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Effect of protein concentration on the surface composition, water sorption and glass transition temperature of spray-dried skim milk powders

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Abstract

The effects of dilution of protein content in skim milk (34–8.5% protein content), by lactose addition, on the surface composition, water sorption property and glass transition temperatures of spray-dried powders were investigated. The X-ray photoelectron spectroscopy (XPS) study of spray-dried powders showed preferential migration of proteins toward the surface of the milk particles whereas the lactose remained in the bulk. Sorption studies showed that the lower protein concentration in milk powders is linked to an increased water adsorption property and lowering of water activity (a_w) for lactose crystallization. Analysis of glass transition temperature (T_g) of the powders sorbed at different humidities showed no distinct change in T_g values, indicating the dominant effect of lactose on the glass transition temperature of all the powders.
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1. Introduction

Current international standards require a minimum of 34% protein in skim milk powder (SMP). However, there is also commercial interest in production (and export) of SMP analogues with lower protein contents, for food ingredient applications. Lactose is the major milk ingredient used to dilute the protein in such products. The effect of altered chemical composition of spray-dried powders, such as milk powders with various fat levels and SMP, with hydrolysed lactose has been studied in terms of physio-chemical behaviour (Fernandez, Schebor, & Chirife, 2003; Jouppila & Roos, 1994a, 1994b, 1997; Kim, Chen, & Pearce, 2002, 2003; Nijdam & Langrish, 2006). However,

the effects of reduced milk protein content on the physio-chemical properties, such as surface composition, sorption behaviour and glass transition temperature (T_g), of spray-dried SMP, that can have some implications for production, processing and storability of the final product, have not been studied.

Spray-drying of milk solution involves the rapid removal of moisture, leading to the formation of dried milk particles. It leads to the concentration of various milk components, such as lactose, fat, protein and minerals as moisture evaporates from the surface, forming a skin. Evaporation of moisture in a drying droplet simultaneously leads to migration of milk components toward the surface to replace the aqueous phase. The concentrations of lactose, fat, protein and moisture at the surface were found to be different from the bulk composition (Faldt & Bergenstahl, 1996; Faldt, Bergenstahl, &

Carlsson, 1993; Kim et al., 2002, Kim, Chen, & Pearce, 2003; Nijdam & Langrish, 2006). The surface compositions of the dried powders largely affect key functional properties, such as stickiness, wettability, particle size distribution, bulk density, and flowability of the powders (Kim et al., 2002; Nijdam & Langrish, 2006). It is important to know the surface composition of major milk components, such as lactose, protein and fat, that will individually, or in combination, affect the resultant properties of these powders. Moisture sorption behaviour and glass transition temperature (T_g) are two important physiochemical properties of spray-dried milk powders that largely determine the processing conditions, product quality (such as stickiness, hygroscopicity and caking behaviour) and stability (storability and handling) of the final product.

In this study, SMPs with reduced levels of proteins, due to standardization with various amounts of lactose, were spray-dried and analysed for their surface compositions using X-ray photoelectron spectroscopy (XPS). Moisture adsorption isotherms and glass transition temperatures of the powders were also measured.

2. Materials and methods

2.1. Sample preparation

Skim milk powder and lactose were purchased from Murray Goulburn Co-operative (MGC), Melbourne, Australia. The bulk composition of SMP, according to MGC, was protein 34%, lactose 50% and fat 1% (as is basis). Aqueous solutions (35%, w/w) of SMP:lactose at ratios of 1:0, 3:1, 1:1 and 1:3 with protein contents of 34%, 25.5%, 17% and 8.5%, respectively, on a dry solids basis, were prepared. Solutions were prepared at temperatures of about 50 °C and spray-dried. The spray-dryer (Saurin Technology, Melbourne, Australia) was a twin fluid nozzle type with 3 l/h water evaporation capacity. The inlet and outlet temperatures of dryer were set at 180 °C and 80 °C, respectively. Powders were collected in a cyclone collector and immediately vacuum-packed in a Cryovac® plastic bag and stored in a dry chamber. The water activity and moisture content of the fresh powder were also measured.

2.2. X-ray photoelectron spectroscopy (XPS) analysis

XPS or electron spectroscopy for chemical analysis (ESCA) is a well-established method for elemental analysis in a variety of materials, including food powders. Detailed description of application of XPS as a method to measure surface composition of dairy powders is given elsewhere (Faldt & Bergenstahl, 1996; Faldt et al., 1993; Kim et al., 2002, 2003; Nijdam & Langrish, 2006). Before analysis, it was assumed that SMP is composed of three major components, namely, lactose, protein and fat, whereas minerals and other organic components were considered to be nil.

All the spray-dried powders, at SMP:lactose at ratios of 1:0, 3:1, 1:1 and 1:3, were analysed in fresh condition in order to prevent any unwarranted changes. Prior to analysis, the samples were outgassed under vacuum for 72 h. The XPS analyses were performed on a Kratos AXIS Ultra with a monochromatic A1 X-ray source at 150 W. Each analysis started with a survey scan from 0 to 1200 eV with a dwell time of 100 ms, pass energy of 160 eV at steps of 1 eV, with a 1 sweep. For the high resolution analysis, the number of sweeps was increased, the pass energy was lowered to 20 eV, at steps of 50 meV, and the dwell time was changed to 250 ms. Data was acquired using a Kratos Axis ULTRA X-ray photoelectron spectrometer, incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was Monochromatic Al X-rays (1486.6 eV) at 225 W (15 kV, 15 ma). Survey (wide) scans were taken at an analyser pass energy of 160 eV and multiplex (narrow) higher resolution scans at 80 eV. Base pressure in the analysis chamber was 1.0×10^{-9} Torr and, during sample analysis, 1.0×10^{-8} Torr.

XPS was applied to measure the relative atomic concentrations of carbon, nitrogen and oxygen in the surface layer of the SMP and SMP/lactose powders. Data from Kim et al. (2002) for elemental composition of the pure components of SMP were used. Those three components were lactose, protein (as sodium caseinate) and fat (as anhydrous milk fat), that make the bulk of the sample. It has been assumed that elemental composition of the pure components is in linear combination with the three major components of the sample (Faldt et al., 1993; Kim et al., 2003). Kim et al. (2002) have verified the surface composition data from XPS by further experimentation, such as measurement of powder surface composition, surface structure studies, fat localization studies, wetting test and measurement of surface oxygen test during storage.

A method described by Faldt et al. (1993), where elemental data from pure components and samples were put into the matrix formula to calculate the relative percentage of each component in the sample, was used. The relative elemental composition data of the pure components, as measured by Kim et al. (2003) using XPS, were used, which were as follows: for lactose – carbon 52.9%, oxygen 47.1% and nitrogen 0%; for protein (sodium caseinate) – carbon 67.4%, oxygen 19.1% and nitrogen 13.5%; and fat (anhydrous milk fat) – carbon 88.4%, oxygen 11.6% and nitrogen 0%. Table 1 shows the relative surface concentrations of

Table 1
A summary of elemental composition of SMP and SMP/lactose powders as measured by XPS

Elements	% Atomic concentration			
	SMP	SMP:lactose (3:1)	SMP:lactose (1:1)	SMP:lactose (1:3)
Oxygen	25.78	26.59	27.09	29.59
Nitrogen	8.24	8.2	7.81	7.64
Carbon	65.97	65.21	65.09	62.76

carbon, oxygen and nitrogen in SMP, SMP:lactose (3:1), SMP:lactose (1:1) and SMP:lactose (1:3), as measured by XPS.

According to Faldt et al. (1993), for each of the elements: C, O and N in the powder sample, the relative amount can be expressed by the following equations (Eqs. (1)–(3)):

$$I_{sample}^{C} = I_{f}^{C} \cdot \gamma f + I_{p}^{C} \cdot \gamma p + I_{l}^{C} \cdot \gamma l \qquad (1)$$

$$I_{sample}^{O} = I_{f}^{O} \cdot \gamma f + I_{p}^{O} \cdot \gamma p + I_{l}^{O} \cdot \gamma l \qquad (2)$$

$$I_{sample}^{N} = I_{f}^{N} \cdot \gamma f + I_{p}^{N} \cdot \gamma p + I_{l}^{N} \cdot \gamma l \qquad (3)$$

where I_{sample}^{C}, I_{sample}^{O} and I_{sample}^{N} are the relative amounts of carbon, oxygen and nitrogen in the sample; I_{f}^{C}, I_{p}^{C} and, I_{l}^{C} are relative amounts of carbon in fat, protein and lactose; I_{f}^{O}, I_{p}^{O} and I_{l}^{O} are relative amounts of oxygen in fat, protein and lactose; and I_{f}^{N}, I_{p}^{N} and I_{l}^{N} are relative amounts of nitrogen in fat, protein and lactose and γf, γl and γp are the fractions of the area covered with fat, lactose and proteins, respectively. The fraction of area covered by each nutrient was estimated by solving the above equation by matrix formula, as previously reported by Faldt et al. (1993).

2.3. Glass transition temperature (T_g)

Differential scanning calorimetry, DSC (Pyris 1 equipped with Intracooler II, Perkin Elmer 7, CT, USA) was used to determine the glass transition temperature of all spray-dried powders. The purge gas used was dry nitrogen (20 ml/min). The onset, mid-point and endset values for glass transition temperature of samples were calculated from the DSC thermogram. Indium and zinc (Perkin Elmer standards) were used for temperature and heat-flow calibration. An empty aluminium pan was used as a reference. About 5–10 mg samples were scanned in hermetically sealed 50 μl DSC aluminium pans (Perkin Elmer). All analyses were done in triplicate. The rate determinations of thermal scanning were carried out in the following order: (1) isothermal at −20 °C for 1 min; (2) heat scanning from −20 °C to a temperature just over the expected T_g at 10 °C/min; (3) cooling rapidly to −20 °C at 50 °C/min; and (4) Heat scanning from −20 °C to 200 °C. The second scanning of each sample was used to reduce the enthalpy relaxation of the amorphous powder which appears in the first scan, thereby enhancing the accuracy of T_g measurement on the DSC thermogram. The transfer of samples from the container to the DSC pan was done in a sealed 'Dry Box' containing silica gel with regular N_2 flushing, to avoid unwanted moisture absorption by the sample.

2.4. Sorption isotherm studies

The spray-dried samples were dried overnight at 70 °C in a vacuum oven, followed by further drying in vacuum desiccators over P_2O_5 for 2 days. To make sure the powders were fully dry, these were further analysed for water activity and residual moisture content. About 2 g of amorphous powders, in triplicates, were transferred into the pre-weighed plastic cups with a screw-cap and placed in evacuated desiccators over P_2O_5 and different saturated salt solutions of LiCl, CH_3COOH, MgCl_2, K_2CO_3, Mg(NO_3)_2, KI and NaCl with respective relative humidities of 11.4%, 23.1%, 33.2%, 44.1%, 52.9%, 68.9% and 75.3% at about 23 °C, giving a_w of 0.01 × %RH (Labuza, Kaanane, & Chen, 1985). The samples were stored for 21 days at 23–24 °C in an air-conditioned room. The samples, after equilibrium was reached, were tightly closed with the screw-cap, weighed and stored in a dry glass chamber containing silica gel prior to further analysis for T_g. The moisture content of each sample was measured and the mean value of triplicates was calculated, as grammes of water per 100 g of dry sample.

2.5. Statistical analysis

Analysis of variance (ANOVA) was used to determine significant effects of different parameters on the materials using a software, Statgraphics package (Statistical Graphic Corporation, 1993, Manugistics Inc., USA). Least significant differences between treatment means were determined by Duncan's multiple range test (DMRT).

3. Results and discussion

3.1. Surface composition

Fig. 1 shows the individual XPS spectrum of oxygen, nitrogen and carbon and also the survey spectrum of all three elements. The binding energies of 1s O, 1s N and 1s C were very close to 528–533, 397–408, and 281–293 eV, respectively, as reported by Chastain (1992). Based on various individual bondings of each element, such as, –C═0, –C–OH, –C–N═, which are characteristics of the binding energy, the relative elemental composition of the milk components on the surface was calculated.

The surface composition of protein, lactose and fat on SMP and SMP/lactose, along with bulk composition, is presented in Table 2. Addition of lactose to SMP decreased the protein and fat contents in the SMP powders. However, there was no linear increase in lactose content or decrease in protein and fat content on the surface of powder. Besides, the compositions on the surfaces of SMP and SMP/lactose were very different from the bulk composition. There was a decrease in surface composition of lactose whereas protein and fat contents were increased in relation to bulk composition.

The most remarkable change in surface composition of milk powder in relation to the bulk was observed in fat content. The surface of SMP and SMP/lactose mixture contains a remarkably higher percentage of fat than does their original composition (Fig. 2). This shows fat is the most preferred milk component to migrate towards the surface. For example, SMP contained only 1% fat, whereas the sur-
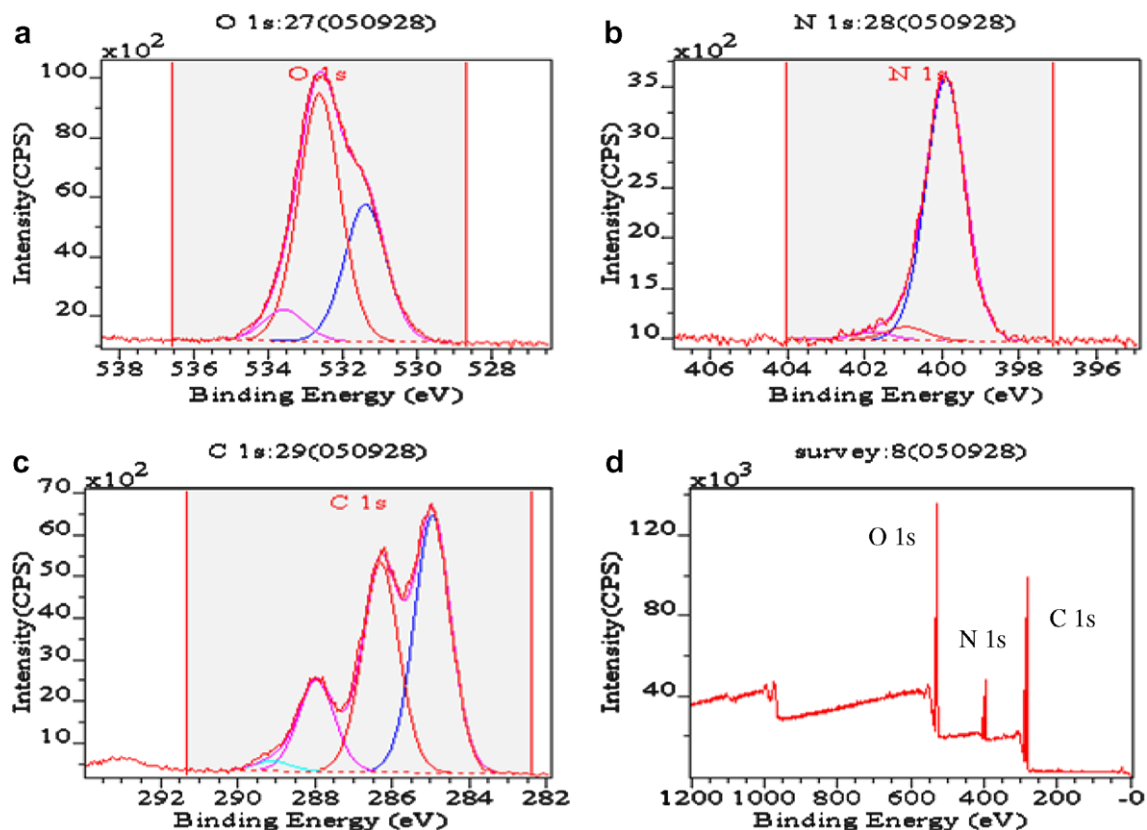
Fig. 1. Surface spectra of individual elements with various bonding positions, as shown by multiple curves, for A – oxygen, B – nitrogen and C – carbon, and D for survey spectra of all elements for SMP.

Table 2
Surface compositions of spray-dried SMP and SMP/lactose mixtures[a]

Parameters	SMP	SMP:lactose (3:1)	SMP:lactose (1:1)	SMP:lactose (1:3)
Protein	61 (34)	61 (26)	58 (17)	57 (9)
Lactose	27 (50)	29 (63)	31 (75)	39 (88)
Fat	12 (1)	10 (0.8)	11 (0.5)	5 (0.25)

[a] Values in parentheses are from bulk composition.

face of the powder had 12% fat (a 12-fold increase). Similarly the surface composition of fat in SMP:lactose (3:1), SMP:lactose (1:1) and SMP:lactose (1:3) ranged from 12 to 22 times higher than the bulk composition. This confirms the previous findings by Nijdam and Langrish (2006) that the small change in the average fat concentration, at low fat concentration, results in a large change in the surface fat coverage. Kim et al. (2002) reported surface compositions of 18%, 98%, 99% and 53% fat in SMP, whole milk powder, cream powder and whey protein concentrate, which originally contained 1%, 29%, 75% and 6% fat, respectively. Nijdam and Langrish (2006) reported the surface coverage of 35% fat in milk powder that had a fat content of 5%.

The result showed a greater rate of migration of fat on the surface during spray-drying of skim milk powder. It has been established that a small change in the fat content in liquid fed to spray-drying significantly affects the surface

fat distribution of SMP. The presence of fat on the surface of milk powder increases the hydrophobicity of the surface, decreasing the wettability of the powders (Faldt & Bergenstahl, 1996). Higher fat content on the surface also renders the powder susceptible to oxidative rancidity (Hardas, Danviriyakul, Foley, Nawar, & Chinachoti, 2000). Fat present on the surface of milk powders is known to cause stickiness due to formation of liquid bridges (Nijdam & Langrish, 2006; Ozkan, Walisinghe, & Chen, 2002).

The concentration of proteins on the surface of the milk powders was also greater than was that of the bulk concentration. Table 2 shows that the surface composition of protein in SMP, SMP:lactose (3:1), SMP:lactose (1:1) and SMP:lactose (1:3) was increased to 61%, 61%, 58% and 57% from the 34%, 26%, 17% and 9%, respectively, originally present in the bulk. It is interesting to see very little change in surface protein content, even when the bulk composition increases from 9% to 34% (Fig. 2). This result suggests that there is rapid diffusion of protein toward the surface, that gets saturated very quickly, so that further increase in protein content does not increase the surface protein level. This confirms the finding of Faldt and Bergenstahl (1994) and Faldt and Bergenstahl (1996) that protein dominates the surface of the dried powder, even at low concentrations of protein in solution. The authors suggested that surface coverage of protein indicates the excess
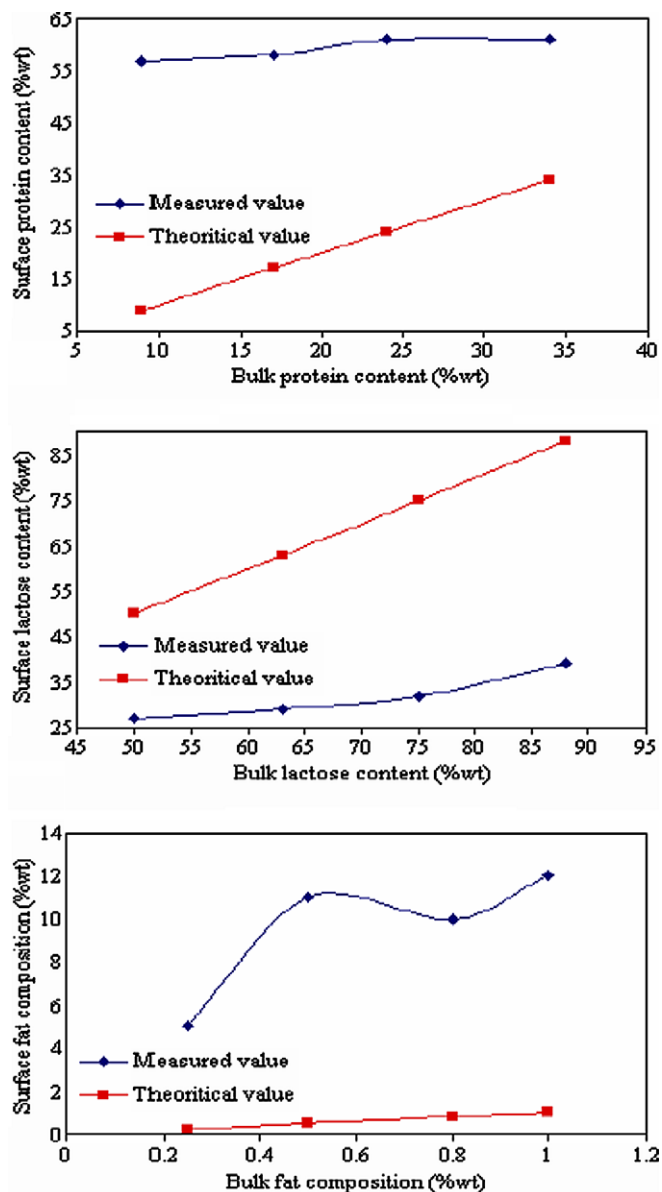
Fig. 2. A comparison of surface coverage of fat, lactose and protein in SMPs with various levels of lactose or protein with the bulk composition.

surface-active protein at the air–water interface of the droplets formed during the spray-drying process. The result presented by Kim et al. (2002) suggested that the amount of protein on the surface of the milk powder is largely determined by the fat content. For example, the surface of SMP that has 58% lactose, 41% protein and 1% fat is covered with 36% lactose, 46% protein and 18% fat. Whereas the whole milk powder that has 40% lactose, 31% protein and 29% fat is almost entirely covered with fat. Nijdam and Langrish (2006) have observed that, in a lactose/protein system, the dominant component at the surface is largely determined by the spray-drying temperature, i.e., protein dominates the lactose on the surface at lower drying temperature and *vice versa*.

Table 2 shows that, unlike fats and proteins, the concentration of lactose on the surface of the particles is lower

than that in the bulk. It was also noticed that only about half of the lactose from the bulk appeared on the surface of the milk powder and the decline of lactose concentration on the surface was almost linear (Fig. 2). Kim et al. (2003) tried to explain the preferential migration of milk components toward the surface or interior of the dry particle, based on the Stoke–Einstein equation. The particle size of free fat is the largest, followed by casein micelles, whey proteins, lactose and salts, while the diffusivity is in the reverse order. Accordingly, the free fat and fat globules very slowly diffuse toward the centre of the milk droplet during drying, followed by casein and lactose. It should be noted that this migration would occur immediately after atomization, but prior to solidification of the droplet. The condition and types of atomization, drying rate and bulk composition are expected to influence the surface property.

3.2. Adsorption isotherm behaviour of SMP/lactose mixtures

Moisture plays an important role in glass transition and crystallization behaviour of amorphous powders, which determines flowability, stickiness or caking and storage stability. The experimental moisture adsorption isotherms of SMP and SMP/lactose mixtures at room temperature (23–24 °C), at equilibrium after 21 days, are given in Table 3 and the trend is also seen in Fig. 3. Comparison of sorption data for SMP with those reported by Jouppila and Roos (1994a), for freeze-dried SMP humidified for 1 day, showed lower water sorptions at all lower water activities. However, it seems inappropriate to compare the present sorption data for spray-dried SMP which has been humidified for 3 weeks with current literature values, such as those of agglomerated SMP humidified until constant weight is reached (Teunou, Fitzpatrick, & Synnott, 1999), freeze-dried SMP humidified for an unknown time period (Fernandez et al., 2003), and freeze-dried SMP humidified for 1 week (Jouppila & Roos, 1997).

The result showed that increase in lactose concentration in SMP significantly ($p < 0.05$) increased the water adsorption in milk powders, except in SMP:lactose (1:3). The sur-

Table 3
Water activity and moisture contents of SMP and SMP/lactose mixtures humidified at different water activities[a,b,c]

Water activity	SMP	SMP:lactose (3:1)	SMP:lactose (1:1)	SMP:lactose (1:3)
0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
0.113	2.4 ± 0.0a	2.9 ± 0.0b	2.9 ± 0.2b	2.2 ± 0.0a
0.225	4.4 ± 0.1a	4.9 ± 0.0c	4.6 ± 0.1b	4.7 ± 0.1b
0.328	6.4 ± 0.2a	7.0 ± 0.1b	6.7 ± 0.1ab	6.6 ± 0.0ab
0.432	8.2 ± 0.2c	5.0 ± 0.2b	3.5 ± 0.3a	3.0 ± 0.2a
0.529	6.9 ± 0.1b	5.8 ± 0.2a	6.1 ± 0.3ab	5.8 ± 0.0a
0.689	12.0 ± 0.1d	10.7 ± 0.1c	9.1 ± 0.3b	6.8 ± 0.4a
0.753	13.1 ± 0.2d	11.9 ± 0.1c	9.8 ± 0.2b	7.4 ± 0.2a

[a] Mean values ± standard deviation of triplicates.
[b] Moisture is presented as gH_2O/100 g dry solid.
[c] Values followed by same letter within a row do not differ significantly ($p > 0.05$).
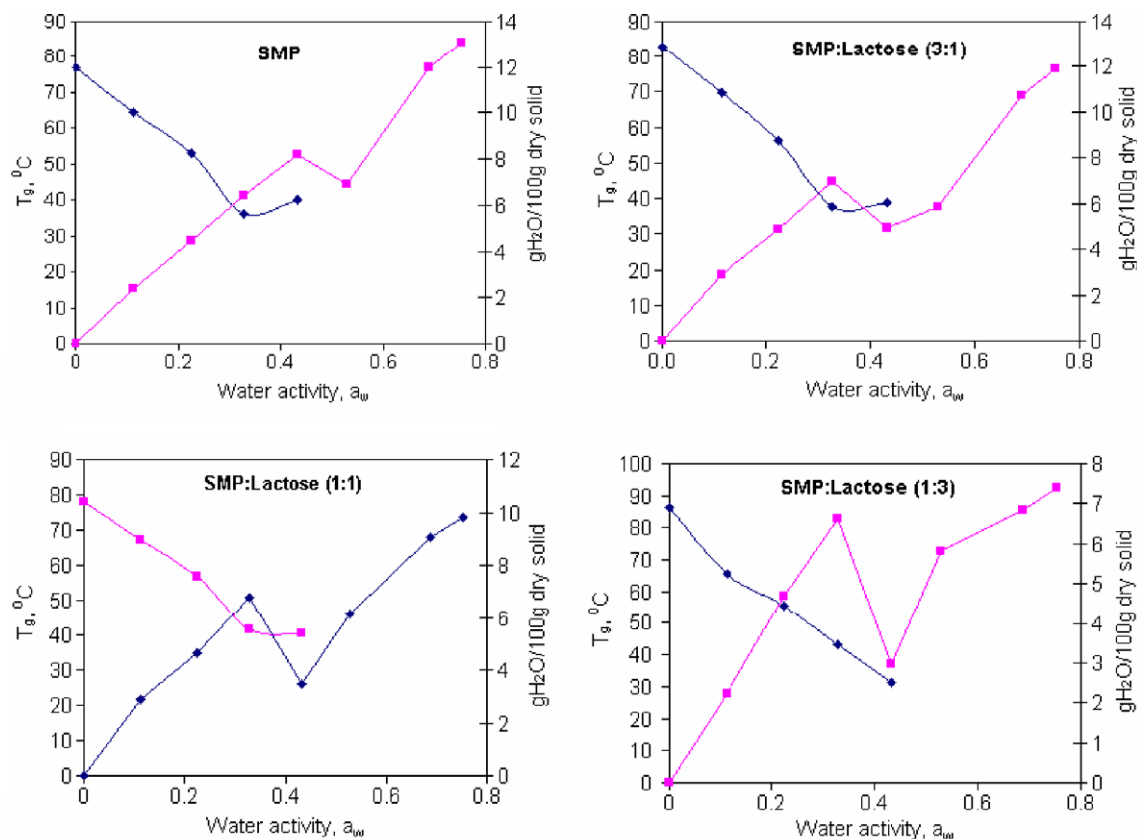
Fig. 3. Moisture sorption behaviour and glass transition temperatures of SMP and SMP/lactose mixtures humidified at various water activities; moisture (■) and glass transition temperature (◆).

face of the SMP and SMP:lactose (3:1 and 1:1) powders had almost similar amounts of protein and fat and these were a little bit different in SMP:lactose (1:3). Since these milk powders were humidified for 3 weeks in saturated salt solutions, the components at the surface might have saturated within a few hours or days and the entire body of the milk particle was involved in the water sorption. Jouppila and Roos (1994a) reported that increased fat (or decreased solid non-fat, SNF) in milk powders significantly reduced the water sorption rate at a corresponding relative humidity. Fat is reported to delay the crystallization of lactose in milk powders (Jouppila & Roos, 1994a); however, it does not affect water sorption by the hydrophilic components (Iglesias & Chirife, 1977). However, it is difficult to claim an effect of surface fat on water sorption in the present study as the original fat content in SMP is very low (1%) and there is very little difference in the percentage of surface covered with fat for all the products.

Fig. 3 shows that increasing the lactose content in SMP lowers the water activity at which crystallization starts. For example, in SMP, crystallization commenced at $a_w \geqslant 0.432$ but in the other three lactose-enriched powders, crystallization occurred at $a_w \geqslant 0.328$. This must be due to interference of protein in the crystallization of lactose. This result is in accord with our previous findings where a_w at which crystallization occurred shifted upwards with an increase in concentration of protein in spray-dried lactose/hydrolyzed whey protein isolate (HWPI) powders: crystallization occurred at $\geqslant 0.432$ for lactose and lactose:HWPI (4:1), at $\geqslant 0.529$ for lactose:HWPI (3:2), at $a_w \geqslant 0.75$ for lactose:HWPI (2:3) and no crystallization at all for lactose:HWPI (1:4) kept at $a_w \approx 1.0$ (Shrestha, Adhikari, Howes, & Bhandari, 2005). Haque and Roos (2004) also reported shifting of a_w to higher levels when proteins were added to lactose. Table 3 also shows that, after crystallization at $a_w \geqslant 0.432$, water content remained significantly ($p > 0.05$) higher for SMP than for other low protein milk powders. This result is also consistent with previous findings by Shrestha et al. (2005) and Haque and Roos (2004). The protein components in SMP/lactose mixtures might have absorbed much of the water remaining after lactose crystallization, which resulted in increased water content in the high protein SMP powders. This finding certainly shed some light on interaction of moisture in standardized SMPs that can have implications for processing and storage performance of low protein SMP powders and the products based on such powders. The high protein SMP may offer better stability to the milk powder as less water would be available to the lactose fraction for plasticization and subsequent crystallization, agglomeration and a resulting sticky product.

3.3. Glass transition temperature (T_g) of SMP/lactose mixtures

The T_g values of spray-dried SMP and SMP/lactose mixtures at corresponding moisture contents are given in Table 4 (and also in Fig. 3). The T_g values of the dry SMP and SMP/lactose were slightly lower than those of SMP or pure lactose reported by other investigators (Hill, Craig, & Feely, 1998; Jouppila & Roos, 1994b; Roos & Karel, 1990). This could be due to improper drying or absorption of moisture by milk powders during handling. Fig. 3 shows a typical gradual and almost linear decrease of T_g values with the increase in water content, up to a_w 0.432. Comparison of T_g values, between the SMP and all SMP/lactose mixtures at similar water activities, showed no significant change in T_g values. Since lactose is the major ingredient of SMP and SMP/lactose mixtures, less change in T_g was expected when lactose was added to SMP. In bulk composition, protein content of milk powder decreased from 34% in SMP to 9% in SMP:lactose (1:3) whereas, on the surface of the powder, it remained almost unchanged at about 60%. Proteins are large molecules that may have some effect on glass transition behaviour of small molecules such as lactose. Our previous study (Shrestha et al., 2005) also showed that proteins (from whey) form incompatible mixtures with lactose with very little interaction between each other and do not affect the T_g value of lactose when measured by DSC.

Fig. 4 shows the DSC thermograms of SMP and SMP/lactose mixtures. It was noticed that increasing or decreasing protein concentration in SMP/lactose mixtures did not affect the endothermic relaxation peaks associated with glass transition of samples. Our previous study showed that when protein concentration is very high in milk powder system (~80% protein in hydrolyzed whey protein isolate/lactose mixtures), it is difficult to detect relaxation peak (and T_g), possibly due to very little change in specific heat capacity (C_p) at the given increment of temperature (Shrestha et al., 2005). However, no such effect was observed in the present study as SMP had 34% protein, much less than the previous study. The endothermic relaxation peaks of all samples kept at water activity 0.432 were very low. This is because all samples stored at this water activity absorbed maximum moisture (Table 3) and were on the verge of mass crystallization.

It is interesting to note very little change in T_g values of SMP and reduced protein milk powders humidified between 0.328 and 0.432 water activities, except in SMP:lactose (1:3) where a significant drop in T_g was observed. Jouppila and Roos (1994a) also reported a T_g value of 34 and 33 °C for SMP humidified at a_w 0.239 (5.6% moisture) and at a_w 0.330 (7.1% moisture), respectively. The levelling off of T_g value in this water activity range was most possibly due to uneven distribution of sorbed water between the amorphous and crystalline state of lactose and also with proteins present in the matrix.

Table 4
Glass transition temperatures (T_g) (°C) of SMP and SMP/lactose mixtures humidified at different water activities[a,b]

Water activity	SMP only			SMP:lactose (3:1)			SMP:lactose (1:1)			SMP:lactose (1:3)		
	Onset	Mid-point	Endset	Onset	Mid-point	Endset	Onset	Mid-point	Endset	Onset	Mid-point	Endset
0	73.9 ± 0.0a	76.9 ± 0.2a	80.0 ± 0.4a	80.1 ± 0.3b	82.8 ± 0.4b	85.6 ± 0.4b	74.6 ± 1.2a	78.2 ± 1.1a	81.9 ± 1.0a	83.9 ± 0.6b	86.5 ± 0.3c	89.3 ± 0.0c
0.113	61.0 ± 3.5a	64.3 ± 3.0a	67.8 ± 2.6a	64.6 ± 2.4a	69.6 ± 2.1a	74.2 ± 2.0a	63.7 ± 0.3a	67.1 ± 0.2a	70.9 ± 0.3a	63.2 ± 0.2a	65.6 ± 0.1a	67.9 ± 0.0a
0.225	51.0 ± 0.4a	53.0 ± 0.3a	54.9 ± 0.1a	54.3 ± 1.2ab	56.3 ± 1.2ab	58.2 ± 1.2ab	55.1 ± 0.0b	57.0 ± 0.1a	58.8 ± 0.1b	53.4 ± 0.1ab	55.4 ± 0.1ab	57.4 ± 0.1ab
0.328	32.4 ± 0.3a	36.3 ± 1.0a	40.0 ± 1.3a	34.4 ± 1.0a	37.8 ± 0.6a	41.3 ± 0.5ab	38.3 ± 0.1b	41.5 ± 0.2b	44.6 ± 0.2bc	40.0 ± 0.1b	43.0 ± 0.1b	46.0 ± 0.2c
0.432	34.9 ± 0.5b	39.9 ± 0.6b	45.9 ± 1.3a	34.9 ± 1.9b	38.9 ± 2.1ab	43.9 ± 2.9a	37.2 ± 0.4b	40.5 ± 0.2b	48.8 ± 0.4a	26.5 ± 1.5a	31.4 ± 1.3a	40.1 ± 0.5a

[a] Mean values ± standard deviation of triplicate samples.
[b] Values followed by same letter within a row for onset, mid-point and endset of each sample do not differ significantly ($p > 0.05$).

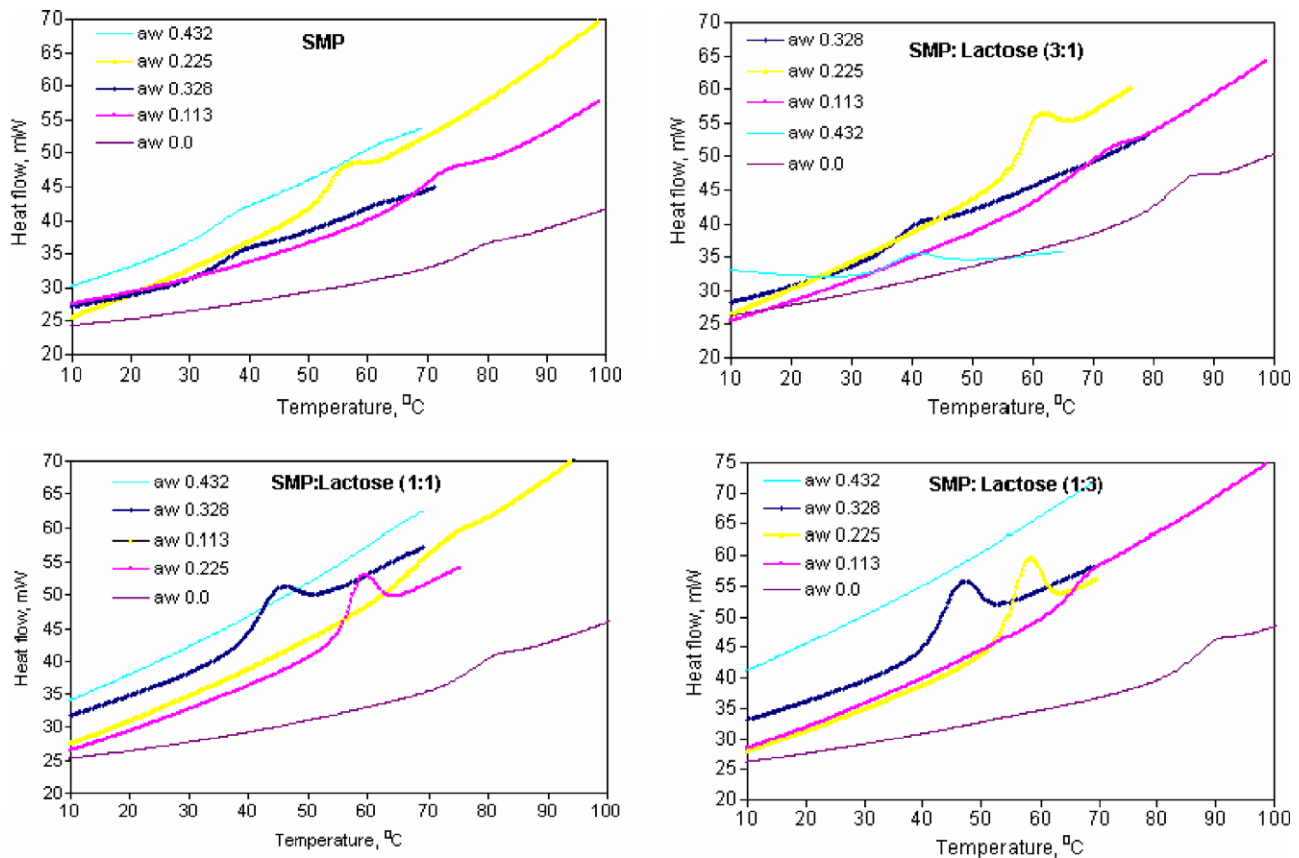Fig. 4. DSC thermograms showing (T_g) of SMP and SMP/lactose mixtures humidified at various water activities (shown in order as given in each figure).

The T_g value of SMP or SMP/lactose mixtures is solely contributed by amorphous lactose which, on the other hand, is largely influenced by the amount of sorbed water. Although the amounts of sorbed water may appear different, e.g., 8.2%, 5% and 3.5% in SMP, SMP:lactose (3:1) and SMP:lactose (1:1), respectively, the amount of water in amorphous lactose may be the same in that particular range of water activity, giving almost similar T_g values. However, if the amount of protein is too low in standardized SMP, such as in SMP:lactose (1:3) at higher humidity, the lactose fraction would have much of the sorbed water, causing more decline in T_g. This product is more likely to be sticky and less stable during processing/storage. This study clearly shows that, except at higher lactose content and at humidity >0.43, the addition of lactose to SMP does not affect the T_g values of the mixtures.

4. Conclusions

This paper investigated the effects of spray-drying on the surface composition of skim milk powders with various protein levels and their sorption as well as glass transition temperatures. X-ray photoelectron spectrophotometry (XPS) revealed that fat and proteins are more likely to migrate toward the surface of the spray-dried powders than is lactose. Decrease in protein or increase in lactose level in milk powders increased the rate of water absorption. It also lowered the water activity range at which the crystallization

occurred, e.g., $a_w \geqslant 0.328$ instead of 0.428 for SMP. However, changing the composition of SMP did not affect the glass transition temperatures of the powders unless the protein content of SMP significantly decreased, such as in SMP:lactose (1:3).

Acknowledgements

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