Supplementary information

1 Supplementary methods

1.1 Preparation of cocoa powder from cocoa press cake

Cocoa press cake was first pre-crushed using a hammer, and then pre-milled with an impact mill (Condux-Werk, Hanau, Germany). The actual milling step to achieve the desired particle sizes was performed with a Multimill including an air classifier, used in the configuration as impact mill 50-ZPS (Hosokawa Alpine, Augsburg, Germany). The applied settings are shown in Table 1.

Table 1. Multimill settings for milling of cocoa press cake.

Speed classifier	2000 rpm
Speed ZPS	8000 rpm
Power classifier	300 W
Power ZPS	200 W
Diff. pressure filter	30 mbar
Airflow	70 $m^3\ h^{-1}$
Int. pressure classifier	Approx. 14 bar

1.2 Preparation of cocoa powder from cocoa nibs

First, the intact cocoa nibs were defatted by adding n-hexane to the nibs in a ratio by weight of 2:1 and stirring for 3 min, after which the hexane was decanted and fresh hexane was added. This was repeated three times. After the hexane was removed by blotting with tissue paper, the nibs were milled to a coarse powder with a commercial blender (model HGB2WTS3, Waring Commercial, Stamford, Connecticut, USA) to enlarge the available surface area and thereby to increase the extraction efficiency. After milling, six additional hexane extraction runs were performed. The duration of the first three extraction intervals was 5 min, followed by two intervals of 20 min, and a final interval of 60 min. The mixture was stirred during extraction intervals. Before decanting the hexane, the powder was allowed to settle for 5 min. The remaining hexane after the last decanting step was removed by use of a vacuum pump and subsequent drying of the powder at room temperature in a fume hood overnight. Particle size was further reduced by use of a commercial blender, as the available amounts (< 100 g) were too little for milling with a high-capacity Multimill.

1.3 Powder fractionation

The two cocoa powders prepared as described in 1.1 and 1.2 as well as a third commercial cocoa powder (Krüger cocoa powder) were fractionated in three size classes (fine, medium and coarse) with an Airjet sieve e200 LS (Hosokawa Alpine, Augsburg, Germany), using sieves with mesh widths of 20, 50 and 100 µm.

1.4 Stability of cocoa particles obtained from different sources

To test the stability of cocoa particles against changes in particle size during the sample preparation procedure, samples with 36% fat were prepared by stirring of different cocoa powders (cocoa powder obtained from cocoa press cake, Krüger cocoa powder and cocoa powder obtained from cocoa nibs) in sunflower oil for 5 min with a 2-bladed propeller stirrer fitted to an IKA RW20 digital overhead stirrer (IKA®-Werke GmbH & Co. KG, Staufen, Germany) at 1200 rpm. Next to stirring at approximately 60°C, samples were also prepared at ambient temperature. The particle size was examined with light microscopy. Sunflower oil instead of cocoa butter was chosen for the sample preparation to facilitate the microscopy imaging.

2 Supplementary discussion

2.1 Disintegration of cocoa powder particles obtained from different sources

By sieving of either commercial cocoa powder (Krüger cocoa powder), cocoa powder obtained from milling of cocoa press cake, or cocoa powder prepared from cocoa nibs, we obtained cocoa powder of three different size fractions (<20 µm, >20 <50 µm and > 50 <100 µm) from several sources. To avoid changes of the PSD during the preparation of the model chocolate samples, the particle size should stay the same under mechanical impact, i.e. not decrease further during subsequent processing steps and rheological measurements. Therefore, before using the powder fractions for sample preparation, the stability of the obtained particles against disintegration upon stirring in oil at 60°C and at ambient temperature was investigated. This was specifically done for the coarse particle fractions. Due to a lack

of material, the test at ambient temperature was not conducted for the powder obtained from cocoa nibs. Figure 1 shows light microscopy pictures of the different samples. Already after very short stirring times at 60°C (Figure 1b), a large proportion of the particles fell apart into smaller fragments for the three different samples. At ambient temperature (Figure 1c), the particle size did not change considerably for the two tested samples, i.e. cocoa powder obtained from cocoa press cake and commercial cocoa powder. The disintegration of the coarse particles at these low temperatures was significantly less than for samples stirred at 60°C.

These results indicate that most of the coarse particles probably consisted of compacted aggregates of finer particles held together by residues of cocoa butter. This could explain why the particle size changed when mechanical impact was combined with elevated temperatures, at which cocoa butter is molten, and not at room temperature (for the tested samples).

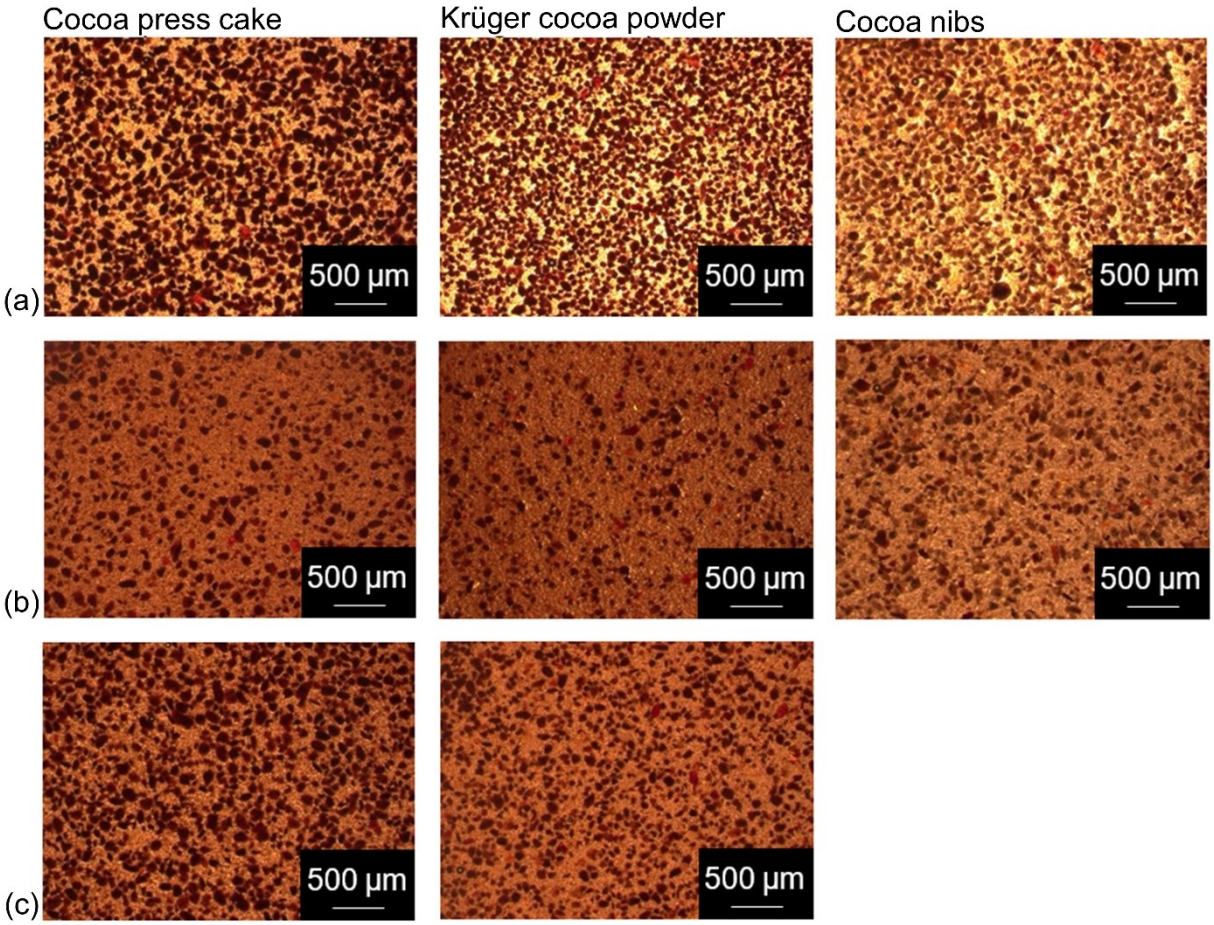

Figure 1. Light microscopy images of coarse cocoa powder fraction obtained from cocoa press cake, Krüger cocoa powder and cocoa nibs in sunflower oil (concentration 0.5 g powder/1 g oil). (a): without treatment; (b): after stirring for 5 min at 60 ± 5 °C; (c): after stirring for 5 min at ambient temperature.