Title	Influence of pre-crystallisation and water plasticization on flow properties of lactose/WPI solids systems
Author(s)	Li, Runjing; Roos, Yrjö H.; Miao, Song
Publication date	2016-03-03
Original citation	Li, R., Roos, Y. H. and Miao, S. (2016) 'Influence of pre-crystallisation and water plasticization on flow properties of lactose/WPI solids systems', Powder Technology, 294, pp. 365-372. doi: 10.1016/j.powtec.2016.02.047
Type of publication	Article (peer-reviewed)
Link to publisher's version	https://www.sciencedirect.com/science/article/pii/S0032591016300894 http://dx.doi.org/10.1016/j.powtec.2016.02.047 Access to the full text of the published version may require a subscription.
Rights	**© 2016, Elsevier B.V. All rights reserved. This manuscript version is made available under the CC BY-NC-ND 4.0 license.** https://creativecommons.org/licenses/by-nc-nd/4.0/
Item downloaded from	http://hdl.handle.net/10468/8040

Influence of pre-crystallisation and water plasticization on flow properties of lactose/WPI solids systems

Runjing Li[1, 2], Yrjö H. Roos[2], Song Miao[1*]

[1] *Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland*

[2] *School of Food and Nutritional Sciences, University College Cork, Cork, Ireland*

*Corresponding author:
Tel.: +353 25 42468
Fax: +353 25 42340
E-mail address: song.miao@teagasc.ie

Abstract

This study investigated the influence of pre-crystallisation and water plasticization on flow properties of lactose/ whey protein isolate (WPI) solids systems. Powder characteristics of lactose/WPI mixtures with different amount of α-lactose monohydrate (1.01%, 11.18%, 29.20%, and 46.84%, w/w) were studied. Dairy powders with higher amounts of crystalline lactose showed larger tapped bulk density and particle density. Morphological characteristics study indicated dairy solids with higher crystallinity had less rounded shape and rougher surface. Increasing protein content or crystalline lactose content could decrease the molecular mobility of dairy solids. Flow function tests indicated that dairy solid with 11.18% crystallinity was more easy-flowing than lactose/WPI mixtures with 1.01%, 29.20% and 46.84% crystallintiy at 0% and 44% relative humidity (RH) storage conditions. Furthermore, dairy solids with higher amount of crystalline lactose showed better resistance to develop cohesive at high RH storage conditions. The friction angle of dairy solid with 1.01% crystallinity increased with increasing water content, while friction angles of lactose/WPI mixtures with higher crystallinity decreased with increasing water content.

Keywords: Pre-crystallisation; Crystallinity; Mechanical properties; Flow properties

1. Introduction

Flow properties of spray-dried dairy solids are very important in handling and processing operations [1,2]. Previous studies indicated that flow properties depend on the composition and physical properties of powders, such as particle size and shape, surface structure, amorphous lactose content, and water content [3-8]. Stickiness and caking of powders usually result from formation of liquid bridges between individual particles [9], and they are responsible for impaired flow properties [10]. Many studies showed that powders with greater amounts of amorphous components, such as amorphous lactose, were more sensitive to absorbing moisture, giving rise to lumping and caking problems [2,4,11,12,13].

Lactose in dairy systems can exist in various crystalline and non-crystalline forms. The crystalline state is a solid state having molecules well arranged in regular lattice. For lactose in amorphous state, the molecular arrangement is disordered. Amorphous lactose is thermodynamically unstable and hygroscopic, absorbing moisture from the surroundings and subsequently plasticizing, while crystalline lactose is thermodynamically stable and significantly less hygroscopic. Reducing stickiness in materials can be achieved through partial or complete crystallisation of sticky components [14]. Bronlund and Paterson [15] stated that crystalline lactose absorbed approximately 100 times less water than amorphous lactose in the same conditions. Therefore, pre-crystallizing those amorphous materials during processing may help to resolve the problem of product stickiness and stability during subsequent storage [16].

Since lactose is around 70% of the dry matter in whey powder, the hygroscopicity of lactose makes whey powder become sticky and adhere to the chamber walls during spray drying [17]. Pre-crystallisation of lactose in whey concentrates before drying is a successful remedial measure in manufacturing process, and is widely used in the production of whey powder in dairy industry [18]. Powder hygroscopicity and caking are brought under control by lowering the level of amorphous lactose.

Moreover, previous studies indicated that particle shape affected the bulk behaviour and flow properties of dairy solids [5,19]. According to the study of Thomas et al. [20], morphological changes, such as surface deformation, occurred due to the build-up of lactose crystals in dairy powders. This difference in the particle shape of crystalline lactose and amorphous lactose may influence the flow properties of dairy powders and subsequently affect the handling and processing operations. Thus, comparing with amorphous lactose, crystalline lactose shows different physical properties and water sorption behaviour during processes of production and storage [15,19], which may finally influence the flow properties of dairy solids.

However, how pre-crystallisation and crystalline components content, such as α-lactose monohydrate, affect the flow properties of dairy solids has not been reported so far. The objectives of this study were to investigate the effect of crystalline lactose content on the flow properties of lactose/whey protein isolate (WPI) solids systems. Pre-crystallisation of lactose before spray drying was used to prepare dairy solids with different amounts of crystalline lactose in this study.

2. Materials and methods

2.1. Materials

α-lactose monohydrate (> 99% purity) was kindly donated by Arla Foods Ingredients (Sønderhøj 10-12, 8260 Viby J, Denmark). WPI, containing 71% β-lactoglobulin and 12% α-lactalbumin, was obtained from Davisco Food International (Le Sueur, MN, USA).

Aluminum oxide calcined powder and α-lactose (≥ 99% purity) were purchased from Sigma−Aldrich (St. Louis, MO, USA).

2.2. Powder preparation

Solution of lactose and lactose/WPI mixtures at the ratio 4:1 were prepared in de-ionized water at 65 °C in a water bath for 2 h with a stirring speed of 500 rpm. The total solid concentration of lactose and lactose/WPI mixtures solution was 40% (w/w). Then the solution of lactose/WPI mixtures was cooled to room temperature (20-22 °C) and kept at room temperature (20-22 °C) for different hours to pre-crystallise. The stirring speed was 150 rpm during pre-crystallisation. The pre-crystallisation time for lactose/WPI mixtures was 0, 3, 15 and 20 h, respectively. They were defined as S2 (0 h), S3 (3 h), S4 (15 h) and S5 (20 h) according to the pre-crystallisation time. Pure lactose without pre-crystallisation and WPI were defined as S1 and S6, repectively. They were all spray-dried by an ANHYDRO spray dryer with a centrifugal atomizer (Copenhagen, Denmark) at the Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland. The inlet air temperature was around 170 ± 2 °C and the outlet temperature around 90 ± 2 °C. Spray-dried solids were kept immediately in evacuated desiccators over P_2O_5 at room temperature. Each analysis was carried out within three months after spray-drying.

2.3. Powder characterisation

2.3.1. Determination of α-lactose monohydrate content in spray-dried lactose/WPI mixtures

The content of α-lactose monohydrate (%C°) in spray-dried lactose/WPI mixtures was determined according to the method of Schuck and Dolivet [21]. In this study, the content of α-lactose monohydrate was used to represent the crystallinity of dairy solids. The water of crystallisation (%) of a powder is the difference between total water and non-bound water. The formula is as below:

$$\% C^{o} = (BWL*19/L)*100 \quad (1)$$

Where
BWL: bound water content in the lactose (g/kg);
L: lactose content (g/kg).

The bound water content in lactose was calculated according to the following formula:

$$BWL=TW-FW-(0.005*WPC) \quad (2)$$

Where
BWL: bound water content in lactose (g/kg);
TW: total water content (g/kg);
FW: non-bound water content (g/kg);
WPC: whey protein content (g/kg); 0.005: 0.50 g of bound water per 100 g of whey protein.

Non-bound water content of lactose/WPI mixtures was measured using GEA Niro analytical method A 1 c [22]. The total water content of lactose/WPI mixtures was determined using a Karl Fischer Titration (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Each analysis was carried out in triplicate.

2.3.2. Powder characteristics

Water content was determined using an HR83 Hologen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland). Powder particle size distribution and specific surface area (SSA) were determined by laser light scattering using a Malver Mastersizer 3000 (Malvern Instruments Ltd., Worcestershire, UK). Powder sample was added to the standard venturi disperser with a hopper gap of 2.5 mm and then fed into the dispersion system. Compressed air at 0.75 bar was used to transport and suspend the powder particles through the optical cell. A measurement time of 10 s was used, and background measurements were made using air for 20 s. The laser obscuration level was at 2-10%.

2.4. Bulk density, particle density and porosity

Loose and tapped (100 taps) bulk densities (ρ_{tapped}) of lactose/WPI solids systems was measured as per GEA Niro [23], using a Jolting volumeter (Funke Gerber, Berlin, Gerrmany). Particle density (ρ_p) was measured as per GEA Niro [24], using a Gas Pycnometer (Accupyc II 1340 Gas Pycnometer, Micromeritics Instrument Corporation, USA). Since the definition of porosity of a porous media corresponds to extra particle void space, the corresponding porosity of dairy solids was calculated as Eq. (3):

$$\varepsilon = 1 - \rho_{tapped} / \rho_p \qquad (3)$$

2.5. Morphological characteristics

Morphological characteristics were determined using a Malvern Morphologi G3 S (Malvern Instruments Ltd, Worcestershire, UK). 5 mm^3 volume powder samples were dispersed on the glass plate. 2.5× objective was used for the measurement in this study. Circularity, convexity and elongation are three commonly used shape factors. One way to measure shape is to quantify how close the shape is to a perfect circle. Circularity is the ratio of perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Several definitions of circularity could be used but for accuracy the software reports HS Circularity (HS for high sensitivity) in addition to circularity. Circularity has values in the range 0-1. A perfect circle has a circularity of 1 while a 'spiky' or irregular object has a circularity value closer to 0. Circularity is sensitive to both overall form and surface roughness. Elongation is defined as [1-aspect ratio] or [1- width/length]. As the name suggests, it is a measure of elongation and again has values in the range 0-1. A shape symmetrical in all axes, such as a circle or square, has an elongation value of 0; shapes with large aspect ratios have an elongation closer to 1. Convexity is a measurement of the surface roughness of a particle. It is calculated by dividing the convex hull perimeter by the actual particle perimeter. A smooth shape has a convexity of 1 while a very 'spiky' or irregular object has a convexity closer to 0. In this study, each sample was measured in triplicate to get the average value.

2.6. Powder preparation for flow function test

Two moisture levels of lactose/WPI solids systems were prepared in a vacuum oven (OV-12, Medline Industries, Inc., Mundelein, Illinois, USA). For dairy solids with low moisture (LM) content, the powders were placed in a vacuum oven at 45 °C for 36 h. For dairy solids with high moisture (HM) content, spray-dried dairy solids were firstly dried at 45 °C in a vacuum oven for 36 h, and then equilibrated over saturated K_2CO_3 solution (giving 44% relative humidity) at 25 °C for 48 h in a vacuum oven. During equilibration, all powders were put in petri dishes with thickness around 8 mm. The final water content was measured in triplicate using an HR83 Hologen Moisture Analyzer (Mettler Toledo International Inc., Im Langacher Greifensee, Switzerland) before measuring the flow properties.

2.7. Glass transition

Glass transition temperatures, T_g (onset), of lactose and lactose/WPI mixtures were determined using a differential scanning calorimeter (DSC Q2000, TA Instruments, Crawley, UK). 10-15 mg of dairy solids was transferred to DSC aluminium pans (Tzero pan and lid, Switzerland). Then DSC pans were hermetically sealed and samples were analysed. An empty pan was used as a reference. At the first scan, the samples were heated over the glass transition temperature region at 5 °C/min and then cooled at 10 °C/min to below glass transition, a 2nd heating scan was then run to above the glass transition temperature at 5 °C/min. All measurements were carried out in duplicate. Glass transition temperatures were determined using TA universal analysis software, version 5.1.2 (TA Instruments, Crawley, UK).

2.8. Dynamic mechanical analysis

A dynamic mechanical analyser (DMA Q800, TA Instruments, Crawley, UK) was used, in conjunction with a gas cooling accessory (GCA) tank, to determine dynamic mechanical properties of spray-dried dairy solids. A rectangular stainless steel powder holder was designed to generate a defined geometry to contain powder with inner dimensions of 60 mm × 11 mm × 1 mm. A pre-weighed mass of dairy solids mixed with aluminum oxide calcined powder at the ratio of 4:1 was evenly spread within this shallow container, and the upper lid was then placed onto the top surface of the powder [25]. As aluminum oxide calcined powder showed no effect on mechanical property results of dairy solids, it was added to protect dairy powder from sticking on the powder holder during the heating test. The sample holder was mounted in the instrument in a dual cantilever clamp so that during measurement, the DMA oscillated the sample perpendicularly to the base plane of the sample holder by a vertical motion of the middle clamp. The measurements were made at a heating rate of 2 °C /min from 0 to 140 °C for dairy solids with low moisture content and from 0 to 120 °C for dairy solids with high moisture content. DMA was operated by a sinusoidal deformation applied to the powder sample holder at a fixed strain. The amplitude was 15 μm. During dynamic heating, the samples were analysed for storage modulus (E’) and loss modulus (E’’) using single frequency 1 Hz.

2.9. Powder flow testing

The flow function of lactose/WPI solids systems was determined using a Powder Flow Tester (PFT) (Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). The axial and torsional speeds for the PFT were 1.0 mm/s and 1 rev/h, respectively. Samples were filled into the aluminium trough of the annular shear cell at room temperature (22-25 °C). Curved- or flat-profiled shaping blades were used to level the powder surface in the trough for flow- or wall fiction-testing, respectively. The mass of the powder was recorded before testing, with axial distance between the lid and the powder used to calculate changes in the volume of powder during testing. Vane- or flat-profiled lids were attached to compression plate of the PFT for flow- or wall friction-testing. Flowability, cohesion and bulk density were measured using standard flow function test. Friction angle was determined using standard wall friction test. For standard flow function test, the involved uniaxial normal stresses were between 0.2 and 4.8 kPa. For standard wall friction test, ten normal stresses, between 0.4 and 4.8 kPa, were applied to measure the wall friction angles.

2.10. Statistical analysis

Measurement of glass transition, and dynamic mechanical analysis were performed in duplicate, with all other analysis performed in triplicate. Results were expressed as mean ± standard deviations (SD). One-way analysis of variance (ANOVA) was used to determine the significant differences between the mean values of each test (Microsoft Office Excel 2010, Microsoft, Inc., WA, USA). A significance level of $P < 0.05$ was used throughout the study.

3. Results and discussion

3.1. Powder characterisation

The powder characteristics of lactose/WPI solids systems are shown in Tab. 1. The amount of crystalline lactose for lactose/WPI mixtures (S2-S5) increased with increasing the pre-crystallised time (Tab. 1). After pre-crystallisation, four kinds of lactose/WPI mixtures with different amounts of α-lactose monohydrate were ready for analysis. As the amount of crystalline lactose was defined as the crystallinity of dairy solids in this study, the crystallinity of lactose/WPI mixtures (S2-S5) were 1.01%, 11.18%, 29.20% and 46.84%, respectively. Lactose (S1) was spray-dried without pre-crystallisation and was assumed to be in the amorphous form. Particle size study showed that the particle size of S3, S4, and S5 was higher than S2 (Tab. 1), which indicated that pre-crystallisation increased the particle size of dairy solids. As specific surface area (SSA) values are typically inferred from particle size data, S2 with 1.01% crystallinity showed the largest SSA value, while WPI powder gave the smallest SSA value. It is well known that particle size influences flowability [6,26]. For example, fine particles tend to be more cohesive and therefore less free-flowing, whereas larger particles tend to be free flowing. Moreover, according to Fitzpatrick et al. [26], the increased surface area per unit mass of powder means more surface area is available for cohesive forces and frictional forces to resist flow. Therefore, the difference in particle size and SSA values of lactose/WPI mixtures with different crystalline lactose content might affect their flowability.

Powder density is an important characteristic for calculating the capacity of packaging materials, containers, hoppers, bins, silos, and also for filling of the die of tableting machines and for capsule filling. Pure lactose (S1) had the largest bulk density and particle density, and the smallest porosity, while WPI powder (S6) gave the opposite results (Tab. 1). For lactose/WPI mixtures (S2-S5), dairy solids with higher amount of crystalline lactose showed larger loose bulk density, tapped bulk density and particle density (Tab. 1). Furthermore, dairy solids with higher crystallinity showed lower porosity (Tab. 1).

3.2. Morphological characteristics

The particle shapes of lactose/WPI solids systems were investigated using a Morphologi G3 S. The Morpholigi G3 S reports a number of particle shape factors. In this study, three morphological characteristics (circularity, elongation and convexity) were used to identify the particle shape of lactose/WPI solids systems. The results in Tab. 2 showed that particles of pure lactose (S1) were more circular than those of lactose/WPI mixtures and WPI. The circularity of particle shape of lactose/WPI mixtures decreased as the crystallinity increased.

Moreover, particle shape of S5 with the highest amount of crystalline lactose had the lowest ratio of width/length and the roughest surface. Those results indicated dairy solids with higher amount of crystalline lactose had less rounded shape, and rougher surface. Fu et al. [19] stated that particle shape significantly affected the flow characteristics of powder over a wide range of stress conditions. Powders consisting of regularly shaped particles flow better than those consisting of irregular shaped particles. Thus, different particle shape of lactose/WPI solids systems may link to their flow behaviours in this study.

3.3. Glass transition

After storage at different humidity conditions, lactose/WPI solids systems with different moisture content were prepared (Tab. 3). There was no trend for the water content of lactose/WPI mixtures with different crystallinity after storage at 44% RH, which might be due to the presence of WPI in dairy powders weakening the effect of crystalline lactose on water sorption behaviour of lactose/WPI mixtures. Water activities of lactose/WPI solids systems with low moisture (LM) content and high moisture (HM) content was around 0.11 a_w and 0.33 a_w, respectively (Tab. 3). Lactose and lactose/WPI mixtures showed significant difference in their glass transition temperatures after storage at different relative humidity conditions (Tab. 3). Water plasticization depressed glass transition temperatures of lactose and lactose/WPI mixtures. For lactose/WPI mixtures (S2-S5), S5 showed the lowest water content after storage at 44% RH, which resulted in the highest T_g value of S5. This might be due to the different water sorption behaviour of amorphous lactose and crystalline lactose. Similar results were also stated by Fitzpatrick et al. [4]. According to their study, the powders with larger amount of amorphous lactose were more sensitive to absorbing moisture when in intimate contact with air. According to Fitzpatrick et al. [2], powders with amorphous components, such as amorphous lactose, may become sticky if the powder temperature is elevated above the components glass transition temperature and into the sticky temperature region. This can lead to the powder becoming much more cohesive and eventually caking, and can also cause a powder to adhere more to a surface. These indicated dairy solids with 46.84% crystallinity sorbed less water during storage, which might give higher T_g values and protect them from stickiness and caking.

3.4. Mechanical properties

The mechanical properties of lactose/WPI solids systems storage at 0% and 44% RH were measured using a DMA. Mechanical α-relaxation of lactose/WPI solids systems occurred above the glass transition and was observed from a decrease in storage modulus and a peak in the loss modulus (Fig. 1). At temperatures above the glass transition, large changes in viscoelastic properties were expected [27,28]. The storage modulus of lactose/WPI solids systems decreased slowly in the amorphous state, while it dropped sharply from the original value at the glassy state to the value at the rubbery state in the glass transition region (Fig. 1A1 and 1B1). There was minor differences in the magnitude of storage modulus change for lactose/WPI mixtures with low moisture content, while pure lactose (S1) with low moisture content showed the most significant change in its storage modulus at the glass transition region (Fig. 1A1). All dairy solids sorbed much water from air during storage at 44% RH (Tab. 3), which resulted in lactose/WPI solids systems showed more significant change in their storage modulus at the glass transition region. The storage modulus of pure lactose still showed the most significant change after storage at 44% RH (Fig. 1B1). However, for lactose/WPI mixtures, S5 with the highest crystallinity showed the smallest change of storage modulus during the glass transition region (Fig. 1B1). Comparing S2 and S5, S2 with lower crystallinity showed higher magnitude of storage modulus change than S5. The magnitudes of modulus changes indicated mechanical α-relaxations which were relative to molecular mobility [28,29]. Higher molecular mobility could contribute to the formation of inter-particle bridges and stickiness [9,28]. Consequently, water plasticization could increase molecular mobility of dairy solids, while increasing protein content or crystalline lactose content of dairy solids could decrease the molecular mobility of dairy solids. In other words, increasing protein content or crystalline lactose content might help dairy solids to delay the formation of stickiness and caking and keep them free-flowing.

Stiffness of materials refers to the ability to carry stress without changing dimension [30]. For the measurement of unconstrained uniaxial tension or compression, Young's modulus can be as a measure of the stiffness of a material. In this study, the change of storage modulus could reflect the change of stiffness for dairy solids. The stiffness of spray-dried dairy solids showed the same trend in change as storage modulus did when temperature increased from 0 to 120 °C. The results of storage modulus indicated that dairy solids with higher crystallinity were stiffer at high moisture content, which might help dairy solids to maintain their flowability after storage at high relative humidity environment.

The changes of loss modulus for lactose/WPI solids systems are shown in Fig. 1A2 and 1B2. Loss modulus of lactose/WPI solids systems showed minor changes in the amorphous state and the rubbery state, while they increased dramatically and reached the peak values in the glass transition region (Fig. 1B1 and 1B2). The magnitudes of loss modulus increased with increasing water content of lactose/WPI solids systems. Although S2 and S5 showed similar water content after storage at 44% RH, S5 with the highest amount of crystalline lactose showed smaller magnitude of loss modulus change. In addition, in this study, the α-relaxation temperatures, T_α, were taken from the temperatures of loss modulus peak (Tab. 3). T_α values of lactose and lactose/WPI mixtures decreased as moisture content increased. S5 showed the highest T_α values, which might be due to its highest crystallinity and lower moisture content. Those results of storage modulus and loss modulus indicated that the crystallinity of dairy solids affected the mechanical properties of dairy solids.

3.5. Flow properties

Standard flow function test and standard wall friction test of lactose/WPI solids systems were conducted using a Powder Flow Tester. The flowability results are shown in Fig. 2. According to Schulze [6], the flowability of powders is usually stress-dependent. For lactose/WPI solids systems with low moisture content, they were easy-flowing or cohesive when the major principle consolidating stress was below 3 kPa, while they were all easy-flowing at major principle consolidating stress > 3 kPa (Fig. 2A). However, for dairy solids with high moisture content, lactose/WPI mixtures with 1.01%, 29.20% and 46.84% amount of crystalline lactose fell into cohesive area even when major principle consolidating stress was over 8 kPa. Therefore, increasing water content decreased flowability of dairy solids, which might be due to the increase in liquid bridges and capillary forces acting between the powder particles. For lactose/WPI mixtures (S2-S5), S3 with 11.18% crystallinity showed more easy-flowing than S2, S4 and S5 after storage at 0% and 44% RH. This could also be derived from the flow index results (Tab. 4). S3 gave higher flow index values than other lactose/WPI mixtures. S4 and S5 with higher amount of crystalline lactose did not show better flowability than S3. According to Fitzpatrick et al. [4], this might be due to the high amount of crystalline lactose for S4 and S5, which gave rise to greater frictional resistance between the particles or the differences in surface moisture contents of crystalline and amorphous lactose producing differences in cohesion due to liquid bridging. In addition, S4 and S5 had smaller particle size and larger SSA values than S3 (Tab. 1), which meant they had more surface area for cohesive forces and frictional forces to resist flow. Furthermore, morphological study showed that dairy solids with lower crystallinity had more rounded shape, and smoother surface (Tab. 2), which might result that S3 was more easy-flowing than S4 and S5.

In addition, for lactose/WPI mixtures with low moisture content, S5 had a significant higher ($P < 0.05$) critical stress value than other lactose/WPI mixtures (S2, S3, and S4) (Tab. 4), indicating that it had a tendency to develop cohesive arches which required greater stress to collapse [6,8]. However, after storage at 44% RH, S5 gave a significant lower critical stress value than other lactose/WPI mixtures (S2, S3, and S4). Moreover, $D_{arching}$ value of S5 with low moisture content was significant higher than other lactose/WPI mixtures (S2, S3, and S4), while S5 gave the opposite result after storage at 44% RH. As a result, S5 with the highest crystallinity showed the smallest change in its critical stress and $D_{arching}$ value with increasing water content. It was clear from these results that dairy solids with higher crystallinity showed better resistance to develop cohesive when storage at high relative humidity conditions.

The bulk densities of lactose/WPI solids systems increased as major principle consolidating stress increased (Fig. 3). All dairy solids became compressed on the application of increasing major principle consolidating stress. There was only minor difference in the bulk density of lactose/WPI mixtures with different crystallinity. Increasing water content decreased the bulk density of lactose (S1) significantly, while the bulk densities of lactose/WPI mixtures and WPI solids only showed minor decrease.

Wall friction is the dominant parameter in determining the minimum hopper angle (between the hopper wall and the horizontal) required to ensure mass flow. In this study, the wall friction angles of lactose/WPI solids systems were also determined at different normal stresses using standard wall friction test (Fig. 4). For lactose/WPI mixtures with low moisture content, friction angles increased as crystallinity was increased at 0.483 kPa (Fig. 4A).

However, for lactose/WPI mixtures with high moisture content, the friction angles decreased with increasing crystallinity at 0.483 kPa (Fig. 4B). Comparing the friction angles of dairy solids with different water content (Fig. 4A and 4B), the friction angles of S2 increased with increasing water content, and the friction angles of S3, S4, and S5 decreased with increasing water content. This might be due to that amorphous powders (S2) were more cohesive with increasing water content. However, for S3, S4, and S5, the increased moisture might act as a lubricant and decreased friction angles for partially crystallised powders [4].

Additionally, the effective angles of internal friction (δ_J) for lactose/WPI solids systems are also shown in Tab. 4. δ_J values of lactose/WPI solids systems increased with increasing water content. For lactose/WPI solids systems (S1-S6) with low water content, pure lactose (S1) showed the smallest δ_J and WPI (S6) showed the largest δ_J, while the opposite result was shown as water content increasing (Tab. 4). This result indicated increasing protein content decreased the effect of water plasticization on the internal friction of dairy solids.

4. Conclusions

As amorphous lactose and crystalline lactose show different physical and mechanical properties, this study investigated the influence of crystalline lactose content and water plasticization on the flow properties of lactose/WPI solids systems. Particle size study indicated that pre-crystallisation increased the particle size of dairy powders. SSA values results showed that S2 with 1.01% crystallinity gave the largest SSA value, while WPI powder showed the smallest SSA value. For lactose/WPI mixtures (S2-S5), dairy solids with higher crystallinity had larger loose bulk density, tapped bulk density and particle density, whereas they gave lower porosity. Moreover, the crystallinity of dairy powders had a minor effect on the particle shape. Those differences in particle size, SSA, bulk density, particle density and particle shape resulting from the crystallinity might affect their flow properties.

The results of mechanical property study indicated that water plasticization could increase molecular mobility of dairy solids, while increasing protein content or crystalline lactose content of dairy solids might decrease the molecular mobility of dairy solids and maintain their stiffness. Therefore, the presence of protein or crystalline lactose might protect dairy solids from stickiness and caking at high relative humidity conditions. Flow function test showed that for lactose/WPI mixtures with different crystallinity, S3 with 11.18% crystallinity was more easy-flowing than S2 (1.01% crystallinity), S4 (29.20% crystallinity) and S5 (46.84% crystallinity) at 0% and 44% RH storage conditions. Increasing water content reduced the flowability of dairy solids with different levels of crystalline lactose. Moreover, dairy solids with higher crystallinity showed better resistance to develop cohesive when they were at high relative humidity conditions. The friction angles of dairy solids with higher crystallinity (S3, S4, and S5) decreased with increasing water content, while the friction angles of S2 increased with increasing water content. Since pre-crystallisation of lactose is widely used in the production of dairy powders, the findings in this study will be very useful in handling and processing of dairy powders.

5. Acknowledgement

This study was supported financially by the Food Institutional Research Measure (FIRM) of the Department of Agriculture, Food and Marine, Ireland, under the project 11-F-001 entitled ‘Formulation and Design for Food Structure and stability’.

Reference

[1] T. M. Knowlton, G. Klinzing, W. Yang, J. Carson, The importance of storage, transfer, and collection, Chemical Engineering Progress;(United States). 90 (1994) .

[2] J. Fitzpatrick, M. Hodnett, M. Twomey, P. Cerqueira, J. O'Flynn, Y. H. Roos, Glass transition and the flowability and caking of powders containing amorphous lactose, Powder technology. 178 (2007) 119-128.

[3] E. H.-J. Kim, X. D. Chen, D. Pearce, Effect of surface composition on the flowability of industrial spray-dried dairy powders, Colloids and Surfaces B: Biointerfaces. 46 (2005) 182-187.

[4] J. Fitzpatrick, K. Barry, P. Cerqueira, T. Iqbal, J. O’neill, Y. H. Roos, Effect of composition and storage conditions on the flowability of dairy powders, International Dairy Journal. 17 (2007) 383-392.

[5] R. Li, Y. H. Roos, S. Miao, The effect of water plasticization and lactose content on flow properties of dairy model solids, Journal of Food Engineering. 170 (2015) 50-57.

[6] D. Schulze, Powders and bulk solids: behavior, characterization, storage and flow, Springer Science & Business Media, 2007.

[7] D. Janjatović, M. Benković, S. Srečec, D. Ježek, I. Špoljarić, I. Bauman, Assessment of powder flow characteristics in incoherent soup concentrates, Advanced Powder Technology. 23 (2012) 620-631.

[8] S. V. Crowley, I. Gazi, A. L. Kelly, T. Huppertz, J. A. O’Mahony, Influence of protein concentration on the physical characteristics and flow properties of milk protein concentrate powders, Journal of Food Engineering. 135 (2014) 31-38.

[9] M. Peleg, Flowability of food powders and methods for its evaluation—a review, Journal of Food Process Engineering. 1 (1977) 303-328.

[10] M. Lazar, A. Brown, G. Smith, F. Wong, F. Lindquist, Experimental production of tomato powder by spray drying, Food Technology. 10 (1956) 129-134.

[11] M. L. Meste, D. Champion, G. Roudaut, G. Blond, D. Simatos, Glass transition and food technology: A critical appraisal, Journal of Food Science. 67 (2002) 2444-2458.

[12] Y. Liu, B. Bhandari, W. Zhou, Glass transition and enthalpy relaxation of amorphous food saccharides: a review, Journal of Agricultural and Food Chemistry. 54 (2006) 5701-5717.

[13] N. Silalai, Y. H. Roos, Roles of water and solids composition in the control of glass transition and stickiness of milk powders, Journal of Food Science. 75 (2010) E285-E296.

[14] D. Chiou, T. Langrish, R. Braham, The effect of temperature on the crystallinity of lactose powders produced by spray drying, Journal of Food Engineering. 86 (2008) 288-293.

[15] J. Bronlund, T. Paterson, Moisture sorption isotherms for crystalline, amorphous and predominantly crystalline lactose powders, International Dairy Journal. 14 (2004) 247-254.

[16] D. Das, T. A. Langrish, Activated-rate theory: Effect of protein inhibition and the temperature dependence of crystallization kinetics for lactose-protein mixtures, Food Research International. 48 (2012) 367-373.

[17] P. L. H. McSweeney, P. F. Fox, Advanced Dairy Chemistry Volume 3. Lactose, water, salts and vitamins, third ed., Springer Publishers, New York, 2008.

[18] K. Roetman, Crystalline lactose and the structure of spray-dried milk products as observed by scanning electron miscroscopy, Netherlands Milk and Dairy Journal (Netherlands). (1979).

[19] X. Fu, D. Huck, L. Makein, B. Armstrong, U. Willen, T. Freeman, Effect of particle shape and size on flow properties of lactose powders, Particuology. 10 (2012) 203-208.

[20] M. E. Thomas, J. Scher, S. Desobry-Banon, S. Desobry, Milk powders ageing: Effect on physical and functional properties, Critical Reviews in Food Science and Nutrition. 44 (2004) 297-322.

[21] P. Schuck, A. Dolivet, Lactose crystallization: determination of α-lactose monohydrate in spray-dried dairy products, Le Lait. 82 (2002) 413-421.

[22] GEA Niro. A1c - Free water content. GEA Process Engineering A/S, Gladsaxevej, Denmark, 2006.

[23] GEA Niro. A2a - Powder Bulk Density. GEA Process Engineering A/S, Gladsaxevej, Denmark, 2006.

[24] GEA Niro. A11c - Particle density, occlided air and interstitial air by air pycnometer, GEA Process Engineering A/S, Gladsaxevej, Denmark, 2006.

[25] D. Mahlin, J. Wood, N. Hawkins, J. Mahey, P. G. Royall, A novel powder sample holder for the determination of glass transition temperatures by DMA, International Journal of Pharmaceutics. 371 (2009) 120-125.

[26] J. Fitzpatrick, T. Iqbal, C. Delaney, T. Twomey, M. Keogh, Effect of powder properties and storage conditions on the flowability of milk powders with different fat contents, Journal of Food Engineering. 64 (2004) 435-444.

[27] P. G. Royall, C. Huang, S. J. Tang, J. Duncan, G. Van-de-Velde, M. B. Brown, The development of DMA for the detection of amorphous content in pharmaceutical powdered materials, Internation Journal of Pharmaceutics. 301 (2005) 181-191.

[28] N. Silalai, Y. H. Roos, Mechanical α-relaxations and stickiness of milk solids/maltodextrin systems around glass transition, Journal of the Science of Food and Agriculture. 91 (2011) 2529-2536.

[29] G. Roudaut, D. Simatos, D. Champion, E. Contreras-Lopez, M. Le Meste, Molecular mobility around the glass transition temperatures: a mini review, Innovative Food Science & Emerging Technologies. 5 (2004) 127-134.

[30] R. O. Ebewele, Polymer science and technology, CRC Press, 2000.

Figure captions

Figure 1 Storage modulus and loss modulus of lactose/WPI solids systems with low moisture (LM) content (A1 and A2) and high moisture (HM) content (B1 and B2). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

Figure 2 Flow function curves showing unconfined strength as a function of major principal consolidating stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

Figure 3 Bulk density as a function of major principal consolidating stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

Figure 4 Fiction angle as a function of normal stress for lactose/WPI solids systems with low moisture (LM) content (A) and high moisture (HM) content (B). S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI (4:1) mixtures with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

Tables

Table 1 Physical characteristics of lactose/WPI solids systems

Systems	**Crystallinity (%)**	**d_{50} (μm)**	**SSA (m^2/kg)**	**Loose bulk density (g/cm^3)**	**Tapped bulk density (g/cm^3)**	**Particle density (g/cm^3)**	**Porosity**
S1	0.00	29.25^{a}±0.25	620.50^{c}±6.50	0.5458^{a}±0.0138	0.7110^{a}±0.0096	1.2900^{a}±0.0055	0.4488^{e}±0.0074
S2	1.01±0.58	22.85^{d}±0.25	714.75^{a}±7.45	0.3282^{d}±0.0027	0.3807^{d}±0.0027	1.2168^{e}±0.0019	0.6871^{b}±0.0023
S3	11.18±0.97	25.35^{b}±0.05	629.95^{c}±0.85	0.3297^{d}±0.0037	0.3731^{e}±0.0023	1.2182^{e}±0.0016	0.6778^{c}±0.0020
S4	29.20±0.92	25.20^{b}±1.20	682.10^{b}±9.30	0.3418^{c}±0.0030	0.4022^{c}±0.0044	1.2443^{d}±0.0014	0.6768^{c}±0.0012
S5	46.84±1.11	23.85^{c}±0.05	695.05^{b}±1.05	0.3614^{b}±0.0070	0.4226^{b}±0.0036	1.2485^{c}±0.0021	0.6615^{d}±0.0031
S6	0.00	26.10^{b}±0.50	536.00^{d}±6.60	0.1916^{e}±0.0007	0.2381^{f}±0.0015	1.2814^{b}±0.0019	0.8142^{a}±0.0018

[1] S1-S6: S1: amorphous lactose; S2-S5: lactose/WPI mixtures at ratio 4:1 with 1.01%, 11.18%, 29.20% and 46.84% crystallinity, respectively; S6: WPI.

[2] Values are mean ± standard deviation (n=3).

[3] $^{a\text{-}f}$ Values within columns with different superscripts are significantly different at P <0.05.

Table 2 Morphological characteristics of lactose/WPI solids systems

Systems	**Circularity**	**Elongation**	**Convexity**
S1	0.9120^{a}±0.0010	0.1590^{c}±0.0010	0.9940^{a}±0.0000
S2	0.8593^{b}±0.0074	0.2477^{b}±0.0082	0.9920^{b}±0.0008
S3	0.8430^{bc}±0.0123	0.2533^{b}±0.0109	0.9900^{bc}±0.0008
S4	0.8473^{bc}±0.0012	0.2507^{ab}±0.0009	0.9903^{bc}±0.0005
S5	0.8350^{c}±0.0071	0.2630^{a}±0.0050	0.9890^{c}±0.0008
S6	0.8355^{c}±0.0055	0.2570^{a}±0.0030	0.9890^{c}±0.0010

[1] S1-S6: Table 1.

[2] Values are mean ± standard deviation (n=3).

[3] $^{a\text{-}c}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

Table 3 Water content, *m*, water activity, a_w, glass transition, T_g, and α-relaxation temperature, T_α of lactose/WPI solids systems storage at different humidity conditions (0% RH and 44% RH).

Systems	***m***		**a_w**		**T_g (ºC)**		**T_α (ºC)**	
	LM	**HM**	**LM**	**HM**	**LM**	**HM**	**LM**	**HM**
S1	1.35±0.01	4.67±0.02	0.16±0.001	0.34±0.002	72.0±0.1	50.0±0.2	122.1±0.04	69.6±0.02
S2	2.21±0.25	4.80±0.21	0.09±0.001	0.32±0.001	68.9±0.2	47.8±0.0	126.6±0.03	69.7±0.03
S3	2.34±0.15	6.14±0.08	0.09±0.002	0.35±0.003	66.1±0.1	35.9±0.2	125.1±0..05	63.2±0.04
S4	2.40±0.04	6.22±0.11	0.11±0.001	0.34±0.000	67.3±0.3	37.0±0.1	127.0±0.02	58.6±0.04
S5	2.11±0.04	4.78±0.12	0.09±0.003	0.33±0.003	71.4±0.2	48.8±0.4	126.3±0.02	73.2±0.05
S6	3.49±0.01	7.87±0.06	0.09±0.001	0.33±0.000	/	/	/	/

[1] S1-S6: Table 1.

[2] Values are mean ± standard deviation (water content: n=3; T_g and T_α: n=2).

Table 4 Values relating to flow properties of lactose/WPI solids systems derived from standard flow function test by Powder Flow Tester ($D_{arching}$: minimum outlet diameter to prevent arching; δ_J: effective angle of internal friction).

Systems	**Critical stress**		**$D_{arching}$ (m)**		**Flow index**		**δ_J**	
	LM	**HM**	**LM**	**HM**	**LM**	**HM**	**LM**	**HM**
S1	0.154^{b}±0.001	0.264^{a}±0.001	0.060^{bc}±0.001	0.113^{b}±0.001	6.25^{c}±0.01	4.17^{bc}±0.01	36.3^{d}±0.1	44.4^{b}±0.1
S2	0.099^{e}±0.000	0.210^{b}±0.003	0.056^{c}±0.000	0.120^{c}±0.002	4.17^{a}±0.01	3.70^{a}±0.00	40.7^{b}±0.1	45.2^{a}±0.0
S3	0.096^{e}±0.001	0.181^{d}±0.001	0.056^{c}±0.001	0.108^{d}±0.002	5.56^{b}±0.20	4.76^{c}±0.00	39.4^{c}±0.1	43.4^{c}±0.0
S4	0.106^{d}±0.001	0.192^{c}±0.001	0.056^{c}±0.001	0.101^{d}±0.001	4.35^{a}±0.00	4.00^{b}±0.01	40.1^{c}±0.1	45.2^{a}±0.0
S5	0.122^{c}±0.000	0.175^{d}±0.001	0.064^{b}±0.001	0.097^{e}±0.001	4.55^{a}±0.00	3.85^{ab}±0.01	40.7^{b}±0.1	44.0^{b}±0.1
S6	0.193^{a}±0.001	0.216^{b}±0.001	0.179^{a}±0.001	0.199^{a}±0.000	6.67^{c}±0.00	6.25^{d}±0.00	41.1^{a}±0.1	40.7^{e}±0.1

[1] S1-S6: Table 1.

[2] Values are mean ± standard deviation (n=3).

[3] $^{a-e}$ Values within columns with different superscripts are significantly different at $P < 0.05$.

***Graphical Abstract (for review)**