

Glass transition and enthalpy relaxation of amorphous lactose glass

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Abstract—The glass transition temperature, T_g , and enthalpy relaxation of amorphous lactose glass were investigated by differential scanning calorimetry (DSC) for isothermal aging periods at various temperatures (25, 60, 75, and 90 °C) below T_g . Both T_g and enthalpy relaxation were found to increase with increasing aging time and temperature. The enthalpy relaxation increased approximately exponentially with aging time at a temperature (90 °C) close to T_g (102 °C). There was no significant change observed in the enthalpy relaxation around room temperature (25 °C) over an aging period of 1 month. The Kohlrausch–Williams–Watts (KWW) model was able to fit the experimental enthalpy relaxation data well. The relaxation distribution parameter (β) was determined to be in the range 0.81–0.89. The enthalpy relaxation time constant (τ) increased with decreasing aging temperature. The observed enthalpy relaxation data showed that molecular mobility in amorphous lactose glass was higher at temperatures closer to T_g . Lactose glass was stable for a long time at 25 °C. These findings should be helpful for improving the processing and storage stability of amorphous lactose and lactose containing food and pharmaceutical products.

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1. Introduction

Most glassy products are manufactured by thermal processing. During this processing, several physical and mechanical changes may occur. Enthalpy relaxation is one such change, and it depends on the processing and storage temperatures, and the time given for the materials to adjust to changes in temperature. Enthalpy relaxation produces changes in the physical properties of the product, such as crispiness, texture, freshness, all of which ultimately determine the quality of the product. Relaxation phenomena are often observed in the region of the glass transition temperature, T_g , during the heating of glassy materials.¹ Amorphous glassy materials are thermodynamically unstable, and during storage their structures tend to relax toward the equilibrium state.^{2–5} Consequently, the enthalpy and volume of a glassy material decrease over time; this phenomenon is often

referred to as physical aging.⁶ It has been observed that increasing the aging temperature to a sufficiently high temperature below T_g , increases the magnitude of the relaxation endotherms observed by DSC.^{2,5,7}

Many studies have been reported on enthalpy relaxation in synthetic polymers.^{6,8–11} Some macroscopic properties, such as density, mechanical strength, and vapor permeability can be affected by enthalpy relaxation in amorphous glassy materials. Noel et al.⁸ reported that enthalpy relaxation can provide information on time-dependent changes in glassy structures, which is related to embrittlement in the glassy state. Kim et al.¹¹ pointed out that the water vapor permeability of glassy starch films decreased with increasing aging time at temperatures below T_g due to enthalpy relaxation.

The phenomena of glass transition and enthalpy relaxation in food components, such as gelatin,⁵ sugars,⁷ starch,^{11–13} and dried glassy fish meat¹⁴ have been studied extensively by many researchers. Kawai et al.⁷ studied the activation-energy-related stability of sugars (trehalose, sucrose, maltose, and glucose), and found

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that the activation energy for glassy trehalose was the highest out of the four sugars and reported that trehalose glass was the most stable sugar glass below the T_g . These authors further suggested⁷ that the activation energy of enthalpy relaxation was related to the mobility of the molecules in the glassy state, which could directly affect the chemical or physical stability of glassy products. Badii et al.⁵ reported that amorphous glassy gelatin aged at various water contents and temperatures below T_g behaved in a similar manner to synthetic polymers and carbohydrates. It has also been proposed that enthalpy relaxation and aging kinetics are highly dependent on the structure and composition of glassy materials.²

Lactose is a carbohydrate that is commonly used in various foods, dairy products, confectionaries, and pharmaceuticals. Lactose containing products may undergo enthalpy relaxation during thermal processing and storage if the conditions are not selected appropriately. Several researchers have investigated the effect of water sorption, T_g , instant and time-dependent crystallization of amorphous lactose on its processing and storage stability.^{15–23} However, very few studies have investigated the storage stability of amorphous lactose by considering the molecular mobility and enthalpy relaxation at and below the T_g . It is thus very important to determine the relaxation properties of lactose as a function of temperature in order to gain a deeper understanding of molecular mobility and stability of lactose glass below T_g .

Several mathematical theories have been developed to calculate and predict the enthalpy relaxation process.^{7,24} The most commonly used theories are the Kohlrausch–Williams–Watts (KWW) theory and the extended Adam–Gibbs theory. The KWW theory was initially developed to describe the dielectric relaxation process.²⁵ Typically, it is generally assumed that this theory can be employed to fit enthalpy relaxation data using the stretched exponential function by non-linear regression, and that it can be used to estimate the mean relaxation time.^{25,26} On the other hand, the extended Adam–Gibbs theory describes the enthalpy relaxation process in the cooperative rearrangement region (CRR) and is used for estimating the minimum and maximum relaxation times. The objective of this present study was to determine the enthalpy relaxation behavior of lactose for various aging temperatures by DSC. In addition, the characteristic relaxation time, and activation energy of enthalpy relaxation were also calculated using the two above-mentioned theories.

2. Experimental

2.1. Sample preparation

Amorphous lactose glasses were prepared by melting α -lactose monohydrate (Sigma Chemical Co. St. Louis,

Mo, USA) in pre-weighed open aluminum DSC pans placed on a hot plate. The temperature of the hot plate was maintained at the melting temperature of the sugar. The molten sugar in the DSC pans was hermetically sealed immediately after being cooled to room temperature. The sample's weights were in the range 7–10 mg.

2.2. DSC measurements

To erase the thermal history of lactose glass, each sample was heated from 60 °C (about 40 °C below T_g) to 140 °C (about 40 °C above T_g) at a heating rate of 5 °C/min, and then immediately cooled to 60 °C at a cooling rate of 10 °C/min. This heating and cooling cycle was repeated using the same heating and cooling rates as before, finally heating the sample to the aging temperature (60, 75, and 90 °C) at a heating rate of 5 °C/min. This procedure was performed using a Perkin–Elmer Diamond DSC (Wellesley, USA); an empty pan was employed as a reference. The DSC was calibrated for temperature using indium (melting point of 156.6 °C), water (melting point of 0.0 °C), and cyclohexane (melting point of –87.0 °C), and for heat flow using indium (ΔH_m , 28.45 J/g) and water (ΔH_m , 334.5 J/g). Erased samples were aged at an isothermal aging temperature in an oven from 12 to 120 h at 60 and 75 °C, and from 2 to 120 h at 90 °C. Aging at 25 °C was also performed from 1 to 30 days. Each measurement was performed using three samples. The onset of T_g and enthalpy relaxation of unaged and aged samples were measured using DSC thermograms obtained from room temperature (20 °C) to 140 °C at a heating rate of 5 °C/min using a Shimadzu (Japan) DSC-50. A schematic representation of the entire temperature program is shown in Figure 1. Alumina placed in the DSC pan was used as a reference for the Shimadzu DSC. The temperature and heat flow calibrations were performed using indium and water. The enthalpy relaxation ΔH_{relax} was calculated from the endothermic peak area around T_g , as indicated on the heating curves shown in Figure 2.

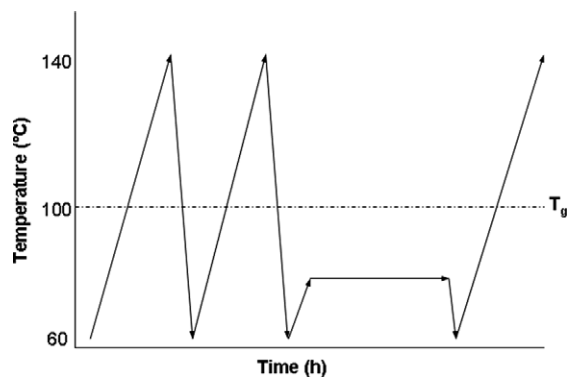


Figure 1. Schematic representation of the temperature programs used to measure the enthalpy relaxation at the glass transition region.

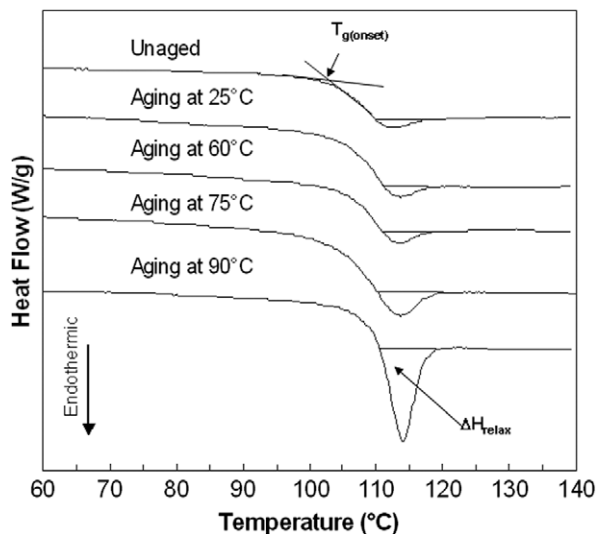


Figure 2. Typical DSC thermograms of unaged and aged (for 24 h) amorphous lactose showing the glass transition and enthalpy relaxation endotherm at the glass transition temperature.

3. Results and discussion

3.1. Glass transition temperature

The glass transition temperature of lactose increased with increasing aging time and temperature (Fig. 3). The increase in T_g with aging time was greater at aging temperatures (90 °C) close to T_g (102 °C), and it decreased slowly as the aging temperatures became further from T_g . No significant changes were observed at the aging temperature (25 °C) close to room temperature. This increase in the glass transition temperature with aging has also been reported by many researchers for a variety of materials. Schmidt and Lammert²⁷ and

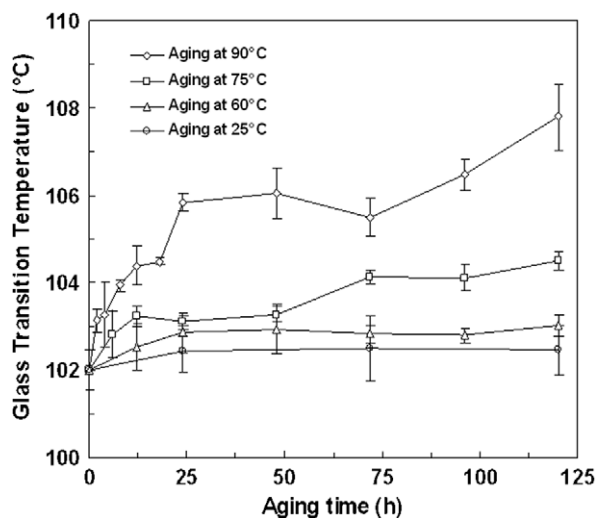


Figure 3. Glass transition temperature as a function of aging time for various aging temperatures.

Lammert et al.²⁸ reported that T_g of maltose increased with increasing aging time, and they observed that the relaxation endotherm shifted to higher temperatures in aged samples. An increase in T_g with increasing aging time was also observed by Chung and Lim^{2,3} in glassy normal and waxy rice starches, and by Liao et al.²⁹ in poly (DL-lactide). They conjectured that the molecular conformation changed during aging in the direction toward the equilibrium state as a result of a decrease in the free volume and molecular mobility in the glassy state. Our results are in agreement with those previously reported results and suggest that during aging, the molecules might have come close together to form a rigid glass with low molecular movement, resulting in an increase in T_g .

3.2. Enthalpy relaxation

Typical DSC thermograms of unaged and aged (for 24 h) anhydrous lactose glass at various temperatures are shown in Figure 2. The unaged samples have a very small endothermic relaxation peak associated with the glass transition, which was also observed in a previous study.²² The size of the relaxation peak, referred to as the recovery of enthalpy relaxation, increased with increasing aging time and temperature. The rate of formation of the relaxation peak was greatest in a sample aged at a temperature (90 °C) close to T_g (102 °C), and it decreased as the aging temperature was lowered from T_g (Fig. 4). There was no significant change in samples aged at a temperature (25 °C) near room temperature for a month. This observation suggests that molecular movement was higher in samples aged at temperatures closer to T_g than those aged at lower temperatures. Our results agree with previous studies, which found that enthalpy relaxation increased with increasing time

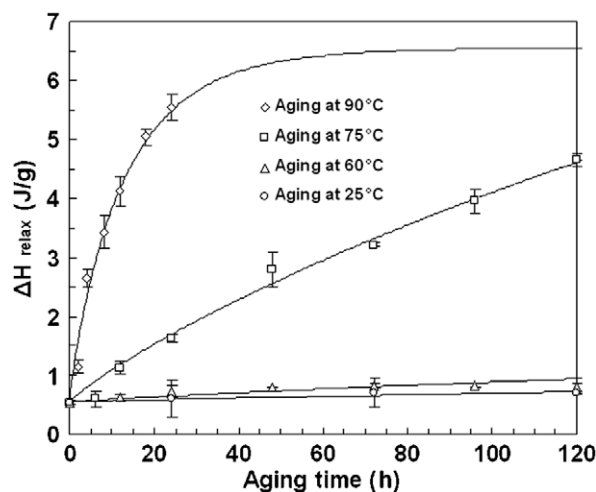


Figure 4. Enthalpy relaxation as a function of aging time for various aging temperatures.

for various amorphous sugar glasses at aging temperatures 10–30 °C below T_g ,⁷ and in freeze-concentrated sucrose–water glass at aging temperatures in the range –55 to –70 °C.³⁰ Chung and Lim³ reported that the recovery of enthalpy relaxation also occurred during aging in glassy normal and waxy rice starches at temperatures 0–75 °C below the T_g . It appears that these aging phenomena occur in both small (monomer and dimer) and large (polymer) amorphous glasses under similar time and temperature conditions. These aging phenomena may change the physical and mechanical properties of glassy materials, as indicated by changes in the relaxation endotherm and T_g .

3.3. Enthalpy relaxation time

Experimental ΔH_{relax} data for anhydrous lactose glass aged at various temperatures up to 120 h are shown in Figure 4. The solid lines in Figure 4 represent the best fits of the KWW equation to the experimental data. The KWW equation is given by²⁵

$$\Delta H_{\text{relax}} = \Delta H_{\infty} [1 - \exp\{- (t/\tau^{\text{KWW}})^{\beta}\}], \quad (1)$$

where t , τ^{KWW} , β are the aging time, characteristic enthalpy relaxation time, and non-exponential parameter, respectively. The non-exponential parameter β is usually considered as the distribution of the enthalpy relaxation time having a value between 0 and 1.^{7,26,31} Both τ^{KWW} , β in KWW equation are adjustable parameters that can be determined by fitting the data to the equation. ΔH_{∞} is the maximum enthalpy recovery at any given temperature and can be calculated from the following equation:

$$\Delta H_{\infty} = \Delta C_p (T_g - T), \quad (2)$$

where ΔC_p is the change in the heat capacity at T_g , and T is the aging temperature. However, the fitting procedure used in this study usually results in a slightly lower estimation of ΔH_{∞} and τ^{KWW} values, and a slightly higher estimation of β as reported by Kawai et al.⁷ and Hancock et al.²⁶ To obtain the best fit to the data, the initial parameters used were $\tau^{\text{KWW}} = 100$ and $\beta = 0.5$ as reported by other researchers.^{7,26}

The range of β values calculated for anhydrous lactose varied between 0.81 and 0.89 depending on the aging temperature and the corresponding τ^{KWW} values. These values were slightly higher than those reported by Kawai et al.⁷ for other sugars, such as glucose, sucrose, and trehalose (0.46–0.75) and by Hancock et al.²⁶ for sucrose (0.4–0.8). However, the calculated enthalpy relaxation data using these values for β , τ^{KWW} , and ΔH_{∞} shown by the solid lines in Figure 4 fitted our experimental data well.

The enthalpy relaxation process was also estimated in the present study using the extended Adam and Gibbs equation (Eq. 3):³²

$$\frac{d(\Delta H_{\infty} - \Delta H_{\text{relax}})}{dt} = -\frac{1}{\tau^{\text{eff}}(t)} (\Delta H_{\infty} - \Delta H_{\text{relax}}), \quad (3)$$

where $(\Delta H_{\infty} - \Delta H_{\text{relax}})$ is the deviation of the enthalpy from its equilibrium value, and $\tau^{\text{eff}}(t)$ is the effective enthalpy relaxation time. The plot of $d(\Delta H_{\infty} - \Delta H_{\text{relax}})/dt$ versus $(\Delta H_{\infty} - \Delta H_{\text{relax}})$ shows an exponential dependence, thus $\tau^{\text{eff}}(t)$ is calculated by using the following equation:

$$\ln \tau^{\text{eff}}(t) = \ln \tau_{\infty}^{\text{eff}} + B(\Delta H_{\infty} - \Delta H_{\text{relax}}), \quad (4)$$

where B and $\tau_{\infty}^{\text{eff}}$ are constants and correspond to the slope and intercept of the plot of $\ln \tau^{\text{eff}}(t)$ versus $(\Delta H_{\infty} - \Delta H_{\text{relax}})$ shown in Figure 5, respectively. The $\tau_{\infty}^{\text{eff}}$ coefficient corresponds to $\tau^{\text{eff}}(t)$ when the enthalpy has relaxed to the equilibrium state [$\Delta H_{\infty} = \Delta H_{\text{relax}}$ in Eq. 4]. The initial (unrelaxed) enthalpy relaxation time, τ_0^{eff} , has also been calculated in the present study in addition to $\tau_{\infty}^{\text{eff}}$. The τ_0^{eff} and $\tau_{\infty}^{\text{eff}}$ coefficients correspond to the relaxation time of the minimum and maximum size of the co-operative rearrangement region (CRR) of the enthalpy relaxation, respectively, during isothermal aging at a given temperature.^{7,32} There was a linear increase in $\ln \tau^{\text{eff}}(t)$ with increasing enthalpy relaxation at all aging temperatures (Fig. 5) as was also observed by Kawai et al.⁷ in various sugar glasses and by Inoue and Suzuki³⁰ in freeze-concentrated sucrose–water glass. This result suggests that the calculated values of τ_0^{eff} and $\tau_{\infty}^{\text{eff}}$ from Eq. 4 are accurate. From the slopes of the plots in Figure 5, the rates of change of $\tau^{\text{eff}}(t)$ with enthalpy relaxation were determined to be –0.09, –0.60, –24.65, and –37.15 at aging temperatures of 90, 75, 60, and 25 °C, respectively. This suggested that enthalpy relaxation was dependent on aging temperature.

It is important to note that the activation energy, ΔE , of enthalpy relaxation is an important parameter for gaining a better understanding of the mobility of molecules in the glass state. This is because the physical

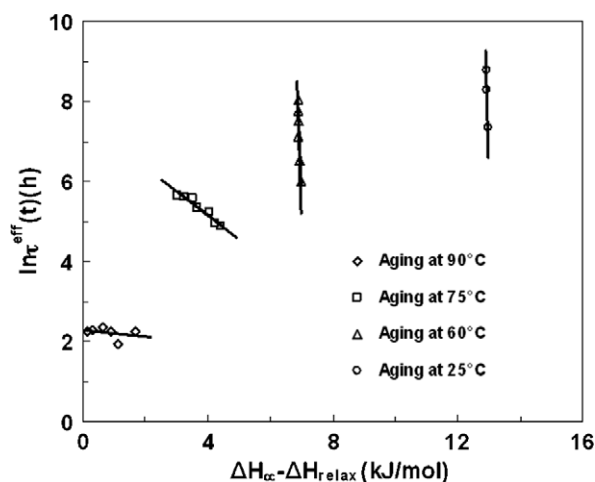


Figure 5. Calculated relaxation time as a function of level of enthalpy relaxation.

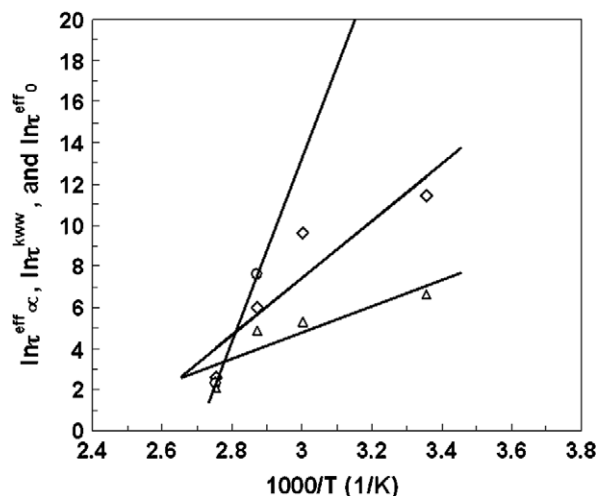


Figure 6. Arrhenius plot of $\ln \tau_{\infty}^{\text{eff}}$ (○) (h); $\ln \tau^{\text{KWW}}$ (◇) (h); and $\ln \tau_0^{\text{eff}}$ (△) (h).

Table 1. Activation energies obtained from the Arrhenius plots of $\tau_{\infty}^{\text{eff}}$, τ^{KWW} , and τ_0^{eff}

Compounds	$\Delta E_{\infty}^{\text{eff}}$ (kJ/mol)	ΔE^{KWW} (kJ/mol)	ΔE_0^{eff} (kJ/mol)
Lactose	370.2	114.9	52.8
Sucrose ^a	320.0	212.2	172.9
Trehalose ^a	589.1	360.8	238.8

^a Data from Kawai et al.⁷

stability of glassy materials may be dependent on molecular mobility to some extent. Therefore, the Arrhenius plots of τ^{KWW} , $\tau_{\infty}^{\text{eff}}$, and τ_0^{eff} (Fig. 6) were analyzed to calculate the activation energy of enthalpy relaxation from the slopes in Figure 6, as was reported by other researchers for various other glassy materials.^{7,30,33} The plots showed good linearity within the measured range of aging temperatures. The ΔE values of lactose shown in Table 1 were significantly lower than other disaccharides, such as sucrose and trehalose reported by Kawai et al.,⁷ with the exception of the $\Delta E_{\infty}^{\text{eff}}$ values of sucrose. However, the $\Delta E_{\infty}^{\text{eff}}$ value of lactose was higher than that for sucrose. The low ΔE values for lactose might be due to low inter-molecular interaction in the glassy state during aging. The lower solubility of lactose compared to those of other sugars also indicates that lactose molecules might have fewer hydrogen bonding sites, which is responsible for inter-molecular interactions. The low ΔE values of lactose also suggest that lactose glass may have low stability compared to other disaccharides. This result suggests that the activation energies of sugar glasses are dependent on molecular structure, level of enthalpy relaxation, and solubility.

To compare the ΔE values, enthalpy relaxation times were also plotted against T_g/T (Fig. 7). These plots show that the enthalpy relaxation time increases in the order of $\tau_{\infty}^{\text{eff}}$, τ^{KWW} , and τ_0^{eff} , and the correspondingly activation energies also increase in the same order. Kawai

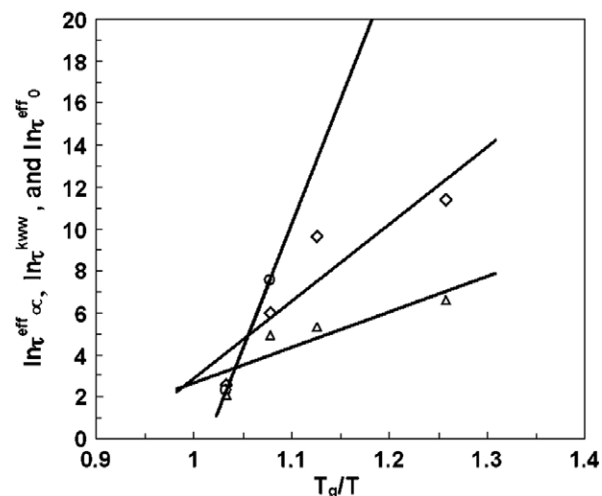


Figure 7. Arrhenius plot of $\ln \tau_{\infty}^{\text{eff}}$ (○) (h); $\ln \tau^{\text{KWW}}$ (◇) (h); and $\ln \tau_0^{\text{eff}}$ (△) (h) as a function of T_g/T .

et al.⁷ observed that the activation energies (ΔE^{KWW}) calculated for various sugars using the KWW equation were between the maximum and minimum activation energies ($\Delta E_{\infty}^{\text{eff}}$ and ΔE_0^{eff}) calculated using the Adams and Gibbs equation. In the present study, the ΔE values also followed the same trend. This result suggests that our data is correct.

4. Conclusions

Enthalpy relaxation and T_g of amorphous lactose glass increased with increasing aging time and temperature. The experimental enthalpy relaxation data were fitted well using the KWW equation. The enthalpy relaxation time was calculated using the KWW equation and the extended Adam and Gibbs equation. The calculated relaxation times varied from a few minutes at an aging temperature close to T_g to a few months at an aging temperature of 25 °C (77 °C lower than T_g). The temperature dependent enthalpy relaxation data obtained in the present study is helpful for gaining a better understanding of molecular mobility in lactose glasses during thermal processing and storage, which can directly affect the physical and mechanical properties of glassy materials.

Acknowledgments

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