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Influence of molecular weight on enthalpy relaxation and fragility of amorphous carbohydrates

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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 fragility indices (m) of glucose, maltose and maltotriose, determined using the DSC glass transition width approach, were 105, 88.1 and 97.6, respectively. The glass transition temperature and mean enthalpy relaxation time increased with increasing molecular weight for the selected carbohydrates studied herein. 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.

1. Introduction

Amorphous foods and food ingredients are produced by many food processing techniques such as dehydration, concentration, extrusion and freezing (Wungtanagorn & Schmidt, 2001a, 2001b). 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 food components results in structural relaxations that achieve a more stable equilibrium state over extended time periods (Gupta, Kakumanu, & Bansal, 2004; Struik, 1978; Wungtanagorn & Schmidt, 2001a, 2001b). 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 (Struik, 1978). This energy can be measured 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 (Gupta et al., 2004). 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 (Struik, 1978). Methods based on identifying the time dependence of these macroscopic properties are often used to monitor the structural relaxations in amorphous systems during their isothermal storage. These techniques include differential scanning calorimetry (Hancock, Shamblin, & Zografi, 1995; Hodge, 1994), modulated differential scanning calorimetry (Craig, Barsnes, Royall, & Kett, 2000; Hourston, Song, Hammiche, Pollock, & Reading, 1996; Hutchinson, 1998; Lammert, Lammert, & Schmidt, 1999), dynamic mechanical thermal analysis (Badii, Martinet, Mitchell, & Farhat, 2006; Chung, Yoo, & Lim, 2005; Ngai & Plazek, 1995; Roland & Ngai, 1991), small deformation dynamic oscillation (Jiang, Kasapis, & Kontogiorgos, 2011; Kasapis, 2006), dielectric thermal analysis (Alegria, Goitiandia, Telleria, & Colmenero, 1997). The changes in macroscopic properties may adversely affect the physicochemical stability during the isothermal storage of low water amorphous foods and food constituents (Farahnaky, Guerrero, Hill, & Mitchell, 2008). Rates of many diffusion-limited physicochemical degradation reactions in amorphous systems can be dependent on molecular mobility and relaxation time (Bell, 2007; Byrn, Xu, & Newman, 2001; Luthra, Hodge, Utz, & Pikal, 2008).

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The '*fragility*' concept introduced by Angell (1985, 1988) 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 such as viscosity, 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 (Hatley, 1997). 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 (Hatley, 1997). 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 (Hancock, Dalton, Pikal, & Shamblin, 1998). Hatley (1997) 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.

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 fragility on molecular weight improves our understanding of the temperature dependency of amorphous carbohydrates at T_g. Amorphous carbohydrates such as maltose, and maltotriose are often used as food ingredients or encapsulating agents due to their high T_g and viscosity (Bayrarn, Bayram, & Tekin, 2005).

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.

2. 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 (25 °C) for 2 days. The moisture content of dry amorphous carbohydrates was analyzed using the vacuum oven method and was ~0.005 kg H_2O/kg sample (Syamaladevi, Sablani, & Swanson, 2010).

2.1. Modulated differential scanning calorimetry (MDSC)

Enthalpy relaxation experiments were conducted using a modulated differential scanning calorimeter (MDSC) (Q2000, TA Instruments, New Castle, DE). 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 min (Lammert et al., 1999). For instance, the melting temperature of glucose, maltose and maltotriose were 149.1, 123, and 200 °C respectively (Roos, 1993). 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. The selected modulation amplitude and modulation period were ±0.5 °C and 45 s, respectively (Lammert et al., 1999). The onset (T_{gi}), midpoint (T_{gm}) and endpoint (T_{ge}) glass transition temperatures of the glucose, maltose and maltotriose were determined using reversible heat flow curve of MDSC thermogram.

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. Then the carbohydrates were annealed isothermally at ($T_{gi}-5$) for selected periods of time (0.5–48 h). 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 (Craig et al., 2000; Hourston et al., 1996; Lammert et al., 1999) (Fig. 1). Non-exponential expressions, such as the Kohlrausch–Williams–Watts (KWW) equation, are used extensively to describe the complex kinetics of enthalpy relaxation in glassy materials during aging (Hancock & Shamblin, 2001; Hancock et al., 1995; Liu, Bhandari, & Zhou, 2007). The KWW equation is expressed as:

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

where $\varphi(t)$ is the relaxation function, indicating the kinetics of non-equilibrium to equilibrium transformation of the system; $\varphi(t)$ provides an estimation of unreleased enthalpy or the extent of enthalpy relaxation at the specific annealing temperature (Liu et al., 2007). 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 (Yoshioka, Aso, & Kojima, 2001). The parameter β characterizes the deviation of the relaxation from exponential behavior. The value of β varies between 0 and 1 (Christensen, Pedersen, & Kristensen, 2002; Van den Mooter, Augustijns, & Kinget, 1999). When $\beta = 1$, the KWW equation is equivalent to an exponential expression. The relaxation function $\varphi(t)$ is expressed as:

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

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

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. The enthalpy relaxation data of glucose, maltose and maltotriose were fitted with the KWW equation to obtain the values of characteristic relaxation time (τ), relaxation distribution parameter (β), and total enthalpy available for relaxation, ΔH_∞ using Statistica® version 5 computer program.

The fragility index (m) is defined as (Angell, 1988):

$$m = \frac{\Delta E}{2.303RT_g} \tag{4}$$

where ΔE is the activation energy for structural relaxations at T_g, and R is the gas constant.

The activation enthalpy of structural relaxation is determined from the glass transition width (Crowley & Zografi, 2001; Moynihan, 1993; Moynihan, Lee, Tatsumisago, & Minami, 1996):

$$\left(\frac{\Delta E}{R}\right)\left(\frac{1}{T_{\rm gi}} - \frac{1}{T_{\rm ge}}\right) = \text{Constant} \tag{5}$$

$T_{\rm gi}$ and $T_{\rm ge}$ 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), Eq. (5) is applicable for a specific q_c/q_h, provided:

$$0.2 \le \left|\frac{q_c}{q_h}\right| \le 5 \tag{6}$$

By studying several material systems, the constant in Eq. (5) was identified as 5 ± 0.5. In the current study, the value of the constant was selected as 5.

The activation enthalpy can also be determined by heating/cooling rate dependence of glass transition temperature (Moynihan, Esteal, Wilder, & Tucker, 1974; Ramos, Taveira-Marques, & Diogo, 2004):

$$\frac{d\ln\left|q_h\right|}{d(1/T_g)} = -\frac{\Delta E}{R} \tag{7}$$

where q_h is the heating rate.

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.

2.2. 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 at a controlled humidity environment. The X-ray diffraction spectra of aged maltose and completely crystalline maltose were obtained using the X-ray diffractometer. 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.

3. Results

3.1. 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 ($T_{\rm gi}$) 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 (Abiad, Carvajal, & Campanella, 2009; Roos & Karel, 1991). Roos and Karel (1991) used Fox and Flory equation to relate increase in T_g of maltodextrins with increase in molecular weight. The T_g of maltodextrins increased from 100 to 188 °C when the molecular weight changed from 500 to 3600 g/mol (Roos & Karel, 1991). Kasapis, Al-Marhoobi, and Mitchell (2003) reported the effect of molecular weight on mechanical glass transition temperature of gelatin/glucose syrup/sucrose mixtures. The T_g of gelatin/glucose syrup/sucrose mixtures ranged from −40 to −16 °C when the molecular weight increased from 29,200 to 68,000 g/mol. The significant increase in T_g of gelatin/glucose syrup/sucrose mixtures with molecular weight was attributed to rapid reduction in the diffusion mobility and free volume as resulted by enthalpic intra-molecular associations by gelatin with increasing molecular weight (Kasapis et al., 2003). No significant difference was observed between the $T_{\rm gi}$ of unaged and aged carbohydrates (Table 1). Aging/annealing at ($T_{\rm gi} - 5$) did not significantly alter the $T_{\rm gi}$ 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 periods of time (Boller, Schick, & Wunderlich, 1995; Craig et al., 2000; Syamaladevi et al., 2010). However, a small increase in the glass transition temperature after aging is observed in selected foods and pharmaceuticals (Chung & Lim, 2003; Haque, Kawai, & Suzuki, 2006; Schmidt & Lammert, 1996). 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 (Haque et al., 2006). A slight decrease in T_g of salicin during aging was reported by Mao et al. (2010). Wungtanagorn and Schmidt (2001a) 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 $T_{\rm gi}$ was observed for glucose aged for selected aging periods (0–48 h). Significant difference in $T_{\rm gi}$ was observed between maltose aged for 12 and 48 h (Table 1). The $T_{\rm gi}$ of maltotriose aged for 48 h was significantly different from the maltotriose aged for 0.5–12 h (Table 1). During the determination of $T_{\rm gi}$, the carbohydrates were heated above their melting points using MDSC, which could result in thermal decomposition, influencing the $T_{\rm gi}$ values (Lee, Thomas, Jerrell, et al., 2011; Lee, Thomas, & Schmidt, 2011). Glass transition temperature width ($T_{\rm ge} - T_{\rm gi}$) of glucose did not change significantly during isothermal aging at ($T_{\rm gi} - 5$) for 0.5–48 h (Table 1). The ($T_{\rm ge} - T_{\rm gi}$) of unaged glucose was significantly different from aged glucose (0.5–48 h). The ($T_{\rm ge} - T_{\rm gi}$) of 2 h aged maltose was significantly different from other aging periods (Table 1). The ($T_{\rm ge} - T_{\rm gi}$) 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 (Fig. 2) (McGonigle, Cowie, Arrighi, & Pethrick, 2005). 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 (Fig. 2). Chung and Lim (2003) observed an increase in ΔC_p with aging time for rice starch. Wungtanagorn and Schmidt (2001b) also observed an increase in ΔC_p at the glass transition with aging of glucose, fructose and mixture of the two. However, a comparatively constant ΔC_p and decrease in ΔC_p with aging are also reported (Barral et al., 1999; Borde, Bizot, Vigier, & Buleon, 2002). Since the equilibrium state has a smaller heat capacity and free energy compared to glassy state, an increase in ΔC_p is expected after aging (Chung & Lim, 2003). 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

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)[a]	$6.3^{h,i}$ (0.29)	78.5^{cd} (1.8)	$10.2^{g,h}$ (1.2)	128.8^{a} (4.1)	$11.4^{f,g,h}$ (3.1)
0.5	36.5^{e} (0.50)	5.0^{i} (0.14)	76.6^{cd} (4.7)	$9.2^{g,h,i}$ (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} (3.7)	$10.2^{g,h}$ (2.5)	134.0^{a} (0.18)	$7.8^{h,i}$ (1.1)
2	36.3^{e} (0.07)	5.0^{i} (0.06)	79.3^{cd} (1.8)	$8.1^{h,i}$ (0.13)	133.4^{a} (1.5)	$6.3^{h,i}$ (0.35)
6	36.4^{e} (0.07)	4.9^{i} (0.05)	76.0^{cd} (2.6)	$11.0^{f,g,h}$ (0.25)	134.8^{a} (1.5)	$7.9^{h,i}$ (0)
12	36.6^{e} (0)	5.1^{i} (0)	81.6^{c} (0)	$9.8^{g,h,i}$ (0.42)	134.9^{a} (0.35)	$8.1^{h,i}$ (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.

[a] Values in parentheses represent the standard deviation of at least two replicates.

the MDSC (Lee, Thomas, Jerrell, et al., 2011; Lee, Thomas, & Schmidt, 2011).

3.2. 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 appears (Wang & Pikal, 2010). The actual enthalpy recovered during the aging process is obtained by subtracting this enthalpy from the enthalpy in the nonreversible heat flow thermogram of aged sample (Wang & Pikal, 2010). The total enthalpy decreased, while the relaxed enthalpy increased with increasing aging time for glucose, maltose and maltotriose (Fig. 3). The rate of enthalpy relaxation of selected carbohydrates decreased gradually during aging due to the decrease in total enthalpy during aging (Fig. 3). The relaxed enthalpy was greater for glucose than maltose and maltotriose during aging (Fig. 3), attributed to its smaller molecular weight and higher specific volume and resulting lower chain rigidity (McGonigle et al., 2005).

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 (Haque et al., 2006). As aging proceeds, the amorphous system reaches the metastable equilibrium state by losing the enthalpy and decreasing the free volume (Yu & Chen, 2000). The KWW equation was used to fit the enthalpy relaxation kinetics of the selected amorphous carbohydrates. The KWW equation described relaxation behavior well for glucose and maltose ($R^2 = 0.98$ and 0.88 respectively); but the equation presented less accurate fit of the relaxation kinetics of maltotriose ($R^2 = 0.72$)

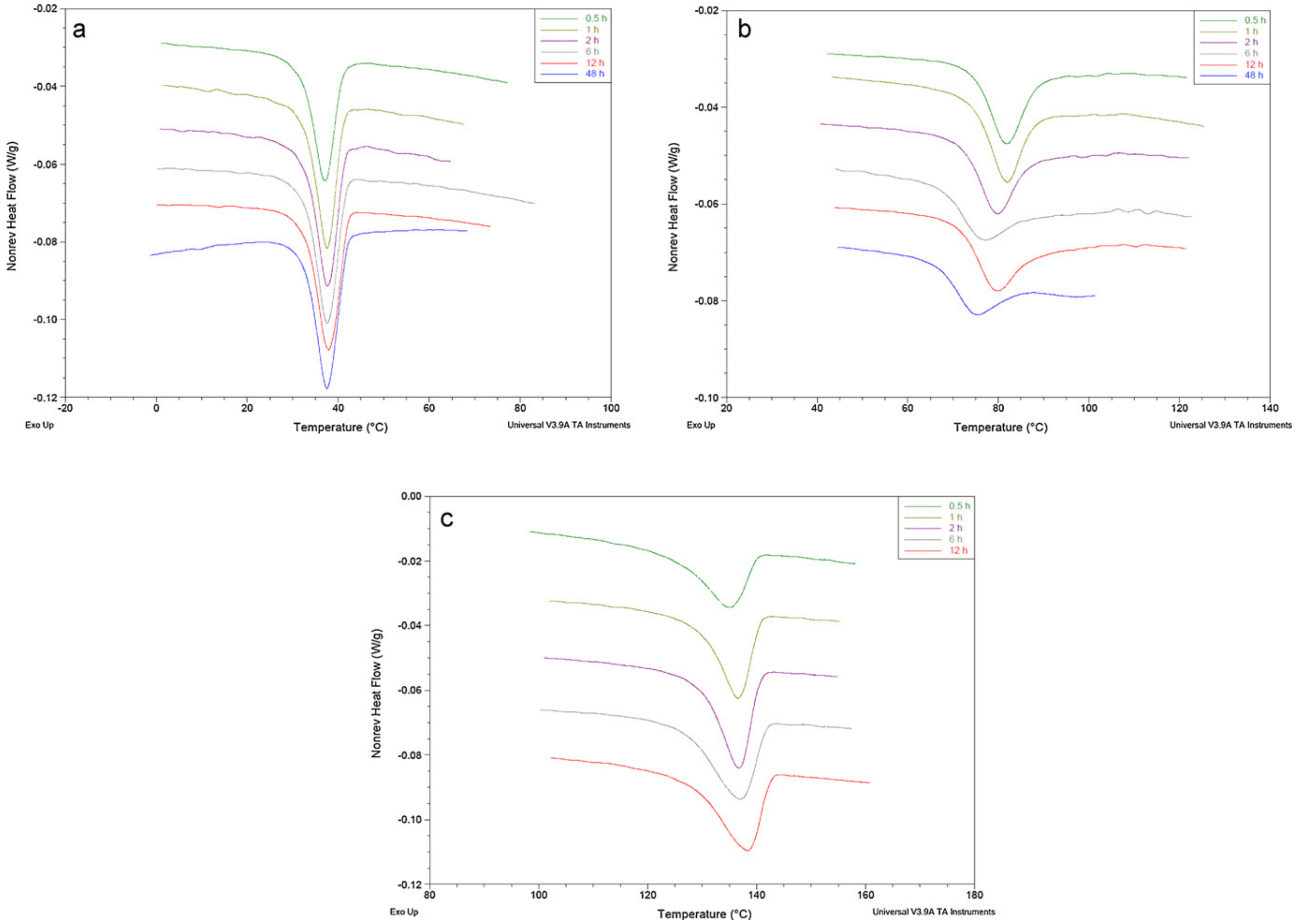

Fig. 1. Original MDSC thermograms showing enthalpy relaxation in: (a) glucose, (b) maltose and (c) maltotriose.

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
Maltose	3.23	38.4	0.33	80.7	536
Maltotriose	2.54	129	0.24	371	2468

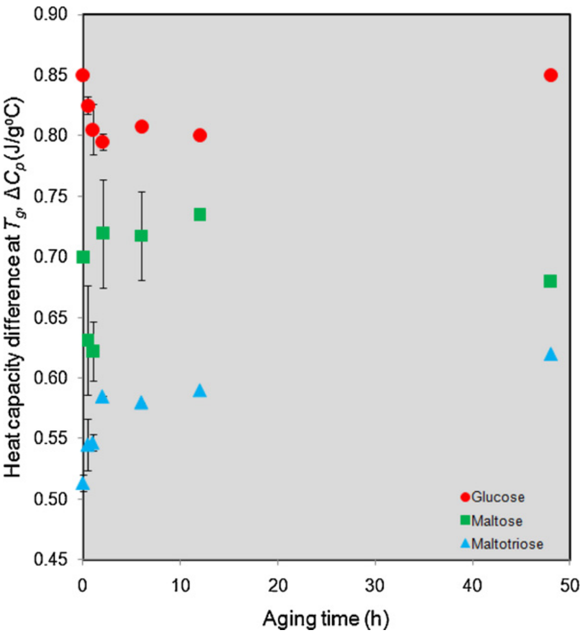

Fig. 2. Variation in specific heat at glass transition temperature (ΔC_p) for selected aging times during aging of glucose, maltose and maltotriose at ($T_g - 5$).

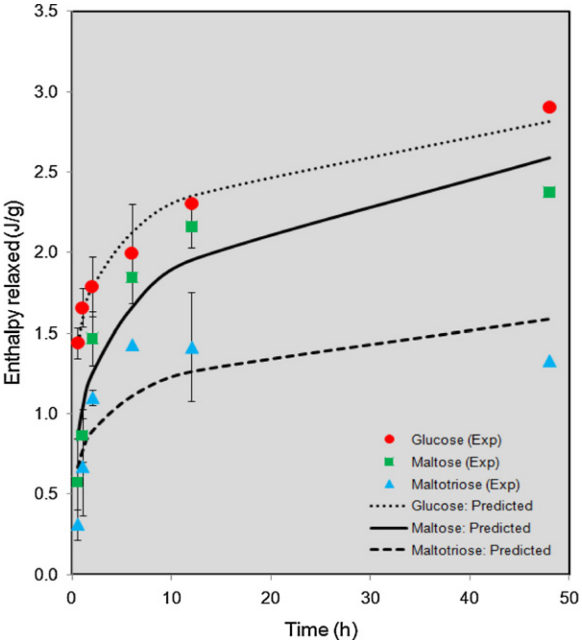

Fig. 3. Amount of relaxation enthalpy after aging of glucose, maltose and maltotriose at ($T_g - 5$) for selected aging times. Experimental (Exp) data was fitted with the KWW equation to obtain predicted (Pred) curves.

(KWW adjustable parameters are presented in Fig. 4 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. 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) (Wungtanagorn & Schmidt, 2001a), but smaller in the case of raspberry powder (e.g. 147.1 h) (Syamaladevi et al., 2010), 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 (Liu, Bhandari, & Zhou, 2006). The relaxation times present an abrupt change at the glass transition, when the β value is close to 1 (Liu et al., 2006). 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 (Arrighi et al., 2005). Smaller values of β represent hydrogen bonding and coupling between relaxing elements of the studied carbohydrates (Arrighi et al., 2005). Hancock et al. (1995) reported the β values for indomethacin, poly(vinylpyrrolidone) (PVP), and sucrose as 0.3–0.6, 0.5–0.8 and

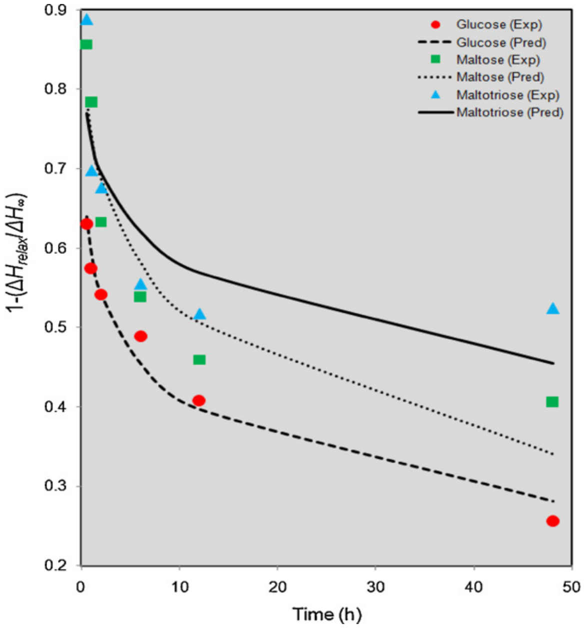

Fig. 4. Variation of $(1 - \Delta H_{\mathrm{relax}}/\Delta H_\infty)$ for selected aging times during aging of glucose, maltose and maltotriose at ($T_{gi} - 5$); experimental (Exp); predicted (Pred).

0.4–0.8 for 16–47 °C below T_g respectively. These β values are greater those of glucose, maltose and maltotriose. Jiang et al. (2011) reported the β values for the polysaccharide (agarose, κ-carrageenan, and deacylated gellan)/glucose syrup with 20% water as 0.36, 0.4 and 0.41 respectively. Also, Kasapis (2006) reported the β value for gelatin/glucose syrup with 22% water as 0.43. The smaller β values for the selected carbohydrates (glucose, maltose and maltotriose) could be due to greater intermolecular coupling originated from the chemical structure and stronger interlinking between segmental chains in their homogeneous structures in comparison to heterogeneous mixtures (Jiang et al., 2011; Kasapis, 2006). Chung, Chang, and Lim (2004) reported the β values for normal and waxy rice starches at 12% water content at an aging temperature of 25 °C below T_g ranged from 0.279 to 0.421. The smaller β values for the glucose, maltose and maltotriose suggest that they have greater amorphous structural composition and broader relaxation time distribution than the starches (Chung et al., 2004). However, an absolute comparison of β values may not be possible since the predicted β values may depend on water content of the sample, aging temperature and relaxation characterization techniques (mechanical vs. enthalpy). The β values of raspberry powder decreased as aging temperature decreased (Syamaladevi et al., 2010). Chung and Lim (2003) observed a decrease in β values as the aging temperature decreased and water content increased. Also, τ and β values are kinetic in nature and may not be related to structure (Brunacci, Cowie, Ferguson, & McEwen, 1997). Shamblin and Zografi (1998) described the inability of KWW equation to predict the relaxation distribution of multicomponent systems. The nonlinear regression algorithm may produce significant error while fitting with the experiential relaxation data (Shamblin & Zografi, 1998). ΔH_∞ may be related to structure and molecular weight of materials during aging (Brunacci et al., 1997; McGonigle et al., 2005). The value of ΔH_∞ decreased linearly with molecular weight for the selected carbohydrates (Table 2). 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 (Liu et al., 2007). 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 (Liu et al., 2007; Syamaladevi et al., 2010). 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. 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.

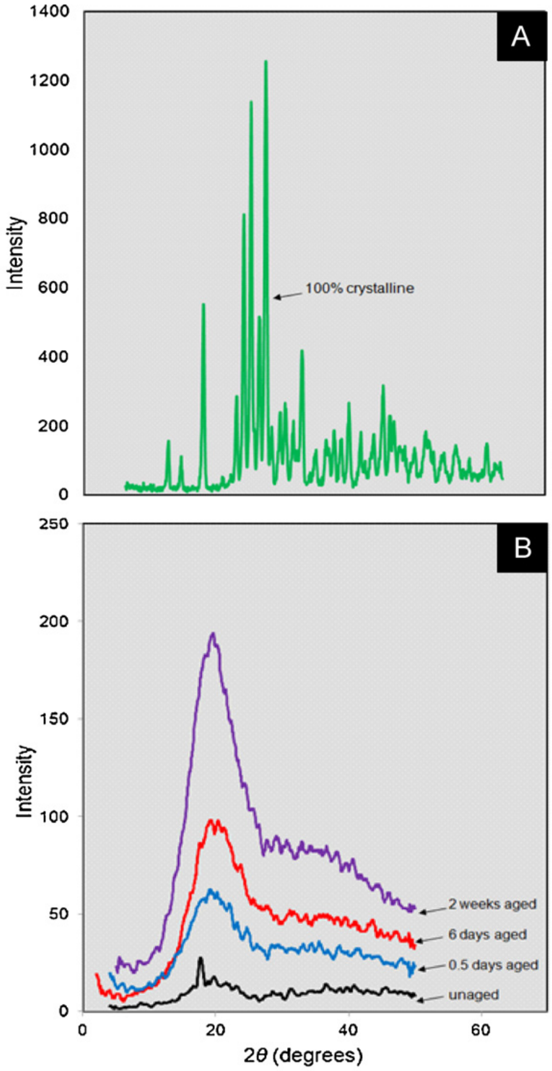

Fig. 5. X-ray diffraction patterns for (A) completely crystalline maltose, (B) maltose stored at $(T_{gi} - 5)$ for selected aging times.

Maltose samples aged isothermally at $(T_g - 5)$ for 0.5, 6, and 14 days were amorphous, however, the intensity of X-ray diffraction (XRD) peaks of aged maltose samples were greater than that of unaged maltose (Fig. 5B). The increased intensity of the aged maltose may be attributed to densification resulting from closer molecular rearrangement and decrease in free volume in the matrix structure as the material approaches equilibrium thermodynamic state during aging (Ambike, Mahadik, & Paradkar, 2005; Lionetto, Maffezzoli, Ottenhof, Farhat, & Mitchell, 2005). The XRD peaks of aged maltose became narrower than for unaged maltose. Ambike et al. (2005) observed no characteristic peak, but significant elevation of diffractograms after 6 months storage of model drug simvastatin in glassy state. Martino, Ruseckaite, & Jimenez (2009) observed poly lactic acid (PLA) and PLA blended with plasticizers (10–20% G206/7 and G206/2) were amorphous during isothermal aging in their glassy state. However, when the polymers were aged just above their glass transition temperature, an initial amorphous to crystalline transition of PLA chains was observed from peaks in X-ray diffractograms. The densification may result in shifting of the peak angle to higher levels and narrowing of the peak in XRD spectra (Lionetto et al., 2005). Further, the XRD spectra of aged maltose were compared with the XRD spectra of completely crystalline maltose (Figs. 5A and 4B). It was interesting to observe that

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
Glucose	105	Fragile	34.5	Strong[a]
Maltose	88.1	Strong[a]	23.5	Strong[a]
Maltotriose	97.6	Strong[a]	28.6	Strong[a]

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

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 (Figs. 5A and 4B).

3.3. *Fragility of amorphous carbohydrates*

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 (Hancock et al., 1998).

Fragile systems exhibit large m values between 100 and 200, while strong systems present small m values between 16 and 100 (Champion, Le Meste, & Simatos, 2000). 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 (Angell, 1985, 1988). The ratio $C_{p(\text{liquid})}/C_{p(\text{glass})}$ of fragile systems is greater than 1.1 (Angell, 1985). Above T_g, strong systems exhibit greater relaxation times, while below T_g, they exhibit smaller dynamic properties and relaxation times (Mao et al., 2010).

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 Eq. (4), 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 Eq. (4). 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 Fig. 6, 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 Eq. (6) were 202.9, 158.3, and 220.1 kJ/mol respectively (Fig. 6). From these ΔE values and using Eq. (6), 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).

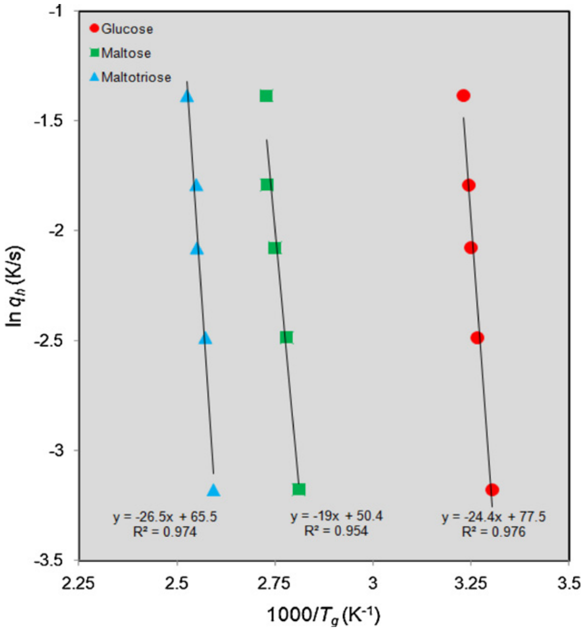

Fig. 6. Heating rate dependence on glass transition temperatures of glucose, maltose and maltotriose in order to find fragility index using Eq. (7). Onset glass transition temperature is assumed as T_g.

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 (Lee, Thomas, Jerrell, et al., 2011; Lee, Thomas, & Schmidt, 2011). Previous literature presents inconsistencies in the fragility predictions by different methods for various systems. There is no definite explanation available for the difference in fragility predictions by different methods (Wungtanagorn and Schmidt, 2001a,b). More research is required for clarification of this discrepancy.

4. Conclusions

The enthalpy relaxed decreased while characteristic relaxation time increased during aging of glucose, maltose and maltotriose at 5 °C below their glass transition temperature. The Kohlrausch–Williams–Watts (KWW) equation was able to describe enthalpy relaxation kinetics of glucose, maltose and maltotriose. The fragility indices (m) of the selected carbohydrates indicated maltose and maltotriose as the strong systems. The molecular weight dependence of enthalpy relaxations and the fragility information of selected amorphous carbohydrates obtained from this study may be useful in relating physicochemical changes in bioactive molecules encapsulated by these carbohydrate systems.

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