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# AFM approach to study the function of PGPR's emulsifying properties in cocoa butter based suspensions

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ABSTRACT

Polyglycerol polyricinoleate (PGPR) often is used as emulsifier in chocolate, but only little is known on the specific interactions between sucrose particles, cocoa butter and PGPR molecules. The most remarkable effect of PGPR on lipophilic suspensions is the enormous decrease in yield value compared to soy lecithin which is not yet understood. A combination of atomic force microscopy (AFM), scanning electron microscopy (SEM), rheological measurements and analysis of immobilized fat content was used to reveal more details on the mechanism of function of PGPR.

It was found that this mechanism is completely different to the one of soy lecithin. On sucrose particle surfaces, PGPR concentration was determined to 0.18 mg/m$^2$ whereas soy lecithin coverage was calculated to 2.69 mg/m$^2$. The interfacial layer obtained by washing separated sucrose particles with acetone contains 83.6 g/100 g cocoa butter which had been immobilized together with or by PGPR molecules. This interaction plays a major role in the mechanism of function of PGPR as an emulsifier. Weakly bound structures consisting of PGPR and cocoa butter were found to form pillow-like structures. They act as spacers between the sucrose particles and reduce particle-particle interaction so that less structure can be built up. That is why flow can be induced very easily. In addition, as particles move along together very well due to steric hindrance of these pillow-like structures, viscosity of the suspension remains low.



## 1. Introduction

Chocolate masses are lipophilic suspensions containing refined sucrose crystals with areas of different surface polarity. These are caused by amorphous and crystalline structures formed during grinding under dry (water free) conditions. Amorphous structures result from a high local energy input during the grinding process (Niediek, 1988). They contribute to aggregation of solid particles and induce phase separation in the suspension (Koglin, 1978). Thus, part of the

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*Abbreviations:* AFM, atomic force microscopy; SEM, scanning electron microscopy; PGPR, polyglycerol polyricinoleate; HPTLC, high performance thin-layer chromatography; PL, phospholipid; PC, phosphatidylcholine; PE, phosphatidylethanolamine.

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continuous phase is immobilized in interparticular spaces of aggregates resulting in increased viscosity (Becker, 1984) and a yield value can be detected (defined as shear strength where crossing of slip flow to shear flow occurs; Windhab, 2000). To control these interactions, emulsifiers are added. They enhance the wettability of the dispersed particles and facilitate their dispersibility in the continuous phase (Johansson & Bergenstahl, 1992).

Macroscopic effects of emulsifiers in lipophilic suspensions have been well-known for years (Weyland, 2008). Factors influencing the rheological behavior are well examined and discussed in detail elsewhere (Chevalley, 1999; Vernier, 1998; Weyland, 2008). It is assumed that these macroscopic effects are caused by covering of sucrose particle surfaces with emulsifier and by reduced amounts of immobilized cocoa butter at the solids (Afoakwa, Paterson, & Fowler, 2007; Johansson & Bergenstahl, 1992). As a result of operating experiences, soy lecithin was found to be the most useful emulsifier for chocolate production. It is a blend of various phospholipids and therefore well adapted to the amphiphilic surface properties of solid particles in chocolate (Schantz, Linke, & Rohm, 2003).

Lecithins can be described as head-tail-emulsifiers. The hydrophilic head groups of the molecules are oriented to the hydrophilic phase of the suspension, fatty acid residues, the *tails*, are lipophilic and oriented to the lipophilic phase. But further details on its mechanism of functions are still unknown. The use of lecithin as an emulsifier is still based on practical experiences.

But less is known about another widely used emulsifier. Polyglycerol polyricinoleate (PGPR) is a very complex mixture of macromolecules consisting of polycondensed ester of vegetable polyglycerol polyricinoleic acid with high molecular mass between 1200 and 2000 g/mol (Bastida-Rodríguez, 2013; Orfanakis et al., 2013). It reduces or even removes yield value without a significant effect on viscosity (Ghorbel, Saïdi, Slema, & Ben Gharsallah, 2011; Rector, 2000; Schantz & Rohm, 2005). It is confirmed that adsorption of PGPR increases the lipophilic nature of sucrose particles via a decrease in acidic character of the surface. As a consequence, particle–particle interactions of sucrose are reduced and fluidity of fat-based suspensions is increased. Since the basic character of lecithin and PGPR is different, it was hypothesized that the oxygen atoms in polycondensed ricinoleic acid play an important role (Rousset, Sellappan, & Daoud, 2002). Other hypothesizes refer to particle repulsion, displacement of additional cocoa butter from particle surfaces or binding of water by PGPR (Rector, 2000). But neither of these could be completely confirmed yet.

Details on the interactions of emulsifiers and sucrose surfaces in a microscopic scale can be obtained by atomic force microscopy (AFM). This technique is based on the measurement of interactions between a sharp tip and the sample's surface (Binnig, Quate, & Gerber, 1986). The tip is moved across the surface in a certain distance (non-contact) or directly in contact to it (contact mode) depending on the surface properties to be determined. In this way, images of e.g. surface topographies up to a resolution of several tenths of a nanometer can be obtained. Besides surface topography and in contrast to other microscopically techniques, AFM is able to reveal various surface properties, e.g. adhesion forces, magnetic properties or surface charges and polarities of surfaces as well (Berger, Butt, Retschke, & Weber, 2009; Butt, Cappella, & Kappl, 2005). Therefore, especially with respect to adhesion forces, AFM offers the opportunity to examine mechanism of function of different emulsifiers.

First experiments with AFM concerning emulsifier adsorption were carried out, recently (Arnold et al., 2013b). It was shown that reduction of particle–particle interactions were in good agreement to results of sedimentation experiments of sugar–oil suspensions and support assumptions from literature. Furthermore, the impact of strongly adsorbed surfactants on particle–particle interactions correlated with previous investigations. They showed that these surfactants were responsible for reduction of rheological parameters in sugar–oil suspensions (Vernier, 1998). Results of another study suggest that the impact of lecithin on adhesive interactions between sucrose particles is responsible for the influence of surfactants on the rheological properties in oil-based suspensions (Arnold et al., 2013b). But it was also mentioned that, in general, AFM measurements were characterized by relatively high deviations, which complicate interpretation of the results.

In this work, we present a different AFM approach to characterize the effect of emulsifier adsorption on sucrose particle surfaces. With respect to chocolate manufacturing, the impact of soy lecithin and PGPR on ground sucrose particle surfaces in liquid cocoa butter was studied. The effect of emulsifier adsorption was investigated on microscopic as well as on macroscopic scale. Flow behavior and fat immobilization were determined and linked to quantitative amounts of emulsifier adsorption on particle surfaces as well as to AFM results. Concerning AFM, in particular topography imaging and force spectroscopy techniques were used. Thus, differences between the application of soy lecithin and PGPR were revealed and more details on the mechanism of function of PGPR were gathered.

## 2. Materials and methods

### 2.1. *Preparation of model suspensions*

For preparation of model suspensions, 0.5% emulsifier related to sucrose content was dissolved in liquid cocoa butter (kindly provided by August Storck KG, Halle, Germany) by stirring at 55 °C and 500 $min^{-1}$. Then, 45% commercially available crystalline sucrose (EC quality I, Nordzucker, Germany) was added and the crystals were ground with a ball mill containing 10 kg steel balls with a diameter of 1.5 cm at 45 °C. The grinding process was performed until mass median diameter of 10–12 μm and a maximum particle size of 30 μm for 90% of the particles was reached.

Afterwards, the suspension was conched for 4 h (DoCorder S300 H, Brabender, Duisburg, Germany) applying airflow of 1500 L/h at 22 °C. Water bath temperature was 75 °C and rotational speed of the kneader was 130 $min^{-1}$.

Besides emulsifier containing model suspensions, two control suspensions without emulsifier addition were also prepared and conched. One of the suspensions was ground as described above, the other one remained unground.

As emulsifiers, Sterncithin F10, a standard soybean lecithin consisting of 62 g phospholipids per 100 g lecithin at minimum