Effects of Heating Conditions on the Glass Transition Parameters of Amorphous Sucrose Produced by Melt-Quenching

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ABSTRACT: This research investigates the effects of heating conditions used to produce amorphous sucrose on its glass transition (T_g) parameters, because the loss of crystalline structure in sucrose is caused by the kinetic process of thermal decomposition. Amorphous sucrose samples were prepared by heating at three different scan rates (1, 10, and 25 °C/min) using a standard differential scanning calorimetry (SDSC) method and by holding at three different isothermal temperatures (120, 132, and 138 °C) using a quasi-isothermal modulated DSC (MDSC) method. In general, the quasi-isothermal MDSC method (lower temperatures for longer times) exhibited lower T_g values, larger ΔC_p values, and broader glass transition ranges (i.e., $T_{g\ end}$ minus $T_{g\ onset}$) than the SDSC method (higher temperatures for shorter times), except at a heating rate of 1 °C/min, which exhibited the lowest T_g values, the highest ΔC_p, and the broadest glass transition range. This research showed that, depending on the heating conditions employed, a different amount and variety of sucrose thermal decomposition components may be formed, giving rise to wide variation in the amorphous sucrose T_g values. Thus, the variation observed in the literature T_g values for amorphous sucrose produced by thermal methods is, in part, due to differences in the heating conditions employed.

KEYWORDS: glass transition (T_g), sucrose, thermal decomposition, standard DSC, quasi-isothermal MDSC

■ INTRODUCTION

Amorphous sugars are essential ingredients in many food and pharmaceutical products due to their useful properties, such as encapsulation ability, high dissolution rate, and high solubility.[1,2] Examples of food ingredients and products containing amorphous sugars are spray-dried flavors, boiled sweets, milk powder, coffee powder, infant formula, and fondants,[3,4] and examples of pharmaceutical ingredients and products are excipients for large-scale tablet and capsule manufacturing[5−11] and fillers in chewable tablets.[12,13]

However, amorphous sugars are known to undergo structural changes induced by heat and/or moisture uptake, leading to undesirable events, such as stickiness, caking, and collapse and recrystallization.[1,10,14] These undesirable events are detrimental to product quality attributes, such as texture, taste, aroma retention, shelf life, and delivery and stability characteristics of drug products, which are critical to final product acceptance. These stability concerns associated with amorphous sugar based products are of practical and economical importance; thus, they have been the subject of much research over the past several years.

A parameter of critical importance to the stability of amorphous materials is the glass transition temperature (T_g), which is the temperature at which a reversible transition occurs between the solid amorphous (glassy) state and the supercooled liquid (rubbery) state. Because the glassy to rubbery transition takes place over a range of temperatures, rather than at a single temperature, it is important to report the onset, midpoint, and end point of the transition and to specify the method and parameters used to obtain the T_g values.[15] Upon inspection of the literature-reported T_g values for the same amorphous material, differences are often observed. For example, the $T_{g\ onset}$ for amorphous sucrose reported by Roos[16] was 62 °C, whereas Slade and Levine[17] reported a value of 52 °C. The dissimilarity between reported T_g values for the same sugar has been ascribed to differences in (1) residual water content, (2) sample handling techniques (e.g., preparation methods), (3) T_g measurement techniques, and (4) T_g analysis conditions and methods.[16,18,19]

The factor influencing T_g of interest in this study is the heating conditions used to produce the amorphous sucrose. The heating conditions used are important because the loss of crystalline structure (usually termed melting) in sucrose is due to the kinetic process of thermal decomposition (termed apparent melting), rather than thermodynamic melting, as shown by Lee et al.[20,21]

Sucrose melting is a time−temperature combination process; that is, in general, thermal decomposition is more extensive under lower temperature−longer time conditions than under higher temperature−shorter time conditions. Thus, depending on the heating condition employed, different amounts and types of thermal decomposition components are formed in the amorphous sucrose and, consequently, give rise to different T_g values. It is important to note that the amorphous sucrose produced by melt-quenching, under all heating conditions (even at temperatures below the literature-reported melting temperature for sucrose), is chemically different from the starting crystalline sucrose, due to the formation of thermal decomposition components produced during heating. The amorphous sample is not just amorphous sucrose, but rather amorphous sucrose plus the resultant decomposition components. However, for convenience and consistency with the literature, the amorphous product produced by melt-quenching sucrose will be referred to as "amorphous sucrose" throughout this paper.

Both Vanhal and Blond,[3] studying sucrose, and Jiang et al.,[22] studying sucrose, glucose, and fructose, applied different heating conditions to these sugars to explore the relationship between thermal decomposition and T_g values. Vanhal and Blond[3] investigated the T_g values for amorphous sucrose prepared by various heating conditions (i.e., final heating temperature, the residence time at the final temperature, and heating rate). The T_g values for amorphous sucrose decreased in the final heating temperature range of 190−210 °C and then increased in the final heating temperature range of 215−225 °C. When sucrose was held for various lengths of time at its melting peak temperature, 190 °C, the T_g values initially decreased and then increased with increasing residence time. Vanhal and Blond[3] attributed the trend of decreasing and then increasing T_g values for amorphous sucrose in these experiments to the formation of different types and amounts of thermal decomposition components. That is, the decrease in T_g values was due to the formation of small molecular weight components via bond breaking (under relatively mild heating conditions), and the increase in T_g values was due to the formation of various high molecular weight components via polymerization (under relatively severe heating conditions). Jiang et al.[22] reported a similar trend of heating condition dependent changes in T_g values for fructose and glucose as well as sucrose. Additionally, Jiang et al.[22] suggested that water formed via dehydration, which occurs during sugar decomposition, as another possible explanation for decreasing T_g values.

The heating conditions (i.e., holding sugar samples for different residence times at different temperatures) employed by Vanhal and Blond[3] and Jiang et al.[22] were carried out at and above the melting peak temperature of the sugars. However, because the loss of crystalline structure in sucrose is due to the kinetic process of thermal decomposition,[20,21] what still needs to be assessed is the effect on T_g values of amorphous sucrose produced under low temperature−long time conditions.

Vanhal and Blond[3] also investigated the effect of heating rates on the T_g values of amorphous sucrose. These researchers found that $T_{g\ mid}$ increased from approximately 61 to 71 °C as a function of heating rate, from 5 to 40 °C/min, respectively. These researchers concluded that at slower heating rates the T_g value was lower because at slower heating rates the sucrose remains for a longer time at each temperature, which resulted in the formation of more thermal decomposition components and, consequently, lower T_g values. However, the effect of the heating rate on the amorphous sucrose T_g values could be confounded

with their selection of a constant final heating temperature of 200 °C, which was applied to all heating rates (5, 10, 20, 30, and 40 °C/min). In DSC analysis, the temperature at which the endothermic melting peak for sucrose, glucose, and fructose is completed depends on the heating rate. In other words, as the heating rate increases, the temperature at which the endothermic melting curve is completed increases. As discussed previously, this is because the loss of crystalline structure of these sugars is due to the kinetic process of thermal decomposition (termed apparent melting), rather than thermodynamic melting. For example, as shown in Figure 1, the final heating temperature required for obtaining the entire apparent melting curve for sucrose was approximately 184 °C at a heating rate of 1 °C/min, whereas it was approximately 206 °C at a heating rate of 25 °C/min. Thus, if a constant final heating temperature (e.g., 206 °C) is applied to both heating rates, the amorphous sucrose heated at a rate of 1 °C/min would still be exposed to heat until the final heating temperature of 206 °C was reached. It remains ambiguous whether a change in the T_g values for the amorphous sucrose was caused only by the heating rate effect or also by the additional heat received to reach the final heating temperature.

Therefore, the objective of this research was to determine (1) the effect of heating rate only on the T_g values for amorphous sucrose (final heating temperature determined by heating rate) using SDSC and (2) the effect on T_g values of producing amorphous sucrose under low temperature (well below the reported melting temperature for sucrose)−long time conditions using quasi-isothermal MDSC.

■ MATERIALS AND METHODS

Materials. High-purity crystalline sucrose (≥ 99.5) was purchased from Sigma-Aldrich Co. (St. Louis, MO) and used without further purification. The water content of sucrose measured by coulometric Karl Fischer titration (with Hydranal Coulomat AG solvent) was 0.004% wet basis (wb).

Methods. Amorphous sucrose samples were prepared by heating at different rates (1, 10, and 25 °C/min) using SDSC and by holding at different isothermal temperatures (120, 132, and 138 °C) using quasi-isothermal MDSC. A DSC Q2000 (TA Instruments, New Castle, DE), equipped with a refrigerated cooling system (RCS 90), was utilized for both SDSC and quasi-isothermal MDSC. Prior to the preparation and measurement of amorphous sucrose, the calibration for enthalpy (cell constant) and temperature was performed with indium ($T_{m\ onset}$ of 156.60 °C, ΔH of 28.71 J/g, TA Instruments). In advance of using the quasi-isothermal MDSC, DSC and MDSC heat capacity calibrations (a modulation amplitude of ± 1 °C and a period of 100 s) were individually conducted using a 22.93 mg sapphire disk (TA Instrument) hermetically sealed in a pan. Hermetic aluminum Tzero pans and lids (TA Instruments) were used for all calibrations, sample preparations, and sample measurements. An empty pan was used as the reference. Dry nitrogen, at a flow rate of 50 mL/min, was used as the purge gas.

Sample Preparation Using Different Heating Rates by SDSC. As previously mentioned in the Introduction, the desired final heating temperature required for obtaining an entire apparent melting peak for sucrose depends on the heating rate employed. The final heating temperature for each heating rate was determined as follows. First, the apparent melting end temperature was determined by linear extrapolation for triplicate measurements at each heating rate. Then, the final heating temperature for each heating rate was calculated as the average end temperature plus 2 standard deviations. The 2 standard deviations were added to account for run-to-run variation, ensuring complete loss of crystalline structure for each measurement. The final heating
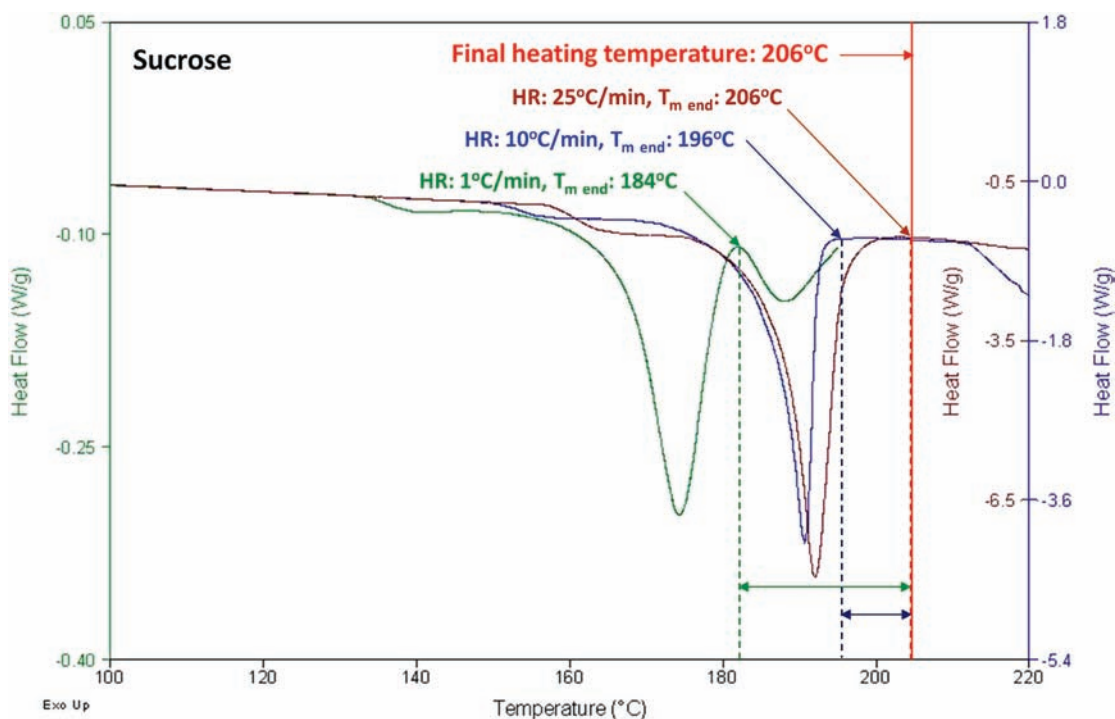
Figure 1. DSC thermograms for sucrose heated at three heating rates (HR), 1, 10, and 25 °C/min, to three different end temperatures using SDSC. The temperature at which the apparent melting for sucrose is completed depends on the HR employed in DSC analysis. Dotted vertical lines are the final temperatures (the average end temperature plus 2 standard deviations) employed at each HR. Arrows illustrate the additional heating that the sucrose samples would experience if the final heating temperature of 206 °C were used for all HRs.

temperatures for each heating rate were 184 °C at 1 °C/min, 196 °C at 10 °C/min, and 206 °C at 25 °C/min.

Crystalline sucrose (approximately 2.75 mg) hermetically sealed in a pan was heated from 25 °C to the final heating temperature calculated for each heating rate. The total heating times at each heating rate were 159 min at 1 °C/min, 78.4 min 10 °C/min, and 7.24 min at 25 °C/min. Immediately after the DSC heat flow signal reached the final heating temperature at each heating rate, the melted sucrose was cooled at a rate of 50 °C/min to −50 °C, equilibrated at −50 °C, and then reheated at a rate of 10 °C/min to 220 °C. The second DSC scan was used to measure the sample T_g parameters. No measurable endothermic melting peak was observed in any of the SDSC amorphous sucrose samples, indicating complete removal of crystalline structure. All amorphous sucrose samples prepared at each heating rate were measured in triplicate. Universal Analysis (UA) software (TA Instruments, version 4.4A) was used to determine the T_g parameters ($T_{g\ onset}$, $T_{g\ mid}$, $T_{g\ end}$, ΔC_p) for the amorphous sucrose samples as follows: $T_{g\ onset}$, the temperature at the intersection of the regression line from the starting point of the specified limit (the first tangent) and the inflection tangent of the step change (the second tangent); $T_{g\ mid}$ (by inflection), the temperature at the steepest slope on the DSC curve between the first tangent and the regression line after the transition (the third tangent); $T_{g\ end}$, the temperature at the intersection of the inflection tangent and the third tangent; and ΔC_p, the difference between the linear extrapolated glass and the liquid heat capacity curves of material at $T_{g\ inflection}$.[23]

Sample Preparation Using Different Isothermal Temperatures by Quasi-isothermal MDSC. To prepare amorphous sucrose samples using quasi-isothermal MDSC, three isothermal temperatures (120, 132, and 138 °C) were chosen on the basis of the results of the stepwise quasi-isothermal MDSC experiment for sucrose conducted in Lee et al.[20,21] In the stepwise quasi-isothermal MDSC experiment, the heat capacity (Rev C_p) signal began to gradually increase at 120 °C, indicating the onset of the loss of crystalline structure in sucrose, and then slightly leveled off at

approximately 143 °C, indicating the removal of all crystalline structure in sucrose (Figure 2). Hence, 120 °C, the onset temperature of the loss of crystalline structure in sucrose, and 132 and 138 °C, the temperatures at which the loss of crystalline structure occurs relatively quickly, were selected as the isothermal temperatures.

Because the loss of crystalline structure in sucrose is caused by the kinetic process of thermal decomposition, as shown in Lee et al.,[20,21] the holding time required for removal of all crystalline structure in sucrose depends on the isothermal temperature employed. Thus, to determine the final holding time for each isothermal temperature, crystalline sucrose (approximately 2.75 mg) hermetically sealed in a pan was isothermally held at 120, 132, and 138 °C using quasi-isothermal MDSC (a modulation amplitude of ±1 °C and a period of 100 s) well over the time at which the Rev C_p signal slightly leveled off. The point at which the Rev C_p signal slightly leveled off was regarded as the time required for removal of all crystalline structure in sucrose at each isothermal temperature. The end holding time was obtained by linear extrapolation for triplicate measurements at each isothermal temperature. Then, the final holding time for each isothermal temperature was calculated as the average end holding time plus 2 standard deviations. As in the case of SDSC, the 2 standard deviations were added to account for run-to-run variation, ensuring complete loss of crystalline structure for each measurement. The final holding times for each isothermal temperature were 3014 min at 120 °C, 883 min at 132 °C, and 510 min at 138 °C (Figure 3).

Crystalline sucrose (approximately 2.75 mg) hermetically sealed in a pan was isothermally held at each isothermal temperature for the corresponding time using quasi-isothermal MDSC (a modulation amplitude of ±1 °C and a period of 100 s). After that, the melted sucrose was immediately cooled at a rate of 50 °C/min to −50 °C, equilibrated at −50 °C, and then reheated at a rate of 10 °C/min to 220 °C. In the second DSC scan, no measurable endothermic melting peak was observed in any of the MDSC amorphous sucrose samples.
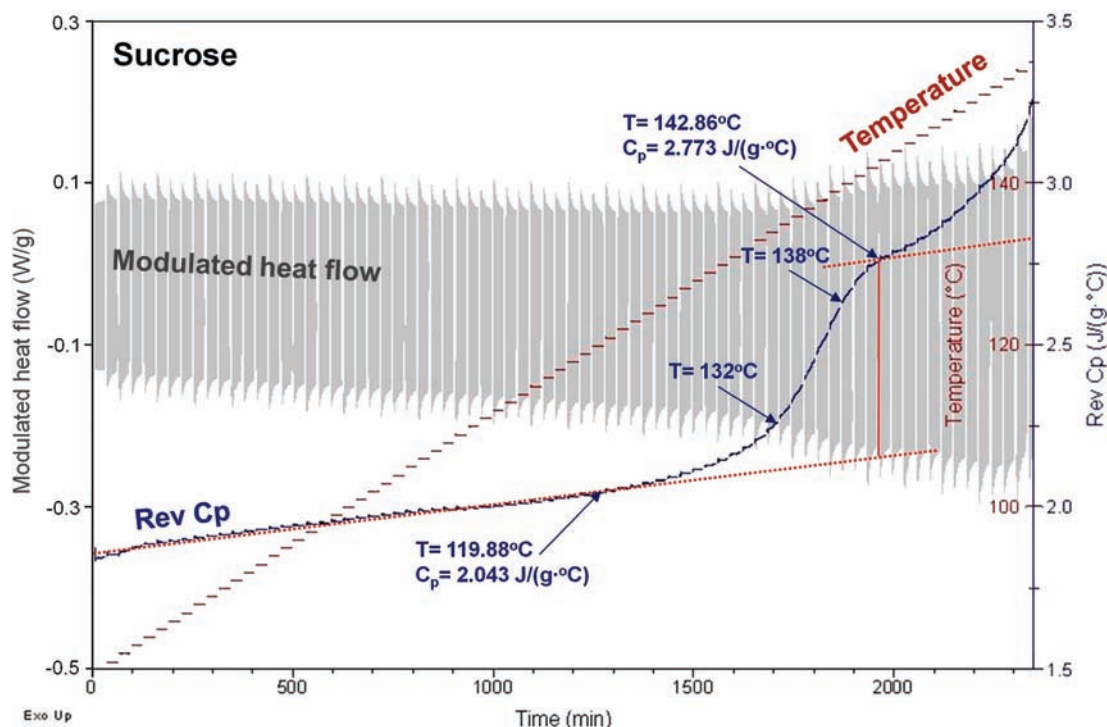
Figure 2. Stepwise quasi-isothermal MDSC thermogram for sucrose (a modulation amplitude of ± 1.0 °C, a period of 100 s, a stepwise temperature - increment of 1 °C, and an isothermal time of 25 min with a data off period of 5 min for initial equilibration) used to determine the three isothermal temperatures (120, 132, and 138 °C) for preparing amorphous sucrose samples using quasi-isothermal MDSC.
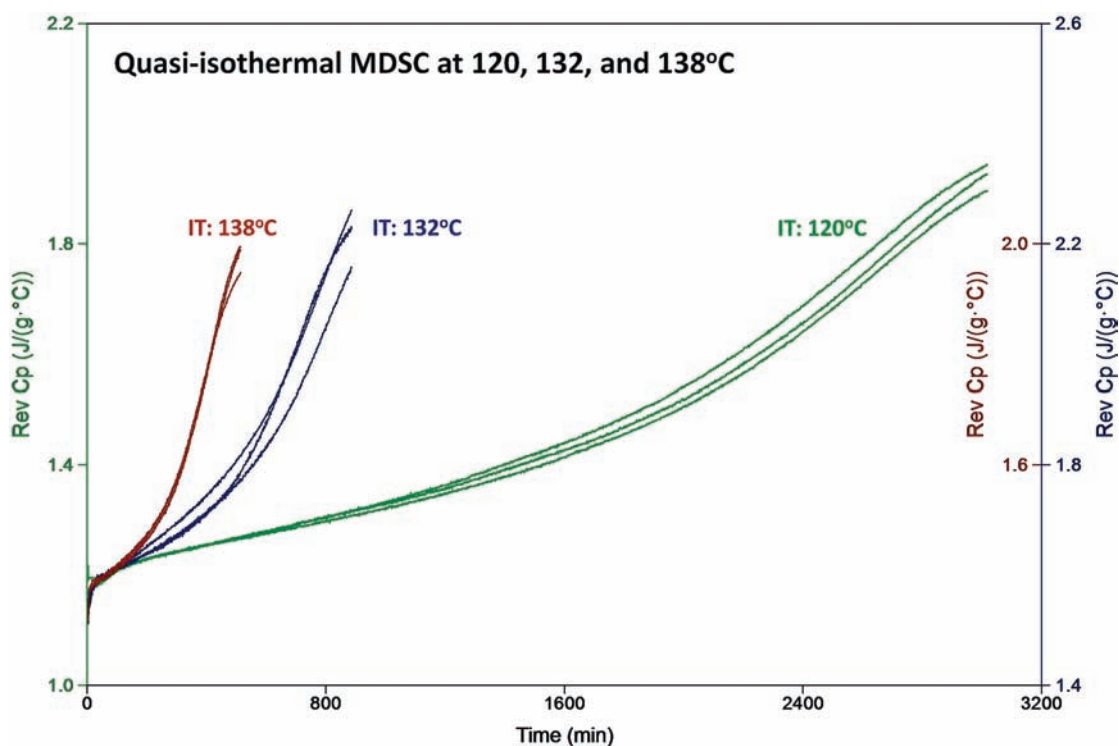

Figure 3. Variations in the Rev C_p change during the loss of crystalline structure in sucrose by holding at isothermal temperatures (IT) of 120 °C for 3014 min, 132 °C for 883 min, and 138 °C for 510 min using quasi-isothermal MDSC.

All amorphous sucrose samples prepared at each isothermal temperature were measured in triplicate. The T_g parameters ($T_{g\ onset}$, $T_{g\ mid}$, $T_{g\ end}$, ΔC_p) for the amorphous sucrose samples were analyzed using UA software as described previously.

Table 1. T_g Parameters ($T_{g\ onset}$, $T_{g\ mid}$, $T_{g\ end}$, and ΔC_p) for Amorphous Sucrose Samples Produced by Employing Three Heating Rates, 1, 10, and 25 °C/min, Using SDSC and by Holding at Three Different Isothermal Temperatures, 120, 132, and 138 °C, Using Quasi-isothermal MDSC, Respectively ($N = 3$ and $n = 3$, where N = Replications and n = Analysis within a Replication)

heating condition for preparing amorphous sucrose samples	$T_{g\ onset}$ (°C)	$T_{g\ mid}$ (°C)	$T_{g\ end}$ (°C)	ΔC_p (J/(g·°C))	$T_{g\ end} - T_{g\ onset}$ (°C)
			T_g parameters[a]		
SDSC Method					
heating at 1 °C/min to 184 °C	25.67 ± 2.08 b4	37.45 ± 0.51 c4	44.84 ± 0.68 c5	0.8684 ± 0.0227 a1	19.17 ± 2.61 a1
heating at 10 °C/min to 196 °C	64.05 ± 1.38 a1	69.83 ± 0.51 a1	75.46 ± 1.72 a1	0.7230 ± 0.0207 b34	11.41 ± 3.01 b34
heating at 25 °C/min to 206 °C	63.83 ± 0.65 a1	68.35 ± 0.43 b1	72.94 ± 0.81 b2	0.7003 ± 0.0223 b4	9.11 ± 1.05 b4
Quasi-isothermal MDSC					
holding at 120 °C for 3014 min	30.92 ± 1.88 b3	39.59 ± 1.57 b3	45.36 ± 1.40 c5	0.7474 ± 0.0164 b3	14.44 ± 1.08 ab2
holding at 132 °C for 883 min	35.26 ± 3.00 a2	44.27 ± 2.86 a2	50.67 ± 2.57 a3	0.7445 ± 0.0088 b3	15.41 ± 1.09 a2
holding at 138 °C for 510 min	34.79 ± 0.59 a2	42.21 ± 0.40 a2	48.38 ± 0.64 b4	0.7844 ± 0.0318 a2	13.59 ± 1.20 b23

[a] Means with the same letter (difference among SDSC method or difference among quasi-isothermal MDSC method) are not significantly different ($p = 0.05$). Means with the same number (difference among both SDSC method and quasi-isothermal MDSC methods) are not significantly different ($p = 0.05$).
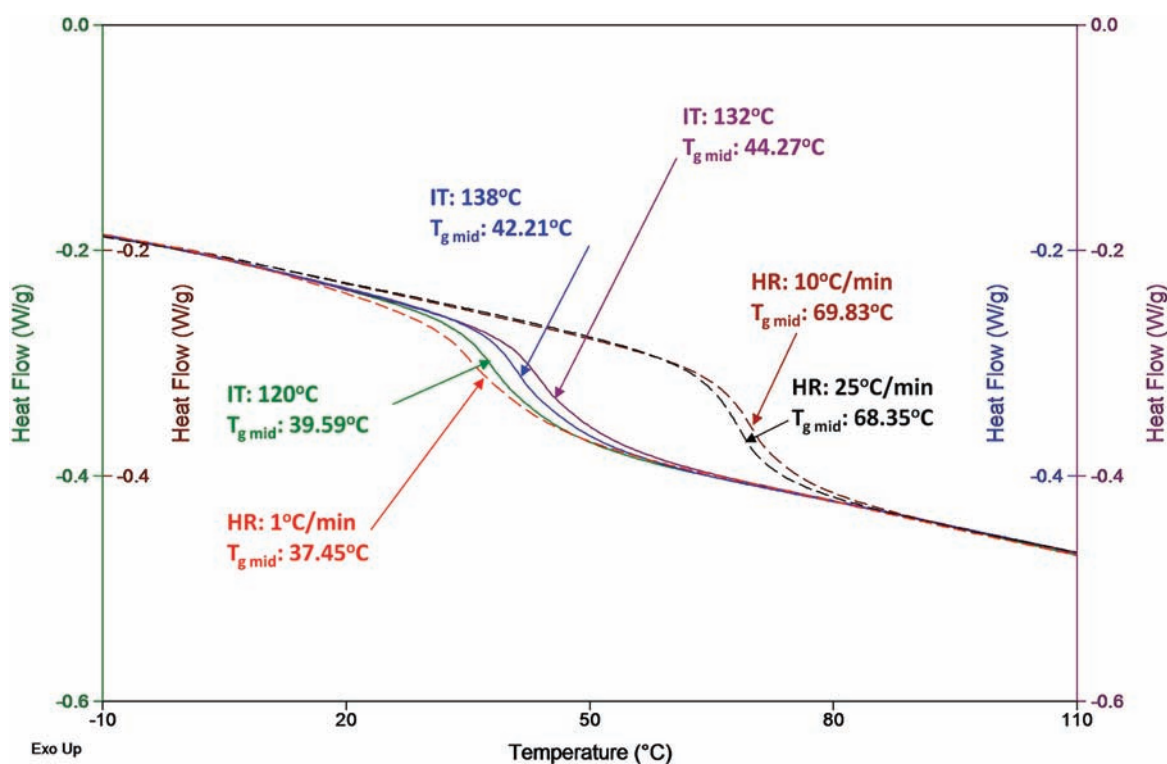

Figure 4. Change in $T_{g\ mid}$ (determined by the inflection method) values for amorphous sucrose samples prepared by employing three heating rates (HR), 1, 10, and 25 °C/min, using SDSC and by holding at three isothermal temperatures (IT), 120, 132, and 138 °C, using quasi-isothermal MDSC.
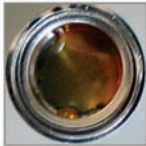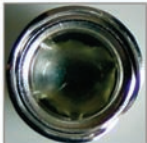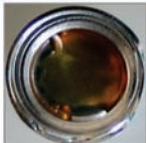
Statistical Analysis. Statistical analyses were carried out using SAS software (SAS 9.2 TS Level, SAS Institute Inc., Cary, NC). The general linear model (GLM) procedure was utilized for the analysis of variance (ANOVA). Tukey's studentized range test was used to determine any significant differences between means at $p = 0.05$.

RESULTS AND DISCUSSION

Effect of Heating Rate on the T_g Parameters for Amorphous Sucrose. The T_g parameters and DSC thermograms for amorphous sucrose samples prepared by employing three heating rates, 1, 10, and 25 °C/min, using SDSC are given in Table 1 and Figure 4, respectively. At 1 °C/min, the amorphous sucrose exhibited the lowest T_g values and the highest ΔC_p. At 10 and 25 °C/min, the amorphous sucrose showed much higher T_g values and lower ΔC_p values, compared to those at 1 °C/min. However, unexpectedly, the T_g parameters for the amorphous sucrose were slightly higher at 10 °C/min than at 25 °C/min; however, their T_g parameters were very close to each other, compared to those at 1 °C/min. It was expected that the slow heating rate would have lower T_g values, because, as discussed in detail below, a slower heating rate is thought to result in more

Table 2. Images of "As Is" and Thermally Treated Sucrose Samples

SDSC sucrose samples			Quasi-isothermal MDSC sucrose samples		
Heating rate (°C/min)	Final heating temperature (°C)	Images	Isothermal temperature (°C)	Holding time (min)	Images
"as is"			"as is"		
1	184		120	3014	
10	196		132	883	
25	206		138	510	

thermal decomposition than a faster heating rate. But, perhaps, the degree of thermal decomposition that occurred at the 10 °C/min heating rate was not different enough compared to the 25 °C/min heating rate to produce a distinguishable difference in the resultant T_g values. The $T_{g \text{ mid}}$ value (69.83 °C) for amorphous sucrose at 10 °C/min obtained in the current study was similar to literature reported $T_{g \text{ mid}}$ values (67.5 °C[3] and 67 °C [24]) for amorphous sucrose prepared and analyzed using similar conditions, except for the use of a higher final heating temperature (200 °C for both studies). In addition, as shown in Table 1, the T_g range increased with decreasing heating rates. According to Vanhal and Blond,[3] as the degree of sucrose thermal decomposition increased, the T_g range (i.e., $T_{g \text{ end}} - T_{g \text{ onset}}$) became broader, indicating an increase in the complexity of the thermal decomposition components.

As shown in Lee et al.,[20,21] the loss of crystalline structure in sucrose is caused by the kinetic process of thermal decomposition. Hence, a slower heating rate allows sucrose to remain for a longer time at each temperature, resulting in the formation of more and different thermal decomposition components. In the early stages of sucrose thermal decomposition, small molecular weight decomposition components (e.g., glucose, fructose, 5-HMF, water, and acids) are produced through a variety of reaction pathways. As heating conditions become more severe, high molecular weight decomposition components are formed through polymerization.[25−36] Consequently, in the present study, a decrease in T_g values and an increase in ΔC_p as heating rate decreases are accounted for by the plasticizing effect of the small molecular weight decomposition components. The plasticizing effect of small molecular weight components, in particular, water, on T_g is a well-known property.[37−41] Both Fang and Angell,[42] studying fructose and galactose, and Okuno et al.,[43]

studying sucrose, reported that the depression of T_g values for these amorphous sugars prepared by melt-quenching may be due to the small molecular weight fragmentation products formed by the decomposition process in the vicinity of their melting temperatures. As shown in Table 1, the ΔC_p at 1 °C/min is higher than the ΔC_p at 10 and 25 °C/min. The higher ΔC_p at 1 °C/min indicates an increase in molecular mobility, which, we hypothesize, is due to the formation of a larger amount of small molecular weight decomposition components. The presence of smaller molecules increases the space between the original molecules by blocking their attractive forces, giving rise to greater free volume and molecular mobility.[18,19]

In addition, it is important to note the use of different final heating temperatures for each heating rate. Different final heating temperatures at each heating rate were used to avoid the effect of the additional heat received to reach a common final heating temperature on the T_g parameters for amorphous sucrose (Figure 1). However, the amorphous sucrose prepared by heating at 1 °C/min to 184 °C exhibited the lowest T_g values and the highest ΔC_p. Thus, it seems that more extensive thermal decomposition occurs at slower heating rates, at which the sucrose sample remained for a longer time at each temperature, compared to faster heating rates to higher final heating temperatures.

Effect of Isothermal Temperature on the T_g Parameters for Amorphous Sucrose. The T_g parameters and DSC thermograms for amorphous sucrose prepared by holding at three isothermal temperatures, 120, 132, and 138 °C, using quasi-isothermal MDSC are given in Table 1 and Figure 4, respectively. As can be seen in Table 1, the T_g values for amorphous sucrose were lower at 120 °C than at 132 and 138 °C. However, the T_g values were slightly higher at 132 °C than at 138 °C, although only statistically different for $T_{g \text{ end}}$. In general, it was expected

that lower temperature—longer time heat treatments would lead to lower T_g values (that is, until extensive polymerization would occur and then the T_g values are postulated to begin to increase), because the thermal decomposition process could take place over a longer period of time. This was the case for the 120 °C isothermal temperature, but not for 132 and 138 °C. However, because both the SDSC and quasi-isothermal MDSC methods used in the present study were the minimum heating conditions required for the complete removal of sucrose crystalline structure, it seems that both methods in terms of the degree of thermal decomposition were not severe enough to cause extensive polymerization (i.e., production of a significant amount of higher molecular weight compounds), where an increase in T_g would be expected, as postulated by both Vanhal and Blond[3] and Jiang and others.[22] In regard to ΔC_p, the amorphous sucrose at 138 °C had a slightly higher value than those at 120 and 132 °C, but the ΔC_p at 132 °C was not statistically different from the value at 120 °C.

Of importance to note is the variability in the data both within each isothermal temperature and between isothermal temperatures. The variation within each isothermal temperature is illustrated by the variation in the triplicate MDSC Rev C_p signals obtained at each isothermal temperature (Figure 3) and the relatively large standard deviations associated with each isothermal temperature (Table 1). The variation between isothermal temperatures is illustrated, as discussed above, by the lack of the expected trend in the T_g values for 132 and 138 °C holding temperatures.

Both sources of variability are attributed to the complex, nonuniform (i.e., nonreproducible) nature of the thermal decomposition reaction. There are a number of factors that can affect both the thermal decomposition reaction pathway and rate, such as aqueous concentration (i.e., water), time, temperature, and presence and concentration of catalysts, natural salts (e.g., chlorides, nitrates), alkaline or acidic substances, reducing sugars (e.g., glucose, fructose), and buffering compounds.[27,28,30,34,44] For example, a number of publications have reported the accelerative effect of water on sucrose hydrolysis.[27,28,30] Kelly and Brown[28] specifically mentioned that the presence of moisture on the surface of sugar crystals seemed to be necessary for thermal decomposition, because the hydrogen ion (H^+) from water is required for sucrose hydrolysis. Thus, because thermal decomposition progresses through a myriad of complex reaction pathways involving a variety of chemical transformations, even a small change in the above factors could lead to different decomposition results and, in turn, increase the variability in the T_g parameters.

Comparison of T_g Parameters Obtained by Heating Rate versus Isothermal Temperature. Overall, compared to the SDSC method, the quasi-isothermal MDSC method resulted in greater sucrose thermal decomposition,[20,21] producing a greater amount of more diverse decomposition components as indicated by the dark brown color of the MDSC samples compared to the SDCS samples (Table 2). Thus, as expected, the quasi-isothermal MDSC amorphous sucrose showed much lower T_g values and higher ΔC_p values than the SDSC amorphous sucrose, except for the amorphous sucrose at a heating rate of 1 °C/min, which took a total of only 159 min but resulted in the lowest T_g values, the highest ΔC_p value, and the broadest glass transition range ($T_{g\ end} - T_{g\ onset}$). Perhaps the relatively slow 1 °C/min heating rate provided a similar initial thermal decomposition scenario as in the MDSC isothermal temperature experiments (low-temperature—long-time conditions), but then

the higher temperatures (due to scanning up to 184 °C) served to accelerate the further stages of the thermal decomposition process. Additional research is needed to fully elucidate the observed dramatic decrease in T_g values for 1 °C/min compared to 10 and 25 °C/min.

It is important to mention that an attempt was made to compare the T_g parameters obtained herein to the T_g parameters for an amorphous sucrose sample prepared by the nonthermal process of freeze-drying and analyzed using a SDSC heating rate of 10 °C/min. It was hypothesized that the freeze-dried sample would exhibit the highest T_g values, because it would have experienced no thermal decomposition, thus no lowering of the T_g values by the formation of small molecular weight components. However, unexpectedly, the freeze-dried sample T_g values ($T_{g\ onset}$ = 53.52 °C, $T_{g\ mid}$ = 60.68 °C, $T_{g\ end}$ = 62.37 °C) were lower than the SDSC samples at heating rates of 10 and 25 °C/min and higher than all of the quasi-isothermal MDSC samples and the SDSC sample at 1 °C/min. The freeze-dried sample ΔC_p value (0.8984 J/g·°C) was slightly higher than the SDSC sample at 1 °C/min, which was the sample with the highest thermal decomposition. This result is ascribed to the relatively high moisture content of the freeze-dried sample. Even after 14 days in a desiccator over P_2O_5, the moisture content of the freeze-dried sample was 2.3% (wb), which lowered the T_g values and raised the ΔC_p value compared to the SDSC samples at heating rates of 10 and 25 °C/min. Further investigation is needed to obtain T_g parameters for an amorphous sucrose sample with a much lower moisture content (as close to zero as possible), which might be produced by increasing the freeze-drying time or by producing a freeze-dried sample directly in a DSC cell.

Conclusions. This research was performed to investigate the effect of heating conditions on the T_g parameters of amorphous sucrose prepared by melt-quenching. As mentioned in the Introduction, the amorphous sucrose produced by melt-quenching, under all heating conditions (even at temperatures below the literature-reported melting temperature for sucrose), is chemically different from the starting crystalline sucrose, due to the formation of thermal decomposition components produced during heating. The amorphous sample is not just amorphous sucrose, but rather amorphous sucrose plus the resultant decomposition components. However, for convenience and consistency with the literature, the amorphous product produced by melt-quenching sucrose was referred to as "amorphous sucrose" throughout this paper. Overall, it was found that the quasi-isothermal MDSC method (lower temperatures for longer times) exhibited lower T_g values, larger ΔC_p values, and broader glass transition ranges (i.e., $T_{g\ end} - T_{g\ onset}$) than the SDSC method (higher temperatures for shorter times), except at a heating rate of 1 °C/min, which exhibited the lowest T_g values, the highest ΔC_p, and the broadest glass transition range for all heating conditions examined herein. Because the kinetic process of thermal decomposition is responsible for the loss of crystalline structure in sucrose, the observed decrease in T_g values was ascribed to the plasticizing effect of small molecular weight decomposition components. It was hypothesized that, perhaps, the relatively slow 1 °C/min heating rate provided a similar initial thermal decomposition scenario as in the MDSC isothermal temperature experiments (low temperature—long time conditions), but then the higher temperatures (due to scanning up to 184 °C) served to accelerate the further stages of the thermal decomposition process. Additional research is needed to fully

elucidate the observed dramatic decrease in T_g values for a heating rate of 1 °C/min compared to heating rates of 10 and 25 °C/min. In addition, this research showed that the heating conditions employed to produce the amorphous sucrose are an additional important contributing factor to explain the wide variation of T_g values observed in the literature. Because glucose and fructose have also been shown to lose their crystalline structure via thermal decomposition,[20,21] the effect of heating conditions on their T_g parameters is hypothesized to be similar to that on sucrose studied herein. This research is useful for better understanding the quality and stability issues associated with heat processed sugar-containing food and pharmaceutical products.

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