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Atomic Force Microscopy study on the effect of different lecithins in cocoa-butter based suspensions

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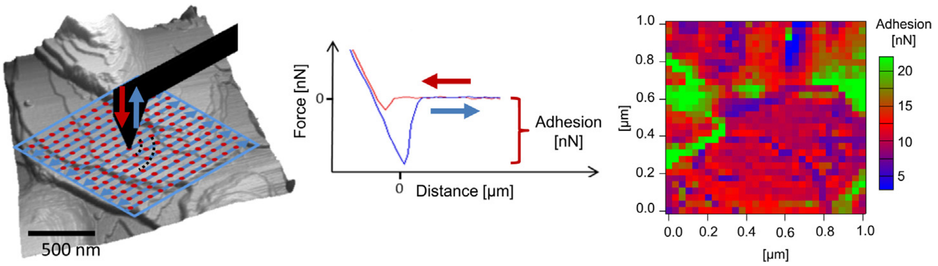
HIGHLIGHTS

- Lecithin adsorption at sucrose surfaces were determined by AFM force spectroscopy.
- Functional differences between soy and sunflower lecithin were found.
- Adhesion force range after PL adsorption from soy lecithin was significantly enlarged.
- PL analysis, rheology and amount of immobilized cocoa butter confirmed AFM results.

GRAPHICAL ABSTRACT



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ABSTRACT

To get a deeper insight into the molecular interactions between sucrose and lecithin's different phospholipids (PL), the impact of soybean and sunflower lecithin on sucrose surfaces ground in liquid cocoa butter was studied. Therefore, flow properties of the cocoa-butter based suspension, immobilized cocoa butter content as well as detailed PL analysis concerning layer thickness and PL content was related to sucrose surface topographies and force spectroscopy measurements performed by atomic force microscopy (AFM).

We found that adsorption of PL from soy lecithin to sucrose resulted in thinner layers with a larger total PL coverage, whereas PL from sunflower adsorbed in smaller amounts but resulted in thicker layers. So, PL covering of the surface is not homogeneous. As a consequence, immobilized fat content after adsorption of PL from soy was found to be smaller than for PL from sunflower lecithin. Also the yield value for suspensions containing soy PL was somewhat lower than for PL from sunflower lecithin. These changes could successfully be traced back to the microscopic scale of the sucrose particle surfaces. AFM surface properties were found to be highly influenced by adsorption of emulsifier molecules in the way that topography dramatically changed and also adhesion properties highly differed after application of soy or sunflower lecithin. By linking these molecular properties of PL from different origin to their behavior at molecular level and to the resulting macroscopic effects, the outcome of this study confirmed some essential differences between the applications of soy and sunflower lecithin with respect to chocolate manufacturing.

1. Introduction

In lipophilic suspensions like chocolate masses, ground sucrose crystals have surface areas of different polarities after grinding in waterless environment. These areas are composed of amor-

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phous and crystalline structures. Whereas crystalline structures are formed during crystal growth, amorphous structures are caused by high local energy inputs during grinding process [1]. Especially amorphous structures contribute to aggregation of solid particles in the suspension resulting in phase separation [2]. Part of the continuous fat phase is immobilized in interparticle spaces of aggregates resulting in increased viscosity, and a yield value can be detected [3,4]. Emulsifiers are added in order to control these interactions during chocolate manufacturing.

The macroscopic effects of emulsifiers in lipophilic suspensions are well-known for years [5], but only little is known on the specific mode of action on a molecular level. The emulsifiers are assumed to cover particle surfaces and reduce immobilization of cocoa butter (CB) at the solid surfaces [6]. Therefore, they are thought to enhance wettability of the dispersed particles by the lipophilic phase and facilitate their distribution in the continuous phase preventing phase separation [6]. A lot of experiences from application indicated that soy lecithin as a blend of various phospholipids (PL) is well adapted to the surface properties of different solid particles in chocolate [7]. Soy lecithin is widely used in chocolate manufacturing, but only little is known about specific interactions of PL fractions with the different sucrose surfaces. Especially, the influence of surface topography and adhesiveness on these interactions is still unknown.

Detailed information on the interaction between emulsifier molecules and sucrose surfaces can be obtained by atomic force microscopy (AFM) [8,9]. First results on the impact of soy lecithin on rheological properties in relation to AFM force-distance-measurements (also called force spectroscopy) and sedimentation experiments of solid particles have already been published [9]. The authors concluded that both disperse and continuous phase affected the impact of lecithin on interparticle interactions. These interactions between sucrose particles were dominated by adhesion forces and lecithin was found to reduce these forces. However, the authors also found that AFM force measurements on sucrose surfaces exhibited relatively high deviations complicating the interpretation of the results. Furthermore, experiments were performed on specific sucrose supports whose shape and surface topography were not directly comparable to the conditions of sucrose particles in chocolate masses. Further work with respect to AFM force-distance measurements was carried out in triglyceride media and soybean oil [10,11]. But these media also have an enormous effect on adhesion forces so that results cannot directly be compared to the different matrix conditions in chocolate masses, as well.

To the best of our knowledge, no detailed information concerning local changes in emulsifier adsorption at sucrose particles have been published yet, especially with respect to potential changes at sucrose surfaces or differences between lecithins of different origin. But it has to be considered that – besides macroscopic properties – surface topography is highly influenced by emulsifier adsorption and that adsorption, in turn, is also highly dependent on the molecular nature of the emulsifier. This has already been shown for PL from soy lecithin in comparison to the polymeric polyglycerol polyricinoleates (PGPR) [12].

It was found that sucrose surfaces were nearly completely covered by PL, whereas PGPR adsorption lead to droplet shaped formations and lower adhesion forces at the surface compared to PL samples. So, adsorption of two different emulsifiers resulted in completely different surface topographies as well as surface adhesion forces. In addition to microscopic surface properties, the amount of adsorbed emulsifier, immobilized fat content and yield value of the resulting model suspensions differed considerably. So, emulsifier's distribution with respect to local surface properties of ground sucrose and the resulting effect on macroscopic suspension properties like flow behavior are important aspects, which have to be considered when analyzing the effect and the impact of an emulsifier.

Table 1
Phospholipid and fatty acid composition of soy and sunflower lecithin used in this study.

Phospholipid	% (w/w)	
	Soy Lecithin	Sunflower Lecithin
PC—Phosphatidylcholine	14.3	12.97
PI—Phosphatidylinositol	11.62	4.27
PE—Phosphatidylethanolamin	7.99	15.06
PA—Phosphatidic acid	3.99	1.54
LPC—Lysophosphatidylcholine	0.81	2.79
LPE—Lysophosphatidylethanolamin	0.5	n.n.
saturated fatty acids	20.92	15.98
mono-unsaturated fatty acids	26.1	21.69
polyunsaturated fatty acids	52.87	61.94

In contrast to already published studies, the aim of this work was to evaluate an AFM approach for characterizing the adsorption and the effects of lecithins derived from different origins. As a practical relevant example for chocolate manufacturing, experiments were carried out with sucrose particles ground in liquid CB. More precisely, emulsifier adsorption at the particle surfaces and the corresponding effect on flow behavior and fat immobilization of the whole suspension was investigated in detail. For this purpose, AFM topography images were captured and force-distance-curves were measured to calculate adhesion forces. For the first time, the AFM technique of local thermal analysis was applied to reveal information on the amorphous and crystalline character of sucrose surface areas. The AFM-data were successfully correlated with macroscopic suspension properties like flow behavior or fat immobilization.

2. Material and methods

2.1. Materials

For preparation of model suspensions, sucrose of EG quality II (Nordzucker, Braunschweig, Germany) was purchased from a local supermarket. CB was kindly provided by August Storck KG Halle, Westfalen, Germany. Its total PL content was <0.001 g/100 g. A commercially available soy lecithin tailored for chocolate production was delivered by Lindt & Sprüngli (Kilchberg, Switzerland). Sunflower lecithin was received from Sternchemie GmbH & Co. KG (LeciStar S 100, Hamburg, Germany). Phospholipid and fatty acid composition of lecithins is shown in Table 1.

2.2. Preparation of model suspensions

550 g CB were molten and 0.5% lecithin related to final sucrose content was dispersed under magnetic stirring at 70 °C. 450 g sucrose were added to the CB and directly ground in this lipophilic phase by ball milling (20 min, 45 °C, 10 kg steel balls of 1.5 cm in diameter; Wienerroto W-1-S, Wiener & Co., Amsterdam, Netherlands). Grinding was performed until 90% of the volume of total solids was smaller than 30 μm ($x_{3,90}$) and 50% smaller than 10 μm ($x_{3,50}$). Particle size distributions were tested using laser diffraction as described in Section 2.3.

After that, suspensions were mechanically treated in order to simulate the conching process as applied during chocolate manufacturing using a Do-Corder-Kneader (S 300 H, Brabender, Duisburg, Germany, air flow 22 °C with 1500 L/h). The kneader jacket was heated up to 75 °C, rotational speed of the kneader was 130 min^{-1} and treatment time was 4 h.