Changes in the Physical State of Sucrose during Dark Chocolate Processing

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Dark chocolate tablets were manufactured using 100% crystalline sucrose, 50% crystalline and 50% amorphous sucrose, and 100% amorphous sucrose. The physical state of sucrose was determined by differential scanning calorimetry (DSC) and X-ray diffraction. DSC scans of dark chocolate samples containing amorphous sucrose were characterized by a glass transition at 63 °C, a sucrose crystallization peak at 105 °C, and a melting endotherm at 188 °C. Independent of the amount of amorphous or crystalline sucrose used for the preparation of dark chocolate, all final chocolate products provided a single melting endotherm at 188 °C and a crystalline X-ray diffraction pattern. These results indicated that sucrose crystallized during production of dark chocolate and that no amorphous sucrose was present in the final chocolate products.

Keywords: *Dark chocolate; amorphous sucrose; sucrose crystallization; differential scanning calorimetry; X-ray diffraction*

INTRODUCTION

Dark chocolate is basically made up of 30−38% cocoa butter with sugar and cocoa particles dispersed through a continuous fat phase. Sugar normally makes up more than 40−50% of the solids dispersed in the fat. The properties of the fat phase as well as the dispersed cocoa, milk, and sugar solids determine the textural and flavor characteristics and thus consumer preferences for these confectionery products (*1*−*4*).

The role of the physical sucrose state (i.e., amorphous vs crystalline) in chocolate has been discussed in the literature (*5*). Functional properties attributed to amorphous sucrose relate to, among others, the flowability of the chocolate mass and the flavor and thermal properties of the chocolate (*6*). It has been reported that chocolate produced with amorphous sugar provides a heat-stable chocolate (*2*).

Considerable skepticism concerning the actual production and existence of amorphous sugar in chocolate processing exists, and is perhaps reinforced by frequent mention of the highly unstable, transitory amorphous state. Amorphous sugar is a metastable form and tends to crystallize under the influence of a number of factors, mainly temperature and moisture. Amorphous sugar may crystallize at temperatures higher than the glass transition temperature (*T*g) but below the melting temperature (*T*m) (*7*). During chocolate processing, amorphous sugar is capable of absorbing water from the environment, other chocolate ingredients, and humid atmosphere, and rapidly recrystallizes (*8*). Hence, it is difficult to measure the presence of the amorphous sucrose state during chocolate manufacture. Differential scanning calorimetry (DSC) (*9*), differential thermal analysis (DTA) (*10*), sorption isotherms (*11*), X-ray diffraction (*12, 13*), and dielectric constant measurements (*14*) have been used to determine the crystalline/amorphous state of sucrose.

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The objectives of this study were to develop a DSC method for determination of amorphous sucrose in dark chocolate and to follow the physical state of sugar during dark chocolate processing.

MATERIAL AND METHODS

Preparation of Amorphous Sucrose. Commercial sucrose (Aarberg AG, Switzerland) was used for the preparation of amorphous sugar. A 10% solution of sucrose was frozen very rapidly by thermal conduction on a steel plate immersed in liquid nitrogen and then freeze-dried for about 48 h. Freeze-dried sucrose was rapidly transferred to hermetically sealed plastic bags under vacuum. The freeze-dried amorphous sucrose was used as an ingredient for dark chocolate preparation. Sucrose amorphism was controlled by DSC and X-ray diffraction.

Preparation of Chocolate Tablets. Dark chocolate tablets were prepared with 100% crystalline sucrose, 50% crystalline and 50% amorphous sucrose, and 100% of amorphous sucrose using a standard formulation (Table 1) and process. The cocoa mass, sugar (crystalline and/or amorphous), cocoa butter (60 °C), soy lecithin, and vanillin were mixed during 10 min, refined (20−25 microns), conched (70 °C), and molded into tablet forms.

Samples were taken during the process after 5 and 10 min of mixing, after refining, after conching, and as final chocolate products (tablets). All samples were rapidly frozen in liquid N_2 and freeze-dried. The freeze-dried samples were stored in a desiccator over P_2O_5 and equilibrated ($a_w = 0$) for at least 2 weeks before DSC and X-ray diffraction analysis.

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry of chocolate samples was performed using a Mettler DSC 820 (Mettler Instrument AG, Volkestwil, Switzerland). Dried chocolate samples (20−30 mg) were weighed directly into 100-mL aluminum crucibles. DSC runs were performed at a heating rate of 10 °C/min within the temperature range of 5 to 210 °C. A high heating rate was used to amplify minor effects, such as the glass transition (*15*). An empty pan was used as reference. Results are the average of duplicate samples.

X-ray Diffraction. Chocolate samples were defatted with light petroleum ether and the solvent was eliminated in a vacuum. Defatted samples were stored in a desiccator over

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Table 1. Composition of Dark Chocolate Samples[a]

ingredients	chocolate 100% CS (%)	chocolate 50% CS + 50% AS (%)	chocolate 100% AS (%)
sucrose: crystalline	49.38	24.69	0
sucrose: amorphous	0	24.69	49.39
cocoa	45.09	45.09	45.09
cocoa butter	5.3	5.3	5.3
vanillin	0.03	0.03	0.03
soya lecithin	0.2	0.2	0.2

[a] CS, crystalline sucrose; AS, amorphous sucrose.

P_2O_5 until analysis. Measurements were carried out with a Philips PW 1820 X-ray diffractometer (Philips, Almelo, The Netherlands) operating at 40 kV, 30 mA with a CuKa radiation ($\lambda = 0.154$). Diffractograms were obtained from 5° 2θ to 50° 2θ with a step size of 0.05° 2θ, counting 2 s on each step. Dried defatted powder samples were pressed into tablets (pressure, 25 t) prior to analysis. Measurements were performed in duplicate. When a sample of amorphous sucrose was extracted with light petroleum ether no changes in physical state of amorphous sucrose and no loss by solubility were observed.

RESULTS AND DISCUSSION

Quantification of Amorphous Sugar. Thermal events during the heating of amorphous sucrose ($a_w = 0$) such as glass transition, crystallization, and melting were reported to occur within the temperature range of 40 °C to 200 °C (*9*, *16*). Crystallized sucrose shows a single melting peak at 188 °C (Figure 1). When amorphous sucrose was heated, it went through its glass transition temperature (*T*g) at 57 °C, crystallized at 105 °C, and started to melt at about 176 °C (onset temperature) to give a melting peak at 183 °C (Figure 1). Similar results were reported by To et al. (*10*) who used the DTA technique to study thermal transition of freeze-dried sucrose. When the sample was cooled to −20 °C and reheated to 200 °C, no exothermic transitions were observed, and the melting enthalpy of the peak at 183 °C corresponded to the melting enthalpy of crystalline sucrose (135 J/g). From this it can be concluded that amorphous sucrose completely crystallized during heating. Therefore, using the exothermic transition at 105 °C, the amount of amorphous sucrose could be quantified in a sample containing an unknown proportion of amorphous and crystalline sucrose:

$$\text{Amorphous sugar (\%)} = \frac{\text{Enthalpy sample (J)} \times 100}{71\ \text{J/g} \times \text{Sample weight (g)}} \quad (1)$$

Where enthalpy sample is enthalpy of the amorphous sucrose peak at 105 °C in the chocolate samples, and 71 J/g corresponds to the enthalpy of the sucrose crystallization peak at 105 °C. This enthalpy value is close to the value (65 J/g) found by Raemy et al (*9*).

X-ray diffraction patterns of freeze-dried sucrose (amorphous) and crystalline sucrose are shown in Figure 2. Crystalline sucrose gave sharp diffraction peaks, whereas freeze-dried amorphous sucrose revealed a broad peak in this region indicating the absence of crystalline sucrose. Several authors have used X-ray diffraction measurements for determining the crystalline-to-amorphous ratio in sucrose. Palmer et al. (*12*) used the height of a defined characteristic sucrose peak to determine sucrose crystallinity, and Chinachoti and Steinberg (*13*) calculated the amount of crystalline

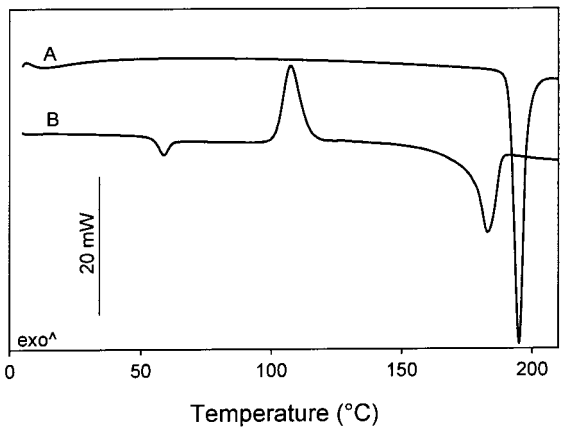

Figure 1. DSC traces of A, crystallized sucrose; and B, amorphous sucrose.

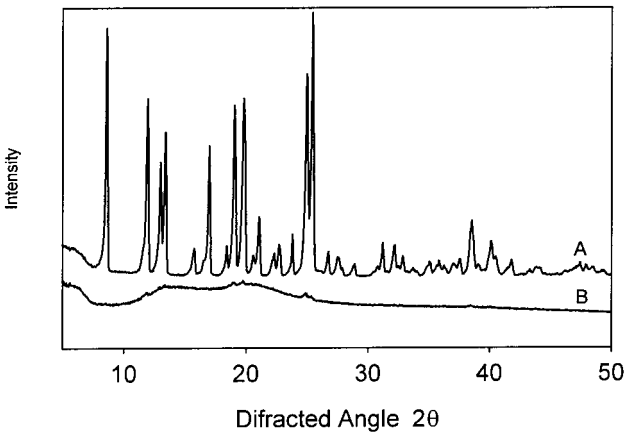

Figure 2. X-ray diffraction pattern of A, crystallized sucrose; and B, amorphous sucrose.

sucrose on the basis of the total area under the diffraction peaks. In this study, data obtained from X-ray diffraction patterns alone were not sufficient to achieve a quantification of amorphous sucrose in the chocolate samples. X-ray diffraction results are affected by the size and perfection of the sugar crystals and the proportion of crystalline/amorphous regions. These parameters were not systematically evaluated in this study. However, X-ray diffraction was used as a qualitative method to determine the presence or absence of crystalline sucrose.

Physical State of Sucrose during Processing of Dark Chocolate. DSC and X-ray diffraction were used to follow the changes in the physical state of sucrose during processing of dark chocolate manufactured with 100% crystalline sucrose, 50% crystalline and 50% amorphous sucrose, and 100% of amorphous sucrose.

DSC scans of dark chocolate samples containing amorphous sucrose were characterized by a glass transition at 63 °C, a sucrose crystallization peak at 105 °C, and a melting endotherm at 188 °C. Chocolate prepared with 100% amorphous sucrose showed a rapid decrease in the enthalpy of the crystallization peak at 105 °C during the mixing process (Figure 3). This decrease in enthalpy can be attributed to the crystallization of amorphous sucrose and corresponds to the presence of 49.0% and 7.4% of amorphous sucrose in the chocolate mass after 5 and 10 min of mixing, respectively. The exothermic crystallization peak was not observed in the samples taken after refining or conching, or in the final

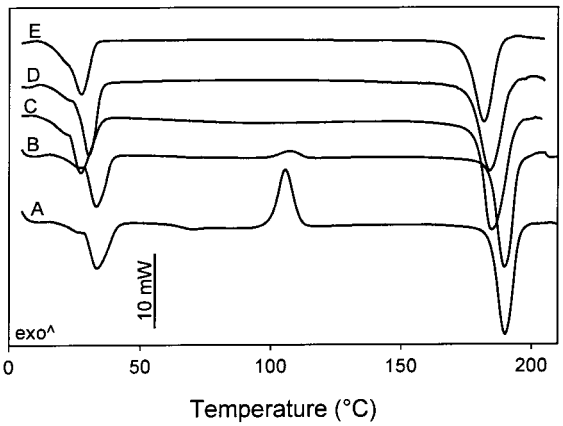

Figure 3. DSC traces of dark chocolate samples made with 100% amorphous sucrose. A, after 5 min of mixing; B, after 10 min of mixing; C, after refining; D, after conching; and E, chocolate tablet.

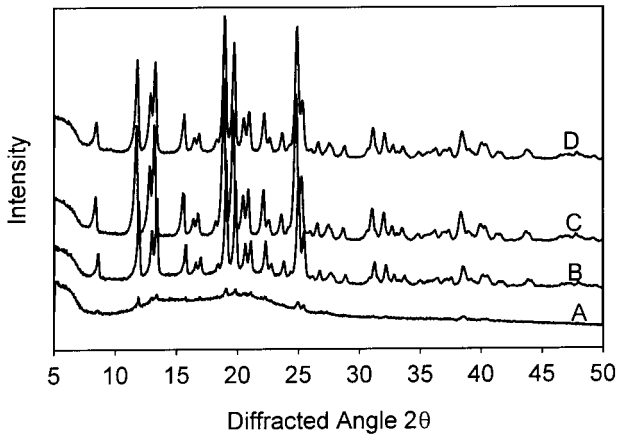

Figure 4. X-ray diffraction pattern of dark chocolate samples made with 100% amorphous sucrose. A, after 5 min of mixing; B, after 10 min of mixing; C, after refining; and D, chocolate tablet.

chocolate tablets. This indicates the absence of amorphous sucrose in these samples.

X-ray diffraction measurements of the chocolate samples made with 100% amorphous sucrose corroborated the findings based on DSC measurements (Figure 4). After 5 min mixing of the chocolate mass, sucrose was still in an amorphous state. After 10 min of mixing, sucrose crystallization appeared to be complete, and sharp X-ray diffraction profiles evidenced the presence of crystalline sucrose after refining and conching, and in the final chocolate product. These events can be explained by the temperature and humidity during processing that favored crystallization of amorphous sucrose (mixing at ~60 °C/~2.0% H_2O; conching at ~70 °C).

When chocolate was manufactured with 50% crystalline and 50% amorphous sucrose, amorphous sucrose crystallized during the early stages of mixing, i.e., after 5 min (Figures 5and 6). This would be consistent with results of Palmer et al. (*12*), who reported that the presence the crystalline sucrose accelerates the crystallization of amorphous sucrose. The sucrose crystals act as nucleation sites favoring the crystallization process. As expected, no amorphous sucrose was detected in samples manufactured with 100% crystalline sucrose (Figures 5 and 6).

From this study, it is concluded that differential scanning calorimetry and X-ray diffraction can be successfully used to determine the physical state of sucrose in dark chocolate. The results indicate that the dark chocolate tablets prepared contained sucrose only in its crystalline state. If amorphous sucrose was used for dark chocolate processing it completely crystallized early in the process, i.e., during mixing, and was not present in the final dark chocolate product.

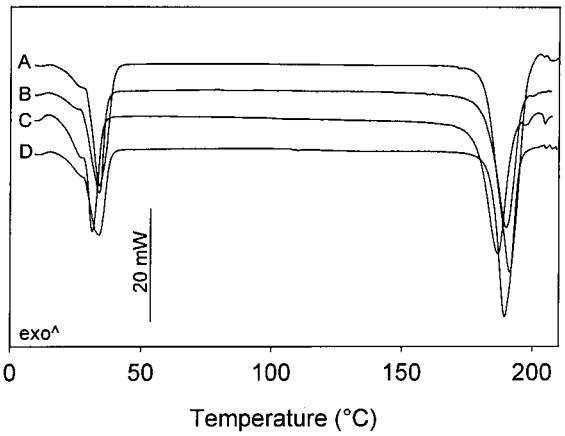

Figure 5. DSC traces of dark chocolate made with 50% amorphous sucrose, A, after 5 min of mixing; B, tablet; and made with 100% crystallized sucrose, C, after 5 min of mixing; D, chocolate tablet.

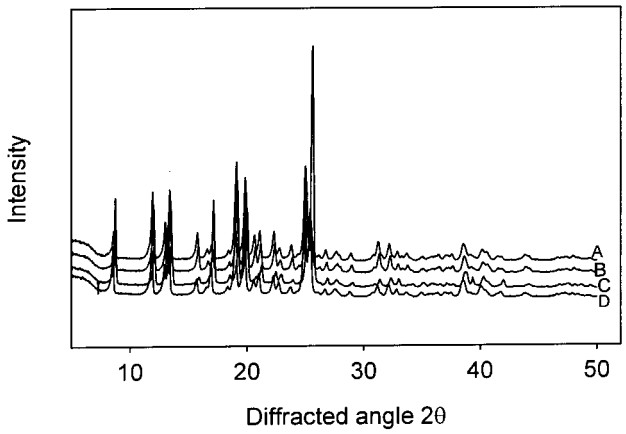

Figure 6. X-ray diffraction pattern of dark chocolate samples made with 50% amorphous sucrose, A, after 5 min of mixing; B, tablet; and made with 100% crystallized sucrose, C, after 5 min of mixing; D, chocolate tablet.

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