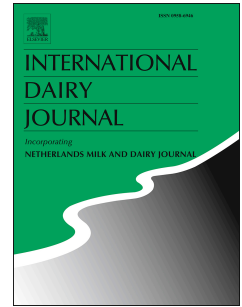


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Influence of particle size on the physicochemical properties and stickiness of dairy powders

Laura T. O'Donoghue, Md. Kamrul Haque, Deirdre Kennedy, Fathima R. Laffir, Sean A. Hogan, James A. O'Mahony, Eoin G. Murphy



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

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7 Laura T. O'Donoghue^{acd}, Md. Kamrul Haque^{ad}, Deirdre Kennedy^a, Fathima R. Laffir^b, Sean
8 A. Hogan^a, James A. O'Mahony^{cd}, Eoin G. Murphy^{ad*}

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12
13 ^a *Teagasc Food Research Centre, Moorepark, Fermoy, Co. Cork, Ireland.*

14 ^b *Materials and Surface Science Institute (MSSI), University of Limerick, Limerick, Ireland.*

15 ^c *School of Food and Nutritional Sciences, University College Cork, Cork, Ireland.*

16 ^d *Dairy Processing Technology Centre (DPTC), Ireland.*

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20
21 *Corresponding author. Tel.: +35 3761112525.

22 *Email address: eoin.murphy@teagasc.ie (E. G. Murphy).*

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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.

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 μm) 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 (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 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 μm) 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 (MgCl_2), potassium carbonate (K_2CO_3) and sodium chloride (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 μm).

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.

156

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]).

163

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 (g.kg^{-1}) and L is the lactose content (g
187 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 (g.kg^{-1}), FW: free water content (g.kg^{-1}), CC: casein content
191 (g.kg^{-1}), WPC: whey protein content (g.kg^{-1}) and MSSC: milk salt solution content (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⁻¹) 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⁻¹ dry air. All analysis was conducted at room temperature (~20 °C).
219 The air velocity (m s⁻¹) passing through each fluid bed in the stickiness apparatus was
220 determined by dividing the total air flow rate (3.5 L m⁻¹) 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⁻¹, cooling from 60 °C to -10 °C at 10
233 °C min⁻¹, 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 μm . However, in
275 DWP, the majority of powder particles were between 250 and 150 μm , compared with WPP
276 and SMP, which mostly contained particles in the range 150 to 75 μm . 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 ± 0.01 , $13.53 \pm$
285 2.29 and 35.55 ± 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 ± 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 (α -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 $x < 75$ μm fraction) compared with larger particles (8.60% of total
294 lactose in $x > 250$ μm fraction). A similar trend was also observed for DWP. Furthermore,
295 representation of SMP crystallinity in terms of α -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 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 $9.56 \pm 1.60\%$, 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 μm)
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 β -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 ± 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

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 μm . The $D[4,3]$ values of
425 the $250 > x > 150$ and $150 > x > 75$ μm fractions of SMP examined in this study were 124
426 and 83.2 μm , 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 ($x < 75$ μm) 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 $150 > x > 75$ μm
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 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 ± 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 ± 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 ± 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

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538

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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 μm , 150 μm and 75 μm 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 ± 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

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.

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) ($^{\circ}\text{C}$)	T ($^{\circ}\text{C}$)	$T-T_g$ ($^{\circ}\text{C}$)	$T-T_g$ (after washing) ($^{\circ}\text{C}$)
DWP	Original	0.34	48.5 ± 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.

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 ($P \leq 0.05$).

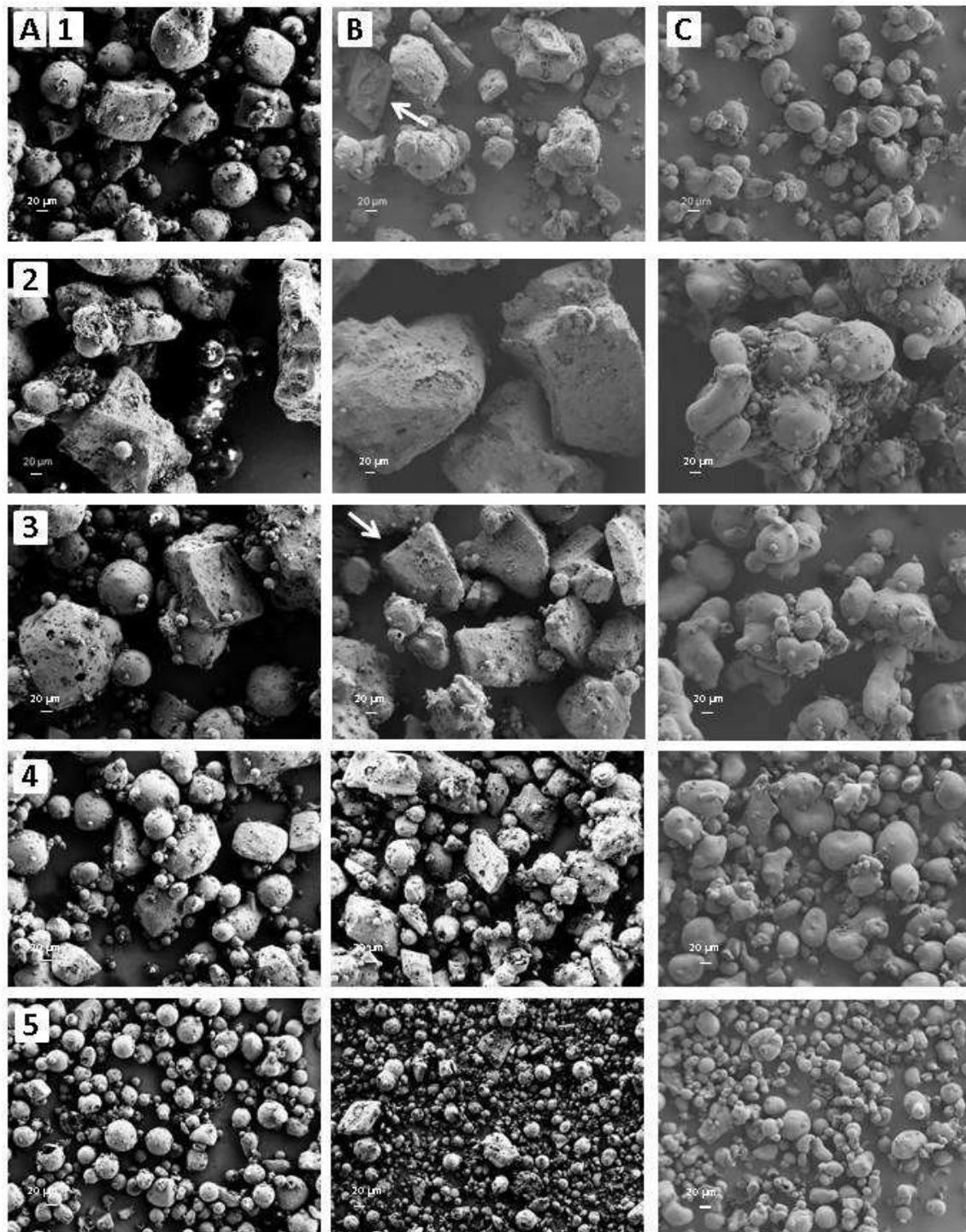


Figure 1

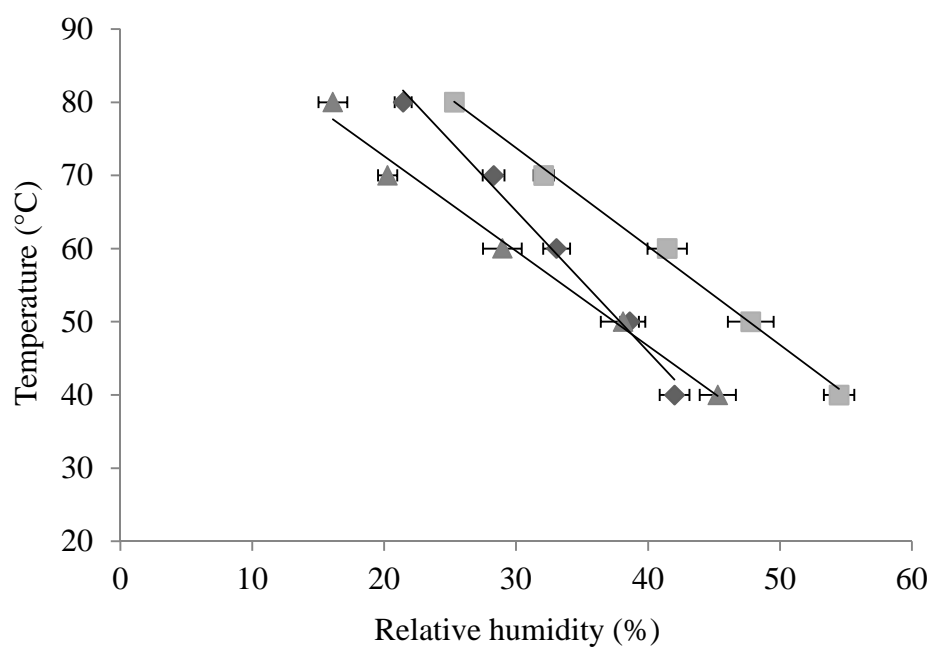


Figure 2

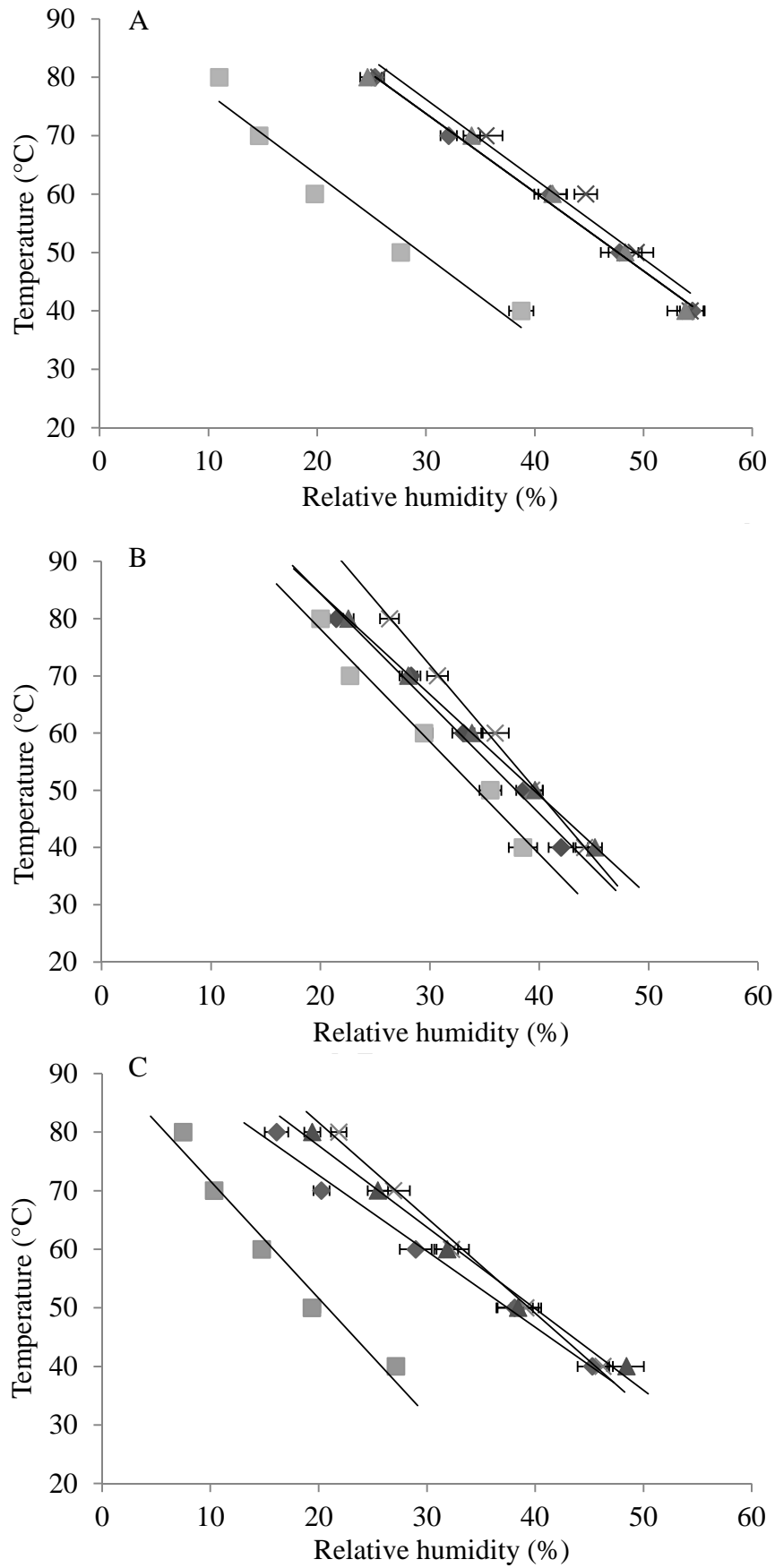


Figure 3

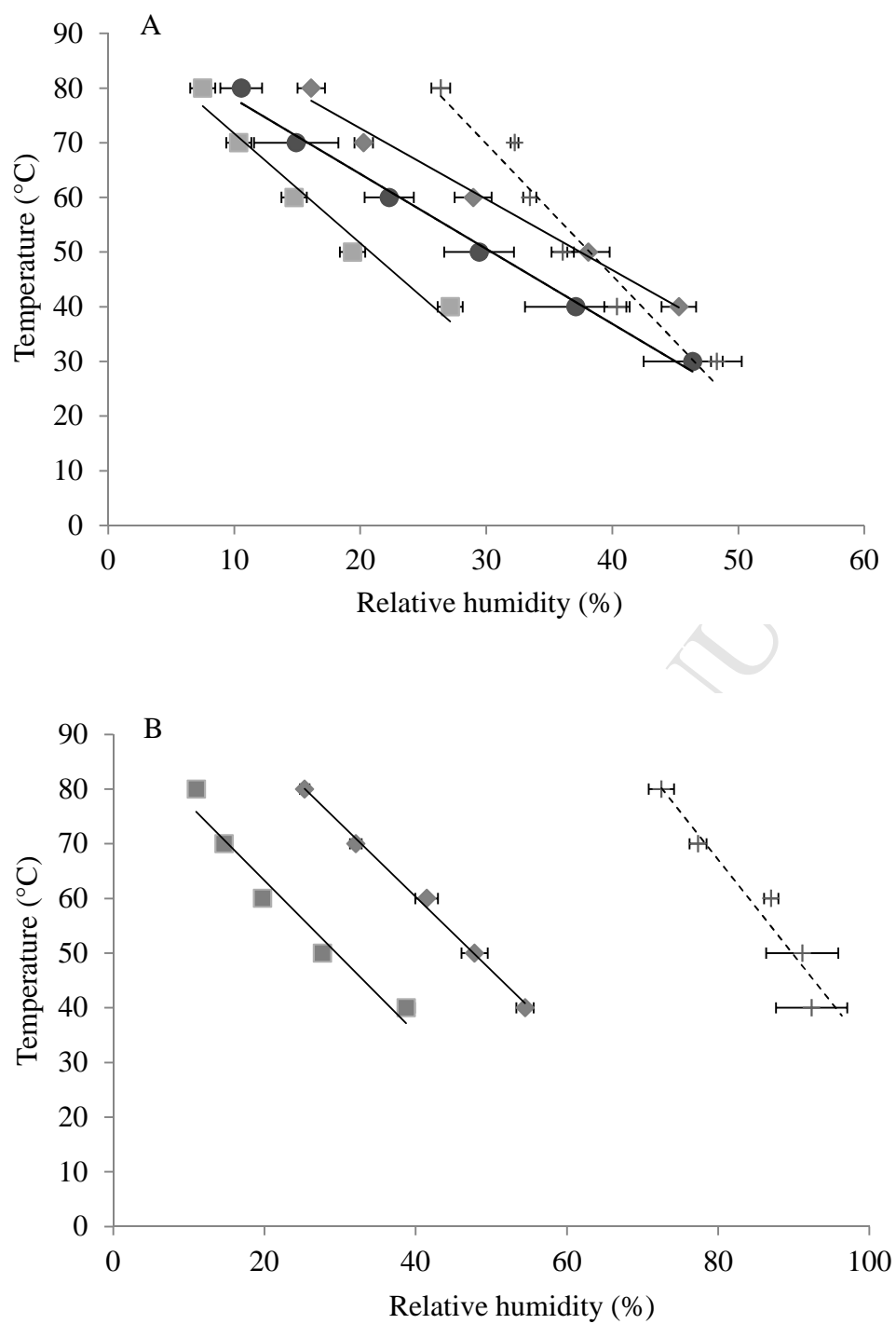


Figure 4