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Storage-induced caking of cocoa powder

J. Petit [a], F. Michaux [a], C. Jacquot [a], E. Chávez Montes [b], J. Dupas [b], V. Girard [b], A. Gianfrancesco [c], J. Scher [a], C. Gaiani [a, *]

[a] *Université de Lorraine, Laboratoire d'Ingénierie des Biomolécules (LIBio), 2, avenue de la Forêt de Haye, TSA 40602, 54518 Vandœuvre-lès-Nancy, France*
[b] *Nestlé Product Technology Center, 1350 3, route de Chavornay, Switzerland*
[c] *Nestlé Research Konolfingen, Nestléstrasse 3, 3510 Konolfingen, Switzerland*

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ABSTRACT

Cocoa powders are highly subjected to caking, a phenomenon of solid particles agglomeration that impairs powder functionalities such as rehydration and flowing properties. This study aimed at identifying the main caking mechanisms occurring during storage of cocoa powders, according to their fat content and water activity, as well as storage temperature. The formation of caked powder was monitored at macroscopic scale by sieve analysis, showing that caking was significant only for fatty powders at 40 °C, in agreement with a caking mechanism controlled by fat melting. The similarity of results obtained at 0.2 and 0.7 water activity indicated that the humidity caking mechanism was not significant for these powders. Observations performed by TEM evidenced the formation of fat bridges, confirming the occurrence of the fat melting mechanism. Then, solvent extraction techniques designed to quantify fat fractions permitted to highlight that storage caused the conversion of encapsulated fat into free fat. At temperatures sufficient to melt cocoa fat (40 °C), this newly formed free fat migrates toward cocoa particle surface, enhancing its fat coverage, hence making cocoa particle sticky and prone to cake. Finally, XPS analysis of the extreme surface of cocoa powders confirmed that two conditions should be met to trigger significant cocoa powder caking: high fat content and elevated storage temperature.

1. Introduction

In the literature, researches on cocoa powders have mainly focused on their health benefices: neuroprotective (Cimini et al., 2013), antioxidant, antimicrobial (Calatayud et al., 2013), cardioprotective activities (Abdi et al., 2013), etc. These health benefices are related to cocoa polyphenols, which are large biomolecules highly sensitive to photo- or thermal oxidation. Thus, cocoa powder processing and storage must be carefully carried out in order to limit bioactive compound and physical properties alterations. The lack of literature studies linking cocoa powder properties to process or storage conditions shows that the understanding of cocoa powder caking during storage requires investigating the impact of storage conditions on cocoa powder structure and surface composition, as well as on their other physicochemical properties (like particle size and shape distributions, fat composition, etc.).

Few works dealing with cocoa powder ageing can be found in the literature. Nevertheless, numerous studies have been published about storage-induced defects of chocolate, mainly those related to polymorphic changes occurring in cocoa fat (Altimiras et al., 2007; Bricknell and Hartel, 1998; Peschar et al., 2004; Tietz and Hartel, 2000): fat bloom, sugar bloom, and swelling. Briefly, fat bloom corresponds to the formation of a white deposit of small fat crystals on the product surface (Hartel, 1999), impairing chocolate visual appearance and texture (Briones and Aguilera, 2005); sugar bloom reflects sugar crystallisation induced by variations of surrounding air humidity and leads to an unpleasant dusty appearance of chocolate surface; and swelling, mostly affecting chocolate texture, is triggered by moisture uptake from the surrounding air and results from water migration, dependently of fat migration and local polymorphic changes (Svanberg et al., 2012).

Chocolate is a product made with cocoa liquor (containing cocoa butter and cocoa solids), with some technological additives and other ingredients in lower proportions. As cocoa powder, obtained from the pressing of cocoa liquor, still contains cocoa butter in variable amounts, it can be assumed that comparable storage-induced defects may occur in cocoa powder and chocolate. Incidentally, these defects can be limited by tempering cocoa-

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* Corresponding author.
E-mail address: claire.gaiani@univ-lorraine.fr (C. Gaiani).

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containing products, which consists in lipid crystallisation (leading to a stable physical state) performed with meticulous time-temperature schedules (Afoakwa et al., 2007; Lonchampt and Hartel, 2006; Talbot, 1999).

Caking designates the formation of a solid bridge between two particles in contact, which is generally the consequence of the solidification of a liquid bridge (Foster, 2002). Caking induces the alteration of food powder use and handling properties (aptitude to reconstitution, agglomeration, handling, conveying, packaging, etc.) (Le Brun et al., 2006). Powder caking is mainly due to a sintering mechanism, i.e. molecular diffusion from amorphous particles to contact zone between particles, driven by the reduction of the surface of particles at constant volume and resulting in a decrease in free energy of the system (Aguilera et al., 1995; Hartmann and Palzer, 2011). Other mechanisms include melting/crystallization of lipids, sugars, or minerals. The particle shape is deeply modified by caking, unless if particles possess an insoluble backbone (e.g., cellulose, silicates, fat, proteins) (Hartmann and Palzer, 2011). Crystallisation may induce water release (like in the case of conversion of monohydrated amorphous lactose into crystallised form), which enhances caking by liquefying local areas of powders, allowing the formation of liquid bridges (Hartmann and Palzer, 2011). Four caking mechanisms, depending on powder composition and environmental conditions, have been identified in the literature for food powders (Foster, 2002): amorphous sugar caking, humidity caking, fat melting caking, and caking caused by protein sticking. Amorphous sugar caking, mostly occurring in hygroscopic powders of amorphous structure, corresponds to the transition from glassy to rubbery state of amorphous sugars when moisture content or temperature is increased, leading to higher particle stickiness and making powders prone to cake. Humidity caking, subsequent to water uptake, consists in water sorption/condensation at the particle surface, inducing the dissolution of surface components up to saturation and the formation of liquid bridges between particles; the latter transform into solid bridges under the action of drying, i.e. when temperature is increased or surrounding air humidity is decreased. Fat melting caking results from the formation of liquid bridges of fat over its melting point (as liquid fat is very sticky), which crystallise when temperature is decreased. Last, protein denaturation and aggregation at elevated temperature may increase particle stickiness and cause powder caking. Cocoa powders, which are highly hydrophobic owing to their large fat content (Omobuwajo et al., 2000), are expected to be affected by the humidity and fat melting caking mechanisms mostly.

Caking induces the formation of powder lumps: at a given caking stage, lumps may be few or numerous, of different sizes and of various degrees of hardness (Aguilera et al., 1995), hence the difficulty to define a unique representative parameter for caking and to monitor caking phenomenon during powder processing or storage. The major analytical techniques for monitoring powder caking are sieve analysis, which permits to quantify the fraction of agglomerated particles, compression tests of a consolidated powder cake, and shear tests of a powder bed under compression, which evaluate the caking-induced decrease in powder flowability (Aguilera et al., 1995; Le Brun et al., 2006).

In this work some physicochemical factors and storage conditions influencing caking of cocoa powders were studied. Three cocoa powders differing in fat content (1, 11, and 21%) were stored in various storage conditions during 2 months. Three storage temperatures (20, 30, and 40 °C) and two surrounding air relative humidities (20% and 70%) were employed to investigate the influence of temperature and water activity on cocoa powder caking, depending on fat content. Structural changes caused by storage in these different conditions were characterised by a multiscale approach. At macroscopic scale, caking was quantified by a sieving procedure. At microscopic scale, mean particle size and shape distribution were evaluated by laser granulometry and morphogranulometry, cocoa powders were imaged by TEM in order to give insight into fat location in particles, and total fat content, along with the distribution of fat within free and encapsulated fractions, were determined by solvent extraction methods. Lastly, at molecular scale, XPS analyses permitted to discuss the evolution of surface fat according to storage conditions. The final objective of this study was to identify the main caking mechanism(s) acting in cocoa powders according to storage temperature and water activity.

2. Material and methods

2.1. Cocoa powders and storage conditions

The influence of fat content on cocoa powder caking was investigated by studying the storage behaviour of three cocoa powders differing in fat content manufactured by De Zaan Cocoa (ADM Cocoa, Rolle, Switzerland):

- defatted (<0.5% fat) alkalised cocoa powder D-00-ZR, called CP1,
- 10–12% fat alkalised cocoa powder D-11-SB, referred as CP11,
- 20–22% fat alkalised cocoa powder D-21-S, named CP21.

Their composition in macronutrients (supplied by Olam Cocoa B.V., Koog aan de Zaan, the Netherlands) is presented in Table 1. Investigated cocoa powders markedly differed in fat content, whereas moisture, theobromine, and caffeine were present in quite similar amounts. Protein, carbohydrate, dietary fibre, and ash contents decreased when increasing the fat content.

Cocoa powders were gently poured in polystyrene Petri dishes (60 mm × 15 mm) so as to form a particle layer of circa 1 cm and stored at controlled temperature and water activity during 56 days. The influence of temperature on caking mechanisms was investigated by storing cocoa powders in hermetically-closed boxes placed in thermostated enclosures regulated at 20, 30, and 40 °C, the latter temperature being considered as critical for complete melting of cocoa butter fat (Jacquot et al., 2016; Wille and Lutton, 1966).

For all temperatures, a potassium acetate (CH_3COOK) saturated saline solution was employed to set powder water activity (a_w) at about 0.2 during storage in hermetically-closed boxes. The influence of water activity on cocoa powder storage-induced caking was investigated at 20 °C by using a potassium iodide (KI) saturated saline solution, fixing the water activity at about 0.7.

All samples have been analysed in triplicates (except for XPS analyses, cf. section 2.3.2) at different storage times up to 56 days.

2.2. Caking monitoring during storage

2.2.1. Powder sieving and caking index

Powder caking was first tracked at macroscopic scale by following the evolution of the fraction of caked powder during storage. To this end, a caking index was defined and determined by sieve analysis, with the purpose of validating a quick and simple tool to put in evidence powder caking.

Powder samples were separated into different granulometric fractions with the vibratory sieve shaker Analysette 3 Spartan (Fritsch, Idar-Oberstein, Germany) at 0.5 mm vibration amplitude for 30 s in permanent mode. Approximately 100 g of powder were initially placed on the top sieve. 20 mm diameter sieves (Fritsch) were employed so as to obtain the following granulometric fractions: > 500 μm; 315–500 μm; 180–315 μm; 100–180 μm; 50–100 μm; 20–50 μm; < 20 μm. Each fraction was weighed to