Glass Transition, Water Plasticization, and Lactose Crystallization in Skim Milk Powder

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ABSTRACT

Effects of water content, storage time, and glass transition (physical state) on lactose crystallization and the resultant crystal forms in skim milk powder were investigated. Samples of freeze-dried skim milk containing amorphous lactose were stored at various relative humidities at room temperature (24°C). Crystallization was observed from time-dependent loss of sorbed water during storage and from increasing intensities and peak areas of X-ray diffraction patterns. Lactose was found to crystallize largely as an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3. At high relative humidities, traces of other crystal forms were also found. The rate of crystallization, up to a maximum extent, which depended on crystallization conditions, increased as the relative humidity during storage increased. The rate of crystallization could be successfully modeled using the Avrami equation when relative humidity was ≥66.2%. The relationship between the extent of crystallization and relative humidity was parabolic; the maximum crystallization occurred at a relative humidity of 70%. The corresponding water content and temperature difference between storage temperature and glass transition temperature were predicted to be 17% (wt/wt) and 61°C, respectively. Glass transition seems to control lactose crystallization in skim milk powder, and the data obtained can be used in predicting lactose crystallization in milk products containing lactose.

(**Key words**: lactose crystallization, milk powder, glass transition, relative humidity)

Abbreviation key: **RH** = relative humidity, $\mathbf{T_g}$ = glass transition temperature, $\mathbf{T - T_g}$ = temperature difference between storage temperature and T_g, **XRD** = X-ray diffraction.

INTRODUCTION

The occurrence of crystallization of amorphous lactose at a constant temperature depends on relative humidity (**RH**) and water content during storage (19). Crystallization has been suggested to occur as a result of water plasticization and depression of the glass transition temperature ($\mathbf{T_g}$) to below storage temperature (18, 23). If the storage temperature is higher than the T_g, crystallization may occur as molecular mobility and diffusion increase and as viscosity decreases exponentially above T_g (23). The rate of lactose crystallization has been suggested to be controlled by glass transition and the extent of supercooling and, therefore, by the temperature difference between storage temperature and T_g ($\mathbf{T - T_g}$) (19, 23).

The effect of RH on the crystallization of amorphous lactose in milk powders has been reported by numerous researchers (3, 10, 11, 15, 24, 27, 28). In most studies, lactose crystallization was observed from the loss of sorbed water as a function of time (10, 11, 15, 24, 27, 28). Several RH values have been reported that allow lactose crystallization in milk powders. Jouppila and Roos (11) reported a critical RH of 37% and a corresponding critical water content of 7.6 g/100 g of SNF for skim milk powder. These critical values were defined as those decreasing the T_g of the material to below 24°C, allowing time-dependent crystallization of lactose. Those researchers also showed that the rate of loss of sorbed water, indicating lactose crystallization, increased as $T - T_g$ increased. Crystallization of amorphous lactose in milk powders impairs the solubility of the powder and often occurs concurrently with various deteriorative changes, such as caking, discoloration, loss of lysine, and lipid oxidation (13, 25, 27).

Amorphous lactose may crystallize into several crystal forms (e.g., as α-lactose monohydrate, anhydrous β-lactose, stable and unstable anhydrous α-lactose, and an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 and 4:1). These forms have been identified using X-ray diffraction (**XRD**) analysis (4, 5, 6, 22). Amorphous lactose in milk powders

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Received February 18, 1997.
Accepted June 13, 1997.

has been reported to crystallize, for example, as α-lactose monohydrate (5, 20, 27, 29), as an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 (5), and as anhydrous β-lactose (20, 27, 29), depending on the RH and temperature during storage. The crystal forms may differ from one another in melting behavior, solubility, density, crystal morphology, and relative sweetness, as reviewed by Nickerson (17).

The objectives of the present study were to investigate effects of RH, storage time, and glass transition (physical state) on lactose crystallization and on the resultant crystal forms of lactose in skim milk powder, using the XRD technique.

MATERIALS AND METHODS

Sample Preparation

Skim milk (Valio Ltd., Helsinki, Finland; according to the manufacturer, 100 g of skim milk contained 3.4 g of protein, 4.9 g of carbohydrates, and 0 g of fat) was dispensed into 5-ml aliquots in 20-ml glass vials and frozen at –80°C for 24 h. Vials were transferred to a freeze-drier (Lyovac GT2; Amsco Finn-Aqua GmbH, Hürth, Germany), and the frozen material was freeze-dried for at least 72 h (pressure <0.1 mbar). Dried samples were placed in desiccators. The desiccators were evacuated, and the materials were stored over P_2O_5 at 24°C for 1 wk before samples were weighed to obtain the dry weights. Drying in vacuum over P_2O_5 was considered to result in dehydration to zero water content. This result was also confirmed from the high T_g (97°C) of the fully dehydrated material (11).

Crystallization Conditions

Dried samples in the vials were placed and stored in vacuum desiccators over saturated salt solutions at 24°C. The salts used were $Mg(NO_3)_2$, $NaNO_2$, NaCl, and KCl (pro analysis; E. Merck, Darmstadt, Germany); respective RH values were 53.8, 66.2, 76.4, and 85.8% (14). At least four replicate samples were removed from vacuum desiccators at intervals, as shown in Figure 1. Samples were weighed to obtain sorbed water contents after storage. Weighed samples were frozen at –80°C and freeze-dried using the same procedure as when samples were prepared. The dried replicate samples were divided into sets of 2, which were combined and powdered using mortar and pestle. The XRD patterns were measured for at least duplicate samples. Powdered samples were placed in 2-ml plastic Eppendorf tubes (Greiner GmbH, Frickenhausen, Germany), and closed tubes were stored not more than 4 h at room temperature (24°C) and RH (<50%) before XRD measurement.

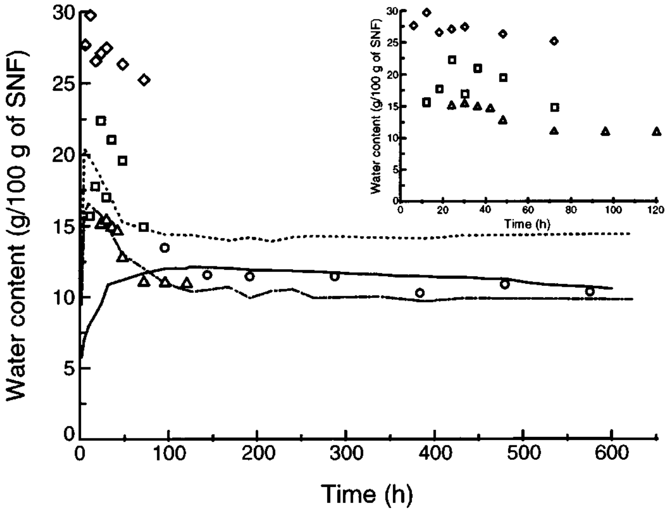

Figure 1. Water sorption of skim milk powder, stored at relative humidities of 53.8 (o), 66.2 (△), 76.4 (□), and 85.8% (◊), as a function of time. Lines indicated show water sorption of skim milk powder stored at relative humidities of 53.8 (—), 66.2 (- · - · -), and 76.4 (· · · ·), as reported by Jouppila and Roos (11). The inset figure shows water contents, at the beginning of storage, of skim milk powder stored at relative humidities of 66.2 (△), 76.4 (□), and 85.8% (◊).

Water Sorption and T_g

Water contents for amorphous skim milk powder that was stored at various RH conditions were estimated using the GAB (Guggenheim-Anderson-de Boer) sorption isotherm model (Equation [1]) (26), with constants m_m of 5.1, C_g of 12.11, and K of 1.08 (10). Prediction of the water sorption was necessary, because lactose crystallization releases sorbed water. The predicted water contents for amorphous skim milk powder were 11.5, 17.3, 28.7, and 69.1 g/100 g of SNF at respective storage RH of 53.8, 66.2, 76.4, and 85.8%.

$$\frac{m}{m_m} = \frac{C_G K a_w}{(1 - Ka_w)[1 + (C_G - 1)Ka_w]}. \qquad [1]$$

The T_g values for amorphous skim milk powder were calculated using the Gordon-Taylor equation, Equation [2] (7) and using T_{g1} of 97°C for amorphous lactose (11); T_{g2} of –135°C for amorphous water (9); a constant (k) of 6.7 (11); and calculated weight fractions of water (w_2) and solids ($w_1 = 1 - w_2$). The estimated T_g values were –4, –28, –56, and –94°C, and corresponding $T - T_g$ values were 28, 52, 80, and 118°C, for amorphous skim milk powder stored at 24°C at 53.8, 66.2, 76.4, and 85.8% RH, respectively. Jouppila and Roos (11) determined experimental T_g values for skim milk powder that was stored at 53.8, 66.2, and 76.4% RH to be –2, –22, and –55°C, respectively, which were quite similar to estimated T_g values. Experimental T_g for skim milk powder that was stored at 85.8% RH could not be determined because of rapid crystallization of lactose.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}. \qquad [2]$$

XRD Measurements

The XRD patterns were recorded for the dehydrated, powdered samples using a Philips X-ray powder diffractometer (PW 1830 generator, PW 1710 diffractometer control, PW 1820 vertical goniometer equipped with graphite reflected beam monochromator, and PC-APD software for Automatic Powder Diffraction Version 3.0; Philips, Eindhoven and Almelo, The Netherlands). The X-ray diffractometer was operated in reflection mode at 40 kV and 50 mA. Samples were slightly pressed on aluminum trays using a 10-mm wide spatula (sample layer, 15 mm × 20 mm × 1.5 mm) and exposed to CuKα radiation (λ = 0.15418 nm) at diffraction angles (2θ) from 10 to 30° (step size 0.02°; time per step 2.5 s). The divergence slit for the primary beam was 1°, and the divergence and receiving slits for the diffracted beam were 1° and 0.2 mm, respectively.

The peak search program of the APD software was used to locate the peaks in XRD patterns by detecting the minima from the second derivative of the diffractogram. Intensity maxima were given as Kα1 net peak height in counts (per step measurement time) at Kα1 position in degrees. The fit profile program of the software was used to fit a profile to a peak and to calculate peak area. Total area was the net area of the Kα1, Kα2, Kα3, and Kα4 components of the fitted profile (in counts), and α1 area was Kα1 net area (in counts).

The lactose crystals that formed in skim milk powder were identified; the location and intensity of the peaks in XRD patterns obtained in the present study were compared with those reported for different crystal forms of lactose (4, 6, 22). The progress of lactose crystallization was observed from increasing intensities of peaks in XRD patterns at diffraction angles of 19, 20, and 22° and from increasing peak areas at a diffraction angle of 22°. Reference XRD patterns showed that α-lactose monohydrate, stable anhydrous α-lactose, and an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 gave a peak at a diffraction angle of 19.1°; intensity of the peak was quite high in both forms (4, 6, 22). Also, both α-lactose monohydrate and an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 gave a peak with a high intensity at diffraction angles of 20.0° (6) and 20.1° (22), respectively; an anhydrous mixture of α- and β-lactose in a molar ratio of 4:1 gave a peak that had very low intensity at a diffraction angle of 20.3° (22). Only an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 gives a peak with a moderate intensity at a diffraction angle of 22.1° (22), although stable anhydrous α-lactose as well as an anhydrous mixture of α- and β-lactose in a molar ratio of 4:1 gave a peak with a very low intensity at diffraction angles of 22.1° (4) and 22.2° (22), respectively.

Kinetics of Lactose Crystallization

The Avrami equation (2), Equation [3], was used in the modeling of lactose crystallization data. The Avrami equation was written in the form of Equation [4],

$$\theta = 1 - e^{-kt^n} \qquad [3]$$

where θ is crystallinity, t is time, k is a rate constant, and n is the Avrami exponent (16),

$$1 - \theta = \frac{I_f - I_t}{I_f - I_0} = e^{-kt^n} \qquad [4]$$

and where I_f = a leveling off value of peak intensity or a leveling off value of peak area occurring at maximum extent of lactose crystallization, I_t = peak intensity or peak area at time t, and I_0 = peak intensity or peak area of 0 counts for a noncrystalline, amorphous sample. Also, half-time ($t_{1/2}$), the time required to achieve 50% of the maximum extent of crystallinity, was calculated using Equation [5].

$$t_{1/2} = \sqrt[n]{-\frac{\ln 0.5}{k}} \qquad [5]$$

The Avrami equation, with I_0 = 0, written in the form of Equation [6], was fitted to the data obtained using a nonlinear regression analysis technique of SAS (21). The SAS system uses the least sum of squares method to fit an equation to the data. The iterative algorithm used was the modified Gauss-

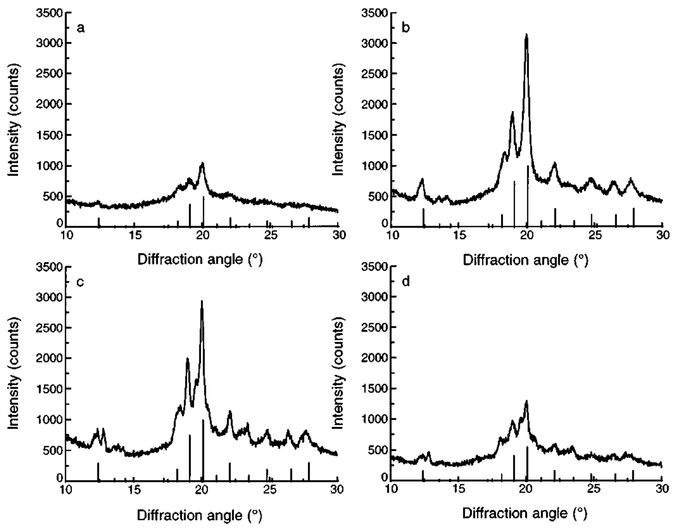

Figure 2. X-Ray diffraction patterns for skim milk powder stored at relative humidities of 53.8 (a), 66.2 (b), 76.4 (c), and 85.8% (d) for 576, 120, 72, and 72 h, respectively. Peaks in the X-ray diffraction pattern for an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 (22), used as a reference, are shown as vertical lines. The height of the line gives intensity of a peak as percentage of the intensity of the highest peak, which is taken as 100%.

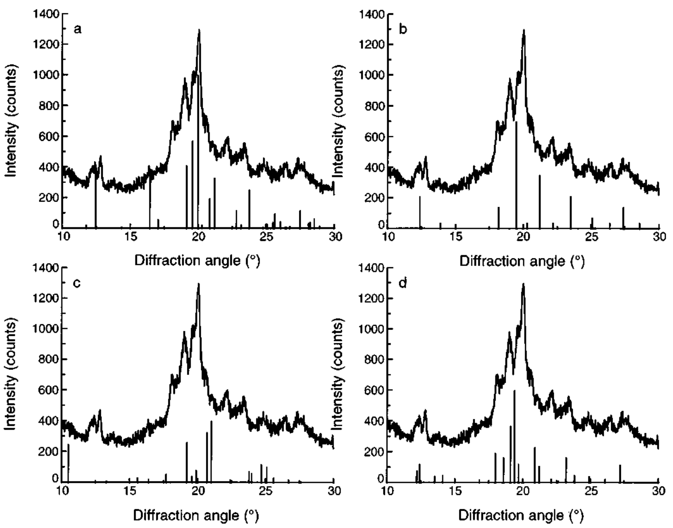

Figure 3. X-Ray diffraction patterns for skim milk powder stored at relative humidity of 85.8% for 72 h (a, b, c, d) compared with reference peaks (vertical lines) of X-ray diffraction patterns of a) α-lactose monohydrate (6), b) an anhydrous mixture of α- and β-lactose in a molar ratio of 4:1 (22), c) anhydrous β-lactose (4), and d) anhydrous stable α-lactose (4). The height of the line gives intensity of a peak as percentage of the intensity of the highest peak, which is taken as 100%.

Newton method, which required specification of the first partial derivates of the model with respect to its parameters (Equations [7] and [8]).

$$I_t = I_f - I_f e^{-kt^n}. \qquad [6]$$

$$\frac{\partial I_t}{\partial k} = I_f e^{-kt^n} t^n. \qquad [7]$$

$$\frac{\partial I_t}{\partial n} = I_f k e^{-kt^n} t^n \ln t. \qquad [8]$$

RESULTS AND DISCUSSION

Lactose crystallization resulted in a loss of sorbed water in skim milk powder during storage at various RH conditions (Figure 1), as has been previously reported (5, 10, 11, 15, 24, 27, 28). The loss rate of sorbed water increased as storage RH and $T - T_g$ increased, as was also reported by Jouppila and Roos (11).

Lactose in skim milk powder was found to crystallize mainly as an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 (Figure 2), as reported by Bushill et al. (5) for skim milk powder that was stored at 55% RH. However, XRD patterns for skim milk powder that was stored at 76.4 and 85.8% RH also suggested the presence of other crystal forms, for example, stable anhydrous α-lactose and an anhydrous mixture of α- and β-lactose in a molar ratio of 4: 1 (Figure 3). Traces of α-lactose monohydrate could also be detected, in skim milk powders that were stored for 48 and 72 h at 85.8% RH, from the unique peak at a diffraction angle of 16.4° (6). In the present study, crystallization of lactose into the form of anhydrous β-lactose could not be observed at any RH from the unique peaks of anhydrous β-lactose at diffraction angles of 10.5 and 21.0° (4). Interestingly, the peak at a diffraction angle of 12.8°, in XRD patterns that were obtained for samples stored at 76.4 and 85.8% RH, was not reported in any XRD reference data used. The peak may be missing from the reference data, or the crystal form may not be known.

Aguilar and Ziegler (1) found that lactose in spray-dried whole milk crystallized as α-lactose monohydrate at 77% RH and 21°C. Also, Vuataz (27) reported that lactose crystallized as α-lactose monohydrate in spray-dried skim milk stored at 57.2% RH and 25°C, but, at 39.1 and 49.3% RH, lactose was reported to crystallize as anhydrous β-lactose. Saito (20) investigated lactose crystallization in spray-dried whole milk at 37°C, and he found that, at 75% RH, α-lactose monohydrate was formed within 1 mo, and, at RH <20%, anhydrous β-lactose was formed within 5 mo. The different crystal forms between previous reports (1, 20, 27) and the present study may be due to the method used for powder production. Temperatures above 50°C are used in the concentration and spray-drying of milk, which may affect the lactose mutarotation occurring in milk; that is, the ratio of the amounts of α- and β-lactose may change as a result of changes in concentration and temperature, as reviewed by Hartel and Shastry (8). Also, concentration of milk prior to drying has been proposed to result in saturation of lactose and formation of nuclei, which may affect the crystallization behavior of lactose in milk powders (11). However, a number of studies have confirmed that lactose crystallization in milk powders occurs at storage RH conditions above 37% at 24°C, which correspond to the critical RH of lactose (3, 11, 15, 24). This result suggests that crystallization, independently of the drying method, is predominantly controlled by glass transition of lactose.

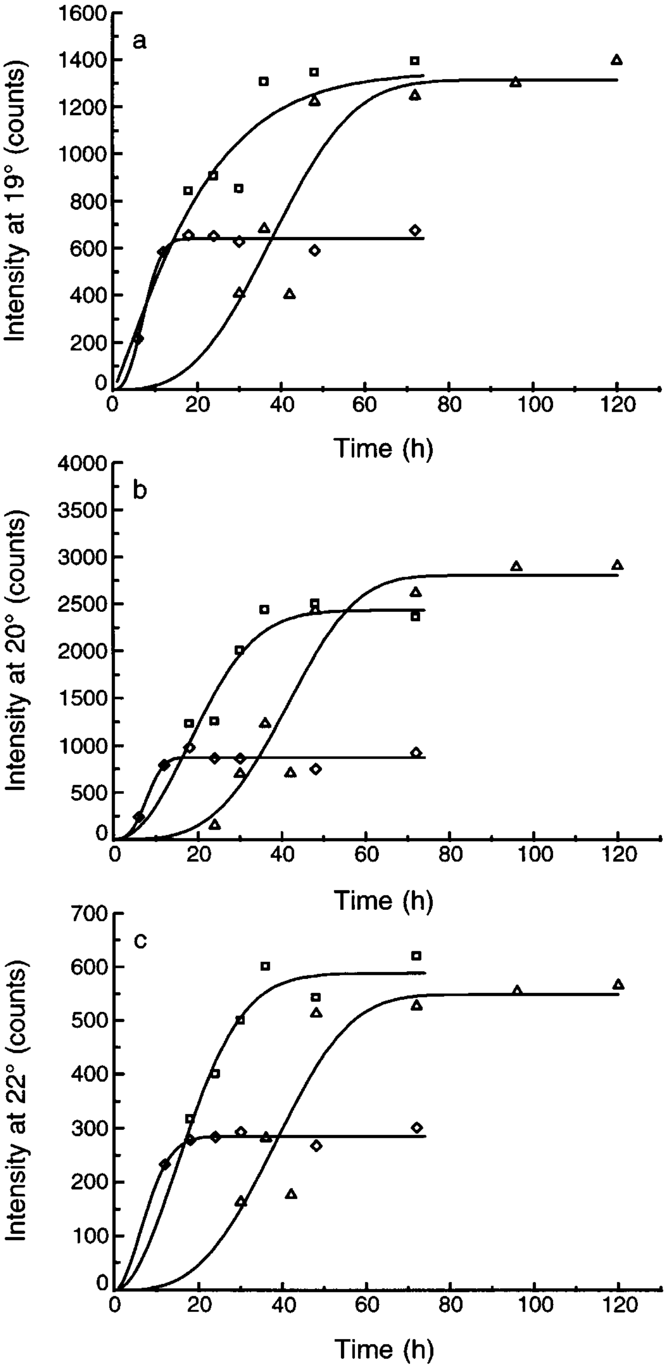

Figure 4. X-Ray diffraction intensities at diffraction angles of 19° (a), 20° (b), and 22° (c), as a function of time, for samples stored at relative humidities of 66.2 (△), 76.4 (□), and 85.8% (◊). The Avrami equation was successfully fitted to the data, as shown by solid lines.

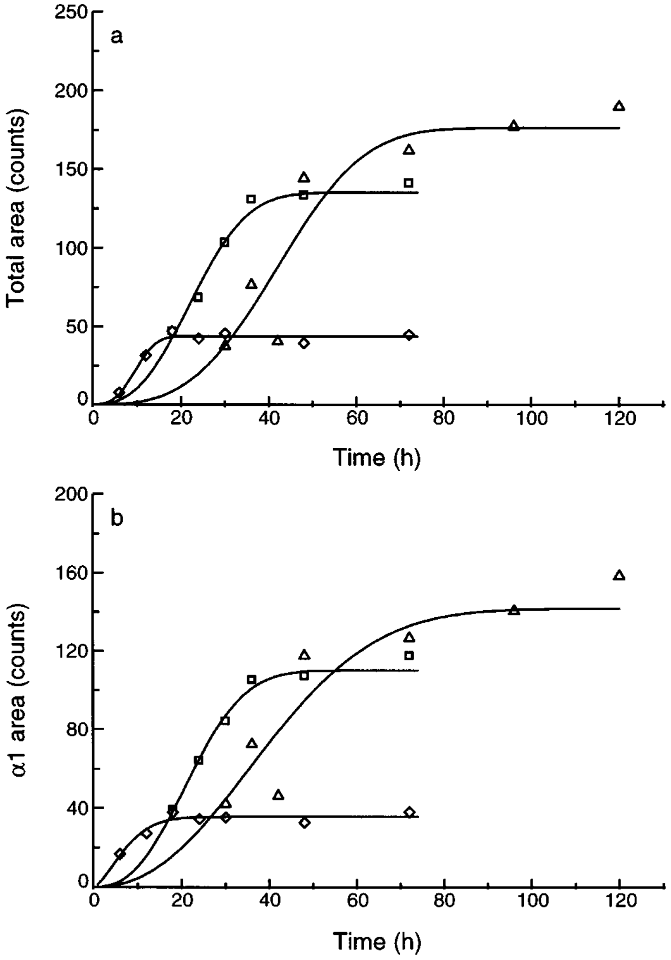

Figure 5. Total (a) and α1 (b) area of the peak at a diffraction angle of 22°, as a function of time, for samples that were stored at relative humidities of 66.2 (△), 76.4 (□), and 85.8% (◊). Total area was the net area of the Kα1, Kα2, Kα3, and Kα4 components of the fitted profile (in counts), and α1 area was Kα1 net area (in counts). The Avrami equation was successfully fitted to the data, as shown by solid lines.

Lactose crystallization occurred in a time-dependent manner (Figures 4 and 5). The intensities of peaks in XRD patterns at diffraction angles of 19, 20, and 22°, and peak areas at a diffraction angle of 22°, leveled off during storage, indicating a maximum extent of crystallization. The extent of leveling off depended on storage RH, and leveling off was reached more rapidly at the storage conditions of higher RH. All of the intensities and peak areas obtained were taken as estimates of total crystallinity in skim milk powder. These estimates were considered to indicate total crystallinity because the amount of anhydrous mixture of α- and β-lactose in a molar ratio of 5:3 was greatest, and the amount of other crystal forms was quite low, even in the skim milk powder that was stored at 85.8% RH. Lactose crystallization data were modeled using the Avrami equation. The Avrami equation fitted well to data obtained at 66.2, 76.4, and 85.8% RH. Lactose crystallization data obtained for samples stored at 53.8% RH could not be modeled using the Avrami equation, probably because of high scatter in the data resulting from the long crystallization time. Fitting the Avrami equation to the data obtained over extended storage time has failed also in previous studies [e.g., (19)]. The leveling off values used in the Avrami equation, the values for constants obtained, and calculated half-times are shown in Table 1. The rate of crystallization, as detected from increasing rate constants and from decreasing half-times, was observed to increase as storage RH, water content, and $T - T_g$ increased, as reported by Roos and Karel (19). However, Slade and Levine (23) suggested that the relationship between the rate of crystallization in amorphous materials and $T - T_g$ was parabolic because, at temperatures close to T_g, nucleation is fast, but crystal growth is slow, and, at temperatures close to T_m, crystal growth is fast, but nucleation occurs slowly. The half-times of lactose crystallization can be used in predictions of storage stability of lactose-containing milk products.

TABLE 1. Leveling off values for the maximum extent of lactose crystallization in skim milk powder that was stored at various relative humidities (RH), values of the constants in the Avrami equation, and half-times of lactose crystallization (time required to achieve 50% of the maximum extent of crystallinity), calculated using the constants, k and n.

Storage RH	Peak intensity (I) or peak area indicating the extent of lactose crystallization[1]	Leveling off value (counts)[2]	Values of the constants in the Avrami equation		Half-time
			k	n	
(%)			(h^{-1})		(h)
53.8	I at 19°	402			
	I at 20°	757			
	I at 22°	209			
	Total area	43			
	α1 area	38			
66.2	I at 19°	1315	1.6×10^{-5}	2.9	40
	I at 20°	2806	1.5×10^{-6}	3.5	42
	I at 22°	549	7.1×10^{-6}	3.2	36
	Total area	177	5.7×10^{-6}	3.1	44
	α1 area	142	1.7×10^{-4}	2.3	37
76.4	I at 19°	1350	2.7×10^{-2}	1.2	15
	I at 20°	2436	1.2×10^{-3}	2.1	21
	I at 22°	588	2.6×10^{-3}	1.9	19
	Total area	135	1.8×10^{-4}	2.7	21
	α1 area	110	2.9×10^{-4}	2.5	22
85.8	I at 19°	640	4.1×10^{-3}	2.6	7
	I at 20°	876	1.7×10^{-3}	2.9	8
	I at 22°	285	1.4×10^{-2}	1.9	8
	Total area	44	8.1×10^{-4}	3.0	9
	α1 area	36	3.7×10^{-2}	1.5	7

[1] Peak intensities at diffraction angles of 19, 20, and 22° are indicated with I and respective diffraction angle. Total and α1 area were determined for the peak at a diffraction angle (2θ) of 22°. Total area is the net area of the Kα1, Kα2, Kα3, and Kα4 components of the fitted profile (in counts), and α1 area is Kα1 net area (in counts).

[2] The number of observations used in calculations with corresponding storage time range is 10 (384 to 576 h), 6 (72 to 120 h), 6 (36 to 72 h), and 10 (18 to 72 h) at relative humidities of 53.8, 66.2, 76.4, and 85.8%, respectively.

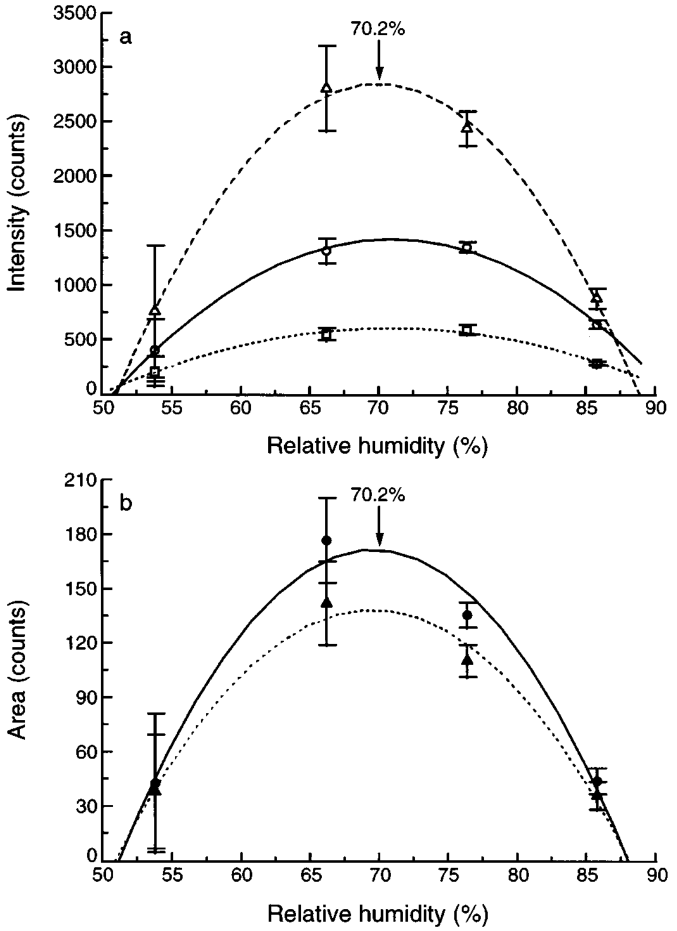

Figure 6. The extent of lactose crystallization in skim milk powder as a function of relative humidity. The extent of lactose crystallization was obtained from the leveled off value for intensity at diffraction angles of 19° (○), 20° (△), and 22° (□) (a) and from the leveled off value for total (●) and $\alpha 1$ (▲) area of the peak at a diffraction angle of 22° (b). The relationship between the extent of crystallization and relative humidity followed a second-order polynomial with average R^2 of 0.987. The maximum extent of lactose crystallization, estimated using the second-order polynomial, occurred at a relative humidity of 70.2%.

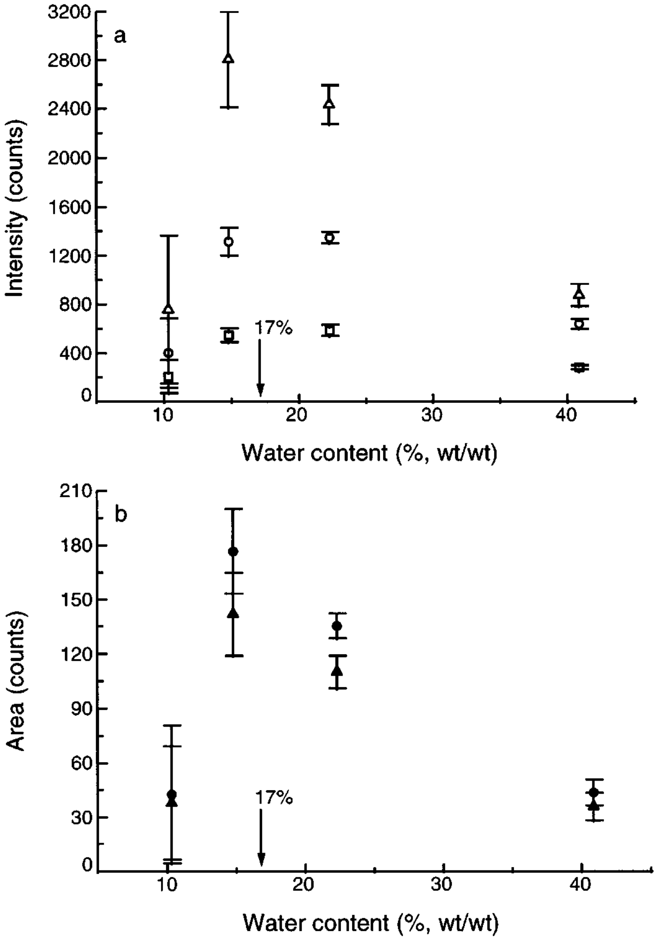

Figure 7. The extent of lactose crystallization as a function of water content in skim milk powder. The extent of lactose crystallization was obtained from the leveled off value for intensity at diffraction angles of 19° (○), 20° (△), and 22° (□) (a) and from the leveled off value for total (●) and $\alpha 1$ (▲) area of the peak at a diffraction angle of 22° (b). The maximum extent of lactose crystallization is predicted to occur at a water content of 17% (wt/wt), which corresponds to a relative humidity of 70.2%, according to the GAB (Guggenheim-Anderson-de Boer) sorption isotherm model.

The leveling off values of peak intensities and areas, indicating the extent of lactose crystallization, were observed to have a parabolic relationship with storage RH (Figure 6), which is similar to data reported for the extent of crystallization in starch (12). The maximum extent of lactose crystallization was estimated to occur at 70% RH, which was the mean value calculated from the five different parabolas shown in Figure 6. The corresponding water content was predicted, using the GAB (Guggenheim-Anderson-de Boer) sorption isotherm, to be 17% (wt/wt), or 20.5 g/100 g of SNF. The relationship between the extent of lactose crystallization and water content was not parabolic (Figure 7), confirming that the maximum extent of crystallization occurs at a water content of 17% (wt/wt). The relationship between the extent of lactose crystallization and $T - T_g$ differed also from a symmetrical parabola, suggesting that the maximum extent of lactose crystallization is obtained at the $T - T_g$ of 61°C (Figure 8), which was predicted using the Gordon-Taylor equation, corresponding to a water content of 17% (wt/wt).

The low extent of lactose crystallization at conditions of low RH and $T - T_g$ was probably due to lower molecular mobility and diffusion, as was also found for crystallization in amorphous starch (12). The crystals that formed during storage may inhibit further crystallization because all lactose molecules may

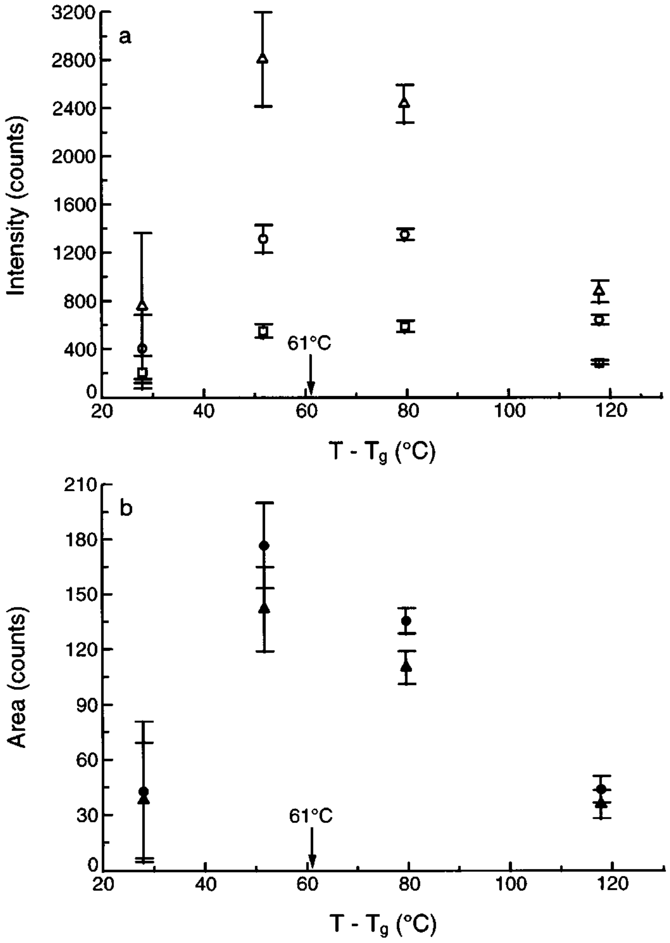

Figure 8. The extent of lactose crystallization as a function of temperature difference between storage temperature and glass transition temperature (T – T_g). The extent of lactose crystallization was obtained from the leveled off value for intensity at diffraction angles of 19° (○), 20° (△), and 22° (□) (a) and from the leveled off value for total (●) and α1 (▲) area of the peak at a diffraction angle of 22° (b). The maximum extent of lactose crystallization is predicted to occur at the T – T_g of 61°C, which corresponds to a relative humidity of 70.2% and a water content of 17% (wt/wt).

not be able to orient themselves into the crystal lattice. At high RH conditions, the extent of lactose crystallization decreased, probably because of increased solubilization of lactose in sorbed water.

CONCLUSIONS

Amorphous lactose crystallized in freeze-dried skim milk, mainly as an anhydrous mixture of α- and β-lactose in a molar ratio of 5:3. At high RH conditions, traces of other crystal forms were also present. The rate of lactose crystallization increased as storage RH, water content, and T – T_g increased. The extent of lactose crystallization was dependent on storage RH, showing a parabolic relationship with a maximum at 70% RH. The predicted water content and T – T_g at 70% RH were 17% (wt/wt) and 61°C, respectively. Low molecular mobility and diffusion at low RH and solubilization of lactose at high RH were proposed to allow crystallization but to result in a lower extent of lactose crystallization. The data obtained in the present study show that crystallization behavior in milk powders is predominantly determined by glass transition of amorphous lactose. The results can be used in modeling and prediction of lactose crystallization phenomena and in evaluation of the probability for crystallization of amorphous lactose in dehydrated milk products and in materials containing lactose during processing (e.g., agglomeration) and storage.

ACKNOWLEDGMENTS

This study has been carried out with financial support from the Commission of the European Communities, Agriculture and Fisheries (FAIR) specific RTD programme, CT96-1085, Enhancement of Quality of Food and Related Systems by Control of Molecular Mobility. The study does not necessarily reflect the views of the Commission and in no way anticipates future policy in this area. Also, the Academy of Finland has financially supported this study. The authors are grateful for the comments and suggestions given by Jorge Chirife, Marcus Karel, and Harry Levine during preparation of the manuscript.

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