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Influence of particle size on the physicochemical properties and stickiness of dairy powders

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ABSTRACT

The compositional and physicochemical properties of different whey permeate (WPP), demineralised whey (DWP) and skim milk powder (SMP) size fractions were investigated. Bulk composition of WPP and DWP was significantly ($P < 0.05$) influenced by powder particle size; smaller particles had higher protein and lower lactose contents. Microscopic observations showed that WPP and DWP contained both larger lactose crystals and smaller amorphous particles. Bulk composition of SMP did not vary with particle size. Surface composition of the smallest SMP fraction (<75 μm) showed significantly lower protein (–9%) and higher fat (+5%) coverage compared with non-fractionated powders. For all powders, smaller particles were more susceptible to sticking. Hygroscopicity of SMP was not affected by particle size; hygroscopicity of semi-crystalline powders was inversely related to particle size. This study provides insights into differences between size fractions of dairy powders, which can potentially impact the sticking/caking behaviour of fine particles during processing.

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1. Introduction

Stickiness and hygroscopicity of powders, especially those with high carbohydrate content, is a major challenge for the dairy industry, particularly during the spray drying process. Sticky powders can become deposited on the walls of the spray drier and block bag-houses and cyclones, decreasing process efficiency, product yield and quality. Stickiness is a surface phenomenon that occurs when the surface of powder particle reaches a critical viscosity (between 10^6 and 10^8 Pa s), which allows for the formation of liquid bridges, causing cohesion between colliding particles and/or adhesion to equipment surfaces (Downton, Flores-Luna, & King, 1982). The viscosity of the particle surface is governed by many factors, such as moisture content, the physical state of lactose and temperature (Downton et al., 1982; Hogan, O'Callaghan, & Bloore, 2009). A wide variety of techniques have been developed over the years to determine the conditions at which powders become sticky, with sticking temperature (T) usually reported as a function of relative humidity (RH) (Boonyai, Howes, & Bhandari, 2006; Hogan et al., 2009; Intipunya, Shrestha, Howes, & Bhandari, 2009; Lazar, Brown, Smith, Wong, & Lindquist, 1956; Murti, Paterson, Pearce, & Bronlund, 2009; Paterson, Bronlund, Zuo, & Chatterjee, 2007; Paterson, Brooks, Bronlund, & Foster, 2005).

Powders containing large amounts of amorphous lactose are particularly susceptible to sticking as amorphous carbohydrates are thermodynamically unstable and undergo a phase transition from a 'glassy' to 'rubbery' state around a critical temperature, known as the glass transition temperature (T_g). This transition is also highly dependent on humidity due to the plasticisation effect of water, which lowers T_g (Haque & Roos, 2004a; Jouppila & Roos, 1994; Ozmen & Langrish, 2002; Roos & Karel, 1991). As the T_g is exceeded, the molecular mobility of the system will increase and the particle surface viscosity will decrease, leading

to the onset of sticking (Foster, Bronlund, & Paterson, 2006). As a consequence of this, stickiness is commonly encountered during spray drying due to high temperature and RH conditions. The temperature difference between the T_g and sticking point temperature, known as the $T–T_g$, has been extensively studied and is often used to describe the sticking behaviour of dairy powders (Hennigs, Kockel, & Langrish, 2001; Hogan et al., 2009; Murti et al., 2009; Ozmen & Langrish, 2002; Paterson et al., 2005, 2007). It should be noted that the $T–T_g$ can vary depending on the measurement technique used (Paterson et al., 2005, 2007) and the composition of the powder (Hogan et al., 2009). $T–T_g$ values reported for SMP vary from 14 to 22 °C, using a thermo-mechanical test (Ozmen & Langrish, 2002), 23.3 °C, using a direct stirrer-type technique (Hennigs et al., 2001), 29 °C, using a fluidised bed apparatus (Hogan & O'Callaghan, 2010; Hogan et al., 2009) to 33.6 °C using a particle gun (Murti et al., 2009).

To minimise processing and product quality challenges associated with stickiness, feeds containing large amounts of lactose, such as whey and whey permeates, are often subjected to a pre-crystallisation step before drying to convert the majority of the amorphous lactose (typically 75–80%) into the more stable, crystalline form. However, due to the presence of impurities (e.g., proteins and minerals), it is not possible to fully crystallise all of the dissolved lactose. Resulting powders are semi-crystalline in nature, as they contain both lactose crystals and a proportion of amorphous lactose (~20–25% of total lactose), in addition to other milk components (Bansal & Bhandari, 2016). These components differ in diffusivity and molecular weight and therefore may not be distributed evenly between size fractions (Meerdink & van't Riet, 1995), leading to differences in stickiness behaviour.

Particle size is thought to play a role in powder stickiness as it has been shown to have a significant effect on the cohesive and adhesive strength of a dairy powders (Rennie, Chen, Hargreaves, & Mackereth, 1999). It is commonly observed in industrial settings that the fines exiting the spray dryer with the exhaust air often stick to the surfaces of the air

filtration systems (e.g., cyclones and bag houses). However, to date, very little research has been carried out investigating the effect of particle size on the stickiness of dairy powders. As part of a study by Hogan et al. (2009) the authors examined the differences in stickiness behaviour between two SMP samples of different particle sizes (D[4,3] values of 130 and 61 µm) but did not find any significant difference between the stickiness of the two size fractions.

The hygroscopicity of a dairy powder describes its final moisture content after exposure to humid air at a constant temperature. Hygroscopicity is closely linked with stickiness, as increased moisture content increases the rate of stickiness development (Murti et al., 2009). Various studies (such as Carpin et al., 2017 and Haque & Roos, 2004b) have investigated the influence of particle size on water absorption by different dairy powders. Haque and Roos (2004b) examined the differences in water uptake of coarse and fine amorphous lactose/protein powders and found that the fine particles absorbed slightly more water than the coarse powder particles at relative vapour pressures (RVP) ≤ 33.2%. Similarly, Carpin et al. (2017) found that for crystalline lactose powders, smaller particles showed an increase in water absorption compared with larger particles at RHs > 50%. Rogé and Mathlouthi (2000) also showed the same effect of particle size on water uptake for crystalline sucrose.

Many studies (Kim, Chen, & Pearce, 2002, 2005, 2009; Nijdam & Langrish, 2006; Shrestha, Howes, Adhikari, Wood, & Bhandari, 2007) have compared the bulk and surface compositions of various dairy powders and found that the proportions of protein, fat and lactose on the surface of the particle can be significantly different from those in the bulk of the powder. While such observations are useful, information on the relationship between particle size and surface composition is limited. Kim et al. (2009) sieved a commercial SMP and examined the surface composition of various size fractions but found no significant effect

of particle size on surface composition. However, the range of particle sizes examined in the study by Kim et al. (2009) was very small (between 0 and 90 µm) and therefore not representative of the range of particle sizes typically found in industrially produced powders. To the author's knowledge, there are no published studies available on the relationships between particle size and surface composition of semi-crystalline dairy powders, such as whey permeates.

The objectives of this study were to characterise the bulk and surface compositions of various size fractions within different dairy powders, and to investigate whether differences exist in the stickiness behaviour and hygroscopicity of these fractions. In particular, the stickiness behaviour of the smaller size fractions, or fines, was of interest, as excessive stickiness in this fraction can be a limiting factor during spray drying.

2. Materials and methods

2.1. Materials

Demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP) were supplied by local dairy ingredient companies. Saturated salt solutions magnesium chloride ($MgCl_2$), potassium carbonate (K_2CO_3) and sodium chloride (NaCl) were purchased from Sigma Aldrich (Co. Wicklow, Ireland).

2.2. Powder fractionation

Powders were sieved using a laboratory test sieve shaker (Octagon 200 test sieve shaker, Endecotts Ltd, London, UK) using three different sieve sizes (250, 150 and 75 µm).

The powders were sieved in batches of 300 g at amplitude 7 for 4 min. The powder in each sieve was then weighed to determine the proportion of each size fraction in the original powder. Two batches of the WPP and four batches of the DWP and SMP were sieved in total. All fractions were well mixed, stored in airtight plastic containers and analysed within 2 months.

2.3. Particle size distribution

The particle size distributions (PSD) of each powder fraction were measured by laser light scattering using a Mastersizer 3000 (Malvern Instruments Ltd., UK), equipped with an Aero S dry powder dispersion unit. Particle size measurements were recorded as the volume mean diameter (D[4,3]).

2.4. Powder composition

Total moisture was determined by Karl-Fischer titration using a 784 KFP Titrino auto-titration system (Metrohm AG, Herisau, Switzerland) as described by GEA (2006). Protein determination was carried out using a LECO Nitrogen Analyser FP-638 (LECO Corporation, Michigan, USA), using a nitrogen-to-protein conversion factor of 6.38. Non-protein nitrogen (NPN) content was measured using the Kjeldahl method, after precipitation of intact proteins using trichloroacetic acid (TCA). In the absence of an accurate method to measure whey:casein ratio in heat treated SMP, the ratio was taken to be 20:80. Lactose content was measured using a lactose assay kit (Megazyme K-LOLAC, Ireland). It should be noted that there was an insufficient amount of powder to test the $x < 75$ μm fraction of the DWP for lactose and NPN, so a simple linear regression was carried out to extrapolate the

data. For the SMP fractions, lactose content was assumed to be the same as the original powder. Fat content was analysed by Röse-Gottlieb (IDF, 1987). Ash content was determined after overnight incineration in a muffle furnace at 550 °C. Water activity (a_w) was determined using a Novasina Labmaster.aw (Novatron Scientific Ltd., UK). Free moisture was determined by oven drying at 86 °C for 6 h.

2.5. Lactose crystallinity

Lactose crystallinity (%) was calculated according to the formula described by Schuck & Dolivet (2002):

$$\frac{BWL.19}{L} \times 100$$

where BWL is the bound water content in the lactose ($g.kg^{-1}$) and L is the lactose content ($g\ kg^{-1}$).

The BWL was calculated according to the following formula:

$$BWL = TW - FW - (0.0152.CC) - (0.005.WPC) - (0.0155.MSSC)$$

where TW: total water content ($g\ kg^{-1}$), FW: free water content ($g\ kg^{-1}$), CC: casein content ($g.kg^{-1}$), WPC: whey protein content ($g\ kg^{-1}$) and MSSC: milk salt solution content ($g\ kg^{-1}$).

2.6. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out with a field-emission scanning electron microscope (FE-SEM, Zeiss Supra 40 VP Gemini, Darmstadt, Germany) at 2.00 kV. Powder samples were mounted on double-sided carbon tape attached to SEM stubs and lightly coated with chromium (Emitech K575X, Ashford, UK) prior to analysis. Images were taken at 500× magnification.

2.7. Stickiness

Powder stickiness was determined using a fluidisation technique previously described by Hogan et al. (2009). Stickiness curves were generated by plotting the air (dry bulb) temperature against the RH (calculated from the saturated air temperature and absolute humidity) at which fluidisation ceased. To determine the effect of surface fat on stickiness behaviour, stickiness curves were generated for powders washed in petroleum ether, as described by Kim et al. (2005).

2.8. Powder fluidisation velocity

Minimum air fluidisation velocities were determined using an Anton Paar MCR 302 rheometer (Graz, Austria), equipped with a powder cell attachment. An 80 mL bed of powder was subjected to an increasing air flow (from 0 to 5 L m^{-1}) and the minimum air velocity required to fluidise the powder was determined by studying the pressure drop across the powder bed and dividing by the cross sectional area. The air used to fluidise the powders in the powder cell was in compliance with ISO 8573.1, class 1.3.1, with a dew point of –20 °C and 0.8 kg moisture kg^{-1} dry air. All analysis was conducted at room temperature (~20 °C). The air velocity (m s^{-1}) passing through each fluid bed in the stickiness apparatus was determined by dividing the total air flow rate (3.5 L m^{-1}) by 5 (for each fluid bed) and then dividing by the cross sectional area of one fluid bed.

2.9. Differential scanning calorimetry

Powders were analysed without pre-equilibration under controlled atmosphere conditions. The water activity (a_w) of the different size fractions varied slightly from 0.34 to 0.36, 0.28 to 0.36 and 0.30 to 0.31 for the DWP, WPP and SMP, respectively. Glass transitions in the three powders were measured using a Q2000 differential scanning calorimeter (DSC; TA Instruments, Crawley, UK) as described by Murphy et al. (2015). Hermetically sealed differential scanning calorimetry (DSC) aluminium pans, containing between 14 and 24 mg of powder, were heated in a nitrogen purged environment using the following method; heating from 0 to 60 °C at 5 °C min^{-1}, cooling from 60 °C to –10 °C at 10 °C min^{-1}, and finally heating at 5 °C to an end temperature of 100 °C. The T_g midpoint values were calculated from the second heating cycle and all analyses were completed in at least duplicate. $T–T_g$ values were calculated as the difference between sticky point temperature (T) and T_g, and represent a single point between both curves at the a_w of the powder. For powders washed with petroleum ether T_g values of the original powder were used.

2.10. Hygroscopicity

Powder hygroscopicity was measured according to the method described by Schuck, Jeantet, and Dolivet (2012). Powder samples (~2 g) were placed in desiccators over saturated salts of K_2CO_3 at 43% RH. The samples were equilibrated and weighed at regular intervals until a constant weight was observed.

Hygroscopicity was calculated using the following formula:

$$\frac{\left((w_2 - w_1 - w_0) \times 1000\right) + (w_1 \times M)}{(w_2 - w_0) \times 10}$$

where w_0 = vial weight (g), w_1 = sample weight (g), w_2 = weight of vial after equilibration (g), M = % free moisture (% w/w)

2.11. Surface analysis of powders

X-ray photoelectron spectroscopy (XPS) measurements were made using a Kratos AXIS Ultra spectrometer (Kratos Analytical Ltd., Manchester, UK) The relative amounts of protein, fat and lactose at the powder surface were determined using a matrix formula created from the elemental compositions of the pure milk components, according to the method described by Faldt, Bergenstahl, and Carlsson (1993). It should be noted that after calculation the WPP tested in this study gave a slight negative surface fat value for all size fractions. Considering that the fat content of the powder was negligible (~0.1%, w/w), the equations were adjusted to remove fat; fat content of WPP surfaces were considered to be "not determined".

2.12. Statistical analysis

All analyses were carried out in at least duplicate. Statistical analysis was carried out by subjecting data sets to one-way ANOVA with a least significant difference (LSD) test using SPSS for Windows Regression Models (IBM Ireland Ltd., Dublin, Ireland) statistical analysis package. A level of confidence of $P \leq 0.05$ was used.

3. Results

3.1. Powder characterisation

3.1.1. Particle size fractions and bulk composition of powders

The proportion of each size fraction in the original powders is shown in Table 1. In all three powders studied, the majority of particles were between 250 and 75 µm. However, in DWP, the majority of powder particles were between 250 and 150 µm, compared with WPP and SMP, which mostly contained particles in the range 150 to 75 µm. Bulk compositional differences were observed between the various size fractions of the original powders (Table 2). For DWP and WPP, smaller particles contained higher levels of protein and lower levels of lactose compared with larger particles. The same trend was not seen for SMP, which showed no significant variation ($P > 0.05$) in bulk composition between size fractions. Mineral content of DWP and WPP was also significantly higher ($P \leq 0.05$) in smaller size fractions. In a similar study by Carpin et al. (2017), the authors also observed higher protein and mineral contents for smaller particles of crystalline lactose powder. The non-protein nitrogen (NPN) content, expressed as a percentage of total nitrogen, was 4.60 ± 0.01, 13.53 ± 2.29 and 35.55 ± 10.59 % across all size fractions of SMP, DWP and WPP respectively.

As expected, DWP and WPP contained a higher amount of lactose (80.2 ± 1.27 and 87.3 ± 0.83%, respectively) compared with SMP (48.5 ± 6.11%). The majority of lactose in DWP and WPP was in the crystalline form (α-lactose monohydrate). This is a result of the pre-crystallisation step that occurs before spray drying, in which the majority of amorphous lactose present is converted into the more stable, crystalline form. However, for all size fractions studied, DWP contained higher levels of non-crystalline lactose compared with WPP. In WPP, the smaller particles contained much higher levels of amorphous lactose (40.1% of total lactose in x < 75 µm fraction) compared with larger particles (8.60% of total lactose in x > 250 µm fraction). A similar trend was also observed for DWP. Furthermore, representation of SMP crystallinity in terms of α-lactose monohydrate is not ideal, as unlike during the manufacture of DWP and WPP, a pre-crystallisation step is not performed prior to drying; therefore any lactose crystals present may contain mixtures of α- and β-lactose

298 (Jouppila & Roos, 1994). Therefore, caution should be exercised when interpreting SMP
299 crystallinity values (as α-lactose monohydrate) from Table 2.
300
301 *3.1.2. Surface composition of powders*
302
303 Surface compositions differed from bulk compositions in the three powders examined
304 (Table 3). Protein and fat contents were higher at the particle surface, while lactose
305 concentrations at the surface were lower than in the bulk. These findings are consistent with
306 other studies in which it was also reported that protein and fat preferentially migrate to the
307 surface of the particle during drying (Nijdam & Langrish, 2006; Shrestha et al., 2007).
308 Many studies have shown that the surface fat content of dairy powders is significantly
309 higher than the bulk composition (Kim et al., 2009; Nijdam & Langrish, 2006). In the present
310 study, fat coverage of the original SMP was found to be 9.56 ± 1.60%, which is considerably
311 higher than the 1.06% fat found in the bulk of the powder. Kim et al. (2009) reported a higher
312 surface fat content of 18% for a commercial SMP with a bulk composition of approximately
313 1% fat, whereas Nijdam and Langrish (2006) reported a surface fat content of approximately
314 8% for a SMP with 1.1% bulk fat content. Foerster, Gengenbach, Woo, and Selomulya
315 (2016) demonstrated that, for industrially spray-dried powders, it is the atomisation stage
316 (and not the subsequent drying stage), which is the primary determinant of surface
317 composition, and is responsible for overrepresentation of surface fat. It is thought that fat
318 globules are ruptured during atomisation and are spread homogenously over the droplet
319 surface, creating a thin film of fat. At lower fat concentrations (between 0 and 5%) small
320 changes in bulk fat content of the powder can also cause significant increases in the fat
321 content at the surface (Nijdam & Langrish, 2006). This may have implications on powder
322 stickiness and caking ability, as a higher fat content at the surface can potentially create a

more cohesive particle and promote the formation of weak bridges between particles (Nijdam & Langrish, 2006).

Particle size can affect surface composition due to differences in droplet drying times, allowing more or less migration of certain milk components to the particle surface. For example, Foerster et al. (2016) reported that protein migration to the particle surface was more prominent in droplets with larger diameters. The authors suggested that this may be due to the surface activity of the protein and differences in diffusivity between the various milk components. In keeping with those observations, Table 3 shows that there was a significant difference ($P \leq 0.05$) in the amount of protein at the surface between the largest and the smallest size fraction of SMP (47.6 ± 1.95% and 43.8 ± 0.49%, respectively). However, in a similar study investigating differences in surface composition of various size fractions of SMP, Kim et al. (2009) observed no significant effect of particle size on surface composition. It should be noted that the particle size range used in their study was very small (0–90 µm) and therefore the differences in size may have not been large enough to show any significant change in surface composition. For DWP and WPP, no clear influence of particle size on surface composition was observed (Table 3). However, disproportionately high levels of crude protein were observed at the surface of WPP powders in comparison with DWP, especially when considering the protein contents of the bulk powders (Table 2). This may indicate a greater diffusivity of nitrogenous compounds in WPP particles during drying.

3.1.3. Particle morphology

Scanning electron micrographs of the three original powders and their size fractions are shown in Fig. 1. For DWP and WPP, the semi-crystalline nature of the powders could be clearly seen, as they consisted of a mixture of sharp-edged lactose crystals and less

regular/more globular amorphous powder particles. The non-crystalline particles in DWP appeared to be more spherical in shape compared with WPP. This may be due to the higher protein content of DWP, as protein formulation has been shown to influence particle morphology (Maa, Costantino, Nguyen, & Hsu, 1997). The $x < 75$ µm fraction of WPP also appeared to be comprised of smaller particles compared with the equivalent size fraction of DWP and SMP (Fig. 1, Sections 5A–C), which could have implications for the flowability of the powder (Fu et al., 2012). SEM images of SMP showed that the powder consisted mostly of agglomerated particles, and that the degree of agglomeration decreased with decreasing particle size.

The scanning electron micrographs from the two semi-crystalline powders also revealed differences in the types of lactose crystals present. In Fig. 1 (section B1) prism shaped crystals can be seen, whereas the crystals seen in Fig. 1 (section B3) had the characteristic tomahawk shape. Factors such as the level of supersaturation (Herrington, 1934; Parimaladevi & Srinivasan, 2014) and the impurities present (Garnier, Petit, & Coquerel, 2002; Visser & Bennema, 1983) during crystallisation can affect the final lactose crystal shape. For example, Parimaladevi and Srinivasan (2014) showed that higher levels of supersaturation promoted the formation of prism shaped crystals, whereas Visser and Bennema (1983) concluded that tomahawk shaped crystals form as a result of the interference of β-lactose on the crystallisation process.

Another distinguishing feature from the SEM micrographs is the presence of small particulates on the surface of the lactose crystals in both of the semi-crystalline powders. This is likely due to the foam of the mother liquor adhering to the crystal surface during spray drying. Similar particulates were also observed by Kalab, Caric, and Milanovic (1991) in DWP, who describe them as ‘lace–like ornamentations’ on the surface of the lactose crystals.

373 *3.1.4. Glass transition temperature*

374

375 Studies have shown that the T_g of a powder containing amorphous sugar is closely
376 associated with the stickiness of that powder (Paterson et al., 2005), as the T_g signifies a
377 decrease in surface viscosity and an increase in molecular mobility (Downton et al., 1982).
378 For the three powders studied, T_g midpoint decreased in the order WPP < DWP < SMP, with
379 values of 56.2 ± 1.26, 48.5 ± 0.03 and 37.7 ± 0.08 °C, respectively. T_g midpoint of the
380 original powders decreased as the amorphous lactose content of the powders increased; this is
381 in keeping with other studies in which amorphous lactose content has been shown to have the
382 greatest influence on T_g (Jouppila & Roos, 1994; Shrestha et al., 2007).

383

384 **3.2. Powder stickiness and hygroscopicity**

385

386 *3.2.1. Stickiness of non-fractionated powders*

387 Stickiness curves were generated for each powder by plotting the RH against the dry
388 bulb temperature at which the powder became sticky. The areas above and below the curves
389 represent the 'sticky' and 'non-sticky' zones respectively. Fig. 2 shows the stickiness curves
390 for the original DWP, WPP and SMP. For all three powders examined, as the dry bulb
391 temperature increased, the RH at which the powder became sticky decreased. The
392 susceptibility of the powders to sticking increased in the order DWP < WPP < SMP, with
393 SMP exhibiting sticky behaviour at the lowest temperature/RH conditions. Similar results
394 were found by Hogan et al. (2009), who compared the stickiness of various dairy powders,
395 including DWP and SMP.

396 Of the two semi-crystalline powders examined, WPP was found to be more
397 susceptible to sticking than DWP, despite the fact that WPP had a higher T_g midpoint and

would therefore be expected to have a higher sticking temperature. This may be explained by the higher protein content of DWP (11.4 ± 0.28%) compared with WPP (3.52 ± 0.05%); increasing the protein content of lactose-containing powders has been shown to significantly increase the $T–T_g$, and therefore protect against sticking (Hogan & O'Callaghan, 2010). This occurs due to the preferential sorption of water by the proteins, which reduces the amount of water available in the system and therefore reduces the rate of plasticisation of amorphous lactose (Hogan & O'Callaghan, 2010; Shrestha et al., 2007). This observation was supported by the $T–T_g$ values obtained in this study for WPP and DWP (Table 4). In relation to surface composition, WPP was found to have a higher percentage of crude protein at the surface compared with DWP. However, this crude protein value is misleading as it is not possible to differentiate between true protein and NPN using XPS. Based on the bulk composition of the powders, it is probable that a greater proportion of the crude protein at the WPP surface is NPN, which may not have had the same retarding effect as higher molecular weight components on T_g and stickiness (Roos & Karel, 1991).

3.2.2. Influence of particle size on stickiness

Fig. 3 demonstrates the relationship between particle size and stickiness. Smaller particles were more susceptible to sticking in all three powders tested. Stickiness is thought to be influenced by particle size as smaller particles have a higher specific surface area (SSA), which promotes interaction and formation of liquid bridges with one another and/or equipment surfaces. Likewise, inter-particle distance in a given volume will also be affected, resulting in an increase in collision frequency for smaller particles. Another explanation for the increased stickiness observed for the smaller fractions of the semi-crystalline powders could be due to a higher amorphous lactose content, compared with the larger fractions (Hogan & O'Callaghan, 2010; Hogan et al., 2009). However, these results do not agree with

the findings by Hogan et al. (2009) who did not observe any effect of particle size on the stickiness of two SMP fractions with D[4,3] values of 130 and 61 µm. The D[4,3] values of the 250 > x > 150 and 150 > x > 75 µm fractions of SMP examined in this study were 124 and 83.2 µm, respectively. A possible explanation for this disparity may the use of a vibrating element in the apparatus used by Hogan et al. (2009), which may have served to disrupt inter-particular cohesion in the smaller size fractions. It should also be noted that the stickiness behaviour of the smallest fraction (x < 75 µm) of each sample could not be determined due to excessive stickiness under ambient conditions (i.e., air channels developed instantly in the powder and no further fluidisation was observed).

For both of the semi-crystalline powders there was no significant difference (P > 0.05) in the amount of lactose present at the surface across the various size fractions (Table 3). However, as previously mentioned, the crystallinity of the lactose in the bulk of the semi-crystalline powders was found to be much higher in larger particles (Table 2). This suggests a higher proportion of amorphous lactose at the surface of smaller particles, which may have contributed to their sticking behaviour (Murti, 2006). This may also explain the increased stickiness and lower $T–T_g$ values (Table 4) observed for smaller size fractions of WPP and DWP. For SMP, slightly lower protein and higher lactose contents at the surface of the smaller particles may have accounted for increased stickiness; however, the surface compositional differences observed between fractions were not sufficient to explain the significant differences seen in Fig 3. For two of the size fractions (i.e., the 150 > x > 75 µm fractions of the DWP and SMP) the $T–T_g$ had a negative value (Table 4), indicating stickiness occurred prior to glass transition – an observation that contradicts many years of published literature. In light of these findings, further investigation was undertaken to determine if these observations were due to a) fluidisation issues or b) contribution of surface fat to stickiness.

To investigate whether the results obtained for the x < 75 µm fraction were due to poor fluidisation characteristics of the powder, the minimum air velocity required to fluidise each powder fraction was determined by measuring the pressure drop across an 80 mL fluid bed using a powder flow rheometer. For all size fractions tested, the minimum air velocity required to fluidise powders in the rheometer (data not shown) was lower than that passing through the fluid beds (0.12 m s^{-1}). These findings suggest that the poor fluidisation observed for the x < 75 µm samples in the stickiness apparatus was likely due to powder stickiness, which inhibited fluidisation due to cohesion between powder particles and/or adhesion of powder particles to the walls of the fluid bed.

Although the amorphous lactose content is considered the predominant cause of stickiness in dairy powders, fat present at the particle surface has also been shown to contribute (Özkan, Walisinghe, & Chen, 2002). To investigate the contribution of surface fat to particle stickiness, a petroleum ether wash was used to remove the surface fat from the 150 < x < 75 µm fractions of all three powders and the x < 75 µm fraction of SMP. The stickiness behaviour of these fractions was then re-tested and the results are presented in Fig. 4. Both DWP and SMP showed significant improvements in stickiness behaviour for all size fractions after washing (i.e., higher temperature and RH conditions were required for the powders to become sticky). In particular, the 150 < x < 75 µm fraction of DWP showed a very significant reduction in stickiness, which may be due to the higher amount of surface fat (26.2%) removed, compared with the equivalent SMP fraction (11.0%). The results for the x < 75 µm fraction of SMP are also particularly significant, as the stickiness of the previous sample containing surface fat could not be determined using the stickiness rig at all. It should also be noted that the stickiness of WPP could not be re-tested due to extreme caking of the powder after washing.

Particle size and lactose crystallinity of the three powder fractions were re-tested after washing to determine whether any other changes in physicochemical properties of the powders might have affected the stickiness results. The results showed that although there was no change in particle size, the lactose crystallinity of each powder did increase slightly, most likely as a result of exposure to atmospheric conditions during evaporation of petroleum ether. The 150 > x > 75 µm fraction of DWP had the greatest increase in crystallinity after washing, from 79.9 to 98.0%. The SMP fractions showed smaller increases in crystallinity, from 8.80 to 11.2% for the 150 > x > 75 µm fraction and 3.66 to 4.05% for the x < 75 µm fraction. The larger increase in lactose crystallinity observed in DWP is likely to have contributed to the considerable improvement in the stickiness behaviour of this powder fraction after washing. Overall, it is difficult to determine the individual influence of the fat removal and the change in lactose crystallinity on the stickiness behaviour of these powder fractions, but considering the magnitude of the change in stickiness behaviour, it is likely a combination of both of these factors. Furthermore, if the surface fat is contributing to stickiness, this, in combination with higher SSA (and contact between small particles), may help explain the increased stickiness observed in the original x < 75 µm fractions.

3.2.3. Hygroscopicity

Hygroscopicity of the powders is shown in Table 5. Of the three powders examined, SMP was the most hygroscopic (7.62 ± 0.03 at 43% RH), classifiable as a 'slightly hygroscopic powder' (Table 5). The values obtained for SMP, at 43% RH, are predominantly due to the amorphous lactose content (46.9%) of the powder (Listiohadi, Hourigan, Sleigh, & Steele, 2005), in combination with relatively high protein content (36.4 ± 0.56%). The two semi-crystalline powders absorbed less moisture than SMP due to their higher crystalline lactose content (Bronlund & Paterson, 2004). Of these, WPP was more hygroscopic (3.74 ±

0.02 at 43% RH) than DWP (2.17 ± 0.00 at 43% RH), which may be due to its higher mineral content (Ibach & Kind, 2007; Shrestha, Howes, Adhikari, & Bhandari, 2008).

Particle size can also affect the hygroscopicity of a powder as moisture occurs primarily on the particle surface. As such, smaller particle sizes have a relatively larger exchange surface for water absorption to occur, and vice versa. In the current study, powder hygroscopicity increased linearly with decreasing particle size for both DWP and WPP (Table 5). Carpin et al. (2017) observed similar water uptake in smaller size fractions of crystalline lactose powders. This water absorption is likely due to the increased amount of hygroscopic components, such as amorphous lactose, proteins and minerals, present in smaller fractions. However, the same pattern was not observed for the SMP sample, which showed very little variation in hygroscopicity across all size fractions (7.6 ± 0.01 to 7.78 ± 0.01 at 43% RH). These results suggest that the influence of particle size on powder hygroscopicity appears minimal, and that differences in hygroscopicity observed between size fractions of the same powder may be primarily due to differences in composition.

4. Conclusions

The results presented show that significant differences in composition, stickiness behaviour and hygroscopicity exist between the various size fractions of SMP, WPP and DWP. There was a clear distinction observed between powders: DWP and WPP were semi-crystalline powders consisting of mixtures of crystalline lactose and non-crystalline particles, while SMP was composed of largely agglomerated, non-crystalline particles. This distinction was a key determinant in both the fractionation and physicochemical behaviours of resultant powders.

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Bulk composition of semi-crystalline powder fractions (DWP and WPP) was greatly affected by particle size; large size fractions were more crystalline compared with smaller fractions, which also had higher protein content. Smaller size fractions exhibited greater tendency towards stickiness and hygroscopicity, leading to the conclusion that differences in bulk composition were the most significant contributory factor to the differences in physicochemical behaviour. In contrast, bulk composition did not vary across SMP size fractions.

Hygroscopicity of all SMP size fractions was relatively constant, again suggesting that bulk composition was the major determinant for water absorption, rather than particle size. Stickiness behaviour of all three powders, however, was closely related to size, with smaller size fractions exhibiting higher stickiness. It was suggested that this was due to a combination of increased particle surface area and fat coverage.

Overall, this study shows that significant differences exist in stickiness and hygroscopic properties of dairy powders as a function of both composition and particle size. The increased susceptibility of fine particles to stickiness/hygroscopicity is particularly interesting and should be better incorporated into spray drying operational procedures.

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Figure legends

Fig. 1. Scanning electron micrographs (500× magnification) of (A) demineralised whey powder, (B) whey permeate powder and (C) skim milk powder and their size fractions: (1) original; (2) x > 250 µm; (3) 250 > x > 150 µm; (4) 150 > x > 75 µm; (5) x < 75 µm.

Fig. 2. Stickiness curves of the three original powders examined in the study: (■) demineralised whey powder; (◆) whey permeate powder; (▲) skim milk powder.

Fig. 3. Stickiness curves showing the original (◆), x > 250 µm (×), 250 > x > 150 µm (▲), and 150 > x > 75 µm (■) fractions of (A) demineralised whey powder, (B) whey permeate powder and (C) skim milk powder.

Fig. 4. Stickiness curves showing the (◆) original, (■) 150 > x > 75 µm (before surface fat removal), (+) 150 > x > 75 µm (after surface fat removal) and (●) x > 75 µm (after surface fat removal) fractions of (A) skim milk powder and (B) demineralised whey powder.

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Table 1

Proportion (%, w/w) of each size fraction in original demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), separated using 250 µm, 150 µm and 75 µm sieves.

Powder	x > 250 µm	250 > x > 150 µm	150 > x > 75 µm	x < 75 µm
DWP (n = 4)	6.52 ± 2.27	69.2 ± 3.74	22.6 ± 5.33	1.65 ± 0.62
WPP (n = 2)	5.36 ± 1.49	21.1 ± 1.79	66.0± 3.77	7.60 ± 0.5
SMP (n = 4)	1.42 ± 0.07	38.1 ± 1.12	54.0 ± 1.85	6.53 ± 0.79

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Table 2

Bulk composition of original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP). [a]

Powder	Size fraction (µm)	True protein (%, w/w)	Fat (%, w/w)	Total lactose (%, w/w)	Ash (%, w/w)	Total moisture (%, w/w)	Free moisture (%, w/w)	Crystalline lactose (%)
DWP	Original	11.4 ± 0.28^{a}	1.11 ± 0.02^{a}	80.2 ± 1.27^{a}	0.70 ± 0.15^{ac}	4.93 ± 0.15^{a}	1.75 ± 0.01^{a}	73.8
	x > 250	8.23 ± 0.04^{b}	0.85 ± 0.00^{b}	88.3 ± 1.05^{b}	0.49 ± 0.15^{ab}	4.93 ± 0.06^{a}	1.34 ± 0.01^{b}	76.2
	250 > x > 150	10.8 ± 0.18^{c}	1.04 ± 0.01^{c}	79.4 ± 0.28^{a}	0.77 ± 0.1^{ac}	4.99 ± 0.22^{a}	1.71 ± 0.05^{a}	76.9
	150 > x > 75	11.8 ± 0.13^{d}	1.16 ± 0.00^{d}	75.4 ± 0.61^{c}	0.79 ± 0.01^{c}	5.10 ± 0.12^{a}	1.86 ± 0.10^{a}	79.9
	x < 75	21.4 ± 0.09^{e}	1.95 ± 0.03^{e}	71.6	1.43 ± 0.11^{d}	5.13 ± 0.08^{a}	3.10 ± 0.26^{c}	50.5
WPP	Original	3.52 ± 0.05^{a}	0.08 ± 0.01^{a}	87.3 ± 0.83^{a}	6.77 ± 0.03^{a}	5.63 ± 0.13^{a}	1.65 ± 0.00^{a}	84.0
	x > 250	0.54 ± 0.02^{b}	0.08 ± 0.01^{a}	99.2 ± 0.94^{b}	1.59 ± 0.02^{b}	5.18 ± 0.28^{b}	0.38 ± 0.00^{b}	91.4
	250 > x > 150	2.89 ± 0.07^{c}	0.11 ± 0.01^{a}	93.1 ± 3.19^{c}	5.89 ± 0.11^{c}	5.57 ± 0.12^{a}	1.46 ± 0.00^{c}	81.6
	150 > x > 75	3.47 ± 0.05^{d}	0.10 ± 0.05^{a}	83.7 ± 1.10^{a}	7.68 ± 0.01^{d}	5.63 ± 0.06^{a}	1.86 ± 0.01^{d}	82.4
	x < 75	6.01 ± 0.01^{e}	0.13 ± 0.01^{a}	70.5 ± 0.06^{d}	12.9 ± 0.12^{e}	5.59 ± 0.1^{a}	3.14 ± 0.00^{e}	59.9
SMP	Original	36.4 ± 0.56^{a}	1.06 ± 0.07^{a}	48.5 ± 6.11	7.31 ± 0.02^{a}	5.52 ± 0.14^{a}	5.05 ± 0.00^{a}	3.28
	x > 250	36.1 ± 0.03^{a}	0.94 ± 0.01^{b}	48.5 ± 6.11	7.19 ± 0.03^{b}	5.57 ± 0.13^{a}	5.04 ± 0.01^{a}	10.9
	250 > x > 150	36.3 ± 0.05^{a}	0.95 ± 0.02^{b}	48.5 ± 6.11	7.24 ± 0.01^{bc}	5.47 ± 0.02^{a}	5.12 ± 0.10^{a}	2.20
	150 > x > 75	36.4 ± 0.05^{a}	0.93 ± 0.02^{b}	48.5 ± 6.11	7.23 ± 0.03^{bd}	5.50 ± 0.04^{a}	5.07 ± 0.01^{b}	8.80
	x < 75	36.5 ± 0.06^{a}	1.00 ± 0.03^{ab}	48.5 ± 6.11	7.25 ± 0.03^{cd}	5.51 ± 0.03^{a}	5.13 ± 0.07^{a}	3.66

[a] For each powder, different superscript letters within the same column represent a significant difference ($P \leq 0.05$). True protein is defined as (Total nitrogen – Non-protein nitrogen) × 6.38; For DWP size fraction x < 75 values for non-protein nitrogen and lactose are extrapolated; for SMP the lactose values are assumed for all size fractions. Crystalline lactose is α-lactose monohydrate as a percentage of total lactose.

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Table 3

Surface composition of original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), given in percentage protein, fat and lactose coverage. [a]

Powder	Size fraction (µm)	Crude protein (%)	Fat (%)	Lactose (%)
DWP	Original	41.2 ± 0.50^{ac}	28.4 ± 2.72^{a}	30.4 ± 2.16^{a}
	x > 250	42.3 ± 1.00^{bc}	28.3 ± 0.85^{a}	29.4 ± 0.21^{a}
	250 > x > 150	44.0 ± 0.50^{b}	26.7 ± 0.44^{a}	29.3 ± 0.93^{a}
	150 > x > 75	41.6 ± 1.00^{ac}	26.2 ± 3.51^{a}	32.1 ± 2.45^{a}
	x < 75	39.4 ± 1.00^{a}	27.9 ± 0.14^{a}	32.3 ± 0.84^{a}
WPP	Original	54.2 ± 0.00^{a}	n.d.	35.4 ± 0.25^{a}
	x > 250	45.8 ± 3.98^{b}	n.d.	36.5 ± 1.27^{a}
	250 > x > 150	54.6 ± 1.49^{a}	n.d.	36.5 ± 0.51^{a}
	150 > x > 75	51.8 ± 3.49^{ab}	n.d.	35.4 ± 0.76^{a}
	x < 75	49.7 ± 0.50^{ab}	n.d.	35.2 ± 1.01^{a}
SMP	Original	52.4 ± 0.98^{a}	9.56 ± 1.60^{a}	35.9 ± 0.56^{a}
	x > 250	47.6 ± 1.95^{b}	18.5 ± 3.25^{b}	32.5 ± 1.43^{b}
	250 > x > 150	47.6 ± 0.00^{b}	12.2 ± 0.84^{ac}	38.7 ± 0.98^{ac}
	150 > x > 75	47.2 ± 0.49^{b}	11.0 ± 1.76^{ac}	40.2 ± 1.13^{c}
	x < 75	43.8 ± 0.49^{c}	14.8 ± 1.20^{bc}	39.7 ± 1.76^{cd}

[a] For each powder, different superscript letters within the same column represent a significant difference ($P \leq 0.05$); n.d., not determined.

Table 4

Water activity (a_w), glass transition temperature (T_g), sticking point temperature (T) and difference between sticking point temperature and glass transition temperature ($T–T_g$) for the original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), before and after surface fat removal. [a]

Powder	Size fraction (μm)	Water activity (a_w)	$T_{g\ (midpoint)}$ (°C)	T (°C)	$T–T_g$ (°C)	$T–T_{g\ (after\ washing)}$ (°C)
DWP	Original	0.34	48.5 ± 0.03[a]	68.1	19.6	n.d[d]
	x > 250	0.36	47.5 ± 0.13[b]	67.7	20.2	n.d[d]
	250 > x > 150	0.34	48.8 ± 0.01[a]	68.5	19.7	n.d[d]
	150 > x > 75	0.35	49.1 ± 0.01[a]	42.9	-6.24	104
	x < 75	0.34	48.6 ± 0.48[a]	n.d.	n.d.	n.e.
WPP	Original	0.27	56.2 ± 1.26[a]	70.9	14.7	n.a.
	x > 250	0.36	50.0 ± 0.83[b]	58.2	8.20	n.a.
	250 > x > 150	0.29	53.7 ± 0.05[c]	68.7	15.0	n.a.
	150 > x > 75	0.28	54.1 ± 0.36[c]	62.5	8.35	n.a.
	x < 75	0.28	56.4 ± 0.30[a]	n.d.	n.d.	n.a.
SMP	Original	0.31	37.7 ± 0.08[a]	58.3	20.6	n.a.
	x > 250	0.30	33.4 ± 0.21[b]	65.1	31.7	n.a.
	250 > x > 150	0.31	39.3 ± 0.12[c]	60.6	21.3	n.a.
	150 > x > 75	0.31	39.3 ± 0.93[c]	30.3	-9.00	27.8
	x < 75	0.31	38.2 ± 0.08[ac]	n.d.	n.d.	11.5

[a] For each powder, different superscript letters within the same column represent a significant difference ($P \leq 0.05$); n.d., stickiness could not be determined and therefore $T–T_g$ could not be calculated; n.e., not enough powder remaining to wash surface; n.a., not analysed.

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Table 5

Hygroscopicity of the original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP) at 43% relative humidity (RH). [a]

Powder	Size fraction (μm)	Hygroscopicity at 43% RH	Classification at 43% RH
DWP	Original	2.71 ± 0.00[a]	Non-hygroscopic
	x > 250	2.00 ± 0.00[b]	Non-hygroscopic
	250 > x > 150	2.61 ± 0.07[c]	Non-hygroscopic
	150 > x > 75	2.94 ± 0.02[d]	Non-hygroscopic
	x < 75	5.00 ± 0.00[e]	Slightly hygroscopic
WPP	Original	3.74 ± 0.02[a]	Non-hygroscopic
	x > 250	0.78 ± 0.01[b]	Non-hygroscopic
	250 > x > 150	3.22 ± 0.05[c]	Non-hygroscopic
	150 > x > 75	4.23 ± 0.02[d]	Non-hygroscopic
	x < 75	7.20 ± 0.03[e]	Slightly hygroscopic
SMP	Original	7.62 ± 0.03[a]	Slightly hygroscopic
	x > 250	7.61 ± 0.02[a]	Slightly hygroscopic
	250 > x > 150	7.78 ± 0.01[b]	Slightly hygroscopic
	150 > x > 75	7.60 ± 0.01[a]	Slightly hygroscopic
	x < 75	7.68 ± 0.03[c]	Slightly hygroscopic

[a] Value ranges for powder hygroscopicity classification at 43% relative humidity (RH) are modified from Schuck, Jeantet, and Dolivet (2012): non-hygroscopic, ≤4.5; slightly hygroscopic, 4.6–8.0; hygroscopic, 8.1–11.0; very hygroscopic, 11.1–14.5; extremely hygroscopic, ≥14.5. For each powder, different letters within the same column represent a significant difference ($P \leq 0.05$).

ACCEPTED MANUSCRIPT

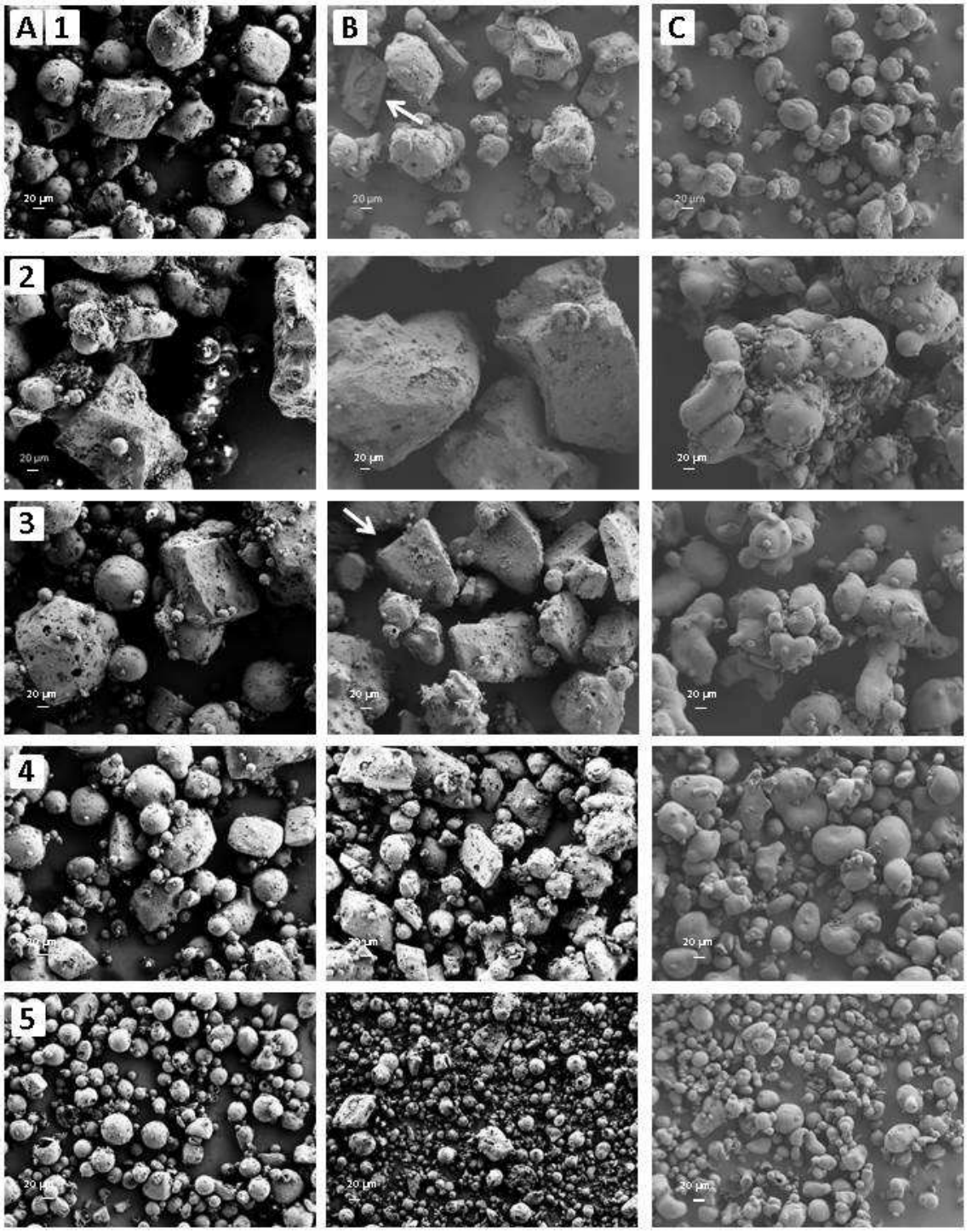


Figure 1

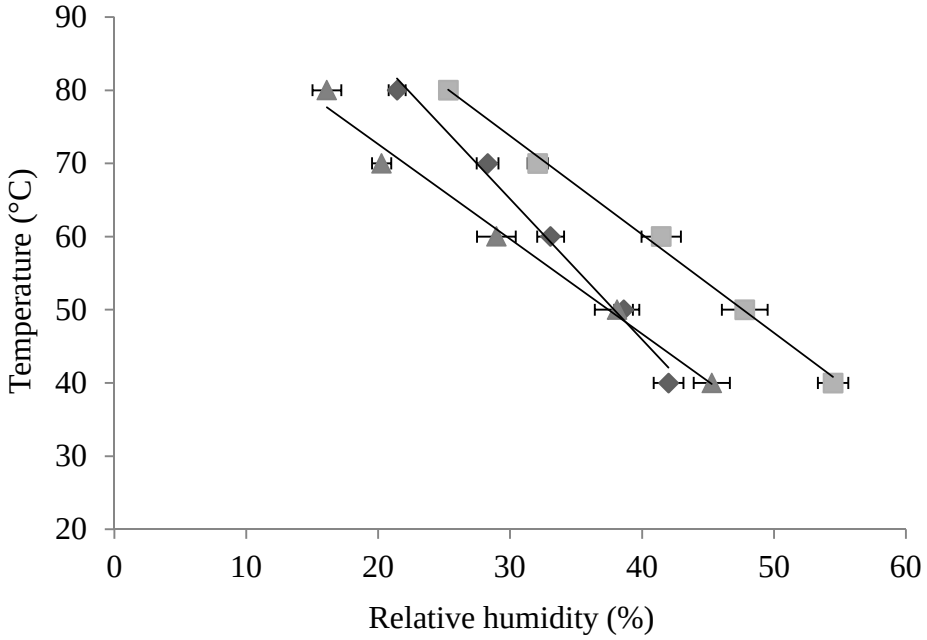


Figure 2

ACCEPTED MANUSCRIPT

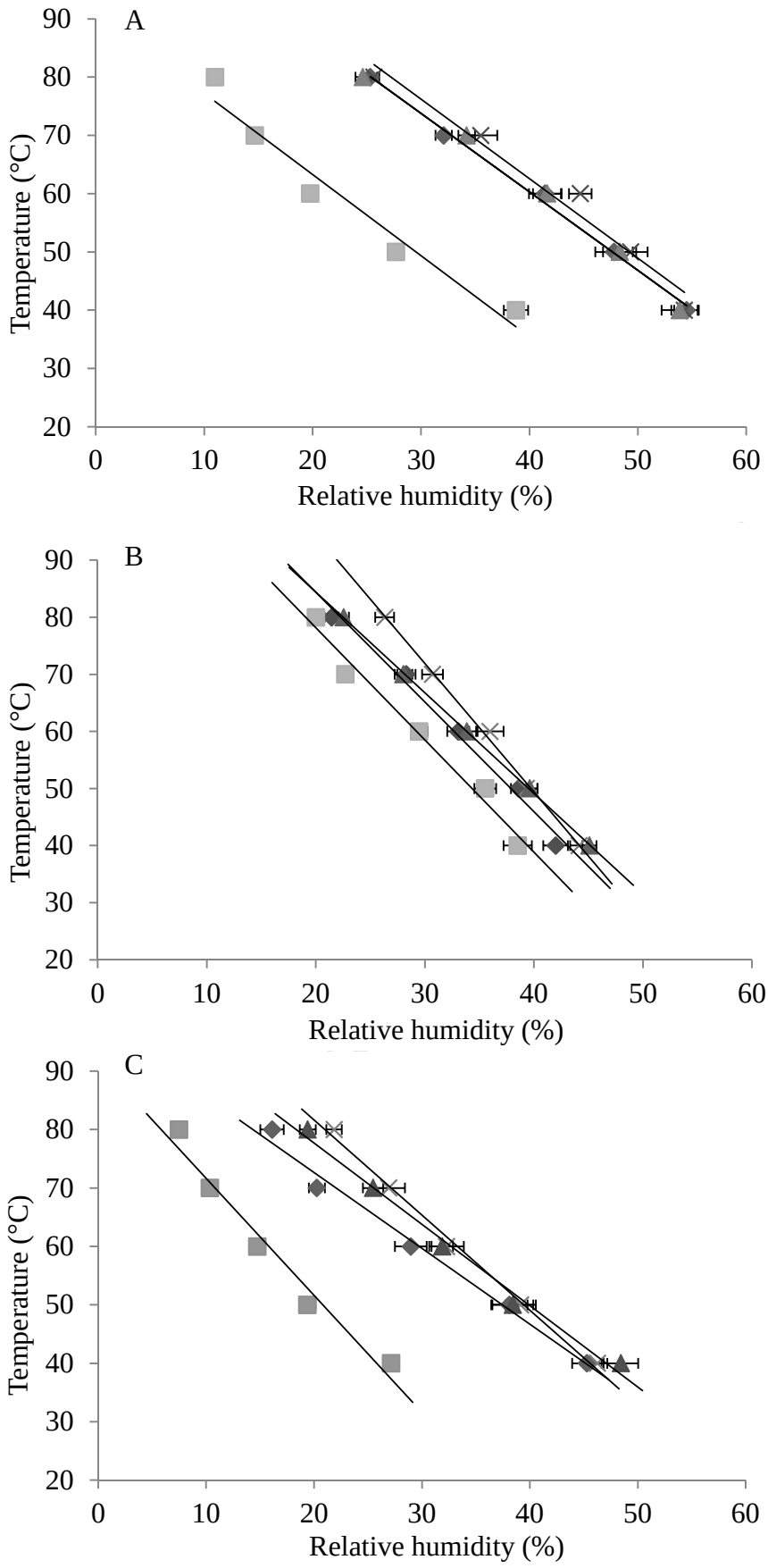

A
B
C
Temperature (°C)
Relative humidity (%)
90
80
70
60
50
40
30
20
0
10
20
30
40
50
60

Figure 3

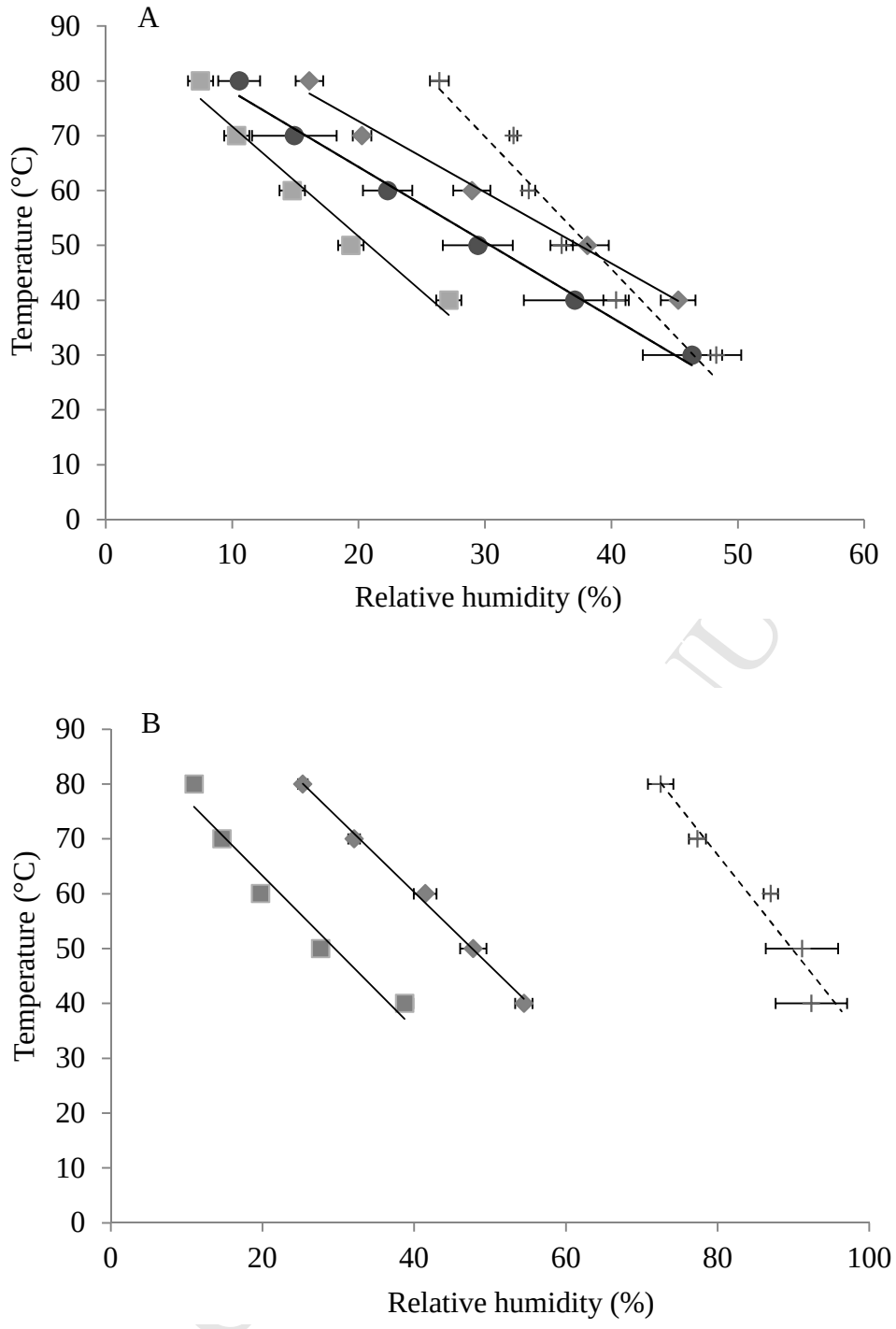

A
Temperature (°C)
Relative humidity (%)
0
10
20
30
40
50
60
70
80
90
0
10
20
30
40
50
60
B
Temperature (°C)
Relative humidity (%)
0
10
20
30
40
50
60
70
80
90
0
20
40
60
80
100

Figure 4