WARREN-SPRING COHESION AND PARTICLE SIZE DISTRIBUTION MEASUREMENTS OF DRY WHEY PROTEIN CONCENTRATE (WPC)

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ABSTRACT

Whey Protein Concentrate 80 (WPC80) is often sold in bags of 20 kg or more. During packing in bags and stacking on pallet, the powder is consolidated. The effect of consolidation on the powder characteristics is dependent on several factors, including powder Particle Size Distribution (PSD).

This introductory study aimed to determine if WPC80 ingredients from two different production sites had significantly different Warren-Spring cohesion and PSD response averages. Quantitative research questions about powder cohesion and PSD responses are relevant to evaluate functional differences between WPC80 ingredients. PSD response values such as Sauter mean diameter-, and Span are relevant in understanding differences in Warren-Spring cohesion after consolidation.

The two WPCs were produced by spray drying liquid whey protein concentrate. This was done at industrial scale and at pilot scale, respectively.

The particle size distributions were measured with Malvern Mastersizer 3000. The Warren-Spring cohesion measurements were executed with an MCR301 rheometer from Anton Paar. It was fitted with a sintered plate for consolidation, and with Warren-Spring vaned paddle for the cohesion measurement. The samples were consolidated with pressure simulating 10 kPa. T-test was used to compare averages for Warren-Spring cohesion (n=9) and PSD (n=16).

Warren Spring cohesion average values for the industrially produced WPC80 were significantly higher than for the WPC80 produced at pilot scale. The sample of industrial scale powder was a more cohesive powder. PSD response average differences showed significantly larger particles, -and a wider Span for the industrially produced WPC80, relative to the pilot scale WPC80. The applied analysis methods are useful for evaluating differences between WPC80 ingredients.

This study describes an MCR method to evaluate cohesion properties in WPC80. Cohesion in such ingredients is associated with poorer powder flow. Powder consolidation occurs in bags, hoppers, and in silos. The analyses described are relevant for process optimization because it is possible to optimize on particle size distribution if the effect on cohesive properties is known.

INTRODUCTION

Spray drying is a common production method to produce WPC80 powder. In this process the liquid protein concentrate feed is turned into solid particles. Drying occurs when droplets are exposed to hot air, with air temperatures often exceeding 180°C. During spray drying the liquid material is sprayed into droplets of varied sizes. Meeting the hot air, the droplets are immediately dried into primary particles. The properties/characteristics of powder particles, like particle size, are influenced by spray drying conditions and type of atomizing equipment[1].

Cohesion properties influence flowability properties of powder. The flowability of powders can be reduced when it is exposed to compressive stress. The measurement of cohesivity in bulk powders is especially important because of problems that can occur after consolidation and storage, in pallet, hopper or silo. An increase in cohesive properties indicate an increased risk of poor silo emptying or even complete stop of flow. Powders with more cohesive properties are more prone to such problems. Malfunction in powder handling equipment can also lead to consolidation of the powder where the powder would otherwise be aerated[2].

Cohesive forces in consolidated powder can be measured directly by the use of a Warren-Spring-Bradford cohesion tester[3]. In a study by Orband and Geldart[3], particle size values were plotted against Warren-Spring cohesion. A distinction was found between free-flowing powder, characterized by size-independent cohesion, and cohesive powders. Cohesive powders exhibited a cohesion value strongly influenced by particle size. For lactose powder they observed a critical limit in the range of 52-60µm average diameter. Below this limit the cohesion increased progressively with decreasing particle size. Above the critical limit, constant values were obtained[3].

Flowability is influenced by slight differences in inter-particle forces. Inter-particle forces can be measured with Warren-Spring cohesion analysis[3-4]. Flowability according to Geldart classification is influenced not only by mean particle size. It is also influenced by other factors, like particle density and the width of the PSD[3, 5], the latter also called the Span. Two qualitative rules often apply: 1) Flowability of bulk solids with the same median diameter (Dv 50) increases with decreasing width of the PSD; and 2) flowability of bulk solids with a PSD of similar shape increases with increasing median diameter (Dv 50). The number of contact points between particles in bulk powder is inversely proportional to the square of the particle diameter. The expectation is that smaller particles give more strength to the powder bed. However, the prediction of powder properties from PSD is difficult, and can sometimes be misleading[4].

In powder with small particles, van der Waals interactions and electrostatic forces have a considerable influence on cohesive forces, binding particles together. Similarly, liquid bridges are forces which bind particles together[4, 6]. The magnitude of the binding force of liquid bridges decreases only slightly with increasing distance between particles, while van der Waals interactions require shorter distances to influence binding forces between particles. Liquid bridges are therefore more important binding forces in powders with relatively large particles[4]. The surface composition, in terms of liquid free fat and liquid water is important, in terms of liquid bridge formation[5].

The two WPC80s investigated in this study were one powder produced in pilot scale (pilot scale powder), and one produced in a full-scale spray drying plant (industrial scale powder). The aim was to investigate differences in PSD and Warren-Spring cohesion average responses between the two powders, and to develop appropriate Warren-Spring and PSD analyses for Norwegian WPC80.

MATERIALS AND METHODS

Pilot plant spray drying

Liquid Whey Protein Concentrate (28.3 % dry matter) was received from a WPC80-producing dairy in Norway. The concentrate was heat-treated at 61-62°C in batches, and then cooled to <10°C. Cooled concentrate was stored for three days at 4°C. Cold concentrate was reheated to 60-63°C in a tube heat exchanger directly before spray drying. The spray dryer used was a GEA Niro type FSD-4.0 co-current spray dryer with fines-return and a two-fluid nozzle atomizing system (GEA Niro, 2014). The liquid was pumped to the nozzle by a NEMA 4X IP66 peristaltic pump (Watson-Marlow Pumps Group, Falmouth, UK, 2014). The 2-step spray dryer included an internal fluid bed suitable for extraction of dried ingredient. The pre-heated concentrate was dried with 181.5°C inlet air temperature and 77°C outlet air temperature to >95 % dry matter (w/w). The temperature in the internal fluid bed was set to 65°C. The chosen nozzle had a 1.3 mm nozzle inner diameter, and the atomizing pressure was set to 2.1 bar with pressurized air.

Powder was packed in ~900 g samples right after extraction from the internal fluid bed. Samples were sealed in vacuum bags without exposure to vacuum (Polyamide, and polyethylene, 90 µm thickness, Maske Emballasjefabrikk, Trondheim, Norway). Vacuum was avoided because exposure would lead to unwanted consolidation of the powder.

WPC80 ingredient samples

One 20 kg bag of industrially produced WPC80 from TINE SA was used. It was initially stored in stable room temp of approximately 20-24 °C for 2 months. (Original 20 kg bag: Two brown paper layers, one blue polyethylene inner liner 70 µm.) After two months the powder was split and repacked in sealed vacuum bags (Polyamide, and polyethylene, 90 µm thickness, Maske Emballasjefabrikk, Trondheim, Norway), then stored for 10 months in a climate-controlled chamber (20°C, 20 % RH. HPP750 eco, Memmert GmbH, Germany, 2021). At the time of powder splitting, the 20 kg bag was brought to a room with controlled air temperature. A 12.5 mm slot, static riffle splitter with 18 slots (Sample splitter RT 12.5, Retch GmbH, Germany, 2021) was used to split the amount into two representative amounts, three times. Energy, fat, carbohydrate, and protein values for commercially available TINE SA WPC80 are described in **Table 1**.

TABLE 1: Nutritional values for industrial scale WPC80, as declared by TINE SA

Nutritional value	**/100g**
Energy	**1650 kJ (390 kcal)**
Fat	6.5 g
Carbohydrate	8 g
Protein	77.4 g

At the time of sample preparation for analysis, the industrial scale powder was 12 months old from production date, and the pilot scale powder was 6 weeks old from production date. Similar amounts of each powder type were split using a coning and quartering method, into 8 bags each, containing equal amounts of powder. The order of the bags was randomized before analyses to reduce the influence of time-dependent variation on the data set.

The powders were produced from the same type of concentrate. Both were industrially produced liquid whey protein concentrates produced on the same processing equipment, but at different production days. The liquid concentrates were cooled to 4°C before storage. Total storage time was different for pilot scale- and industrial scale powder. The pilot spray drying process was designed to be as similar to the industrial scale process as possible in terms of temperature process parameters. Inherent differences caused by dissimilarity in processing equipment was not possible to avoid.

Malvern Mastersizer

A Malvern Mastersizer 3000 (S.nr. MAL1083189, Malvern, UK, 2013) equipped with an Aero S dry powder disperser was used to analyse particle size distributions in 16 replicates. Particle absorption index was set to 0.005 and refractive index to 1.461. 40 second measuring time per sample at 90% feed rate. Dispersion of 8 grams of sample at 0.3 bar pressurized air. 2 mm height of the feed opening. The red laser had a wavelength of 632.8nm, and the blue laser had a wavelength of 470nm.

The responses of interest were the diameter responses Dv 50, D [3,2] and Span, describing two points in the PSD volume distribution and the width of the distribution, respectively. Dv 50 is the median diameter value in the volume distribution. Sauter mean diameter D[3,2] is a surface weighted mean diameter value[7].It is more sensitive to the presence of fine particles in the particle size distribution[6,8]. The calculation of the Span was done with the following equation:

$$Span = \frac{d(v, 0.9) - d(v, 0.1)}{d(v, 0.5)} \quad (1)$$

$d(v, 0.1)$: Value under which 10 % of the powder volume has shorter diameter
$d(v, 0.5)$: Value under which 50 % of the powder volume has shorter diameter
$d(v, 0.9)$: Value under which 90 % of the powder volume has shorter diameter
$d(v, 0.5)$ corresponds to Dv 50 in results and discussion below

To avoid static charge build up, a grounding wrist strap and cord (1MΩ, RS Pro, RS Group London, UK) was used, during Mastersizer and MCR analyses.

Warren-Spring cohesion measurement

A Physica MCR301 rheometer (Paar Physica, Anton Paar, Stuttgart, Germany, 2010) was used to analyse the Warren-Spring cohesion in nine replicates of WPC80. A Powder Flow Cell with an uncoated glass tube (Anton Paar, Stuttgart, Germany, 2020) held the powder sample. The Warren-Spring cohesion measurement must be done in the top part of the consolidated powder bed when using this method. The original number of samples for this analysis was 16. In several cases the vaned paddle did not stop after 10 mm penetration into the powder bed, during analysis. In these cases, the results were excluded from the dataset.

A modified sample preparation method was developed. An analysis sieve (2mm opening width, stainless steel, approved for ISO 3310/1, Retsch, Haan, Germany) and a limiting ring with 7.5 mm inner diameter were used. The powder was sieved directly into the powder cell. A glass rod with a rounded end was used to vibrate the sieve manually in a similar way for each sample. The glass rod was pushed gently against the sieve mesh, outside the limiting ring, and small circle motions were made. The glass rod was also used to even out the powder in the limiting ring before vibration. As a result, the powder bed of each sample was aerated before the consolidation step. The alternative was to use a measuring cell fluidization set. Formation of air channels in the powder bed was observed in fluidization trials with the fluidization set.

The powder bed was consolidated using an air-permeable sintered steel disc (Anton Paar, Stuttgart, Germany, 2020). Consolidation lasted for one minute at 18.1 N normal force. A Warren-Spring vaned paddle (ST36-8V-10/PCC/WS. 36 mm outer diameter. Anton Paar, Stuttgart, Germany, 2020) was used to penetrate the consolidated powder bed 10 mm. Torque was applied to the vaned paddle. During the automated Warren-Spring cohesion analysis the rheometer measured the highest resistance to torque force (curve maximum). Curve maximum indicated the time when the force broke the powder and rotated the powder within the vanes.

The calculation of the Warren-Spring cohesion in Pa was done with the following equation (notation as used by Anton Paar):

$$S_{WS} = \frac{3 \cdot M}{2\pi \left(R_O^3 - R_I^3\right)} \tag{2}$$

S_{WS}: Warren-Spring cohesion in Pa
M: Torque in Nm
R_O: Outer diameter of the Warren-Spring vaned paddle in m
R_I: Inner diameter of the Warren-Spring vaned paddle in m

During analysis, coning and quartering of these samples the temperature was 19-22 °C and relative humidity in the air was 34-43 % RH.

Dry matter, bulk density, tapped density and Hausner ratio

Dry matter was calculated from weights before and after dehydration (102°C, 4 hours). Tapped- and bulk density were measured for 50 g of sample (Tamping volumeter, J. Engelsmann Ag, Germany, 2021). Hausner ratio was calculated as Hausner ratio = Powder tapped bulk density / Powder poured (loose) bulk density[9].

Data analysis

Data from Malvern Mastersizer was evaluated with Malvern panalytical software, to ensure that the quality of the analyses was good (Weighted residual 0.16. Good fit). The full dataset was analysed in R Studio (V 4.1.3) with Student's t-test. Student's t-test null hypothesis for all responses were: "True difference in mean values between pilot scale powder and industrial scale powder is equal to 0."

RESULTS

Particle size distribution responses

In **Fig. 1.** The PSD for pilot scale powder has a mode slightly further to the left, indicating that the volume of relatively smaller particles is slightly larger than for industrial scale powder.

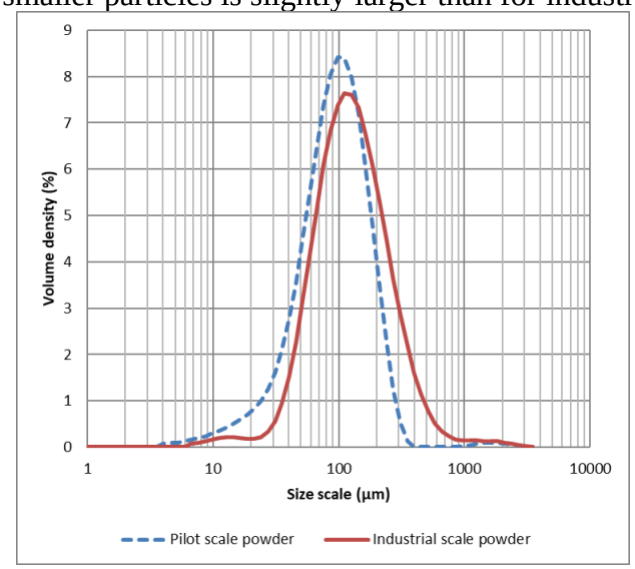

FIGURE 1: Particle size distribution (average values) for pilot scale powder (left mode) and industrial scale powder (right mode)

Both powder PSDs could be considered monomodal (**Fig. 1.**). The industrial scale powder had a tendency towards a secondary mode for finer particles (7-12 µm). The Sauter mean diameter (D[3,2]) average values showed that the pilot scale powder had a significantly ($P<0.05$) shorter average particle diameter length than industrial scale powder (**Table 2.)**. Significant difference was also found for median diameter (Dv 50; $P<0.05$). Pilot scale powder had significantly smaller particles than industrial scale powder. Average Span response value was significantly lower ($P<0.05$) for pilot scale powder than for industrial scale powder. Pilot scale powder had a narrower particle size distribution than the industrial scale powder. Both distributions showed presence of particles >1 mm diameter (probably agglomerates).

TABLE 2. Average PSD response values and P-values for T-test comparisons

Response	Pilot scale powder average values	Industrial scale powder average values	P-values. Student's t-test
Dv 50	100 µm	131 µm	$<2.2e^{-16}$
D[3,2]	67 µm	100 µm	$<2.2e^{-16}$
Span	1.63	2.02	$<2.2e^{-16}$

Warren-Spring cohesion

The shape of the penetration curve was evaluated for each sample. Each penetration curve had a sharp maximum before 6 seconds. Industrial scale powder had a significantly higher Warren-Spring cohesion average value than pilot scale powder (**Fig. 2**).

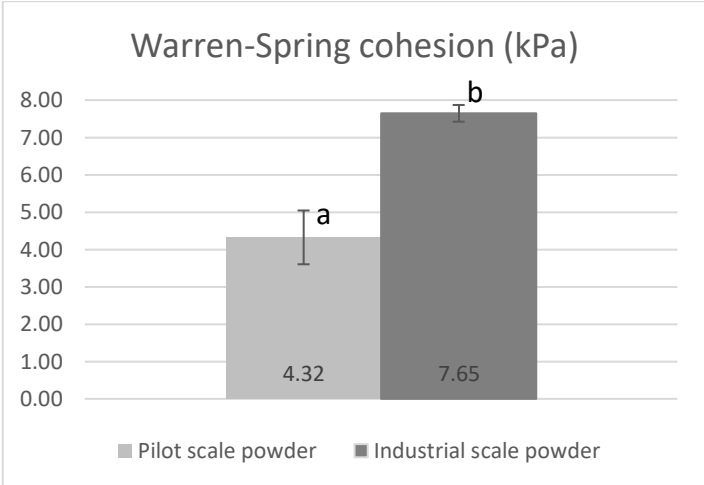

FIGURE 2: A column chart representation of Warren-Spring cohesion mean values with error bars (n=9). The dark column represents industrial scale WPC80, and the light column represents pilot scale powder. S_{WS} mean values are presented in kPa. Different letters on top of columns indicate significant difference ($P<0.05$) between mean values (n=9)

Dry matter, bulk density, tapped density and Hausner ratio

Dry matter in the samples were 95.45 g/100g for pilot scale powder and 95.50 g/100g for industrial scale powder. Pilot scale powder had a tapped density (525 taps) of 0.44 g/ml. Industrial scale had a value of 0.51 g/ml. The bulk density was 0.34 for the pilot scale powder and 0.39 g/mL for the industrial scale powder. Both calculated to a Hausner ratio of 1.3. A Hausner ratio of 1.3 is generally associated with the description "passable" flowability[9].

DISCUSSION

The two powders analysed in this study were significantly different in terms of Warren-Spring cohesion and PSD-responses. When exposed to consolidation, simulating packing in pallets, the industrial scale powder was more cohesive.

The particle diameter values were in the expected range (100 and 131 um). Hazlett et al. 2021[10] found that the Dv 50 value for agglomerated WPC (Carbery Ingredients, Ballineen, Cork, Ireland) was 209 µm and that D[3,2] diameter was 165 µm. When compared to these diameters, smaller particles were found in the less agglomerated Norwegian WPC80.

Pilot scale powder had significantly shorter median diameter than industrial scale powder. It was expected that significantly shorter average diameter of particles would coincide with relatively higher cohesion values. Unexpectedly, pilot scale powder had a significantly lower Warren-Spring cohesion mean value compared to industrial scale powder. Schulze[4] refers to a thumb of rule that smaller particles generally increases number of contact points between particles, and increase tendency towards cohesion. Schulze[4] emphasizes, however, that it can be difficult to predict the strength of the powder bed only based on PSD-data. The PSD Span response describes the width of the PSD distribution. A narrower PSD results in a lower Span value[5, 7]. The wider PSD span for the industrial scale powder (2.02) than for the pilot scale powder (1.63) could, however, lead to a higher Warren-Spring cohesion, as a wider Span means larger differences in particle size. If enough small particles fill voids between larger particles, the result is an increase in number of particle-particle interactions.

A wider Span is compatible with increase in cohesive properties, but cohesion is also influenced by other factors such as particle shape and bulk density[5]. Pilot scale powder had lower bulk density and tapped density values than industrial scale powder. This indicates a higher porosity in the pilot scale powder bulk. Voids between particles and voids within particles would take up more space in more porous powder beds. This could possibly influence cohesion because less close arrangement of particles contributes to a lower number of particle-particle interactions[6].

Liquid bridges are important binding forces in powder beds[4]. It is possible that water liquid bridge interactions could contribute in a small way to the difference between powders, in terms of powder cohesivity. However, the difference in dry matter content for the two powders were only 0.05 g/100g and thus the effect would be limited.

The purpose of the study was to compare WPC samples, to develop a Warren-Spring MCR method and to evaluate future analytical opportunities for comparisons of industrial scale powder and pilot scale powder. The methods developed and described in this study can be applied in future studies on WPC80, and possibly other powders.

CONCLUSION

The MCR methods developed were appropriate for measuring Warren-Spring cohesion for WPC80 powders.

The study's limited range of analyses could only elucidate a selection of impacting factors influencing Warren-Spring cohesion in Whey Protein Concentrates, like PSD particle diameters and the width of the Span. To study the effect of particle size on Warren-Spring cohesion in WPC an experiment comparing more similar powders is required. A wider spectrum of analyses would be required to understand the complex phenomenon of WPC powder cohesivity. More research is needed.

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