

# Differential Scanning Calorimetry Study of Phase Transitions Affecting the Quality of Dehydrated Materials<sup>†</sup>

Yrjö Roos and Marcus Karel\*

Department of Food Science, Rutgers—The State University of New Jersey, P.O. Box 231, New Brunswick, New Jersey 08903

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Differential scanning calorimetry was used to determine the phase transitions of dried and rehumidified amorphous lactose, sucrose, and a mixture of sucrose and Amioca. Glass-transition, crystallization, and melting temperatures decreased with increasing moisture content. The time to crystallization of amorphous lactose held isothermally above the glass-transition temperature decreased as the temperature was increased. Isothermal crystallization time of lactose was a function of the temperature difference between the holding temperature and the glass-transition temperature independently of moisture content. Amorphous biological materials are metastable showing temperature, moisture content, and time-dependent phase transitions that affect their drying behavior, stickiness, storage stability, and quality.

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## Introduction

The water content of biological materials can be reduced by concentration, freezing, and drying. Both freezing and drying reduce the water activity to levels at which the growth of microorganisms is inhibited. Therefore, water is not available to microorganisms but may have an effect on physical and chemical changes in the material. Usually the separation of water leads to the formation of a highly viscous, metastable, amorphous state, which can be either a "glass" or a "rubber" depending on the final temperature and moisture content. The physical state and its effect on various changes have been discussed by White and Cakebread (1), Karel (2), Levine and Slade (3, 4), and Simatos and Karel (5).

During freezing, evaporation, or sublimation processes, the material is in a continuously changing state, which is determined by temperature, moisture content, and time. In various studies, the physical changes, e.g., collapse and stickiness during drying, have been proved to affect the quality of the final product (6-10). Carbohydrate materials, especially mono- and disaccharides and products in which these are the main components like fruit juices, are difficult to dry because of their sensitivity to temperature and moisture (11, 12).

At low moisture contents, both carbohydrates and proteins may exist in an amorphous state. This state is extremely sensitive to water, which plasticizes the amorphous structure (1, 3). The temperature at which the structure changes from the glass to the more liquidlike rubber is a function of molecular weight and the amount of plasticizer (3). This change, known as glass transition ( $T_g$ ), is specific to each amorphous material and composition. At the glass-transition temperature, the free volume and the mobility of the molecules of the amorphous matrix increase at a rapid rate (13). This causes an endothermic change in the apparent specific heat that can be detected by using differential scanning calorimetry. Also, changes in the physical properties such as vis-

cosity occur at the glass-transition temperature. The temperature dependence of mechanical relaxation processes in amorphous polymers above the glass-transition temperature follows the Williams-Landel-Ferry (WLF) equation (13).

During dehydration, physical changes that may have a profound effect on technological properties and the quality of the materials occur. These changes are related to the molecular mobility and glass-transition temperature during and after dehydration. The glass-transition temperature is affected by various factors of which the composition of the material, molecular weight, and plasticizers are most important. These effects have been extensively discussed in the literature (3-5, 14, 15). Plasticizers decrease the glass-transition temperature, and thus, e.g., water in dried sugars affects also diffusional properties.

The purpose of this study was to determine glass-transition, crystallization, and melting temperatures of amorphous lactose, sucrose, and a gelatinized mixture of sucrose (80%) and Amioca (20%) as a function of moisture content and to determine the temperature dependence of the crystallization time with use of differential scanning calorimetry. These transitions are of importance to drying behavior, water sorption, and storage stability. It will be shown that glass-transition, crystallization, and melting temperatures of the amorphous materials decrease with increasing water content and are affected by the composition of the material. Crystallization of amorphous sugars is a temperature-dependent phenomenon having a relaxation time dependent on the mobility of the crystallizable molecules above  $T_g$ . The crystallization of amorphous sugars occur isothermally from the rubbery state above  $T_g$ , being faster as the holding temperature is increased. Thermal transitions give information of temperature, moisture content, and time-dependent changes in the amorphous materials during drying and storage.

## Materials and Methods

**Amorphous Food Models.** The model food materi-

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**Table I. Glass-Transition Temperatures ( $T_g \pm$  Standard Deviation) for Amorphous  $\alpha$ -Lactose, Sucrose, and a Gelatinized Mixture of Sucrose (80%) and Amioca (20%) Equilibrated to Varying Moisture Contents over Saturated Salt Solutions**

salt	$a_w^b$	material					
		$\alpha$ -lactose		sucrose		sucrose/Amioca	
		H <sub>2</sub> O g/100 g	$T_g$ , °C	H <sub>2</sub> O g/100 g	$T_g$ , °C	H <sub>2</sub> O g/100 g	$T_g$ , °C
P <sub>2</sub> O <sub>5</sub>	0.00	0.0	101.2 $\pm$ 0.9	0.0	56.6 $\pm$ 3.4	0.0	58.4 $\pm$ 4.3
LiCl	0.11	1.2	65.0 $\pm$ 1.6	1.4	37.4 $\pm$ 8.0	0.5	32.6 $\pm$ 3.6
CH <sub>3</sub> COOK	0.23	3.4	43.7 $\pm$ 2.6	3.8	27.9 $\pm$ 2.4	1.1	20.4 $\pm$ 1.4
MgCl <sub>2</sub>	0.33	5.9	29.1 $\pm$ 6.4	4.7	12.6 $\pm$ 0.9 <sup>a</sup>	4.4	10.5 $\pm$ 1.0
K <sub>2</sub> CO <sub>3</sub>	0.44	8.0	17.5 $\pm$ 1.1 <sup>a</sup>		<i>a</i>	6.5	-5.1 $\pm$ 1.5

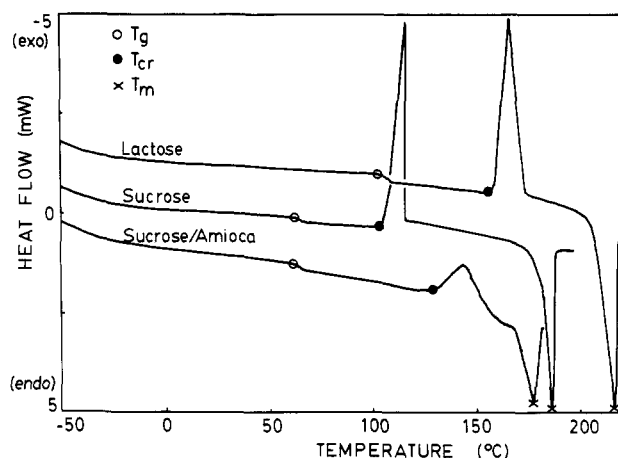
<sup>a</sup> Moisture content allows crystallization at room temperature. <sup>b</sup> Water activity at 25 °C.

sucrose (Sigma Chemical Co.; anhydrous, grade II), and a mixture of sucrose (80%) and Amioca (20%) (a high amylopectin starch (1.8% amylose); National Starch and Chemical Corp.). The materials were dissolved into distilled water as a 10% solution, and the mixture containing sucrose and Amioca was gelatinized. Weighing bottles containing 10 g of respective solutions were subsequently frozen at -20 °C overnight, tempered over dry ice for 3 h, and freeze dried on shelves for 24 h at a pressure below 0.1 mbar with a laboratory freeze drier (Virtis, Benchtop 3 1). After the samples were freeze dried, the vacuum was broken with dry nitrogen, and the weighing bottles were transferred into a vacuum desiccator and dried over P<sub>2</sub>O<sub>5</sub> (Fisher; Certified ACS) for at least 1 week.

**Differential Scanning Calorimetry.** Differential scanning calorimetry (DSC) was used to determine the glass transition, crystallization, and melting of the amorphous model foods and to determine the isothermal crystallization time of amorphous lactose at varying moisture contents above respective glass-transition temperatures. The DSC used was a Perkin Elmer Model DSC-2 equipped with Intracooler II and Perkin-Elmer Model 3600 data station. Dynamic measurements were made using the Perkin-Elmer TADS standard software and isothermal measurements using the isothermal software. Perkin-Elmer hermetically sealable 20- $\mu$ L aluminum sample pans were used in all measurements with an empty aluminum pan as the reference sample. The DSC was calibrated for temperature and heat flow with distilled water (distilled several times, mp = 0.0 °C,  $\Delta H_m$  = 333 J/g), gallium (mp = 29.8 °C, Aldrich Chemical Co.), and indium (mp = 156.6 °C,  $\Delta H_m$  = 28.45 J/g; Perkin-Elmer standard). The drybox of the DSC was dried with desiccant and a flush of dry nitrogen. The sample head was purged with a flow of dry nitrogen (20 mL/min) to avoid condensation of moisture.

**Sample Preparation for Differential Scanning Calorimetry.** The amorphous materials dried over P<sub>2</sub>O<sub>5</sub> were extremely hygroscopic, and samples were placed in the DSC pans (2-3 mg) in the dry box and hermetically sealed before weighing. Samples of varying water contents were prepared by weighing 2-3 mg of the dried material into open DSC pans. Samples in the open pans were equilibrated over saturated salt solutions in vacuum desiccators for 24 h. The salts used were LiCl, CH<sub>3</sub>COOK, MgCl<sub>2</sub>, and K<sub>2</sub>CO<sub>3</sub> (Fisher; Certified ACS) giving the following water activities respectively: 0.11, 0.23, 0.33, and 0.44 (Table I). After equilibration, the pans were hermetically sealed and weighed. The water content of the samples was obtained from the increase in weight (16).

**Dynamic Measurements.** The samples were scanned at a rate of 5 °C/min from -50 °C until melting was completed. The thermograms obtained were typical of amor-



**Figure 1.** Dynamic DSC curves for dried amorphous lactose, sucrose, and a gelatinized mixture of sucrose and Amioca. The thermograms show glass transition, crystallization, and melting. Scanning rate was 5 °C/min.

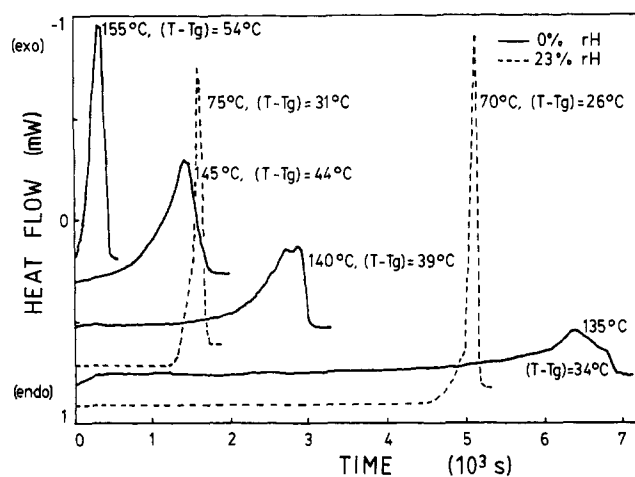
mined as the onset temperature of an endothermic shift in the apparent specific heat),  $T_{cr}$  (determined as the onset temperature of an exothermic peak), and  $T_m$  (determined as the peak temperature of the broad melting endotherm). At least four replicates were used, and the results were calculated as the mean value  $\pm$  the standard deviation.

**Isothermal Measurements.** The isothermal crystallization time ( $\theta_{cr}$ ) of amorphous lactose at varying temperatures and moisture contents was determined to obtain the temperature dependence of the crystallization time and its dependence on the  $T_g$ . Samples of varying moisture contents were heated from ambient temperature to a predetermined final temperature at 40 °C/min, and isothermal data was collected at 5 °C intervals below  $T_{cr}$  until a crystallization exotherm was completed (Figure 2).  $\theta_{cr}$  was determined as the time at the peak of the exotherm. At least four replicates were used at each temperature and moisture content, and the results were calculated as the mean value for each experimental point.

**Temperature Dependence of Crystallization Time.**  $\theta_{cr}$  of amorphous lactose at different temperatures was used to determine the temperature dependence of the crystallization time at each relative humidity. The dynamic measurements showed that crystallization occurs at a constant value for  $T_{cr} - T_g$ . Therefore, the temperature dependence of  $\theta_{cr}$  was assumed to follow the WLF equation (1), which is proved to establish

$$\log \left( \frac{\theta_{cr}}{\theta_g} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (1)$$

the temperature dependence of mechanical relaxation processes above  $T_g$  of amorphous polymers (13).  $\theta_g$  used to



**Figure 2.** Isothermal DSC curves for amorphous lactose at various temperatures after equilibration at 0% and 23% relative humidity. The thermograms show exothermal crystallization of amorphous lactose having a peak at  $\theta_{cr}$  that is specific to each  $T - T_g$ .

tion (1) for all experimental points of each moisture content, and the average time obtained for crystallization at  $T_g$  was used. Thus,  $\theta_{cr}$  to the WLF-type behavior could be calculated:

$$\log \theta_{cr} = \log \theta_g + \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (2)$$

Both experimental and calculated values of  $\theta_{cr}$  were used to show the temperature dependence of the crystallization time.

## Results

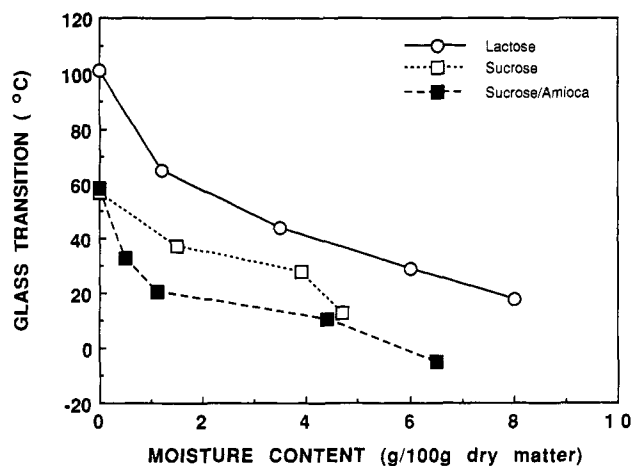
**Glass-Transition Temperature.** The drying of the materials studied led to the formation of an amorphous, glassy state, which could be analyzed and proved by using DSC (Figure 1).  $T_g$  was found to be affected by water plasticizing the materials studied.  $T_g$  was found to be a function of moisture content, decreasing with increasing moisture.  $T_g$  and the respective moisture content of the materials studied are given in Table I. The effect of moisture content on  $T_g$  is shown in Figure 3.

**Crystallization and Melting.** The  $T_{cr}$  and  $T_m$  are given in Table II. They were found to be functions of moisture content decreasing with increasing moisture. The increase in moisture content caused about an equal decrease in  $T_g$  and  $T_{cr}$ .

**Temperature Dependence of Crystallization Time.** The time to crystallization of amorphous lactose at temperatures  $T_{cr} > T > T_g$  was found to be a function of temperature (Figure 2).  $\theta_{cr}$  for amorphous lactose followed the WLF equation at the temperature range studied, and the  $\theta_{cr}$  values were plotted against  $T - T_g$  (Figure 4). However, a linear temperature dependence of the crystallization time on  $T - T_g$  of the data points also gives a good correlation and is consistent with an Arrhenius-type temperature dependence.

## Discussion

The properties of amorphous food materials during and after dehydration depend on a number of factors. Many of these are similar to those well-defined for polymers (3, 15). The important factors related to food materials have been reviewed by Karel and Flink (17) and King et al. (18). The glass-transition temperature is related to



**Figure 3.** Effect of moisture content on the glass-transition temperature of amorphous lactose, sucrose, and a gelatinized mixture of sucrose and Amioca.

dependence of the mobility of amorphous sugars as measured by time to recrystallization under isothermal conditions above  $T_g$  have not been reported.

The glass-transition temperature of amorphous food materials has been reported to have an effect on drying behavior and properties of the dried products (16, 19). It has been shown in various studies that the final quality, flavor retention, and stickiness as well as the final moisture content are functions of the drying temperature, structure of the material, including its molecular weight, and time. Lactose crystallization is an important defect in dried dairy products. This can be predicted by the relationship between the glass-transition temperature, moisture content, and time to crystallization. In this study various carbohydrate materials were dried, and the thermal behavior was determined for samples of different moisture contents. The results showed similar dependence of  $T_g$  on moisture content as Tsourouflis et al. (11) reported for the collapse temperature of freeze-dried materials and Downton et al. (20) for the sticky point in spray drying. These temperatures are decreased by the presence of moisture, which plasticizes the amorphous materials (Figure 3).

$T_g$  decreases with increasing moisture content and theoretically reaches the  $T_g$  of pure water. Most of the work on food-related materials has been done with frozen solutions, and the glass-transition temperatures for the freeze concentrated solutions have been reported (4). However, estimation of drying conditions and storage stability requires knowledge of the effects of very small amounts of moisture on  $T_g$ . The effects of moisture on  $T_g$  of wheat gluten has been reported by Hosney et al. (21) and on dried strawberries by Roos (16). For the carbohydrate materials in this study, an increase in water content from "zero" to 1% decreased  $T_g$  20–40 °C. As the  $T_g$  is decreased below ambient temperature, collapse and, in some cases, crystallization of amorphous sugars occur during storage. In sorption isotherms of amorphous sugars, this is shown as loss of moisture.

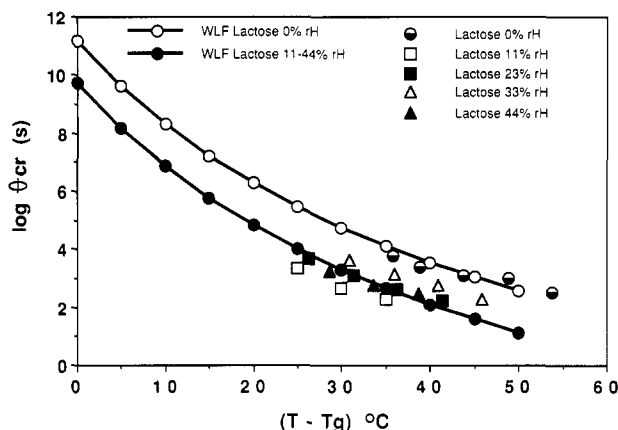
In drying, the evaporation of water keeps the product temperature low. As the water content is reduced, a dried amorphous surface layer is formed. The moisture content of the dried layer depends on the vapor pressure in the drying environment, which also determines the moisture content of the dried product and affects its physical state. In a proper drying process, the dried surface is probably transformed into a very viscous glass directly



**Table II. Crystallization and Melting Temperatures ( $T_{cr}$  and  $T_m \pm$  Standard Deviation) for Amorphous  $\alpha$ -Lactose, Sucrose, and a Gelatinized Mixture of Sucrose (80%) and Amioca (20%) Equilibrated to Varying Moisture Contents over Saturated Salt Solutions**

salt	material					
	$\alpha$ -lactose		sucrose		sucrose/Amioca	
	$T_{cr}$ , °C	$T_m$ , °C	$T_{cr}$ , °C	$T_m$ , °C	$T_{cr}$ , °C	$T_m$ , °C
P <sub>2</sub> O <sub>5</sub>	162.5 ± 1.1	214.1 ± 0.4	104.4 ± 2.3	183.5 ± 1.2	129.5 ± 8.1	178.1 ± 2.2
LiCl	113.3 ± 6.1		83.7 ± 7.6	172.1 ± 4.2	104.7 ± 2.0	167.6 ± 2.0
CH <sub>3</sub> COOK	93.3 ± 1.1		75.1 ± 4.1	165.0 ± 2.1	100.3 ± 2.8	156.7 ± 1.8
MgCl <sub>2</sub>	74.7 ± 5.6		57.4 ± 1.2 <sup>a</sup>		73.4 ± 3.6	144.2 ± 2.8
K <sub>2</sub> CO <sub>3</sub>	64.9 ± 1.5 <sup>a</sup>		a		49.6 ± 3.6	138.4 ± 2.6

<sup>a</sup> Moisture content allows crystallization at room temperature.



**Figure 4.** Time to crystallization of amorphous lactose rehumidified to various moisture contents at varying relative humidities as a function of  $T - T_g$ . The solid lines show the time to crystallization as predicted by the WLF equation.

(20) have related collapse in freeze drying and stickiness in spray drying to viscosity changes. Soesanto and Williams (22) showed that the viscosity of an amorphous mixture of sucrose and fructose above  $T_g$  is characterized by the WLF equation. Thus, if the moisture content and the product temperature are increased above the specific collapse temperature or sticky point, the viscosity of the material is rapidly decreased, and it dries into the rubbery state. This leads to collapse, decreased water removal, decreased drying rate, and increased stickiness, and both product quality and flavor retention are impaired.

To and Flink (12) reported the collapse temperatures for dried lactose and sucrose to be 101.1 and 55.6 °C, respectively. In this study, the  $T_g$  of the dried lactose and sucrose were found to be at about the same temperatures. Samples having a glass-transition temperature below room temperature were both collapsed and sticky. The similarities of glass transition, collapse, and stickiness are obvious, and  $T_g$  as a well-characterized transition of amorphous materials could be used to predict drying, agglomeration, and storage conditions.

At sufficient moisture contents above  $T_g$ , the molecular mobility is rapidly increased, and some materials may crystallize during storage, probably due to decreased viscosity. Crystallization of amorphous sucrose and lactose occurred at room temperature above 0.33 $a_w$  and 0.44 $a_w$ , respectively. Crystallization was not observed for the mixture of sucrose and Amioca but may occur probably at higher moisture contents or slowly during storage. It was also found that the Amioca increased the  $T_{cr}$  of amorphous sucrose about 25 °C and decreased the melting temperature. The crystallization exotherm was broad

The time to crystallization of amorphous lactose seems to be determined by the temperature difference between the holding temperature and glass-transition temperature ( $T - T_g$ ). The crystallization rate is probably determined by the mobility of lactose molecules. Viscosity is known to decrease with increasing temperature according to the WLF equation, and it is likely that the diffusivity of lactose in our system behaves similarly. The results of this study show that a completely dry lactose is more difficult to crystallize than amorphous lactose plasticized by water even when compared at the same  $T - T_g$  value. This observation may be due to the following process: the formation of crystals releases water since the isotherm for amorphous sugars shows moisture contents, at the same activity, that are much higher than those for crystalline materials (23-25). This water plasticizes the remaining amorphous material and facilitates crystallization. In the case of anhydrous lactose, this does not occur.

The crystallization time of amorphous food materials depends on  $T - T_g$ , which makes their sorption behavior time-dependent as shown in Figure 5. This is of importance to the quality of dried food products, which often contain crystallizable and noncrystallizable amorphous solids, as has been already noted for the case of sucrose-containing foods by Karel (26), who constructed a time-dependence diagram based on the data of Makower and Dye (23). They showed that crystallization time of amorphous sucrose at room temperature depends on moisture content. Crystallization time was increased with decreasing moisture content, and at  $a_w = 0.12$ , sucrose remained amorphous at least almost 3 years. The crystallization of amorphous sucrose at  $a_w = 0.24$  and 25 °C was noticed after about 300 days. According to our results, the  $T_g$  of sucrose at  $a_w = 0.24$  is very close to 25 °C, and if we combine this with the data of Makower and Dye (23), we note that crystallization is clearly a function of  $T - T_g$  following the WLF-type temperature dependence. At higher  $a_w$  values above  $T_g$ , amorphous sucrose was reported to become sticky. In this study crystallization of amorphous lactose occurred above  $T_g$ , and it was faster the higher was the isothermal holding temperature. The results also indicated that the temperature dependence of  $\theta_{cr}$  is close to Arrhenius type when studied at temperatures well above  $T_g$ . However,  $\theta_{cr}$  closer to  $T_g$  should be determined, since it appears that the WLF equation predicts  $\theta_{cr}$  better than the Arrhenius relation extrapolated to  $T_g$ .

Glass-transition temperature seems to be one of the most important factors governing the stability of amorphous materials. Because of their high sensitivity to moisture content and temperature, both water sorption properties and the temperature and time-dependent changes in the physical state determine the drying behavior and

