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AFM-based local thermal analysis is a suitable tool to characterize the impact of different grinding techniques on sucrose surface properties

D. Middendorf [a, *], U. Bindrich [a], P. Mischnick [b], K. Franke [a], V. Heinz [a]

[a] German Institute of Food Technologies, Prof.-v.-Klitzing-Str. 7, D-49610 Quakenbrueck, Germany
[b] Technische Universität Braunschweig, Institute of Food Chemistry, Schleinitzstr. 20, 38106 Braunschweig, Germany

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ABSTRACT

Influence of roller and ball mill grinding technology applied for sucrose particles in a lipophilic suspension was investigated considering both particle properties and suspension's flow behavior. Especially particle surfaces after grinding were analyzed using a novel approach by combining atomic force microscopy (AFM) and AFM-local thermal analysis (AFM-LTA). This technique is able to characterize local distributions of different surface states on sucrose particles in nano- and microscale by determining local softening temperatures. For the first time, it was possible to demonstrate on molecular level that applied grinding technologies resulted in different surface characteristics with respect to adhesion forces and state of sucrose using AFM-LTA. Differences in flow behavior despite same particle size distributions and solid contents were traced back to the distribution of crystalline and amorphous areas on sucrose particle surfaces.

1. Introduction

Disperse systems consisting of a continuous lipophilic phase of e.g. cocoa butter (CB) and a disperse phase of ground solid particles, e.g. sucrose, play an important role in many confectionery products, like chocolate (Beckett, 2009). A maximum particle size of 15–30 μm is required in such suspensions to obtain high quality products without a sandy mouthfeel (Afoakwa et al., 2007). Therefore, solid particles of the disperse phase in these suspensions have to be subjected to a size reduction by a grinding process.

During grinding of the solids within the lipid phase, new surfaces are generated which can differ in their properties depending on the grinding process. A common grinding method used for this type of suspension is the roller grinding. In roller mills, solids are deformed and broken by compression and shear in parallel (Afoakwa, 2010). The maximum particle size after this type of grinding is determined by the width of the last gap of the roller mill. A frequently used alternative to roller grinding is ball mill grinding. In this case, the solid particles are smashed or broken due to an impact caused by collision of individual balls or between a ball and the wall of the mill (Mohos, 2010).

In general, grinding of sucrose particles in such suspensions leads to at least a partial amorphization of their surfaces (Newell et al., 2001; Beckett, 2009; Tang et al., 2012). However, due to differences in the dynamics of particle breakage in roller mill (relatively slow pressure increase and shear) and in ball mill (short, but high energy impacts), particle surfaces vary (Beckett, 2009).

Furthermore, different grinding techniques result in different flow behavior of the suspensions (viscosity and yield value) even if volume fraction of solids and the particle size distribution are the same (Braun, 2000). As already known, different interparticular interactions and interactions between particles and the surrounding lipid phase have an influence on the flow behavior of the suspensions (viscosity and yield value; Mewis and Wagner, 2009).

Based on this knowledge, it can be assumed that the impact dynamics during grinding process influence the extent as well as local distribution of the amorphous regions after grinding and that the different amorphous parts have an effect on interparticular interactions as well as the interaction between particles and a surrounding lipid phase. However, the correlation between grinding type, amorphous surface state and resulting flow behavior of the suspension is not clear so far.

Up to now, a number of different methods has been used for the detection and quantification of amorphous components including e.g. X-ray powder diffraction (XRPD) isothermal micro-calorimetry

* Corresponding author.
E-mail address: d.middendorf@dil-ev.de (D. Middendorf).

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(IMC), Raman spectroscopy, near infrared spectroscopy (NIRS), solid state nuclear magnetic resonance (SS-NMR), conventional differential scanning calorimetry (DSC), modulated temperature DSC (MTDSC), or high speed DSC (hyper-DSC). However, many of these methods are bulk techniques and are not sensitive enough to determine whether the amorphous material is located at the surface in a very small layer (Dai et al., 2009; Lappalainen, 2010).).

A powerful tool to characterize particle surfaces on molecular level is atomic force microscopy (AFM). AFM is based on the measurement of interactions between a sharp tip at the end of a cantilever and the sample's surface (Binnig et al., 1986). The tip is scanned across the surface so that images up to a resolution of several tenths of a nanometer can be obtained (molecular level). Besides surface topography and in contrast to other microscopic techniques, AFM is able to reveal various other surface properties, e.g. adhesion forces, magnetic properties or surface charges and polarities of surfaces as well (Eaton and West, 2010). These techniques have already been used to characterize food systems (Rousseau, 2006; Shimoni, 2008; Liu and Wang, 2011; Arnold et al., 2013; Middendorf et al., 2015, 2016). A relatively new AFM technique called local thermal analysis (LTA) enables measurement of softening temperatures of distinct surface areas so that the respective surface state, e.g. amorphous or crystalline material, can be determined in parallel to surface topography (Harding et al., 2007). For this purpose, the sample is locally heated with increasing temperature at the point where the tip contacts the surface by raising the voltage (Harding et al., 2008). At a certain tip temperature, the surface begins to soften and the tip penetrates it. The measurement is terminated as soon as a predefined penetration depth has been detected (King et al., 2002; Fischinger et al., 2014). Output of the AFM software is the resistance between tip and surface resulting from the heating voltage which is applied at the softening point. The resistance can be converted into the softening temperatures of the specific surface area by calibration (Fischinger et al., 2014; King et al., 2013).

So, the aim of our study is to characterize the local surface properties of sucrose particles after application of two different grinding techniques. We ground the sucrose particles directly in a suspension of liquid CB to prevent the newly generated sucrose surfaces from humidity so that potential amorphous parts will remain as such. The resulting surface properties after grinding were linked to the macroscopic behavior of the whole suspension, especially flow properties. The results of our study will enable a better understanding of the interplay between particle surface properties after grinding and macroscopic suspension properties.

2. Materials and methods

2.1. Materials

Sucrose of EU quality II (Nordzucker, Braunschweig, Germany) was purchased from a local supermarket. In all experiments, the same lot was used. Sucrose was stored at about 22 °C and 50% rH ensuring that possibly amorphous regions are completely recrystallized (Carstensen and van Scoik, 1990). CB was kindly provided by August Storck KG Halle, Westfalen, Germany. Besides sucrose, fructose (Merck, Darmstadt, Germany) and anhydrous glucose (α-D-(+), AppliChem, Darmstadt, Germany) were used for calibration of the AFM-LTA system.

2.2. Preparation of model suspensions

For ball mill grinding, 450 g crystalline sucrose and 550 g molten CB were ground in a vertical ball mill (Wienerroto W-1-S, Wiener & Co., Amsterdam, Netherlands) at controlled temperature of 45 °C preserved by the double-jacket cylinder. The total inner volume of the ball mill was 6.5 L. Grinding media were 10 kg of steel balls of 1.5 cm in diameter agitated with a speed of 260 min^{-1}.

Roller grinding was performed with a 3-roller-refiner (WLDH 300, Lehmann, Aalen, Germany) at 40 °C roller temperature. Roller speed was 35, 96 and 265 min^{-1} for rollers 1, 2 and 3. The gap size could not be adjusted to a defined value, but is a result of roll contact pressure which was 50 bar. Roller-milling was started with an initial fat content of the suspension of about 30%.

Grinding with both techniques was performed until 90% of the volume of total solids was smaller than 30 μm ($x_{90,3}$) and 50% smaller than 10 μm ($x_{50,3}$) which was reached approx. after 20 min of ball milling or multiple passes of suspension through the roller mill. Particle size distributions (PSD) were analyzed using laser diffraction as described below. After reaching the desired PSD by roller milling, grinding process was terminated and fat content was enhanced to 55% with CB. A reference suspension remained unground (reference).

All suspensions were subjected to a kneading and stirring process for 4 h at a temperature of 75 °C using Do-Corder-Kneader (S 300 H, Brabender, Duisburg, Germany) at 130 min^{-1}. Additionally, dry air was blown into the kneader with a flow rate of 1500 L/h and a temperature of 22 °C. This process ensures de-agglomeration of solid particles (Afoakwa, 2010).

To ensure that sucrose surface is protected from recrystallization due to moisture sorption, excess of CB was used so that a lipid CB-layer was always around the particles (also during grinding, kneading, and stirring). Relative humidity was carefully controlled during roller milling to stay below 25% rh, as no recrystallization is expected under these conditions (Carstensen and van Scoik, 1990). Model suspensions were prepared in duplicate.

2.3. Laser diffraction analysis

Particle size distribution (PSD) was determined using a laser diffraction spectrometer (Mastersizer, 2000; with dispersion unit Hydro, 2000S, Malvern Instruments Ltd., Worcestershire, UK). For this purpose, molten model suspensions (45 °C) were predispersed in mineral oil (kinematic viscosity 22 mm^2/s at 40 °C, refractive index 1.450) with a concentration of 0.02 g/100 g for 5 min using ultrasound (40 kHz, Branson 3200, Scientific Support Inc., Hayward, CA, USA). Then, a small amount of suspension covering the tip of the spatula was added to the dispersion unit of the spectrometer. Volume distribution, Sauter mean diameter D [3,2] and specific surface area [SSA] were calculated according to Mie model (Mie, 1908) using the manufacturer provided software (21 CFR Part 11, particle density 1.586 g/cm^3 (Bubnik et al., 1995), refractive index 1.51 according to Malvern Instruments). Obscuration was about 10 ± 2%. PSD were determined four times per sample. Based on the assumption of spherical non-porous particles, D[3,2] is the diameter of a sphere that has the same volume/surface area ratio as a particle of interest and is calculated by D[3,2] = 6/SSA. SSA is defined as the surface area relative to the mass of a sphere and can be calculated by the total surface area A, the total particle volume V: SSA = A/V.

2.4. Differential scanning calorimetry

DSC analysis of melting properties of the different carbohydrates used for calibration of AFM-LTA system was carried out using the MDSC 2920 instrument from TA Instruments (New Castle, USA). Approximately 5–10 mg of sample was weighed into a standard 40 μL aluminum crucible (Mettler Toledo, ME-26763, Gießen, Germany) and hermetically sealed. Measurement was carried out in