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Particle size and fat encapsulation define the colloidal dispersibility and reconstitution of growing-up milk powder

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ABSTRACT

Growing-up milk (GM) powders of contrasting colloidal behavior in aqueous suspension were studied by laser diffraction under wet and dry conditions. The reconstitution of the GM powders considered the interdependencies between particle size and the presence of encapsulated fat. The GM powders of low dispersibility presented fines associated with large particles. By contrast, the highly dispersible GM powder included fat encapsulated with fine particles ($20 - 80 \mu m$). Complementary analyses (morphological, SEM, spectroscopic, and thermal, DSA) analyses showed that the fine particles with free fat were more adhesive and presented poorer dispersibility, and lower soluble concentrations of macronutrients, eventually reducing the dispersibility in water.

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1. Introduction

Milk powder obtained by spray-drying results in different morphology and size, including spherical fines and agglomerates [1]. Large particles and agglomerates typically have a mean diameter in the range of 200–500 μ m but can reach up to 1 mm in size [2,3]. Fines or small particles are associated to diameters <125 μ m [4]. Importantly, agglomerates have been observed to improve the reconstitution properties of milk powders in water [1,5]. On the contrary, due to their stickiness, fines lead to poor rehydration and represent a challenge in handling [4,6].

As an example of milk powder, infant formula (IF) powder is composed of typical components, including macronutrients (lactose, fat, and milk proteins) and micronutrients (minerals and vitamins) needed for the optimal development and growth of the infants [7]. Based on the age of the infants and growth nutritional needs, various stages are classified, and these include stage 1 (0–6 months, IF), stage 2 (6–12 months, follow-on formula, FF), and stage 3 (12–36 months, growing-up milk, GM) [8]. Further, the stability of macronutrients is significantly influenced by the relative humidity, thus causing physical and functional properties to change [9]. IF powder should have consistency in chemical composition [8], which typically includes fat (about 26%) [9] in close proximity to whole milk powder (WMP) [10]. Upon reconstitution, an ideal milk powder should wet quickly, sink into water, become fully dispersed (within a short period of time) and should show no traces of lumps or residual, insoluble materials [11,12]. The factors affecting dispersibility, defined as the capacity of wet particles to disperse uniformly in contact with water [13], remain as important subjects for elucidation given the utilization and delivery prospects of milk powders after reconstitution.

Besides particle size distribution [14] and structural porosity [15], other factors influence the dispersibility of milk powders, such as particle density [2,15] and composition [16,17]. Particle density refers to that of a single particle; however, a "density" can also assigned to a group of particles. To determine particle density of large particles and a group of fines, an immiscible solvent is poured into a container and the fine fractions is demonstrated for its higher free-fat content compared to the larger particles [18], leading to stronger adhesion between them. Thus, due to an increase in the surface area-to-volume ratio, the smaller the size, the more the solvent is needed to disperse the particles, assuming the large and fines particles had the same mass. Thus, the presence of low particle density in fines slow precipitation, thus indicating milk powders of poor dispersibility [19]. As an essential composition in the milk powder, the presence of fat on the surface of milk powder affects reconstitution [20], particle cohesion [21] and prevents water wetting given the low surface energy [12,22]. An increased free fat content in the powder further reduces the dispersibility of whole milk powder (WMP) [23,24]. The cohesion of milk powder consisting of 26% fat was found to increase when the size of the particles was reduced from



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239 µm to 59 µm [10]. In addition, the dispersibility of IF powder was significantly impeded by the breakdown of agglomerates through a combination of increased surface free fat and a reduction in the interstitial air volumes, both of which limit the water diffusion into the powder bulk during reconstitution [25].

Several studies have investigated powder dispersibility, but still little is known about the interrelation that exist between particle size distribution and bulk fat. Particle size distribution has been characterized by using various methods, such as sieving/screening and laser diffraction [26]. In efforts to fractionate WMP, it was noted that the sieving efficiency was reduced by the cohesive properties of the powder [27]. On the other hand, laser diffraction (LD) offers several advantages, including high reproducibility, fast and simple operation, versatility, adaptability, and suitability for a broad range of sample types [28,29]. Laser diffraction-based measurements, which use air as dispersion medium (dry condition), has the advantage of eliminating the effect of changing particle morphology that otherwise occurs in the presence of a liquid phase [30]. Controlling the air pressure to avoid particles to breaking apart is critical to correctly determine the particle size distribution [31]. This latter effect is minimized in laser diffraction in wet conditions [31], which is also suitable for cohesive powders [32], that can properly studied by selecting the dispersing medium [29]. Laser diffraction have been extensively applied to milk powder and operation in wet conditions have been found to be effective in determining the particle size of infant formula powders (IF) [31]. For instance, the particle size distribution of WMP and skim milk powders (SMP) have been compared by using ethanol as a dispersant [14]. Recently, particle sizing-based laser diffraction by both dry and wet conditions was applied and determined that a high dispersibility was associated with fat-filled milk powders (FFMP), which after sieving had fewer fines compared to FFMP of low dispersibility [33].

Despite previous efforts, correlations between particle size analyses and distribution are still lacking, subject that is addressed in this study. Here, we compare two contrasting growing-up milk (GM) powders, one which showed no lumps during reconstitution (herein termed as "welldispersing growing-up milk or WDG") and another GM, which showed lumps (termed as "poorly-dispersing growing-up milk or PDG"). Solid particle size characterization was performed using dry and wet LD. The experimental results suggested different mechanisms acting on the formation of lumps after reconstitution of WDG and PDG powders, respectively. Fines were found to comprise stable encapsulated fat, which resulted in the formation of lumps (WDG powders) under gentle agitation during reconstitution. In addition, unencapsulated or free fat in the fines of PDG powders played a dominant role in the formation of insoluble lumps upon reconstitution, irrespective of the energy applied during agitation. We find that particle type and bulk fat are critical factors affecting GM powder dispersibility.

2. Materials and characterizations

2.1. Materials

Spray-dried growing-up milk (GM) powders were obtained from Valio, Ltd. (Lapinlahti, Finland). The powder was obtained to meet the stage 3 for nutritional needs of the children from 12 to 36 months. The GM powder composition (g/100 g) included fat (vegetable oils, 21.5), lactose (52.7), milk proteins (17.4 with casein: whey = 60:40), ash (4.7), and moisture (2.4). After manufacturing, the growing-up milk (GM) powders were initially evaluated for their reconstitution properties at the factory. The powders were placed in a bottle-feeding child, simply reconstituted at 40° C, and manually shaken, similarly to what the consumers would do. After simple reconstitution, the samples were classified as GM powders showing no lumps, thereafter labelled as WDG. The powders that showed lumps were termed as PDG. Different GM batches were produced at different times, i.e., batch 1, 2, and 3, and were classified as WDG or PDG. Accordingly, the samples (6 in

total) are herein referred to as "WDG" or "PDG" followed by the batch number: WDG-1, WDG-2, and WDG-3 for well-dispersing GM powders and PDG-1, PDG-2, and PDG-3 for the poorly dispersing GM powders, as accessed qualitatively. The samples were thereafter placed in a tight plastic bags at room temperature (RT, 22° C) in the dark room for further characterization.

2.2. Characterization

The characterization of WDG and PDG powders were performed four times, unless otherwise stated, and included particle sizing, morphological evaluation (SEM), spectroscopic (FTIR) and thermal (DSC) analyses, as introduced next.

2.2.1. Particle size analysis by sieving

The WDG and PDG samples (200–300 g each), were fractionated through a series of sifters using a Retsch sieve shaker (Retsch GmbH, Germany). A series of meshes with characteristic aperture size (500, 355, 250, 212, 160, 125, 80 and 63 μ m) were used and a metal pan placed underneath the classification system collected the fractionated GM powders. Prior to sieving, the powder was shaken at least 1 min to homogenize the sample. The powder fractionation was performed for 10 min with under vibrating amplitude of 1.2 mm. The fractionated GM powder collected from each sample was used for particle analyses, namely, laser diffraction using the wet and dry method as well as subjected to compositional and dispersibility analyses.

2.2.2. Particle size analysis, wet method

Particle size distribution of the WDG and PDG samples was obtained by using isopropanol as dispersing medium using a Mastersizer 2000 operated at both wavelengths of 466 and 633 nm (Malvern Instruments Ltd., U.K). The refractive index of isopropanol was assumed to be 1.38 [32]. In addition, the refractive index of milk particle and its absorption coefficient were 1.46 and 0.001, respectively [34,35]. The given GM powder was added dropwise into the sample tank containing isopropanol until the system reached 5% laser obscuration. The powder-isopropanol system was kept mechanically agitated at 2000 rpm and following this procedure, particle sizes were determined by light diffraction according to the volume mean diameter (VMD) or d [4.3] as well as d(0.1), d(0.5) and d(0.9).

2.2.3. Particle size analysis, dry method

Similar to the wet method, particle size distribution was carried out by using a laser-based instrument, Hydro Scirocco 2000 (Malvern Mastersizer Scirocco 2000, Malvern Instruments Ltd., U.K). In contrast to the wet method, air was utilized as a carrier to suspend the WDG and PDG particles and the respective size distribution was determined. The GM powder (20 g) was mounted on the sample holder and two air pressures, 2 and 6 bar, respectively, were applied to transport the powder into the sampler. Similar to the wet method, the particle sizes are reported as VMD, d (0.1), d (0.5), and d (0.9).

2.2.4. Spectroscopy analysis

The GM powder (13 g) was added into a 90 mL water in the feed bottle at 40° C, according to the IDF standard 87 [36] with some modifications. The reconstituted powder was allowed to disperse for 6 min and gently agitated with an orbital shaker. In addition, this mechanical agitation can be controlled from a speed of "1" (low agitation), of "3" (gentle), and of "6" (robust). The reconstituted sample was settled for 30 s and filtrated using a 315 μ m sieve. The formation of lumps was checked during the filtration. The filtrate was thereafter characterized using the Milko Fourier Transform (FT) scan analysis to determine the total solid content (% TS). The dispersibility was calculated according to the following equation:

$$D(\%) = \frac{692 \times \% TS}{100 - (\% TS + \% mc)}$$
(1)

where *TS*, *mc*, and % D represent the total solids (lactose, fat, and protein), moisture content of the sample, and percentage of dispersibility, respectively. Further, the powders demonstrated % D > 85 [37] were classified as 'more dispersible', otherwise they were classified as 'less dispersible'. The samples tested included non-fractionated as well as WDG and PDG fractions obtained from sieving, as previously described. To simplify the calculation, the moisture content of the powder fractions was assumed to be similar to their non-fractionated powders. The dispersibility analysis was performed in duplicate.

2.2.5. Scanning electron microscope (SEM)

The morphology of the WDG and PDG powders was accessed with a scanning electron microscope, SEM (JSM-7500FA Jeol, Japan) operated at accelerating voltage of 2 kV. The samples were mounted on the double-sided adhesive carbon black. To ascertain a firm attachment between samples and adhesive carbon black, the GM powders were blown with N_2 gas under a pressure of 2.5 bar. Later, they were sputtered with a gold (Au) layer with a thickness of 5 nm (Leica EM, ACE 200, Germany). The characterization was performed once.

2.2.6. Differential scanning calorimetry (DSC)

Bulk fat composition of both representative fractions of WDG and PDG powders as well as vegetable oil blends was characterized using a DSC 3+ (Mettler Toledo, AG, Schwerzenbach, Switzerland) facilitated with STARe thermal analysis software. The samples (3–5 mg) were weighed in 40 μ L aluminum pans. They were cooled and heated at 10 K/min. They were heated from 20° to 70° C, hold for 5 min at 70° C, cooled to -50° C, and once again heated to 70° C under N₂ atmosphere. The thermal characterization was performed once.

2.2.7. Statistical analysis

Differences between measurements were tested with one-way analysis of variance (ANOVA). The significance of the differences was thereafter tested with Tukey's honest significance test at p < 0.05. All statistical tests were performed using Minitab Statistical (LCC, Pennsylvania, USA) software.

3. Results and discussion

3.1. Particle size analyses (sieving, laser diffraction, and SEM)

Each of the growing-up milk (GM) powders classified as well dispersing growing-up (WDG) and poorly dispersing growing-up (PDG) powder, respectively, were sieved into fractions ranging from the largest (500 μ m aperture) to the smallest (63 μ m) mesh sizes (Table 1).

Table 1

Fraction (µm)	Mass fraction (%)							
		Growing-up milk (GM) powders						
	Well-dispersing GM powders			Poorly dispersing GM powders				
	WDG-1	WDG-2	WDG-3	PDG-1	PDG-2	PDG-3		
500	0.3	0.7	0.4	0.6	0.6	0.6		
355	4.6	6.8	8.3	3.5	9.6	13.3		
250	35.3	28.4	35.4	30.5	45.7	54.1		
212	24.1	18.9	25.8	28.1	32.2	26.5		
160	21.6	25.3	17.2	28.8	11.2	5.3		
125	7.3	10.4	5.2	8	0.6	0.2		
80	6.4	8.8	7.3	0.5	0	0		
63	0.5	0.7	0.6	0	0	0		

After sieving, the largest size fraction (500 µm) of both WDG and PDG, represented a relatively similar contribution to the mass distribution, between 0.3 and 0.7% (Table 1). Poorly dispersing growing-up powders displayed a larger mass fraction corresponding to the 355-µm size, 9.6 and 13.3% for samples PDG-2 and PDG-3, respectively. Compared to WDG powders at 250 µm, powder PDG-2 and PDG-3 further showed larger mass fraction, 45.7 and 54.1%, respectively. However, the WDG samples contained more fines (sieving with a sifter of 80 µm or 63 µm, Table 1). As will be discussed in later sections, our results are in contrast with others who indicate that fat-filled milk powders had fewer fines after sieving [33]. In this latter case, the powders were stabilized emulsions made from blends of skim milk, lactose, proteins, high fat content (vegetable oils), minerals, and vitamins. The powders with good dispersibility showed low level white flecks, while those poorly dispersed demonstrated high level of flecking [33].

The non-fractionated WDG and PDG, and their powder fractions, were characterized using laser diffraction, spectroscopic, and calorimetric methods. Accordingly, the particle size distribution (PSD), dispersibility, and thermal properties were obtained. We assumed that the results of dispersibility and thermal properties were similar within the respective group.

Particle sizing by the wet method of non-fractionated WDG and PDG powders as well as their fractions is shown in Fig. 1. Both, nonfractionated and fractionated WDG displayed a narrow size distribution (Fig. 1). The volume mean diameter (VMD) or mean particle diameter of non-fractionated WDG powders was larger than that of PDG (Fig. 1a, Table 2). Similarly, WDG displayed larger mean particle diameter than the PDG in the size range between 160 and 250 µm (Table 2). However, mean particle diameter of PDG samples overlapped each other at 355 µm (Table 2). In contrast to the size distribution of WDG, shoulders and larger end tails areas were observed for PDG powders in the 355- and 250-µm fractions, respectively (Fig. 1b and c, black arrow). These tail areas seen in the PSD profiles are assigned to the presence of "fines" (wet method) [32]. In our characterization, shoulders and larger tails areas are hypothesized to result from the attachment of fines to the large particles in the 355- and 250-µm size fractions.

From the PSD profiles of the WDG, particle sizes calculated as d[0.1], [0.5], and d[0.9], showed particle distributions larger than PDG (Table S1-S3). In the 160–355 μ m size range, PDG-2 and PDG-3 powders included particles with d[0.1] < 95 μ m, namely, fines (wet method, Table S1). However, a notable exception was PDG-1 powder, containing fines, d[0.1] < 95 μ m in a narrower range fraction, i.e., 160–250 μ m (Table S1). In contrast to the sieving results (Table 1), the wet sizing method revealed more fines for PDG than for WDG powders fractions at 355- and 250- μ m, as observed by shoulders and larger tail areas, respectively (Fig. 1b and c). We note that particles with smaller diameters than the sieve aperture may cause blinding, thereby resulting in a lowered sieving capacity (during sieving, blinding occurs when small particles clog the sieving mesh) [38].

A previous study revealed that high surface fat coverage leads to milk powders with poor functional properties [16]. Milk powders with a high surface fat content become very sticky, resulting in few powder particles passing the sifter during powder fractionation. In our study, sticky, individual fines in PDG (Fig. 2b and d) accumulated in the large sifters, i.e., 355 µm and 250 µm, allowing more GM powders to be collected during sieving (Table 1).

Scanning electron microscopy (SEM) revealed attachment of spherical fines to the larger particles, in both WDG-2 and PDG-2 powders in the 355-µm fraction (Fig. 2a and b) and in the 250-µm fraction (Fig. 2c and d), respectively. However, for these two larger fractions, WDG-2 powder demonstrated much larger agglomerates (Fig. 2a and c) compared to PDG-2 powder (Fig. 2b and d). An inert gas, N₂, was blown onto the particles in the two fractions, which were mounted on a carbon adhesive tape to assess the attachment strength between the fines and the large particles (Fig. 2a-2d).



Fig. 1. Mean particle diameter of GM powder dispersed in isopropanol (wet method). The samples included the (a) non-fractionated samples and the fractions obtained by screening with the (b) 355-µm mesh, (c) 250-µm mesh, and (d) 160-µm mesh. The black arrow denotes tail areas representing the presence of fines in the given system.

The GM powders were blown at low pressure at room temperature (RT, 21° C). The fines that were strongly bound to the large particles remained agglomerated (Fig. 2a and c), while the weakly-bound fines were detached from the large particles and transferred to the carbon tape, as individual or free fines. Many free fines were observed for PDG-2 powder (Fig. 2b and d); free fines were absent in WDG-2 (Fig. 2a and c) in the 355- and 250-µm fractions, respectively. When dispersing these larger fractions in isopropanol, the cohesive individual fines formed aggregates of given sizes or adhered to large particles, as indicated by the shoulders (Fig. 1b) and the end tails observed in the particle size distribution (Fig. 1c). By analogy, the interactions between the free fines or those with large particles are expected to induce the formation of lumps during reconstitution in water, which partly explains the limited dispersibility, to be discussed in next sections. No

significant differences in particle geometry were observed for WDG-2 (Fig. 2e) and PDG-2 powders (Fig. 2f), respectively, the fractions of 80 μ m.

Besides the wet particle analysis, WDG and PDG particle sizing was carried out under airflow at a pressure of 6 bar (dry method) (Fig. S1, Supplementary Information). Compared to the wet method (Fig. 1), the size distribution obtained by the dry method, using the non-fractionated and the several sieving fractions obtained from WDG and PDG powders, were not significantly different (Fig. S1, Supplementary Information). Interestingly, the WDG and PDG powders, as determined by the dry method, showed much smaller mean particle diameter (Table S7, Supplementary Information) than those obtained with the wet method (Table 2). Shoulders and larger end tails indicate the presence of fines in PDG, 250-µm fraction, as shown in the wet method

Table 2

Volume mean diameter, d[4.3] of well-dispersing GM and poorly dispersing GM powders obtained by laser diffraction using the wet method.

Non-fractionated/Fraction (µm)	Volume mean diameter (VMD), d[4.3]*							
	Growing-up milk (GM) powders							
	Well-dispersing GM powders			Poorly dispersing GM powders				
	WDG-1	WDG-2	WDG-3	PDG-1	PDG-2	PDG-3		
Non-fractionated 355 250 212 160 80	$\begin{array}{c} 259 \pm 5^{b} \\ 484 \pm 13^{a} \\ 338 \pm 3^{b} \\ 234 \pm 2^{a} \\ 197 \pm 1^{b} \\ 137^{a} \end{array}$	$\begin{array}{c} 272 \pm 3^{a} \\ 468 \pm 10^{ab} \\ 354 \pm 5^{a} \\ 226 \pm 1^{b} \\ 214 \pm 1^{a} \\ 126 \pm 1^{b} \end{array}$	$\begin{array}{c} 270 \pm 2^{a} \\ 452 \pm 10^{b} \\ 313 \pm 2^{c} \\ 217 \pm 1^{c} \\ 176 \pm 1^{c} \\ 128^{ab} \end{array}$	$\begin{array}{c} 215\pm5^c\\ 464\pm14^{ab}\\ 294\pm2^d\\ 197\pm1^d\\ 156\pm1^d\\ 106^c \end{array}$	$\begin{array}{c} 199 \pm 4^{d} \\ 313 \pm 6^{c} \\ 245 \pm 4^{e} \\ 164 \pm 2^{e} \\ 142 \pm 1^{e} \\ n.a \end{array}$	$\begin{array}{c} 212 \pm 5^c \\ 294 \pm 7^c \\ 226 \pm 1^f \\ 155 \pm 1^f \\ 137 \pm 2^f \\ n.a \end{array}$		
63	n.a	84	n.a	n.a	n.a	n.a		

* mean \pm SD (n = 4), samples sharing the same subscript in the same row are not statistically different (p > 0.05); n.a = not analyzed.

WDG-2 powder

PDG-2 powder



Fig. 2. SEM images of GM powder fractions obtained by sieving using the (a,b) 355-µm, (c,d) 250-µm, and (e,f) 80-µm meshes. Well-dispersing GM (WDG-2) and poorly dispersing GM (PDG-2) powders were used as representative in each category.

(Fig. 1c), but not detected with the dry test (Fig. S1b, Supplementary Information). In addition, SEM images displayed agglomerates in WDG and PDG, particle diameter (d) $> 300 \,\mu\text{m}$ at 355 μm and 250 μm , respectively (Fig. 2a-d), confirming the particle size distribution at d[0.9] from the wet method analysis (Table S3, Supplementary Information). Overall, the results point to the fact that the wet method is better suited for particle sizing of GM powder.

In agreement with the mean particle diameter of WDG and PDG, the sizes calculated as d[0.1], d[0.5], and d[0.9] decreased when the particles were subjected to a high air pressure (6 bar, dry method) (Table S4-S6, Supplementary Information). Interestingly, the mean particle diameter of non-fractionated WDG (Fig. 3a) and PDG (Fig. 3b) did not increase when lowering the air pressure to 2 bar. Given that no significant differences in PSD was found for tests at low pressure (Fig. 3), it can be concluded that a low pressure might be sufficient to disperse the fragile agglomerates into smaller particles, thus reducing the PSD (Fig. 3). In contrast to our PSD results from the dry method, Kwak et al. (2009)

[31] found that the mean particle diameter and particle size at d[0.1], d[0.5], and d[0.9]), respectively, increased when reducing the air pressure in the dry method. The authors hypothesized that large agglomerates broke down under high air pressure. Our PSD results are, however, in good agreement with Kwak et al. [31] that indicated the benefits of the wet methodology. Besides pressure, other factors may influence the PSD profiles obtained by laser diffraction, under different working conditions, wet and dry, such as sphericity, geometry, and particle orientation. The effect of particle geometry on large agglomerates and fines was not considered in our particle analyses under both conditions and further studies are needed to determine their influence in the particle analyses of GM powders.

3.2. Dispersibility of WDG and PDG powders

Fourier transform infrared (FTIR) spectroscopic analysis has been used to direct measurement of fat, lactose, and protein in the emulsion



Fig. 3. Mean particle diameter of (a,c) well-dispersing GM (WDG-2) and (b,d) poorly-dispersing GM (PDG-2) powders by using the wet and dry methods. The black arrow denotes the end tail area, indicating the presence of the fines.

using a double beam spectrophotometer, thus providing a complete analysis of a product covering ash, solid non-fat (SNF), and total solid (TS) contents [39]. The spectroscopy measures absorption energy by specific functional groups existing in fat, lactose, and protein, respectively [39]. To evaluate powder dispersibility using FTIR spectroscopy analysis, both WDG and PDG powders were reconstituted in water at 40° C. The dispersibility was evaluated following the formation of the lumps under the influence of gentle agitation of a controlled orbital shaker. In addition, the % dispersibility, or % D (Fig. 5) was calculated, according to Eq. (1), upon reconstitution of WDG and PDG. The values of %D refer to the amount of GM powder (expressed on dry mass basis) that was dispersed in a specified volume of water, under controlled conditions.

Lumps were observed for both non-fractionated WDG and PDG during reconstitution under gentle agitation (Table 3). Lumps were also

Table 3

Formation of lumps during reconstitution with gentle agitation in water of well-dispersing GM and poorly dispersing GM powders.

Sample	Formation of lumps ^a					
	Growing-up milk (GM) powders					
	Well-dispersing GM powders			Poorly dispersing GM powders		
	WDG-1	WDG-2	WDG-3	PDG-1	PDG-2	PDG-3
Non-fractionated	Yes	Yes	Yes	Yes	Yes	Yes
250 µm	No	No	No	Yes	Yes	Yes
212 µm	Yes	Yes	Yes	Yes	Yes	Yes
160 µm	Yes	Yes	Yes	Yes	Yes	Yes

 $^{\rm a}\,$ Reconstitution temperature $=40^{\rm o}\,$ C and measurements were performed in duplicates.

observed for the 212-µm size fraction of both WDG and PDG powders (Table 3). However, the 250-µm fraction of WDG did not show any lumps (Table 3). This finding confirms that WDG agglomerates (Fig. 2c) rapidly disperse and form a colloidal suspension under gentle agitation. In contrast to the reconstitution of WDG powders (250-µm fraction), lumps were evident when reconstituting PDG powders of the same size fraction (Table 3). Although non-fractionated WDG powders showed lumps during reconstitution under gentle agitation (Table 3), they had a higher % D compared to that of PDG (Fig. 4a). The higher the percentage of powder dispersibility, the more dispersible the powder is. In sum, comparable % D results were recorded for both WDG and PDG powders.

Sharma et al. (2012) [37] indicated that for whole milk (WMP) to be classified as an instant powder, it should give at least % D > 85. The percentage dispersibility of WMP powder could thus be applied to our GM powder. Our 250-µm WDG fraction demonstrated a higher % D than the respective PDG powder (Fig. 4b). Eventually, the 212-µm fraction of WDG powder displayed a higher % D than that of PDG powder under reconstitution using a controlled agitation (Fig. 4b). The dispersibility results (Fig. 4) indicate no clear correlation between %D and the presence of lumps (Table 3). Lumps were still observed when reconstituting non-fractionated WDG and PDG under gentle agitation (Table 3), even though % D > 85 for these samples (Fig. 4a). However, poor dispersibility of non-fractionated GM powder is indicated by two findings, firstly, the formation of lumps under a controlled agitation (Table 3) and secondly, % D < 85. It is worth noting that the dispersibility analysis indicate that the smaller particles, the lower their dispersion, as indicated by % D (Fig. 4b). Similar to our finding, Kinsella and Moor (1984) [40] found that powder dispersibility increased with particle size.



Fig. 4. Dispersibility, measured as % D (Eq. (1)) of (a) non-fractionated well-dispersing GM (WDG-1, WDG-2, WDG-3) and poorly-dispersing GM (PDG-1, PDG-2, PDG-3) powders. (b) % D as a function of particle size fraction (µm) during reconstitution under gentle agitation. The histogram sharing the same lower-case letter is not statistically different (p > 0.05).

3.3. Bulk fat in WDG and PDG powders

Differential scanning calorimetry (DSC) has been previously used as a routine thermal analysis to identify fats and edible oils with a high sensitivity and reproducibility [41]. Thus, the bulk fat in WDG-2 and PDG-2 powders, respectively, was determined by using DSC (Fig. 5). Therein, the thermal properties of large and small size fractions, 355- and 80-µm, were determined at a cooling/heating rate of 10 K/min. The thermal behavior of vegetable oil blends, as a reference, was also characterized (Fig. S4) and compared to that of these representative samples. The exothermic region showed different crystallization peaks for WDG-2 powder, 355-µm and 80-µm fractions, indicating different fat crystals. The formation of fat crystals in this sample, in these two fractions, occurred at $T_{crys} < 0^{\circ}$ C (Fig. 5a). Both crystallization profiles differed from that of vegetable oil blends (Fig. S4a). In contrast to WDG-2, the fat crystallization of PDG-2 at 80-µm fraction began early, at $T_{crys} > 0^{\circ}$ C (Fig. 5b). Interestingly, the crystallization profile of vegetable oil blends under cooling (Fig. S4a) matched closely that of the fines of PDG-2 at 80-µm fraction, with initial $T_{crys} > 0^{\circ}$ C (Fig. 5b). Previously, Vignolles et al. 2008 [42] carried out a DSC thermal analysis to



Fig. 5. Thermogram of bulk fat of (a,c) well-dispersing GM powder (WDG-2) and (b,d) poorly-dispersing GM powder (PDG-2) using DSC to show the main exothermic (cooling) and endothermic (melting) transitions.

identify edible oil in two different samples, homogenized and nonhomogenized, respectively, emulsions. They found that compared to the case of homogenized emulsion droplets, the crystallization profile of non-homogenized emulsion droplets occurred earlier, at 12.8° C. The authors further noted that the non-homogenized milk emulsion showed a greater free fat content, indicating an unstable fat organization dispersed in the particle matrices. Thus, this later characteristic might be taken as indicator of poor dispersibility [42]. It is likely that fat droplets in our PDG-2 fines (Fig. 5b) were not completely encapsulated by milk proteins during spray drying process, thus showing similar cooling behavior compared to that of vegetable oil blends (Fig. S4).

At a heating rate of 10 K/min, the melting profile of a 355-µm fraction of WDG-2 powder showed no significant difference with the 80µm fraction (Fig. 5c). However, the endotherms of PDG-2 powder showed a large difference in melting fats, considering the large and small size fractions, i.e., 355- and 80-µm, respectively (Fig. 5d). As noted earlier, unstable fat droplets in the PDG-2 fines influenced not only the crystallization behavior of fat (Fig. 5b), but also their melting profile (Fig. 5d). A more limited GM dispersion in water at 40° C is thus expected with the presence of unstable fat.

DSC profiles revealed that bulk fat in the agglomerates and the fines of WDG powder are more stable supramolecular organizations, as indicated by the similarities in the endothermic profiles of agglomerates and fines (Fig. 5c). Nevertheless, it is possible to explore different fat polymorphisms (α , β , and γ) and thus polymorphic stabilities of the vegetable oils in these WDG and PDG fines, which would be interesting subjects for investigation.

The relationship between thermal properties and dissolution of milk powders have been studied by dissolution calorimetry [43], which indicated that a higher fat level in the milk powders produced larger endothermic enthalpies (therefore, smaller dissolution enthalpies). The negative effect of a reduced dissolution enthalpy is associated with poorer reconstitution. In our case, the bulk fat in WDG-2 at 80-µm fraction displayed endothermic areas (Fig. 5c) that are larger compared to those of the 350-µm fraction. Considering that lumps formed during reconstitution of non-fractionated WDG (Table 3), and given the presence of fines, it follows that one needs to apply strong mechanical energy to overcome the large enthalpic barrier. Indeed, no lumps of nonfractionated WDG were visible (WDG-2, Table S8) or dramatically decreased in size (WDG-1 and WDG-3, Fig. S3a) when reconstituting under strong agitation. However, PDG lumps were not removed during reconstitution under the influence of robust agitation using a controlled orbital shaker (Fig. S3b).

According to Syll et al. (2013) [6], the cohesion forces between small particles are stronger than those with large ones, thus leading to slower dispersion. In our case, fines (Fig. 2b and d) may interact with each other, thus forming aggregates of different sizes; alternatively, they may strongly attach to large particles in PDG powders, as confirmed by the wet method, Fig. 1b and c, causing poor dispersibility. Fines consisting of stable, encapsulated fat in WDG powders demonstrated suitable colloidal dispersion since no lumps or very small lumps were observed during reconstitution under robust agitation (Table S8, Fig. S3a). By contrast, fines with unencapsulated fat (Fig. 5b and d) in PDG powders clearly caused poor dispersibility. High levels of unencapsulated fat on the particle surface tend to stick together, thus forming lumps [44]. In addition, many large lumps were detected during reconstitution (Fig. S3b), even under the application of strong agitation. In sum, particle size and bulk fat are essential aspects influencing dispersibility of growing-up powders.

4. Conclusions

Growing-up milk (GM) powders demonstrated different behaviors according to their particle size distribution, dispersibility, and thermal properties. WDG powders contained more fines than PDG powders, as measured from the small sieve fraction, i.e., 80 µm. However, a higher mass contribution was found in the PDG size fractions corresponding to 355-µm and 250-µm meshes. Laser diffraction following the wet method revealed shoulders and large tail areas for the PDG size fractions corresponding to 355-µm and 250-µm. They resulted from the contribution of non-agglomerated fines in PDG powder, as confirmed by SEM imaging. In contrast to the wet method, laser diffraction using air carrier was insensitive to the particle size distribution of GM powders, when analyzed at two different air pressures.

During reconstitution under gentle agitation, WDG powders showed no lumps (250-µm), while they were observed for PDG powders of the same size fraction. In addition, the non-fractionated WDG powders presented higher dispersibility than the non-fractionated PDG powders. Following thermal analysis, free fat was detected in the PDG fines; meanwhile, encapsulated, or stable fat existed in the WDG fines. These effects contribute to the dispersibility of GM powder in water at 40° C. Under strong agitation, the fines in WDG powders showed no significant effect. By contrast, the fines with free fat in PDG significantly minimized the powder dispersibility during reconstitution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.powtec.2021.06.008.

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