Changes in surface chemical composition relating to rehydration properties of spray-dried camel milk powder during accelerated storage

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Highlights

- Spray-dried camel milk powders were stored at 11.15-32.27% RH (37°C) over 18 weeks.
- An increase in surface lipid caused an increase in surface hydrophobicity.
- Wettability was not affected, and dispersibility and solubility dropped during storage.
- There was a strong correlation between surface lipid content and powder solubility.
- Powder property changes were more profound at 32.27% RH than at lower RH levels.

Changes in surface chemical composition relating to rehydration properties of spray-dried camel milk powder during accelerated storage

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Abstract

In this study, alterations in surface chemical composition relating to rehydration properties of spray-dried camel milk powders during accelerated storage (11 - 32% RH, 37^{o}C) over 18 weeks were investigated. The results showed that the surface of the fresh spray-dried camel milk powder was dominated by lipids (approximately 78%), followed by proteins (approximately 16%). During storage, the surface protein and lactose content decreased while the surface lipid content increased, resulting in an increase in surface hydrophobicity and slight agglomeration of the powder, especially for powder kept at 32% RH. Although fresh camel milk powder had very poor wettability, it displayed very high dispersibility and solubility. During storage, dispersibility and solubility declined with increasing storage time and increasing RH levels, which correlated with an increase in surface lipid content. However, at the end of the storage period, camel milk powder still retained very high solubility (>93%).

Keywords: Camel milk powder, surface chemical composition, rehydration property, accelerated storage.

1. Introduction

Camel milk is well known for its high nutritional content. As compared with other ruminant milk, camel milk is low in cholesterol, high in minerals (K, Na, Fe, Cu, Zn, and Mg), and high in vitamin C (Kaskous, 2016). The lipid content in camel milk mainly consists of long-chained poly-unsaturated fatty acids. A good indicator of the nutritional quality of milk is the ratio of unsaturated fatty acids to saturated fatty acids. This ratio is 0.43 to 0.45 in camel milk, which is much higher than that of cow milk (e.g. 0.30) (Gorban and Izzeldin, 2001). Proteins in camel milk are rich in essential amino acids, lack allergenic β-lactoglobulin, and contains many protective proteins (lactoferrin, lactoperoxidase, lysozyme, and immunoglobulins), thus providing camel milk with antibacterial, antiviral, antidiabetic, anti-ageing, and anticarcinogenic properties (Abrhaley and Leta, 2018; Kaskous, 2016). However, the global supply of camel milk is very limited as camels are typically raised in countries with arid conditions as found in deserts (FAO, 2016). One of the optimal approaches to extend shelf life, reduce transportation cost, and expand applications of camel milk is the production of camel milk powder that can be distributed globally. There are a few camel milk powder products on the market produced by small-scale freeze and spray drying. However, research studies on the production of camel milk powder and changes in its functional properties during storage are limited. To the best of our knowledge, there are only a few studies focused on the effects of drying conditions on physical and nutritional properties of camel milk powder (Al-Juboori et al., 2013; Ibrahim and Khalifa, 2015; Kaskous, 2016; Sulieman et al., 2014), and none of them investigated the stability of camel milk powder during storage.

One of the most important functional properties of milk powder is rehydration, as this is a prerequisite for the incorporation of milk powder in food products (Thomas et al., 2004). Rehydration of milk powder includes a number of sub-processes (e.g. wettability, sinkability, dispersibility, and solubility), which can overlap with each other and are difficult to measure and study in isolation (Fitzpatrick et al., 2016). Wettability refers to the ability of a powder to be wetted on the surface by water, while sinkability refers to the ability of powder particles to overcome the surface tension of water and sink into the water. The terms “sinkability” and “wettability” are often interchangeable, because the powder is usually considered to be wetted from the point when it starts to sink into solution (Selomulya and Fang, 2013). The wettability of a powder can be determined through wetting time measurement, the Washburn method, dynamic contact angle measurement, and the turbidity method (Fitzpatrick et al., 2016). Dispersibility is the ease with which the lumps and agglomerates of powder break into individual particles in water and can be measured via the International Dairy Federation standard method, optical fibre sensor, and particle sizing instrument e.g. Malvern Particle Sizer (Selomulya and Fang, 2013). Solubility refers to the ability of a powder to be dissolved into liquid to form a stable solution. There are several methods to determine powder solubility, including measurement of dissolved solids content over time, turbidity, and particle size (static light scattering) measurements (Fitzpatrick et al., 2016). Rehydration ability is influenced by many factors, in particular the chemical composition (both in bulk and on the surface) and physical properties of milk powder and even measurement methods.

During storage of milk powder, rehydration properties of milk powder are greatly affected by physical processes and chemical reactions associated with lactose and protein and lipid components, such as crystallisation of lactose, oxidation of lipids, and Maillard reaction (Tehrany and Sonneveld, 2010). In addition, the migration of lipids on the milk powder surface is responsible for poor rehydration of milk powder during storage (Gaiani et al., 2007). The rate of these changes is dependent on the water activity (a_w) of milk powder, which is greatly affected by the surrounding relative humidity (RH) due to the hygroscopic nature of the milk powder, and is accelerated at high storage temperature (Gonzales et al., 2010; Stapelfeldt et al., 1997; Thomsen et al., 2005). Thus, milk powder must be stored at low RH levels to preserve its functional properties. In a previous study (Ho et al., 2019), the effects of different RH levels (11 - 32% RH, 37^{o}C) on the physiochemical properties of spray-dried camel milk powders (e.g. true density, colour, fat oxidation, lactose crystallisation, particle morphology), especially solubility during storage, were reported. However, changes in chemical composition on the surface of the powders, which is also expected to play an essential role in the rehydration process, have not been investigated. In this study, we examined the changes in surface chemical composition (e.g. lactose, lipid, and proteins) in relation to rehydration properties (wettability, dispersibility, and solubility) of spray-dried camel milk powder during storage at the same conditions reported in the previous study (11 - 32% RH, 37^{o}C) using X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

Raw camel milk was obtained from a camel farm in Queensland, Australia. The milk was kept at 5^{o}C during transportation and storage. The milk was subjected to spray drying within 48 h after collection. All chemicals used in this study were analytical grade and were purchased from Sigma Aldrich (New South Wales, Australia).

2.2. Production of camel milk powder

A pilot anhydrous spray drier (The University of Queensland, Australia) with a water evaporation capacity of 3 to 4 L/h equipped with a twin fluid nozzle was used to dry camel milk. The compressed air inlet of the atomizer was set at 40 kPa. The inlet and outlet temperature of the drying air were controlled at 160 and 70°C, respectively. The powders collected from the cyclone were kept in vacuum-sealed aluminium pouches for further analyses and stored at -80^{o}C.

2.3. Storage of spray-dried camel milk powder

The changes in rehydration and surface chemical composition of spray-dried camel milk powder kept at 11, 22 and 32% RH at 37^{o}C over 18 weeks were investigated. Spray-dried camel milk power (35 g) was evenly spread into a 2-cm layer in a polystyrene petri dish (20 cm in diameter). For each RH level, six such petri dishes were prepared corresponding to six time intervals (week 3, 6, 9, 12, 15, and 18) for sample analyses. The petri dishes were placed on the platform of plastic boxes (high density polyethylene, 25 L) in which RH was controlled at 11, 22 and 32% using oversaturated salt solutions of LiCl, CH_3COOK, and $MgCl_2$, respectively. The oversaturated salt solutions were prepared at least 2 days before commencing the experiment and were checked for a_w (AquaLab 3 Water Activity Meter, Decagon Devices, Inc., Pullman, USA). The RH in the headspace of the container was monitored to ensure that the desired RH levels were achieved (Digital hygrometer, KT-908, Ozstock, Australia). All boxes were tightly closed and placed in an incubator (HettCube 400R, LabGear, Australia) to maintain temperature at 37^{o}C during storage. For each time interval, one petri dish sample at each storage condition was removed from the plastic box, transferred to a 10-mL plastic container, and then kept at -80^{o}C for further analyses.

2.4. Determination of spray-dried camel milk powder properties

2.4.1. Gross composition of camel milk powder

Moisture, protein, lipid, and lactose content were determined by the vacuum oven method [AOAC (2005), 925.10], Kjeldahl method [AOAC, (2005), 2001.14], Gerber method [AOAC, (2005), 989.05], and titrimetric method (AS, 1994), respectively.

2.4.2. Surface properties of spray-dried camel milk powder

a). X-ray photoelectron spectroscopic (XPS) analysis

Surface atomic chemical elements of carbon, oxygen, and nitrogen of camel milk powder (approximately 10-nm surface depth) were determined using a KRATOS Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromatic Al Kα X-ray (hν =1486.6 eV) operated at 150 W. Camel milk samples were sprinkled onto the surface of the sample holder using sticky carbon tape and were then outgassed under a very high vacuum overnight. The analysis was performed with a survey scan from 0 to 1200 eV with a dwell time of 100 ms, pass energy of 160 eV at steps of 1 eV, with a single sweep. The obtained spectra were analysed using CasaXPS software (Casa Software Ltd., United Kingdom) to determine the relative percentage (%) of carbon (C), nitrogen (N) and oxygen (O) elements on the sample surfaces (Figure S.1 in supplementary material).

From the relative atomic percentages of the elements (C, O, and N), the relative amounts (%) of protein, lipid, and lactose at the powder surface were determined using a classical matrix formula (Gaiani et al., 2006; Nawaz et al., 2016).

However, it was difficult to isolate and purify lactose, protein, and lipid components from spray-dried camel milk powder samples and these pure components are not commercially available. Therefore, for the purpose of comparison among camel milk powder samples, the values of pure cow milk powder components (anhydrous milk fat, lactose [Sigma-Adrich], and pure milk proteins) were used for calculation. These values were reported by Gaiani et al. (2006) as follows: lactose (C = 61.6, O = 38.4, N = 0), milk proteins (C = 68.2, O = 18.5, N = 13.3), and anhydrous milk fat (C = 87.0, O = 12.3, and N = 0.7). The results are the mean of two independent repeats. Each analysis scanned an area of 600 x 600 µm, meaning that one experiment is already the mean of the surface of hundreds of particles.

b). Scanning electron microscopy (SEM)

SEM analysis of samples was performed using a Hitachi SU3500 Scanning Electron Microscope (Hitachi High-Technologies Europe GmbH, Germany). The samples were fixed on double-sided carbon tape and kept in a desiccator with silica gel for at least 24 h before observing under SEM. Samples were coated with iridium using a Quorum Q150T metal coater (Quorum Technologies Ltd., UK). The accelerating voltage during SEM scanning was set at 5 kV. The selected images are representative of at least five images observed.

2.4.3. Rehydration properties of spray-dried camel milk powder

a). Wettability

The wettability of spray-dried camel milk powders was evaluated via wetting time and dynamic wettability measurement (Ji et al., 2016). The wetting time is defined as the time required to obtain the complete wetting of 6 g of powder dropped on the surface of 100 mL water contained in a 400 mL glass beaker at room temperature (25^{o}C).

A modified Washburn method was applied for dynamic wettability measurement. Approximately 1.5 g of powder was carefully placed into a pre-weighed borosilicate cylindrical glass tube (15 cm in length and 0.1 cm inside diameter) with the bottom end covered with a piece of filter paper and gauze. The powder was packed into the tube via tapping the glass tube containing the powder on the bench surface 10 times. Then, the glass tube was fixed on a burette stand such that its bottom end just contacted the water surface by which water can penetrate into the powder via capillary forces. After 15 min, the amount of water adsorbed by the powder was determined from the difference in the weight of the tube containing wetted powder and the total weight of the empty tube and initially used powder. Wettability was expressed as the percentage of the amount of water adsorbed by the powder with respect to that of the initially used powder.

An optical microscope (Scientific Instruments & Optical Sales, Australia) with a 5.0 MP camera system using TSView7 software (Fuzhou Tucsen Image Technology Co., Ltd., China) connected to the video entry port of a computer was used to take an image of the powder just after the particles contacted with water. The water was placed on a glass slide and a few camel milk powder particles were then dropped on the water surface. Images were taken with a 20X objective without a cover slip such that the powder particles were not disturbed. The selected images were representative of at least 10 images observed.

b). Dispersibility

Dispersibility was determined by measuring the changes in particle size distribution (PSD) of the powder dispersed in water during agitation at constant speed (2000 RPM) using a laser light scattering analyser (Malvern Mastersizer 2000, Malvern Instruments Ltd., Worcestershire, UK) (Mimouni et al., 2009). Approximately 8 mg of camel milk powder was dispersed into a 100-mL beaker (used as dispersion unit) containing 80 mL of milliQ water such that a desirable obscuration level of 15% can be achieved. The PSD was continuously measured at 2-min intervals until no change in PSD, which took approximately 60 min.

c). Solubility

Powder solubility was determined following the method reported by Ho et al. (2019). Aqueous solutions (5% w/w) of camel milk powders were prepared by mixing the powder in distilled water using an overhead stirrer (400 RPM, Heidolph RZR 2050, Kelheim, Germany) attached to a five-blade propeller. During stirring, the temperature of the solutions was maintained at 30^{o}C in a water bath. The solutions were stirred for 30 min to completely disperse the powders into water. Then, approximately 45 mL of the stirred solution was taken and centrifuged (Eppendorf Centrifuge, 5702, Thermal Fisher Scientific, Australia) at 1000 x *g* for 15 min at 20^{o}C. All supernatant and separated fat were carefully removed. Any residual fat around the centrifugal tubes was wiped out with tissue paper without disturbing the insoluble solids at the bottom of centrifuge tubes. The insoluble solids were flushed with distilled water and transferred to pre-weighed moisture pans. The moisture pans were dried in a Thermoline vacuum oven (Scientific Equipment, Australia) at 105°C (absolute pressure 80 kPa) overnight and then weighed after cooling in a desiccator. An increase in the weight of the moisture pan was the amount of insoluble solids. Total solids in the dispersion before centrifugation were determined by vacuum oven drying of approximately 5 g of dispersion at 105°C until constant weight (drying overnight). The solubility (S, %) of camel milk powder was calculated using following equation (eq. 1).

$$S\ (\%) = \frac{W_{ts} - W_{is}}{W_{ts}} * 100 \qquad \text{(eq. 1)}$$

Where W_{ts} is the weight of total solids (soluble and insoluble) in the solution (g) and W_{is} is the weight of insoluble solids (g).

2.5. Experimental design and statistical analysis

The experiments were performed following a fully randomized design with three replications. Experimental data were subjected to analysis of variance (ANOVA) at a significance level of p = 0.05 using the Minitab Express statistical programme (Minitab Inc., USA). For the characterization of inclusion complexes, each criterion was repeated at least two times.

3. Results and discussion

3.1. Chemical composition of spray-dried camel milk powder

After spray-drying, camel milk powder had about 25% (w/w) of protein, 23% (w/w) of fat, 45% (w/w) of lactose and 5% of moisture content (wet basis) corresponding to 0.34 a_w. During storage, the moisture content of camel milk powder changed differently depending on RH levels. At the end of the storage period (week 18), the moisture content of camel milk powder kept at 11, 22 and 32% RH was 2.73, 3.49 and 4.85%, respectively.

3.2. Surface properties of spray-dried camel milk powder

3.2.1. XPS

The surface elemental composition (C, O, and N) of camel milk powders kept at different conditions is shown in Table 1. These elements were calculated from O_{1s}, N_{1s}, and C_{1s} peaks from XPS spectra with binding energies of 528 - 533, 397 - 408, and 281 - 293 eV, respectively. Due to very good detection sensitivity of the XPS equipment, there was a peak for Cl element (Cl_{2p}) (Figure S.1 in supplementary material) in the XPS spectra of some camel milk samples. The presence of chlorine in camel milk powder possibly comes from either the sanitisers/disinfectants used in the dairy farm for cleaning the containers or milk minerals. However, this was found at extremely low concentration (< 0.1%) and was disregarded in the calculation of the surface element composition. Although the results showed that RH levels did not affect changes in element composition on the milk powder surface, a significant increase in C content and a decrease in N and O levels were observed over the storage period, especially at week 18. These results are consistent with those reported by Kosasih et al. (2016) on spray-dried whole cow milk powders ($a_w = 0.22$) kept at 37^oC over 18 weeks in zipped aluminium bags. However, this contrasts with findings reported by Kim et al. (2002) for spray-dried dairy powders (skim milk powder, whole milk powder, cream powder, and whey protein concentrate). Kim et al. was observed that during storage at 40^oC in an oven for 2 days, the O content on the surface of all powders increased by 0.14% to 1.5% due to fat oxidation and oxygen chemisorption. The differences in the reported results are probably due to dissimilarity in material properties and storage conditions.

From the percentage of elemental composition (Table 1), the surface chemical composition (lipid, protein, and lactose) were calculated and the changes in these composition during storage at different conditions are illustrated in Figure 1. The surface of fresh camel milk powder (week

0) was dominated by lipids (approximately 78%), followed by proteins (approximately 16%), and lactose (approximately 6%). These results are consistent with the majority of those reported in the literature, as other studies revealed an overrepresentation of lipids at the surface in comparison with the bulk (Kim et al., 2002 and Gaiani et al., 2007). Nevertheless, Kosasih et al. (2016) reported different results for spray-dried whole cow milk powders in which lipids, proteins, and lactose at the surface of the powders were either 58.1%, 15.4%, and 26.5%, respectively. These differences may be attributed to differences in spray-drying processes, milk properties, and even the matrix formula used to calculate the surface chemical composition. Kim et al. (2009) observed that surface chemical composition of milk powder were largely determined by spray-drying conditions such as feed solid concentrations, drying temperatures, size of droplets, and degree of homogenisation (e.g. size of fat globules). A high surface lipid content in fresh camel milk powder could be the results of spray drying at high outlet temperature (e.g. 70°C), which could make the temperature of the powder surface higher than the melting temperature of lipids in camel milk powders (range 10 to 46°C) (Rahman et al., 2012). Thus, lipids can exist in fluid form during spray drying, which led to the preponderance of lipid on the powder surface (Gaiani et al., 2007).

As shown in Figures 1 (a, b, and c), the surface chemical composition of camel milk powders changed over the storage period. The surface fat content increased while the surface protein and lactose content decreased. After week 12, the surface lipid content was significantly different than that at week 0 ($p < 0.05$). These changes were the results of the migration of lipid towards the powder surface caused by the melting of some lipid fractions in the powder as stored at high temperature (Murrieta-Pazos et al., 2012). The decline in surface lactose and protein contents was a compensation for the increase in surface fat content. It was observed that spray-dried camel milk powder was in an amorphous form and the lactose components in the powder experienced a slight crystallisation during storage (Ho et al., 2019). Crystallisation of lactose causes stress to the oil droplets inside the powder particles and forces the lipid to spread onto the powder surface (Fäldt and Bergenståhl, 1996).

As indicated in Figure 1d, a C/O ratio related to surface hydrophobicity of camel milk powder increased steadily during storage. The most significant change ($p < 0.05$) in surface hydrophobicity occurred at the end of storage period (week 18). The increase in surface hydrophobicity of camel milk powder during storage was caused not only by lipid migration, but also by the partial unfolding of proteins that expose the hydrophobic residues on the surface (Fyfe et al., 2011). In addition, changes in surface hydrophobicity of the powder are caused by Maillard compounds that modify surface composition. Our previous study (Ho et al., 2019) revealed that during storage of spray-dried camel milk powder, the secondary structure of proteins unfolded from α-helices to β-sheets, loops and β-turns, and Maillard reaction was initiated.

Changes in surface chemical composition and surface hydrophobicity of camel milk powders kept at different RH levels were not significant ($p > 0.05$). As reported, the rate of many deteriorating reactions in the milk powder during storage is minimum at $a_w < 0.35$. Stapelfeldt et al. (1997) observed that when whole cow milk powder was kept at $a_w = 0.11$ to 0.33 and 25 to 45^{o}C for 2 months (except for storage at $a_w = 0.33$ and 45^{o}C which induced a marked alteration in lipid oxidation, Maillard reaction, and sensory properties), the overall quality of powder was completely retained at most storage conditions.

3.2.2. SEM

Spray-dried camel milk powders consisted of different sized spherically shaped particles with wrinkled and folded surface (Figure 2). There were some dents and large vacuoles containing small dried milk particles on the surface of the particles. These morphological characteristics are common in spray-dried cow whole milk powders (Kosasih et al., 2016). However, the shape of the spray-dried milk powder particles changed with changes in the atomization process, drying conditions, and material composition (Langrish et al., 2006). Although the shape of the camel milk particles were almost unchanged over the storage period, the agglomeration of the powder was likely increased, especially those kept at 32.27% RH. The agglomeration of spray-dried camel milk powders is possibly due to the increase of lipid content on the surface of the particles (Bhandari, 2007). This is consistent with the XPS analytical results that indicated an increase in surface lipid content during the storage period.

3.3. Rehydration properties of spray-dried camel milk powder

3.3.1. Wettability

All spray-dried camel milk powder samples did not entirely immerse into water (a large proportion of the powder still floated on the water surface) after 10 min. As they were not wetted in less than 120 seconds (Schuck et al., 2012), it can be concluded that they are non-wettable. The poor wettability of spray-dried camel milk powder could be due to the hydrophobic properties on the particle surface (high C/O ratio values) caused by the presence of a large amount of surface lipids. These results were similar to those reported by Kosasih et al. (2016), in which spray-dried whole cow milk powders did not wet within 5 min. However, wettability of milk powder is dependent on particle size, density, porosity, surface charge, surface area of powder, and presence of amphipathic substances (Kim et al., 2002). During contact with water, a layer (the black layer as seen in Figure S.2 in supplementary document) was immediately formed surrounding the powder particles. These layers could be non-hydrated regions which kept the powder floating on the water surface and prevented water from penetrating inside the powder particles. A similar phenomenon was reported for dispersing high-protein milk powder in water (Ji et al., 2016).

The Washburn method was applied to further differentiate these powders with poor wettability behaviour. As shown in Figure 3a, the amount of water adsorbed was not significantly different among the samples and ranged from 1.5 to 2.5% (w/w) ($p > 0.05$). This indicates that the storage conditions (RH level and storage time) did not affect wettability of camel milk powders. The high amount of lipid on the powder surface was a reason for the poor wettability of camel milk powders.

3.3.2. Dispersibility

At t = 0 min, which was counted as when all powder particles were immersed into water (e.g., approximately 30s), the PSD of powder was the broadest (ranging from 0.04 to 1.0 µm, shown as three peaks indicated by (1), (2) and (3) symbols in Figure 3b). An increase in measurement time led to a gradual decline in peaks (1) and (3) and a steady increase in peak (2). After 50 min, peaks (1) and (3) almost disappeared and the PSD displayed only peak (2) with a much narrower distribution range. These changes were observed for all camel milk powder samples. These results indicate that under the mechanical force due to stirring, the agglomerated powder particles gradually broke up and started to disperse into water as individual particles, while the small separated particles dissolved into water (Selomulya and Fang, 2013).

Typically, d(0,5) values (which are the size at which 50% of the particles are smaller and 50% are larger) are selected to investigate the dispersibility of high protein dairy powders (Ji et al., 2015; Ji et al., 2016). However, changes in d(0,5) values in our study were too small to distinguish among the powder samples, while alterations in d(0,9) values (which are the size of particles below which 90% of the samples lie) were much larger. Thus, d(0,9) values were used to evaluate the dispersibility of camel milk powders. Because d(0,9) values measured at t = 0 min were different among the powder samples, to compare the dispersibility among the camel milk powder samples, all d(0,9) values were converted to d(0,9) ratios by dividing the d(0,9) at time t (min) to that at t = 0 min. The changes in d(0,9) ratios during the dispersion of the camel milk powders in water over 60 min are shown in Figure S.3 (supplementary material).

As shown in Figure S.3, the decline rate of d(0,9) ratios occurred rapidly within the initial 10 min of dispersion for all powder samples. Therefore, for comparison purposes, the slopes of the regression lines for the dispersion data up to 10 min were calculated (Table 2). The higher absolute slope values indicate faster dispersibility of the powder. For each RH level, the slope values decreased with an increase in storage time, indicating decline in dispersibility. This was especially apparent for powders kept at 22% and 32% RH longer than 12 weeks. The wettability of the powder in water has a strong correlation with the hydrophilicity of the powder surface while dispersibility of the powders in water under mechanical force were mainly determined by the powder surface charge (zeta-potential) and specific gravity (e.g. particle size) of powder (Mitsui and Takada, 1969).

3.3.3. Solubility

As shown in Figure 3(c), fresh powder dissolved almost completely in water with a solubility of 98.62 ± 1.47%. This solubility level was almost unchanged until week 9 for all RH levels. From week 9, solubility started to gradually decline, especially that of powders kept at 22 and 32% RH (decline to 91.21 ± 4.78 and 90.85 ± 4.09 %, respectively) at the end of storage period. These results indicate that in long-term storage (e.g. more than 12 weeks), the solubility of camel milk powder is affected by storage RH conditions in which the higher RH level resulted in greater reduction in solubility. The reduction in solubility of the milk powder could be caused by cross-linking of proteins (Anema et al., 2006), Maillard reaction (Le et al., 2011), crystallisation of lactose, or the presence of a high amount of lipid on the powder surface (Thomas et al., 2004). In a previous study (Ho et al., 2019), storage of spray-dried camel milk powder at 11% to 32% RH (37^{o}C) over 18 weeks resulted in unfolding of proteins, slight crystallization of lactose, and

Maillard reaction. Similarly, due to the migration of free fat to the powder surface and the spreading of fat on the surface, during storage at 37°C the solubility of spray-dried whole cow milk powder ($a_w = 0.2$) reduced by approximately 15% over 18 weeks of storage (Kosasih et al., 2016).

3.4. Correlation of surface chemical composition and solubility of camel milk powders

Solubility is the final stage of the rehydration process of milk powder, thus solubility is a more reliable criterion than wettability and dispersibility to evaluate the rehydration property of milk powder. To evaluate if there is any correlation between surface chemical composition and rehydration ability of camel milk powder, regression analyses between the surface lactose and lipid and the powder solubility were performed (Figure 4). While surface proteins and lactose displayed a much lower degree of correlation ($R^2 = 0.5565$ and $R^2 = 0.5565$, respectively), surface lipid showed a very strong correlation with powder solubility ($R^2 = 0.7856$). An increase in surface lipid led to powder solubility decline. An increase in surface hydrophobicity caused by migration of lipid may be the reason for the declining power solubility. Fyfe et al. (2011) reported that the increase in hydrophobicity at the surface appeared to contribute to the decrease in the solubility of high protein milk powder during storage. In addition, Gaiani et al. (2007) reported that during storage of native phosphocaseinate powder, the increase in wetting time was due to migration of lipid on the powder surface.

4. Conclusions

Here we report the effects of accelerated storage at 11% to 32% RH and 37°C on the surface characteristics of spray-dried camel milk powder over an 18-week period. The XPS results indicated there was a change in surface chemical composition (protein, lipid, and lactose), especially at week 18. During storage, the increase in surface lipid content led to an increase in surface hydrophobicity and agglomeration of powder particles (SEM results). For rehydration properties, due to a preponderance of surface lipid (e.g. 78%) of camel milk powder, which formed non-hydrated regions that prevented the powder from wetting, it was impossible to determine the wettability of camel milk powder via measurement of wetting time. The Washburn method did not distinguish the wettability among the powder samples. However, the dispersibility and solubility of the powder exhibited the effects of storage time and RH levels. When compared to fresh camel milk powder, powders kept at 22% to 32% RH showed a marked decline in dispersibility and solubility from week 15. The increase in surface lipid content could explain the decrease in solubility of camel milk powder as there was a strong correlation between them.

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References

AOAC (2005). Official methods of analysis AOAC International (18th ed.). Gaithersburg, MD: Association of Official Agricultural Chemists.

AS 1994. Methods of chemical and physical testing for the dairying industry. Method 4.10: Dried milk and dried milk products - Determination of lactose - Titrimetric method. Australia: Standards Australia committe on chemical analysis of dairy products.

Abrhaley, A., and Leta, S. (2018). Medicinal value of camel milk and meat. *Journal of Applied Animal Research* **46**, 552-558. https://doi.org/10.1080/09712119.2017.1357562.

Al-Juboori, A. T., Mohammed, M., Rashid, J., Kurian, J., and El Refaey, S. (2013). Nutritional and medicinal value of camel (Camelus dromedarius) milk. *Food and Environment Ii: The Quest for a Sustainable Future* **170**, 221-232. https://10.2495/fenv130201.

Anema, S., Pinder, D., Hunter, R., and Hemar, Y. (2006). Effects of storage temperature on the solubility of milk protein concentrate (MPC85). *Food Hydrocolloids* **20**, 386-393. https://doi.org/10.1016/j.foodhyd.2005.03.015.

Bhandari, B. R. (2007). Stickiness and caking in food preservation. *In* Handbook of Food Preservation, pp. 387-401. CRC Press Boca Raton.

Fäldt, P., and Bergenståhl, B. (1996). Changes in surface composition of spray-dried food powders due to lactose crystallization. *LWT-Food Science and Technology* **29**, 438-446. https://doi.org/10.1006/fstl.1996.0067.

FAO (2016). Food and Agriculture Organization of the United Nations - Statistic Data. Vol. 2018. Food and Agriculture Organization of the United Nations.

Fitzpatrick, J. J., van Lauwe, A., Coursol, M., O'Brien, A., Fitzpatrick, K. L., Ji, J., and Miao, S. (2016). Investigation of the rehydration behaviour of food powders by comparing the behaviour of twelve powders with different properties. *Powder Technology* **297**, 340-348. https://doi.org/10.1016/j.powtec.2016.04.036.

Fyfe, K. N., Kravchuk, O., Le, T., Deeth, H. C., Nguyen, A. V., and Bhandari, B. (2011). Storage induced changes to high protein powders: influence on surface properties and solubility. *Journal of The Science of Food and Agriculture* **91**, 2566-2575. https://doi.org/10.1002/jsfa.4461.

Gaiani, C., Ehrhardt, J. J., Scher, J., Hardy, J., Desobry, S., and Banon, S. (2006). Surface composition of dairy powders observed by X-ray photoelectron spectroscopy and effects on their rehydration properties. *Colloids and Surfaces B: Biointerfaces* **49**, 71-78. https://doi.org/10.1016/j.colsurfb.2006.02.015.

Gaiani, C., Scher, J., Ehrhardt, J. J., Linder, M., Schuck, P., Desobry, S., and Banon, S. (2007). Relationships between dairy powder surface composition and wetting properties during storage: importance of residual lipids. *Journal of Agricultural and Food Chemistry* **55**, 6561-6567. https://doi.org/10.1021/jf070364b.

Gonzales, A. S. P., Naranjo, G. B., Leiva, G. E., and Malec, L. S. (2010). Maillard reaction kinetics in milk powder: Effect of water activity at mild temperatures. *International Dairy Journal* **20**, 40-45. https://doi.org/10.1016/j.idairyj.2009.07.007.

Gorban, A. M., and Izzeldin, O. M. (2001). Fatty acids and lipids of camel milk and colostrum. *International Journal of Food Sciences and Nutrition* **52**, 283-287. https://doi.org/10.1080/09637480020027000-3-5.

Ibrahim, A. H., and Khalifa, S. A. (2015). Effect of freeze-drying on camel's milk nutritional properties. *International Food Research Journal* **22**, 1438-1445.

Ji, J., Cronin, K., Fitzpatrick, J., Fenelon, M., and Miao, S. (2015). Effects of fluid bed agglomeration on the structure modification and reconstitution behaviour of milk protein isolate powders. *Journal of Food Engineering* **167**, 175-182. https://doi.org/10.1016/j.jfoodeng.2015.01.012.

Ji, J., Fitzpatrick, J., Cronin, K., Maguire, P., Zhang, H., and Miao, S. (2016). Rehydration behaviours of high protein dairy powders: The influence of agglomeration on wettability, dispersibility and solubility. *Food Hydrocolloids* **58**, 194-203. https://doi.org/10.1016/j.foodhyd.2016.02.030

Kaskous, S. (2016). Importance of camel milk for human health. *Emirates Journal of Food and Agriculture* **28**, 158-163. https://doi.org/10.9755/ejfa.2015-05-296

Kim, E. H.-J., Chen, X. D., and Pearce, D. (2009). Surface composition of industrial spray-dried milk powders. 2. Effects of spray drying conditions on the surface composition. *Journal of Food Engineering* **94**, 169-181. https://doi.org/10.1016/j.jfoodeng.2008.10.020.

Kim, E. H. J., Chen, X. D., and Pearce, D. (2002). Surface characterization of four industrial spray-dried dairy powders in relation to chemical composition, structure and wetting property. *Colloids and Surfaces B: Biointerfaces* **26**, 197-212. https://doi.org/10.1016/S0927-7765(01)00334-4.

Kosasih, L., Bhandari, B., Prakash, S., Bansal, N., and Gaiani, C. (2016). Effect of whole milk concentrate carbonation on functional, physicochemical and structural properties of the resultant spray dried powder during storage. *Journal of Food Engineering* **179**, 68-77. https://doi.org/10.1016/j.jfoodeng.2016.02.005

Langrish, T. A. G., Marquez, N., and Kota, K. (2006). An investigation and quantitative assessment of particle shape in milk powders from a laboratory-scale spray dryer. *Drying Technology* **24**, 1619-1630. https://doi.org/10.1080/07373930601031133.

Le, T. T., Bhandari, B., and Deeth, H. C. (2011). Chemical and physical changes in milk protein concentrate (MPC80) powder during storage. *Journal of Agricultural and Food Chemistry* **59**, 5465-5473. https://doi.org/10.1021/jf2003464.

Mimouni, A., Deeth, H. C., Whittaker, A. K., Gidley, M. J., and Bhandari, B. R. (2009). Rehydration process of milk protein concentrate powder monitored by static light scattering. *Food Hydrocolloids* **23**, 1958-1965. https://doi.org/10.1016/j.foodhyd.2009.01.010.

Mitsui, T., and Takada, S. (1969). On factors influencing dispersibility and wettability of powder in water. *Journal of the Society of Cosmetic Chemists* **20**, 335-351.

Murrieta-Pazos, I., Gaiani, C., Galet, L., and Scher, J. (2012). Composition gradient from surface to core in dairy powders: Agglomeration effect. *Food Hydrocolloids* **26**, 149-158. https://doi.org/10.1016/j.foodhyd.2011.05.003.

Nawaz, M. A., Gaiani, C., Fukai, S., and Bhandari, B. (2016). X-ray photoelectron spectroscopic analysis of rice kernels and flours: Measurement of surface chemical composition. *Food Chemistry* **212**, 349-357. https://doi.org/10.1016/j.foodchem.2016.05.188.

Rahman, M. S., Al-Hakmani, H., Al-Alawi, A., and Al-Marhubi, I. (2012). Thermal characteristics of freeze-dried camel milk and its major components. *Thermochimica Acta* **549**, 116-123. https://doi.org/10.1016/j.tca.2012.09.005.

Schuck, P., Jeantet, R., and Dolivet, A. (2012). "Analytical methods for food and dairy powders," West Sussex: John Wiley & Sons.

Selomulya, C., and Fang, Y. (2013). Food powder rehydration. *In* "Handbook of food powders", pp. 379-408. Cambridge: Elsevier.

Stapelfeldt, H., Nielsen, B. R., and Skibsted, L. H. (1997). Effect of heat treatment, water activity and storage temperature on the oxidative stability of whole milk powder. *International Dairy Journal* **7**, 331-339. https://doi.org/10.1016/S0958-6946(97)00016-2.

Sulieman, A. M. E., Elamin, O. M., Elkhalifa, E. A., and Laleye, L. (2014). Comparison of physicochemical properties of spray-dried camel’s milk and cow's milk powder. *International Journal of Food Science and Nutrition Engineering* **4**, 15-19. https://doi:10.5923/j.food.20140401.03.

Tehrany, E. A., and Sonneveld, K. (2010). Packaging and the Shelf Life of Milk Powders. *In* "Food Packaging and Shelf Life: A Practical Guide" (L. R. Gordon, ed.), pp. 128-137. CRC Press, New York.

Thomas, M. E. C., Scher, J., Desobry-Banon, S., and Desobry, S. (2004). Milk powders ageing: effect on physical and functional properties. *Critical Reviews in Food Science and Nutrition* **44**, 297-322. https://doi.org/10.1080/10408690490464041.

Thomsen, M. K., Lauridsen, L., Skibsted, L. H., and Risbo, J. (2005). Temperature effect on lactose crystallization, Maillard reactions, and lipid oxidation in whole milk powder. *Journal of Agricultural and Food Chemistry* **53**, 7082-7090. https://doi.org/10.1021/jf050862p.

Table captions

Table 1: Surface elemental composition (%) of carbon (C), oxygen (O), and nitrogen (N) of camel milk powders kept at different RH conditions (*).

Table 2: Slope values obtained from regression curves indicating changes in d(0,9) ratios during dispersion of camel milk powders (stored at 11-32% RH) in water (*).

Table 1: Surface elemental composition (%) of carbon (C), oxygen (O), and nitrogen (N) of camel milk powders kept at different RH conditions(*).

Storage time (week)	11% RH			22% RH			32% RH		
	C	**N**	**O**	**C**	**N**	**O**	**C**	**N**	**O**
0	83.68 ± 0.22	2.39 ± 0.47	13.94 ± 0.69	83.68 ± 0.22	2.39 ± 0.47	13.94 ± 0.69	83.68 ± 0.22	2.39 ± 0.47	13.94 ± 0.69
3	84.48 ± 0.54	2.11 ± 0.01^{c}	13.42 ± 0.55	84.27 ± 0.52	2.30 ± 0.11	13.44 ± 0.42	84.46 ± 0.19	2.23 ± 0.01	13.32 ± 0.20
6	84.02 ± 0.30	2.14 ± 0.21^{c}	13.85 ± 0.08	84.44 ± 0.13	2.14 ± 0.13	13.43 ± 0.01	84.37 ± 0.25	2.12 ± 0.05	13.52 ± 0.30
9	85.12 ± 0.76	2.10 ± 0.07^{c}	13.29 ± 0.03	84.92 ± 0.51^{d}	1.95 ± 0.15	13.14 ± 0.35	84.36 ± 0.11	2.18 ± 0.13	13.46 ± 0.24
12	85.54 ± 0.40^{b}	1.63 ± 0.28^{c}	12.84 ± 0.13	85.19 ± 0.01^{d}	1.99 ± 0.08	12.83 ± 0.06	85.09 ± 0.12^{g}	1.87 ± 0.23	13.05 ± 0.35
15	85.51 ± 0.39^{b}	1.26 ± 0.08^{c}	13.25 ± 0.30	84.70 ± 0.12	2.14 ± 0.12	13.17 ± 0.00	86.17 ± 0.66^{g}	1.62 ± 0.06	12.22 ± 0.71^{h}
18	86.15 ± 0.24^{b}	1.32 ± 0.11^{c}	12.54 ± 0.13	86.41 ± 0.21^{d}	1.38 ± 0.11^{e}	12.21 ± 0.08^{f}	86.56 ± 0.35^{g}	1.49 ± 0.34	11.96 ± 0.00^{h}

For each column, b, c, d, e, f, g and h letters indicating significant difference when compared with week 0 ($p < 0.05$).

Table 2: Slope values obtained from regression curves indicating changes in d(0,9) ratios during dispersion of camel milk powders (stored at 11-32% RH) in water (*).

Storage time (week)	**11% RH**	**22% RH**	**32% RH**
0	-0.067 ± 0.005 (**)	-0.067 ± 0.005	-0.067 ± 0.005
3	-0.062 ± 0.006	-0.069 ± 0.002	-0.065 ± 0.001
6	-0.066 ± 0.003	-0.063 ± 0.004	-0.063 ± 0.003
9	-0.054 ± 0.000	-0.066 ± 0.000	-0.062 ± 0.005
12	-0.055 ± 0.007	-0.053 ± 0.004[a]	-0.055 ± 0.005[b]
15	-0.058 ± 0.004	-0.048 ± 0.004[a]	-0.061 ± 0.000
18	-0.056 ± 0.002	-0.059 ± 0.003[a]	-0.052 ± 0.000[b]

(**) Minus (-) before the numbers indicates reduction of d(0,9) values during dispersion process. For each column (RH level), a, b indicate a significant difference when compared with week 0 ($p < 0.05$).

Figure captions

Figure 1: Surface chemical composition (%) of lactose (a), proteins (b), and lipid (c) and changes in C/O ratio (d) of camel milk powders kept at different RH conditions (11-grey for 11%, 22-red for 22%, and 33-blue for 32% RH). For each RH level and criteria, $^{(*)}$ indicates a significant difference when compared with week 0 ($p < 0.05$).

Figure 2: SEM of fresh spray-dried camel milk powder (a) and of powders kept at 11, 22 and 32% RH at week 18 (b, c, and d, respectively).

Figure 3: Wettability determined by Washburn method (a), representative changes in particle size distribution of power particles dispersed in water, and solubility (c) of spray-dried camel milk powder kept at different conditions. For each RH level, a and b indicate significant difference when compared with week 0 ($p < 0.05$).

Figure 4: Regression analyses between the surface chemical composition and the solubility of camel milk powders. S - solubility, Li - lipids, P - proteins, La - lactose.

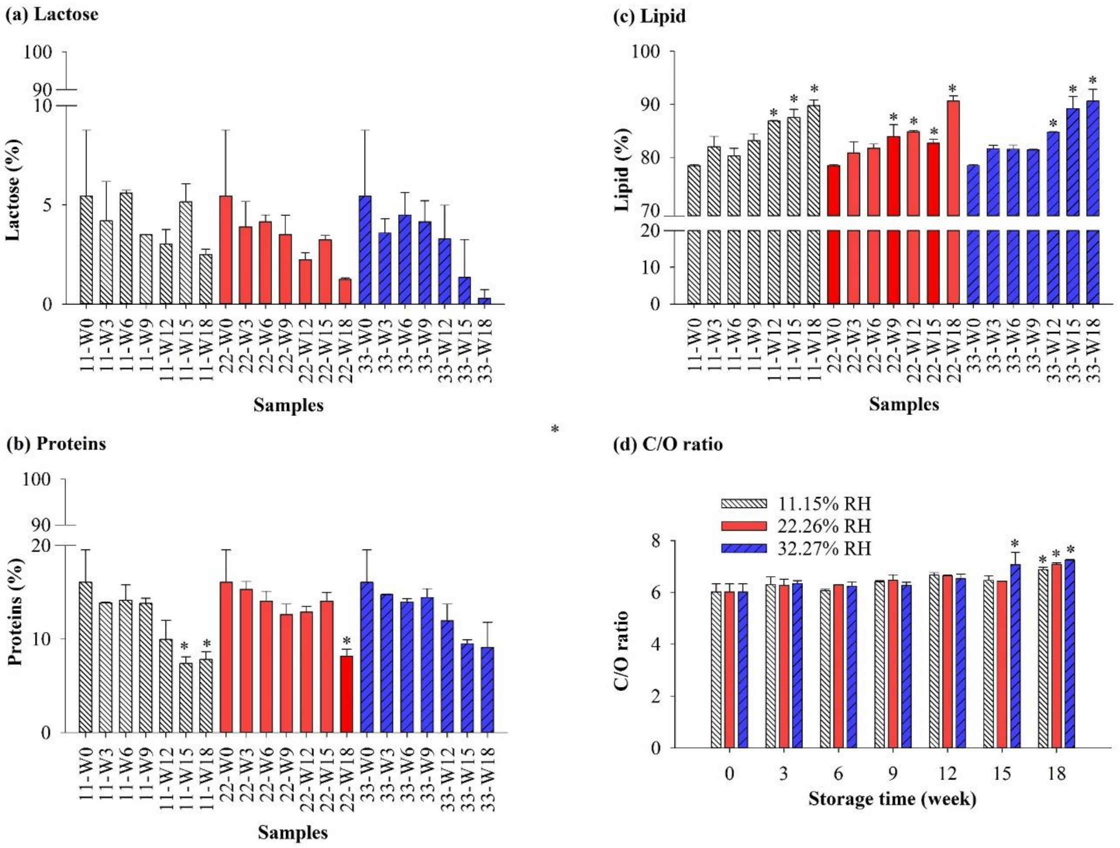
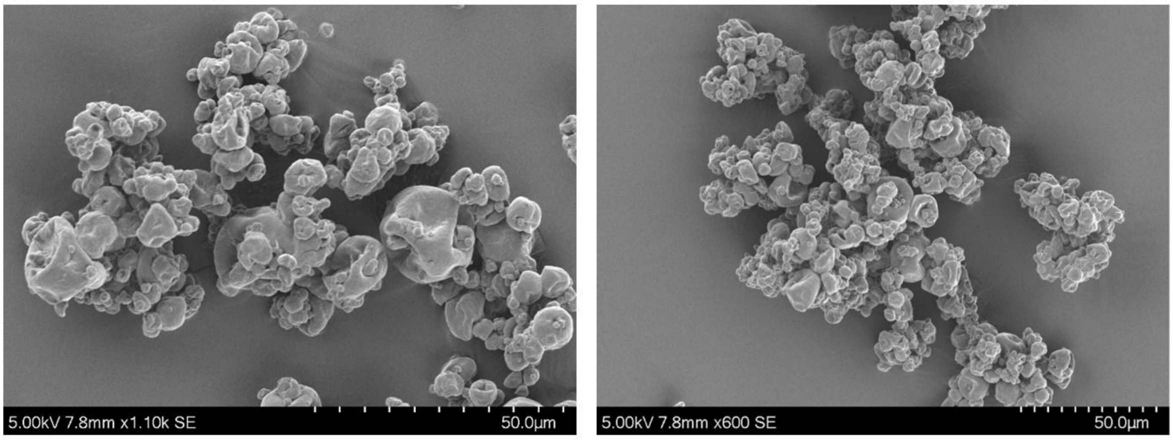
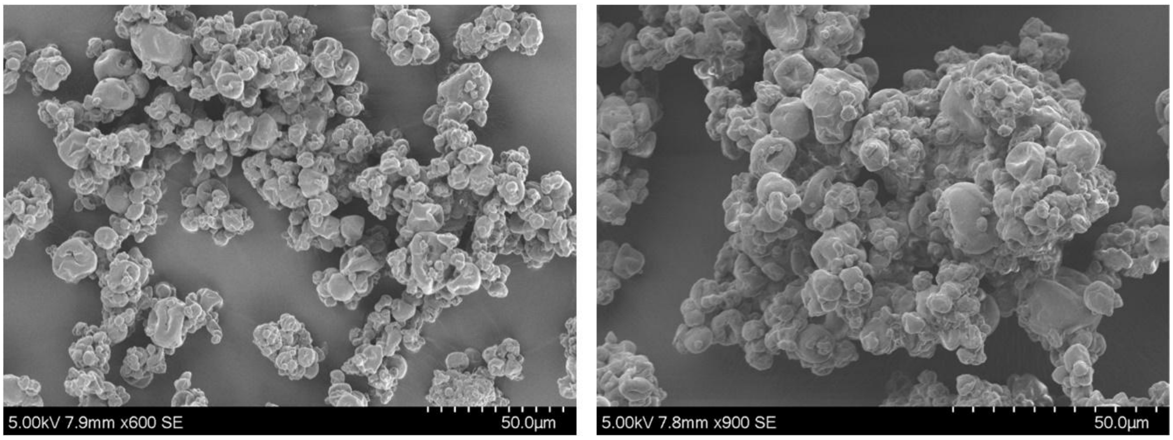


Figure 1: Surface chemical composition (%) of lactose (a), proteins (b), and lipid (c) and changes in C/O ratio (d) of camel milk powders kept at different RH conditions (11-grey for 11%, 22-red for 22%, and 33-blue for 32% RH). For each RH level and criteria, (*) indicates a significant difference when compared with week 0 ($p < 0.05$).



(a) Week 0

(b) Week 18 – 11% RH

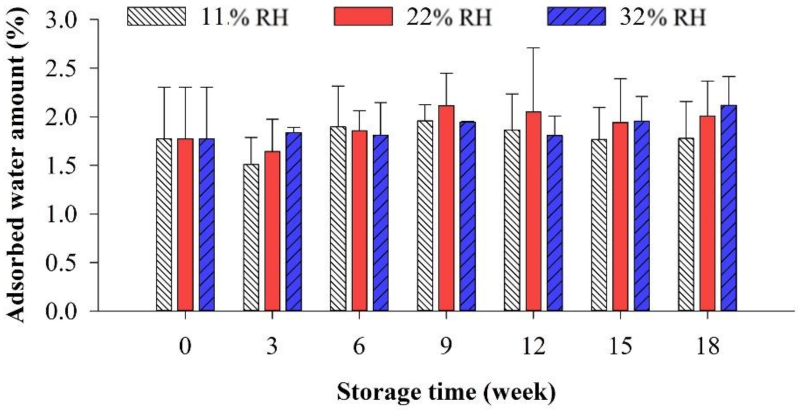


(c) Week 18 – 22% RH

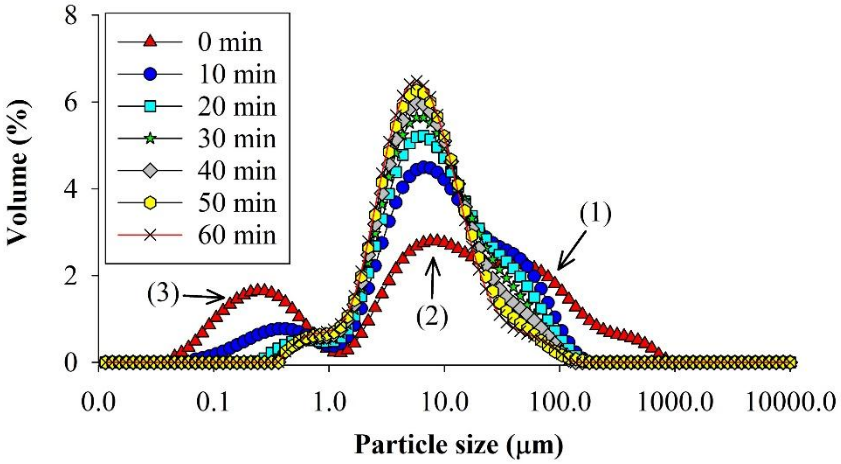
(d) Week 18 – 32% RH

Figure 2: SEM of fresh spray-dried camel milk powder (a) and of powders kept at 11, 22 and 32% RH at week 18 (b, c, and d, respectively).

(a) Wettability



(b) Change PSD during dispersion of the powder



(c) Solubility

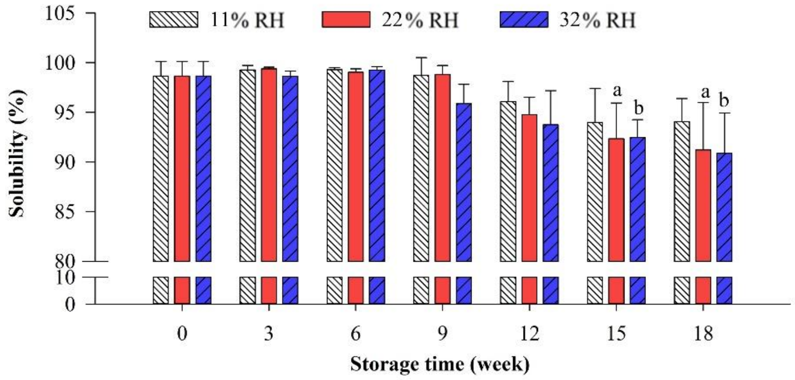


Figure 3: Wettability determined by Washburn method (a), reprsentative changes in particle size distribution of power particles dispersed in water (b), and solubility of spray-dried camel milk powder kept at different conditions (c). For each RH level, a and b indicate significant difference when compared with week 0 ($p < 0.05$).

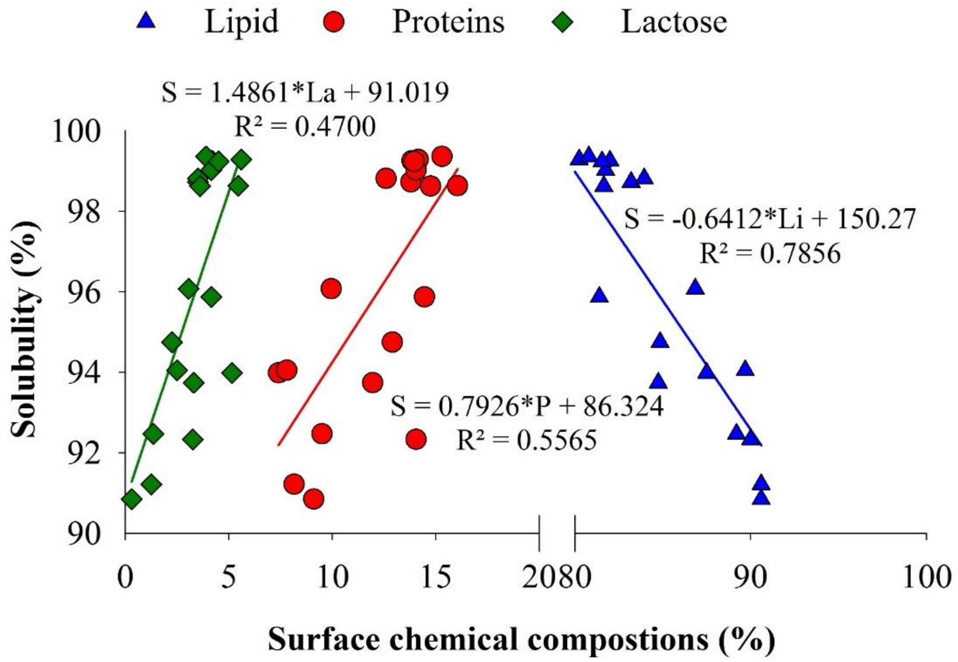


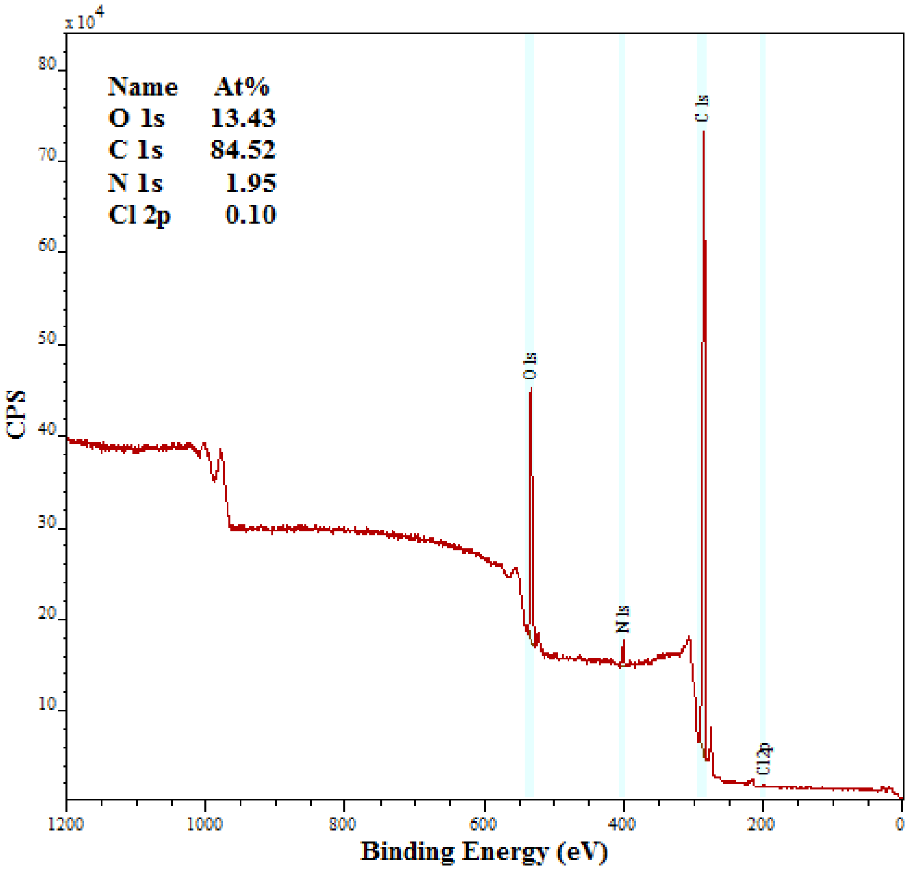
Figure 4: Regression analyses between the surface chemical composition and the solubility of camel milk powders. S - solubility, Li - lipids, P - proteins, La - lactose.

Supplementary material

Figure S.1: Typical XPS spectrum performed with a survey scan of camel milk powder.

Figure S.2: Optical images of camel milk powder particles dispersing on the water surface (scale bar = 20 µm).

Figure S.3: Changes in d(0,9) ratios of spray-dried camel milk powders kept at different RH levels after they were dispersed in water for 60 min.



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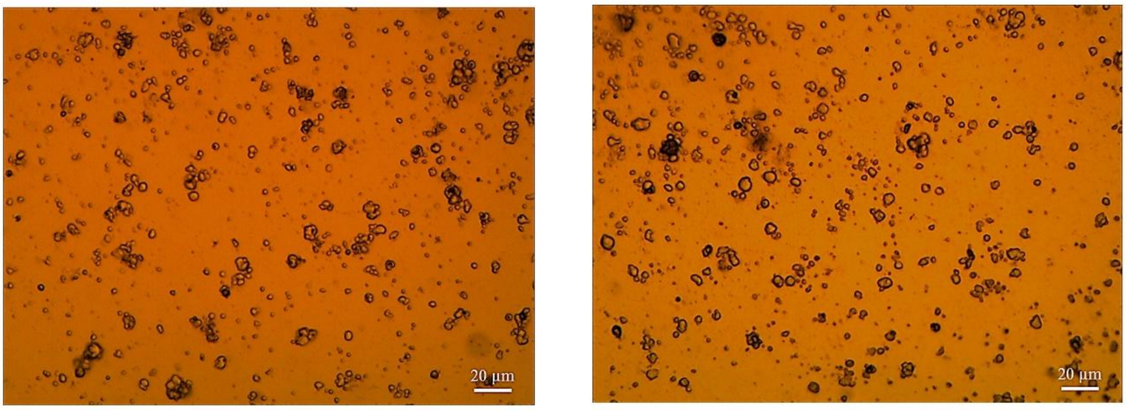
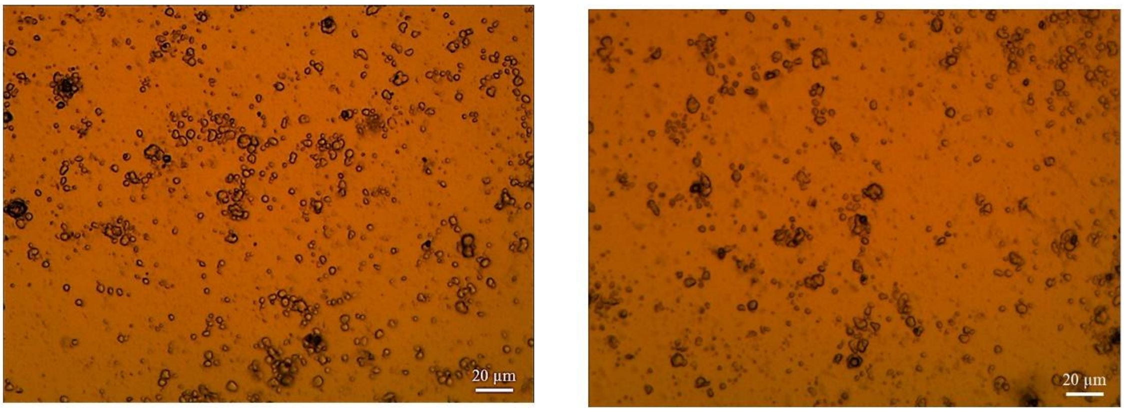


(a) Week 0

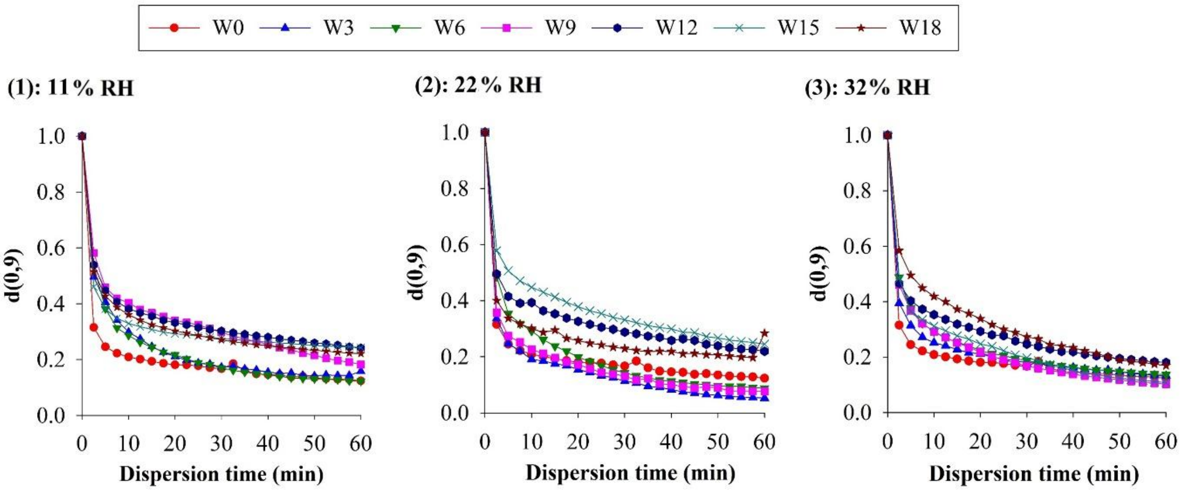
(b) Week 18 – 11% RH



(c) Week 18 – 22% RH

(d) Week 18 – 32% RH

Figure S.2: Optical images of camel milk powder particles dispersing on the water surface (scale bar = 20 µm).



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***Declaration of Interest Statement**

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: