Characterization of Milk Powder – Chapter 1: Dissolution of Infant Formula and the Final Milk Product

Relevant for: Characterization of Powders and Granular Media, Food Industry, Chemical Industry, Pharmaceutical Industry

Knowing the properties and behavior of powders and granular media is essential for many industrial applications. Powder behavior is not only critical for the manufacturing process and transportation, but it also influences the product's final use. Thus, properties influencing the solubility of infant and toddler formula are important parameters to be investigated. This application report presents multiple characterization methods such as specific surface area, particle size, and permeability, to define the nature of infant/toddler milk powder with respect to formulation. Furthermore, the particle size and rheological behavior of the final dissolved milk powder, prepared based on the manufacturers' instructions, were investigated. Those results provide important information about the milk flow out of the baby bottle during consumption as well as the texture of the fluid.

1 Introduction

Not only is powdered milk a commonly used basic food item in situations where fresh milk is not available, but powdered infant formula is very important for infants and toddlers either as supplementation to or as a substitution for breast feeding, especially for those cared for in a nursery. Infant formula needs to meet the nutritional requirements of children's bodies by resembling the composition of breast milk through its special formulation.

Experiments were carried out using two milk powder samples: an infant formula, suitable for the first six months of life, and a toddler formula, for kids above the age of one.

Generally infant formula is mostly pure milk powder, but the nutritional needs of toddlers warrant a higher energy intake. This is addressed by the addition of sugars (most commonly maltodextrin). This in turn changes the structure, texture, and flow behavior of the formula (both in its powdered state and when dissolved) and critically affects the dissolution behavior as well.

Milk powder quality plays an important role in manufacturing processes and is dependent on the raw product (fresh milk). The powder behavior also influences product transportation and the characteristics of the final liquid milk product.

In this report the aim was to show a complete picture of the dissolution process and the variables governing it, as well as to depict the products' state and behavior in solution in order to illustrate the final application as experienced by the customer.

1.1 Powder Characteristics Influencing Dissolution

The solubility of a product such as infant/toddler formula is determined by chemical factors (like surface chemistry, surface charge, temperature, and pH) and by physical powder characteristics. Some of these physical characteristics are discussed below.

1.1.1 Permeability

Permeability is determined by how well the solvent (in this case water) is able to access the individual particles of the powder. The higher the permeability, the better the sample matter is accessible.

This parameter was measured using the combination of an Anton Paar rheometer and a powder flow cell, by pumping a defined air flow across the particle bed at a fixed pressure gradient. This indicates the amount of accessibility that the water has to the product, which influences the process of dissolution. A product with high permeability in this sense prevents the undesired formation of knots and nodules of undissolved powder while dissolving. These lumps of undissolved powder are the result of a barrier layer forming when water is taken up within mostly secondary agglomerates (see free fall vs Venturi particle sizes in the results section 3.1.2), which slows down the process of dissolution. Since formula should be prepared in a speedy matter, this is highly undesirable, making this an important parameter in regards to the quality of the product.

1.1.2 Particle size

Particle size impacts solubility in different ways. First, both single particle size and the size of agglomerates are correlated to the permeability of the powder; and hence, they also impact the accessibility of the sample matter by the solvent. Secondly, the size of the individual particles in the powder determines the surface area to volume ratio and is therefore critical for the speed of dissolution itself.

The particle size was measured using a laser diffraction method, which can be used in two different modes: free fall mode to investigate agglomerates and Venturi mode for the characterization of the primary particles.

1.1.3 Surface Area

Once the solvent reaches the single particles of the powder, the surface area is critical, as it defines the area available for the interaction between the solvent and the solute particles. The surface area is not only a function of particle size and shape, but it can differentiate porosity from the bulk sample.

Surface area in particular can be measured using vacuum volumetric methods. This technique measures the amount of gas or vapor (adsorbate) adsorbed onto the solid surface of the adsorbent (milk powder) at a defined absolute temperature and pressure. Measurements of the gas or vapor uptake amount versus pressure at a constant temperature, is known as the “adsorption isotherm”. This isotherm is used to determine the accessible surface area by applying the BET (Brunauer-Emmett-Teller) equation (1). In addition, pore size distribution and many more physical properties also influence the adsorption or desorption (reverse of adsorption) process.

Taken together, these three parameters form a picture of the dissolution process in its component parts and therefore give engineers the ability to tune the product and further address individual quality control issues.

1.2 Characterization of Milk – the Dissolved Powder

The final infant/toddler milk needs to meet various criteria concerning quality. Apart from nutritional aspects, quality is further reflected in the texture and stability of the milk. Additionally its flow behavior when being filled into a bottle and especially when it is sucked out of the bottle by the child is of great importance when judging the “experience” and effort needed to draw the liquid. This, in turn, is dependent on the particulates present within the dissolved formula which can change according to the nutritional needs of the child.

1.2.1 Particle size: Dynamic Light Scattering

If powdered milk or baby formula is reconstituted in water, an oil/water emulsion exists whereby the protein and fat globule particles are dispersed. The particle size distribution of these particles can be determined by using dynamic light scattering. The particle size of reconstituted milk formula influences its texture and flow behavior. These characteristics depend on manufacturing, processing conditions, drying, storage, and formulation instructions, which can all affect the particle size. This in turn influences the rheology of the dissolved product.

1.2.2 Rheology

The liquid’s flow through the bottle into the child’s mouth, as well as the intensity of sucking required, differs depending on the viscosity and flow behavior of the milk product. The viscosities at shear rates which are representative of the milk flowing out of the small hole in the feeding bottle provide important information. Furthermore, viscosity in general plays a role in the formula’s texture and its dispersion stability.

The methods for characterization of powder and liquid dispersion presented in this report will guide users to describe the characteristics of milk powder and its final milk product.

2 Sample Preparation and Experimental Setup

2.1 Powder Characteristics Influencing Dissolution

Before the measurement, both samples were stored at 70 °C overnight in a drying oven to prevent environmental moisture from influencing the sample.

2.1.1 Permeability

Permeability was investigated using an Anton Paar rheometer in combination with a powder flow cell (see Figure 1).

Figure 1: The powder flow cell mounted on an Anton Paar rheometer

Permeability is a powder property representing specifically its porous portions. It can be defined as the flow rate across a particle bed at a fixed pressure gradient. As such, it follows the relation of Darcy's law (Equation 1) and can be calculated via the viscosity of air, the cross section of the cell and the pressure differential compared to the empty cell. Substances that show high permeability allow high flow rates through the material bed, whereas lower flow rates are observed in less permeable powders. While air permeability is an important factor for filling, aerosolization processes and compaction processes (and these are employed in the production of formula), its importance in this study stems from the equality of the underlying infiltration process inherent with Darcy's law for both gas and liquid infiltration, and therefore for the dissolution process.

$$Q = \frac{KA}{\eta L} \Delta p$$

Equation 1: Darcy's law.

In Equation 1, Q is the volumetric flow rate, K is the permeability, A is the cell area, η is the viscosity of air, L is the gap width and Δp is the pressure drop.

For determining the permeability, a sample volume of 60 mL is recommended. The measuring geometry used for permeability measurements was a compression tool with an air permeable disk. All measurements were performed at ambient temperature.

2.1.2 Particle size: Laser Diffraction

The dry dispersion unit of a particle size analyzer (PSA) was used to carry out the measurements. The Venturi setup was employed to determine the particle size of primary particles, while the free fall method was used to analyze the agglomeration rate.

In the Venturi (also termed Dry Jet) dispersion mode, the powder is fed into a chamber and ejected through a Venturi tube using compressed air, the pressure of which can be set by the user between 50 and 6000 mbar. To adequately disperse the sample without causing particle breakage, the Venturi pressure was set here to 50 mbar and the vibrator parameters were set to a duty cycle of 50 % and to a frequency of 43 Hz and 39 Hz for the infant formula and the toddler formula, respectively.

In the free fall dispersion mode, the particles are conveyed by vibration down a manifold, the extremity of which is placed directly above the camera opening. The particles then fall in front of the detector, moved solely by gravity – no pressure is applied. The vibrator parameters were set here for both samples to a frequency of 44 Hz and a duty cycle of 50 %.

The commonly-used Fraunhofer reconstruction mode was applied in order to convert the diffraction pattern into a particle size distribution.

2.1.3 BET surface area

For the Kr adsorption experiment using a vacuum volumetric surface area analyzer, at least one gram of sample is needed. The measurements were performed using a relative pressure range from 0.05 to 0.3 (P/P_0). Therefore a linear plot of $1/[W(P_0/P)-1]$ vs. P/P_0 was used to apply the BET equation to determine the surface area and BET C constant (1).

2.2 Characterization of Milk – the Dissolved Powder

2.2.1 Particle size: Dynamic Light Scattering

The milk formulas were prepared as suggested by the instructions shown on the product boxes. For this purpose, water was heated and then cooled down to approximately 50 °C. Afterwards, 9 g of the infant formula were dispersed in 60 mL of water and 23 g of toddler formula were mixed and dissolved with 150 mL of water.

Since the samples were very turbid, they were further diluted for testing using filtered (0.2 µm) ultrapure water at a 1:40 ratio. The particle size measurements were carried out with the Litesizer 500 using quartz cuvettes at 37 °C. The angle, filter and focus position were automatically set by the instrument. The measurements were carried out in triplicate.

2.2.2 Rheological Measurements

The milk was prepared in the same way as for dynamic light scattering, but without further dilution of the product.

The measurements were done in an Anton Paar Modular Compact Rheometer (MCR) equipped with a concentric cylinder (CC27) measuring system and a Peltier temperature controlling device. After filling the milk into the measuring cup, the sample was heated to 37 °C and the temperature was held constant for 15 minutes in order for equilibrium to be reached. Afterwards, flow curves at 37 °C with shear rates between 0.7 and 2000 s^{-1} were performed.

A maximal shear rate of 2000 s^{-1} was chosen to represent the shear rate while sucking the milk out of a baby bottle. The shear rate was calculated by using the formula of Hagen and Poiseuille (2) (Equation 2).

$$\dot{\gamma} = \frac{4*V}{\pi*R^3*t} = \frac{4*5*10^{-6}}{\pi*(1*10^{-3})^3*3.3} = 1929\ s^{-1}$$

Equation 2: Calculating the shear rate based on Hagen and Poiseuille.

Where $\dot{\gamma}$ is the shear rate, *V* is the volume of an infant's sip (assumed to be 5 mL), *R* is the radius of the hole in the nipple (assumed to be 1 mm), *t* is the time to take one sip of milk (assumed to be 3.3 s).

3 Results

3.1 Powder Characteristics Influencing Dissolution

3.1.1 Permeability

Figure 2 and Table 1 show the permeability results, representing the powders' air flow resistances under different compaction forces. The infant formula is not only notably more permeable, but it is also much more dependent on the compaction, showing a significant change.

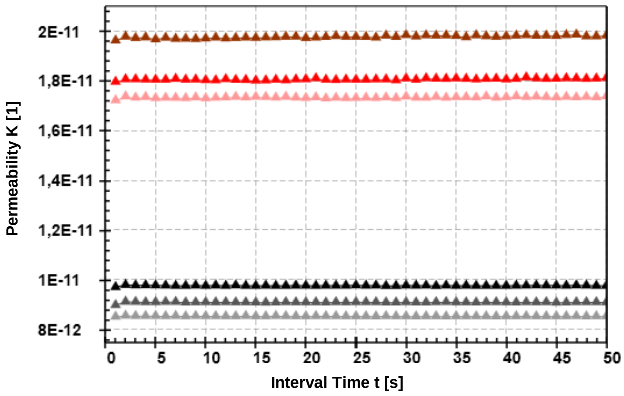

Figure 2: Permeability – toddler formula (black to gray curves) and infant formula (red curves) measured at compressions of 3 kPa, 6 kPa and 9 kPa (from darkest to lightest).

Generally, the permeability decreased with increasing normal stress during compression, and the infant formula showed significantly higher permeability (by more than a factor of 2) than the toddler formula. In itself, this could be an indication of higher particle size diversity (see section 3.1.2). However this could also be a function of chemical composition. A higher amount of carbohydrates in the composition (as is the case with the toddler formula) would naturally change the morphology of the particles, in this case leading to less free volume and therefore lower permeability.

The dependence on compression (Figure 2) shows the vulnerability of some powders to compaction. It can be expected that the infant formula will be more likely to produce clots after prolonged storage compared to fresh infant formula. However, the toddler formula shows worse dissolution behavior irrespective of applied stress and thus will exhibit clotting either way. This was also observed subjectively in the dissolution steps.

Table 1: Results of the permeability measurements.

Sample	Permeability [$10^{-12}m^2$] at 3 kPa consolidation	Permeability [$10^{-12}m^2$] at 6 kPa consolidation	Permeability [$10^{-12}m^2$] at 9 kPa consolidation
Infant	19.8	18.1	17.4
Toddler	9.8	9.1	8.5

3.1.2 Particle Size: Laser Diffraction

Figure 3 shows the differences in particle size distribution for infant and toddler formulas. The primary aggregates (measurements in Venturi mode) of the toddler formula are found in a smaller size range than the primary particles of the infant formula.

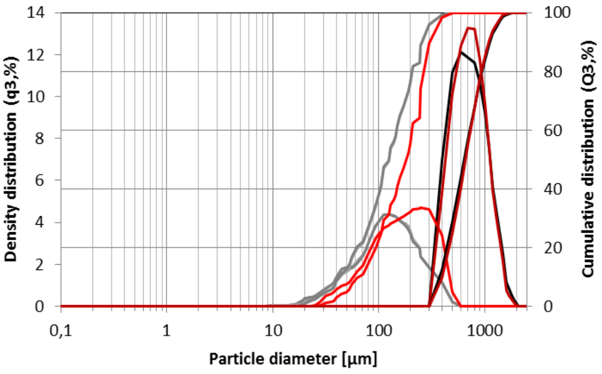

Figure 3: Particle density distribution (q3,%) and cumulative distribution (Q3,%) of both infant and toddler formulas. The infant formula measured via the Venturi mode is shown in light red, and via free fall is shown in dark red. The toddler formula measured by the Venturi mode is in grey, and by the free fall mode is in black

The analysis of D10, D50 and D90 values for the samples measured in free fall revealed only minute size differences between the two powders (see Table 2). Still, a shift towards a smaller size range for the primary particles of the toddler formula was observed.

As shown in the porosity (permeability) experiments, the different sugar composition of the two milk samples had an impact on the particle size and surface area of both samples. In fact, infant formula, which contains more lactose, had bigger particles and therefore a lower surface area than toddler formula. The bigger particles further suggest higher porosity for infant formula.

Table 2: Summary of D-volume weighted data of laser diffraction for the infant (I) and toddler (T) formula.

Infant (I) and Toddler (T) Formula				
		D10 [µm]	D50 [µm]	D90 [µm]
Venturi	I	72	189	402
	T	48	130	315
Free fall	I	501	765	1193
	T	478	746	1222

3.1.3 BET Surface Area

The calculated BET-accessible surface area values for the experimental Kr adsorption isotherm (Figure 4) were 0.041 m^2/g and 0.074 m^2/g for infant and toddler formula, respectively. With the low surface areas of the milk powders, low values of the BET *C* constant (4.14 and 7.05) were consistent with similar organic compositions which display weak adsorbate-adsorbent interactions.

Infant formula having smaller surface area complies with the particle characterization results showing a bigger particle size.

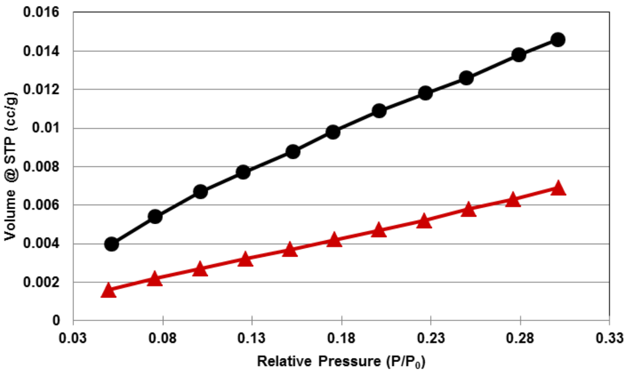

Figure 4: Kr adsorption isotherms at 77 K for toddler (black circles) and infant (red triangles) formula.

Together these results show clear particle size and morphologic differences between the samples, leading to the conclusion that the toddler formula has a higher solubility overall, but is prone to form clots during dissolution due to its low permeability.

This is corroborated subjectively through their behavior in the subsequent preparation steps in the following liquid analyses.

3.2 Characterization of Milk – the Dissolved Powder

3.2.1 Particle size: Dynamic Light Scattering

Both formulas contain milk proteins, carbohydrates (from milk or other sources), plant oils and minerals, in varying proportions. The two milk formulas showed clear differences in their particle size distribution, as measured by the Litesizer (see Figure 5). For infant formula, a single peak was measured at 666 nm. In contrast, toddler milk showed peaks at 108 nm, 604 nm and 2179 nm.

The peak present in toddler formula at 108 nm also coincides with a minor shoulder in the infant formula's particle size distribution. These particles likely correspond to the well characterized casein micelles, the dominant protein component of cow's milk (3). Fat globules in milk are known to range in size from 100 nm to 10 µm (3). As both formulas contain the same plant oils, and as the fat content only differs slightly, it is assumed that the fat globules are found in the overlapping peaks.

Lactose is present in both formulas, and because its solubility in water is poor, could be the main constituent of the largest particles observed in reconstituted milk. However, the peak at 2179 nm is only detected in toddler milk. This means that these large particles are likely not composed of lactose, but of other, more complex polysaccharides. In fact, toddler milk is known to contain high amounts of maltodextrin, which is added to increase the feeling of satiety in older infants (4) (5). Therefore this complex sugar might be the main component of the peak at 2179 nm.

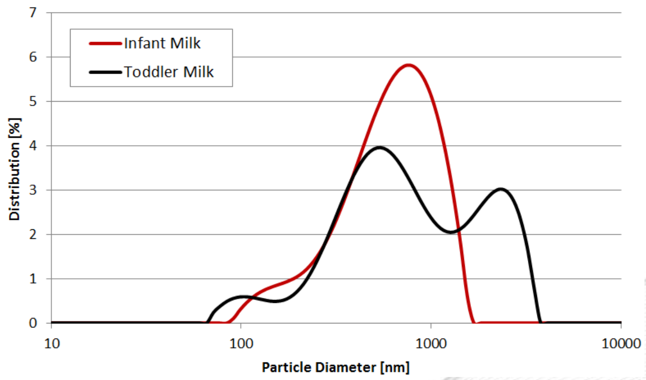

Figure 5: Representative particle size distributions for infant (red) and toddler (black) formula.

3.2.2 Rheological Measurements

The flow curves in Figure 6 reveal different flow behavior for the two liquid milk samples. Infant milk showed only slight shear-thinning flow behavior while the toddler milk was significantly shear-thinning (more than an order of magnitude decline in viscosity). Further, the absolute viscosity values of the toddler milk were consistently higher than those of the infant milk.

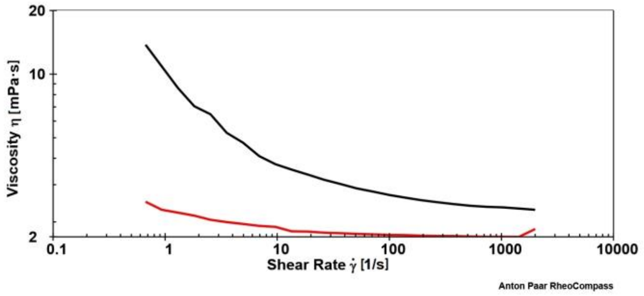

Figure 6: Flow curve of infant milk (red) and toddler milk (black) at 37 °C.

The almost Newtonian flow behavior of the infant milk can be explained by the uniform particulate size distribution in the solution. The highly shear-thinning behavior of the toddler milk is likely due to the insoluble carbohydrate ingredients like maltodextrin in the milk powder.

Considering the geometry of a baby bottle, the tip of the nipple is the most sensitive part where most of the shear rate is applied (see 2.2.2 for the calculation).

Considering the high shear rate applied, designing formula to be shear-thinning (advertently or inadvertently) is a prudent decision. Also considering the stronger muscular development of toddlers versus infants, a higher viscosity overall might be desirable as well.

4 Conclusion

4.1 Powder Characteristics Influencing Dissolution

Two different milk powder samples as well as the milk formula derived from those samples were comprehensively analyzed using solely Anton Paar instruments.

The different sugar composition of the milk samples had an impact on the samples' particle sizes and surface areas. In fact, the infant formula, with a higher content of lactose, had bigger particles and therefore a lower surface area than the toddler formula. Furthermore, a higher permeability was shown for this infant formula sample compared to the toddler formula. This goes in line with the general assumption of a better flow across the particle bed when the average particle size is enhanced.

Summarizing the results from the powder characterization, the solubility of the infant formula from a physical point of view is favored based on higher permeability. But the smaller particle size and enhanced surface area of the toddler formula benefits the area of interaction between the solvent and the solute particles, but at the cost of being more prone to form clots during dissolution.

4.2 Characterization of Milk – the Dissolved Powder

The occurrence of bigger particles in the toddler milk, where complex carbohydrates like maltodextrin are present in higher amounts, matches well with the highly shear-thinning behavior of the toddler formula. With increasing shear rate, the particles align and therefore the viscosity decreases.

In summary, the methods from Anton Paar presented in this report resulted in the successful characterization of milk powder. The powder and liquid dispersion characteristics, especially regarding solubility, were described, giving a depiction of the milk powders before and during dissolution. Furthermore, the properties of the final milk products were also analyzed and can provide insight into the qualities of the final product, as experienced by the user.

5 References

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