

Relationships between Dairy Powder Surface Composition and Wetting Properties during Storage: Importance of Residual Lipids

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The relationships between powder surface composition and powder rehydration properties under variable conditions of storage are investigated in this paper. A rheological approach was used to evaluate the modifications induced by storage on the rehydration properties of native phosphocaseinate powder. Concurrently, the powder surface composition (i.e., lactose, proteins, and lipids) was evaluated by X-ray photoelectron spectroscopy (XPS). A strong correlation was found between the powder wetting time lengthening and the migration of lipids on the powder surface during storage. XPS studies indicated also an over-representation of lipids on the powder surface (6%) in comparison with total lipids (0.4%) even on fresh powder before storage. Detailed investigation of powder lipids revealed the presence of high levels of polar lipids (66% compared with <1% in milk lipids). Their amphiphilic nature and their melting points could explain the extensive enrichment of lipids observed at the powder surface during processing and storage.

KEYWORDS: Dairy powder; lipids; rehydration; storage; XPS

INTRODUCTION

There is a continuous need to develop innovative dairy-based ingredients. Native phosphocaseinate (NPC) is one of them thanks to the developments in membrane filtration processing (1). This powder constitutes an interesting ingredient for the food industry due to its high protein content and presents also an excellent capacity for cheesemaking (2). However, the variation of its rehydration properties during storage could involve practical difficulties for an industrial use (3). Therefore, more information about the rehydration behavior of this powder during storage can make its applications more effective.

The dissolution properties of a powder can be studied by a rheological approach as for hydrocolloids (4–6) or dairy-based products (3, 7, 8). These approaches allow the determination among other things of the wetting, which is the first step in the powder rehydration process. Indeed, powder rehydration is an essential quality attribute (9) and depends on different steps: the wettability, which is the ability to absorb water; the sinkability, which is the ability to sink into the water; the

dispersibility, which is the ability to disperse in single particles throughout the water; and the solubility, which is the ability to dissolve in water (10). Much knowledge on this phenomenon has been accumulated recently on the basis of rheology, static light scattering, and microscopy studies (3).

Storage conditions of milk powders are often established to warrant microbiological safety or to keep an acceptable appearance. Consequently, the modifications induced by storage on functional properties of the powders and especially rehydration properties have been poorly investigated (11). Within the past 10 years, X-ray photoelectron spectroscopy (XPS) has been successfully applied for investigating the surface composition of dairy powders at an elemental level (13, 14). To the best knowledge of the authors, only a few works concern dairy powder surface investigation by XPS during storage (12, 13). From the C, O, and N percentages, surface contents in proteins, lactose, and lipids were deduced. In early studies, the classical way to characterize the surface of a dairy powder was the use of scanning electron microscopy (SEM). However, distinction between the various compounds or their quantification was seldom possible (15), and SEM was used only to visualize the surface topography. The presence of surface lipids was characterized by solvent extraction, but it was shown that the extractable lipids obtained originate from the powder surface and also from the bulk of the particle (16). Consequently, despite

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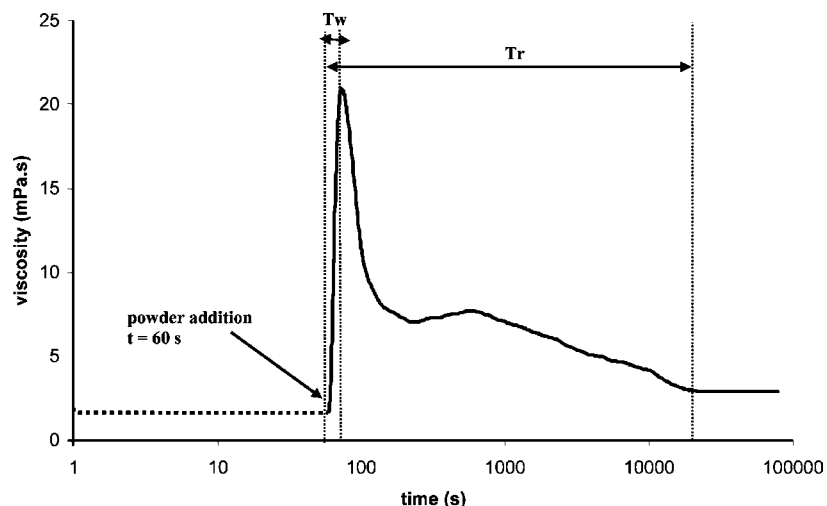


Figure 1. Example of a viscosity profile as a function of log time during rehydration of a casein powder in distilled water at 24 °C for 80000 s. Tr, rehydration time; Tw, = wetting time; ---, below rheometer sensitivity.

its crucial importance, knowledge of the surface composition of a dairy powder is very limited.

To study the modifications induced by storage on rehydration properties of the powders, the powder wetting time (Tw) was investigated concurrently with the powder surface composition. For this purpose (1) the viscosity profiles obtained during powder rehydration under different conditions of storage were interpreted in terms of wetting time, (2) the surface composition (i.e., lactose, lipids, and proteins) of the powder was followed by XPS during storage, and (3) an in-depth analysis of the residual lipids present in the powder is presented.

MATERIALS AND METHODS

Powder Fabrication Steps. NPC Concentrate Preparation. The NPC concentrate was separated from skimmed milk (1200 L) by tangential membrane microfiltration followed by purification through water diafiltration (17, 18) and supplied by UMR STLO (Unité Mixte de Recherche, Sciences et Technologie du Lait et de l'Oeuf, INRA Rennes, France).

NPC Spray-Drying. The spray-drying of concentrates was performed at Bionov (Rennes, France) in a three-stage pilot-plant spray-dryer (GEA, Niro Atomizer, St Quentin en Yvelines, France). The temperature of the product before drying was around 40 ± 2 °C. The atomizer was equipped with a pressure nozzle (0.73 mm diameter orifice) and a four-slot core (0.51 mm nominal width), providing a 60° spray angle. The pressure at the nozzle was 16 MPa. Inlet temperature was 215 ± 5 °C, integrated fluid bed air temperature was 70 ± 1 °C, and outlet temperature was 70 ± 1 °C. Inlet air humidity was controlled and adjusted by a dehumidifier (Munters, Sollentuna, Sweden).

Powder Storage. Freshly manufactured NPC powder was packed in 200 g bags. Two kinds of bags were used: a watertight bag and a standard bag. Storage was performed at room temperature (20 °C) and at 50 °C (the glass transition temperature of the powder determined by differential scanning calorimetry).

Characterization of the Powders. Chemical Analysis. The water content was measured by weight loss after drying 1 g samples of powder at 105 °C for 5 h. The total nitrogen (TN), the soluble nitrogen at pH 4.6 (non-casein nitrogen or NCN), and the 12% TCA-soluble nitrogen (non-protein nitrogen or NPN) were determined according to the Kjeldahl method (19). Casein and whey protein were determined as follows: $(TN - NCN) \times 6.38$ and $(NCN - NPN) \times 6.38$, respectively. Lactose content was obtained by enzymatic method using an Enzytec Lactose/d-Galactose kit (Diffchamb France SARL, Lyon, France), and the total lipid concentration was determined according to the Röse Gottlieb (20) and Folch (21) methods. Ashes were measured after incineration at 550 °C during 5 h.

Lipid Class Analysis. Lipid classes were separated on chromarods-SIII and quantified using a thin layer flame ionization detection (TLC-FID) Iatroscan apparatus MK V (Iatroscan Laboratory Inc., Tokyo, Japan). Lipids were extracted according to the Röse Gottlieb and Folch methods and collected in chloroform (5 mg mL⁻¹). A 1 μ L glass minicap pipet (Hirschmann Laborgeräte, Germany) was used to spot samples onto the chromarods. Lipids were submitted to migration in the following two systems at 20 °C (triplicate analyses): hexane/diethyl ether/formic acid (80:20:0.2 v/v/v) to separate neutral lipids and chloroform/methanol/water/ammonia (47:20:2.5:0.28 v/v/v/v) to separate polar lipids.

The air and hydrogen flow rates were set at 200 and 160 mL min⁻¹, respectively, and the scanning speed was 30 cm scan⁻¹. Data acquisition and processing were performed by a compatible PC equipped with dedicated software (SCPA GmbH, ChromStar Integrator, version 4.14). The following standards (Sigma-Aldrich Chemie GmbH) were used to identify the sample components: tripalmitin, cholesterol, L- α -phosphatidylcholine (PC), 3-*sn*-phosphatidylethanolamine (PE); L- α -phosphatidyl-L-serine (PS); L- α -phosphatidylinositol (PI); sphingomyelin (SM).

Rheological Study. A rehydration method was developed and described in detail elsewhere (3, 8). Briefly, a rheometer (Reologica AB, Lund, Sweden) was equipped with a custom-built paddle stirrer and a C25 cup. Rehydration processes include stirring at constant shear rate (100 s⁻¹). The experiments were carried out using a protein concentration of 5% in an 18 mL cup containing distilled water. The powder was dispersed in the cup 60 s after the rheometer had been started. The temperature was kept constant at 24 °C.

An example of viscosity profile as a function of log time is presented in **Figure 1**. The powder is poured at 60 s into water under stirring. This powder addition increases quickly the viscosity until a maximum. This first phase is related to the powder wetting (Tw). Next to this stage, another increase occurred followed by a slow and regular decrease of viscosity until stabilization indicating the end of rehydration (Tr). The final product obtained is a stable colloidal suspension of casein micelles (8).

XPS Analyses. XPS Equipment. The XPS analyses were carried out with a Kratos Axis Ultra (Kratos Analytical, Manchester, U.K.) spectrometer using a monochromatic Al K α source. The powder samples were attached to the sample holder using a double-sided conductive tape and then evacuated overnight prior analyses. Spectra were analyzed using Vision software from Kratos (Vision 2.2.2). A Shirley baseline was selected to subtract the background, and Gaussian-Lorentzian (70–30%) shapes were used for spectral decomposition. Quantification was performed using the photoemission cross sections and the transmission coefficients given in the Vision package.

Table 1. Chemical Composition of the Native Phosphocaseinate Powder Used (Mean of Three Determinations \pm SD)

	wt (g 100 g ⁻¹)		wt (g 100 g ⁻¹)
water	9.7 \pm 0.1	ashes	7.8 \pm 0.2
casein	80.1 \pm 0.6	lactose	1.5 \pm 0
whey	0.5 \pm 0.1	lipids ^a	0.4 \pm 0.1

^a Obtained with the Röse Gottlieb method.

Application of XPS to the Surface Content in Lactose, Protein, and Lipids. The underlying principle of the technique and its application to dairy powder have been described elsewhere (13, 14). Briefly, the relative atomic concentrations of carbon, oxygen, and nitrogen in the surface layer (~10 nm) of the powder were quantified and used in a matrix formula related to the surface content of the different compounds making up the sample (i.e., lactose, proteins, and lipids). Ca_{2p}, S_{2p}, and P_{2p} have been detected at levels lower than 1% for all of the powders. Consequently, elements other than C, O, and N were neglected in the quantification procedure.

$$A^C = \alpha P \cdot A^{C_P} + \alpha' L \cdot A^{C_L} + \alpha'' F \cdot A^{C_F} \quad (1)$$

$$A^O = \alpha P \cdot A^{O_P} + \alpha' L \cdot A^{O_L} + \alpha'' F \cdot A^{O_F} \quad (2)$$

$$A^N = \alpha P \cdot A^{N_P} + \alpha' L \cdot A^{N_L} + \alpha'' F \cdot A^{N_F} \quad (3)$$

$$100 = \alpha P + \alpha' L + \alpha'' F \quad (4)$$

In these equations, according to the chemical stoichiometry, $\alpha P = (\text{mol of C} + \text{mol of O} + \text{mol of N}) / \Sigma (\text{mol of C} + \text{mol of O} + \text{mol of N})$ in proteins; the same equations hold for lipids and lactose. In the following, this ratio will be defined as $\alpha =$ surface content. A^C , A^O , and A^N are the mole fractions of carbon, oxygen, and nitrogen in the sample surface; values were obtained from the areas of the C_{1s}, O_{1s}, and N_{1s} XPS peaks. A^{C_P} , A^{C_L} , and A^{C_F} are the mole fractions of carbon in proteins, lactose, and lipids; A^{O_P} , A^{O_L} , and A^{O_F} are the mole fractions of oxygen in proteins, lactose, and lipids; and A^{N_P} , A^{N_L} , and A^{N_F} are the mole fractions of nitrogen in proteins, lactose, and lipids.

Experimental values obtained from the reference samples (casein, anhydrous milk fat, and monohydrated lactose) were estimated. The following elemental compositions have been used to carry out these calculations: (lactose) C, 61.6; O, 38.4; (casein) C, 68.2; O, 18.5; N, 13.3; (lipids) C, 87.0; O, 12.3; N, 0.7 (22). By solving the matrix, (αP), ($\alpha' L$), ($\alpha'' F$), respectively, the proteins, lactose, and lipid surface contents were determined. Because there are differences between the molecular weights of carbon (12), oxygen (16), and nitrogen (14), the relative coverage was calculated to be mass-based for direct comparison with the bulk composition of the powders.

Statistical Analyses. Statistical analysis was carried out by using the software KyPlot version 2.0 (Koichi Yoshioka, Department of Biochemistry and Biophysics, Graduate School of Allied Health Sciences, Tokyo, Japan). For comparisons between fresh NPC powder and stored NPC powder, a parametric multiple test (Dunnnett test with fresh NPC powder as control) was performed. The significance levels were ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$; and NS, $P > 0.05$.

RESULTS

Powder Characterization. The chemical composition of the powder is reported in **Table 1**. NPC is a high protein content powder with 80% casein and also fat (0.4%), whey (0.5%), and lactose (1.5%) traces. The colloidal minerals are collected in the ash fraction (7.8%). The humidity is relatively high, around 10%. Lipid composition was determined on fresh powder by Iatroscan TLC-FID. The first development of chromarods in hexane/diethyl ether/formic acid resulted in the separation of three or four peaks depending on the extraction method [**Table 2**: Röse Gottlieb extraction, triacylglycerols (32%), diacylg-

Table 2. Iatroscan TLC/FID Separation of the Lipids Contained in the Fresh Powder: (a) Solvent System Hexane/Diethyl Ether/Formic Acid (80:20:0.2 v/v/v); (b) Solvent System Chloroform/Methanol/Water/Ammonia (47:20:2.5:0.28 v/v/v/v) Found after Röse Gottlieb and Folch Extractions (Mean of Three Determinations \pm SD)

lipid class	wt % of the total lipids	
	found by Folch extraction	found by Röse Gottlieb extraction
triacylglycerol	28.3 \pm 1.8	32.3 \pm 2.4
diacylglycerol	2.5 \pm 0.3	2.3 \pm 0.4
monoacylglycerol	0	0
fatty acids	nd	nd
phospholipids ^a	67.7 \pm 2.1	65.3 \pm 2.6
PE	36.4 \pm 1.1	23.8 \pm 1.6
PI	5.0 \pm 1.3	0
PS	0	0
PC	27.9 \pm 1.5	20.5 \pm 1.9
SM	30.7 \pm 0.8	43.1 \pm 0.9
cholesterol	1.5 \pm 0.2	0

^a PC, phosphatidylcholine; PE, phosphatidylethanolamine; PI, phosphatidylinositol; PS, phosphatidylserine; SM, sphingomyelin.

lycerols (2%), and polar lipids (65%); and Folch extraction, triacylglycerols (28%), diacylglycerols (2%), cholesterol (1%), and polar lipids (68%]. Polar lipids were separated after partial burning of chromarods to eliminate the neutral lipids from the sample. The development of these rods in chloroform/methanol/water/ammonia resulted again in three or four peaks depending on the extraction method [**Table 2**: Röse Gottlieb extraction, PE (23.8%), PC (20.5%), and SM (43.1%); and Folch extraction, PE (36.4%), PI (5.0%), PC (27.9%), and SM (30.7%]. Whatever the method of extraction, the relative concentration of polar lipids (about 66% of total lipids) found was very high in comparison with the value of milk (0.2–1%).

Powder Wetting Time Determination from the Viscosity Profiles. From each viscosity profile (**Figure 2**), the wetting time was determined as the time included between powder pouring and the maximum viscosity. A correlation between the determination of the wetting time with this methodology and standard (23) is described in detail elsewhere (3, 8). All of the wetting times obtained during storage are summarized in **Table 3**.

Watertight Bag Packaging. As shown in **Figure 2A**, the wetting time of the powder stored at 20 °C is not modified after 15 and 30 days of storage: all of the powders are wetted in 12 s. The maximum viscosities noted were, respectively, around 21 mPa·s after 15 days and 19 mPa·s after 30 days of storage. From 60 days, a shift is observed with a wetting time around 35 s. If the powder is stored at 50 °C (**Figure 2B**), the shift observed from 60 days is higher and around 148 s. Before 60 days of storage, no differences in Tw are observed in comparison with the fresh powder. The maximum of viscosity decreased during storage; around 21, 15, 11, and 10 mPa·s, respectively, after 0, 15, 30, and 60 days.

Standard Bag Packaging (Figure 2C,D). From 30 days of storage, a slight shift of the wetting time starts to appear at 20 and 50 °C (Tw = 66 s). When the powder is stored for a longer period, the wetting time is significantly lengthened ($P < 0.01$) at 20 °C from 66 to 73 s. At 50 °C, the wetting time is also significantly ($P < 0.001$) delayed from 68 to 265 s. The maximum of viscosity still decreased for the two temperatures during storage.

Powder Surface Composition from XPS Analysis. In **Figure 3A**, the survey scan of the freshly produced NPC powder

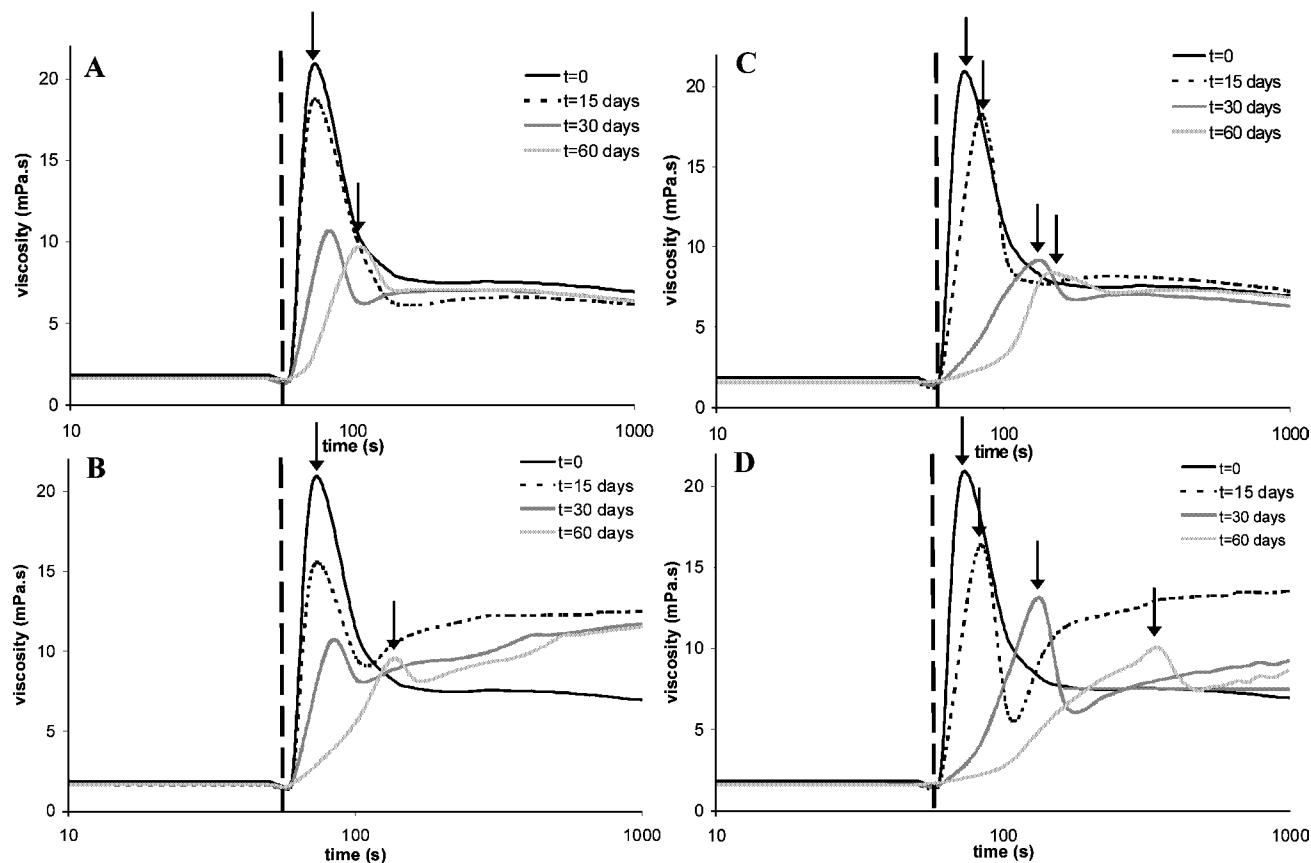


Figure 2. Viscosity profiles as a function of log time during rehydration of the powder in distilled water at 24 °C for 1000 s allowing the wetting time (T_w) determination: (A) watertight bag at 20 °C; (B) watertight bag at 50 °C; (C) standard bag at 20 °C; (D) standard bag at 50 °C.

Table 3. Evolution of the Powder Wetting Time during Storage in Comparison with the Wetting Time of the Same Powder before Storage (Fresh Powder, 0 Days) (Mean of Triplicate Analyses)^a

temperature of storage (± 1 °C)	packaging	0 days	15 days	30 days	60 days
20	watertight bag	12	13 ^{NS}	19 ^{NS}	35*
20	standard bag	12	14 ^{NS}	66*	73**
50	watertight bag	12	19 ^{NS}	14 ^{NS}	148***
50	standard bag	12	15 ^{NS}	68*	265***

^a***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$; NS, nonsignificant.

is represented as an example with the identification of the O_{1s} , Ca_{2p} , N_{1s} , C_{1s} , S_{2p} , and P_{2p} peaks. The detection of Ca_{2p} , S_{2p} , and P_{2p} elements was possible thanks to the high sensitivity of the XPS equipment used here. The concentration of these three elements was found below 1% for all of the powders. Consequently, elements other than C, O, and N were neglected in the quantification procedure. Representative peaks of the principal elements are presented in **Figure 3B–D**. According to a model for biochemical compounds, the C, O, and N peaks were decomposed (24). The C_{1s} peak was decomposed in four peaks corresponding to the \underline{C} –(C, H), \underline{C} –(O, N), $\underline{C}=\text{O}$, and $\text{O}=\underline{C}=\text{O}$ functions. The O_{1s} peak was decomposed in three peaks attributed to the $\text{O}=\underline{C}$, $\text{O}=\underline{C}$, and H_2O or $\text{O}=\underline{C}=\text{O}$ functions. The N_{1s} peak was decomposed in $\text{C}=\underline{N}\text{H}$ and $\text{C}=\underline{N}\text{H}^{2+}$ functions. From the carbon, oxygen, and nitrogen percentages, the surface content in proteins, lactose, and lipids was calculated from eqs 1–3.

Watertight Bag Packaging (Table 4). After 15 and 30 days of storage at 20 and 50 °C, no differences in powder surface composition were observed in comparison with fresh powder.

The protein, lactose, and lipid percentages were, respectively, at 94, 0, and 6%. From 60 days of storage, lipids started to migrate on the powder surface: 11% of lipids were measured for powders stored at 20 °C and 14% for powders stored at 50 °C. Consequently, the protein percentage at the surface diminished, respectively, at 89 and 86%.

Standard Bag Packaging (Table 4). After 15 days of storage at 20 and 50 °C, no differences in powder surface composition were observed. From 30 days of storage, the surface lipids increased from 6 to 13%. After 60 days of storage, lipids were around 17% whatever the temperature of storage. The protein percentage at the surface was lower and at 83% instead of 94%.

DISCUSSION

It has been shown that on fresh powder, the surface lipids found by XPS (6%) are significantly higher than the average lipid content (0.4%). A lipid over-representation on NPC powder surface was also visualized by confocal scanning laser microscopy (CSLM), confirming XPS results (data not shown). From XPS and CSLM results, it appears that lipids are transported toward and accumulate at the surface of the powder during drying. Differential scanning calorimetry (DSC) measurements (25) indicated that the melting points of lipids in dried milk are around 25 and 45 °C for low- and high-melting lipids, respectively. During powder fabrication, the outlet temperature (90 °C) of the spray-dryer, corresponding to a powder surface of around 70 °C, was above the melting points of lipids. Consequently, the lipids should be in a fluid form throughout the spray-drying process, and this fluid form could explain the lipid over-representation on the powder surface. Other authors have observed a similar trend (12, 22, 26, 27). The affinity of proteins with the air–water interfaces (surface active compo-

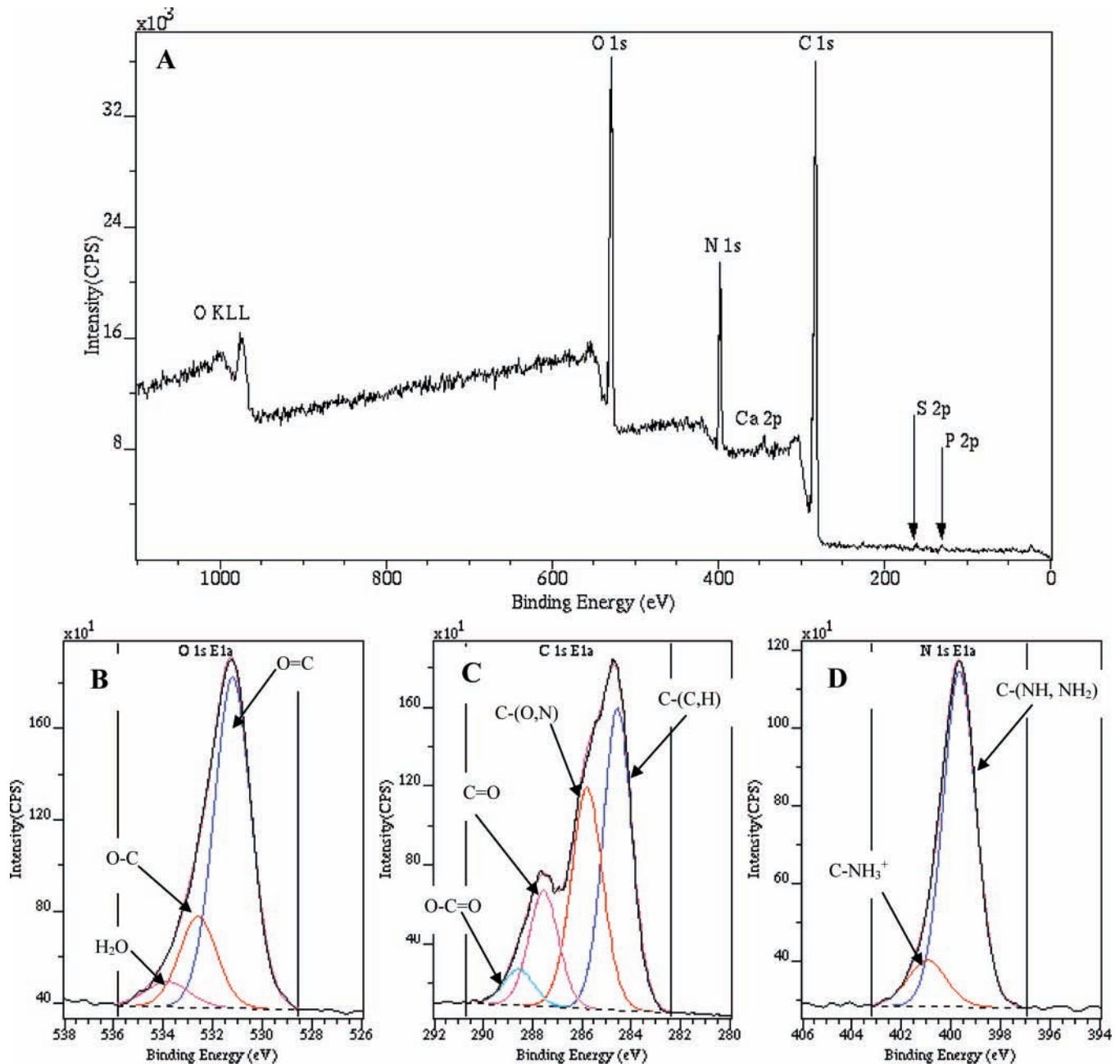


Figure 3. XPS spectra obtained for the fresh powder: (A) survey scan; (B, C, D) narrow spectra of O_{1s}, C_{1s}, and N_{1s} levels, respectively.

nents) of the droplets could explain their high presence on the powder surface at the expense of lactose. Indeed, lactose is generally found encapsulated in the particle even at high concentration. Note that the presence of lactose on the powder surface is known to strongly influence the caking of milk powder during storage (27) or the wettability (12, 13, 22, 28).

During storage, a strong correlation seems to appear between the changes in surface lipid coverage and the wetting properties (Figure 4). Indeed, when the wetting time increased significantly, lipid migration on the powder surface increased also significantly. This tendency is observed for all of the powders whatever the packaging (watertight or standard) and the temperature of storage (20 or 50 °C). It is well-known that surface lipids deteriorate the wetting properties of the powders (12, 22), but, for the first time, we demonstrated this relationship during powder storage.

To find out whether the powder wetting time lengthening observed during storage could be attributed to lipid migration on the powder surface, the lipids were analyzed by Iatroscan. We found that 66% of the lipids in the powder are polar lipids, whereas lipids of milk contain 99% triglycerides and <1% polar lipids, which are mainly associated with the milk fat globule membrane (MFGM). This complex membrane is a layer consisting of many different compounds (mainly polar lipids, proteins and enzymes) that surrounds a spherical core (predominantly composed of neutral lipids) (29). MFGM contains the major part of the milk polar lipids (29, 30). It was demonstrated that physical and mechanical treatments may affect compositional and structural changes in the MFGM during milk processing. These changes could involve a loss of membrane components also called "fat globule damage" (31). During processing, the MFGM could be ruptured and migrate toward the water phase, resulting in a low-fat product rich in polar lipids (32). Consequently, the surprising differences found in lipid

Table 4. Surface Composition of the Powder Stored during 60 Days in Comparison with the Fresh Powder (Days = 0) (Mean of Duplicate Analyses)

packaging	storage (days)	temperature (°C)	surface composition ^{a,b} (%)		
			proteins	lactose	lipids
watertight bag	0		94	0	6
	15	20	94 ^{NS}	0 ^{NS}	6 ^{NS}
		50	94 ^{NS}	0 ^{NS}	6 ^{NS}
	30	20	94 ^{NS}	0 ^{NS}	6 ^{NS}
		50	94 ^{NS}	0 ^{NS}	6 ^{NS}
	60	20	89*	0 ^{NS}	11*
50		86**	0 ^{NS}	14**	
standard bag	0		94	0	6
	15	20	94 ^{NS}	0 ^{NS}	6 ^{NS}
		50	94 ^{NS}	0 ^{NS}	6 ^{NS}
	30	20	87*	0 ^{NS}	13*
		50	88*	0 ^{NS}	12*
	60	20	83**	0 ^{NS}	17**
50		83**	0 ^{NS}	17**	

^a Surface composition found by XPS. ^b **, $P < 0.01$; *, $P < 0.05$; NS, nonsignificant.

composition could be due to a fractionation of polar and neutral lipids upon processing, allowing a concentration of lipids from globule membrane (33). For example, heating treatments (34), homogenization, and agitation (31), which are part of the natural processes used to produce the powder, were found to seriously affect the MFGM. However, polar lipid proportions in natural milk were found to be far from constant, and the differences observed could not be attributed to only the

processing (34). Both the amphiphilic nature of lipids (mainly polar lipids) and the storage temperature (above or equal to the lipid melting point) may explain the lipid migration on the powder surface during processing and also storage.

The major external factors influencing NPC powder rehydration are temperature, concentration, and time (8). These factors were constant in this study. Nevertheless, lipid localization at the surface may not be the only foundation to explain the wetting properties of the powder. For example, changing the composition of the powder by adding hygroscopic material (lactose or minerals) could significantly improve the wetting properties (22). During the storage of milk powders, much physicochemical damage occurred and could also modify the wetting properties. These damages are closely connected with the physical structure of the powder (3, 9, 11, 35). In this study, the bulked and packed densities were, respectively, around 340 and 395 kg m⁻³ for the fresh powder, and the median size distribution of the particles was around 285 μm. After storage (6 months), the densities and particle size were similar and could not explain the evolution of the wetting properties during storage. However, particle collapse and caking, which are mainly dependent on lactose glass transition, could also decrease the rehydration properties during storage. For the powders studied, the lactose amount was low (1.5%) and could not have a great influence. The mechanical stresses involved during storage may also enhance protein unfolding, which is detrimental to rehydration properties (36). Consequently, the physical state of milk components could also be implied and need to be investigated more precisely.

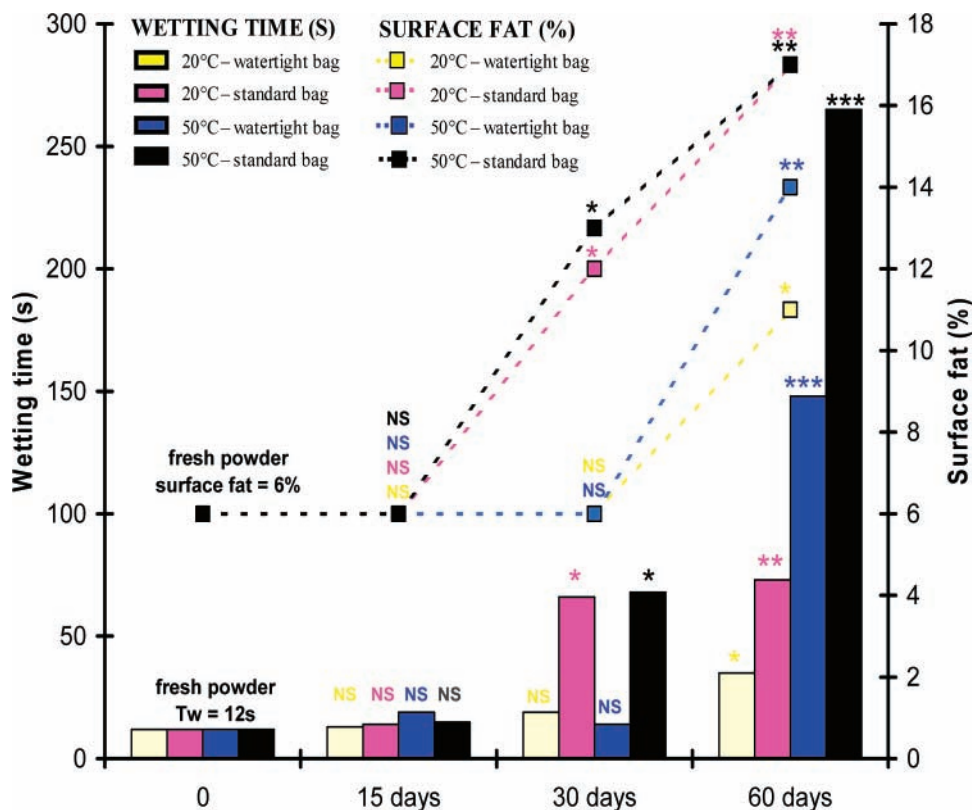


Figure 4. Relationship between lipid migration on powder surface and the wetting time increase during storage. ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$; NS, nonsignificant.

ABBREVIATIONS USED

NPC, native phosphocaseinate powder; PC, phosphatidylcholine; PE, phosphatidylethanolamine; PI, phosphatidylinositol; PS, phosphatidyl-L-serine; SEM, scanning electron spectroscopy; SM, sphingomyelin; Tr, rehydration time; Tw, wetting time; XPS, X-ray photoelectron spectroscopy.

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LITERATURE CITED

- (1) Fauquant, J.; Maubois, J. L.; Pierre, A. Microfiltration du lait sur membrane minérale. *Tech. Lait*. **1988**, *1028*, 21–23.
- (2) Maubois, J. L. Techniques séparatives appliquées à la valorisation du lait. *Ind. Aliment. Agric.* **2000**, 32–37.
- (3) Gaiani, C. Etude des mécanismes de réhydratation des poudres laitières : influence de la structure et de la composition des poudres. Ph.D. Thesis, INPL, Vandoeuvre-lès-Nancy, France, 2006.
- (4) Larsen, C. K.; Gaserod, O.; Smidsrod, O. A novel method for measuring hydration and dissolution kinetics of alginate powders. *Carbohydr. Polym.* **2003**, *51*, 125–134.
- (5) Wang, Q.; Ellis, P. R.; Ross-Murphy, S. B. Dissolution kinetics of guar gum powders. I. Methods for commercial polydisperse samples. *Carbohydr. Polym.* **2002**, *49* (2), 131–137.
- (6) Kravtchenko, T. P.; Renoir, J.; Parker, A.; Brigand, G. A novel method for determining the dissolution kinetics of hydrocolloid powders. *Food Hydrocolloids* **1999**, *13*, 219–225.
- (7) Ennis, M. P.; O'Sullivan, M. M.; Mulvihill, D. M. The hydration behaviour of rennet caseins in calcium chelating salt solution as determined using a rheological approach. *Food Hydrocolloids* **1998**, *12*, 451–457.
- (8) Gaiani, C.; Scher, J.; Schuck, P.; Hardy, J.; Desobry, S.; Banon, S. The dissolution behaviour of native phosphocaseinate as a function of concentration and temperature using a rheological approach. *Int. Dairy J.* **2006**, *16* (12), 1427–1434.
- (9) King, N. Dispersibility and reconstitutability of dried milk. *Dairy Sci. Abstr.* **1966**, *28* (3), 105–118.
- (10) Freudig, B.; Hogeckamp, S.; Schubert, H. Dispersion of powders in liquids in a stirred vessel. *Chem. Eng. Process.* **1999**, *38*, 525–532.
- (11) Thomas, M. E. C.; Scher, J.; Banon, S.; Desobry, S. Milk powders ageing: effect on physical and functional properties. *Crit. Rev. Food Sci. Nutr.* **2004**, *44* (5), 297–322.
- (12) Kim, E. H.-J.; Chen, X. D.; Pearce, D. Surface characterization of four industrial spray dried dairy powders in relation to chemical composition, structure and wetting properties. *Colloids Surf. B: Biointerfaces* **2002**, *26* (3), 197–212.
- (13) Fäldt, P. Surface composition of spray dried emulsions. Ph.D. Thesis, Lund University, Department of Food Engineering, Lund, Sweden, 1995.
- (14) Fäldt, P.; Bergenståhl, B.; Carlsson, G. The surface coverage of fat on food powders analysed by ESCA (electron spectroscopy for chemical analysis). *Food Struct.* **1993**, *12*, 225–234.
- (15) Mistry, V. V.; Hassan, H. N.; Robinson, D. Effect of lactose and protein on the microstructure of dried milk. *J. Food Struct.* **1992**, *11*, 73–82.
- (16) Buma, T. J. Free fat in spray-dried whole milk. 1. General introduction and brief review of literature. *Neth. Milk Dairy J.* **1971**, *25*, 33–41.
- (17) Pierre, A.; Fauquant, J.; le Graet, Y.; Piot, M.; Maubois, J. L. Préparation de phosphocaseinate natif par microfiltration sur membrane. *Lait* **1992**, *72*, 461–474.
- (18) Schuck, P.; Piot, P.; Méjean, S.; Fauquant, J.; Brulé, G.; Maubois, J. L. Déshydratation par atomisation de phosphocaseinate natif obtenu par microfiltration sur membrane. *Lait* **1994**, *74*, 375–388.
- (19) AOAC. *Official Methods of Analysis*; Association of Official Analytical Chemists: Washington, DC, 1984; Kjeldahl method.
- (20) NORM IDF. Dried milk, dried whey, dried buttermilk & dried butterserum—determination of fat content—Röse-Gottlieb reference method; International Dairy Federation: Brussels, Belgium, 1987; 9C.
- (21) Folch, J.; Lees, M.; Stanley, H. S. A simple method for the isolation and purification of total lipides of animal tissues. *J. Biol. Chem.* **1957**, *226*, 497–509.
- (22) Gaiani, C.; Ehrhardt, J. J.; Scher, J.; Hardy, J.; Desobry, S.; Banon, S. Surface composition of dairy powders observed by X-ray photoelectron spectroscopy and effects on their rehydration properties. *Colloids Surf. B: Biointerfaces* **2006**, *49* (1), 71–78.
- (23) NORM IDF. Dried milk—determination of dispersibility and wettability; International Dairy Federation: Brussels, Belgium, 1979; no. 087.
- (24) Gerin, P. A.; Dengis, P. B.; Rouxhet, P. G. Performance of XPS analysis of model biochemical compounds. *J. Chim. Phys.* **1995**, *92*, 1043–1065.
- (25) Innocente, N.; Blecker, C.; Deroanne, C.; Paquot, M. Langmuir film balance study of the surface properties of a soluble fraction of milk fat globule membrane. *J. Agric. Food Chem.* **1997**, *45*, 1559–1563.
- (26) Kim, E. H.-J.; Chen, X. D.; Pearce, D. Effect of surface composition on the flowability of industrial spray-dried dairy powders. *Colloids Surf. B: Biointerfaces* **2005**, *46*, 182–187.
- (27) Nijdam, J. J.; Langrish, T. A. G. The effect of surface composition on the functional properties of milk powders. *J. Food Eng.* **2006**, *77*, 919–925.
- (28) Fäldt, P.; Bergenståhl, B. Spray-dried whey protein/lactose/soybean oil emulsions. 2. Dispersability, wettability and particle structure. *Food Hydrocolloids* **1996**, *10*, 431–439.
- (29) Rombaut, R.; Dewettinck, K. The milkfat globule membrane—methodologies for measuring milkfat globule (membrane) damage. *Int. Dairy J.* **2006**, *16*, 1362–1373.
- (30) Mather, I. H. A review and proposed nomenclature for major proteins of milk fat globule membrane. *J. Dairy Sci.* **2000**, *83*, 203–247.
- (31) Evers, J. M. The milkfat globule membrane—compositional and structural changes post secretion by the mammary secretory cell. *Int. Dairy J.* **2004**, *14*, 661–674.
- (32) Rombaut, R.; Camp, J. V.; Dewettinck, K. Analysis of phospho- and sphingolipids in dairy products by a new HPLC method. *J. Dairy Sci.* **2005**, *88*, 482–488.
- (33) Rombaut, R.; Camp, J. V.; Dewettinck, K. Phospho- and sphingolipid distribution during processing of milk butter and whey. *Int. J. Food Sci. Technol.* **2006**, *41* (4), 435–442.
- (34) Ye, A.; Singh, H.; Taylor, M. W.; Anema, S. Characterization of protein components of natural and heat-treated milk fat globule membranes. *Int. Dairy J.* **2002**, *12*, 393–402.
- (35) Baldwin, A. J.; Sanderson, W. B. Factors affecting the reconstitution properties of whole milk powder. *N. Z. J. Dairy Sci. Technol.* **1973**, *8* (92), 92–100.
- (36) Thomas, M. E.; Scher, J.; Desobry-Banon, S.; Desobry, S. Milk powders ageing: effect on physical and functional properties. *Crit. Rev. Food Sci. Nutr.* **2004**, *44* (5), 297–322.

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