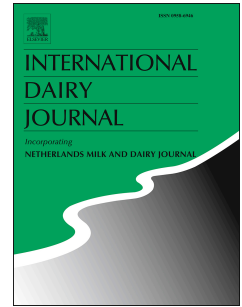


# Accepted Manuscript

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

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PII: S0958-6946(19)30159-1

DOI: <https://doi.org/10.1016/j.idairyj.2019.07.002>

Reference: INDA 4536

To appear in: *International Dairy Journal*

Received Date: 19 March 2019

Revised Date: 2 July 2019

Accepted Date: 2 July 2019

Please cite this article as: O'Donoghue, L.T., Haque, M.K., Kennedy, D., Laffir, F.R., Hogan, S.A., O'Mahony, J.A., Murphy, E.G., Influence of particle size on the physicochemical properties and stickiness of dairy powders, *International Dairy Journal*, <https://doi.org/10.1016/j.idairyj.2019.07.002>.

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1 **Influence of particle size on the physicochemical properties and stickiness of dairy**  
2 **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 ( $<75 \mu\text{m}$ ) 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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## 51 1. Introduction

52

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

69 Powders containing large amounts of amorphous lactose are particularly susceptible  
70 to sticking as amorphous carbohydrates are thermodynamically unstable and undergo a phase  
71 transition from a 'glassy' to 'rubbery' state around a critical temperature, known as the glass  
72 transition temperature ( $T_g$ ). This transition is also highly dependent on humidity due to the  
73 plasticisation effect of water, which lowers  $T_g$  (Haque & Roos, 2004a; Jouppila & Roos,  
74 1994; Ozmen & Langrish, 2002; Roos & Karel, 1991). As the  $T_g$  is exceeded, the molecular  
75 mobility of the system will increase and the particle surface viscosity will decrease, leading

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

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

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

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

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

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

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

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

137

## 138 **2. Materials and methods**

139

### 140 *2.1. Materials*

141

142 Demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk  
143 powder (SMP) were supplied by local dairy ingredient companies. Saturated salt solutions  
144 magnesium chloride ( $\text{MgCl}_2$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ) and sodium chloride ( $\text{NaCl}$ )  
145 were purchased from Sigma Aldrich (Co. Wicklow, Ireland).

146

### 147 *2.2. Powder fractionation*

148

149 Powders were sieved using a laboratory test sieve shaker (Octagon 200 test sieve  
150 shaker, Endecotts Ltd, London, UK) using three different sieve sizes (250, 150 and 75  $\mu\text{m}$ ).

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

### 157 2.3. *Particle size distribution*

158  
159 The particle size distributions (PSD) of each powder fraction were measured by laser  
160 light scattering using a Mastersizer 3000 (Malvern Instruments Ltd., UK), equipped with an  
161 Aero S dry powder dispersion unit. Particle size measurements were recorded as the volume  
162 mean diameter (D[4,3]).

### 164 2.4. *Powder composition*

165  
166 Total moisture was determined by Karl-Fischer titration using a 784 KFP Titrino  
167 auto-titration system (Metrohm AG, Herisau, Switzerland) as described by GEA (2006).  
168 Protein determination was carried out using a LECO Nitrogen Analyser FP-638 (LECO  
169 Corporation, Michigan, USA), using a nitrogen-to-protein conversion factor of 6.38. Non-  
170 protein nitrogen (NPN) content was measured using the Kjeldahl method, after precipitation  
171 of intact proteins using trichloroacetic acid (TCA). In the absence of an accurate method to  
172 measure whey:casein ratio in heat treated SMP, the ratio was taken to be 20:80. Lactose  
173 content was measured using a lactose assay kit (Megazyme K-LOLAC, Ireland). It should be  
174 noted that there was an insufficient amount of powder to test the  $x < 75 \mu\text{m}$  fraction of the  
175 DWP for lactose and NPN, so a simple linear regression was carried out to extrapolate the



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

181

## 182 2.5. *Lactose crystallinity*

183

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

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

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

188 The BWL was calculated according to the following formula:

$$189 \text{ BWL} = \text{TW} - \text{FW} - (0.0152.\text{CC}) - (0.005.\text{WPC}) - (0.0155.\text{MSSC})$$

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

192

## 193 2.6. *Scanning electron microscopy*

194

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

200

201 2.7. *Stickiness*

202

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

209

210 2.8. *Powder fluidisation velocity*

211

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

222

223 2.9. *Differential scanning calorimetry*

224

225 Powders were analysed without pre-equilibration under controlled atmosphere  
226 conditions. The water activity ( $a_w$ ) of the different size fractions varied slightly from 0.34 to  
227 0.36, 0.28 to 0.36 and 0.30 to 0.31 for the DWP, WPP and SMP, respectively. Glass  
228 transitions in the three powders were measured using a Q2000 differential scanning  
229 calorimeter (DSC; TA Instruments, Crawley, UK) as described by Murphy et al. (2015).  
230 Hermetically sealed differential scanning calorimetry (DSC) aluminium pans, containing  
231 between 14 and 24 mg of powder, were heated in a nitrogen purged environment using the  
232 following method; heating from 0 to 60 °C at 5 °C min<sup>-1</sup>, cooling from 60 °C to -10 °C at 10  
233 °C min<sup>-1</sup>, and finally heating at 5 °C to an end temperature of 100 °C. The  $T_g$  midpoint values  
234 were calculated from the second heating cycle and all analyses were completed in at least  
235 duplicate.  $T-T_g$  values were calculated as the difference between sticky point temperature (T)  
236 and  $T_g$ , and represent a single point between both curves at the  $a_w$  of the powder. For powders  
237 washed with petroleum ether  $T_g$  values of the original powder were used.

238

### 239 2.10. Hygroscopicity

240

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

245 Hygroscopicity was calculated using the following formula:

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

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

248

249 2.11. *Surface analysis of powders*

250

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

260

261 2.12. *Statistical analysis*

262

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

267

268 **3. Results**

269

270 3.1. *Powder characterisation*

271

272 3.1.1. *Particle size fractions and bulk composition of powders*

273 The proportion of each size fraction in the original powders is shown in Table 1. In all  
274 three powders studied, the majority of particles were between 250 and 75  $\mu\text{m}$ . However, in  
275 DWP, the majority of powder particles were between 250 and 150  $\mu\text{m}$ , compared with WPP  
276 and SMP, which mostly contained particles in the range 150 to 75  $\mu\text{m}$ . Bulk compositional  
277 differences were observed between the various size fractions of the original powders (Table  
278 2). For DWP and WPP, smaller particles contained higher levels of protein and lower levels  
279 of lactose compared with larger particles. The same trend was not seen for SMP, which  
280 showed no significant variation ( $P > 0.05$ ) in bulk composition between size fractions.  
281 Mineral content of DWP and WPP was also significantly higher ( $P \leq 0.05$ ) in smaller size  
282 fractions. In a similar study by Carpin et al. (2017), the authors also observed higher protein  
283 and mineral contents for smaller particles of crystalline lactose powder. The non-protein  
284 nitrogen (NPN) content, expressed as a percentage of total nitrogen, was  $4.60 \pm 0.01$ ,  $13.53 \pm$   
285  $2.29$  and  $35.55 \pm 10.59$  % across all size fractions of SMP, DWP and WPP respectively.

286 As expected, DWP and WPP contained a higher amount of lactose ( $80.2 \pm 1.27$  and  
287  $87.3 \pm 0.83\%$ , respectively) compared with SMP ( $48.5 \pm 6.11\%$ ). The majority of lactose in  
288 DWP and WPP was in the crystalline form ( $\alpha$ -lactose monohydrate). This is a result of the  
289 pre-crystallisation step that occurs before spray drying, in which the majority of amorphous  
290 lactose present is converted into the more stable, crystalline form. However, for all size  
291 fractions studied, DWP contained higher levels of non-crystalline lactose compared with  
292 WPP. In WPP, the smaller particles contained much higher levels of amorphous lactose  
293 ( $40.1\%$  of total lactose in  $x < 75$   $\mu\text{m}$  fraction) compared with larger particles ( $8.60\%$  of total  
294 lactose in  $x > 250$   $\mu\text{m}$  fraction). A similar trend was also observed for DWP. Furthermore,  
295 representation of SMP crystallinity in terms of  $\alpha$ -lactose monohydrate is not ideal, as unlike  
296 during the manufacture of DWP and WPP, a pre-crystallisation step is not performed prior to  
297 drying; therefore any lactose crystals present may contain mixtures of  $\alpha$ - and  $\beta$ -lactose

298 (Jouppila & Roos, 1994). Therefore, caution should be exercised when interpreting SMP  
299 crystallinity values (as  $\alpha$ -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  $9.56 \pm 1.60\%$ , 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 homogeneously 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

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

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

342

### 343 3.1.3. Particle morphology

344

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

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

357 The scanning electron micrographs from the two semi-crystalline powders also  
358 revealed differences in the types of lactose crystals present. In Fig. 1 (section B1) prism  
359 shaped crystals can be seen, whereas the crystals seen in Fig. 1 (section B3) had the  
360 characteristic tomahawk shape. Factors such as the level of supersaturation (Herrington,  
361 1934; Parimaladevi & Srinivasan, 2014) and the impurities present (Garnier, Petit, &  
362 Coquerel, 2002; Visser & Bennema, 1983) during crystallisation can affect the final lactose  
363 crystal shape. For example, Parimaladevi and Srinivasan (2014) showed that higher levels of  
364 supersaturation promoted the formation of prism shaped crystals, whereas Visser and  
365 Bennema (1983) concluded that tomahawk shaped crystals form as a result of the interference  
366 of  $\beta$ -lactose on the crystallisation process.

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

372



#### 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  $56.2 \pm 1.26$ ,  $48.5 \pm 0.03$  and  $37.7 \pm 0.08$  °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

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

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

412

### 413 3.2.2. Influence of particle size on stickiness

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

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

432 For both of the semi-crystalline powders there was no significant difference ( $P >$   
433 0.05) in the amount of lactose present at the surface across the various size fractions (Table  
434 3). However, as previously mentioned, the crystallinity of the lactose in the bulk of the semi-  
435 crystalline powders was found to be much higher in larger particles (Table 2). This suggests a  
436 higher proportion of amorphous lactose at the surface of smaller particles, which may have  
437 contributed to their sticking behaviour (Murti, 2006). This may also explain the increased  
438 stickiness and lower  $T-T_g$  values (Table 4) observed for smaller size fractions of WPP and  
439 DWP. For SMP, slightly lower protein and higher lactose contents at the surface of the  
440 smaller particles may have accounted for increased stickiness; however, the surface  
441 compositional differences observed between fractions were not sufficient to explain the  
442 significant differences seen in Fig 3. For two of the size fractions (i.e., the  $150 > x > 75$   $\mu\text{m}$   
443 fractions of the DWP and SMP) the  $T-T_g$  had a negative value (Table 4), indicating stickiness  
444 occurred prior to glass transition – an observation that contradicts many years of published  
445 literature. In light of these findings, further investigation was undertaken to determine if these  
446 observations were due to a) fluidisation issues or b) contribution of surface fat to stickiness.

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

456 Although the amorphous lactose content is considered the predominant cause of  
457 stickiness in dairy powders, fat present at the particle surface has also been shown to  
458 contribute (Özkan, Walisinghe, & Chen, 2002). To investigate the contribution of surface fat  
459 to particle stickiness, a petroleum ether wash was used to remove the surface fat from the 150  
460  $< x < 75 \mu\text{m}$  fractions of all three powders and the  $x < 75 \mu\text{m}$  fraction of SMP. The stickiness  
461 behaviour of these fractions was then re-tested and the results are presented in Fig. 4. Both  
462 DWP and SMP showed significant improvements in stickiness behaviour for all size fractions  
463 after washing (i.e., higher temperature and RH conditions were required for the powders to  
464 become sticky). In particular, the  $150 < x < 75 \mu\text{m}$  fraction of DWP showed a very  
465 significant reduction in stickiness, which may be due to the higher amount of surface fat  
466 (26.2%) removed, compared with the equivalent SMP fraction (11.0%). The results for the  $x$   
467  $< 75 \mu\text{m}$  fraction of SMP are also particularly significant, as the stickiness of the previous  
468 sample containing surface fat could not be determined using the stickiness rig at all. It should  
469 also be noted that the stickiness of WPP could not be re-tested due to extreme caking of the  
470 powder after washing.

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

487

### 488 3.2.3. *Hygroscopicity*

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

496 0.02 at 43% RH) than DWP ( $2.17 \pm 0.00$  at 43% RH), which may be due to its higher mineral  
497 content (Ibach & Kind, 2007; Shrestha, Howes, Adhikari, & Bhandari, 2008).

498 Particle size can also affect the hygroscopicity of a powder as moisture occurs  
499 primarily on the particle surface. As such, smaller particle sizes have a relatively larger  
500 exchange surface for water absorption to occur, and vice versa. In the current study, powder  
501 hygroscopicity increased linearly with decreasing particle size for both DWP and WPP  
502 (Table 5). Carpin et al. (2017) observed similar water uptake in smaller size fractions of  
503 crystalline lactose powders. This water absorption is likely due to the increased amount of  
504 hygroscopic components, such as amorphous lactose, proteins and minerals, present in  
505 smaller fractions. However, the same pattern was not observed for the SMP sample, which  
506 showed very little variation in hygroscopicity across all size fractions ( $7.6 \pm 0.01$  to  $7.78 \pm$   
507  $0.01$  at 43% RH). These results suggest that the influence of particle size on powder  
508 hygroscopicity appears minimal, and that differences in hygroscopicity observed between  
509 size fractions of the same powder may be primarily due to differences in composition.

510

#### 511 **4. Conclusions**

512

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

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

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

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

536

### 537 **Acknowledgements**

538

539 This work was supported by the Irish State through funding from the Enterprise  
540 Ireland (EI) Technology Centres programme - grant number TC/2014/0016. The authors  
541 would like to thank Anne Marie McAuliffe of the Technical Services Laboratory, Teagasc  
542 Moorepark, Co. Cork for her assistance in the fat determination and the removal of the  
543 surface fat.

544

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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)  $x > 250 \mu\text{m}$ ; (3)  $250 > x > 150 \mu\text{m}$ ; (4)  $150 > x > 75 \mu\text{m}$ ; (5)  $x < 75 \mu\text{m}$ .

**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 (◆),  $x > 250 \mu\text{m}$  (×),  $250 > x > 150 \mu\text{m}$  (▲), and  $150 > x > 75 \mu\text{m}$  (■) fractions of (A) demineralised whey powder, (B) whey permeate powder and (C) skim milk powder.

**Fig. 4.** Stickiness curves showing the (◆) original, (■)  $150 > x > 75 \mu\text{m}$  (before surface fat removal), (+)  $150 > x > 75 \mu\text{m}$  (after surface fat removal) and (●)  $x > 75 \mu\text{m}$  (after surface fat removal) fractions of (A) skim milk powder and (B) demineralised whey powder.

**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  $\mu\text{m}$ , 150  $\mu\text{m}$  and 75  $\mu\text{m}$  sieves.

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

**Table 2**

Bulk composition of original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP).<sup>a</sup>

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

<sup>a</sup> 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  $\alpha$ -lactose monohydrate as a percentage of total lactose.

**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. <sup>a</sup>

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

<sup>a</sup> 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. <sup>a</sup>

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

<sup>a</sup> 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.

**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).<sup>a</sup>

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

<sup>a</sup> 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 ( $P \leq 0.05$ ).

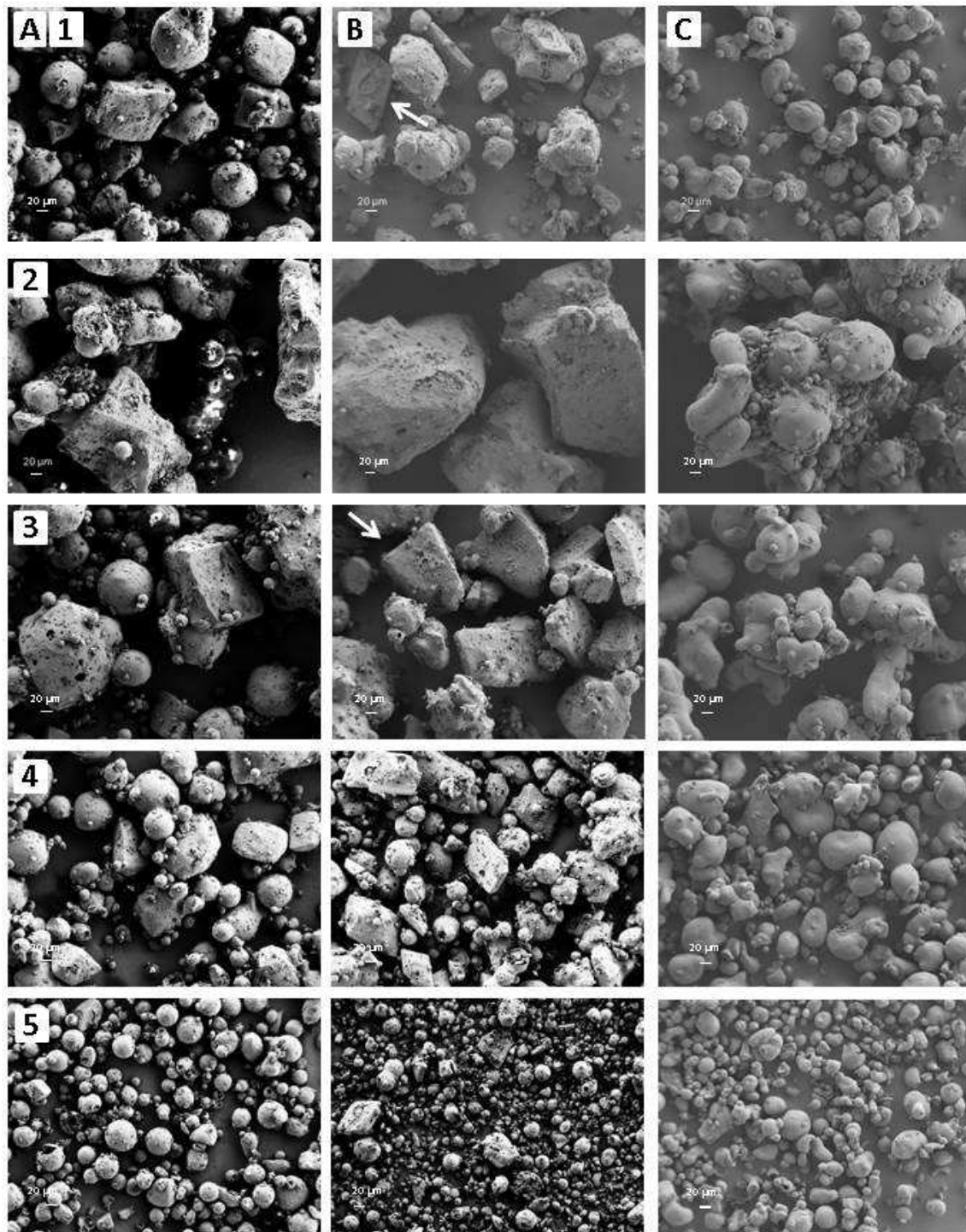


Figure 1

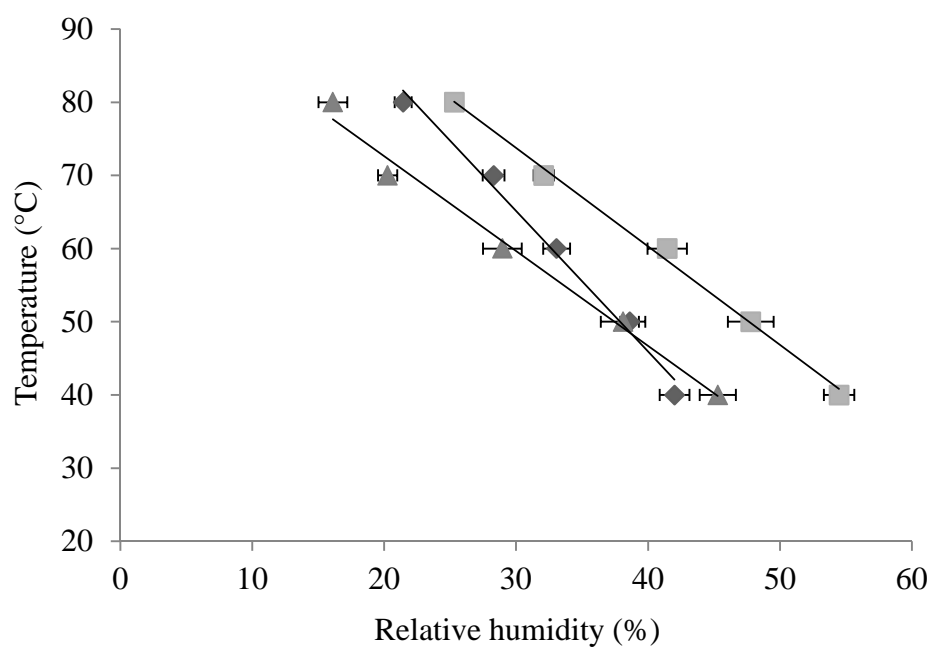


Figure 2

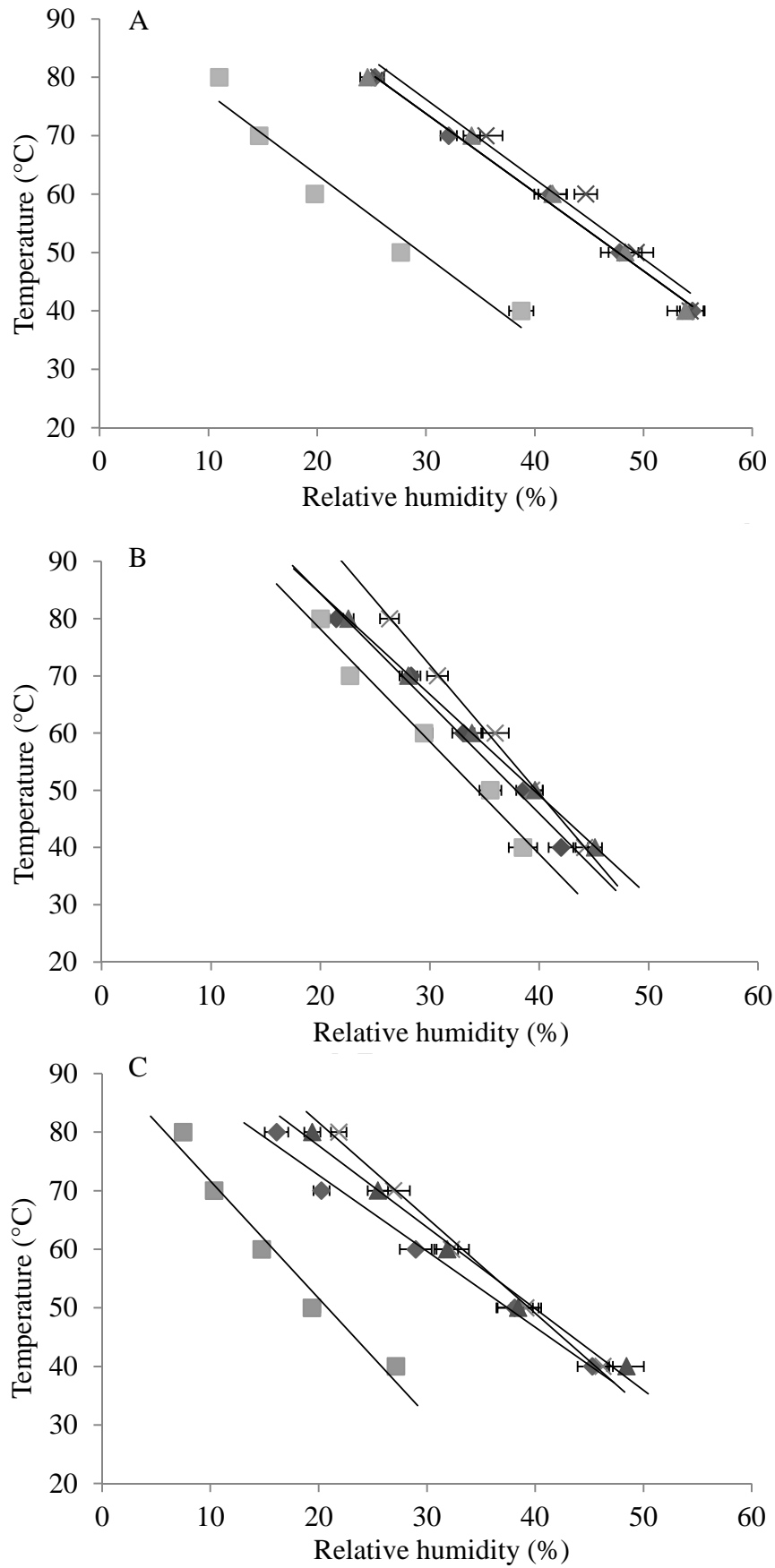


Figure 3

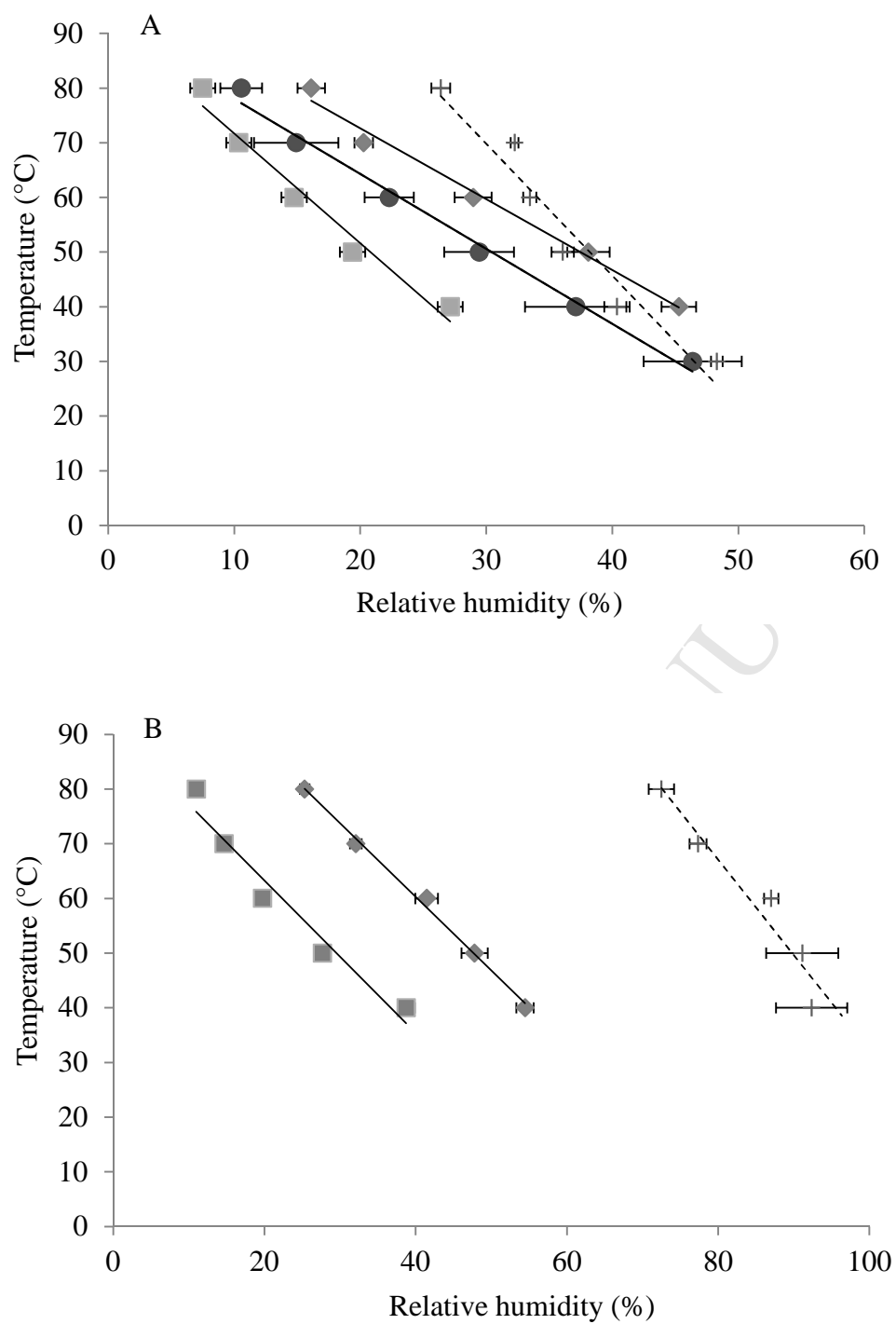


Figure 4