A Combined Rheological and Tribological Study of Different Types of Chocolate

Relevant for: Food Tribology, Food Oral Processing, Chocolate, Suspensions, Particle Size

The tribological behavior of a lubricated system depends on various factors, such as the properties of the mating surfaces and the lubricant, with the latter being governed by its own rheological characteristics. This study deals with combining rheological properties of the lubricant – chocolate in this particular case – with the tribological behavior of the tribosystem and the particle size distributions.

1 Introduction

Understanding the influence of structural factors on food systems during food oral processing is relevant for comprehending and optimizing the sensory perception of food during intake, mastication, and swallowing (1). Sensory perception of food during oral intake can be depicted with tribological and rheological measurements. Tribology, in particular, considers the interaction occurring during bolus formation and processing, whereas rheological measures enable for drawing conclusions on how foodstuff behaves during swallowing (2). During food oral processing, the tongue is pressed against the palate and moves relatively to the latter (see Figure 1). The tribosystem is lubricated by the mixture of food and saliva, named bolus. Understanding how tribological behavior and rheological properties complement each other can be a key to a comprehensive understanding of food oral processing.

2 Chocolate Samples

Chocolate masses vary in their composition and the respective manufacturing process, e.g. roller or ball mill refining (3), (4). They are highly concentrated polydisperse suspensions, usually consisting of cocoa and sugar particles, cocoa butter, milk fat, milk particles, emulsifiers and flavors (5) and additional ingredients.

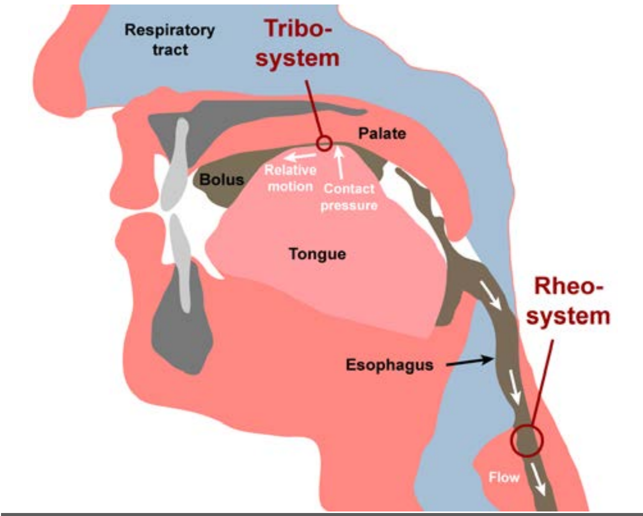

Figure 1: Food oral processing: food intake represented by a tribo-system with tongue/bolus/palate, and swallowing represented by a rheo-system.

For this study, three commercially available chocolate samples and one cocoa butter were used. The samples and their respective fat content are listed in Table 1. In case of the dark chocolate with fat filling, the fat portion consists of cocoa butter, palm kernel fat, coconut fat and clarified butter. The fat portions of the other samples consist of cocoa butter.

Sample	Fat Content [w/w-%]
Whole milk chocolate	38
99 % cocoa chocolate	51
Dark chocolate with fat filling	47
Cocoa butter	100

Table 1: Fat content of chocolate and cocoa butter samples.

3 Experimental Setup

The interacting solids are named specimen, whereas the liquid chocolate masses and the cocoa butter are named samples.

3.1 Tribological Setup

The tribological tests were carried out on an MCR Tribometer from Anton Paar equipped with a tribology cell with Peltier temperature control. A ball-on-three-pins test configuration, as shown in Figure 2, was used. In addition, a Peltier-controlled temperature hood was also used.

Within this study, the tongue/palate tribopair (see Figure 1) was simulated by a glass ball (soda lime glass, 12.7 mm in diameter) pressed against Polydimethylsiloxane (PDMS) pins (see Figure 2). The PDMS pins are made of Sylgard 184 (Dow Corning) with a PDMS : curing agent mixing ratio of 8:1, cured in a furnace for 1 h at T = 70 °C.

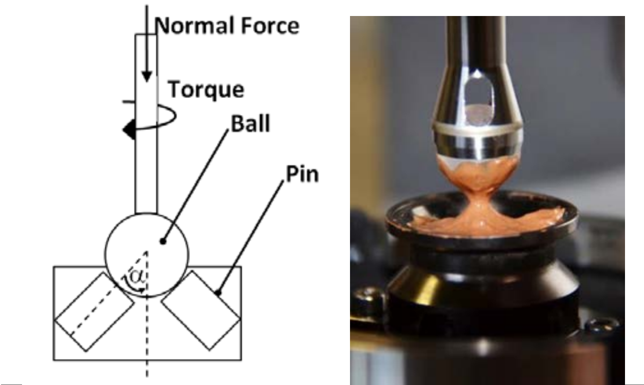

Figure 2: Schematic of the ball-on-three pins test configuration (left) and a picture of the setup filled with chocolate sample (right).

3.2 Rheological Setup

The rheological measurements were carried out on a Modular Compact Rheometer (MCR) from Anton Paar equipped with a Peltier Temperature Device (PTD) and a CC27 measuring system.

3.3 Particle Size Measurements

The particle size distributions of the chocolate samples were measured with an Anton Paar PSA 1190 L laser diffraction particle size analyzer.

4 Experimental Procedure

4.1 Tribological Measurements

The surfaces of tongue and palate are relatively soft, and the contact pressures experienced there are in the range of 3 to 27 kPa (6). Here, such soft contact conditions are simulated by using relatively soft PDMS specimen and by applying a low normal force of 1 N. The tribological tests are carried out in four steps.

1. The measuring shaft is lowered until the glass ball surface touches the PDMS pins. This is achieved by lowering the measuring shaft until a normal force of 0.5 N is detected. This low normal force load avoids shock loading or sudden impacts on the specimen surfaces.
2. The load is increased to the test load of 1 N. The system is then held at the test load for 5 min to enable for partial relaxation of stresses produced at contact by applying the test load.
3. The sliding velocity is increased logarithmically from 10^{-5} mm/s to 10^{3} mm/s (80 data points, logarithmically decreasing measurement point duration from 10 s to 1 s).
4. The measuring shaft is lifted to break contact with sample and PDMS pins.

This procedure is repeated three times with breaking contact between each run. Repeating the procedure enables for a running-in of the tribosystem. Each repetition is called a run. During the entire test, the sample remains in the sample holder. Measurements were carried out in double determination using a new set of PDMS specimen for each repetition.

4.2 Rheological Measurements

Rheological measurements were carried out in shear-rate-controlled mode. These measurements determine the viscosity curves of the respective samples. The data were interpreted to obtain yield point values by fitting the measurements to the Casson model. The measurement procedure includes five steps. Evidence for reproducibility is given by duplicate measurements.

1. Filling the sample in the cylinder and lowering the bob.
2. 5 min waiting.
3. Pre-shearing for 30 s at 1 s^{-1}.
4. 5 min waiting.
5. Shear rate ramp from $3 \cdot 10^{-2}$ s^{-1} to 100 s^{-1} (22 data points, logarithmically decreasing measurement point duration from 60 s to 2 s).

4.3 Particle Size Measurements

The particle size distribution measurements were carried out in liquid mode. Therefore, the chocolate samples were molten and dispersed in sunflower oil before the measurement. The pump and stirrer was at minimum speed. For evaluation, the average of two measurements and the Fraunhofer model was used.

5 Results and Discussion

Extended Stribeck curves can be divided into static and dynamic friction regimes (7). The transition point indicates how much force is required to overcome static friction and set the system into motion. The minimum force required here is the breakaway, or the limiting force, and the corresponding friction is known as the limiting friction of the system. Once the system is set into motion, the Stribeck curve can be further divided into boundary, mixed and hydrodynamic lubrication regimes.

5.1 Limiting Friction and Yield Point

In Figure 4, the sliding distance is plotted against the torque values. The sliding distance is calculated from the deflection angle and the radius of the glass ball. In the graph, the limiting friction is identified as the point of inflection of the curve. Before reaching the limiting friction, the tribosystem mainly undergoes deformation. The highest value for the limiting friction of the tribosystem is observed for whole milk chocolate. A possible explanation is the complex structure within the sample, perhaps due to steric particle interactions, which need to be destroyed before the system is set into motion. The maximum limiting friction correlates well with the yield point determinations, since the whole milk chocolate yield point is also the highest (see Table 2). The same order of limiting friction and yield point is observed for 99 % cocoa chocolate and dark chocolate with fat filling.

Sample	Yield Point [Pa]
Whole milk chocolate	16
99 % cocoa chocolate	11.5
Dark chocolate with fat filling	1.4
Cocoa butter	not observed

Table 2: Yield point of samples from fits to Casson model (values represent mean values from replicate viscosity curve measurements).

For the cocoa butter, the deviation from continuous sliding distance increase occurs at the lowest frictional forces. This could be due to the fact, that cocoa butter does not contain particles and, hence, there is no structure, which may counteract the onset of macroscopic motion, in line with the absence of a yield point.

In contrast to the other samples, the dark chocolate with fat filling shows a sharp increase in the sliding distance (see Figure 3).

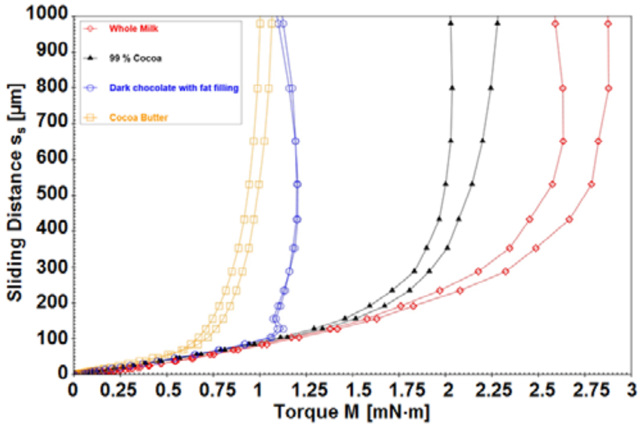

Figure 3: Sliding distance plotted against torque of the glass/chocolate/PDMS tribosystems at T = 37 °C (lin-lin plot, 3rd runs).

Right at the beginning of the sharp increase, at approximately 1.1 mN·m, the curve shows a kink. Interestingly the sliding distance covered by this kink is approximately 50 µm. This is in the size range of bigger particles, which were only detected in the dark chocolate with fat filling sample. One could discuss, whether this particular behavior is connected to the presence of bigger particles in the dark chocolate with fat filling, since bigger particles may counteract the onset of macroscopic motion of the tribosystem.

The particle size distributions of the chocolate samples are shown in Figure 4. The wideness of the distributions differs: Dark chocolate has the widest distribution; the 99 % cocoa has the narrowest. The dark chocolate shows the biggest particles with a d90 at 26 µm.

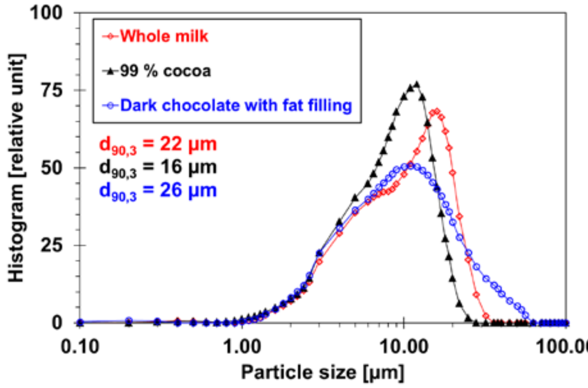

Figure 4: Particle size distribution of the chocolate samples.

5.2 Dynamic Friction and Viscosity

The results from sliding velocity ramps in the form of extended Stribeck curves are shown in Figure 5. The tribosystem with the whole milk sample shows the highest frictional resistance over the entire sliding velocity range. Within the intermediate sliding velocity regime, the whole milk chocolate and the 99 % cocoa chocolate show a distinctively different frictional behavior, whereas in the hydrodynamic regime, the curves show similar trends (increasing almost in parallel with the sliding velocity).

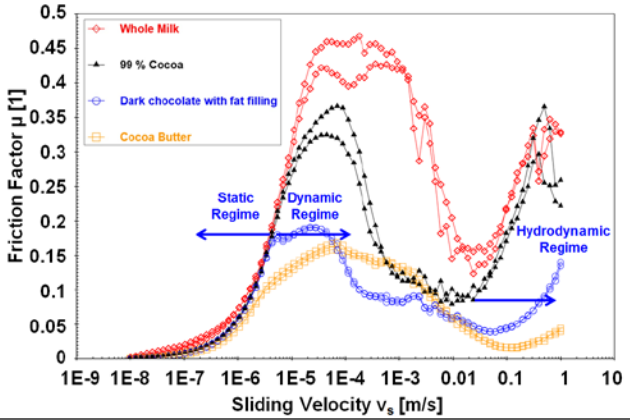

Figure 5: Extended Stribeck curves of the glass/chocolate/PDMS tribosystems at T = 37 °C (lin-log plot, 3rd runs). The respective friction regimes are marked for the dark chocolate with fat filling system.

In contrast to the 99 % cocoa chocolate, the Stribeck curves for the whole milk chocolate show stick slip events at intermediate sliding velocities.

Cocoa butter yields the lowest friction, except during intermediate sliding velocity range, where the friction factor with dark chocolate with fat filling is even lower. This cannot be correlated with differences in the sample viscosities, since cocoa butter shows the lowest viscosity over the entire shear rate range (see Figure 6). The 99 % cocoa chocolate and the dark chocolate with fat filling have similar fat contents (51 % respectively 47 %). However, the viscosity of the 99 % cocoa chocolate is clearly higher. One possible explanation could be the even broader particle size distribution of the dark chocolate with fat filling. In the case of broad particle size distributions, small particles may fill the voids between bigger particles and, thereby, enable a higher maximum packing fraction (Farris effect). This, again, yields a lower viscosity of the suspension.

The authors propose two possible explanations for the observed tribological behavior:

- One possible explanation could be the development of structural domains within the dark chocolate with fat filling sample sliding against each other resulting in lower friction factors.
- Another possible explanation could be spherical cocoa particles rolling against each other with the effect of friction factor reduction (like in ball bearings).

For higher sliding velocities, the tribosystems undergo a transition towards the hydrodynamic friction regime (see Figure 4). Within the hydrodynamic friction regime, the frictional behavior, as expected, is influenced by the viscosity of the sample. With increasing sample viscosity, the transition into the hydrodynamic regime occurs at a smaller sliding velocity, at $v_s \approx 30 \frac{mm}{s}$ for the whole milk and the 99 % cocoa chocolate, at $v_s \approx 80 \frac{mm}{s}$ for the dark chocolate with fat filling and $v_s \approx 200 \frac{mm}{s}$ for the cocoa butter. The friction factor values at sliding velocities greater than 200 $\frac{mm}{s}$ follow the same trend as their viscosity values (see Figure 5 and Figure 6).

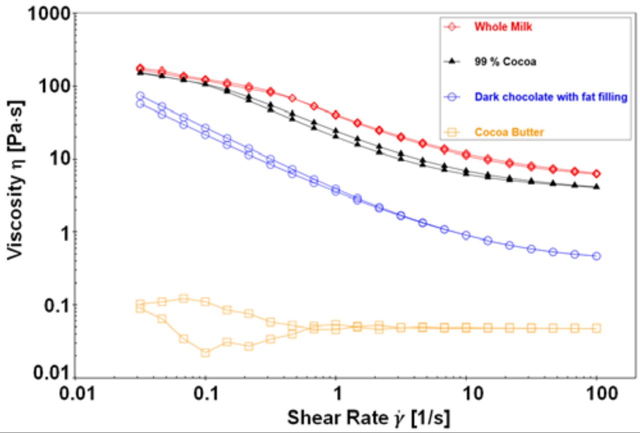

Figure 6: Viscosity curves of molten chocolate samples at T = 37 °C (shear-rate-controlled measurement).

6 Conclusions and Outlook

It could be shown that combining results from tribological and rheological tests provides a comprehensive understanding of the behavior of tribosystems. At very low sliding velocities, as well as in the hydrodynamic regime, interrelationships between rheological properties of the molten chocolate sample and the tribological behavior could be found. Further on, there are distinct regimes of the extended Stribeck curves, namely within the intermediate sliding velocity range, where tribological measurements allow additional insights into the system behavior in addition to solitary rheological data. The following points can be stated:

- Even though there are similarities in terms of particle size distribution and rheological behavior, the tribological behavior may differ. This allows for additional information through tribological studies.
- Polydispersity plays a role in the rheological behavior of chocolate samples (Farris effect).

Beyond this, extended Stribeck curves enable estimation of the frictional behavior during the transition from static to dynamic friction (7).

The methods presented above are currently being used in both quality control, and research and development of food and beverages. An even more comprehensive understanding of food oral processing could be achieved by combining tribological measurements and mouthfeel attributes as presented elsewhere (8) with rheological measurements. Since cocoa particles are known to be abrasive, there could be possible applications of interest for plant engineering, such as refiners or pumps.

From a structural point of view, it could be of interest to investigate the influence of steric and interfacial interactions of the solid and fluid ingredients of the chocolate masses and the comprising surfaces.

This application report only deals with the influence of the food sample itself. One could extend the scope of this study by taking into account further influencing factors, created by addition of components such as saliva, to mimic scenarios closer to the real-life applications.

7 References

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