). The (T_{ge}-T_{gi}) of maltotriose aged for 48 h was significantly different from rest of the aged maltotriose (Table 1).

In the MDSC thermograms of glucose, maltose and maltotriose, the difference in C_p values between glassy and rubbery states is measured as the heat capacity change (ΔC_p). The heat capacity change (ΔC_p) at T_g of maltotriose was smaller than the other selected carbohydrates, attributed to its higher chain rigidity and molecular weight[43] (Figure 4). A slight increase in the heat capacity change (ΔC_p) at T_g with aging time was observed for maltose and maltotriose, while a fluctuating trend in ΔC_p was observed for glucose (Figure 4). Chung and Lim[38] observed an increase in ΔC_p with aging time for rice starch. Wungtanagorn and Schmidt[1] also observed increase in ΔC_p at glass transition with aging of glucose, fructose and their mixture. However, a comparatively constant ΔC_p and decrease in ΔC_p with aging are also reported[44,45]. Since the equilibrium state has a smaller heat capacity and free energy compared to glassy and rubbery states, an increase in ΔC_p is expected after aging[38]. In the current study, the difference in the trends in ΔC_p with aging time could possibly be due to thermal decomposition resulting from heating the carbohydrates above their melting points in the MDSC[41,42].

Molecular weight dependence of enthalpy relaxation time

The selected aging temperatures (T_g-5) for glucose, maltose and maltotriose were 29.5, 73.5 and 123.8°C, respectively. In the nonreversible heat flow thermogram of an unaged sample, an endotherm called "frequency effect" appears[46]. The actual enthalpy recovered during the aging process is obtained by subtracting this "frequency effect" from the enthalpy in the nonreversible heat flow thermogram of aged sample[46]. The total enthalpy decreased, while the relaxed enthalpy increased with increasing aging time for glucose, maltose and maltotriose (Figure 5). The rate of enthalpy relaxation of selected carbohydrates decreased gradually during aging due to the decrease in total enthalpy during aging (Figure 5). The relaxed enthalpy was greater for glucose than maltose and maltotriose during aging (Figure 5), attributed to its smaller molecular weight and higher specific volume and resulting smaller chain rigidity[43].

The rate of enthalpy relaxation and the quantity of relaxed enthalpy for a given aging time are the highest when the aging temperature is close to T_g[40]. As aging proceeds, the amorphous system reaches the metastable equilibrium state by losing the enthalpy and decreasing the free volume[47]. The KWW equation was used to fit the enthalpy relaxation kinetics of the selected amorphous carbohydrates; KWW adjustable parameters are presented in Figure 6 and Table 2. The τ values determined for glucose, maltose and maltotriose were 16.9, 38.4 and 128.6 h, respectively. An exponential relationship between τ and molecular weight of the selected amorphous carbohydrates was obtained (Figure 7). The larger τ value for maltotriose may be attributed to its smaller specific volume, resulting in more restriction of its relaxing elements during aging. The molecular mobility of glassy maltotriose may be smaller than the molecular mobility of glucose and maltose at a specific aging temperature. The τ value obtained for glucose is higher than previously reported literature values (e.g. 3.35 h)[1], but smaller in the case of raspberry powder (e.g. 147.1 h)[36], in which glucose is one of the major constituents. This difference may be attributed to the presence of other constituents and complex interactions between them.

In the current study, β values obtained for glucose, maltose and maltotriose were 0.23, 0.33 and 0.24, respectively. A β value much smaller than 1 shows the non-exponentiality and broad distribution of the enthalpy relaxations[6]. The relaxation times present an abrupt change at the glass transition, when the β value is close to 1[6]. The β value obtained for glucose is smaller than that of raspberry powder. The β values of carbohydrates may be also related to the degree of co-operativity between relaxing elements[48]. Smaller values of β represent hydrogen bonding and coupling between relaxing elements of the studied carbohydrates[48]. However, τ and β values are kinetic in nature and may not be related to structure[49]. ΔH_∞ may be related to structure and molecular weight of materials during aging[43,49]. The value of ΔH_∞ decreased linearly with molecular weight for the selected carbohydrates (Table 2 and Figure 8). The greater ΔH_∞ of glucose is attributed to its higher ΔC_p at T_g.

The relaxation time corresponding to 50% of the maximum enthalpy ($\tau_{\varphi(t)=50\%}$) and 99% of the maximum enthalpy ($\tau_{\varphi(t)=99\%}$) during the aging process is determined at (T_{gi}-5) from τ and β values[9]. The $\tau_{\varphi(t)=50\%}$ values were 50.9, 80.7 and 371.4 h, while $\tau_{\varphi(t)=99\%}$ values were 338.4, 535.9 and 2467.6 h for glucose, maltose, and maltotriose respectively. The increasing $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=99\%}$ values of the selected higher molecular weight amorphous carbohydrates indicate they may be used as encapsulants and ingredients to reduce the structural relaxations during storage.

The $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=99\%}$ values obtained for glucose are smaller than $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=99\%}$ values of raspberry powder attributed to the complex interactions of components in the raspberries compared to interactions among pure components[9,36]. The $\tau_{\varphi(t)=50\%}$ value from the KWW equation depends more on β than τ. A small increase/decrease in β affects the $\tau_{\varphi(t)=50\%}$ significantly, since β is an exponential coefficient in the KWW model. The $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=99\%}$ values obtained for glucose, maltose and maltotriose may provide important indications that affect their selection as food ingredients and encapsulants, since they play crucial roles in long term storage stability at room temperature.

Intensity of *X*-ray diffraction (XRD) peaks of maltose aged for 0.5, 6, and 14 days at (T_g-5) were significantly greater than that of unaged maltose (Figure 9B). The increased intensity of the aged maltose may be attributed to the closer molecular rearrangement during aging[50,51]. The XRD peaks of aged maltose became narrower than for unaged maltose. During aging, densification resulting from closer molecular rearrangement may occur. Ambike et al.[50] observed no characteristic peak, but significant elevation of diffractograms after 6 months storage of model drug simvastatin in glassy state. The densification may result in shifting of the peak angle to higher levels and narrowing of the peak in XRD spectra[51]. Further, the XRD spectra of aged maltose were compared with the XRD spectra of completely crystalline maltose (Figure 9A and 9B). It was interesting to observe that the peak angles of completely crystalline maltose ($19.85<2\theta<20.1$) and aged maltose ($17.95<2\theta<22.35$) were in the similar range (Figure 9A and 9B).

Fragility of amorphous carbohydrates

In the current study, selected methods were used to determine the fragility of the glucose, maltose and maltotriose (Table 3). Fragility of an amorphous system is generally determined by analyzing variations in specific properties at T_{gi}. Using equation (6), the activation enthalpy of structural relaxations (ΔE) of glucose, maltose and maltotriose at the glass transition temperature were 692.8, 593.2 and 750.9 kJ/mol, respectively. Fragility indices (m) of glucose, maltose and maltotriose determined using the glass transition width approach were 105, 88.1 and 97.6, respectively (Table 3). The m values of the selected amorphous carbohydrates indicate the fragile behavior of glucose, while maltose and maltotriose are comparatively stronger in nature. No linear relationship between m values and molecular weights of the amorphous carbohydrates was observed. Maltose and maltotriose exhibited similar, but higher glass transition widths (T_{ge}-T_{gi}) than glucose. So the ΔE of maltose was smaller than the ΔE of maltotriose calculated using equation (6). Hence, the m of maltose was smaller than the m of maltotriose and glucose.

Fragility indices (m) of glucose, maltose and maltotriose were also determined using a method based T_g dependence on heating rate (q_h) used in the DSC. As presented in Figure 10, a linear relationship was observed between ln q_h and 1000/T_g of amorphous carbohydrates. The values of ΔE calculated for glucose, maltose and maltotriose using equation 8 were 202.9, 158.3, and 220.1 kJ/mol respectively (Figure 10). From these ΔE values and using equation 5, fragility indices of glucose, maltose and maltotriose were 34.5, 23.5 and 28.6 respectively (Table 3). The m values calculated using T_g dependence on heating rate were smaller than the m values determined using glass transition width approach, but the trend remains the same (Table 3). The m values calculated using T_g dependence on heating rate indicate, glucose, maltose and maltotriose are fragile in nature (Table 3).

For glucose, maltose and maltotriose, the $C_{p(liquid)}/C_{p(glass)}$ values (The ratio of the heat capacity of material system in the rubbery state to the heat capacity of the material system in the glassy state) were determined as 2.21, 1.65 and 1.24 (Table 3) respectively, indicate the fragile behavior of selected amorphous carbohydrates[45]. The fragility of the selected carbohydrates increased as molecular weight increased with regard to the $C_{p(liquid)}/C_{p(glass)}$ ratio (Table 3). Glucose, maltose and maltotriose exhibited a small ΔC_p at T_g and are categorized as fragile. A greater ΔC_p at T_g for maltotriose demonstrates its stronger nature in comparison to glucose and fructose. Raspberry powders present strong behavior where the main components, glucose and fructose, may encourage complex interactions among components[36].

Bohmer et al.[52] proposed a simple empirical relationship relating β and fragility index (m) as:

$$m = 250 - 320\beta \tag{8}$$

The β values for glucose, maltose and maltotriose using equation (8) and fragility indices from glass transition width approach are 0.45, 0.51 and 0.47, respectively. This empirical relationship between m and β depends on the fragility index determination method and provides a rough approximation of β[53]. The smaller β value indicates a more fragile behavior of glucose in comparison to maltose and maltotriose.

One possible explanation for this discrepancy in the fragility of glucose, maltose and maltotriose could be the thermal decomposition of carbohydrates to smaller components resulting from heating them above their melting points, which may have influenced the fragility determination[41,42]. Previous literature presents inconsistencies in the fragility predictions by different methods for various systems. There is no definite explanation is available for the difference in fragility predictions by different methods[1,2]. More research is required for clarification of this discrepancy.

DISCUSSION

The relaxation enthalpies are much smaller and hence the τ values of maltotriose are much larger than the relaxation enthalpies and τ values of glucose and maltose. Hence, maltotriose may be preferably used in food formulations to reduce structural relaxation during storage. The enthalpy relaxation behavior of amorphous carbohydrates with molecular weights between glucose and maltotriose might be predicted using the enthalpy relaxation data of glucose, maltose and maltotriose. By studying the enthalpy relaxation behavior of different molecular weight carbohydrates, a database of enthalpy relaxation in relation to molecular weight may be developed.

The molecular weight dependence of enthalpy relaxations and the fragility information of selected amorphous carbohydrates obtained from this study are useful tools for selecting these carbohydrates as ingredients or encapsulants for various food formulations. The enthalpy relaxation data of the current study might be used to predict the enthalpy relaxation behavior of selected amorphous carbohydrates with molecular weight in between glucose and maltotriose. Also the estimated relaxation times may be used to predict the physicochemical stability of amorphous carbohydrates, which also can reduce the cost and time of complex experiments[51]. However, a relationship between relaxation times and rates of physicochemical degradation reactions should be established for such a comparison[51]. Thus, enthalpy relaxation time and fragility information obtained may be used to predict various physicochemical changes in selected carbohydrates during their long-term glassy state storage.

SAFETY

No specific safety or toxicological concerns are associated with the current research.

ACKNOWLEDGEMENTS

This activity was funded, in part, by an Emerging Research Grant from Washington State University, College of Agricultural, Human, and Natural Resource Sciences.

REFERENCES

1. Wungtanagorn, R.; Schmidt, S. J. Thermodynamic properties and kinetics of the physical aging of amorphous glucose, fructose and their mixture. *J. Therm. Anal. Cal.* ***2001a***, *65*, 9-35.
2. Wungtanagorn, R.; Schmidt, S.J. Phenomenological study of enthalpy relaxation of amorphous glucose, fructose, and their mixture. *Thermochim. Acta*, ***2001b**, 369*, 95-116.
3. *Physical aging in amorphous polymers and other materials*; Struik, L. C. E. Elsevier Scientific Pub. Co: Amsterdam, 1978.
4. Gupta, P.; Kakumanu, V. K.; Bansal, A. K. Stability and solubility of Celecoxib-PVP amorphous dispersions: A molecular perspective. *Pharm. Res.* ***2004***, *21(10)*, 1762-1969.
5. Farahnaky, A.; Guerrero, A.; Hill, S. E.; Mitchell, J. R. Physical aging of cray fish flour at low moisture contents. *J. Therm. Anal. Cal.* ***2008**, 93(2)*, 595-598.
6. Liu, Y. T., Bhandari, B., Zhou, W. B. Glass transition and enthalpy relaxation of amorphous food saccharides: A review. *J. Agric. Food Chem.* ***2006***, *54(16)*, 5701-5717.
7. Hancock, B. C., Shamblin, S. L., Zografi, G. Molecular mobility of amorphous pharmaceutical solids below their glass transition temperatures. *Pharm. Res.* ***1995**, 12(6)*, 799-806.
8. Hancock, B. C.; Shamblin, S. L. Molecular mobility of amorphous pharmaceuticals determined using differential scanning calorimetry. *Thermochim. Acta*, ***2001***, *380*, 95-107.
9. Liu, Y., Bhandari, B., Zhou, W. Study of glass transition and enthalpy relaxation of mixtures of amorphous sucrose and amorphous tapioca starch syrup solid by differential scanning calorimetry (DSC). *J. Food Eng.* ***2007***, *81*, 599-610.

10. Van den Mooter, G.; Augustijns, P.; Kinget, R. Stability prediction of amorphous benzodiazepines by calculation of the mean relaxation time constant using Williams-Watts decay function. *Euro. J. Pharm. Biopharm.* ***1999***, *48*, 43-48.
11. Yoshioka, S.; Aso, Y.; Kojima, S. Usefulness of the Kohlrausclh-Williams-Watts stretched exponential function to describe protein aggregation in lyophilized formulations and the temperature dependence near the glass transition temperature. *Pharm. Res.* ***2001***, *18(3)*, 256-260.
12. Christensen, K. L.; Pedersen, G. P.; Kristensen, H. G. Physical stability of redispersible dry emulsions containing amorphous sucrose. *Euro. J. Pharm. Biopharm.* ***2002,*** *53(2)*, 147-153.
13. Bansal, S. S.; Kaushal, A. M.; Bansal, A. K. Co-relationship of physical stability of amorphous dispersions with enthalpy relaxation. *Pharmazie*, ***2008***, *63(11)*, 812-814.
14. Zhou. D., Zhang, G. G. Z., Law, D., Grant, D. J. W., Schmidt, E. A. Thermodynamics, Molecular Mobility and Crystallization Kinetics of Amorphous Griseofulvin. *Mol. Pharm.* ***2008***, *5(6)*, 927-936.
15. Byrn, S.R.; Xu, W.; Newman, A.W. Chemical reactivity in solid-state pharmaceuticals: formulation implications. *Ad. Drug Del. Rev.* ***2001***, *49 (1)*, 115–136.
16. Luthra, S. A.; Hodge, I. M.; Utz, M.; Pikal, M. J. Correlation of annealing with chemical stability in lyophilized pharmaceutical glasses. *J. Pharm. Sci.* ***2008***, *97 (12)*, 5240–5251.
17. Bell, L. N. Moisture effects on food's chemical stability. In: *Water activity in foods: fundamentals and applications*; Barbosa-Canovas, G. V., Fontana, A. J. Jr., Schmidt, S. J., Labuza, T. P., Eds; Blackwell Publishing Ltd: Ames, 2007; pp 177-198.

18. Angell, C. A. Spectroscopy simulation and scattering, and the medium range order problem in glass. *J. Non-Crystal. Sol.* ***1985***, *73,* 1-17.

19. Angell, C. A. Perspective on the glass transition. *J. Non-Crystal. Sol.* ***1988****, 49(8),* 863-871.

20. Hatley, R H. M. Glass fragility and stability of pharmaceutical preparations-Excipient selection. *Pharm. Dev. Technol.* ***1997****, 2(3)*, 257-264.

21. Champion, D.; Le Meste, M.; Simatos, D. Towards an improved understanding of glass transition and relaxations in foods: molecular mobility in the glass transition range. *Trends Food Sci. Technol.* ***2000****, 11(2)*, 41-55.

22. Hancock, B.C.; Dalton, C. R.; Pikal, M. J.; Shamblin, S. L. A pragmatic test of a simple calorimetric method for determining the fragility of some amorphous pharmaceutical materials. *Pharm. Res.* ***1998****, 15(5)*, 762-767.

23. Mao, C.; Chamarthy, S. P.; Byrn, S. R.; Pinal, R. Theoretical and experimental considerations on the enthalpic relaxation of organic glasses using differential scanning calorimetry. *J. Phys. Chem.* ***2010****, 114*, 268-279.

24. Moynihan, C. T.; Lee, S. K.; Tatsumisago, M.; Minami, T. Estimation of activation energies for structural relaxation and viscous flow from DTA and DSC experiments. *Thermochim. Acta*, ***1996***, *280*, 153-162.

25. Moynihan, C. T. Correlation between the width of glass transition region and the temperature dependence of the viscosity of high-T_g glasses. *J. Am. Cer. Soc.* ***1993***, *76(5)*, 1081-1087.

26. Crowley, K. J.; Zografi, G. The use of thermal methods for predicting glass former fragility. *Thermochim. Acta*, ***2001***, *380(2)*, 79-93.

27. Moynihan, C. T.; Esteal, A. J.; Wilder, J.; Tucker, J. Dependence of the glass transition temperature on heating and cooling rates. *J. Phys. Chem.* ***1974***, *76*, 2673-2677.

28. Moura Ramos, J. J.; Taviera-Marques, R.; Diogo, H. P. Estimation of the fragility index of indomethacin by DSC using heating and cooling rate dependency on glass transition. *J. Pharm. Sci.* ***2004***, *93(6)*, 1503-1507.

29. Bayram, O. A.; Bayram, M.; Tekin, A. R. Spray drying of sumac flavor using sodium chloride, sucrose, glucose and starch as carriers. *J. Food Eng.* ***2005***, *69(2)*, 253-260.

30. Syamaladevi, R. M.; Sablani, S. S.; Tang, J.; Powers, J.; Swanson, B. G. State diagram and water adsorption isotherm of raspberry (*Rubus idaeus*). *J. Food Eng.* ***2009,*** *91,* 460-467.

31. Shamblin, S. L.; Tang, X.; Chang, L.; Hancock, B. C.; Pikal, M. J. Characterization of the time scales of molecular motion in pharmaceutically important glasses, *J. of Phys. Chem.* ***1999***, *103*, 4113-4121

32. Lammert, A. M., Lammert, R. M., Schmidt, S. J. Physical aging of maltose glasses as measured by standard and modulated differential scanning calorimetry. *J. Therm. Anal. Calorimet.* ***1999***, *55*, 949-975.

33. Roos, Y.H.; Karel, M. Water and molecular weight effects on glass transitions in amorphous carbohydrates and carbohydrate solutions. *J. Food Sci.* ***1991***, *56(6)*, 1676-1681.

34. Abiad, M. G.; Carvajal, M. T.; Campanella, O. H. A review on methods and theories to describe the glass transition phenomenon: Applications in food and pharmaceutical products. *Food Eng. Rev.* ***2009***, *1(2),* 105-132.

35. Boller, A.; Schick, C.; Wunderlich, B. Modulated differential scanning calorimetry in the glass transition region. *Thermochim. Acta*, ***1995**, 266,* 97-111.

36. Syamaladevi, R. M.; Sablani, S. S.; Swanson, B. G. Aging of amorphous raspberry powder: Enthalpy relaxation and fragility. *J. Food Eng.* ***2010***, *101*, 32–40.

37. Craig, D. Q. M.; Barsnes, M.; Royall, P. G.; Kett, V. L. An evaluation of the use of modulated temperature DSC as a means of assessing the relaxation behavior of amorphous lactose. *Pharm. Res.* ***2000***, *17(6)*, 696-700.

38. Chung, H. J.; Lim, S. T. Physical aging of glassy normal and waxy rice starches: Effect of aging time on glass transition and enthalpy relaxation. *Food Hydrocol.* ***2003***, *17(6)*, 855-861.

39. Schmidt, S. J.; Lammert, A. M. Physical aging of maltose glasses. *J. Food Sci.* ***1996***, *61(5)*, 870-875.

40. Haque, M. K.; Kawai, K.; Suzuki, T. Glass transition and enthalpy relaxation of amorphous lactose glass. *Carbohydr. Res.* ***2006***, *341*, 1884-1889.

41. Lee, J. W., Thomas, L. C., Schmidt, S. J. (2011a). Investigation of the heating rate dependency associated with the loss of crystalline structure in sucrose, glucose and fructose using a thermal analysis approach (Part I). *Journal of Agricultural and Food Chemistry*, 59, 684-701.

42. Lee, J. W., Thomas, L. C., Jerrell, J., Feng, H., Cadwallader, K. R., Schmidt, S. J. (2011b). Investigation of thermal decomposition as the kinetic process that causes the loss of crystalline structure in sucrose using a chemical analysis approach (Part II). *Journal of Agricultural and Food Chemistry*, 59, 702-712.

43. McGonigle, E. A.; Cowie, J. M.G.; Arrighi, V.; Pethrick, R. A. Enthalpy relaxation and free volume changes in aged styrene copolymers containing hydrogen bonding co-monomer. *J. Mat. Sci.* ***2005***, *40*, 1869-1881.

44. Barral, L.; Cano, J.; Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Abad, M. J.; Ramirez, C. Physical aging of an epoxy/cycloaliphatic amine resin. *Euro. Polym. J.* ***1999***, *35(3)*, 403-411.

45. Borde, B.; Bizot, H.; Vigier, G.; Buleon, A. Calorimetric analysis of the structural relaxation in partially hydrated amorphous polysaccharides I. Glass transition and fragility. *Carbohydr. Polym.* ***2002**, 48,* 83-96.

46. Wang, B.; Pikal, M. The impact of thermal treatment on the stability of freeze-dried amorphous pharmaceuticals: I. Dimer formation in sodium ethacrynate. *J. Pharam. Sci.* ***2010***, *99(2)*, 663-682.

47. Yu, T. L.; Chen, Y. S. Physical aging of epoxy resin blended with poly(ether sulfone): Effect of poly(ether sulfone) molecular weight. *J. Polym. Res.-Tai.* ***2000***, *7(4)*, 257-266.

48. Arrighi, V.; Cowie, J. M. G.; Ferguson, R.; McEwen, I. J.; McGonigle, E. A.; Pethrick, R. A.; Princi, E. Physical aging in poly(4-hydroxy styrene)/poly(vinyl methyl ether) blends. *Pol. Int.* ***2005***, 55, 749-756.

49. Brunacci, A.; Cowie, J. M. G.; Ferguson, R.; McEwen, I. J. Enthalpy relaxation in glassy polystyrenes: 1. *Polym.* ***1997**, 38(4)*, 865-870.

50. Ambike, A. A.; Mahadik, K. R.; Paradkar, A. Physico-chemical characterization and stability study of glassy simvastatin. *Drug Dev. Ind. Pharm.* ***2005***, *31*, 895-899.

51. Lionetto, F.; Maffezzoli, A.; Ottenhof, M.; Farhat, I. A. Mitchell, J. R. The retrogradation of concentrated wheat starch systems. *Starch*, ***2005***, *57*, 16-24.

52. Bohmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. Nonexponential relaxations in strong and fragile glass formers. *J. Chem. Phys.* ***1993***, *99(5)*, 4201-4209

53. Miller, D. P. Lechuga-Ballesteros, D. Rapid assessment of the structural relaxation behavior of amorphous pharmaceutical solids: Effect of residual water on molecular mobility. *Pharm. Res.* ***2006***, *23(10)*, 2291-2305.

FIGURE CAPTIONS

Figure 1 Enthalpy relaxation experimental protocol for amorphous carbohydrates.

Aged experiment: Glucose, maltose and maltotriose were scanned to (T_g+100°C) to remove their thermal history after equilibration at 25°C for 5 minutes. Then the carbohydrates were scanned to (T_{gi}-50) at 3°C/min to make a carbohydrate glass. The carbohydrates were scanned to (T_{gi}-5) and annealed isothermally at (T_{gi}-5) for selected periods of time (0.5 to 48 h). After aging, samples were cooled to (T_{gi} -50). After equilibrating the carbohydrates for 1 min, they were reheated to (T_{gi}+50) at a rate of 3°C/min.

Unaged experiment: Glucose, maltose and maltotriose were scanned to (T_g+100°C) to remove their thermal history after equilibration at 25°C for 5 minutes. Then the carbohydrates were scanned to (T_{gi}-50) at 3°C/min to make a carbohydrate glass. Then the samples were were reheated to (T_{gi}+50) at a rate of 3°C/min.

Figure 2 Identification of onset, midpoint, and endpoint glass transition temperatures (T_{gi}, T_{gm}, and T_{ge} respectively) and relaxed enthalpy (ΔH_{relax}) from MDSC thermogram.

Figure 3 Identification of onset, and endpoint glass transition temperatures (T_{gi}, and T_{ge} respectively) and heat capacity change at glass transition temperature (ΔC_p) for the determination of fragility of amorphous carbohydrates by glass transition width approach

Figure 4 Variation in specific heat at glass transition temperature (ΔC_p) for selected aging times during aging of glucose, maltose and maltotriose at (T_g-5).

Figure 5	Amount of relaxation enthalpy after aging of glucose, maltose and maltotriose at (T_g-5) for selected aging times. Experimental (Exp) data was fitted with the KWW equation to obtain predicted (Pred) curves.
Figure 6	Variation of (1-$\Delta H_{\mathrm{relax}}/\Delta H_{\infty}$) for selected aging times during aging of glucose, maltose and maltotriose at (T_{gi}-5); experimental (Exp); predicted (Pred).
Figure 7	Characteristic relaxation time (τ) dependence on molecular weight of glucose, maltose and maltotriose during isothermal aging at (T_{gi}-5).
Figure 8	Total enthalpy available for relaxation, ΔH_{∞} (J/g) dependence on molecular weight effect of glucose, maltose and maltotriose during isothermal aging at (T_{gi}-5).
Figure 9	X-ray diffraction patterns for (A) completely crystalline maltose, (B) maltose stored at (T_{gi}-5) for selected aging times.
Figure 10	Heating rate dependence on glass transition temperatures of glucose, maltose and maltotriose in order to find fragility index using equation 8. Onset glass transition temperature is assumed as T_g

Table 1. Onset (T_{gi}) glass transition temperatures of glucose, maltose and maltotriose aged at (T_{gi}-5) for selected times

Time t, (h)	Glucose		Maltose		Maltotriose	
	T_{gi} (°C)	(T_{ge}-T_{gi}) (°C)	T_{gi} (°C)	(T_{ge}-T_{gi}) (°C)	T_{gi} (°C)	(T_{ge}-T_{gi}) (°C)
0	34.5^{e} (0.20)*	$6.3^{h,i}$ (0.29)	78.5^{cd} (1.75)	$10.2^{g,h}$ (1.18)	128.8^{a} (4.13)	$11.4^{f,g,h}$ (3.09)
0.5	36.5^{e} (0.50)	5.0^{i} (0.14)	76.8^{cd} (4.90)	$9.2^{g,h,i}$ (0.59)	131.7^{a} (0.14)	$7.7^{h,i}$ (0.71)
1	36.2^{e} (0.35)	4.6^{i} (0.23)	76.3^{cd} (3.70)	$10.2^{g,h}$ (2.52)	131.6^{a} (4.51)	$7.8^{h,i}$ (1.13)
2	36.3^{e} (0.07)	5.0^{i} (0.06)	79.1^{cd} (1.90)	$8.1^{h,i}$ (0.13)	133.4^{a} (1.47)	$6.3^{h,i}$ (0.35)
6	36.4^{e} (0.07)	4.9^{i} (0.05)	76.0^{cd} (2.60)	$11.0^{f,g,h}$ (0.25)	132.4^{a} (4.20)	$7.9^{h,i}$ (0)
12	36.6^{e} (0)	5.1^{i} (0)	81.6^{c} (0)	$9.8^{g,h,i}$ (0.42)	132.7^{a} (3.79)	$8.1^{h,i}$ (0)
48	36.1^{e} (0)	5.2^{i} (0)	72.7^{d} (0)	$13.8^{f,g}$ (0)	113.7^{b} (0)	15.4^{f} (0)

Same superscripts within a column indicate there is no significant difference in values

*Values in parentheses represent the standard deviation of at least two replicates

Table 2. Experimental values of ΔH_∞, τ, β, $\tau_{\varphi(t)=50\%}$, and $\tau_{\varphi(t)=1\%}$ calculated for glucose, maltose and maltotriose

Amorphous system	KWW equation				
	Total enthalpy available for relaxation, ΔH_∞ (J/g)	Characteristic relaxation time, τ (h)	Relaxation distribution parameter, β	The relaxation time corresponding to 50% of the maximum enthalpy, $\tau_{\varphi(t)=50\%}$ (h)	The relaxation time corresponding to 99% of the maximum enthalpy, $\tau_{\varphi(t)=1\%}$ (h)
Glucose	3.94	16.9	0.23	50.9	338.4
Maltose	3.23	38.4	0.33	80.7	535.9
Maltotriose	2.54	128.6	0.24	371.4	2467.6

Table 3. Fragility prediction for selected amorphous carbohydrates by selected methods

Amorphous system	Fragility parameter (*m*) using activation enthalpy at glass transition temperature	Fragility prediction based on *m* value	Fragility parameter (*m*) using glass transition dependence on heating rate	Fragility prediction based on *m* value	$^{*}C_{p(liquid)}/C_{p(glass)}$	Fragility prediction based on $C_{p(liquid)}/C_{p(glass)}$ value
Glucose	105	Fragile[a]	34.5	Strong[a]	2.21	Fragile[b]
Maltose	88.1	Strong[a]	23.5	Strong[a]	1.65	Fragile[b]
Maltotriose	97.6	Strong[a]	28.6	Strong[a]	1.24	Fragile[b]

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

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

*Ratio of heat capacity of material system in the rubbery state to heat capacity of the material system in the glassy state

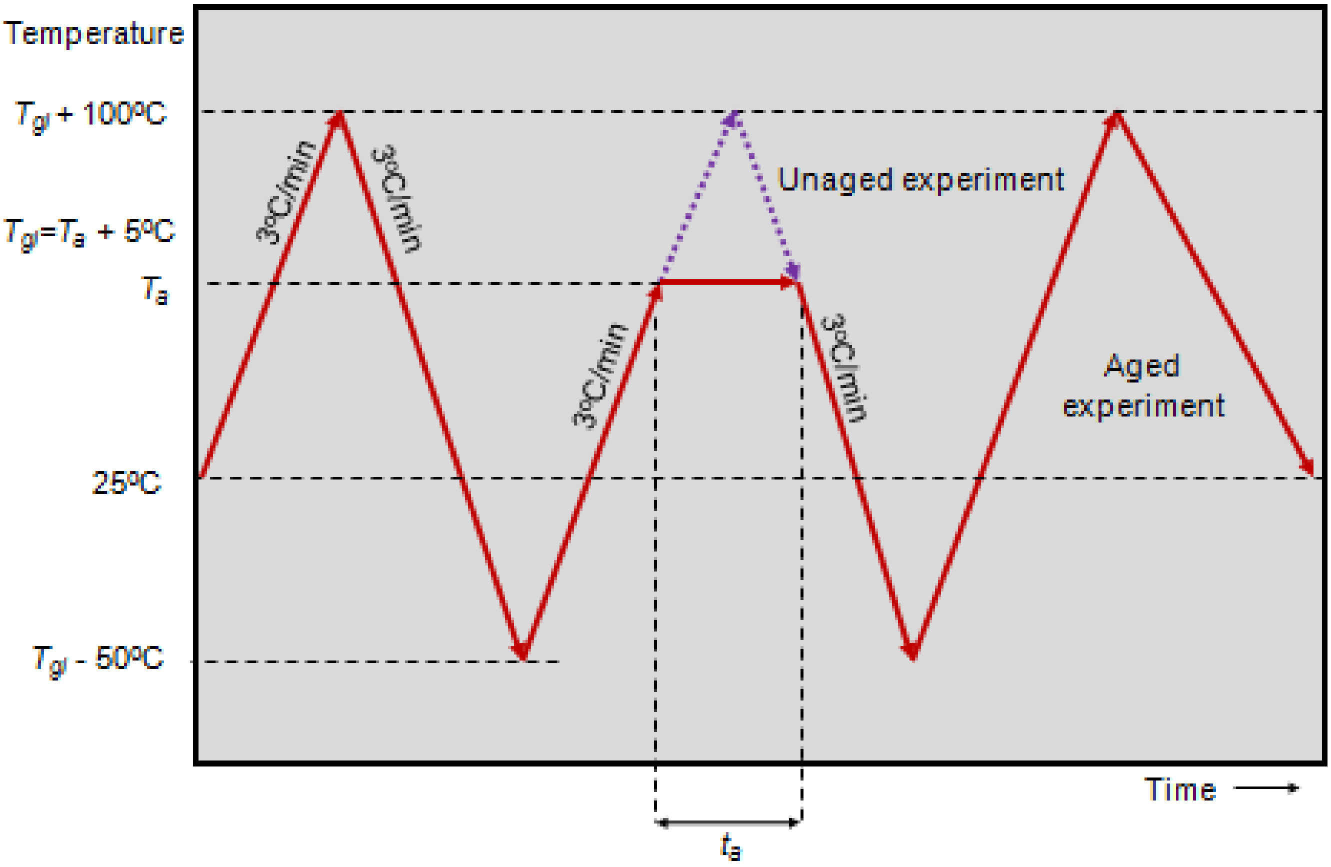
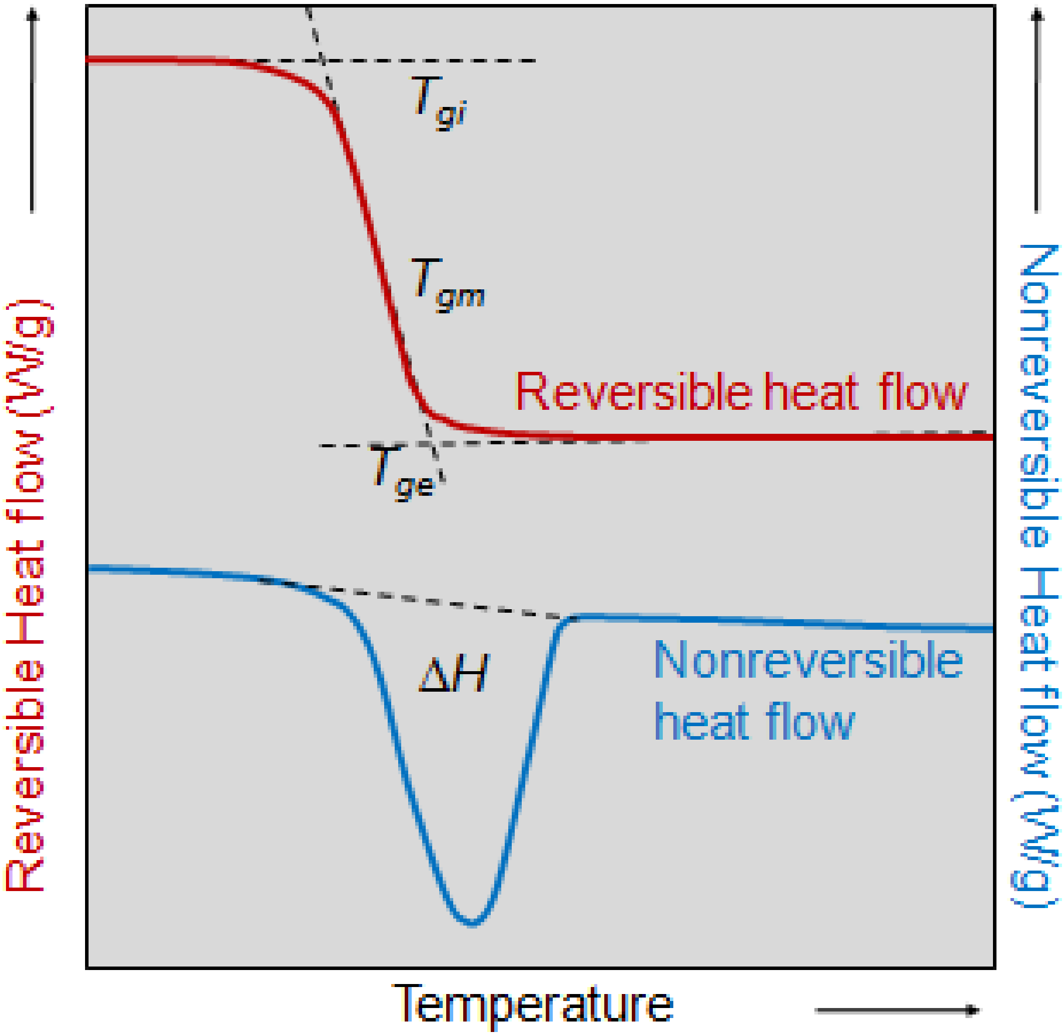

Temperature
T_{gl} + 100ºC
T_{gl}=T_a + 5ºC
T_a
25ºC
T_{gl} - 50ºC
3ºC/min
3ºC/min
3ºC/min
3ºC/min
Unaged experiment
Aged experiment
t_a
Time

Figure 1



T_{gi}
T_{gm}
Reversible heat flow
T_{ge}
ΔH
Nonreversible heat flow
Reversible Heat flow (W/g)
Nonreversible Heat flow (W/g)
Temperature

Figure 2

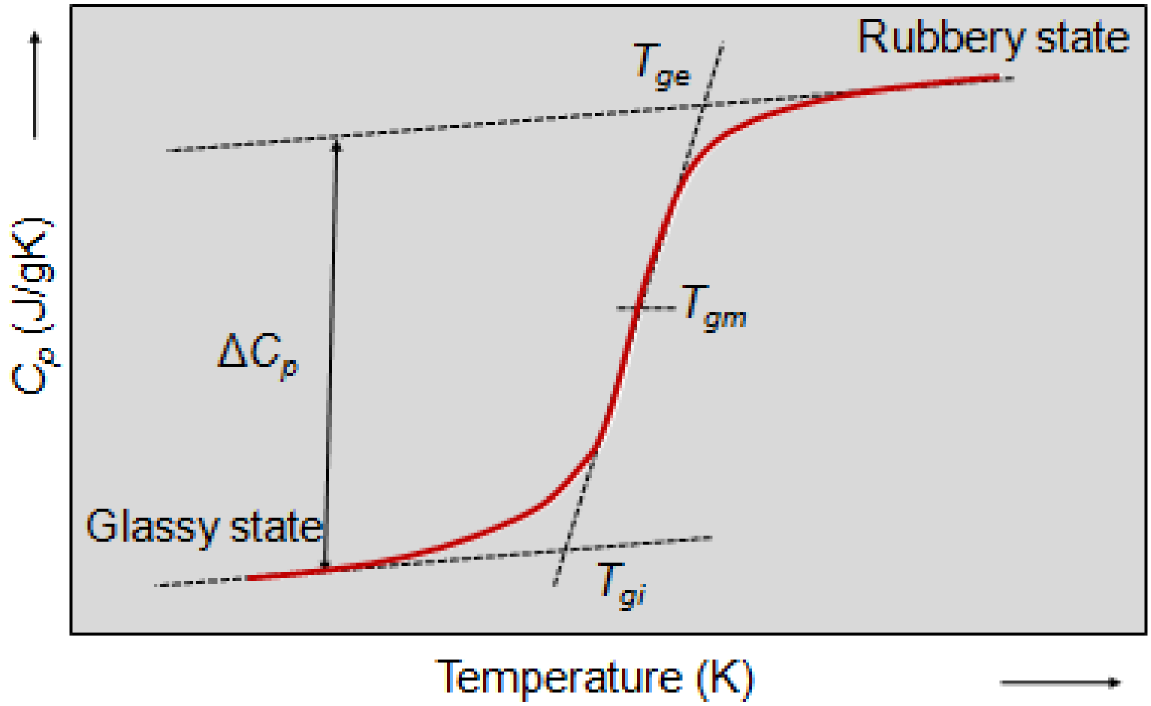

Rubbery state
T_{ge}
T_{gm}
ΔC_p
Glassy state
T_{gi}
C_p (J/gK)
Temperature (K)

Figure 3

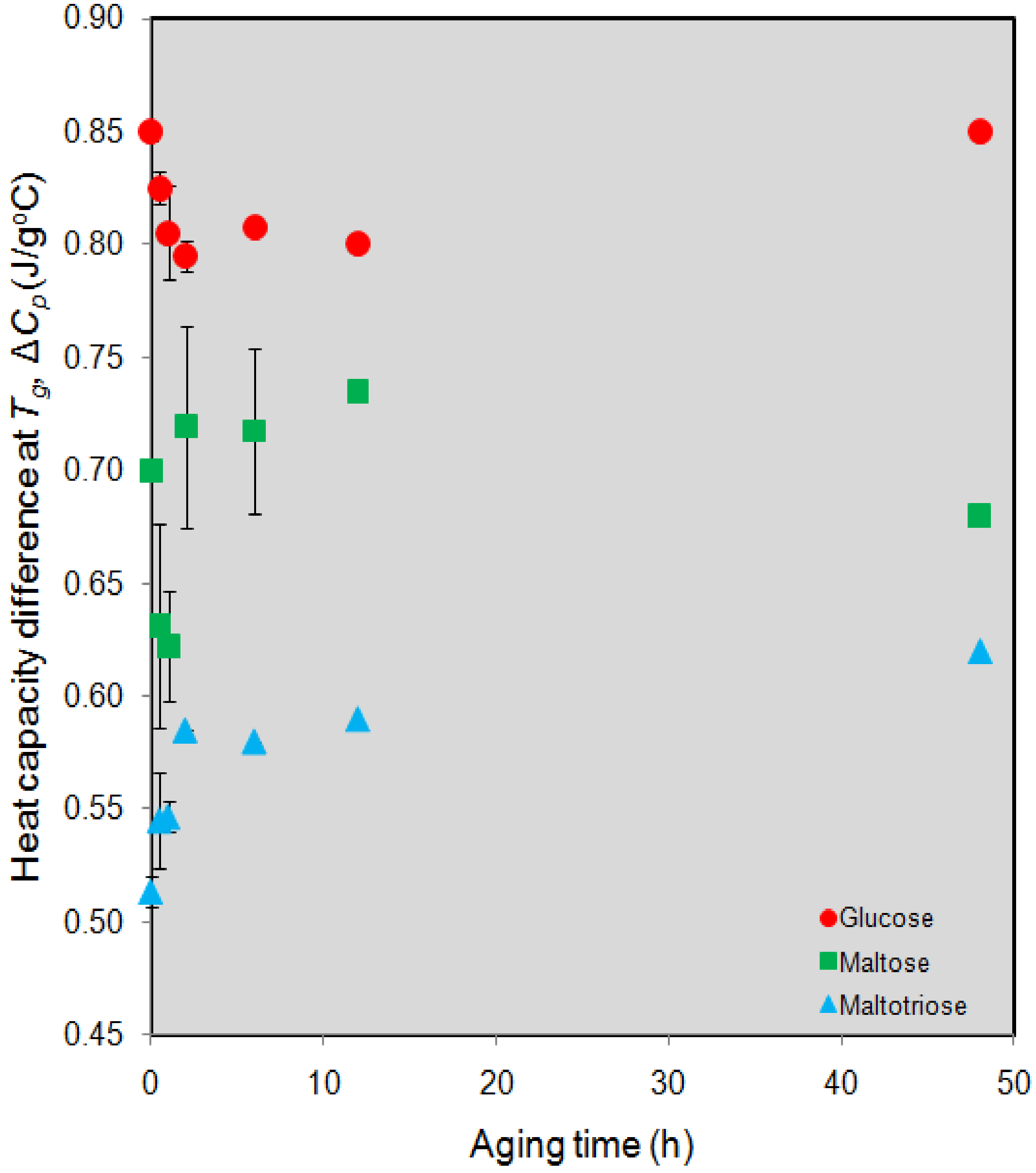
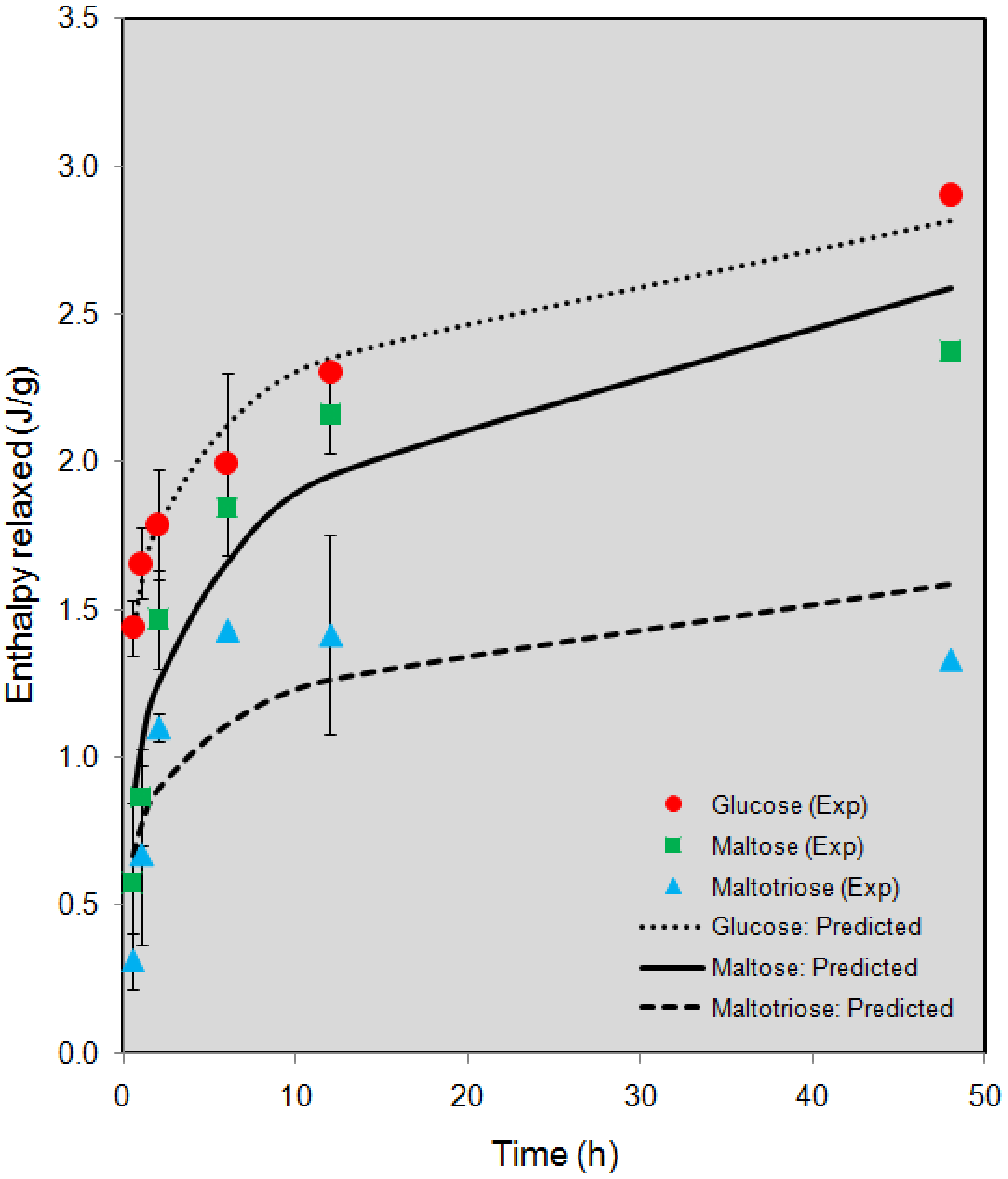

0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
Heat capacity difference at T_g, ΔC_p (J/g°C)
0
10
20
30
40
50
Aging time (h)
● Glucose
■ Maltose
▲ Maltotriose

Figure 4



3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Enthalpy relaxed (J/g)
0
10
20
30
40
50
Time (h)
● Glucose (Exp)
■ Maltose (Exp)
▲ Maltotriose (Exp)
Glucose: Predicted
Maltose: Predicted
Maltotriose: Predicted

Figure 5

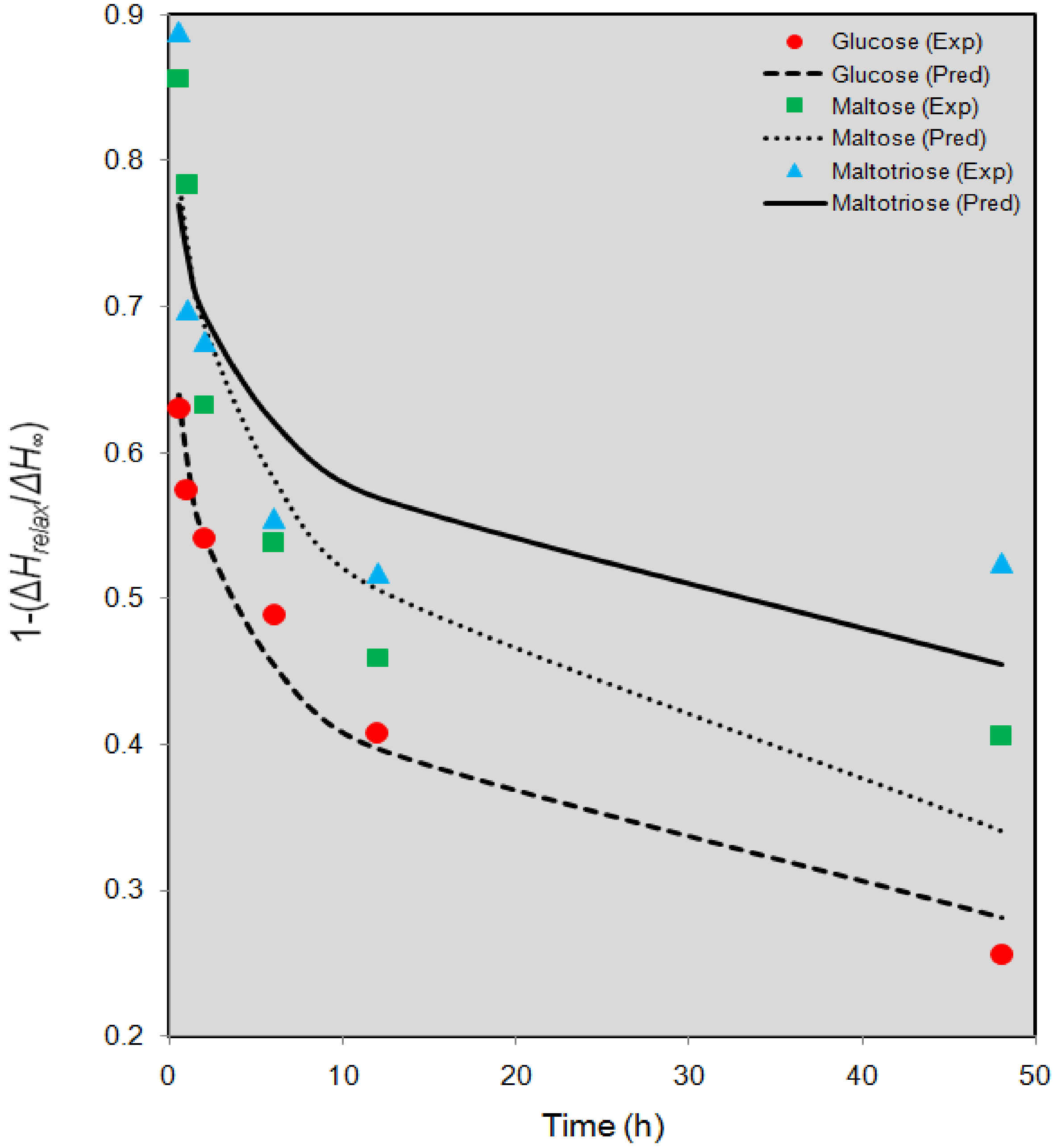

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
$1-(\Delta H_{relax}/\Delta H_{\infty})$
0
10
20
30
40
50
Time (h)
● Glucose (Exp)
Glucose (Pred)
■ Maltose (Exp)
Maltose (Pred)
▲ Maltotriose (Exp)
Maltotriose (Pred)

Figure 6

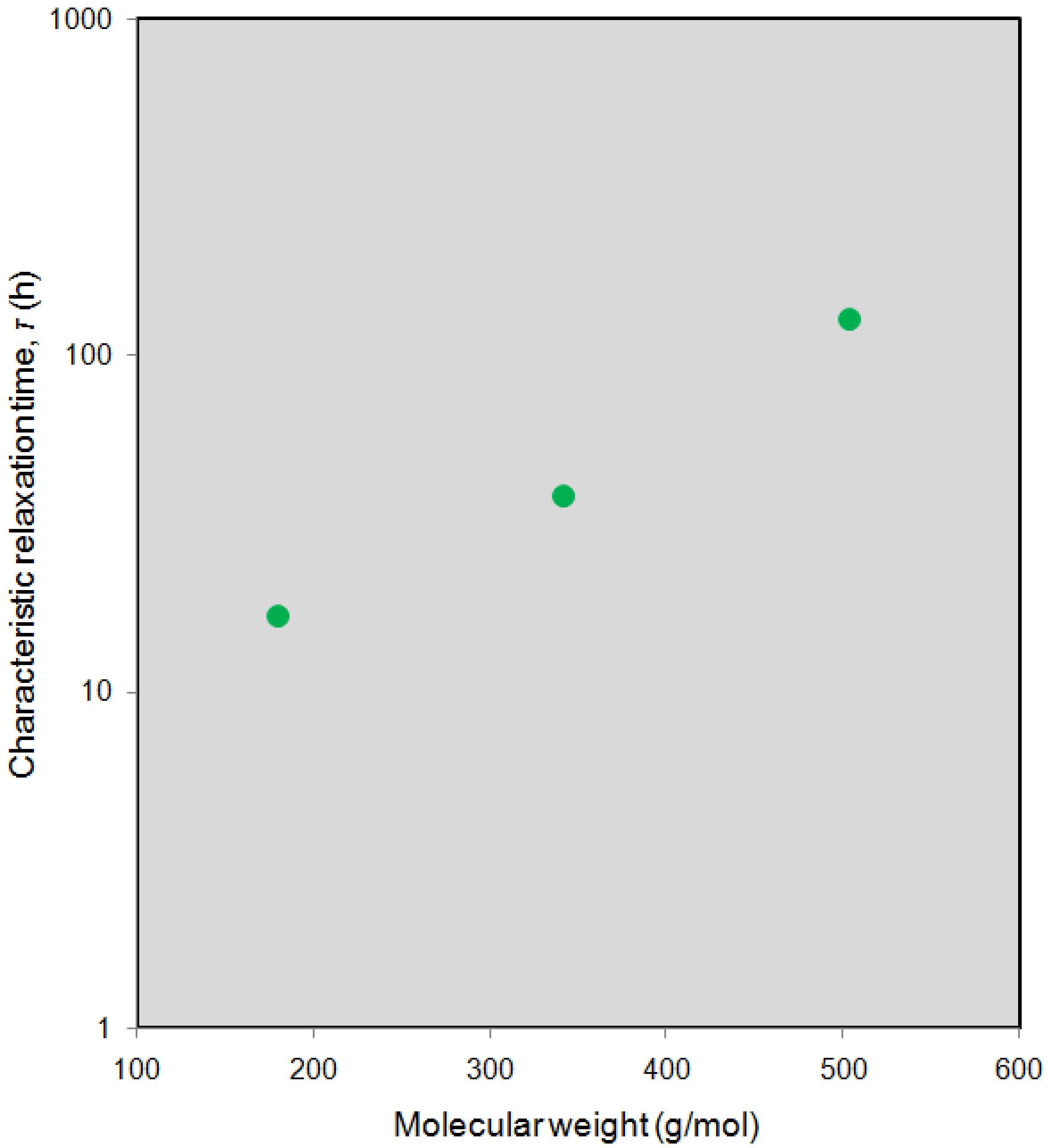

1000
100
10
1
100
200
300
400
500
600
Characteristic relaxation time, τ (h)
Molecular weight (g/mol)

Figure 7

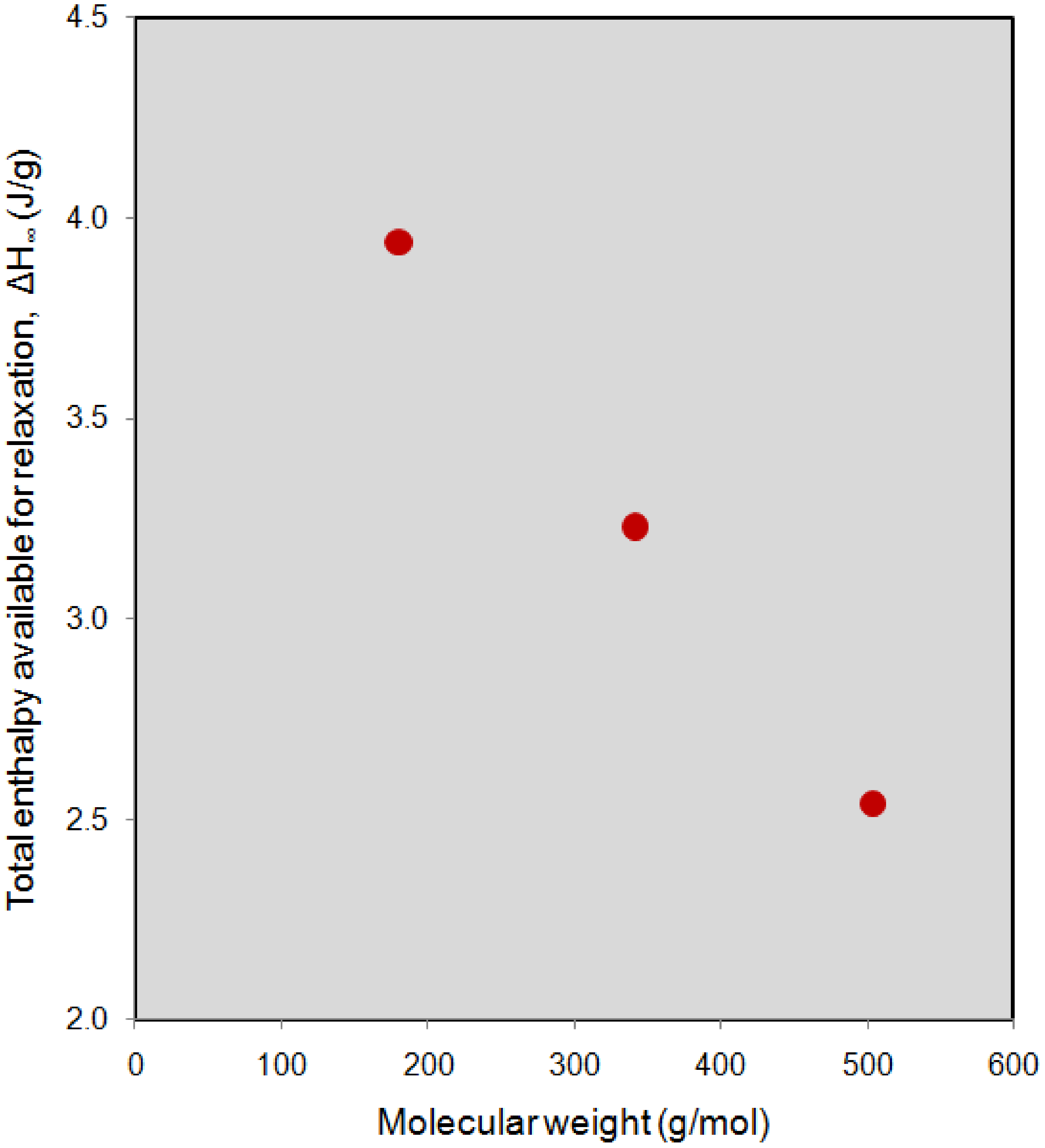

4.5
4.0
3.5
3.0
2.5
2.0
0
100
200
300
400
500
600
Total enthalpy available for relaxation, ΔH_∞ (J/g)
Molecular weight (g/mol)

Figure 8

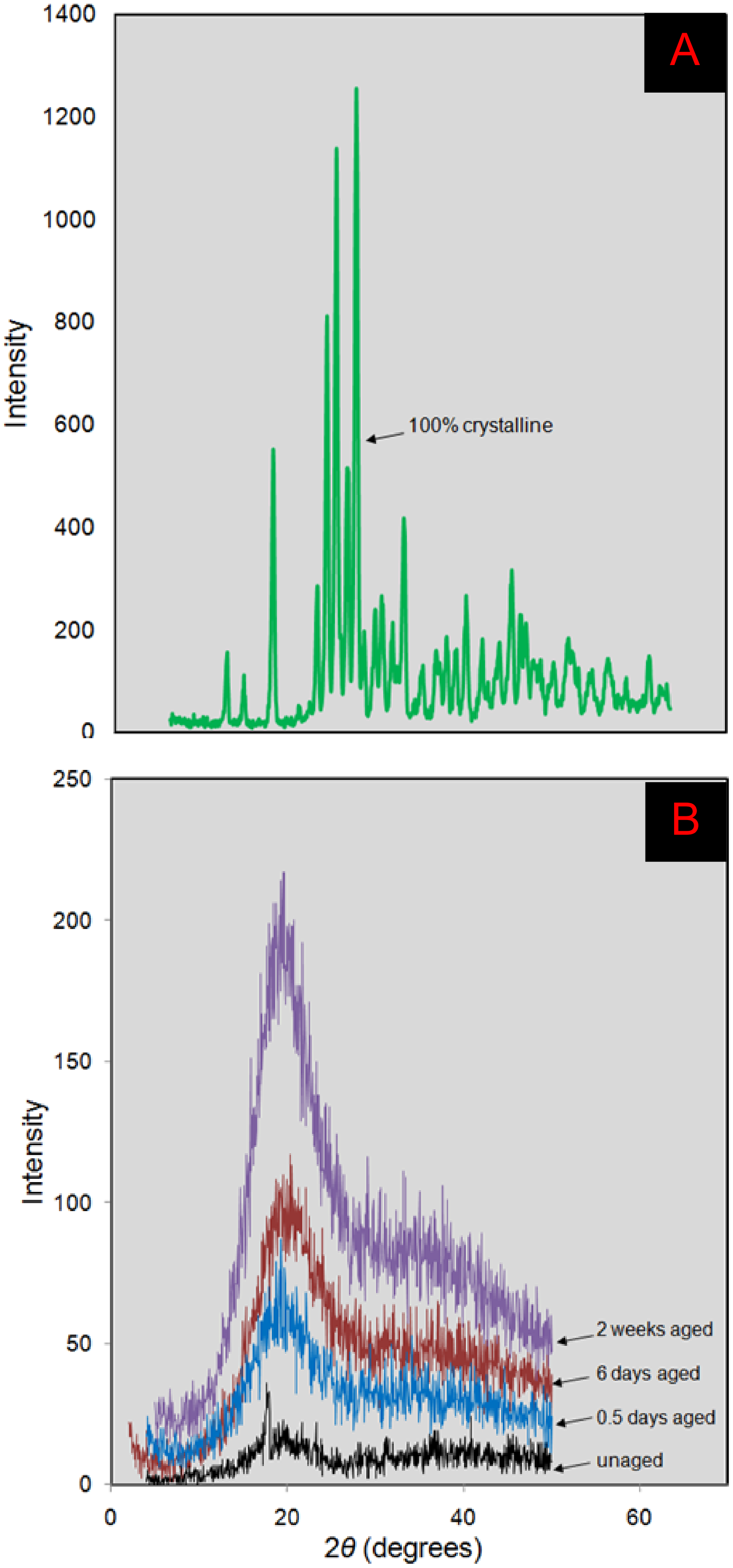
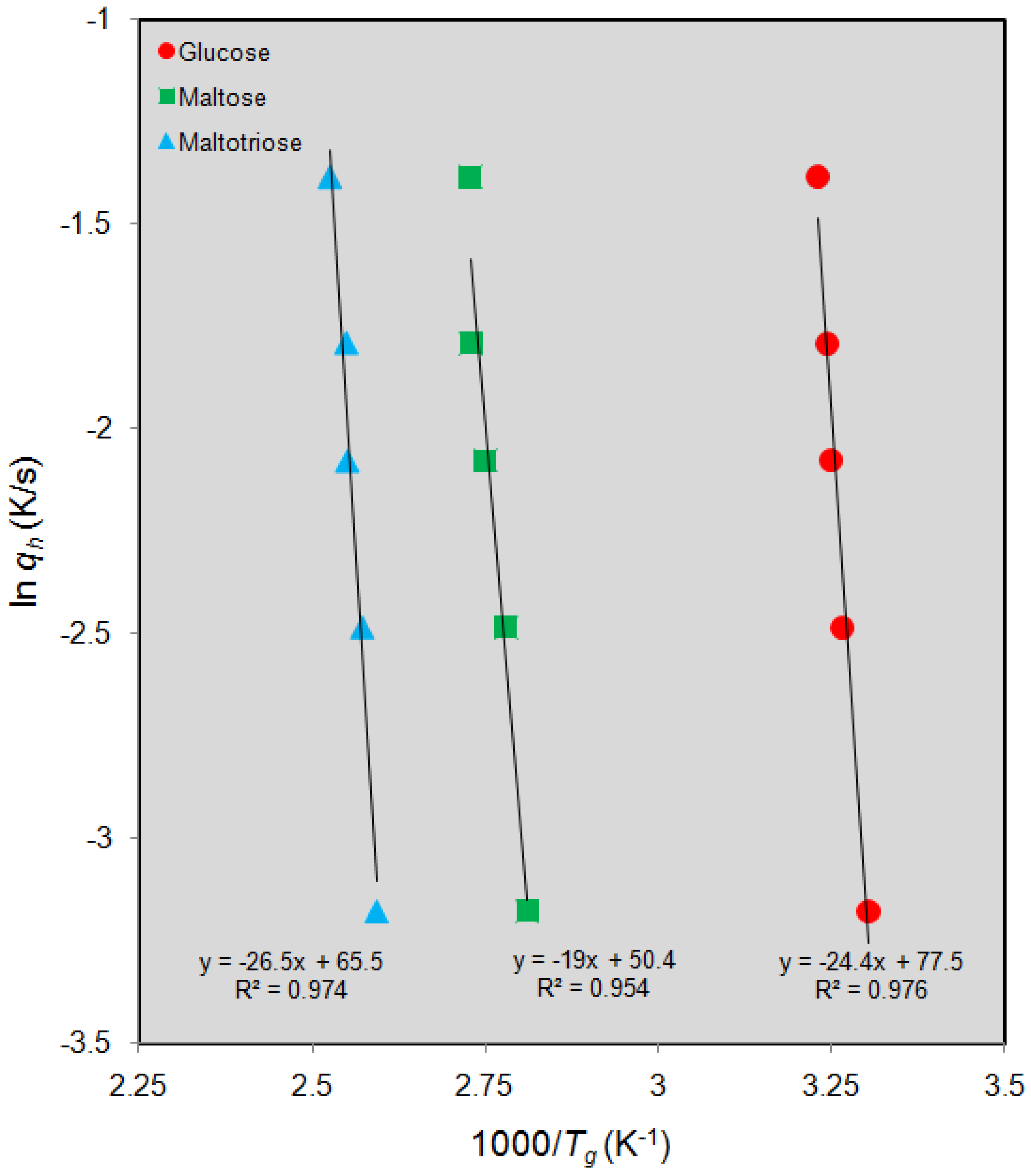

A
Intensity
0
200
400
600
800
1000
1200
1400
100% crystalline
B
Intensity
0
50
100
150
200
250
2 weeks aged
6 days aged
0.5 days aged
unaged
0
20
40
60
2θ (degrees)

Figure 9



Glucose
Maltose
Maltotriose
y = -26.5x + 65.5
R² = 0.974
y = -19x + 50.4
R² = 0.954
y = -24.4x + 77.5
R² = 0.976
-1
-1.5
-2
-2.5
-3
-3.5
2.25
2.5
2.75
3
3.25
3.5
ln q_h (K/s)
1000/T_g (K^{-1})

Figure 10