Milk Powder Characterization – Chapter 2: Packaging, Transport, and Storage

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 can change during manufacturing processes or can vary depending on environmental conditions. This application report presents multiple characterization methods such as tapped density, static volumetric water uptake, particle size, cohesion strength and compressibility, in order to define the nature of infant/toddler milk powder with respect to manufacturing, storage, filling, and formulation.

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 maltodextrine). This in turn changes the structure, texture, and flow behavior of the formula (both in its powdered state and when dissolved).

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

In this report the aim was to show a complete picture of the powder characteristics which are critical for production, packaging, transport, and storage of the product.

1.1 Packaging and Transport

For packaging and transport, powder characteristics like the bulk density, flowability, and the interaction with the silo wall are crucial parameters influencing the production process and need to be considered during product development and construction of the production site.

Multiple techniques were employed to illustrate differences that arose from the samples' various chemical and morphological differences.

Tapped density

Many materials (such as powders) often display complex shapes or are too small to measure their dimensions accurately enough to determine their densities with a high certainty. Tapped density measurements can be used to predict flow and compressibility properties. This value is obtained by mechanically tapping a volumetric vessel containing a known amount of sample a fixed distance until no visible change in its volume is observed. The material's compressibility index and Hausner ratio can then be calculated. Free flowing powders generally show little difference between the bulk and tapped densities.

True density

The true density of a material can be determined using Archimedes' method of displacement. However, many samples interact with the usual displacement fluid which is water. Therefore, gases such as helium or nitrogen can be used as the displacement fluid, and Boyle's law can be applied to determine a material's true volume, and then calculate its density. The true density can then be used to directly assess the chemical composition and morphology of a material in a quality control step.

Compressive density

Compressibility is a measure of the relative volume change of a sample when normal stress is applied or changed. It describes the relationship between bulk density and the applied pressure. Several factors influence the compressibility of powders including particle size, shape, elasticity, water content, temperature, etc. This simple test gives information about the powder flow behavior.

Cohesion Measurement

Cohesion in the sense of the bulk solid is the powder's innate resistance to displacement. It is usually influenced by the preconditions of the powder such as temperature, moisture content, or precompaction. For example, a powder previously compacted will be at the bottom instead of at the top of a container and will exhibit a different cohesion. Especially the development of cohesion as the precompaction is increased yields insight into how a powder will flow after protracted storage.

Wall friction

Wall friction is also an essential aspect of assessing a powder's behavior in a given process or use.

Because, in most processes and applications, powders will interact with solids in one way or another (storage bins, packaging materials, silos or even measurement equipment), measuring how it interacts with these surfaces is crucial. It is also critical in the design of hoppers or dosing mechanisms. An improperly designed hopper will lead to improper discharges, retaining material from previous batches.

Further, information about the maximum packing density, which is important for the filling of the milk powder, was assessed.

1.2 Storage – the Influence of Moisture on the Powder

Producing materials in high quantities and shipping them to distributers for selling involves long storage times, which ought not to affect the quality of the product. Appropriate packaging is needed to avoid influences from outside environmental conditions. But before the product is packaged into its final wrapping, it has already interacted with the environment. In addition, the customer may not use the whole product at once, but may rather store it after opening.

An especially influential environmental factor for powder properties is the relative humidity. It varies not only at different geographic locations, but also between different buildings and outdoors.

Furthermore, the shelf life of milk powders can be influenced by both temperature and relative humidity. Determining the amount of water adsorbed into the milk powder can be monitored volumetrically using a static volumetric vapor sorption analyzer. Fixed or variable temperatures and relative humidities (RH) can mimic storage conditions and reveal how much water uptake or release occurs throughout a specific time period.

The physical changes of powders due to environmental conditions like relative humidity can be modelled by the measurement of particle sizes using a particle size analyzer. Applying two different measurement modes (Venturi vs. Free-fall) enables the description of both size and the changes in size for not only primary particles but also for agglomerates. Size enlargement by agglomeration is the main goal of milk powder producers. This is usually achieved in a fluidized bed granulator; but an excessive increase of inter-particle cohesion limits the optimal packing, the porosity and moreover the flowability during powder processing.

2 Sample Preparation and Experimental Setup

2.1 Packaging and Transport

Before measurement, the powdered milk samples were dried at 70 ºC overnight in an oven.

2.1.1 Tapped density, true density and compressive density

Tapped density

The dried milk formulas were briefly stirred with a glass rod prior to adding it to the sample vessel using a funnel. For tapped density, 70 mL of milk powder was added to a 100 mL graduated cylinder and weighed prior to tapping. Using a Dual Autotap, the cylinder was lifted and dropped from a height of 3.0 mm for each tap (ASTM and USP standards).

True density

An Anton Paar pycnometer was used for true density measurements. Approximately three-fourths of the large sample cell (>45 g) was filled and the sample

was degassed with N_2 for one minute prior to density measurements using N_2 for analysis.

Compressive density

Compressibility is a measure of the relative volume change of a sample when normal stress is applied or changed. It describes the relationship between bulk density and the applied pressure.

Further, the compressibility measurements are yielded using the MCR powder cell in the calculation of the Carr index and the Hausner ratio. The Carr index and the Hausner ratio are characteristic values of a powder's compressibility, which is often used as an indicator for the flowability. For the calculation of those values, see Equations 1 and 2.

$$C = \frac{V_B - V_T}{V_B} * 100$$

Equation 1: Calculation of the Carr Index

$$H = \frac{\rho_T}{\rho_B}$$

Equation 2: Calculation of the Hausner ratio

Here, V_B and V_T are respectively the unconsolidated and consolidated volumes; and ρ_T and ρ_B are the tapped (consolidated) and bulk (unconsolidated) densities. Note that these values can differ from tapped density experiments.

In those experiments, an air-permeable piston was used for compression.The applied normal force was 3, 6 and 9 kPa.

2.1.2 Warren Spring Cohesion

Warren Spring Cohesion gives information about the cohesiveness of a powder in a consolidated state, and therefore information about the powder's flowability and its behavior during storage.

Warren Spring Cohesion is determined by compressing the powder for a defined period of time using an air-permeable piston at 6 kPa. This ensures the reproducibility of measurement results by producing a comparable initial state. After the consolidation step, the measuring system is replaced by the Warren Spring geometry (see Figure 1).

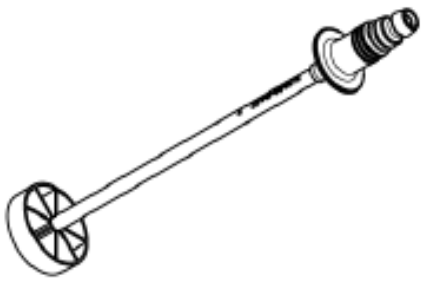

Figure 1: Warren Spring geometry.

The Warren Spring geometry penetrates into the powder bed with a predefined immersion depth. Then, the torque is measured while rotating the measuring system at a speed of 0.1 rpm (see Figure 2). Those torque values reach a maximum in an early state of each measurement when the rotation overcomes the cohesion forces between the powder particles as the powder flow is initiated. After this point, the particles are able to move freely and are in a flowing or dynamic state. The torque decreases and reaches a constant final value. For the calculation of the Warren Spring Cohesion, the recorded maximum torque is multiplied by a factor based upon geometry as shown in Equation 3.

$$S_{WS} = \frac{3 * M}{2\pi * (R_O^3 - R_I^3)}$$

Equation 3: Calculation of the Warren Spring Cohesion

Here, S_{ws} is the Warren Spring Cohesion value, M is the torque, R_o and R_I are the outer and inner diameters of the Warren Spring geometry. This gives a comprehensive single value for the flowability of the powder in a compressed state.

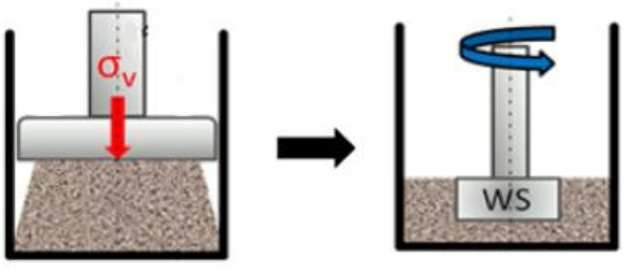

Figure 2: Compression of powder with the preparation set (left) at a certain normal stress (σ_v); shearing the sample with the Warren Spring geometry (right).

2.1.3 Wall Friction Angle

Wall friction describes the friction between a granular media and a solid body. It is measured by compressing the sample at a defined normal stress. The compression tool used is called “Preparation Set” and the disc is made of stainless steel. While rotating the disc, the torque is recorded and thereby the shear stress.

The resulting Wall Friction angle is an important parameter in hopper design with the aim of preventing core flow and achieving mass flow. The disc used for the measurement can be replaced easily, allowing the analysis of the friction between any wall material and the bulk material.

2.2 Storage – the Influence of Moisture on the Powder

2.2.1 Vapor sorption

Approximately 100 mg of each sample were used for the static volumetric vapor sorption experiment performed on the VSTAR instrument. The samples were degassed at 298 K for 16 hours under vacuum prior to the measurement. Water uptake was measured at 95% RH at 25, 35, and 45 °C and the kinetics were monitored. Full water sorption isotherms were also measured at 25 °C.

2.2.2 Particle size: Laser diffraction

The dry milk powder was investigated on samples which were stored at 70 °C overnight in the oven. Further, the samples were placed in an environmental chamber at 25 °C with 95 % RH and the effect of moisture was examined after 30 min, 1 h, 2 h and 3 h.

The dry dispersion unit of a particle size analyzer (PSA) was used to carry out the measurements.

The Venturi set-up was employed to determine the particle size of primary particles while the Free-fall method allowed agglomeration rate analysis. In the Free-fall dispersion mode, the particles flowed through a manifold that allowed them to fall in front of the laser when no pressure was applied. The vibrator parameters were set for both samples to a frequency of 44 Hz and a duty cycle of 50 % in order to optimize the dispersion. In the Venturi (also termed “Dry Jet”) dispersion mode, the powder is fed into a chamber and ejected through a Venturi tube at a controlled air pressure (user-set between 50 and 6000 mbar). To improve the dispersion without causing particle breakage, the vibrator parameters were set for the infant milk to a frequency of 43 Hz and a duty cycle of 50 %, while the Venturi pressure was set to 50 mbar. For the toddler milk, the frequency and the duty cycle were respectively set at 39 Hz and 50 %, with the pressure at 50 mbar.

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

3 Results

3.1 Packaging and Transport

3.1.1 Tapped density, true density and compressive density

The initial bulk densities for the milk powders were similar at 0.43 and 0.42 g/cm³ for infant and toddler powder formulas, respectively. After tapping with the Dual Autotap, they reached respective tapped densities of 0.56 and 0.55 g/cm³. This change in density, following ASTM protocol, enabled calculations of their compressibility and Hausner ratio of 24.29 and 1.32 for the infant formula, and 25.0 and 1.33 for the toddler formula. These values are good for the dry state of milk powder to allow fairly easy handling for packing. The true densities of 1.19 and 1.08 g/cm³, which were determined by the Anton Paar pycnometer, were nearly twice the tapped density for both formulas, revealing the natural packing phenomena of these materials.

Compressibility measurements using the MCR powder cell revealed the dependence of the bulk density on applied normal stresses. Figure 3 and Table 1 show the bulk densities for different normal stresses for infant and toddler formula.

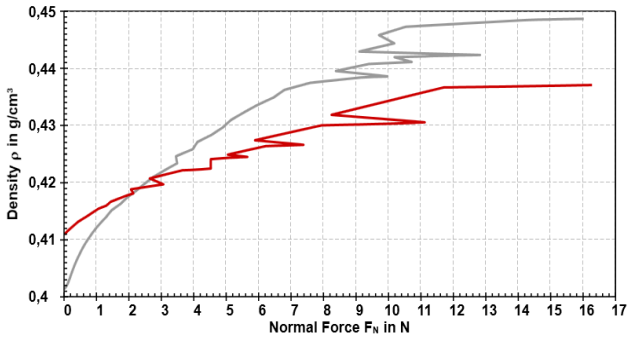

Figure 3: Bulk density of toddler formula (grey curve) and infant formula (red curve).

The initial bulk density, without normal stress applied on the sample, was higher for the infant formula. With increasing normal stress, the bulk density of toddler formula was more affected, leading to a higher bulk density of the toddler formula when normal stress was applied. This behavior represents the higher compressibility of the toddler formula.

Sample	Bulk Density (g/cm³)
Infant	0.411 / 0.424 / 0.430 / 0.437
Toddler	0.401 / 0.432 / 0.441 / 0.449

Table 1: Results of the bulk density measurements at 0, 3, 6, and 9 kPa.

Based on the compressibility measurements with the MCR powder cell, the Hausner Ratio and the Carr index were calculated.

The Carr Index of infant formula was lower than that of the toddler formula (see Figure 4 and Table 2), which makes sense with the better compressibility of the toddler formula as observed with the bulk density measurements.

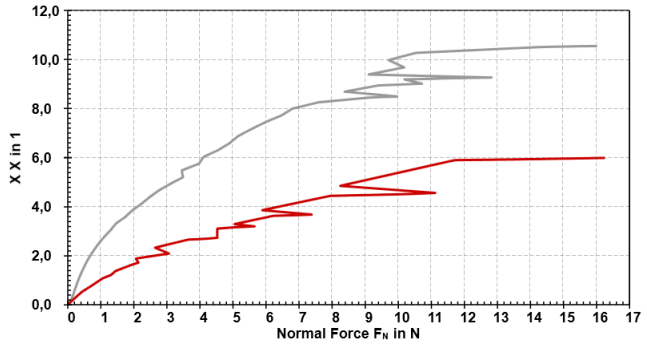

Figure 4: Carr Index of toddler formula (grey curve) and infant formula (red curve).

Also, the Hausner Ratio was slightly smaller for the infant formula (see Table 2). Generally, in both samples, the Hausner Ratio and the Carr Index were positively correlated with the applied pressure.

The lower Carr Index and Hausner Ratio of infant formula suggest slightly better flowability of this powder compared to the toddler formula. As the infant formula was not compressed as easily, the likelihood of ratholing and arching is lower, which facilitates smoother movement of the material (for example out of a silo).

Sample	Hausner Ratio	Carr Index
Infant	1.03 / 1.05 / 1.06	3.2 / 4.5 / 6
Toddler	1.08 / 1.10 / 1.12	7.1 / 9.0 / 10.6

Table 2: Results of the Hausner Ratio and Carr Index at 3, 6, and 9 kPa.

Comparing the measurements from the Dual Autotap and the compressibility measurement in the MCR powder cell, the results showed the same trends (namely that the toddler formula was much more compressible than the infant formula).

The difference in the absolute values can be explained by the different measurement principles and sample preparation procedures for the different instruments. For bulk density and tapped density (determined by the Dual Autotap), the compression was based on tapping; while in the MCR powder cell, compression was achieved by applying pressure onto the sample.

The starting values were consistent, as shown in Table 3.

Sample	Bulk Density at 0 kPa (g/cm³) in the MCR	Non-Tapped Bulk Density (g/cm³) in the Dual Autotap
Infant	0.411	0.43
Toddler	0.401	0.42

Table 3: Comparing the bulk density at 0 kPa in the MCR to the non-tapped bulk density measured with the Dual Autotap.

3.1.2 Warren Spring Cohesion

Although the Warren Spring Cohesion of the infant formula (4.02 ± 0.27 kPa) was slightly higher than that of the toddler formula (3.75 ± 0.31 kPa), the standard deviation was such that a definitive comparative statement cannot be made. In general, the two values were similar. This is depicted in Figure 5 and Figure 6.

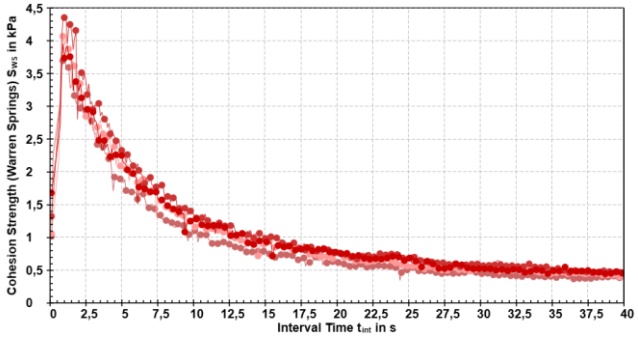

Figure 5: Reproducible measurements of the Warren Spring Cohesion at 6 kPa for infant formula.

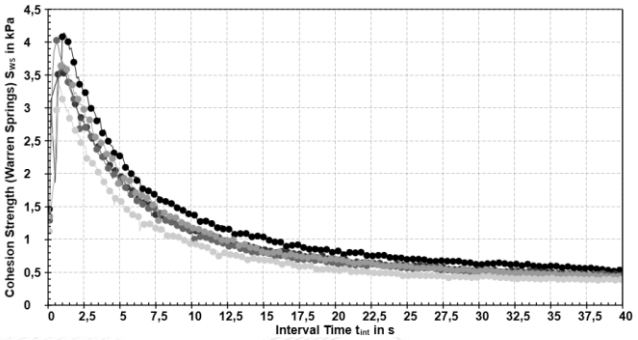

Figure 6: Reproducible measurements of the Warren Spring Cohesion at 6 kPa for the toddler formula.

3.1.3 Wall Friction Angle

The shear stress at the point where the wall yield locus intersects with the axis is called adhesion (τ_{ad}) which is shown in Figure 7.

When $\tau_{ad} > 0$, it indicates high adhesive forces, where the bulk solid can adhere to vertical walls. The τ_{ad} of infant formula was slightly higher than that of the toddler formula.

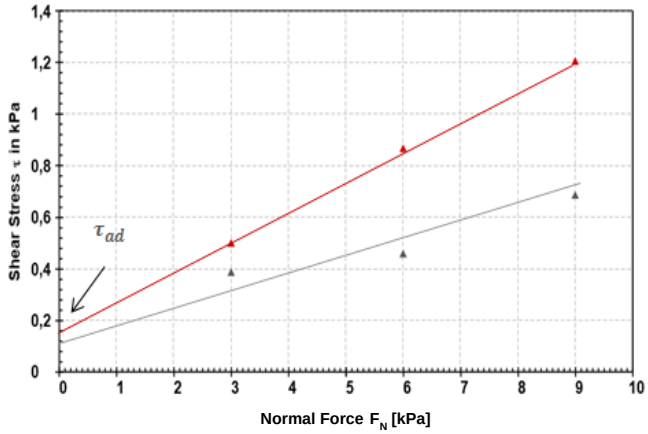

Figure 7: Measurement of the Wall Friction angle for toddler formula (grey curve) and infant formula (red curve).

Both milk powders showed a low adhesion behavior to vertical walls. The infant formula showed a slightly higher Wall Friction angle of 8.3º than the toddler milk powder of 4.5º; but overall, the values were within a similar range.

Parameter	Infant	Toddler
Warren Spring cohesion [Pa]	4.02 ± 0.27	3.75 ± 0.31
Wall Friction angle [°]	8.3	4.47

Table 4: Summary of rheological measurement results.

3.2 Storage – the Influence of Moisture on the Powder

Milk powders are inherently prone to hydration with all of its hydrophilic functional moieties and sugars. This impacts its processing, transportation weight, granularity, stickiness, and longevity.

3.2.1 Vapor sorption

The vapor sorption experiments were carried out on dry milk powder sample at 95 % RH at temperatures of 25, 35, and 45 ºC. With increased exposure time to 95 % RH, the sample mass increased. The mass change in percent is depicted in Table 5.

Time (h)	Milk Powder Mass Change %		
	25 ºC	35 ºC	45 ºC
24	21.72	24.72	24.78

Table 5: Milk powders' % mass change at 95% relative humidity at given temperatures.

All samples increased by 20 % to 25 % of their original mass after 24 hours of exposure to 95 % RH at different temperatures. Higher uptake amounts were achieved with higher temperature, suggesting that storage of milk powders at lower temperatures will reduce its likelihood of adsorbing excess moisture.

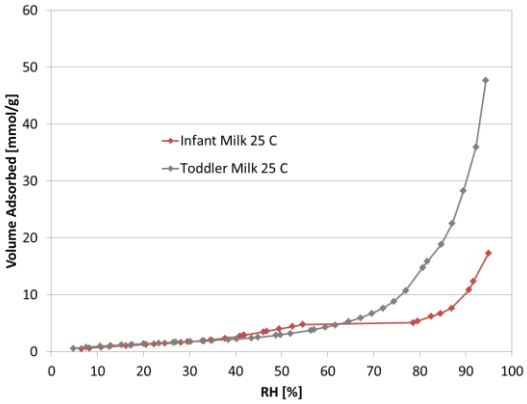

Figure 8: Water vapor adsorption isotherms of milk powders at 25 °C.

The full water sorption isotherms of the infant and toddler formulas were measured at 25 °C and are shown in Figure 8. Clear differences are seen between the two formulas with the toddler formula adsorbing more water at higher RH. In addition, the infant formula isotherm shows an unusual step in the adsorption branch starting between 50-60 RH% that is most probably related to a lactose phase transition, confirming that the two formulas have different compositions.

3.2.2 Particle size: Laser diffraction

Dry sample

Figure 9 shows the differences of particle size distribution in the dry infant and toddler milk samples. The primary aggregates (measurements in Venturi mode) of the toddler formula were found in a smaller size range than the primary particles of the infant formula.

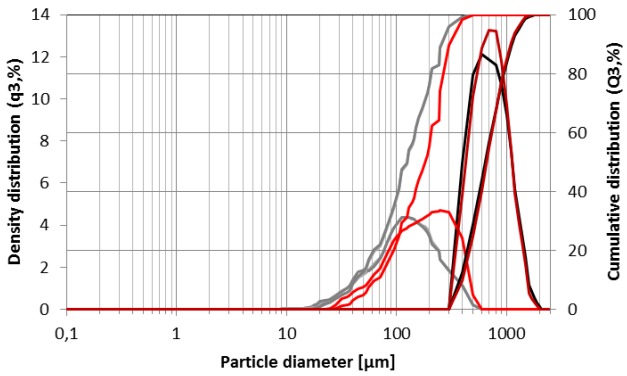

Figure 9: Particle density distribution (q3, %) and cumulative distribution (Q3,%) of the infant formula measured in Venturi (light red) and in Free-fall (dark red) as well as of the toddler formula (Venturi: grey, and Free-fall: black).

The analysis of D10, D50 and D90 of the samples in Free-fall mode indicated only small size differences between the aggregates of the two powders (see Table 6), while the shift towards a smaller size range for primary particles in the case of the toddler formula was observed.

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

Table 6: Summary of D-volume weighted data of laser diffraction for the infant (I) and toddler (T) formula.

Samples exposed to humidity

The results obtained for the infant formula sample are listed in Table 7 and Figure 10. In Venturi, the increase of D-values over time indicates that the primary particles started to progressively swell due to moisture uptake. The Free-fall results indicate the bigger size and stability of the formed agglomerates after 3 h of conditioning.

Infant (I) Milk				
		D10 [µm]	D50 [µm]	D90 [µm]
Venturi	After 30 min	75.61	208.57	437.55
	After 1 h	79.84	211.36	438.51
	After 2 h	82.10	221.04	444.76
	After 3 h	84.51	223.12	442.68
Free-fall	After 30 min	319.42	547.63	878.83
	After 1 h	331.42	568.42	891.20
	After 2 h	405.29	618.34	1099.76
	After 3 h	374.91	519.69	1062.84

Table 7: Summary of D-volume weighted data of laser diffraction for the infant (I) milk after conditioning at 25 °C, 95 % RH at different times. Results of measurements performed in Venturi and Free-fall are displayed.

In Figure 10, the direct comparison of the infant formula after 30 min and after 3 h of moisture conditioning indicated that only a slight shift towards a higher particle size range was observed. The agglomerates present after 30 min became bigger over time and consolidated after 3 h.

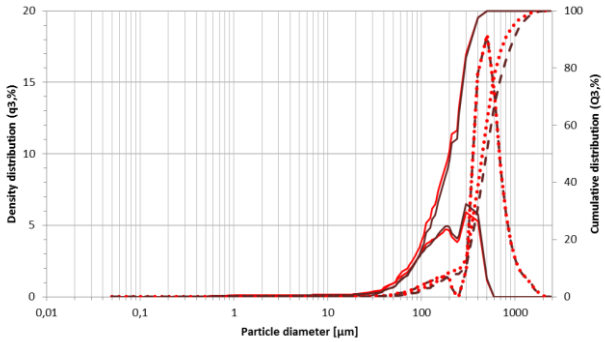

Figure 10: Particle size distribution (q3,%) and cumulative distribution (Q3,%) of the infant formula measured after 30 min in Venturi (light red) and Free-fall (light red, dotted line) as well as after 3 h (Venturi: dark red, solid line, and Free-fall: dark red, dashed line) conditioning at 25 °C, 95 % RH.

In the case of the toddler formula, a slight swelling of the primary particles with exposure to increased humidity could be observed (see Table 8). Opposed to that, no change in the size of aggregates could be seen between 30 min and 3 h of humid environment exposure. The latter is underlined by overlaying curves in Figure 11.

Toddler (T) Milk				
		D10 [µm]	D50 [µm]	D90 [µm]
Venturi	After 30 min	46.44	138.65	359.38
	After 1 h	45.47	136.62	360.25
	After 2 h	48.90	139.70	358.49
	After 3 h	49.51	140.19	360.24
Free-fall	After 30 min	199.28	613.17	1162.01
	After 1 h	169.64	561.28	919.96
	After 2 h	195.89	603.32	1035.47
	After 3 h	186.90	608.78	1107.16

Table 8: Summary of D-volume weighted data of laser diffraction for the Toddler (T) milk after conditioning at 25 °C, 95 % RH for different times. Results of measurements performed in Venturi and Free-fall are displayed.

Comparing the two milk powders, primary particles and agglomerates of the toddler formula were generally smaller than those of the infant formula (dry and humid state). In both samples the primary particles slightly swelled when exposed to elevated humidity and might have even taken up further moisture when exposed for longer than 3 h, as the measurement with the vapor sorption analyzer suggests.

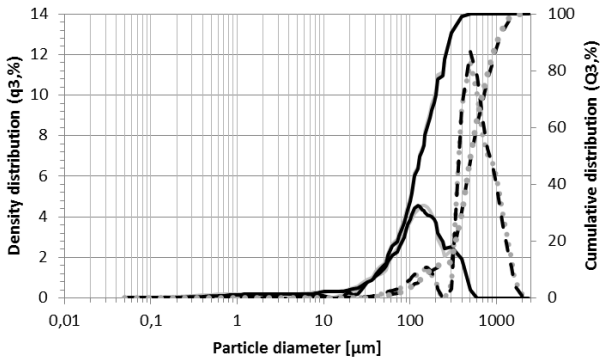

Figure 11: Particle density distribution (q3,%) and cumulative distribution (Q3,%) of the toddler milk measured after 30 min in Venturi (grey) and Free-fall (grey dotted line); and after 3 h (Venturi: black, and Free-fall: black dashed line) conditioning at 35 °C, 95 % RH.

The bigger sizes of aggregates in the dried samples derived from caking, which occurs when humid powder samples are dehydrated. Apparently, the humidity in the laboratory in Graz was sufficient to create this effect. Opposed to this, the samples exposed to increased humidity for defined periods of time had not been dried before and thus lacked this enhanced caking effect when being dried. This effect is applied in fluidized bed granulators: The initial particles are fluidized in rising hot air while a liquid (binder solution or water) is sprayed on their surface, making them locally sticky. The collisions between fluidized wet “sticky” particles allow for adhesion and the formation of agglomerates through liquid bridges. Consolidated structure formation occurs by simultaneously drying particles in the hot air stream. For this reason, particle size is controlled by the drying procedure to avoid collapsing the particle bed (due to insufficient drying) and to avoid a lack of agglomeration (due to excess drying). Further, the smaller particle size and higher surface area of the toddler formula (see Chapter 1 for results) were consistent with the higher and faster moisture uptake as determined by the vapor analyzer, when compared to the infant formula.

While no change in agglomerate size occurred for the toddler formula between 30 min and 3 h of exposure to 95 % RH, the infant formula agglomerates increased within the same time period. This may relate to the higher permeability of the infant formula (also see Chapter 1), which allows water molecules to enter the space between particles and promotes adhesion to each other.

4 Conclusion

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

Different techniques of characterizing the unconfined density and the bulk density of the powders were applied. The findings describe the differences between the two milk formula samples and underline the influence of the powder treatment and the resulting density.

Furthermore, the Wall Friction Angle and the Warren Spring Cohesion showed similar behavior between the samples. The lower Carr Index curve indicated that the infant formula had better flowability. This needs to be addressed to ensure smooth production and application.

Finally, the water adsorptions were described, which fit well with previous findings about the solubility of the two powders. In addition, the differences in the response to exposure to elevated relative humidity were described, showing different trends for primary particles and agglomerates.

To put it in a nut shell: In this report, a complete picture of powder characteristics critical for production, packaging, transport and storage of the milk formulas was shown.

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