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Cocoa powder surface composition during aging: A focus on fat

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ABSTRACT

The surface of 11 wt.% fat cocoa particles was thoroughly investigated during a 2-month storage at 20 and 40 °C and at $a_w = 0.2$. Surface fat migration was evidenced only for powders stored at 40 °C by X-ray Photoelectron Spectroscopy. This was confirmed by ToF-SIMS, which allowed visualizing bigger fat patches at the surface of 40 °C-stored powders. These observations emphasize that fat need to be under a melted form to move toward the surface during storage. However, an increase in the free fat content was observed at both 20 °C and 40 °C. These results suggest rearrangements of particle structure during storage; free fat being more accessible to solvents at both temperatures. Confirmation was done by Scanning and Transmission Electron Microscopy images. Free and encapsulated fat were also extracted and analyzed during storage and no significant difference in fatty acids distribution (C16, C18, C18:1, C18:2) was observed by gas chromatography.

1. Introduction

Cocoa powder is obtained from cocoa beans, which are the seeds of three varieties of *Theobroma cacao*. After harvest, cocoa beans are freed from their shell to obtain the nibs. Nibs are then grounded, roasted and pressed to obtain cocoa liquor. Cocoa powder consists of the (partially) defatted fraction of cocoa liquor [1].

Cocoa powder composition is strongly affected by the quality of cocoa beans and processing parameters such as pressing time, and degree of alkalization. Disparate values in literature concerning cocoa composition are reported [2–6]. Polysaccharides are the major cocoa components (ranging between 34 and 60%), among which only few sugars (<2.5%). The major sugars found in cocoa beans are fructose and sucrose, with a higher amount of fructose [7]. In cocoa shells, total dietary fibers represent between 50 and 57% of the total composition [8,9]. Insoluble fibers are mainly constituted by glucose and uronic acid, but lower amounts of galactose, arabinose, xylose, and mannose are also present, which allows concluding that cellulose and pectin are the most abundant polysaccharides [6]. Proteins represent the second most abundant constituent of cocoa beans. Cocoa proteins can be divided into 4 fractions; the main fractions are water-soluble albumin (52%) and salt-soluble globulins (43%) [10]. Cocoa also contains some alkaloids: theobromine (3,7-dimethylxanthine) and caffeine (1,3,7-trimethylxanthine). Theobromine is a biologically-active metabolite of caffeine and both have different impacts on human metabolism by acting upon the central nervous system [11].

Most of the cocoa beans fat is contained in the nib. Of course, the fat content in cocoa powder is highly dependent on the type and yield of the defatting process. The total fat content of cocoa mass is typically about 55%, while it is between 11 and 22% for standard cocoa powders and less than 1% for highly-defatted cocoa powders [12]. The powder fat content is directly influenced by the pressing parameters and usually determines the cocoa powder designation, according to three categories (highly fat reduced, fat reduced and cocoa powders) but sometimes four (with breakfast cocoa containing more than 22% of fat) depending on the country and local legislation.

For many food powders (e.g., milk, cereal, starch), surface composition and more particularly surface fat content often plays a major role for powder functional properties [13]. As for other food powders, cocoa powders are known to present defects during processing and/or storage (caking, sticking, etc.). Indeed, the stickiness phenomenon may have a particular importance during drying or powder handling [14]. Powder stickiness is a surface property. Five main stickiness mechanisms are listed in the literature: intermolecular and electrostatic forces, mobile liquid bridges, immobile liquid bridges, solid bridges, and mechanical interlocking [14]. The main cause of stickiness for amorphous powder is water plasticization of particle surfaces [14]. Caking is also observed for cocoa powders and induces the alteration of use and handling properties, such as abilities to rehydrate or agglomerate, as well as flow properties that are critical for powder handling, conveying, and easiness of packaging [15]. Powder caking is mainly due to a sintering mechanism (molecular diffusion from the bulk of amorphous

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particles to contact points between particles) driven by the minimization of the particle surface area at constant volume that lowers the free energy of the system [16,17]. Four caking mechanisms (induced by humidity, protein sticking, fat melting and/or sugar phase transition) depending on powder composition and environmental conditions, are identified in the literature [18].

The main concern about cocoa powder in the literature, deals with health benefices of cocoa extracts: neuroprotective effects [19], antioxidant and antimicrobial action [20], cardioprotective effects [21], etc. These health benefits are strongly linked to the high content in polyphenols of cocoa powders. Unfortunately, no work focused on the relationship between aging, structure, and properties of cocoa powders has been directly identified in the literature, even though it is a very important technological question.

The objectives of this work were to thoroughly evaluate chocolate powdered product surfaces in order to better control its behavior during storage. This work opens a new window in the field of a food powder, whose surface has rarely been studied in spite of the substantial industrial market of chocolate products. To this aim, some analytical techniques, already used for other food powders (mainly, milk powders), were adapted to cocoa powders in order to follow the evolution of surface properties of a medium-fat powder (10–12%) during a 2-month storage at 20 and 40 °C.

2. Materials and methods

2.1. Cocoa powders and storage conditions

Industrial cocoa powder containing 11% fat (D-11-SB Dark Brown Cocoa), called CP11 in this work, was supplied by ADM Cocoa, Netherlands. During 2 months of storage, the temperature was controlled at 20 or 40 °C (±2 °C) in order to have a fat fraction under a solid or liquid state and to be close to industrial storage conditions. A saturated salted solution of potassium acetate (CH_3COOK) was used to set the relative humidity of the surrounding air in equilibrium so as to fix the water activity of the powder at $a_w = 0.2$.

2.2. Powder moisture content

Powder moisture content was determined by weighting 1 g of cocoa powder in a previously dried and weighted dish containing sand [1]. The sample was dried in an oven at 102 ± 2 °C for 4 h. The dish was then put in a dessicator and finally weighted.

Moisture content (MC) was calculated as follows:

$$MC\ (\%) = \frac{m_1 - m_2}{m_1 - m_0} * 100 \quad (1)$$

Where:

m_0 weight of empty and dry (dish + sand)
m_1 weight of (dish + sand + powder)
m_2 weight of dry (dish + sand + powder)

2.3. Powder imaging

For Scanning Electron Microscopy (SEM) analyses, powders were spread on a sticky plastic circle fixed on a support and was then coated with gold–palladium (Bio-Rad type SC 502). Finally, powders were analyzed with a Hitachi SEM S-4800 instrument operating from 15 to 20 kV.

For Transmission Electron Microscopy (TEM) analyses, powders were first dehydrated in ethanol and propylene oxide. Then, cocoa powders were pre-impregnated with a mixture of 2/3 Epon-embedded 812 resin and 1/3 propylene oxide for 5 h, and included in pure resin for 16 h. Resin polymerization was finally performed at 56 °C for 48 h. Thin slices (80 nm) were colored and contrasted in 3% uranyl acetate aqueous solution. Slices were put on copper grids covered with a carbon film. Finally, examinations were carried out with a Philips CM12 microscope operating at 80 kV.

2.4. Powder surface investigations

2.4.1. XPS

XPS was used in this study to measure the surface elemental composition of cocoa powders (up to 5–10 nm depth). It provides elemental and chemical state data in solid samples. This technique was never used for cocoa powders, but it had previously been well developed on other food powders [22–24]; in this work, the XPS technique was adapted to cocoa powders on the basis of these pioneer works

XPS is performed in ultra-high vacuum (10^{-8} Pa). The sample is irradiated with photons from a soft X-ray source of well-defined energy. The method is based on the irradiation of the material surface that causes a complete transfer of X-ray photon energy to atomic electrons of the sample. When the electron binding energy (E_b) is lower than the photon energy ($h\nu$), the electron is emitted from the atom with a kinetic energy (E_k) equal to the difference between the photon kinetic energy and the electron binding energy minus the spectrometer work function Φ:

$$E_k = h\nu - E_b - \Phi \quad (2)$$

XPS was carried out with a Kratos Axis Ultra (Kratos Analytical, Manchester, UK) photoelectron spectrometer. The instrument uses a monochromatic Al K_α X-ray source. Cocoa powder samples were attached to a sample holder with a double-side conductive tape. Spectra were analyzed using the Vision software from Kratos (Vision 2.2.0). Quantification of peak areas was performed using the photoemission cross-section and transmission coefficients given in the Vision package.

2.4.2. TOF-SIMS

TOF-SIMS measurements were performed using a commercial TOF-SIMS V time-of-flight mass spectrometer (ION-TOF GmbH, Münster, Germany). Again, this technique has never been used on cocoa powders, but was already tested on milk powders [25]. This spectrometer is supplied with a bismuth liquid metal ion gun (LMIG) delivering Bi_3^+ ions. Primary ions, extracted from the source, reach the sample surface. Secondary ions, accelerated up to an energy of 2 keV, are reflected with a single-stage reflector before being post-accelerated to 10 keV just before hitting the entrance surface of the hybrid detector. A low-energy electron flood gun is activated between each primary ion pulse in order to neutralize the sample surface with minimum damage. Images of fresh and aged cocoa powders surface with a field of view of 200 μm × 200 μm were recorded without stage movement just by randomly rastering the primary ion beam. Because of the very thin kinetic energy distribution of the secondary ions, the relationship between the time-of-flight and the square root of the mass-to-charge ratio m/z is linear over the whole mass range. The processing and data acquisition software was the SurfaceLab 6.3 (ION-TOF GmbH, Münster, Germany). The color scale is defined by normalizing the count signal: the maximum number of counts corresponds to white spots, and no count was associated with black spots. The amplitude of the color scale corresponds to the maximum number of counts m_c and could be read as $[0, m_c]$. t_c is the total number of counts recorded for a specified m/z value; in other words, it is the sum of counts in whole image.

2.5. Fat extraction, fat quantification and fatty acids analysis

Fat extraction techniques, already used for other food powders, were adapted to cocoa powders in this work [13,26,27].