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## Fast crystallization of lactose and milk powder in fluidized bed dryer/crystallizer

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**Abstract** The rationale of this study has been to produce stabilized dairy powders for longer-term ambient storage by partial crystallization of the sticky amorphous lactose component in vibrated fluidized beds. Various combinations of temperatures, humidities, and processing times were used to crystallize lactose and milk powder in a fluidized bed dryer/crystallizer to achieve different degrees of amorphicity of powder. Under these conditions, lactose crystallinity and the crystallinity of the lactose portion in milk powder were found to increase significantly compared with the amorphous powders that were produced by conventional spray dryers. Different analytical techniques were used to investigate the degree of amorphicity and the improvement in powder crystallinity, such as modulated differential scanning calorimetry, water-induced crystallization, and Raman spectroscopy. The resulting powders were not sticky and were produced by different experimental conditions of processing temperature as 50–70 °C and 40% relative humidity in 30–60 min processing time. This technique is able to crystallize amorphous lactose and lactose-containing powder after spray drying in a reasonable processing time.

### 流化床干燥器/结晶器中乳糖和乳粉的快速结晶

**摘要** 本研究是基于粘稠无定形乳糖成分在振动流化床中部分结晶的原理从而生产出能在室温下长期保存的奶粉。温度、适度以及处理时间等参数的不同组合用来调试以获得不同无定形度的粉末。在本实验条件下，乳糖结晶度和奶粉中乳糖成分的结晶度比传统的喷雾干燥器生产出的无定形粉末有了显著的提高。研究采用多种分析手段，如调制式差示扫描量热技术、水诱导结晶以及拉曼光谱，来研究粉末的无定形度以及结晶度的改进。此技术生产的粉末不具粘性，能在50–70 °C、40%相对湿度以及30–60分钟处理时间的实验条件范围内生产得到。此项技术可以用来在合理处理时间内，对无定形乳糖以及传统喷雾式干燥技术得到了参杂粉末的乳糖进行结晶化处理。

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**Keywords** Milk powder · Lactose · Crystallization · Fluidized bed dryer

**关键词** 奶粉 · 乳糖 · 结晶 · 流化床干燥器

## 1 Introduction

Spray drying is widely used in the food-processing industry (and other industries) to produce dry powder from slurries or food solutions. Due to the short drying time in the drying chamber, most of the sugar-containing powders that are produced by the spray-drying technique have insufficient time to make a thermodynamically stable arrangement in two or three dimensions (crystalline form); therefore, an amorphous powder is typically formed. Although amorphous materials have some desirable properties, such as porosity, good solubility, and bioavailability, they are unstable and have a tendency to sorb moisture from the environment, causing the formation of bridges between particles and making agglomerated powders. The sticky powders and caked powders are not free-flowing, causing significant problems in powder handling and storage (Aguilera et al. 1995). The stickiness of powders may be reduced by partial or complete crystallization of the amorphous components after processing.

Many researchers have recommended that the amorphous lactose fraction could be treated in a crystallization facility after spray drying to crystallize lactose-containing powders and thus limit the caking tendency of the powder (Ibach and Kind 2007). Although the main morphological structure forms in the spray-drying chamber, many researchers have reviewed post-drying crystallization of lactose and milk powder in different temperatures and humidities. Langrish and Wang (2006) and Joupilla and Roos (1994) have studied crystallization of milk powder in a sorption box at different temperatures and water activities to assess the crystallization rate and time. The crystallization times that have been measured for skim milk powder and amorphous lactose in a sorption box (packed bed) ranged from several hours to a week (Jouppila et al. 1997). Ibach and Kind (2007) have found crystallization times that are as low as 1 min for pure lactose at 100 °C and 80% relative humidity, but they also found that the proteins and salts in whey and whey permeate slowed down the crystallization process under the same conditions to 5 min. On the other hand, the crystallized powders after this long process became hard cakes and agglomerated particles that were not suitable for further use. However, the time scale for the crystallization process appears to be longer than that for the drying process (Langrish 2008).

It has been established that changes like stickiness or the crystallization of amorphous lactose occur at temperatures above the glass-transition temperature (Jouppila et al. 1997). The temperature at which the transition from an amorphous solid state to a viscous rubbery state that occurs is known as the glass-transition temperature ( $T_g$ ) and is specific to each amorphous material and composition. The glass-transition temperature is affected by various factors, of which the composition of the material, molecular weight, and the presence of plasticizers (like water) are most important. The  $T_g$  can be estimated by the Gordon–Taylor equation (1952); when amorphous materials sorb water, the glass transition falls and crystallization may occur if  $T_g$  falls below the ambient temperature.

The Williams–Landel–Ferry (WLF) equation can be applied to conditions that give both drying and crystallization (Chiou et al. 2008; Williams et al. 1955), where

the rate of crystallization is related to the temperature difference ( $T - T_g$ ) of material temperature and the glass-transition temperature at relevant moisture content. The WLF equation shows that the rate of crystallization can be increased by increasing the temperature difference ( $T - T_g$ ). This temperature difference can be raised by increasing the inlet gas temperature to the fluidized bed dryer, or increasing the moisture content of the powders by supplying more moisture with high-humidity fluidization air. The difference between the glass-transition temperature and the powder temperature can be adjusted either by adding a plasticiser to lower  $T_g$ , or by heating the sample to raise  $T$ . Higher humidity within the fluidized bed dryer may mean higher moisture contents in the particles (by sorption), and according to the Gordon–Taylor equation (1952), higher moisture contents will decrease the glass-transition temperatures of the particles and enhance the crystallization rate.

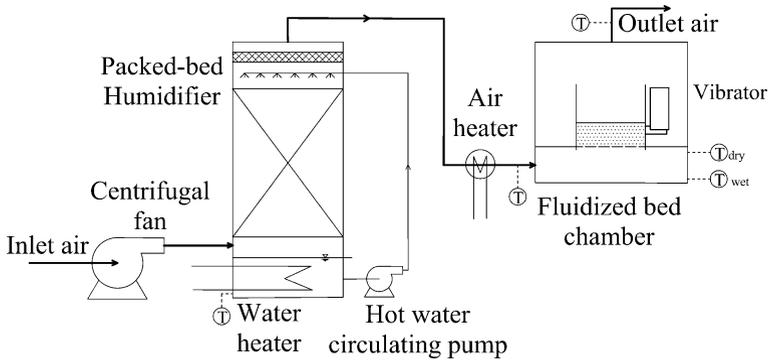
Vibrating fluidized bed dryers are used in milk powder production processes to further dry and cool the milk powder after spray drying. Fluidized bed technology has been widely used in the processing industries since the 1970s (Kunii and Levenspiel 1991). High heat and mass-transfer rates, high yields and lower residence times are advantages that have made this technique into a robust and efficient industrial technique. Some researchers have recommended that the amorphous lactose fraction could be treated in a crystallization facility after spray drying to crystallize lactose-containing powders and thus limit the caking tendency of the powder (Hynd 1980; Nijdam et al. 2008; Roetman 1979). No attempt was reported (Hynd 1980; Nijdam et al. 2008) to decrease the degree of amorphicity or assess the progressive change in crystallinity of lactose or milk powder during processing at different temperatures and humidities in fluidized beds. Fluidization of amorphous powders is very sensitive to process parameters like temperature, air velocity and humidity. Palzer tried to assess if the glass-transition concept could be useful for improving fluidized bed agglomeration (Palzer 2005). A commonly found problem is the collapse of the bed at a high relative humidity of the air within the bed, due to cake formation from the cohesion of all the particles in the bed. Palzer (2005) shows that the whole powder bed will collapse immediately when reaching the calculated critical moisture level when using air having a relative humidity of 90%. In addition, Nijdam et al. (2008) found that a bed of amorphous whey powder could not be re-fluidized by a further increase in air velocity after a slight increase in air humidity above the fluidization limit. This humidity limit represents a point above which no amount of additional mechanical energy, either in the form of air flow or mechanical force (by vibration or stirring), can fluidize the milk powder in the fluidized bed.

This work investigates the fast crystallization of skim milk powder and amorphous lactose powder in a vibrated fluidized bed at different temperatures and humidities. Improvements in powder crystallinity will be assessed by conventional evaluation techniques.

## 2 Materials and methods

### 2.1 Fluidized bed setup

A vibrated fluidized bed (Fig. 1) has been used to fluidize the powders with hot humid air. A variable speed centrifugal fan (0.75 kW motor and 50 cm fan



**Fig. 1** A schematic diagram of the fluidized bed system

diameter, Western Electric Australia, ABB speed controller), a counter-current humidifier column (a packed-bed vessel with circulating hot water (Thermoline, Australia), constructed in our laboratory) and a 1 kW electrical heater coil (constructed in our laboratory) have been used to generate the hot humid air. The supplied air was able to be conditioned to have a temperature range from 25 to 100 °C, a relative humidity from 10% to 95% and a fluidization air velocity within the fluidization column from 0.1 m s<sup>-1</sup> up to 5 m s<sup>-1</sup> at ambient conditions. The inside diameter of the fluidized bed column is 100 mm with a height of 50 mm. A stainless steel mesh (45 µm) plate with a diameter of 100 mm (Endecotts, UK) has been used as a bed support (air distributor). A small vibrated motor (IKA-werk, Germany) with a 2-cm unbalanced crankshaft was joined to the column and used to agitate the bed at 500 Hz to break up the channels in the bed during processing and create smooth fluidization. The fluidization column wall and bed support have been made from stainless steel. Heating insulation has been used on all pipes and connections between the humidifier, the electrical heater and the fluidized bed chamber and fluidized bed body. Five RTD thermocouples (Pyrosales, Australia) have been connected to the system to measure the temperature of the humidifier, the air heater, the inlet fluidization air (dry bulb), the wet-bulb temperature of the inlet air to the fluidization chamber and the outlet air. All sensed temperature data were transferred to a computer by a data logger (Datataker DT-505, Datataker Pty Ltd, Australia). The dry-bulb and wet-bulb temperature of the fluidization air have been reported here as the process air temperature. The wet-bulb temperatures of the inlet air were measured, and the dry-bulb temperature of the outlet air was also measured. No significant temperature difference was noticed between the inlet and outlet dry-bulb temperatures in the well-insulated short fluidized bed. No significant differences were found between the inlet and outlet wet-bulb temperatures, because typically 1 g of moisture was adsorbed or desorbed in a 30-min period, during which 3.4 kg of air (0.2 m/s through 10 cm diameter bed during 30 min) flowed through the bed. The whole setup was run for 2 h to reach steady state (temperature and humidity) before feeding the powders, and all inlet process variables were normally kept constant during each experiment. The aeration time for fluidizing the samples was up to 1 h, and during this time material was well agitated with continuous vibration.

## 2.2 Fresh amorphous lactose

Fresh amorphous lactose was produced by the spray drying of lactose solutions. A 15% ( $w \cdot w^{-1}$ ) lactose solution was prepared using pure lactose monohydrate ( $C_{12}H_{22}O_{11} \cdot H_2O$ ) (analytical-grade reagent, CAS no.: 63-42-3, Univar, Australia, batch no.: 0903237). Based on the results of recent publications on changing the crystallinity of spray-dried lactose (Imtiaz-UI-Islam and Langrish 2008), a solution of 15%  $w \cdot w^{-1}$  of lactose at 25 °C was fed into a Buchi B-290 spray dryer (Buchi Labortechnik, Switzerland) with an inlet air temperature of 160 °C, an outlet air temperature of 70 °C, a feed pump rate of 30% ( $9 \text{ mL} \cdot \text{min}^{-1}$ ) and an aspiration (main air flow) rate of 100% ( $38 \text{ m}^3 \text{ h}^{-1}$ ). Spray-dried amorphous lactose has been collected from a collection vessel at the bottom of the main product collection cyclone and stored in a sealed container in a refrigerator to keep the material below the glass-transition temperature. The fluidization experiment was done within 24 h of the production of the lactose to retain the freshness of the amorphous lactose.

## 2.3 Fresh spray-dried skim milk powder

Fresh spray-dried skim milk powder was produced from the spray drying of fresh skim milk from a local supplier (Coles, Sydney). Based on the results of recent publications on the surface composition of spray-dried milk powder (Nijdam and Langrish 2005), fresh skim milk ( $0.1 \text{ g fat} \cdot 100 \text{ mL}^{-1}$ ) at 25 °C was fed into a Buchi B-290 spray dryer (Buchi Labortechnik, Switzerland) with an inlet air temperature of 140 °C, an outlet air temperature of 63 °C, a feed pump rate of 20% ( $6 \text{ mL} \cdot \text{min}^{-1}$ ) and an aspiration rate of 100% ( $38 \text{ m}^3 \text{ h}^{-1}$ ). Fresh spray-dried milk powder was collected from a collection vessel at the bottom of a cyclone and instantly fed to the fluidized bed.

## 2.4 Crystalline $\alpha$ -lactose monohydrate and mostly crystallized skim milk powder

To define the upper limits of fluidization for the crystalline powders and compare the fluidization ability of amorphous and crystalline lactose-containing powder,  $\alpha$ -lactose crystals (Analytical reagent, CAS no.: 63-42-3, Univar, Australia, batch no.: 0903237) and crystallized skim milk powder, that were produced by the following technique, have been used.

A mass of 80 g fresh spray-dried skim milk powder was placed in a Petri dish and stored in a sorption box with a saturated NaCl solution (25 °C and 75% relative humidity) for 2 weeks. Every day the bulk material was gently agitated to break up the caked materials and to mix the powders, exposing all particles to the moisture in the air. Joupila and Roos (1994) and Langrish and Wang (2006) showed that the amorphous lactose in skim milk powder is mostly crystallized under such conditions in 2 weeks.

## 2.5 Sorption test

Time-dependent mass changes (percent; based on dry material) have been plotted for each of the samples. Moisture sorption behaviour was studied with two repeat samples of the raw and processed powders. A mass of 3–3.5 g of the powder was placed on a 150-mm diameter borosilicate glass Petri dish and spread uniformly in a layer that was

as thin as possible to cover the dish surface (the powder layer thickness was around 1 mm), and the mass change as a function of storage time was recorded once per minute over a period of 2–3 days to reach a constant mass by using a four-figure analytical balance ( $\pm 0.0001$  g, Mettler Toledo, AB 204-S, Switzerland). The sample and the balance were placed in a sealed sorption box (constructed in our laboratory), where the relative humidity (RH=70–75%) and the temperature (24.5–25 °C) were kept constant using a saturated solution of sodium chloride and electric light bulbs, respectively. A small fan was used for air circulation to keep the air conditions uniform within the sorption box. The sorption box has been described in previous work (Ibach and Kind 2007).

The curve of mass change versus time indicates amount of moisture sorbed by amorphous component in the powders. The end of the crystallization process can be determined by the point where the sorption curve reached a plateau region (Lehto et al. 2006). All changes in moisture content, including the peak heights, have been reported as being relative to the mass at the plateau value. The amount of sorbed moisture was divided by the final dry mass (oven dried) to calculate the percentage mass change. All the mass changes and moisture contents that have been reported in this paper are based on the dry basis (mass) of the material. This procedure has been used and reported by Imtiaz-Ul-Islam and Langrish (2008), Lehto et al. (2006), and Saleki-Gerhardt et al. (1994).

## 2.6 Glass-transition temperatures and crystallization energy

The glass-transition temperatures and degrees of amorphicity of the powders were determined by modulated differential scanning calorimetry (MDSC). MDSC samples were prepared according to standard procedures using aluminium hermetically sealed pans. Five samples of each material were analysed. An empty pan was used as a reference. The samples were heated from 0 to 300 °C using a ramp rate of 5 °C·min<sup>-1</sup> with a 1 °C modulated signal every 60 s using a modulated differential scanning calorimeter (TA Instruments Q1000, DE, USA). The scans were normalised by the system according to the sample mass. The midpoint temperatures of the glass-transition inflections were considered as the  $T_g$  values and the integrated peak energies were used to compare the differing degrees of amorphicity (according to the latent heat of crystallization) between raw and processed (treated) products.

## 2.7 Raman spectroscopy

Raman spectroscopy was used to evaluate the crystallinity of lactose on the surfaces of the particles (Murphy et al. 2005). The Raman spectra were collected using a Raman Station 400 F (PerkinElmer, CA, USA). The samples were analysed using a power of 100% with a 785 nm laser and 1 s exposure time with four exposures over a range of wavelengths from 200 cm<sup>-1</sup> to 3,200 cm<sup>-1</sup>. The spectra were analysed using the software Spectrum v6.3.4.0164.

## 2.8 Moisture content

Moisture content (dry basis) was measured by weighing 3 g of a sample before and after drying in an oven (Labec, Australia) at 85 °C for 2 days. The skim milk was

dried at a temperature of 85 °C, as suggested by DIN 10321, instead of 102 °C as suggested by IDF standard 26A: 1993, to prevent degradation and browning of the skim milk powder (Ozmen and Langrish 2003; Reh et al. 2004). The measured moisture contents, of the skim milk were adjusted by adding 0.371% ( $w \cdot w^{-1}$ ) to the moisture content determined by the decrease in mass, to compare with moisture contents of material dried at 102 °C, as recommended by De Knecht and Van Den Brink (1998). Each test was carried out in duplicate.

## 2.9 Particle size analysis

The particle size distribution was measured by laser diffraction using a Malvern Mastersizer S (Malvern Instruments, UK) with a dry powder feeder unit. Each test was carried out three times, and the average mean particle size was reported. The differences in the mean particle size between the tests were less than 5% of the average particle size.

## 2.10 Process conditions

Table 1 shows all the experiments performed for this study. The powder processing was a batch process. Amorphous powders were produced by spray drying, then the fluidized bed dryer was used to process the powders further. A mass of 7–10 g of powders (milk powder or lactose) was used for each batch of the fluidization process. The process temperature and humidity were chosen within the limits of fluidization, as will be explained later (Section 3.1). The fluidization air velocity was based on conventional minimum and maximum fluidization velocity calculations (Kunii and Levenspiel 1991). The degrees of amorphicity for processed powders have been investigated by the techniques described above. Samples were taken after the fluidization process was completed. Samples were immediately used for analytical tests (moisture content, DSC analysis and gravimetric moisture analysis), otherwise they were kept in sealed bags and in a refrigerator to do Raman spectroscopy on the following day. Each experiment was done in triplicate to assess

**Table 1** Experimental conditions used to process the powders in the fluidized bed

Material	Fluidization air <sup>a</sup> temperature (°C)	Fluidization air RH (%)	Fluidization time (min)	Initial moisture content % $w \cdot w^{-1}$ (dry basis)	Final moisture content % $w \cdot w^{-1}$ (dry basis)
Lactose	50	40±1	30	3.0	2.8±0.1
	60	40±1	30	3.0	2.9±0.1
	60	40±1	60	2.9	2.7±0.1
FSDMP	60	40±1	30	5.2±0.1	5.3±0.2
	70	40±1	30	5.2±0.1	4.2±0.2
	70	40±1	60	5.2±0.1	3.1±0.1

<sup>a</sup> Fluidization air velocity was 0.3 m·s<sup>-1</sup> for all experiments

FSDMP fresh spray-dried skim milk powder

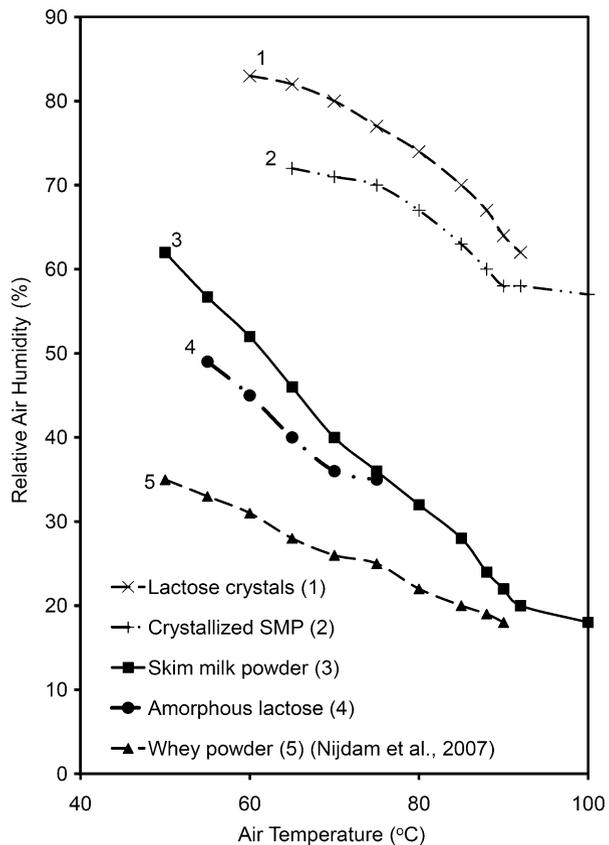
the repeatability, and the average value and the standard deviation have been reported.

### 3 Results and discussion

#### 3.1 Fluidization limits and final moisture contents

To assess the upper limits of fluidization for lactose-containing materials, hot humid air at different temperatures and humidities has been used. Figure 2 shows the stickiness and fluidization limits for (a) fresh spray-dried skim milk powder, (b) pure amorphous lactose, (c) crystallized skim milk powder, and (d) crystallized lactose, as measured in the fluidized bed chamber. Combinations of different humidity and temperature were used while vibrating the bed to prevent channelling. The sticky point and upper limit of fluidization that caused the material to collapse and prevented re-fluidization was measured visually (collapsed-bed pictures are not shown).

**Fig. 2** The upper limit of fluidization on the relative humidity of process air, under lactose-base which materials can be fluidized

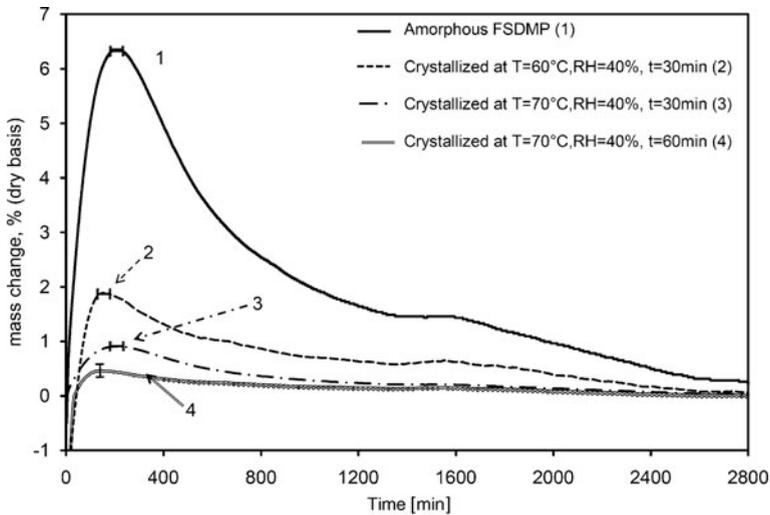


Nijdam et al. (2008) showed that the difference between the upper limits of fluidization for partially crystallized whey powder and fully crystallized whey powder was that fully crystallized whey powder can be fluidized up to a relative humidity of approximately two times greater than that of partially crystallized whey powder at any given air temperature. In this study, the same behaviour has been found for crystallized skim milk powder and amorphous fresh spray-dried skim milk powder, in the sense that fully crystallized skim milk powder can be fluidized up to a relative humidity that is approximately two times higher than fresh spray-dried skim milk powder at any corresponding air temperature. Since fresh spray-dried skim milk powder shows the same behaviour as the amorphous and the crystalline lactose, these fluidization limits show the effect of crystallinity on stickiness and agglomeration. For the design of experiments, the process conditions (temperature and humidity) should be selected below the upper limits of fluidization.

### 3.2 Moisture sorption tests

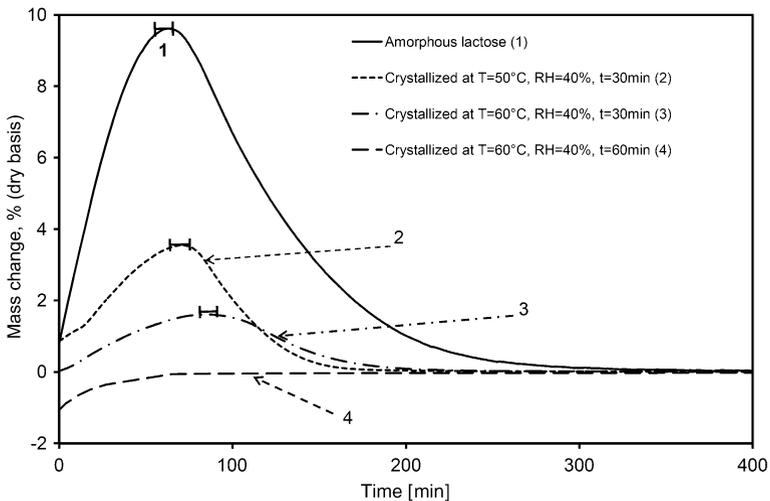
It has been established (Imtiaz-Ul-Islam and Langrish 2008; Lehto et al. 2006) that the moisture-adsorption peak heights (changes in moisture content, percent ( $100 \times \text{kg} \cdot \text{kg}^{-1}$  dry basis)) represent the degree of amorphicity for the samples. The size of the initial sorption peak, the mass change, represents the amount of sorbed moisture by amorphous materials, which characterises the degree of amorphicity for lactose. It has been compared with other available analytical techniques (gravimetric moisture sorption, Raman spectroscopy, and calorimetric methods), and the reliability and validity of these results has been demonstrated (Lehto et al. 2006). The net percentage changes in mass (dry basis) as a function of time for fresh spray-dried milk powder, pure lactose and skim milk powder (commercial type) processed in this fluidized bed are displayed in Figs. 3 and 4. The results are reproducible in terms of the peak heights and maximum moisture intakes, with a standard deviation of 0–3% of the peak height. Some peak shifts in time ( $\pm 40$ – $60$  min) were observed with repeat samples, but the peaks had similar heights (Tables 2 and 3). These time differences are the results of different ( $\pm 500$   $\mu\text{m}$ ) thicknesses of powder layers on the Petri dishes or the different powder particle sizes that change the moisture diffusion rates through the powder layers on the Petri dishes. By having the same peak height, the percentages of amorphous content appear to be the same, thus the sorption peak heights show the amounts of water that were sorbed by the amorphous material (lactose and proteins). However, the bed/bulk diffusion times were different for thicker layers of powders, and correspondingly the powder reached a state of maximum sorption at different times. The best test preparation is making the thinnest possible mono-layer of powders with uniform particle sizes to reduce these complications, which was done here.

In the sorption Figs. 3 and 4, the initial sharp increase in the moisture content is due to the dominating adsorption process by amorphous powder material (Burnett et al. 2004). By sorbing moisture (increasing moisture content), the glass-transition temperature of material decreases to below the ambient temperature, and the crystallization process can occur at the ambient temperature (25 °C), when the amount of sorbed moisture is sufficient. After that (at the peak point of the curve), the material begins to crystallize, leading to a loss in the mass. The moisture content



**Fig. 3** Results of moisture sorption tests for amorphous fresh spray-dried skim milk powder (FSDMP) before processing and the fresh spray-dried skim milk powders that were processed after being exposed to different conditions in the fluidized bed (sorption test at 25 °C and 75% relative humidity). The error bars on the curves represent the time shift on peak point

decreases until the crystallization process reaches an equilibrium state at the storage conditions (75% RH and 25 °C) with water, amorphous lactose and the monohydrate form (Burnett et al. 2004; Jouppila et al. 1997). In the following graphs (Figs. 3 and 4), the change in moisture content after the peak of each curve depends on the degree of amorphicity for the materials (Saleki-Gerhardt et al. 1994). Hence, the peak height (the distance between the peak and the plateau of the crystallization process) for each powder characterises the degree of amorphicity for that material



**Fig. 4** Results of moisture sorption tests for pure amorphous lactose before processing and lactose powders that were processed after being exposed to different conditions in the fluidized bed (sorption test at 25 °C and 75% relative humidity). The error bars on the curves represent the time shift on peak point

**Table 2** Summary of the statistical analysis for the moisture sorption peak heights of all the experimental conditions (Table 1) for skim milk powders with respect to the sorption peak heights of FSDMP (base case)

Milk powder				Run	Run	Run	Average	STDV	Improvement
Curve no. <sup>a</sup>	Fluidization air temperature (°C)	Fluidization air relative humidity (%)	Processing time (min)	1	2	3			(%)
1	Amorphous			6.353	6.394	6.330	6.359	0.032	–
2	60	40	30	1.902	1.912	1.922	1.912	0.010	70
3	70	40	30	0.908	0.929	0.911	0.916	0.011	86
4	70	40	60	0.463	0.473	0.452	0.463	0.010	93

<sup>a</sup> Corresponding numbers to the curves in Fig. 3

(Lehto et al. 2006). After crystallization, all the amorphous lactose was changed to  $\alpha$ -lactose monohydrate, and there was no tendency to sorb/desorb further moisture. The long-term plateau line shows the consistency of mass after crystallization.

The lactose powders sorption curves in Fig. 4 show the progressive decreases in amorphicity and the lower amount of sorption that were caused by greater processing times and higher temperatures/humidities. The similar progressive results for the fresh spray-dried milk powder (FSDMP) demonstrated the significant decrease in amorphicity (less sorption) after processing the powders at different temperatures and humidities (Fig. 3). There were significant changes between different samples that were processed (crystallized) at different humidities and temperatures in the fluidized bed environments with the same residence time or with the same temperature, as shown in Figs. 3, 4 and Tables 2, 3. For FSDMP, the powders that were processed at 60 °C and 40% relative humidity for 30 min had 70% lower peak heights compared with the fresh amorphous milk powder (Table 2). The lowest peak height was for the milk powder that was crystallized at 70 °C and 40% relative

**Table 3** Summary of the statistical analysis for the moisture sorption peak heights of all the experimental conditions (Table 1) for lactose powders with respect to the sorption peak heights of fresh amorphous lactose (base case)

Lactose				Run	Run	Run	Average	STDV	Improvement
Curve no. <sup>a</sup>	Fluidization air temperature (°C)	Fluidization air relative humidity (%)	Processing time (min)	1	2	3			(%)
1	Amorphous			9.602	9.657	9.587	9.615	0.037	–
2	50	40	30	3.546	3.553	3.536	3.545	0.009	63
3	60	40	30	1.608	1.610	1.606	1.608	0.002	83
4	60	40	60	0.005	0.005	0.006	0.006	0.000	100

<sup>a</sup> Corresponding numbers to the curves in Fig. 4

humidity for one hour, which shows a peak height that is 93% lower compared with the raw powder. In one series of experiments, the residence time and relative humidity were kept constant, and the only variable parameter was the air temperature. By increasing the process temperature and/or increasing the water activity by sorbing more moisture at a higher relative humidity,  $T - T_g$  increased and the crystallization time decreased, according to the Gordon–Taylor and Williams–Landel–Ferry (Gordon and Taylor 1952; Williams et al. 1955) equations. Therefore, as the results show, by increasing the temperature from 60 to 70 °C, the sorption peak height decreased, suggesting that less amorphous lactose (the most hygroscopic component) remained in the milk powder. The lactose powder that was processed at 60 °C for 1 h (Fig. 4) had low levels of amorphous material, as shown by the low moisture sorption peaks. The reductions in the amounts of amorphicity (peak height) are 100% compared with the fresh amorphous lactose (Table 3). As other analytical techniques will show later, curves 4 in both figures (Figs. 3 and 4) represent the most crystalline (least amorphous) powder. There is no moisture desorption for these types of crystallized (nonamorphous) powders. Mostly crystalline FSDMP (Fig. 3, curve 4) shows more initial moisture sorption compared with pure lactose. This moisture sorption could occur because of amorphous proteins in the milk powder structures (Bronlund and Paterson 2004).

After forming lactose crystals during fluidized bed crystallization of FSDMP and lactose, the initial moisture-adsorption processes in the sorption box were enough to cause polymorph transformation, changing the anhydrous crystal form to a more stable  $\alpha$ -lactose monohydrate form. The other possible hypothesis is mutarotation of  $\beta$ - to  $\alpha$ -lactose monohydrate, which is more stable at ambient conditions. In this case, and related to the very long sorption/desorption times for the powder, the solid-phase mutarotation process may occur in different layers of internal  $\beta$ -lactose sorbing moisture, forming the  $\alpha$ -lactose monohydrate crystals and releasing water to the other layers. The steps involved in changing  $\beta$ -lactose to the monohydrate form are firstly mutarotation to the anhydrous alpha form then crystallization as the monohydrate form in the presence of adequate amount of water. According to Table 1, the processed (crystallized) powders from the fluidized bed dryer are relatively dry (2.7–5.3%  $w \cdot w^{-1}$  moisture content, dry basis), therefore the initial moisture sorption is due to the difference between the equilibrium moisture content and the actual moisture content of the initially partly amorphous powders.

The moisture sorption peak heights were statistically analysed to assess their differences compared with the base case (amorphous fresh spray-dried milk powder or fresh amorphous lactose) in terms of the improvements in amount of the crystallinity. The comparative peak heights (improvements) and standard deviations for each series of experiments have been reported in Tables 2 and 3. ANOVA tests have shown that there are significant differences between the powders processed under different conditions and the amorphous powders at a 95% confidence level.

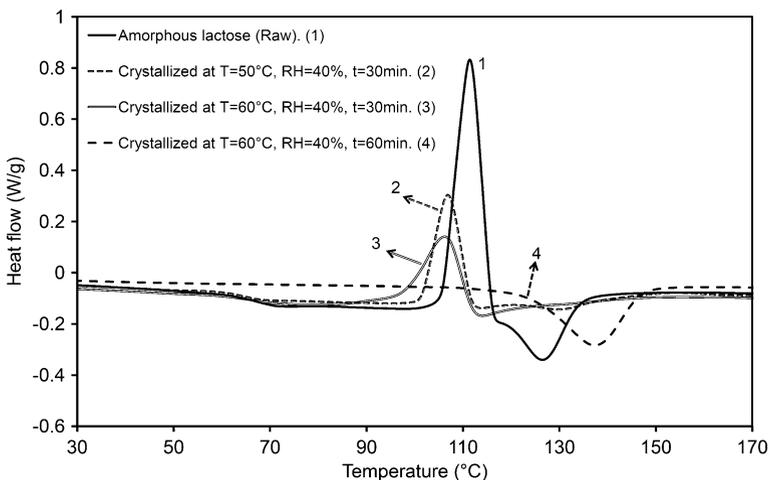
Most of the sorption curves became flat from around 3,000 min, showing steady behaviour and no sorption (associated with lactose crystallization) for the raw FSDMP and the processed FSDMP (Fig. 3). Moisture sorption curves for amorphous lactose and processed lactose become flat from around 300 min (Fig. 4). This time difference is possibly because of the complex structure of milk powder and lactose/protein interaction (Jouppila and Roos 1994).

### 3.3 Glass-transition temperatures and MDSC results

Many researchers have investigated the thermal analysis of pure lactose and its different anomers and polymorphs and lactose in milk powders (Gombas et al. 2002; Haque and Roos 2004; Jouppila and Roos 1994). The reported transition temperatures include mostly the glass-transition temperatures and the crystallization/re-crystallization temperatures of pure lactose and the lactose mixtures (lactose-containing materials) with different moisture contents.

In this work, MDSC analysis results for mostly crystallized lactose powder, amorphous lactose powder and processed (with different amount of amorphicity) powders, show significant changes in the crystallization peaks. Figure 5 illustrates the glass-transition inflection and crystallization peaks for the different kinds of powders.

MDSC analysis results for FSDMP and processed milk powder are not given here for the following reason. There are many transition peaks in milk powder calorimetric scanning due to the different thermal transitions of different materials. Therefore the crystallization peaks or the glass-transition temperatures were overlaid by other diffused peaks. Many researchers have studied the thermal analysis of binary systems or the effect of other components on the crystallization temperature and delayed transitions. Jelen and Coulter (1973) studied the retarding effect of high salt concentrations on lactose crystal formation. Arvanitoyannis and Blanshard (1994) showed delayed crystallization of amorphous sucrose with the addition of lactose. Jouppila and Roos (1994) found that milk proteins delayed lactose crystallization in milk powders. Haque and Roos (2004) reported different crystallization temperatures and shifts in mixtures of lactose/WPI, lactose/albumin, lactose gelatine and lactose/casein. The reported thermal transitions at 160–180 °C are related to different forms of transformations during MDSC analysis, including the transformation of the amorphous to the crystalline state, or the mutarotation of  $\alpha$ - to  $\beta$ -lactose in the solution formed from the released water and the consequent



**Fig. 5** The full range DSC analysis results for different types of lactose powders

**Table 4** Summary of the results of the MDSC analysis for different types of processed lactose and amorphous lactose

Material	Process conditions			MDSC results			
	Fluidization air temperature (°C)	Fluidization air RH (%)	Fluidization time (min)	$T_g$ (midpoint)	Crystallization temperature (°C)	Latent energy of crystallization (J/g)	Curve no. <sup>a</sup>
Lactose	Amorphous lactose			65±3	111±4	71±7	1
	50	40	30	65±1	106±2	30±2	2
	60	40	30	64±1	105±2	21±3	3
	60	40	60	–	–	–	4

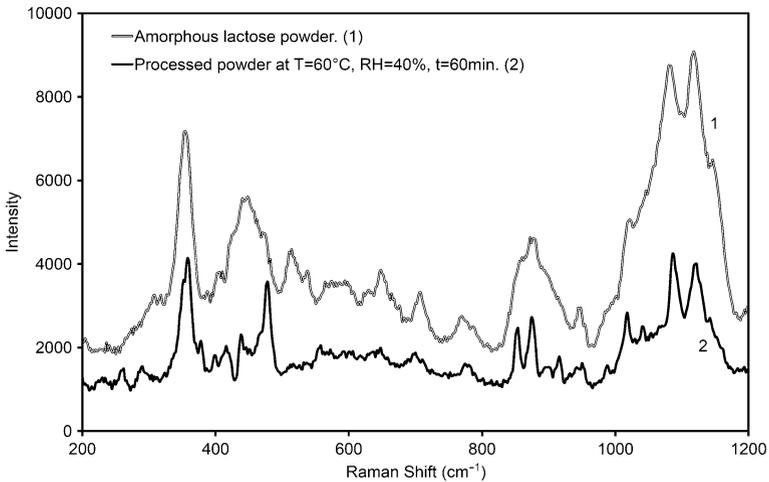
<sup>a</sup> Corresponding numbers to the curves in Fig. 5

crystallization of the  $\beta$ -lactose and the crystallization of unstable anhydrous  $\alpha$ -lactose into crystalline  $\alpha/\beta$ -mixtures ( $\alpha/\beta=1:1$ ).

The crystallization peak of the amorphous lactose powders at 111 °C was observed with lower exothermic latent energies of crystallization for the processed powders, which were related to the lower amounts of amorphous lactose in the processed powders (Table 4). In the raw powder, the crystallization peak had larger under-peak surface areas (71±7 J/g latent heats of crystallization) compared with the processed powders (such as 21±3 J/g latent heats of crystallization for the lactose powders that were crystallized at 60 °C and 40% relative humidity for 30 min). The different integrated peak energies (different amount of latent heats of crystallization) show different amounts of amorphous lactose in different processed powders compared with amorphous lactose powder.

In Fig. 5, the amorphous lactose, the lactose crystallized at 50 °C and a relative humidity of 40% for 30 min, and the lactose crystallized at 60 °C and a relative humidity of 40% for 30 min, all show inflections at 60–70 °C which may be glass-transition temperatures. Only the lactose crystallized at 60 °C and a relative humidity of 40% for 60 min shows no inflection. There were no crystallization peaks or glass-transition temperature inflections detected for processed (crystallized) lactose that was processed at 60 °C and 40% relative humidity for 1 h. The absence of MDSC crystallization peaks and moisture sorption peak indicates that the amorphous powders that were processed under these conditions had become crystalline. The endothermic peaks around 125 and 140 °C are associated with dehydration (free moisture and crystalline moisture) of lactose powders.

In skim milk powder, the crystallization peaks were not recognizable among the other peaks due to other components, but the peaks in the expected places have lower peak areas (data not shown). In most of the relevant literature, the crystallization peak for lactose in dry milk powder was mentioned to occur at around 170 °C (Gombas et al. 2002; Haque and Roos 2004). Milk protein may delay lactose crystallization because of competitive water sorption. Also, for skim milk powders, there is more than one crystallization peak in that region due to the presence of different proteins, salts and lactose; and other transformation peaks, including melting or mutarotation, which overlap with each other.

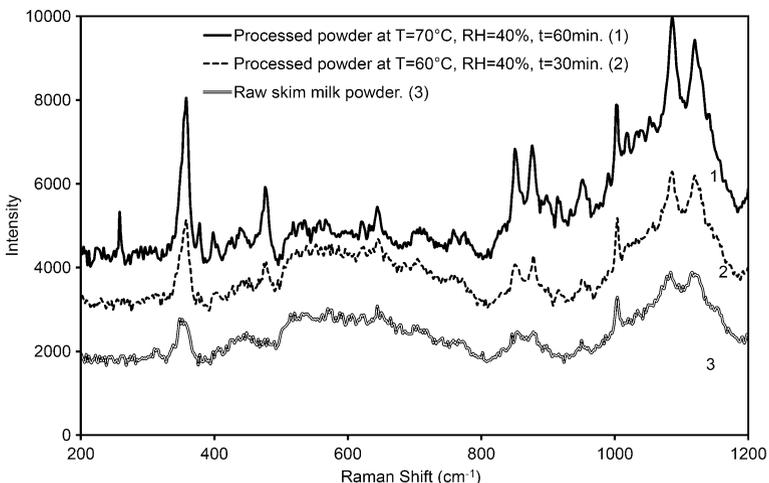


**Fig. 6** Raman spectra of the amorphous lactose and the processed (crystallized) powder showing the difference in lactose crystallinity

### 3.4 Crystallinity assessment by Raman spectroscopy

The Raman spectra, shown in Figs. 6 and 7, indicate that the processed powder particles are more similar to the crystalline powders than to the raw powders.

Clearly defined and visually distinguishable peaks on the Raman spectra for different lactose anomeric (Kirk et al. 2007; Susi and Ard 1974) and crystalline (Murphy et al. 2005) forms allow the identification of different lactose forms in the samples. Kirk et al. (2007), Murphy et al. (2005) and Susi and Ard (1974) found characteristic peaks for  $\alpha$ - and  $\beta$ -lactose, which are due to the characteristic stretching and bending vibrations of the bridge COC grouping. The characteristic peaks and significant differences occur at 1,100 and 350 cm<sup>-1</sup> for  $\alpha$ - and  $\beta$ -lactose (Susi and Ard 1974). While comparing the crystallographic nature of amorphous lactose with crystalline  $\alpha$ -lactose monohydrate,



**Fig. 7** Raman spectra of the amorphous skim milk powder and the processed (crystallized) powder showing the difference in powder crystallinity

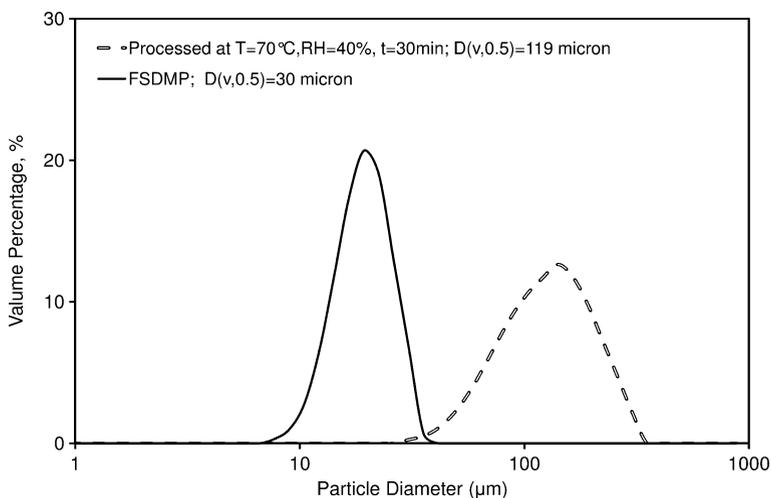
Murphy et al. (2005) found similar Raman spectra with single characteristic sharp peaks (except for the peak at  $350\text{ cm}^{-1}$ , which appear to have split into a minor doublet, as an influence of experimental parameters (Kirk et al. 2007)) for crystalline  $\alpha$ -lactose monohydrate as seen in the above study by Susi and Ard (1974), but broadened peaks appeared at similar Raman shifts for amorphous lactose.

However, for comparisons and quantification purposes, Murphy et al. (2005) calculated the polarization ratios at  $865$  and  $1,082\text{ cm}^{-1}$  Raman shifts, which correspond to bending vibrations of the COC group and stretching vibrations of the COC group, respectively. Murphy et al. (2005) found that the Raman bands at those positions are significantly depolarized for amorphous samples. They explained that, due to the local symmetry of the nuclei, the Raman bands become polarized when in solution and in amorphous solids. This supports the occurrence of a similar single peak at  $350\text{ cm}^{-1}$  and a range of peaks in-between  $1,500$ – $1,200\text{ cm}^{-1}$  for both amorphous lactose (Murphy et al. 2005) and lactose solutions (Susi and Ard 1974).

The comparison between the amorphous lactose and the crystallized lactose and also the FSDMP and the processed milk powders, in Figs. 6 and 7, show the significant reduction in powder amorphicity, by having clear and sharp peaks in  $350$  and  $1,100\text{ cm}^{-1}$ . The processed lactose spectrum shows a single peak but with a small doublet peak, which indicates the dominant existence of the  $\alpha$ -anomer with a small amount of the  $\beta$ -anomer. In the FSDMP spectra, the characteristic and clear doublet peaks are hard to recognize, and the spectra have many noise components that could be due to other complex materials in the milk powder. It is also possible that the presence of proteins in the powder has masked the characteristic peaks of the lactose.

### 3.5 Final moisture content

It may be a point of concern using this approach if the use of high humidities leads to high final moisture contents. This situation may occur if the solid state (amorphous or crystalline) stays the same during processing. However, this is not



**Fig. 8** Particle size distributions for a processed skim milk powder and fresh spray-dried milk powder

the case here. In terms of the experimental evidence, according to Table 1, reasonably low final moisture contents (3.1–5.3%) were achieved despite using high humidities, which was necessary to induce crystallization. These final moisture contents may have occurred because crystallization may have caused moisture to be expelled from the materials during crystallization. To reduce the final moisture content below these values, further drying is required.

### 3.6 Particle size analysis

Particle size analysis of processed materials has shown some particle agglomeration for the processed powders compared with the fresh spray-dried skim milk powder. The agglomeration and size enlargement was observed for all types of processed powders due to processing at high humidity conditions that causes particles to stick together during the process. Figure 8 indicates the particle size distribution for one type of processed powder (at  $T=70\text{ }^{\circ}\text{C}$ ,  $\text{RH}=40\%$ ,  $t=30\text{ min}$ ) compared with the raw powder (FSDMP) that was measured with a Malvern Mastersizer S. The size distribution charts for the same experimental conditions at different temperatures and humidities are all very similar, in the sense of significant size increases and little generation of fines. The particles have been enlarged from a size of  $30\text{ }\mu\text{m}$  ( $D_{50}$  for FSDMP) to  $100\text{--}200\text{ }\mu\text{m}$  ( $D_{50}=119\text{ }\mu\text{m}$  for a processed skim milk powder at  $T=70\text{ }^{\circ}\text{C}$ ,  $\text{RH}=40\%$ ,  $t=30\text{ min}$ ). For processed lactose, the particles have been enlarged from the size of  $18\text{ }\mu\text{m}$  ( $D_{50}$  for fresh amorphous lactose) to  $100\text{--}200\text{ }\mu\text{m}$  ( $D_{50}=158\text{ }\mu\text{m}$  for a processed lactose powder at  $T=60\text{ }^{\circ}\text{C}$ ,  $\text{RH}=40\%$ ,  $t=30\text{ min}$ ).

The agglomeration and particle enlargement is not the result of crystallization of lactose in milk powder; however agglomeration is not avoidable in this technique due to processing by high-humidity air and at temperature above the glass-transition temperature of the powders.

## 4 Conclusions

Lower degrees of amorphicity were obtained for powders of pure lactose and laboratory fresh spray-dried milk powder that was processed (crystallized) in a fluidized bed dryer by hot and humid air. The results from the analytical techniques showed significant reduction in the amorphicity for the processed powders. The DSC analysis and the gravimetric moisture sorption test for the processed powders (milk powders and lactose powders) show a 60–100% reduction in the degree of amorphicity for different processing combinations of temperature and humidity. The crystallized powders show very little moisture sorption from the environment, meaning easier storage for the final products. It can be concluded that fluidized bed processing by hot and humid air may be utilized to decrease the amorphicity of powders after spray drying.

## References

- Aguilera JM, Valle JMD, Karel M (1995) Caking phenomena in amorphous food powders. *Trends Food Sci Technol* 6:149–155

- Arvanitoyannis I, Blanshard JMV (1994) Rates of crystallization of dried lactose–sucrose mixtures. *J Food Sci* 59:197–205
- Bronlund J, Paterson T (2004) Moisture sorption isotherms for crystalline, amorphous and predominantly crystalline lactose powders. *Int Dairy J* 14:247–254
- Burnett DJ, Thielmann F, Booth J (2004) Determining the critical relative humidity for moisture-induced phase transitions. *Int J Pharm* 287:123–133
- Chiou D, Langrish TAG, Braham R (2008) The effect of temperature on the crystallinity of lactose powders produced by spray drying. *J Food Eng* 86:288–293
- De Knecht RJ, Van den Brink H (1998) Improvement of the drying oven method for the determination of the moisture content of milk powder. *Int Dairy J* 8:733–738
- Gombas Á, Szabó-Révész P, Kata M, Regdon G, Erős I (2002) Quantitative determination of crystallinity of  $\alpha$ -lactose monohydrate by DSC. *J Therm Anal Calorim* 68:503–510
- Gordon M, Taylor JS (1952) Ideal copolymer and the second-order transition of synthetic rubbers. I non-crystalline copolymers. *J Appl Chem* 2:493–500
- Haque MK, Roos YH (2004) Water plasticization and crystallization of lactose in spray-dried lactose/protein mixtures. *J Food Sci* 69:FEP23–FEP29
- Hynd J (1980) Drying of whey. *Int J Dairy Technol* 33:52–54
- Ibach A, Kind M (2007) Crystallization kinetics of amorphous lactose, whey-permeate and whey powders. *Carbohydr Res* 342:1357–1365
- Intiaz-Ul-Islam M, Langrish T (2008) The effect of the salt content on the crystallization behaviour and sorption fingerprints of spray-dried lactose. *Food Bioprod Process* 86:304–311
- Jelen P, Coulter ST (1973) Effects of certain salts and other whey substances on the growth of lactose crystals. *J Food Sci* 38:1186–1189
- Jouppila K, Roos YH (1994) Water sorption and time-dependent phenomena of milk powders. *J Dairy Sci* 77:1798–1808
- Jouppila K, Kansikas J, Roos YH (1997) Glass transition, water plasticization, and lactose crystallization in skim milk powder. *J Dairy Sci* 80:3152–3160
- Kirk JH, Dann SE, Blatchford CG (2007) Lactose: a definitive guide to polymorph determination. *Int J Pharm* 334:103–114
- Kunii D, Levenspiel O (1991) Fluidization engineering. Butterworth-Heinemann, Newtown
- Langrish TAG (2008) Assessing the rate of solid-phase crystallization for lactose: the effect of the difference between material and glass-transition temperatures. *Food Res Int* 41:630–636
- Langrish TAG, Wang EH-L (2006) Crystallization of powders of spray-dried lactose, skim milk and lactose-salt mixtures. *Int J Food Eng* 2:1–15
- Lehto V-P, Tenho M, Vähä-Heikkilä K, Harjunen P, Päällysaho M, Väliisaari J, Niemelä P, Järvinen K (2006) The comparison of seven different methods to quantify the amorphous content of spray dried lactose. *Powder Technol* 167:85–93
- Murphy BM, Prescott SW, Larson I (2005) Measurement of lactose crystallinity using Raman spectroscopy. *J Pharm Biomed Anal* 38:186–190
- Nijdam JJ, Langrish TAG (2005) An investigation of milk powders produced by a laboratory-scale spray dryer. *Dry Technol* 23:1043–1056
- Nijdam J, Ibach A, Kind M (2008) Fluidisation of whey powders above the glass-transition temperature. *Powder Technol* 187:53–61
- Ozmen L, Langrish TAG (2003) An experimental investigation of the wall deposition of milk powder in a pilot-scale spray dryer. *Dry Technol* 21:1253–1272
- Palzer S (2005) The effect of glass transition on the desired and undesired agglomeration of amorphous food powders. *Chem Eng Sci* 60:3959–3968
- Reh C, Bhat SN, Berrut S (2004) Determination of water content in powdered milk. *Food Chem* 86:457–464
- Roetman K (1979) Crystalline lactose and the structure of spray-dried milk products as observed by scanning electron microscopy. *Neth Milk Dairy J* 33:1–11
- Saleki-Gerhardt A, Ahlneck C, Zografis G (1994) Assessment of disorder in crystalline solids. *Int J Pharm* 101:237–247
- Susi H, Ard JS (1974) Laser-Raman spectra of lactose. *Carbohydr Res* 37:351–354
- Williams ML, Landel RF, Ferry JD (1955) The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *J Am Chem Soc* 77:3701–3707