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LUBRICATION OF CHOCOLATE DURING ORAL PROCESSING

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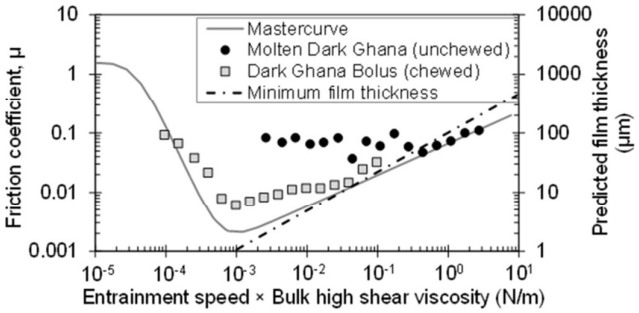
GRAPHICAL ABSTRACT

Oral processing transforms the structure of dark chocolate from a fat-continuous suspension to a saliva-continuous emulsion, which results in lower viscosities, thinner films and reduced friction.



ABSTRACT

The structure of chocolate is drastically transformed during oral processing from a composite solid to an oil/water fluid emulsion. Using two commercial dark chocolates varying in cocoa solids content, this study develops a method to identify the factors that govern lubrication in molten chocolate and saliva's contribution to lubrication following oral processing. In addition to chocolate and its individual components, simulated boluses (molten chocolate and phosphate buffered saline), *in vitro* boluses (molten chocolate and whole human saliva) and e*x vivo* boluses (chocolate expectorated after chewing till the point of swallow) were tested. The results reveal that the lubrication of molten chocolate is strongly influenced by the presence of solid sugar particles and cocoa solids. The entrainment of particles into the contact zone between the interacting surfaces reduces friction such that the maximum friction coefficient measured for chocolate boluses is much lower than those for single-phase Newtonian fluids. The addition of whole human saliva or a substitute aqueous phase (PBS) to molten chocolate dissolves sugar and decreases the viscosity of molten chocolate so that thinner films are achieved. However, saliva is more lubricating than PBS, which results in lower friction coefficients for chocolate-saliva mixtures when compared to chocolate-PBS mixtures. A comparison of *ex vivo* and *in vitro* boluses also suggests that the quantity of saliva added and uniformity of mixing during oral processing affect bolus structure, which leads to differences in measured friction. It is hypothesized that inhomogeneous mixing in the mouth introduces large air bubbles and regions of non-emulsified fat into the *ex vivo* boluses, which enhance wetting and lubrication.

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INTRODUCTION

Research on oral processing has long since recognised that in addition to the mechanical properties of food, texture perception is also affected by friction between the tongue, bolus and palate [1,2]. Oral processing involves several interacting surfaces in relative motion, for example, grinding teeth, tongue and palate, tongue and teeth, teeth and food, and tongue and food [3]. This process of mastication and bolus formation through to post-swallow is considered to involve both rheological (flow) and tribological (lubrication) mechanisms, whereby a mixture of food and saliva is squeezed and sheared at multiple length scales.

A study by De Wijk, Janssen and Prinz found that mechanisms of texture perception differ depending on whether the attribute is related to bulk properties or surface properties of the bolus [4]. Sensations that reflect bulk properties (e.g. “coldness” and “thickness”) are detected quickly and are therefore perceived earlier in the chewing sequence, when the food is still intact. On the other hand, sensations related to surface properties (e.g. “fattiness” and “melting”) require additional oral processing to sufficiently degrade the food before they are perceived. Certain attributes (e.g. “fatty after-feel”) are only fully developed after the bolus has been swallowed. As a result, surface-dominated attributes are detected much later in the chewing sequence compared to bulk-dominated attributes [4].

Chen and Stokes linked this division in attributes to a dynamic transition in the oral perception of texture from rheology to tribology [5]. They proposed that during the early stages of oral processing, the food is still large in size and bulk (large gap/ thick film), such that breaking and large deformation processes dominate these stages. Consequently, the textures perceived during early chewing are mostly related to the rheological or mechanical properties of food. As chewing progresses, particle size is reduced and fluid foods are diluted with saliva. Changes in length scale, particularly a decreasing film thickness, mean that shearing surfaces begin to interact and rheology becomes less relevant. Instead, surface friction and lubrication dominate mouthfeel and afterfeel during the later stages of oral processing [3,5,6].

Previous studies have linked oral lubrication to perceived texture in liquid and semi-solid foods. Kokini et al. [7–9] developed a model in which fluid food functions as a lubricant in the movement of the tongue against the surface of the hard palate. Their research suggests tribological measurements are related to the sensory texture attributes of “thickness”, “smoothness”, “slipperiness” and “creaminess”. The textural properties of fluid foods were described by two physical parameters: friction factor (tribology) and viscous factor (rheology). “Thickness” was defined by the perceived viscosity of food and depends on bulk deformation and flow properties (rheology). “Smoothness” was correlated to the reciprocal of the friction force between oral surfaces, and depends on lubrication (tribology). “Slipperiness” was correlated to the reciprocal of the sum of the viscous and friction forces, and therefore depends on a combination of rheological and tribological factors. The same was also true for “creaminess”, which was correlated to a combination of “thickness” and “smoothness” [7–9]. De Wijk and Prinz also reported that reduced lubrication leads to a decrease in the intensity of “creaminess” and “fattiness”, and an increased intensity of perceived “roughness” [10]. Furthermore, it has been proposed that the perception of “grittiness”, described as the sensation of hard particles, can be suppressed by increasing lubricant viscosity [1].

Solid chocolate undergoes multiple changes during oral processing that transform it into an oil-in-water emulsion by the point of swallow [11]. This structural transformation involves the mechanisms of comminution and agglomeration commonly observed during chewing [12], as well as sugar dissolution and a phase change from solid to liquid. As such, the final bolus is composed of a

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continuous saliva phase containing discrete oil droplets and insoluble cocoa solids. The lubrication properties of chocolate boluses are expected to relate to certain mouthfeel attributes such as “smoothness”, which is a key driver of consumer appreciation and acceptance in chocolate products. Consequently, this study aims to develop a method to elucidate the mechanisms that control the lubricating ability of melted dark chocolate, and saliva's contribution to lubrication during oral processing.

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MATERIALS AND METHODS

Chocolates

250g blocks of Whittaker's Dark Block (50% Cocoa) and Whittaker's Dark Ghana (72% Cocoa) chocolate were used in this work. The products were composed of the same core ingredients, but in different proportions, as detailed in Table 1. A standard sample size of a single piece of chocolate (25 × 16 × 9 mm, 5.7 ± 0.6 g) was used to prepare samples from both types of chocolate.

Particle Size Measurements

The particle size distribution of Whittaker's dark chocolates was measured by laser diffraction (Mastersizer 2000, Malvern, UK). Sunflower oil was used as a dispersant to prevent sugar dissolution. 1 ± 0.05 g of chocolate was placed into a falcon tube and 15 ml of sunflower oil was added to it. The sample was thoroughly mixed for 10 minutes using an ultrasonic bath (Unisonics, Australia; level 20) at room temperature (20–22 °C) to obtain a dispersion before the measurements [13]. The tubes were then placed on a roller mixer (Ratek, Australia; speed 5) to maintain a uniform dispersion for the duration of the measurements. Three separate replicates were performed per sample.

Sample Preparation

Three types of boluses were tested in this study: simulated, *in vitro* and *ex vivo*.

Simulated boluses were produced by mixing melted chocolate with Phosphate Buffered Saline (PBS), which was employed as a simple substitute for saliva focusing on its dilution effect. PBS solution was prepared by dissolving a PBS tablet (AMRESCO, USA) in 100 mL of double-filtered deionised water[1]. To determine the effect of dilution on chocolate's tribological response, a series of diluted chocolate-PBS mixtures at 100%, 50%, 35% and 20% (w/w) chocolate were tested. For each sample, 4 pieces of chocolate were chopped, transferred into a 250 mL glass beaker (68 cm inner diameter × 95 cm high) and weighed. The corresponding mass of PBS solution required was calculated and measured in a glass dish. The beaker was placed on a hot plate at 45 °C to avoid cooking the chocolate, and continuously stirred for 2–3 minutes till the chocolate melted. During this time, the pre-measured PBS solution was also placed on the hot plate and allowed to heat to the same temperature. The PBS solution was then manually mixed into the molten chocolate with a teaspoon, stirring steadily for 2 minutes at 2 revolutions per second to obtain a homogeneous mixture. Two repeats were performed for each chocolate. In the event that both repeats yielded different measurements, additional runs were conducted as necessary and outliers were discarded.

The components of chocolate were also tested individually to determine which component dominates its flow and lubrication behaviour. Chocolate-and-PBS mixtures diluted to 35% chocolate were centrifuged at 8500 rpm for 60 minutes to separate their components into cocoa butter (yellow liquid on top), a suspension of fine cocoa solids in water (dark brown liquid in middle), and heavy cocoa solids (solid layer at the bottom). The liquid layers were extracted and tested separately, with two repeats conducted for each type of chocolate.

In vitro boluses at the point of swallow were prepared by mixing chocolate with expectorated whole human saliva. 4 pieces of chocolate were chopped, transferred into a 250 mL glass beaker (68 cm inner diameter × 95 cm high), weighed and melted over the hot plate at 45 °C. The aim of this study was to develop methodologies to evaluate the influence of saliva on the properties of the

[1] AMRESCO reports on the bottle label that the resulting solution has a composition of 137 mM NaCl, 2mM KCl and 10 mM phosphate buffer and a pH of 7.4 ± 0.1.

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chocolate bolus. However, as saliva composition and rheology vary within and between individuals, we assessed the variation in chocolate-stimulated saliva properties between 8 individuals of differing oral processing strategies when eating chocolate (sucking, chewing etc.). While saliva flowrate, G' and G'' increased after stimulation with Dark Ghana chocolate compared to the resting state, limited variation was observed in saliva G' and G'' between individuals irrespective of oral processing strategy, as detailed elsewhere [14]. On that basis, and for simplicity so that technique-development could be focused on, we limited the scope of the current study to a single saliva donor. Chocolate-stimulated saliva was collected from a 25-year-old woman with healthy dentition and good general health. Human whole saliva (HWS) was collected at the same time of day (between 1500–1800 hrs) to minimise diurnal variation, and at least 1.5 hours after a meal. The subject rinsed her mouth with water, chewed and swallowed a piece of chocolate. The mouth-rinse was repeated to clear most of the chocolate debris in the oral cavity. The donor then expectorated saliva into a sterillin tube for a period of 3 minutes. This was repeated for 4 pieces of chocolate to ensure that the volume of saliva collected was sufficient to produce a 50% HWS-50% chocolate *in vitro* bolus, and was mixed in the same way as simulated boluses (described above). Three repeats were conducted for each type of chocolate.

For *ex vivo* boluses, the subject first masticated chocolate samples to the point of swallow *in vivo* in her mouth and then expectorated the mouthful into a 70 mL sterilin container. This was repeated for 6 pieces of chocolate and mixed together to obtain sufficient sample volume for tribological, rheological, and moisture content testing. Water was used to rinse the mouth between chews. The samples were mixed in a beaker for a minimal duration (10 revolutions) in order to obtain a homogeneous volume from the 6 consecutive mouthfuls but avoid changing the structure of the bolus through excessive shearing. The mastication time for each sample was also recorded and found to be consistent between repeats (Dark Block = 27.1 ± 1.9 s, Dark Ghana = 31.6 ± 0.9 s). The samples were tested *ex vivo* immediately after being produced. Three repeats were conducted for each type of chocolate.

This work was approved by the University of Auckland Human Participants Ethics Committee (UAHPEC; reference number 010854), and the participant gave her informed consent.

Tribology

The lubrication of all samples was tested immediately on a mini-traction machine (MTM2, PCS Instruments Ltd, UK). A sample volume of 20 mL was used per test, with the inclusion of the pot filler. A ball-and-disk tribopair fabricated from PDMS elastomer was used to implement soft-contact tribology, following the method developed by Bongaerts et al. [15] and used by Selway & Stokes to test yoghurts, custards and thickened creams [16]. Both PDMS surfaces were smooth and hydrophobic. A comparison of increasing and decreasing entrainment speed revealed that decreasing speed generally produced sharper transitions between lubrication regimes. Consequently, friction force was measured as a function of decreasing entrainment speed from 1000–1 mm/s at logarithmic intervals, which was repeated 5 times during the test and averaged to obtain the Stribeck curve. A slide-to-roll ratio of 50% was used to obtain a combination of sliding and rolling motion between the PDMS surfaces, along with a constant ball load of 2 N. All tests were run at 37 °C. Before and between runs, the tribopair parts were thoroughly cleaned with a sequence of rinses in an ultrasonic bath, beginning with warm water, isopropanol, deionised water, 1% SDS solution, deionised water and ending with double-filtered deionised water. The machine pot and metal parts were also cleaned with multiple rinses of hot water, isopropanol and double-filtered deionised water between samples to avoid contamination effects. No transient wear was

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observed in the tribopair between tests on chocolate, as monitored by measuring the Stribeck curve for water at the start of each testing day.

Rheology

The steady-shear rheology of all samples was tested on a stress-controlled rheometer (HAAKE MARS III, Thermo Scientific, MA, USA), between 35 mm-diameter smooth flat plates at a gap size of 250 μm. A "narrow" gap was used because of the need to obtain a sufficiently high shear rate (> 1000 s^{-1}) in the rheometer so as to access a high-shear plateau in viscosity, which was subsequently required to analyse the tribological data. Preliminary tests conducted on molten chocolate at different gap sizes (2000, 1000, 250 and 100 μm) showed good agreement between flow curves, so a gap size of 250 μm was chosen for all further tests. Viscosity was measured as a function of increasing shear stress from 0.1–23,000 Pa (maximum limit of the machine). All tests were run at 37 °C. Due to the narrow gap size used during tests, a gap error from misalignment and/or squeeze flow of air during gap-zeroing procedures can significantly affect the obtained results [17,18]. As previously demonstrated, the gap was zeroed at a normal force of 4 N to overcome the resistance associated with air present in the gap [19]. Furthermore, the residual gap error was estimated by Kravchuk and Stokes' statistical approach [18] and varied between 8–14 μm. Viscosity was corrected for gap error by multiplying measurements with the ratio of (gap size + gap error)/gap size [20].

Bolus Moisture Content

Gravimetric analysis was used to determine the moisture content of the *ex vivo* chocolate boluses. Samples were placed in aluminium drying dishes and covered with perforated foil to limit the loss of volatile fats. The samples were weighed and then dried in an oven at 105 °C for 22 hours, allowed to cool to room temperature and reweighed. Moisture and saliva content were calculated on a wet basis from the mass lost during drying.

Microscopy

The structure of molten chocolate and the three types of chocolate boluses were viewed under an optical microscope (Olympus BX40, Olympus Corporation, Tokyo, Japan). A small drop of the sample volume prepared for tribological and rheological testing was placed on a glass slide, gently covered with a cover slip and examined with transmitted light.

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RESULTS

Components of Chocolate

The results from narrow gap rheology presented in Figure 1 and Table 2 indicate that at oral temperature, chocolate has an apparent yield stress (~10 Pa for 100% Dark Ghana & Dark Block) and is shear-thinning with a relatively high high-shear viscosity plateau (η_{HS}), as expected based on literature [11,13,21,22]. The data indicates that diluted chocolate (35% chocolate, 65% PBS) also displays shear thinning behaviour up to a shear stress of 2 Pa. In contrast, the liquid components of simulated boluses are Newtonian. In the absence of solids, cocoa butter is Newtonian and several times more viscous than water (50 mPa.s). The fine suspension of cocoa solids extracted from centrifuged samples also exhibits Newtonian behaviour, but has a much lower viscosity (8 mPa.s), closer to that of water (0.7 mPa.s).

Figure 2 presents friction coefficient as a function of entrainment speed for tribological measurements performed on chocolate, its individual components, and upon dilution/mixing in PBS solution. Figure 2a shows the measured data, and figure 2b presents the data with the entrainment speed multiplied by the *sample's* high-shear viscosity plateau. This provides a basis for comparison against the assumption that the sample behaves as a continuum, whereby the hydrodynamic component of the tribological response is governed by the sample's high-shear viscosity; this is not necessarily true at all speeds given the multiphase nature of the fluid and the decrease in gap occurring with decreasing speed. The product of viscosity and entrainment speed is also an indication of the film thickness between tribopairs within the elastohydrodynamic regime, as predicted in the model of De Vicente et al. [23,24]. The data plotted in this way is compared to an empirical 'master curve' obtained for the same tribopair using water and glycerol solutions across boundary, mixed and hydrodynamic lubrication regimes [15]. Deviation from the master curve in the hydrodynamic regime is an indicator that the tribological response is not governed by the bulk high-shear viscosity of the sample.

Figure 2a shows that the friction coefficients for chocolate and the simulated chocolate bolus (35% solids) are just under 0.1, but vary from the friction coefficient of their individual components. The Stribeck curves for cocoa butter and the cocoa-solids/water suspension show a decrease in friction with increasing entrainment speed at low speeds until a minimum is reached, followed by an increase in friction with increasing speeds. This behaviour is characteristic of mixed and hydrodynamic lubrication respectively. When normalised by multiplying entrainment speed by the sample's high-shear viscosity in figure 2b, there is good alignment between the hydrodynamic regions of plain melted chocolate, cocoa butter, the cocoa solids suspension and that of the master curve generated using simple Newtonian lubricants (i.e. glycerol-water solutions). However, the onset of mixed lubrication occurs at much higher values of $U\eta_{HS}$ for the molten chocolate samples compared to the isolated chocolate components. We explain this to indicate that as film thickness decreases with reducing speed in the hydrodynamic region, a critical gap is reached whereby the melted chocolate exhibits a fluctuating friction coefficient associated with the entrainment of sugar and cocoa particles. These particles provide a barrier to direct surface contact and prevent further reduction in film thickness (contrary to the predictions for simple Newtonian fluids). Diluting chocolate with PBS solution (35% chocolate) decreases its viscosity, but essentially the same behaviour is obtained, albeit extended down to lower values of $U\eta_{HS}$. However, the measured friction coefficient at the lowest speed is 0.06–0.09, which is several orders of magnitude lower than the boundary coefficient for water between the same tribopairs ($\mu_{b,water}$~2). This is most likely because insoluble cocoa solids and oil droplets within the chocolate-PBS emulsions continue to prevent full asperity contact between the PDMS surfaces.

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Dilution of Chocolate

Images of melted chocolate and chocolate-PBS mixtures (Figure 3) reveal that chocolate phase inverts upon dilution and its sugar particles dissolve in water-based solutions, concurring with previous findings of expectorated chocolate [11]. Angular sugar particles can be distinguished in both chocolates, along with dark specks of cocoa solids. Corresponding measurements obtained from the Mastersizer are presented in Figure 4, and reveal that dark chocolate displays a bimodal distribution in particle size, which is associated with cocoa solids and sugar particles respectively. Deconvolution of the curves indicates that the size of the cocoa solids lies between 0.5–30 μm (peak = 9 μm), while that of sugar ranges from 3–110 μm (peak = 33 μm).

The results from rheology measurements are presented in Figure 5 and Table 3. When PBS solution is mixed into chocolate and transforms its structure into an oil-in-water emulsion, its apparent viscosity and yield stress decrease. The greater the amount of PBS added, the larger the observed decrease. Furthermore, the flow index (n, Table 3) of chocolate-PBS mixtures increases with increasing dilution, which suggests a tendency towards Newtonian behaviour (n = 1) as the solid phase volume decreases.

The Stribeck curves for simulated chocolate-PBS boluses, shown in Figure 6, demonstrate a shift from “mixed-hydrodynamic” lubrication to “boundary-mixed” lubrication with increasing water content. Diluting chocolate with water lowers its viscosity, which in turn decreases its ability to fully support the normal load through hydrodynamic forces. The friction coefficient in the “boundary-mixed” regime plateaus at ≈ 0.07.

Upon closer inspection, it appears that the film thickness at which mixed lubrication transitions to elastohydrodynamic lubrication varies between different dilutions of the same type of chocolate. Adding a greater volume of water to chocolate shifts this transition to lower $U\eta_{HS}$ values, particularly for dilutions of 20% and 35% chocolate. For example, the mixed-EHL transition is observed at a film thickness of ~ 50 μm for molten Dark Ghana chocolate, 20 μm for Dark Ghana diluted to 35% chocolate, and 10 μm when it is diluted to 20% chocolate. We have previously noted that the sugar particles vary in size from 3–110 μm, with the mode at 33 μm. This is of similar order to the film thickness of 100% chocolate, indicating that friction in the mixed regime, where the sample no longer behaves as a continuum, is influenced by the entrainment of undissolved sugar particles. In contrast, 20% chocolate is sufficiently diluted to dissolve all the sugar particles, and therefore exhibits this transition at a lower film thickness which corresponds to the size of the cocoa solids (0.5–30 μm).

Comparison of Simulated, *In vitro* and *Ex vivo* Boluses

Simulated, *in vitro* and *ex vivo* chocolate boluses were viewed under an optical microscope for a quick glance of their structure. The images, presented in Figure 7, imply that mixing chocolate with saliva leads to a finer dispersion of oil droplets in the resulting emulsion compared to mixing chocolate with PBS solution. Furthermore, *ex vivo* mixing in the mouth also appears to differ from *in vitro* mixing in a beaker in terms of droplet size, although the extent of the difference cannot be discerned since images of the *ex vivo* bolus do not show well-defined droplets. Images of the same boluses viewed at lower magnifications (refer Figure 8) show that air bubbles are present in both *in vitro* and *ex vivo* boluses containing saliva, but not the simulated boluses containing PBS.

Rheological measurements of the boluses (Figure 9 and Table 4) suggest that, across all bolus types, Dark Ghana boluses are more viscous than their Dark Block equivalents due to the higher percentage of cocoa solids present in Dark Ghana. Furthermore, for the same mass of added liquid, chocolate-saliva mixtures *(in vitro* boluses*)* also appear to be more viscous than chocolate-PBS mixtures (simulated boluses). Comparing the results of *in vitro* and *ex vivo* chocolate boluses,

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it appears that saliva content also affects bolus viscosity: a greater quantity of added saliva leads to a less viscous bolus. This explains why the *ex vivo* Dark Ghana bolus has a lower viscosity than its *in vitro* counterpart, while the *ex vivo* Dark Block bolus has a higher viscosity than its *in vitro* counterpart. *In vitro* boluses were diluted to a fixed moisture content of 50% during preparation. However, when chewed in the mouth and expectorated, the resulting *ex vivo* bolus had a moisture content greater than 50% in the case of Dark Ghana, and less than 50% in the case of Dark Block. Chocolate-saliva boluses also exhibit improved lubrication compared to chocolate-PBS boluses, as evident by lower friction coefficients in the Stribeck curve (Figure 10). Mixing in the mouth further enhances this effect, such that reported friction coefficients are lowest for *ex vivo* boluses out of the three types of samples tested.

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DISCUSSION

Effect of Cocoa Solids

The effect of solid particles on chocolate rheology can be discerned by comparing measurements of melted chocolate with those of cocoa butter. Based on the results obtained in the current study, it can be concluded that the addition of sugar and cocoa solids to cocoa butter not only dramatically increases its viscosity, but also alters its behaviour from Newtonian to shear-thinning. The same is true for PBS-diluted chocolate — as the quantity of liquid added increases, sugar dissolves and the concentration of cocoa solids decreases, resulting in lower viscosities and a shift towards Newtonian behaviour. Furthermore, dilutions of Dark Block were generally less viscous than those of Dark Ghana diluted to the same degree since Dark Block had a lower percentage of cocoa solids. This change in flow behaviour can affect the perceived texture of a food product; for example, increasing the concentration of solid particles dispersed in xanthan gum has been shown to increase its measured viscosity and influence perceived "creaminess" [25].

The results obtained from the current study also indicate that solid particles have a significant effect on boundary lubrication in chocolate, which has been reported in previous studies. Lee et al. reported that the high concentration of particles present in chocolate dominates friction between two soft PTFE surfaces by increasing lubricant viscosity and deforming the surfaces, since crystalline sucrose is hard enough to deform PTFE [26]. A detailed study by Yakubov et al. concluded that the addition of spherical glass particles to an aqueous lubricant significantly reduces the sliding friction coefficient between smooth PDMS surfaces at low speeds [27] — the presence of spherical particles was found to reduce friction in the boundary regime by as much as four times. This is because particles confined in the gap, assisted by favourable surface interactions and substrate compliance, transform sliding of the surfaces into rolling of particles [27]. Consequently, it is not surprising that molten chocolate yields much lower friction coefficients than the Stribeck curve generated from simple Newtonian fluids (master curve) in the current study. A very low volume of particles can produce this effect in boundary lubrication [27], which concurs with the same phenomenon being observed in a fine suspension of cocoa solids when compared against the master curve obtained for water and glycerol solutions (Figure 2).

The volume of particles in a lubricant also determines the critical film thickness at which mixed lubrication transitions to elastohydrodynamic lubrication. Within the elastohydrodynamic regime at high speeds where the suspension behaves as a continuum, lubrication is determined by the viscosity of the sample. As the film thickness progressively decreases with decreasing entrainment speed, there is a point at which film thickness is roughly equal to the average particle size within the suspension. At this critical film thickness, the suspension ceases to behave as a continuum and "jumps" to mixed lubrication due to the confinement of particles in the direction normal to fluid flow [27]. Based on the results of the current study, this occurs at a similar entrainment speed regardless of the degree of dilution (20, 35 or 50% chocolate, Figure 6a). However, when the entrainment speed is multiplied by lubricant viscosity (Figure 6b), the transition value of $U\eta_{HS}$ and thus film thickness decreases with increasing dilution for chocolate-PBS mixtures.

Effect of Phase Inversion

Previous studies have analysed the lubrication of oil and water emulsions (without insoluble particles) between soft elastohydrodynamic contacts. De Vicente et al. found that for sunflower oil-in-water emulsions where the oil viscosity is greater than 5.8 times that of the aqueous dispersion medium, it is the oil phase that dominates friction [28]. This is because hydrophobic elastomers are wetted by oil and, due to the high oil:water viscosity ratio, the droplet interface is relatively non-deformable. Consequently, the oil droplets are entrained into the contact zone whereby they coalesce to form a pool of viscous oil that supplies the lubricating film [28]. A later study by Douaire

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et al. studied water-in-sunflower oil emulsions between similar surfaces and found that even in an oil-continuous medium, some of the dispersed water droplets are entrained in the contact zone, but the amount of water entrained depends on total water content rather than droplet size [29]. The entrained droplets reduce boundary friction by increasing the viscosity of the film within the contact zone [29].

Comparing the results of plain melted chocolate with that of PBS-diluted chocolate, it is clear that the rheology and lubrication of chocolate are significantly altered upon mixing with an aqueous fluid. This change, expressed as a large decrease in apparent viscosity and a difference in lubrication regimes, not only relates to a decrease in solid phase volume via sugar dissolution, but also a change in the suspension matrix. The simultaneous melting of cocoa butter combined with the progressive incorporation of saliva into the chocolate bolus during chewing causes its structure to phase invert from a fat-continuous suspension to a water-continuous emulsion, as is evident in microscope images of chocolate before and after dilution. Water has a much lower viscosity (0.7 mPa.s) than cocoa butter (49.8 mPa.s). Since water is the continuous phase in the resulting emulsion, it follows that diluting chocolate with an aqueous solution results in viscosities lower than that of cocoa butter, as observed for 35% chocolate-PBS mixtures.

The decrease in viscosity also produces a shift in the lubrication regimes seen on the Stribeck curves for melted chocolate and PBS-chocolate dilutions (Figure 6). In tribological testing, high viscosity fluids like molten chocolate are expected to have a large gap width in the hydrodynamic lubrication regime unless a large load is applied to displace it from the contact zone [1]. Consequently, it is only after dilution with PBS that boundary and mixed lubrication can be clearly identified on the Stribeck curves for chocolate samples. A comparison of chocolate and its centrifuged components reveals that the Stribeck curves of molten chocolate greatly differ in appearance to those of its components (Figure 2). Both cocoa butter and the fine suspension of cocoa solids also exhibit much lower friction coefficients than diluted chocolate. In the case of cocoa butter, this is attributed to a higher viscosity, which is known to decrease friction at a specific entrainment speed in mixed lubrication [3]. In contrast, the solid suspension exhibits boundary lubrication and, due to the suggested entrainment and normal-confinement of ground cocoa solids described in the previous section, demonstrates much lower friction coefficients than the master curve obtained for water/glycerol mixtures of equivalent viscosity. However, the fine suspension also displays lower friction coefficients than melted chocolate, and may be linked to the difference in matrix viscosity after phase inversion. Water (suspension matrix) is several times less viscous than cocoa oil (chocolate matrix), which will affect particle movement and thus the entrainment of particles into the gap between the PDMS surfaces.

Role of Saliva in Lubrication

Since solid particles modulate the lubrication of chocolate at narrow gap sizes, it was hypothesised that the primary role of saliva in the chocolate bolus from a tribological viewpoint may be sugar dissolution. This hypothesis was tested by comparing the results obtained for chocolate-PBS mixtures with those of *in vitro* chocolate-saliva mixtures and expectorated *ex vivo* boluses. Since both PBS and saliva dissolve sugar, obtaining similar Stribeck curves across the three types of samples would support this hypothesis.

The results of the current study demonstrate reduced friction when saliva is added to chocolate instead of PBS. This is attributed to differences in the lubricating ability and interfacial activity of saliva when compared with PBS. During mastication and swallowing, the tongue is pressed against the palate, giving a perception of friction in which saliva provides the lubrication [30,31]. Saliva is known to be highly lubricating, a characteristic that is thought to be essential for its functionality in protecting oral surfaces from irritation and wear, and efficiently transporting food through the oral

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cavity [32]. When adsorbed onto substrates, saliva forms a multi-layered protein-rich film composed of a dense anchoring inner layer and highly-extended, lubricating outer layer [33]. In soft hydrophobic contact measured between PDMS surfaces, lubrication by mechanically-stimulated human whole saliva was found to have a boundary friction coefficient $\mu \sim 0.02$, which is two orders of magnitude lower than that for water tested at the same conditions [34]. Boundary friction coefficients for acid-stimulated saliva are reported to be even lower, with $\mu \sim 0.01$ [6].

Saliva has also been confirmed to rapidly emulsify oils upon consumption. In-vivo fluorescence imaging of the residue on the tongue's surface after orally processing corn and castor oil show clear evidence of emulsification occurring within the mouth [35]. Previous studies have shown that the frictional properties of plain molten chocolate is strongly influenced by the addition of emulsifiers such as lecithin [26,36]. Lee et al. suggest this is because emulsifiers enable better mixing of hydrophilic particles (e.g. sugar) with the lipophilic fat phase in chocolate, which in turn reduces its viscosity and friction by facilitating more liquid-like behaviour as a lubricating film [36]. It is also possible that salivary proteins lead to differences in droplet entrainment between simulated and *in vitro* boluses, which may account for the variation in their lubrication behaviour. The deformation of dispersed droplets entering the contact zone depends on the elasticity of the oil-water interface, which in turn is influenced by the presence of emulsifiers i.e. surface active molecules which are able to stabilise an increased surface area when the drop is deformed [29].

Furthermore, *in vivo* mixing during oral processing appears to produce a bolus with improved lubricating ability compared to *in vitro* mixing, shifting closer to the lubrication response obtained from cocoa butter alone. This may be attributed to differences associated with mixing boluses in a beaker *in vitro* compared to *in vivo* mixing in the mouth. Due to their short residence time in the mouth, emulsions that are orally processed are expected to involve inhomogeneous mixing of the emulsion with saliva [37]. In the case of chocolate, which also requires melting of the continuous cocoa butter phase to form an emulsion, inhomogeneous mixing in the mouth produces heterogeneous boluses that might still contain solid chocolate particles at the point of swallow. These may lead to regions of non-emulsified fat being included in the *ex vivo* boluses, which would affect their tribological response.

The incorporation of air into the bolus during chewing may also play a role in reducing its friction. Due to the nature of inhomogeneous mixing, masticated emulsions will inevitably include a fraction of air [38]. Low magnification images of the boluses prepared in this study (refer Figure 8) reveal air bubbles are present in both saliva-diluted boluses (*in vitro* and *ex vivo*) but not the PBS-diluted boluses (simulated), and that uncontrolled mixing in the mouth results in larger air bubbles compared to controlled mixing in a beaker. Droplets are proposed to release oil by spreading onto the surface of the air-water interface [38]. This has been confirmed by the observation of a layer of fat droplets coating the air bubbles in whipped emulsions [39]. The same process is expected to occur during the mastication of a food emulsion, with the release of oil causing a decrease in friction [38]. Increased wettability has also been observed to enhance fluid entrainment and thus extend the mixed-EHD transition to lower film thickness (indicated by $U\eta_{HS}$) [34], which concurs with the results obtained in the current study.

Comparing *ex vivo* boluses for both chocolates, Dark Ghana shows a much steeper decrease in friction coefficient at the EHD-mixed lubrication transition point compared to Dark Block. This is linked with a shorter chewing duration for Dark Block compared with Dark Ghana, leading to less saliva being added to the Dark Block bolus by the point of swallow. Saliva is reported to increase the wettability of PDMS substrates through adsorption and enhance lubrication [33,34], so it follows that the bolus with a higher saliva content has a lower friction coefficient.

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The structure of an emulsion can also be altered by flocculation and coalescence during oral processing. Oral manipulations during mastication include shearing the bolus between the tongue and palate, which can cause emulsion droplets to rapidly coalesce [30,38,40–42]. The coalescence of emulsion droplets is accompanied by a release of oil that affects the coating on oral surfaces during chewing [38], and may contribute to the observed difference in lubrication between *in vitro* and *ex vivo* boluses from the present study. Shear-induced coalescence is proposed to promote oil spreading and deposition on the tongue surface, thereby lowering friction and making it more hydrophobic [2,38,43,44]. Consequently, it is possible that shearing the bolus between oral surfaces during mastication may lead to droplet coalescence and oil release in expectorated chocolate boluses, which could explain why the *ex vivo* boluses displayed lower friction coefficients than their *in vitro* counterparts.

When an emulsion is mixed with saliva, either *in vitro* outside the mouth or *in vivo* during oral processing, it has been observed to flocculate within the time scales relevant to chewing [2,30,38,42,45–47]. The type and degree of saliva-induced flocculation generally varies depending on the net charge of the emulsion droplets and presence of other charged molecules [30]. Droplets have even been observed to become incorporated into “slimy” strings of mucous structures associated with saliva [38]. The aggregation of droplets in an emulsion causes an increase in viscosity [45] that is considered more prominent in *ex vivo* boluses compared to *in vitro* boluses [42]. Emulsion flocculation has been previously observed in expectorated boluses of a less mouthcoating milk chocolate, but not in a more mouth-coating alternative of similar composition [11]. It was proposed that different interactions between saliva and chocolate ingredients (particularly those adsorbed at droplet interfaces in competition with salivary proteins), lead to the formation of large flocs which do not effectively adhere to oral surfaces in the less mouthcoating chocolate. However, the relevance of flocculation to chocolate lubrication in the present study is questionable, particularly after considering that the high shear used in rheological and tribological testing will easily disrupt weak flocculation.

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CONCLUSIONS

In this study, we develop the method and techniques required to understand the lubrication of chocolate during oral processing. The results reveal that the lubrication of molten chocolate is strongly influenced by the presence of solid sugar particles and cocoa solids. Its Stribeck curve is dominated by fluctuations associated with these particles entering the contact zone between the moving surfaces. The addition of saliva (or a substitute like PBS solution) to chocolate dissolves sugar and decreases the spatial concentration of cocoa solids, such that boundary and mixed lubrication are observed. However, insoluble cocoa solids prevent full asperity contact between the PDMS surfaces and transform surface sliding into particle rolling to reduce friction, even at dilutions of 20% chocolate. Therefore, the maximum friction coefficients measured for all chocolate boluses are lower than those of water and glycerol solutions measured with the same tribopair and testing conditions.

From a tribological viewpoint, the role of saliva in the chocolate bolus extends beyond sugar dissolution. Saliva is more lubricating than PBS solution, and this confers lower friction coefficients to chocolate-saliva mixtures when compared with chocolate-PBS mixtures. Comparing the results of *ex vivo* and *in vitro* boluses, it appears that the quantity of saliva and uniformity of mixing lead to differences in friction. Expectorated boluses are expected to contain regions of non-emulsified fat. Furthermore, mixing with saliva incorporates air bubbles in the bolus regardless of whether it is mixed *in vitro* in a beaker or *in vivo* in the mouth. Fat droplets are proposed to cover the air-water interface of bubbles with oil, thereby enhancing wetting and lubrication. As a result, orally-processed chocolate boluses exhibit the lowest friction coefficient of the three types of boluses tested.

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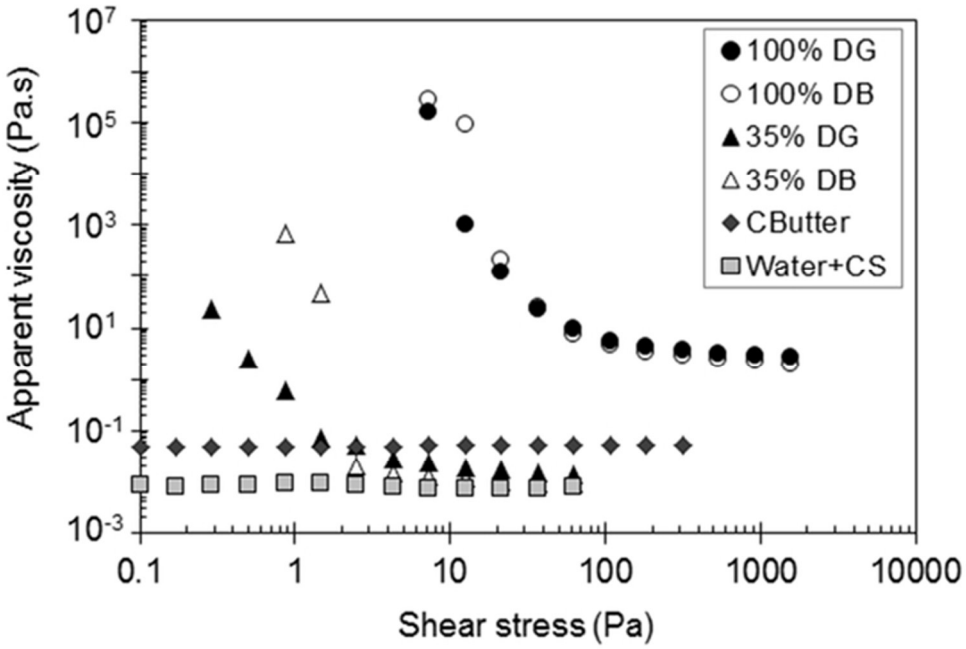

Plot of apparent viscosity against shear stress for extracted components of Dark Ghana (DG) and Dark Block (DB) chocolate, diluted to 35% chocolate with Phosphate-Buffered Saline (PBS) and centrifuged to separate its phases. "CButter" = Cocoa butter and "Water+CS" = Fine suspension of cocoa solids in water. Each series represents an average of two repeats. Note that "100% DG" and "100% DB" refer to plain melted chocolate without the addition of PBS.

Figure 1
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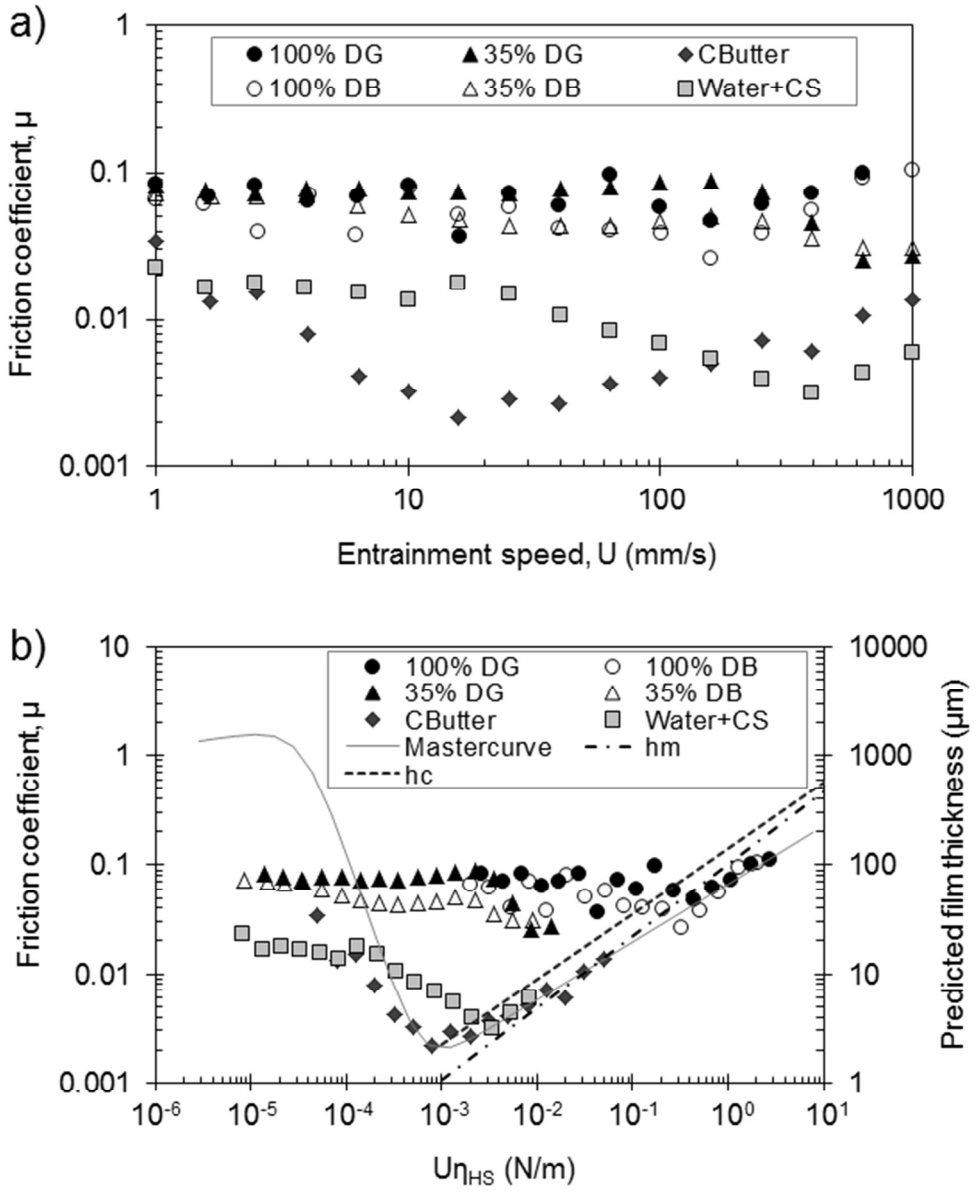

Stribeck curves for individual components of chocolate extracted from centrifuged samples, plotted against a) entrainment speed and b) entrainment speed × lubricant viscosity at high shear. "100% DG" and "100% DB" = melted Dark Ghana (DG) and Dark Block (DB) chocolate respectively, "35% DG" and "35% DB" = chocolate-PBS mixtures containing 35% chocolate and 65% Phosphate-Buffered Saline (PBS), "CButter" = Cocoa butter and "Water+CS" = Fine suspension of cocoa solids in water. Each series represents an average of two repeats. The master curve (solid line) was derived from an empirical model fitted to measurements of water and glycerol solutions. The dashed lines represent the predicted film thickness (minimum and central) for elastohydrodynamic lubrication in microns.

Figure 2
204x246mm (300 x 300 DPI)

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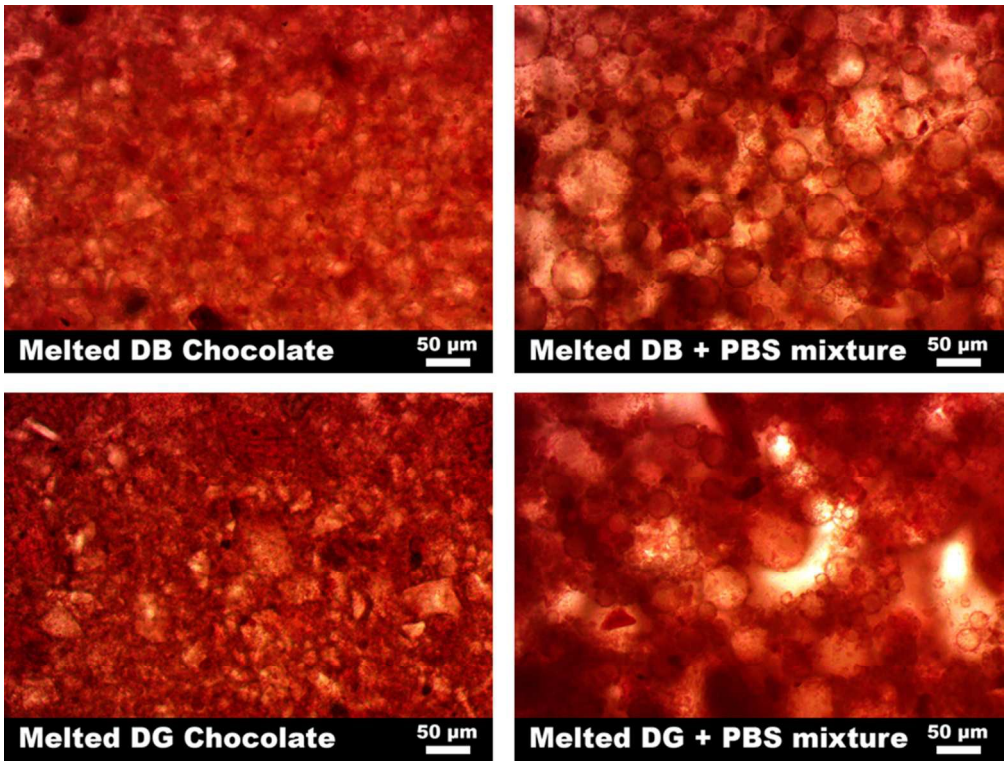

Microscope images of melted (left) and PBS-diluted (right) Dark Block and Dark Ghana chocolate, viewed with transmitted light. Note: DB = Dark Block, DG = Dark Ghana and PBS = Phosphate-Buffered Saline.
Figure 3
131x99mm (300 x 300 DPI)

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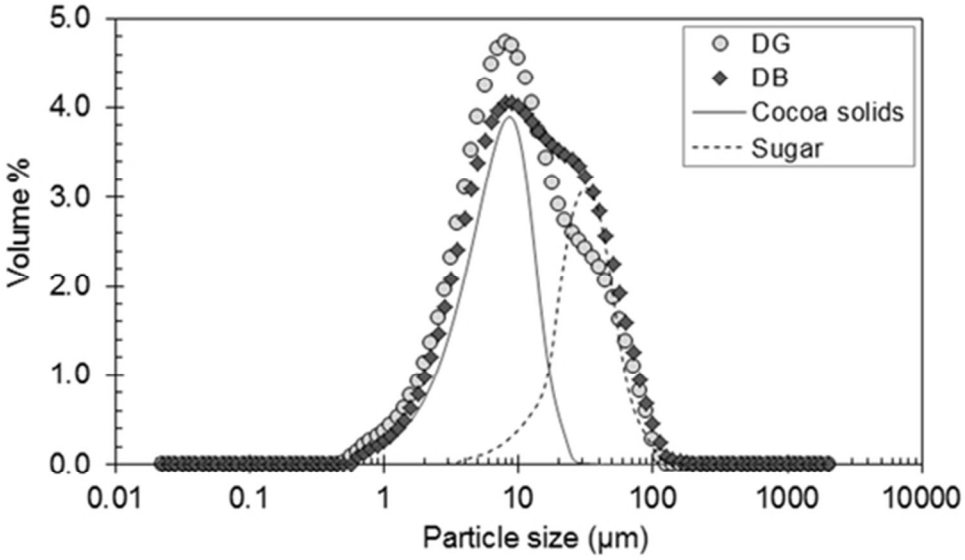

Bimodal distribution of Whittaker's dark chocolates as measured by the Mastersizer, showing individual peaks for cocoa solids and sugar particles after curve deconvolution (Gauss distribution assumed). Based on these measurements, the estimated size of the cocoa solids is between 0.5 – 30 μm (peak = 9 μm), while sugar varies from 3 – 110 μm (peak = 33 μm). The shape of the curves also indicates that Dark Ghana chocolate (72% cocoa) contains a greater volume of cocoa solids compared to Dark Block (50% cocoa), as expected. Note: DG = Dark Ghana and DB = Dark Block.

Figure 4
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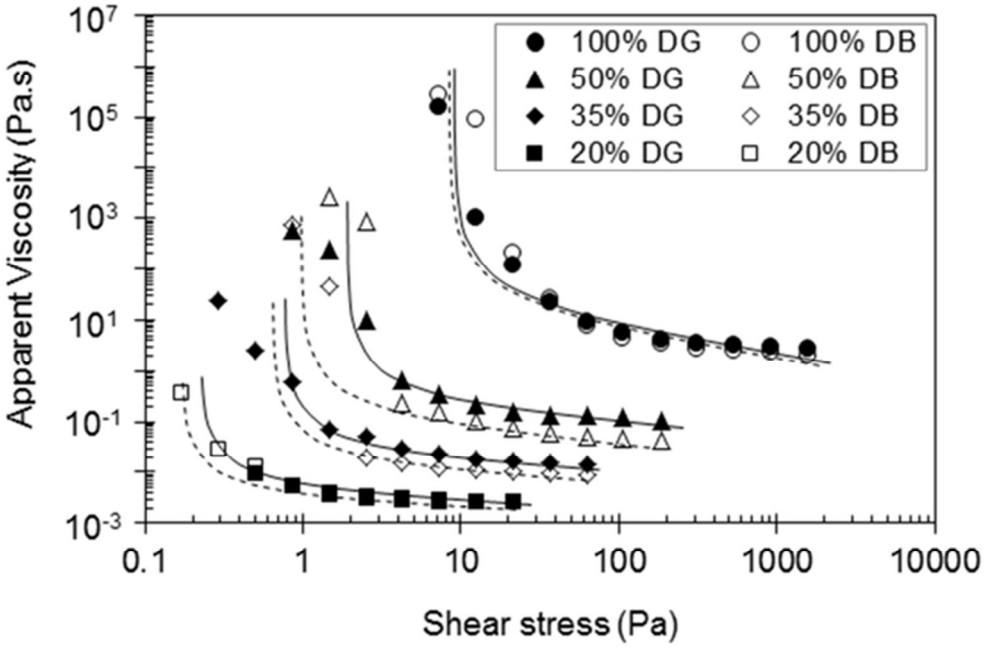

Plot of apparent viscosity against shear stress for Dark Ghana (DG) and Dark Block (DB) chocolate diluted with Phosphate-Buffered Saline (PBS) solution to varying degrees. Each series represents an average of two repeats. Note that "100% DG" and "100% DB" refer to melted Dark Ghana and Dark Block without the addition of PBS. The lines represent Herschel-Bulkley model fits to the data for Dark Ghana (solid) and Dark Block (dashed); fitting parameters are reported in Table 3.

Figure 5

55x36mm (300 x 300 DPI)

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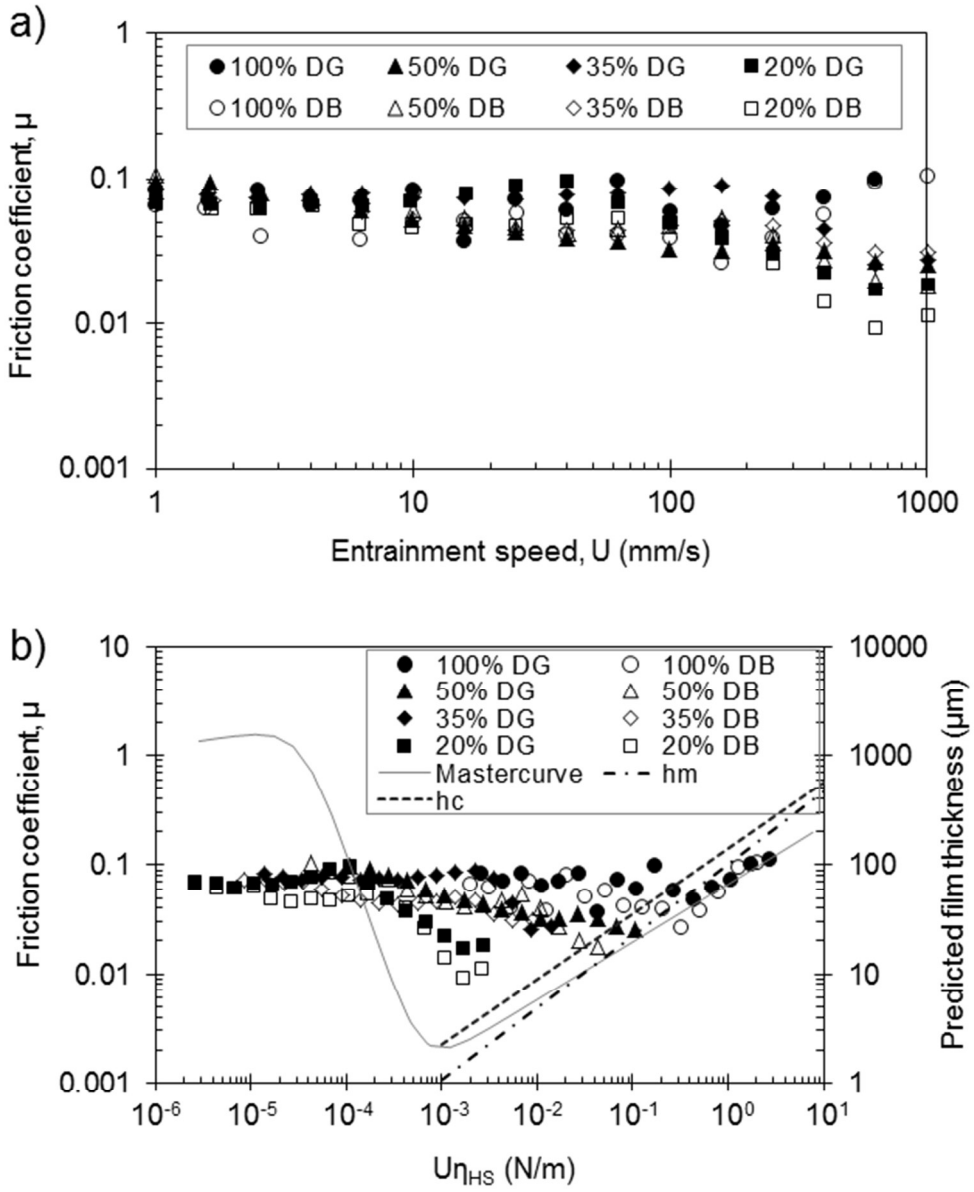

Stribeck curves for Dark Ghana (DG) and Dark Block (DB) chocolate diluted with Phosphate-Buffered Saline (PBS) solution to varying degrees, plotted against a) entrainment speed and b) entrainment speed × lubricant viscosity at high shear. "100% DG" and "100% DB" = melted Dark Ghana (DG) and Dark Block (DB) chocolate respectively, "35% DG" and "35% DB" = chocolate-PBS mixtures containing 35% chocolate and 65% Phosphate-Buffered Saline (PBS), and so on. Each series represents an average of two repeats. The master curve (solid line) was derived from an empirical model fitted to measurements of water and glycerol solutions. The dashed lines represent the predicted film thickness (minimum and central) for elastohydrodynamic lubrication in microns.

Figure 6
204x246mm (300 x 300 DPI)

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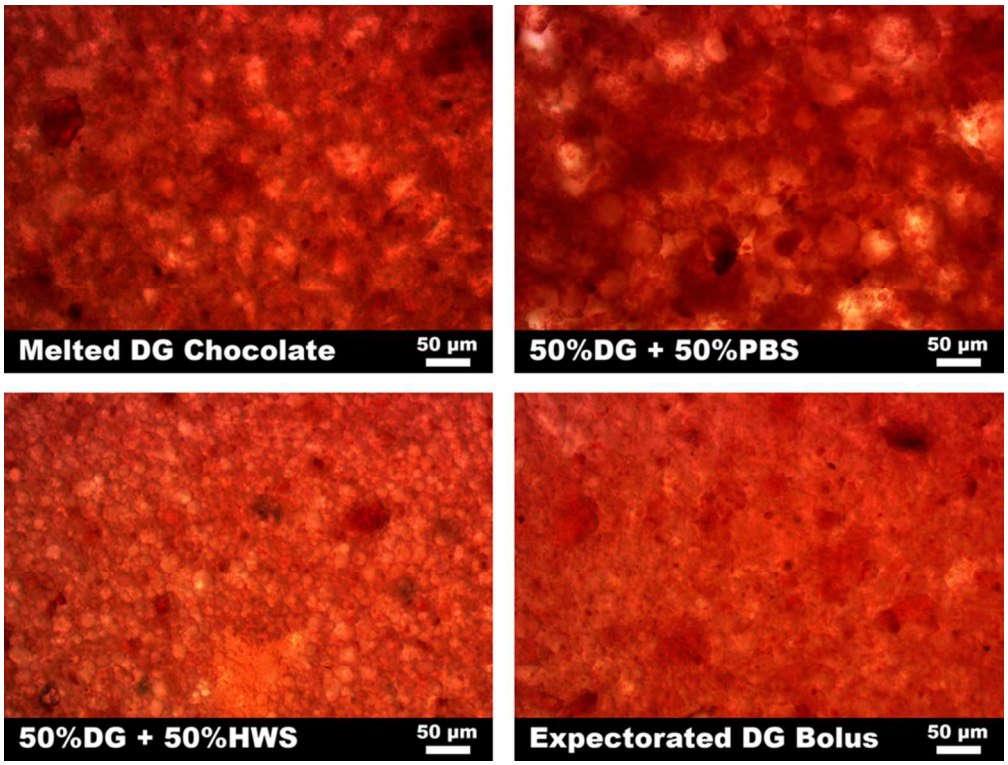

Microscope images of Dark Ghana chocolate and its corresponding simulated (PBS), in vitro (HWS) and ex vivo (expectorated) boluses, viewed with transmitted light. Note: DG = Dark Ghana, DB = Dark Block, PBS = Phosphate-Buffered Saline, HWS = Human Whole Saliva.
Figure 7
129x97mm (300 x 300 DPI)

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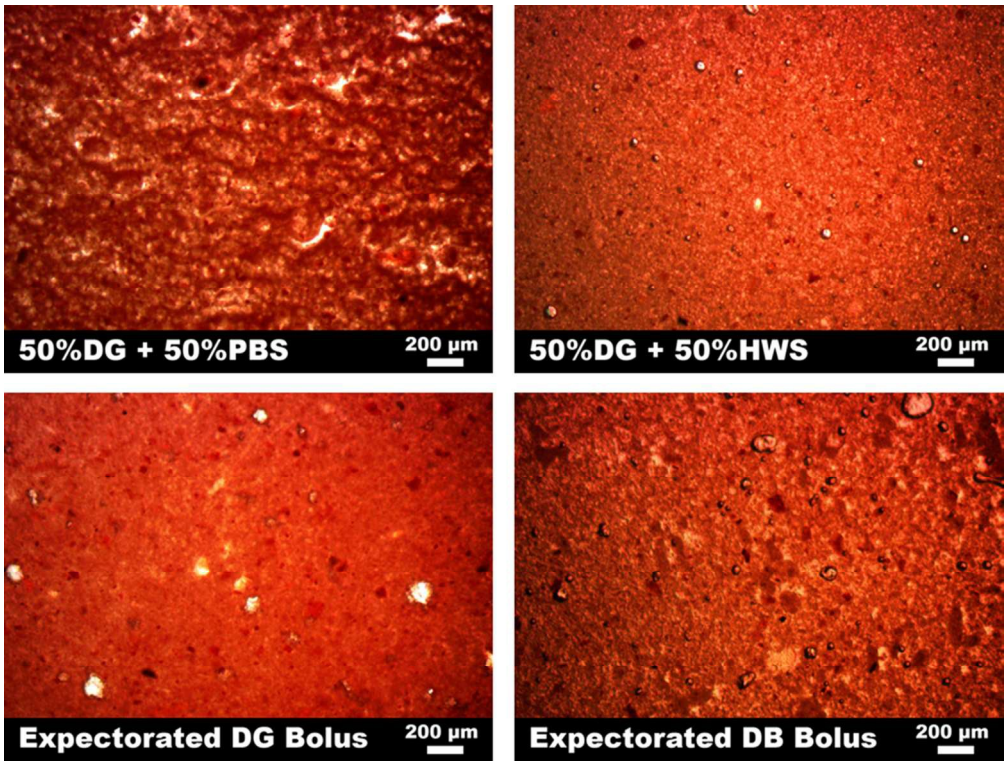

Microscope images of simulated (PBS), in vitro (HWS) and ex vivo (expectorated) boluses viewed with transmitted light under low magnification, showing the presence of several air bubbles in samples containing saliva. Note: DG = Dark Ghana, DB = Dark Block, PBS = Phosphate-Buffered Saline, HWS = Human Whole Saliva.

Figure 8

129x97mm (300 x 300 DPI)

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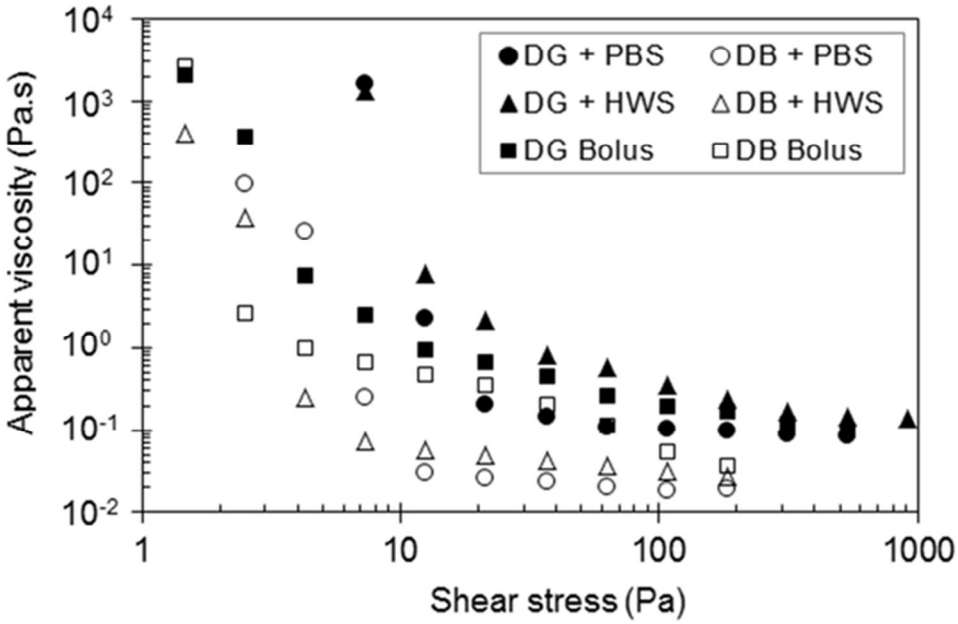

Plot of apparent viscosity against shear stress for simulated (PBS), in vitro (HWS) and ex vivo chocolate boluses. Each series represents an average of three repeats. Note: DG = Dark Ghana, DB = Dark Block, HWS = Human Whole Saliva and PBS = Phosphate-Buffered Saline.
Figure 9
55x36mm (300 x 300 DPI)

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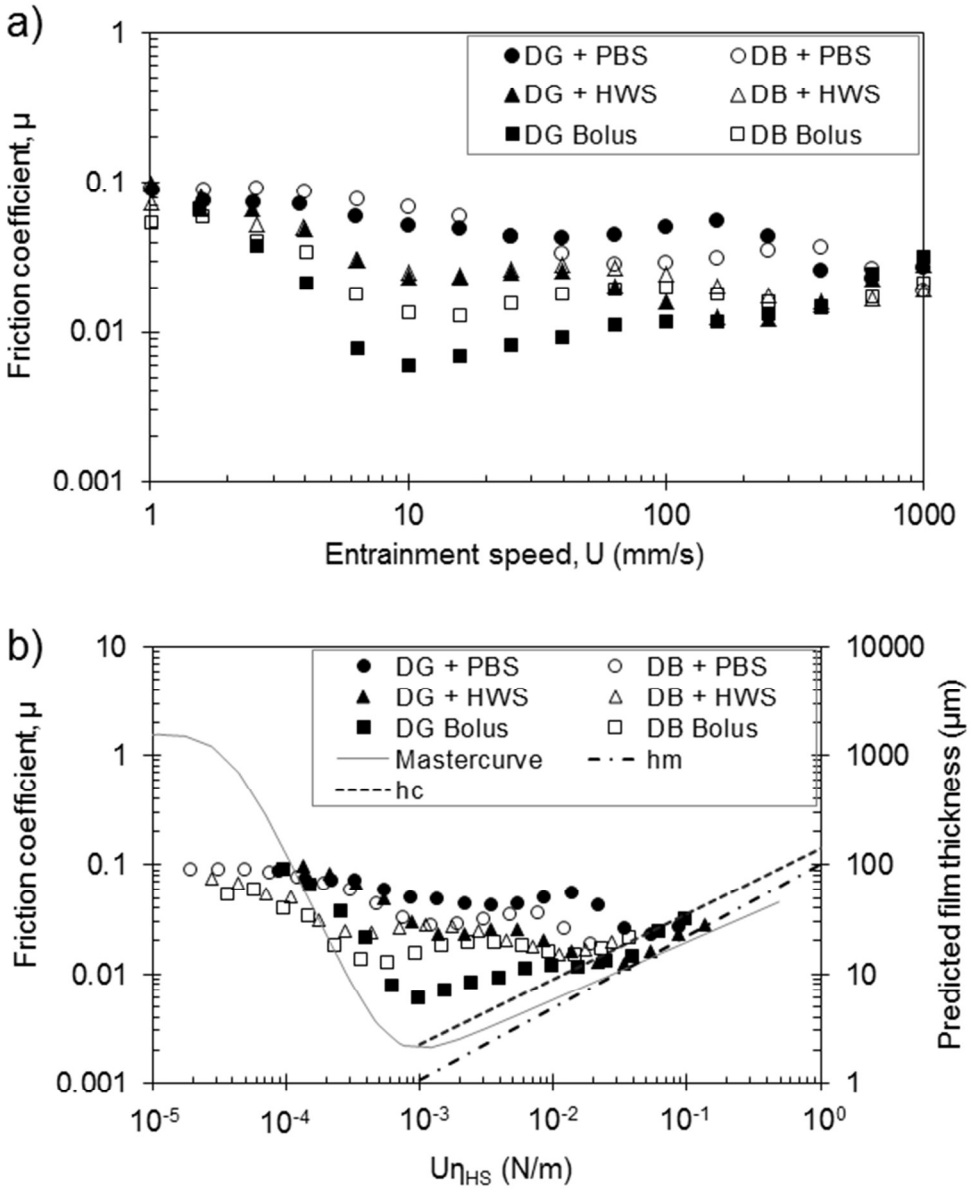

Stribeck curves for simulated (PBS), in vitro (HWS) and ex vivo chocolate boluses, plotted against a) entrainment speed and b) entrainment speed × lubricant viscosity at high shear. Each series represents an average of two repeats. The master curve (solid line) was derived from an empirical model fitted to measurements of water and glycerol solutions. The dashed lines represent the predicted film thickness (minimum and central) for elastohydrodynamic lubrication in microns. Note: DG = Dark Ghana, DB = Dark Block, HWS = Human Whole Saliva and PBS = Phosphate-Buffered Saline.

Figure 10
204x246mm (300 x 300 DPI)