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Frictional behaviour of molten chocolate as a function of fat content†

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Soft tribology is used to probe the lubrication behaviour of molten chocolate between soft contacts, analogous to in-mouth interactions between the tongue and palate. Molten chocolate is a concentrated suspension of solid particles (sugar, cocoa and milk solids) in cocoa butter. We hypothesise that the complex frictional behaviour of molten chocolate depends on its particulate nature and thus solid volume fraction (sugar & cocoa solids/fat content). In this work, we assess the properties of molten chocolate as a function of fat content by diluting milk chocolate containing 26, 27 and 29% fat with cocoa butter. The tribological behaviour of molten chocolate deviates notably from the typical Stribeck curve of Newtonian fluids. Additional transitions are observed in mixed and elastohydrodynamic lubrication which are respectively attributed to the effect of shear-thinning rheology (*i.e.* breakdown of aggregates) and the selective entrainment or exclusion of particles depending on interfacial gap height. These transitions are more pronounced in chocolate of high solid fraction, and correlate with the influence of particle aggregation on rheology. In addition, we assess oral lubrication by preparing model chocolate boluses with aqueous buffer, which produces a ternary system of oil droplets and insoluble cocoa solids dispersed within a continuous aqueous phase. The frictional behaviour of chocolate boluses is determined by the viscosity ratio between cocoa butter and aqueous phase, in agreement with previous findings for oil-in-water emulsions. We provide a conceptual model to interpret how fat content influences the oral lubrication and mouthfeel of chocolate during consumption.

1. Introduction

Soft tribology is a useful technique for evaluating the sensory performance of chocolate as it probes friction between sliding surfaces as a function of interfacial separation (lubricant film thickness), analogous to oral processing of food and dilution with saliva.[1,2] Indeed, tribological studies of foods ranging from dairy products[3,4] and hydrogel emulsions[5] to wine[6] have discovered correlations to sensory attributes like *smoothness*, *chalkiness*, *creaminess* and *astringency*.[1] More specifically, milk chocolates that are perceived as less *mouthcoating* have been linked to a higher friction coefficient in soft–hard (PDMS-steel) sliding contact.[7,8] Yet, it is not easy to interpret the mechanisms that contribute to the frictional behaviour of complex multiphase fluids like chocolate. In its molten form, milk chocolate is a concentrated suspension of various solid particles (sugar crystals, non-fat milk solids and cocoa nibs) dispersed in fat. During tribological measurements, certain components can be confined or excluded from the contact, particularly from the decreasing gap associated with decreasing entrainment speed. Consequently, the Stribeck curve for chocolate does not follow the shape of a typical Stribeck curve, as shown by our previous work on dark chocolate.[9]

An accumulation of particles at the inlet in sliding contact has been observed for slurry-type particle/oil systems, measured between hard surfaces.[10,11] While a fraction of the solid particles were swept around the track and another fraction bypassed the contact zone, it was still possible for some particles to enter the contact area. The number of particles that passed through the sliding contact was found to depend on particle properties (size, shape and material *e.g.* hardness, hydrophobicity), velocity and load. Previous tribological studies on chocolate have also assessed the effect of particle size, lecithin content, milk fat:cocoa butter ratio and conching type on the frictional properties of chocolate between different combinations of surfaces.[12–14] The authors concluded that the static and dynamic frictional properties of chocolate are pri-

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marily determined by its particle size distribution and lecithin content, and suggest that frictional differences in a highly mobile slurry-type system correlate to differences in particle entrainment.

There is no universal rule for the effect of particle entrainment on measured friction, as particle–surface interactions vary depending on particle (size, modulus), fluid (viscosity, phase volume) and surface properties (roughness, modulus, hydrophobicity, charge).[2,15] We surmise that several outcomes are possible, wherein the solid particles of chocolate can either:

1. Enter the contact zone and convert sliding of the surfaces to rolling of particles, which reduces friction[15]
2. Accumulate at the inlet and block the supply of fat into the contact, or be swept around the sliding track without rolling, either of which leads to increased friction[13]
3. Cause abrasive wear of sliding surfaces softer than the particles, which increases friction[13]

In this work, we unravel the mechanisms that affect the frictional behaviour of chocolate by analysing particle entrainment as a function of fat content with soft contact tribology, a technique which measures friction between elastomer surfaces to approximate shearing of food between soft oral surfaces such as the tongue and palate. Non-commercial samples of milk chocolate containing 26, 27 and 29% fat were diluted with either cocoa butter or phosphate-buffered saline to simulate saliva. In our approach, we also compare the Stribeck curves of diluted chocolate to those of individual components, with the goal of identifying potential drivers of in-mouth lubrication during oral processing.

2. Materials and methods

2.1 Chocolates

Non-commercial milk chocolates of varying fat content (26, 27 and 29% fat) were manufactured by a mid-scale process and supplied by Mondelēz International. Samples were melted over a hot plate set at 45 °C and tested in their molten state. To gain a better understanding of lubrication mechanisms, we performed further testing on chocolate diluted with cocoa butter (Cocoa Butter Buttons, Absolute Organic). Diluted chocolate samples were prepared by separately melting chocolate and cocoa butter on a hot plate set at 45 °C, and then combining the two together with continued heating over the hot plate.

When chocolate is mixed with saliva during oral processing, it forms an emulsion.[7–9] We create model boluses by diluting molten chocolate with phosphate-buffered saline (PBS tablets, AMRESCO§) under similar ionic conditions to those found in-mouth. As the tablets produce a 150 mM buffer solution at pH 7.4, a single tablet was dissolved in double the amount of recommended water to prepare a solution of similar ionic strength to whole human saliva (~70 mM). Diluted chocolate samples were prepared by separately heating chocolate and buffer on a hot plate set at 45 °C, and then mixing the two together with continued heating over the hot plate. This method of pre-heating the buffer prior to mixing with molten chocolate was required to prevent the mixture from "seizing" *i.e.* fat solidification and separation from aqueous phase. Dilutions of 70 and 50% chocolate were selected for tribological testing, since the chocolate–PBS mixture seized above 70% chocolate. In addition to testing chocolate–PBS mixtures, we also measured the friction of their aqueous and non-aqueous phases (isolated from the mixtures) to identify the mechanisms that influence oral tribology during chewing. The mixtures were prepared, placed into 50 mL centrifuge tubes and centrifuged at 8500 rpm for 60 minutes. Two liquid phases were obtained after centrifugal separation, including an oil phase (mainly cocoa butter) and an aqueous suspension of fine solids which resembled chocolate milk in appearance.

§AMRESCO PBS solution has a composition of 68.5 mM NaCl, 1 mM KCl and 5 mM phosphate buffer and a pH of 7.4 ± 0.1

2.2 Rheology

Viscosity was measured on the Haake Mars III (Thermo Scientific) between 35 mm diameter smooth plates and a gap of 250 μm. Measurements were stress-controlled from low to high stress within the range of 0.1–1000 Pa. Tests were performed at 37 °C, and included a pre-shear at 10 s^{-1} for 60 s followed by 60 s equilibration time; each stress was measured for a maximum of 30 s. The measured viscosity was adjusted for gap error following the technique of Davies and Stokes.[16–18] Chocolate and its dilutions were modelled as a Herschel–Bulkley fluid to predict viscosity at a given shear rate. We use the predictions at 1 and 1000 s^{-1} to describe viscosity at low shear (η_{LS}) and high shear (η_{HS}), respectively.

2.3 Soft tribology

The friction of chocolate was measured on a mini-traction machine (MTM2, PCS Instruments Ltd) with a ball-and-disk tribopair fabricated from polydimethylsiloxane (PDMS) elastomer.[19] Both PDMS surfaces were smooth and hydrophobic. A sample volume of 20 ml was used for all chocolate samples with the inclusion of the pot filler. Friction coefficient was measured as a function of decreasing entrainment speed from 1000–1 mm s^{-1} followed by increasing speed from 1–1000 mm s^{-1}, and repeated 5 times during each test. A slide-to-roll ratio of 50% was used to obtain a combination of sliding and rolling motion between the surfaces, and the load was set at 2 N. Additionally, the data was filtered to ensure measurements were within ± 10% of these conditions, *i.e.* slide-to-roll ratio between 45–55%, load between 1.8–2.2 N and traction coefficient greater than zero. All tests were run at 37 °C to ensure chocolate was molten during measurements. A comparison of measurements collected from increasing *versus* decreasing entrainment speed revealed that decreasing speed generally produced sharper transitions in friction coefficient between lubrication regimes. Consequently, the measurements are presented as a function of decreasing entrainment speed from 1000–1 mm s^{-1} (and average of 5 repeats from the test). A minimum of two replicates were conducted per chocolate and averaged to obtain its Stribeck curve. An aqueous mastercurve was also generated for the same tribopair using glycerol solutions of varying viscosity to encompass all three regimes of lubrication.[2,19]

3. Results and discussion

3.1 Lubrication of molten chocolate

Friction is not a fundamental property of materials (*e.g.* viscosity), but rather a system property that depends on substrate properties and testing conditions.[1,2,20] However, tribology allows us to analyse differences in material properties provided the same tribopair and testing conditions are used for all samples. Friction coefficient is typically measured as a function of increasing fluid entrainment speed, which correlates to increasing film thickness between the interacting surfaces and gives rise to three distinct regimes: boundary (BL), mixed (ML) and elastohydrodynamic lubrication (EHL). The Stribeck curve for an aqueous Newtonian liquid across all three lubrication regimes is demonstrated by an empirical 'master curve' (refer to ESI†), obtained by testing water and glycerol solutions between the same tribopair used to test chocoloate.[2,19] In the case of simple Newtonian fluids, the fluid behaves as a continuum across all entrainment speeds, and bulk viscosity governs measured friction within the EHL regime. However, this is not true for multiphase fluids such as molten chocolate where individual phases may dominate friction at different entrainment speeds. Large differences are observed between the friction of chocolate and pure cocoa butter, as shown in Fig. 1a.

Previous work on chocolate[9] and microparticulate dairy dispersions[21] has shown that the Stribeck curves of different samples align when plotted as a function of $U\eta_{HS}$, since friction under elastohydrodynamic lubrication at high entrainment speeds (*i.e.* where the interacting surfaces are completely separated by the lubricant) is a function of the lubricant's high-shear viscosity. After differences in viscosity at high shear (1000 s^{-1}) are accounted for in Fig. 1b, the soft lubrication of molten chocolate of varying fat content collapses with the behaviour of water and cocoa butter in the EHL region, but diverges when $U\eta_{HS} < 0.04$ N m^{-1}. This indicates that chocolate lubrication is dominated by bulk viscosity at high shear in EHL, which we term "*thick-film lubrication*". In contrast, for $U\eta_{HS} < 0.04$ N m^{-1}, the frictional behaviour of chocolate deviates from the 'master curve', marking a transition to mixed lubrication that we refer to as "*thin-film lubrication*" henceforth.

The key to understanding why the frictional response of molten chocolate deviates from the 'master curve' is to consider the dependence of its viscosity on shear rate, given that cocoa butter is Newtonian. Molten chocolate is a concentrated suspension of solid particles (sugar, cocoa and milk) dispersed within a continuous liquid (cocoa butter). Its complex rheology is described by a yield stress and shear-thinning behaviour, which we have studied as a function of solid phase volume for the same milk chocolates investigated here and concluded is strongly influenced by particle aggregation.[22] The presence of

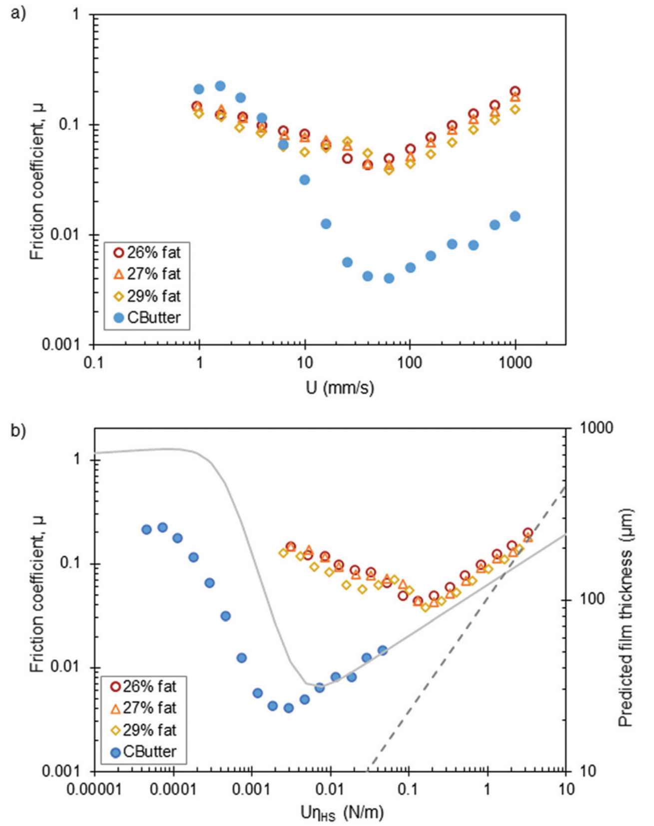

Fig. 1 Friction coefficient as a function of (a) entrainment speed and (b) entrainment speed × bulk high-shear viscosity at 1000 s^{-1} for chocolates of varying fat content. The master curve (solid line) was derived from an empirical model fitted to measurements of aqueous glycerol solutions. The dashed line represents minimum film thickness as a function of $U\eta$, predicted by de Vicente *et al.*[24,25] for elastohydrodynamic lubrication in the same setup.

particle interactions above roughly 50% solids is supported by the results of Shewan *et al.*[22], as it corresponds to the point of deviation away from the theoretical Maron Pierce Quemada (MPQ) model for non-interacting hard spheres.

We anticipate that the unique frictional response of molten chocolate arises from particle presence, which has a two-fold effect on lubrication through number of particles (solid volume fraction) and breakage of aggregates (demonstrated by shear thinning behaviour in Fig. 2). As such, solid particles are responsible for the deviation of chocolate from cocoa butter observed in thin-film lubrication, which we propose is caused by selective entrainment of solid particles smaller than the gap and shear-induced breakdown of aggregates which do enter the contact zone. Previously, we have shown that the tribological behaviour of shear-thinning lubricants in the absence of particles exhibits a similar secondary transition within the mixed lubrication region.[23] In shear-thinning fluids, the $U\eta$ value corresponding to this transition correlates with low-shear viscosity at 1 s^{-1}, which is much lower than the shear rate expected at the interfacial separation by convention.[23] We believe the same phenomenon occurs here so that the devi-

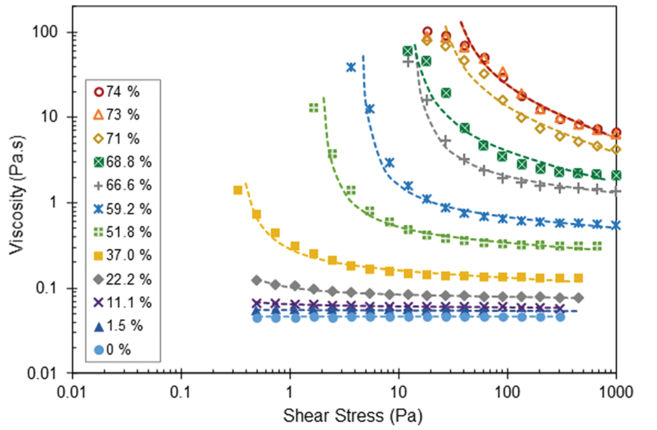

Fig. 2 Viscosity of chocolate as a function of solid fraction (w/w %), determined by diluting 26% fat chocolate with cocoa butter to produce mixtures from 71% to 1.5% solids. 0% corresponds to the viscosity of pure cocoa butter, while 71–74% correspond to the chocolate samples (26–29% fat). Dashed lines represent viscosity predicted by the Herschel–Bulkley model.

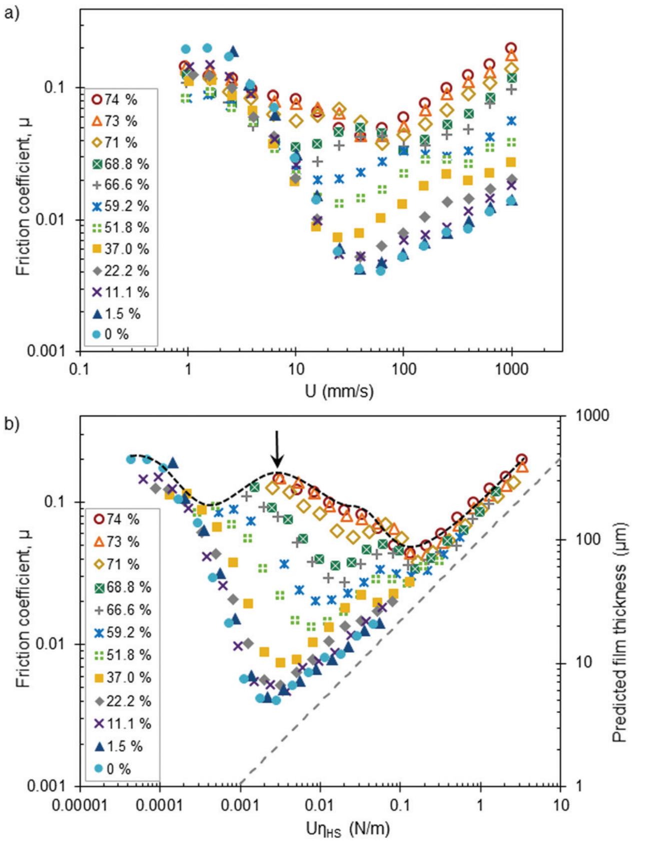

Fig. 3 Friction coefficient of chocolate as a function of solid fraction (w/w %) determined by diluting 26% fat chocolate with cocoa butter, shown in (a) friction coefficient as a function of entrainment speed and (b) friction coefficient as a function of entrainment speed multiplied by high-shear viscosity at 1000 s^{-1}. 0% corresponds to pure cocoa butter, while 71–74% correspond to the original chocolates (26–29% fat). The grey dashed straight line represents minimum film thickness in the contact (secondary axis on right) as a function of $U\eta$, predicted by de Vicente *et al.*[24,25] for elastohydrodynamic lubrication in the same setup. The black curve has been added as a guide for the eye.

ation of molten chocolate from the typical Stribeck curve is a function of its non-Newtonian rheology, caused by the presence of aggregated particles.

Additionally, since previous studies on chocolate tribology have revealed that solid particles are squeezed out of the contact zone by repeated back and forth motions,[13,14] we also reasonably expect that a fraction of particles are excluded from the sliding-rolling contact between ball and disk with decreasing gap size. All three chocolates transition from EHL to mixed lubrication at the same $U\eta_{HS}$ (~0.1 N m^{-1}, Fig. 1b), corresponding to a film thickness of ~30 μm. As a general rule for suspensions, particle confinement occurs when the gap is of similar order of magnitude to particle size – this is true for glass spheres, microgels, insoluble fibres and even plant cells.[2] In this case, 30 μm is relatively close to the chocolate's maximum particle size (~50 μm), which is roughly the same for the chocolates of varying fat content (data provided in ESI†).

3.1.1 Role of non-Newtonian rheology and particle entrainment. To further investigate the influence of shear-thinning behaviour and particle presence, we measured the tribological response of a series of samples prepared by diluting the 26% fat chocolate with increasing amounts of cocoa butter. The subsequent decrease in solid phase volume influences both rheology and tribology as demonstrated in Fig. 2 and 3, respectively. Solid fraction (w/w %) was estimated by assuming all 26% fat is in the continuous phase, such that solid particles account for the remaining 74%. The shear-thinning behaviour of chocolate is associated with the breakage of aggregated particles into smaller clusters. As chocolate is increasingly diluted with cocoa butter, both its yield stress and degree of shear-thinning decrease (Fig. 2, Table S1†). The decrease in viscosity leads to a decrease in measured friction (Fig. 3a) at the same speed, and the shape of the Stribeck curve shifts closer to the response of pure cocoa butter (Fig. 3b) as the solid content approaches zero. Furthermore, when the particle phase volume is decreased below a certain threshold (roughly 20% from Fig. 3a), the particles cease to visibly affect lubrication—the Stribeck curves for chocolate with 1.5 and 11% solids are nearly identical to that of pure cocoa butter, in agreement with rheology (Fig. 2) where 20% solids marks the transition from shear-thinning to Newtonian behaviour. This indicates there is a degree of correlation between the rheological and tribological behaviours of molten chocolate, which is not surprising given that both are strongly dependent on the presence of particles, its volume fraction and the degree of aggregation.

Closer inspection of the curves presented in Fig. 3b reveals that the secondary ML-EHL transition ('hump' marked by black arrow) is only observed in chocolate containing more than 20% solids, and its position varies with solid phase volume. Our hypothesis is that the secondary transition arises from complex fluid-surface interactions which create local

EHL contacts between surface asperities as opposed to a continuous fluid film; we refer to this phenomenon by the term "*local EHL*". The emergence of the 'hump' in the Stribeck curves marks the solids concentration at which molten chocolate begins behaving as a non-Newtonian lubricant. Under these conditions, large particles are either excluded from the gap, or if the large particles are aggregates, they break down into smaller clusters so that lubricant entrainment into the contact zone is governed by non-Newtonian fluid mechanics. Consequently, the rheology of molten chocolate under low shear must also be considered when interpreting its tribological response, following the same method of analysis as non-Newtonian lubricants.[23] Specifically, viscosity at low shear (η_{LS}, represented by viscosity at 1 s^{-1}) is used to scale the Stribeck measurements and replotted in Fig. 4a. To investigate the influence of solid phase volume, the critical $U\eta_{LS}$ value corresponding to the onset of this secondary transition is derived graphically (shown by the blue arrow in Fig. 4a as an example for 51.8% solids chocolate), and the results are plotted as a function of low-shear viscosity in Fig. 4b. A linear relationship is seen between critical $U\eta_{LS}$ and η_{LS}, in agreement with our previous observations for model shear-thinning lubricants.[23] This indicates that the secondary transition phenomenon is reasonably interpreted to result from the shear-thinning behaviour of molten chocolate, which leads to complex fluid-surface interactions including local EHL behaviour. Considering that molten chocolate is a suspension of hard, aggregated particles, we anticipate this deviation from the typical Stribeck curve relates to the breakdown of large aggregates during fluid entrainment, which ultimately also contributes to its shear-thinning rheology.

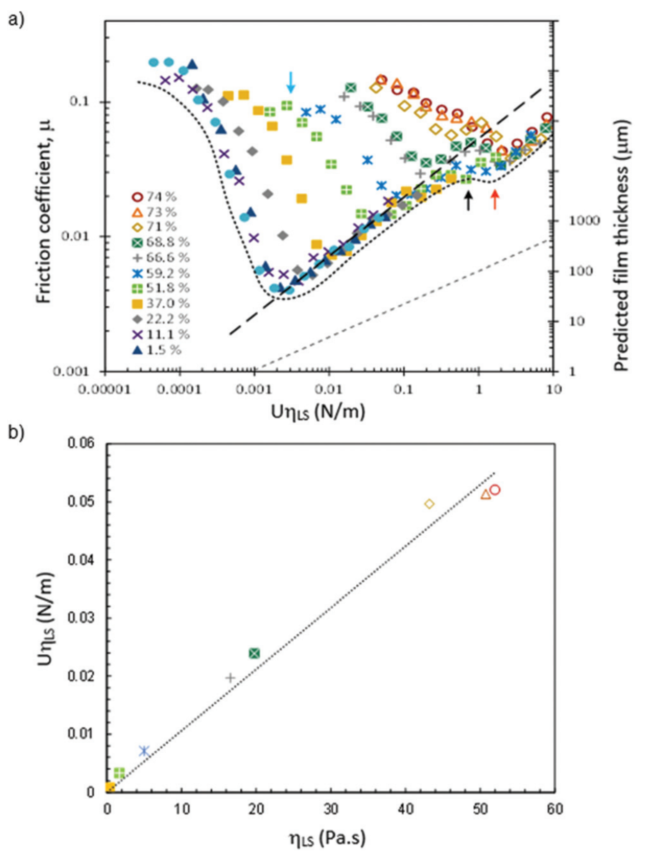

Fig. 4 Friction coefficient of chocolate as a function of solid fraction (w/w %) determined by diluting 26% fat chocolate with cocoa butter, shown in (a) friction coefficient as a function of entrainment speed multiplied by low-shear viscosity at 1 s^{-1} and (b) critical $U\eta_{LS}$ as a function of low-shear viscosity at 1 s^{-1}. 0% corresponds to pure cocoa butter, while 71–74% correspond to the original chocolates (26–29% fat). The grey dashed straight line represents minimum film thickness in the contact (right axis) as a function of $U\eta$, predicted by de Vicente *et al.*[24,25] for elastohydrodynamic lubrication in the same setup. The additional black dashed lines in plot (a) are provided to guide the eye, while the line in plot (b) indicates a linear relationship. The arrows on plot (a) mark the local EHL transition (blue arrow), transition within EHL lubrication (black arrow) and onset of macro-EHL (red arrow).

Normalising the Stribeck curves with low-shear viscosity identifies an alternate transition within the EHL regime, indicated by the bump in the sketched curve in Fig. 4a (black arrow). This transition is absent in the Stribeck curves of model suspensions[23] where the lubricant is shear-thinning but does not contain particle aggregates (*i.e.* no yield stress). Interestingly, this transition in the EHL regime cannot be fully attributed to shear-thinning behaviour as in Fig. 4b, since the data in Fig. 5a does not follow a linear relationship as was previously demonstrated for non-Newtonian lubricants. Closer inspection of Fig. 4a reveals that the tribological response of molten chocolate follows a behaviour similar to the EHL regime up to a critical $U\eta_{LS}$ when scaled with low-shear viscosity (black arrow, Fig. 4a). Above this critical value, a transition occurs (red arrow, Fig. 4a) whereby lubrication switches to another EHL region that is not governed by the low-shear viscosity. One possible explanation is that, since the gap is predicted to be of the same order of magnitude as particle size (refer Fig. 3), aggregated particles may be entrained along with the fluid into the contact zone and break down under shear. This breakdown of aggregates would mean that the lubricant's viscosity within the contact zone is actually lower than the low-shear viscosity used to scale the data in Fig. 4a, which explains the observed shift to higher $U\eta$ when the curves are compared to the EHL behaviour governed by low-shear viscosity (indicated by dashed straight line, Fig. 4a). At sufficiently high $U\eta$, chocolate lubricant enters the true EHL regime that is largely dependent on high-shear viscosity, such that the curves for molten chocolate collapse in the EHL regime when the measurements are scaled by high-shear viscosity (Fig. 3). We anticipate that, if this EHL transition in the Stribeck curve results from the entrainment of aggregated particles, the onset of the true EHL (red arrow, Fig. 4a) should scale with the amount of particles in the fluid *i.e.* the solid content of molten chocolate. For systems with a higher proportion of aggregates or larger-sized aggregates, a higher $U\eta$ (*i.e.* larger gap separation) is required to entrain them into the contact zone. Fig. 5b indicates a power-law relationship exists between the critical $U\eta_{LS}$ (for the onset of true EHL) and solid fraction of chocolate rather than a linear relationship. The power-law

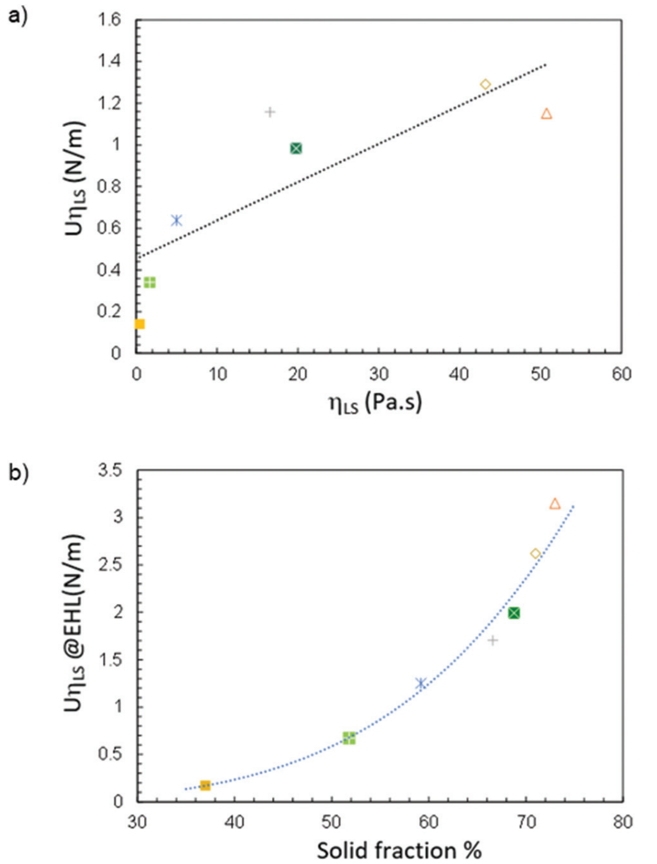

Fig. 5 (a) Critical $U\eta_{LS}$ for the EHL transition (marked by black arrow in Fig. 4a) plotted as a function of low-shear viscosity at 1 s^{-1}. The dashed line represents a linear relationship; and (b) critical $U\eta_{LS}$ for the onset of true-EHL (indicated by red arrow in Fig. 4a) plotted as a function of solid content (w/w%). The dashed line represents a power-law relationship with exponent = 4. Legend is the same as Fig. 3a.

dependency is not surprising given that when the solid volume fraction of a particle suspension approaches the maximum packing fraction, its overall rheology becomes more solid-like – this eventually stops fluid entrainment and pushes the critical $U\eta$ for transitioning to true EHL to an infinite value.

Based on the observed trend, we suggest that a greater concentration of particles, a higher viscosity at low shear and a greater degree of shear-thinning generally increase friction between sliding surfaces in the case of chocolate. This concurs with recent findings by Samaras *et al.*[26] who also concluded that the friction coefficient of molten chocolate increases with increasing cocoa solids content using a reciprocating PDMS disk on glass plate setup. In Fig. 3, pure cocoa butter (a Newtonian liquid without particles) demonstrates much lower friction coefficients when compared to molten chocolate (characterised as a Herschel–Bulkley fluid that contains particles). Lee *et al.*[12] concluded that liquid-like behaviour at the sliding interface results in smooth sliding for chocolate, which reduces measured friction. On the other hand, solid-like behaviour leads to an irregular "stick-slip" motion which increases friction.[12] Hence, it follows that more particles are entrained into the gap as the solid phase volume of chocolate increases, and increases measured friction under thin-film lubrication conditions as observed on Fig. 1b. On a more subtle note, the presence of particles in a suspension can also reduce friction by converting sliding of surfaces to rolling of particles.[15] Commonly referred to as the "ball-bearing" lubrication mechanism, this has been suggested to occur in suspensions of softer particles such as microparticulated whey protein (MWP),[27] and because of their lubricating ability, small MWP particles may positively contribute to the perception of *creaminess.*[28]

3.1.2 Influence of particle interactions. The role of particle aggregates in the soft lubrication of molten chocolate can be investigated by controlling the inter-particle attractive forces. Attractive interactions between hydrophilic sugar particles in a continuous fat (hydrophobic) medium result in particle aggregation. This has been demonstrated by Shewan *et al.*[22] for the same 26% and 29% fat chocolates, as well as biscuit creams. In relation to chocolate friction, we hypothesise that a lower degree of aggregation will reduce the degree of shear-thinning behaviour and thus lead to lower friction, shifting towards the tribological response of Newtonian lubricants. Emulsifiers such as lecithin or polyglycerol polyricinoleate (PGPR) are known to minimise particle–particle attractions and decrease viscosity. To test our hypothesis, we added between 0.3 to 1% PGPR (Danisco) to 26% fat chocolate to study the effects of reduced aggregation on friction.

Rheological measurements reveal that the addition of PGPR reduces low-shear viscosity and degree of shear-thinning (proven by the reduced exponent of the Herschel–Bulkley fitting in Fig. 6, reported in Table S2†). Fig. 7 shows that, by adding PGPR to molten chocolate, its tribological response shifts closer towards the behaviour of Newtonian lubricants (the transition in the mixed-EHL regime becomes less pronounced), which we propose arises from the reduced low-shear viscosity and lower degree of shear-thinning. Lee *et al.*[12] also found that the addition of 0.4% lecithin to chocolate leads to better mixing of hydrophilic particles (*e.g.* sugar and

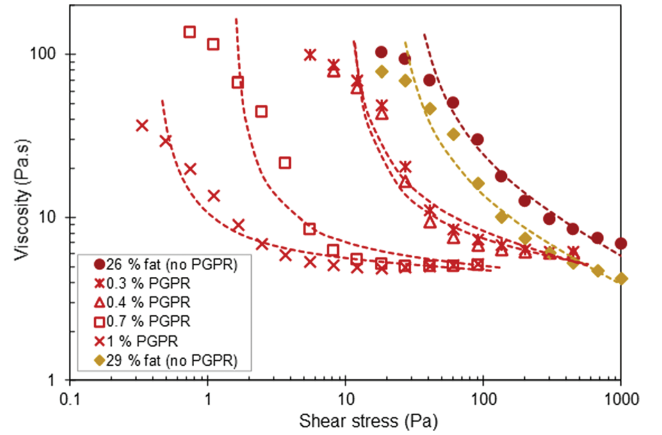

Fig. 6 Viscosity plotted as a function of shear stress for PGPR added to 26% fat chocolate. Note: %PGPR = mass of PGPR/(mass of PGPR + mass of chocolate).

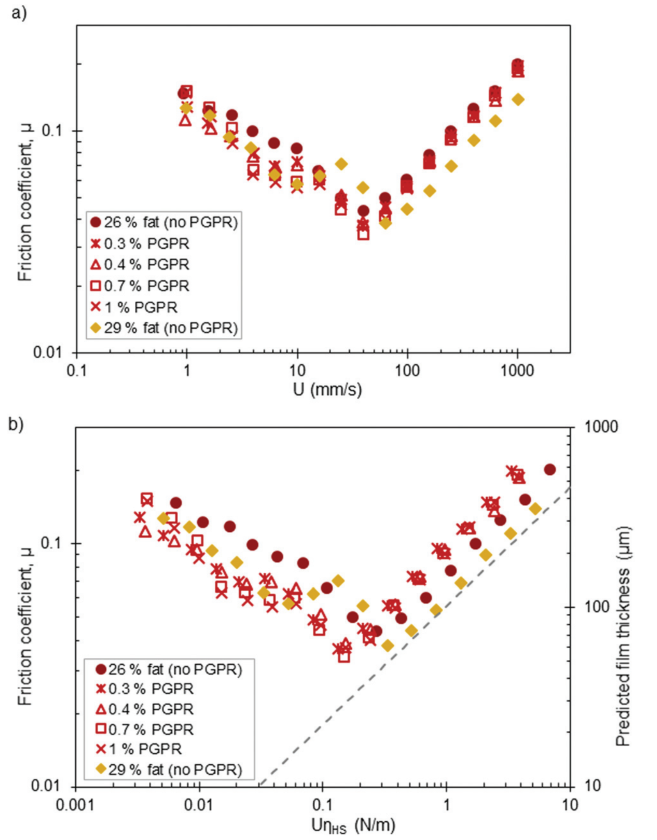

Fig. 7 Friction coefficient as a function of (a) entrainment speed and (b) entrainment speed × bulk high-shear viscosity at 1000 s^{-1} for 26% fat chocolate with PGPR added to it. The dashed line represents the minimum film thickness for elastohydrodynamic lubrication predicted by de Vicente *et al.*[24,25] Note: 0% PGPR represents 26% fat chocolate without PGPR; 29% fat without PGPR is added for comparison.

milk powder) with the continuous fat phase, which reduces particle aggregation, viscosity and friction at the sliding interface. While the addition of PGPR has little effect on high-shear viscosity (*i.e.* curves converge at high shear rates), 29% fat chocolate has a lower viscosity than 26% fat chocolate at both low and high shear. Yet, increasing the amount of PGPR added to 26% fat chocolate produces a larger drop in friction under thin-film lubrication ($U\eta \sim 0.02$ N m^{-1}). This supports our hypotheses that (1) the variation in friction in thin film lubrication is the result of particle exclusion and/or the breakdown of aggregates during their entrainment into the ball-disk contact, and (2) particle entrainment promotes solid-like behaviour at the sliding-rolling contact and thus increases the friction of molten chocolate. Additionally, the thin-film regions of Stribeck measurements for 26% fat chocolate containing 0.7 and 1% added PGPR overlap with that of 29% fat chocolate without PGPR, which suggests that the friction of low-fat chocolate can be moderated by controlling aggregation.

3.2 Friction in relation to oral processing

While certain sensory attributes (*e.g. thickness*) are strongly correlated to changes in viscosity, other attributes (*e.g. creaminess, mouthcoating*) are not as easily explained.[29] It is reasonable to hypothesise that a more viscous fluid will be perceived as more *mouthcoating* because it is not as easily dislodged from oral surfaces. However, the interaction of emulsion droplets with oral surfaces means that tribology also influences perceived mouthfeel.[29] A previous study by Carvalho-da-Silva *et al.*[7] comparing two milk chocolates of identical viscosity linked the less *mouthcoating* chocolate to higher friction coefficient measured at high speed (elastohydrodynamic lubrication regime). Low-fat milk chocolate is generally perceived as more *bitter* and, surprisingly, more *fatty/oily* in terms of texture, the latter of which is most likely because panellists associate fat with *viscous* and *mouthcoating*.[30] A more recent study by Qian *et al.*[31] has revealed that the perceived *smoothness* of chocolate is strongly correlated to the lubricating properties of model chocolate boluses (50% chocolate–50% artificial saliva) – smoother chocolates were linked to a lower average coefficient of friction. Furthermore, chocolates of increasing cocoa concentration demonstrated higher friction coefficients and were linked to lower perceived *smoothness*.[31]

Our previous work on dark chocolates has shown that the EHL region of the tribological response is governed by the sample's high-shear viscosity, but with decreasing gap size, the curve transitions to mixed lubrication at a film thickness which corresponds to particle size and solid phase volume.[9] The same is observed in milk chocolates in Fig. 8; undiluted chocolate transitions from EHL to mixed lubrication at a film thickness of ~30 μm, but this transition shifts to thinner films (~8 μm) after it is diluted with PBS to 50% chocolate. This is linked to dissolution of sugar upon dilution with an aqueous solution, which dramatically decreases bulk viscosity. The particle size distribution of the milk chocolates (refer ESI†) suggests a bimodal distribution composed of two peaks at approximately 20 and 5 μm, which coincide with the expected particle size of sugar particles and insoluble cocoa nibs respectively based on our previous work.[9]

Undiluted chocolate (particle suspension) and its boluses (oil-water emulsion) are shear-thinning up to a dilution of 50% chocolate, but the degree of shear-thinning behaviour decreases upon further dilution (Fig. 8a). Fig. 8b reveals that the reduction in viscosity which results from dilution with PBS shifts the Stribeck measurements towards boundary lubrication, as observed previously for chocolate.[9] Furthermore, the tribological difference observed between 26, 27 and 29% fat chocolate before dilution disappears when it is diluted to 70% chocolate, but reappears upon further dilution to 50% chocolate and, remarkably, is amplified. The difference observed in thin-film lubrication of 50% chocolate boluses of varying fat content follows the same trend as undiluted chocolate (*i.e.* 29% fat demonstrates lower friction compared to 26% fat chocolate), albeit to a larger extent in boundary lubrication. For oil–water emulsions between hydrophobic surfaces, lower friction generally relates to the formation of an oil film coating the interacting surfaces.[32] In this context, it is not surprising that 29% fat chocolate is more lubricious than its 26% fat counterpart. Closer inspection of the 70% model boluses shows a similar transition in the EHL regime (black arrow, Fig. 8b) to that observed in

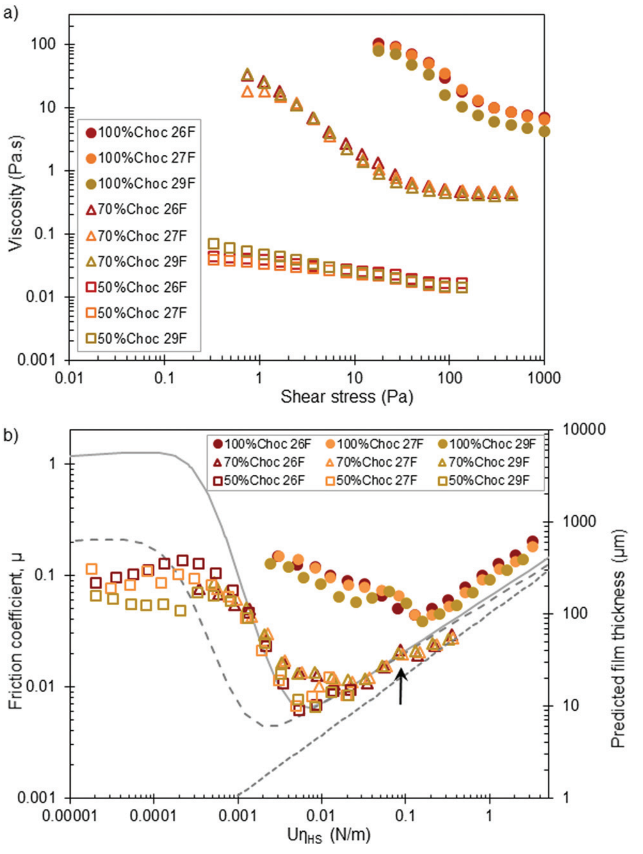

Fig. 8 (a) Viscosity plotted as a function of shear stress for model bolus systems, prepared by diluting molten chocolate with PBS. % indicates the mass of chocolate/(mass of chocolate + mass of PBS), 26F, 27F and 29F represent 26, 27 and 29% fat. (b) Friction coefficient as a function of entrainment speed × bulk high-shear viscosity for model bolus systems. The empirical master curve represents the lubrication of aqueous solutions (solid line) and cocoa butter (dashed line). The dashed straight line represents the minimum film thickness for elastohydrodynamic lubrication, as predicted by de Vicente *et al.*[24,25] The black arrow indicates a transition within the EHL regime.

cocoa-butter chocolate dilutions (black arrow, Fig. 4a). We suggest this transition arises from the exclusion of large-sized aggregates/droplets from the interfacial gap as gap size decreases below $U\eta_{HS} \sim 0.1$ N m^{-1} (*i.e.* 20 μm).

In order to interpret these findings, the Stribeck curves of chocolate boluses should be considered in relation to that of their individual components. Before dilution, the dispersed phase (sugar, cocoa and milk solids) in chocolate is effectively non-deformable and thus increases friction when entrained into the ball-disk contact zone. There are two dispersed phases in chocolate bolus emulsions – cocoa solids and oil droplets – the latter of which can be deformed by the normal load on the ball depending on the oil : water viscosity ratio. De Vicente *et al.*[32] studied the friction of oil-in-water emulsions between hydrophobic PDMS surfaces and concluded that friction varies significantly based on the following two scenarios:

1. The aqueous phase enters the sliding contact and dominates film formation (and measured friction) when the viscosity of dispersed oil droplets is less than or comparable to that of the continuous water phase.

2. The oil phase enters the contact zone and dominates measured friction when the dispersed oil is at least four times more viscous than the continuous water phase.

At high viscosity ratios, the dispersed droplets are non-deformable; they enter the contact inlet area, collide with each other and coalesce to form a pool of viscous liquid. The pool then acts as a reservoir to supply the contact zone since the lower viscosity fluid is not able to displace it (viscous shear stress is too small).

Cocoa butter is an order of magnitude more viscous than the aqueous phase, but both are Newtonian (refer ESI†). The general sequence in order of decreasing viscosity is 100% chocolate (most viscous), 70% chocolate–PBS mixture, cocoa butter, 50% chocolate–PBS mixture and aqueous phase (least viscous), as shown in Table 1. The aqueous phase in 70% chocolate boluses (~100 mPa s on average) is 3 times more viscous than cocoa butter (~46 mPa s), so it follows that the continuous aqueous phase dominates friction. However, when chocolate is further diluted to 50% of the bolus, the viscosity of the aqueous phase decreases (~5 mPa s) to 9 times less than that of cocoa butter. Consequently, the aqueous phase is preferentially squeezed out of the gap and the fat phase dominates thin film lubrication in chocolate boluses, so that reduced friction is observed between sliding surfaces for 29% fat chocolate when compared to 26 and 27% fat chocolate.

3.2.1 Conceptual model of bolus-oral surface interactions. Based on these findings, we propose different mechanisms dominate the oral tribology of chocolate, shown in Fig. 9 as a function of increasing dilution with saliva in relation to increasing chewing time. In general, the Stribeck curve for chocolate can be divided into either thick-film lubrication measured at high entrainment speeds where bulk hydrodynamics dominate, or thin-film lubrication measured at low entrainment speeds where separate components (*e.g.* particle aggregates) dictate the interaction between the sliding surfaces.

– ***Before dilution with saliva***: Chocolate acts as a bulk fluid in thick films, but larger particles are excluded from the sliding contact area in thin films such that the Stribeck curve deviates from the typical shape (measured friction decreases with fewer entrained solids). The shear-thinning behaviour of chocolate leads to a secondary transition in ML region.

Table 1 Viscosity of bulk chocolate–PBS model boluses compared against the viscosity of its constituent fluid phases (aqueous and cocoa butter). Reported values in mPa s represent Herschel–Bulkley predictions of viscosity at 1000 s^{-1}

Chocolate	70% Choc bulk	70% Choc aqueous	50% Choc bulk	50% Choc aqueous	Cocoa butter
26% fat	349	112	22	6	46
27% fat	367	104	20	5	—
29% fat	328	95	21	5	—

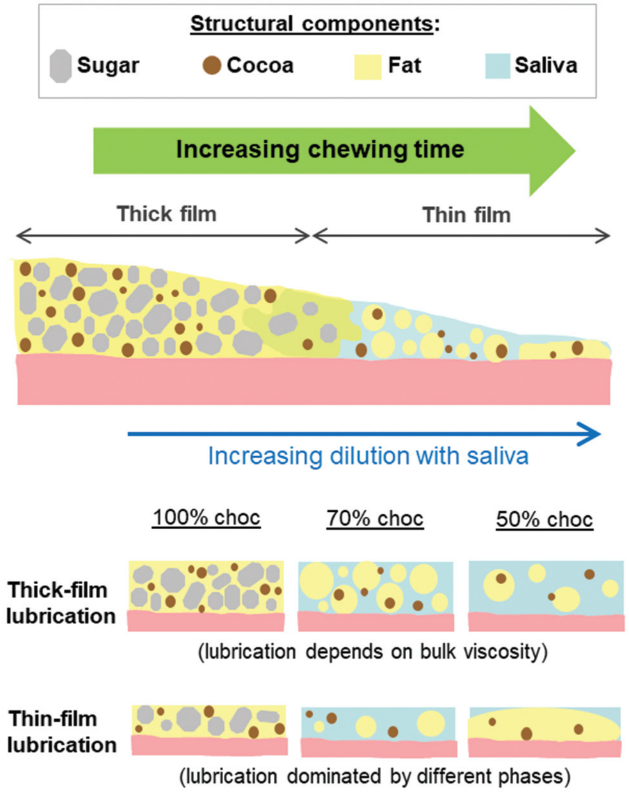

Fig. 9 Schematic diagram illustrating the proposed mechanisms that determine lubrication in chocolate as a function of increasing dilution with saliva. In thick-film lubrication (high entrainment speed), the measured friction for all chocolate and corresponding boluses is determined by bulk viscosity. In contrast, thin-film lubrication behaviour (low speed) deviate from bulk hydrodynamics such that individual phases dominate measured friction. The dominating phase progresses from solid particles in undiluted chocolate, to the aqueous phase in 70% chocolate boluses due to inversion of the emulsion, and then the oil phase in 50% chocolate boluses (~point of swallow).

– ***After dilution with saliva to 70% chocolate***: Chocolate inverts to form an oil-in-water emulsion. The bulk emulsion determines friction under thick film conditions, while the continuous aqueous phase occupies most of the contact area in the fluid entrained between the sliding surfaces and therefore dominates thin-film lubrication.

– ***After further dilution to 50% chocolate***: Chocolate is an oil-in-water emulsion comprising a low fraction of oil (<15% w/w) and low-viscosity aqueous phase. Bulk viscosity determines lubrication in thick films, but the dispersed oil phase coalesces and coats the interacting surfaces, thereby controlling lubrication in thin film conditions.

4. Conclusions

This study has deconvoluted the complex tribological response of molten chocolate, which has implications to its performance during oral processing. The frictional behaviour of chocolate is complicated by the confinement and exclusion of its components from the contact zone at decreasing gap height. By diluting chocolate with cocoa butter, we have investigated the relationship between solid phase volume and measured friction. Cocoa butter is an effective lubricant for hydrophobic surfaces, demonstrating low friction under boundary conditions. In comparison, the tribological behaviour of molten chocolate includes additional transitions in mixed and elastohydrodynamic lubrication linked to the exclusion of large particles and breakdown of entrained aggregates within the interfacial gap. Particle entrainment is promoted by increasing solid phase volume, but a fraction of the particles is excluded from the gap once confinement begins in thin films. Decreasing gap height drives the transition from bulk fluid to particle-excluded fluid, and likely promotes further exclusion of particles from the contact as fluid viscosity decreases and thinner films are achieved. Consequently, the Stribeck curve for chocolate can be rationalised as a series of Stribeck curves corresponding to entrained suspensions of different particle volume and/or viscosity due to the shear-induced breakdown of aggregates within the sliding contact.

Reducing the fat content of chocolate increases its effective solid phase volume, which promotes particle entrainment and increases friction in the thin-film regime. Furthermore, the difference in the thin-film friction of chocolate of varying fat content is amplified once chocolate has been sufficiently diluted with an aqueous buffer to form an oil-in-water emulsion. Given the link between chocolate tribology and mouthfeel attributes,[7,31] we expect that the frictional mechanisms identified in this study will contribute towards sensory differences between reduced-fat and regular chocolate during oral processing. In relation to chocolate boluses, we propose that different phases dominate oral lubrication depending on the degree of dilution and corresponding film thickness, which suggests certain sensory differences (*e.g. mouthcoating, oily, bitter*) may only be detected after a certain time-point in the chewing sequence.

While we have investigated the specific effects of phase volume and particle aggregation on soft lubrication in chocolate, the influence of other factors remain to be studied. We observe that particle entrainment increases measured friction – this is most likely associated with angular-shaped sugar particles, which comprise a major fraction of the solids in chocolate (47% w/w of chocolate, ~66% of solids). As the shape of a particle will affect its ability to roll, the use of spherical particles with a low aspect ratio may be a potential lever for modulating friction in low-fat chocolate. Moreover, there are several food systems with a similar structure to chocolate, for example: nut butters, concentrated purees and pastes. Thus, the conclusions and approach presented in this study are not only relevant to chocolate, but are applicable to other multiphase systems too.

Author contributions

Sophia A. Rodrigues: Conceptualization, methodology, investigation, analysis, writing – original draft. Heather M. Shewan:

Conceptualization, analysis, writing – reviewing & editing. Yuan Xu: Analysis, writing – reviewing & editing. Nichola Selway: Project administration, supervision, writing – reviewing & editing. Jason R. Stokes: Funding acquisition, resources, supervision, analysis, writing – reviewing & editing.

Conflicts of interest

No conflicts of interest to declare.

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