Journal of Food Engineering 139 (2014) 24-30

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Soft tribology of oil-continuous emulsions

M. Douaire*, T. Stephenson, I.T. Norton

Department of Chemical Engineering, the University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

Article history: Received 17 September 2013 Received in revised form 26 February 2014 Accepted 14 April 2014 Available online 2 May 2014

Keywords: Emulsion Lubrication Tribology Oral behaviour

ABSTRACT

Lubrication behaviour of foodstuff is related to mouthfeel perception and consumer appreciation. Soft tribology of food related products has mainly been investigated with semi-solid food, polymer solutions and water continuous emulsions, and this is the first study aimed at investigating soft tribolocigal behaviour of oil continuous emulsions. All the emulsions considered here exhibit the same trends in terms of lubrication behaviour, where little boundary lubrication is observed at the entrainment speed considered. The volume of dispersed aqueous phase affects overall tribology of oil continuous emulsions via an increase in their dynamic viscosity. Increasing the phase volume leads to an increase in friction in the elastohydrodynamic regime whereas the lubrication in the boundary regime is improved. Elastohydrodynamic lubrication is independent of the aqueous phase composition and the type of emulsifier present at the water-oil interface. These parameters affect boundary lubrication of emulsion systems exhibiting droplet size bigger than the elastohydrodynamic oil film thickness. This is expected to have a significant impact on the design of low fat emulsions that match the lubrication properties of their full fat version.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Tribological behaviour of many food and personal care products plays an important part in their sensory perception. It dictates how a cosmetic cream feels upon skin application, and relates to the mouthfeel of food products. Consequently, there is currently much ongoing research which attempts to use the field of tribology to accurately predict the mouthfeel properties of a semi-solid through the material's behaviour as a lubricant (Dresselhuis et al., 2007; Malone et al., 2003; van Aken et al., 2007). De Wijk and Prinz showed that oral perception of semi-solid foods is related to their lubrication behaviour (de Wijk and Prinz, 2005). This is of crucial importance for low fat food, since creaminess and thickness, attributes that are usually provided by the fat content, are perceived through friction.

Emulsions are ubiquitous in foods and cosmetic products and have proven useful in the areas of fat reduction and time/pressure dependent release of flavour compounds, nutrients or vitamins. Their frictional behaviour is not only related to the percentage of fat but also the viscosity of the emulsion (Bongaerts et al., 2007; van Aken et al., 2007). However, emulsions are mostly shear thinning, rending the prediction of their lubrication behaviour difficult.

In the area of tribological behaviour of food related products, several studies have been published, aimed at understanding lubrication of polymer solutions (Cassin et al., 2001; de Vicente et al., 2005, 2006a; Mills et al., 2013), fluid gels and gelled particles (Chojnicka et al., 2008; Fernández Farrés et al., 2013; Gabriele et al., 2010; Garrec and Norton, 2012) and oil in water emulsions (de Vicente et al., 2006b). Lubrication behaviour of mayonnaise, a fairly ubiquitous water continuous food emulsion, was examined by Giasson and co-workers (Giasson et al., 1997). Their results show that friction depends mainly on the properties of the dispersed particles, such as size, stiffness and hydrophobicity. de Vicente et al., 2006b showed that soft lubrication behaviour of water continuous systems also depends on the viscosity ratio between the two immiscible phases, with the dispersed phases determining the friction properties when its viscosity is high enough.

The tribology of water-in-oil emulsions has thus far only been studied in the context of aqueous impurities in an oil lubricant (Benner et al., 2006; Liu et al., 1994). Under heavy contact loads (hundreds of Newtons), and for conventional tribology it has been shown that water in oil emulsions behave as pure oil (Benner et al., 2006) for emulsions containing up to 30% water. The hydrody-namic film thickness is similar to pure oil systems for most emulsions, with the exception of emulsions containing dispersed water droplets which are smaller or of the same scale as the pure oil film itself, in which case the film gets thicker (Wan et al., 1984). Other studies suggest that bigger droplets form patches in the contact zone, decreasing the effective viscosity of the emulsion system (Kimura et al., 1996; Liu et al., 1994). Fat continuous systems







^{*} Corresponding author. Tel.: +44 1214145284. E-mail address: m.douaire@bham.ac.uk (M. Douaire).

containing particles have also been investigated. Luengo and coworkers studied tribology of chocolate and related its lubrication behaviour to the constitution of the continuous fat phase and the average size of sugar crystals, cocoa solids and lactose particles (Luengo et al., 1997).

However, the above studies refer to tribological experiments using hard contacts (steel-steel or steel-glass), unlike most studies aimed at relating sensory perception to friction, which involves evaluation of the latter through soft tribology (steel-elastomer contact). This paper presents the first study, to the author's knowledge, of soft tribology analysis of water in oil emulsions. This study is aimed at investigating the effects of ball load as well as emulsion formulation, such as phase volume, emulsifier type and concentration, aqueous phase composition, on soft lubrication behaviour.

The above studies refer to tribological experiments using hard contacts (steel-steel or steel-glass) to characterise lubrication of oil continuous systems. However, most studies aimed at relating sensory perception to friction in food applications have been realised with the aid of soft tribology (steel-elastomer contact) to characterise the friction. This paper presents the first study, to the author's knowledge, of soft tribology analysis of water in oil emulsions. This study is aimed at investigating the effects of ball load as well as emulsion formulation, such as phase volume, emulsifier type, emulsifier concentration and aqueous phase composition, on soft lubrication behaviour.

2. Material and methods

2.1. Emulsion preparation

PRPG and kCarrageenan were obtained from Cargill (US), Tween 80, alginate and potassium chloride from Sigma (UK) and hydrophobic silica particles from Wacker Chemie AG (Germany). Sunflower oil was bought from the local store. Emulsions were realised with a high shear mixer (Sylverson, UK) with emulsifying time (up to 10 min) and rotation speed (up to 10,000 RPM) adjusted depending on the desired droplet size.

2.2. Physical properties

The droplet sizes were measured using a High Performance Particle Sizer (Mastersizer, Malvern Instruments, UK). Sample viscosity was measured using a Gemini HR Nano stress-controlled rheometer (Malvern Instruments, UK).

2.3. Tribology

The friction coefficient (a measure of lubricity) of a material can be determined through the use of a tribometer. The working part of a tribometer is composed of two moving components; for soft, semi-solid samples these are usually a ball and a disk. These components rotate in the same direction such that any fluid or semisolid material placed in the sample chamber will be entrained between the two moving parts. Depending on the entrainment speed and especially the viscosity of the sample, the mode of lubrication can be determined.

Frictional properties were measured using a Mini Traction Machine (MTM, PCS Instruments, UK). A 3/4 in. AISI 400 stainless steel ball (PCS Instruments, UK) was loaded against the face of a silicone flat disc (Samco Silicone Products Ltd, UK). These selected materials are known to provide a strong correlation between frictional data and oral response (Malone et al., 2003). The load (W) was set to 3N except when testing the effect of load on friction, where it was set to either 1, 3 or 7N. The Slide-Roll Ratio was set

to 50% for all experiments and each set of measurements was performed in triplicates to ensure repeatability.

Frictional behaviour is usually shown in the form of a Stribeck curve (Fig. 1) as presented in the works of Chen and Stokes (2012), Selvway and Stokes (2013) and de Vicente et al. (2006a), where three main regimes of lubrication can be observed: boundary (at low entrainment speeds and low viscosities), mixed (moderate entrainment speeds and viscosities), and hydro/elasto-hydro-dynamic (high entrainment speeds and viscosities). Boundary lubrication is prevalent when there is very little fluid between the surfaces, meaning that there is a large amount of contact between the two surfaces themselves. The hydrodynamic regime exists at higher entrainment speeds, where there is enough lubricant of sufficient viscosity entrained between the surfaces to ensure that the pressure in the fluid prevents the surfaces from touching (Dresselhuis et al., 2007).

The parameters investigated in this study, as well as details on emulsions preparation, are summarised in Table 1.

3. Results

3.1. Effect of ball load on Stribeck curves

The friction coefficient as a function of entrainment speed for 40% water in oil emulsions at various ball loads is shown in Fig. 2. In the case of water in oil emulsions, the region where the boundary regime is observed is limited, if not nonexistent, indicating that for the range of entrainment speeds studied, fluid is entrained between the ball and disc. As the entrainment speed increases, fluid entrainment becomes more significant, thus reducing the friction coefficient. Considering the high variability of data in this so-called mixed regime, the decrease in friction coefficient cannot be statistically attributed to the load variation. A further increase in entrainment speed results in even more fluid entrained, leading to an increase in friction coefficient; this is the hydrodynamic regime. The entrainment speed required to enter the hydrodynamic regime is increased for higher loads. This is because the film of fluid created between the moving parts needs to be able to sustain an increasing load, therefore requiring higher fluid pressure. However, the friction coefficient is somewhat higher for reduced load. Depending on the applied load, the transition to elastohydrodynamic lubrication occurs at different entrainment speeds: 60 mm s⁻¹ for loads of 1N and 3N, and 100 mm s⁻¹ for



Fig. 1. Idealised sketch of a Stribeck curve, where μ is the friction coefficient (–), *U* the entrainment speed (mm s⁻¹), η the fluid dynamic viscosity (Pa s) and *W* the applied load (N).

| Table 1 | |
|------------|---------------|
| Parameters | investigated. |

| Parameter | Range | Emulsion formulation |
|------------------------------|--|---|
| Ball load Phase volume | 1N, 3N and 7N 0%, 20%, 40% and 60% water | 40% water, 4% PGPR 4% PGPR Fixed PGPR/water ratio = 0.1 For each set of emulsions, the emulsification time and energy were adjusted to keep droplet size constant |
| Doplet size | 0.5 μm and 10 μm | 40% water 60% water For each set of emulsions, the emulsification time and energy were adjusted to keep droplet size constant, with a fixed PGPR/water ratio of 0.1 |
| Dispersed phase viscosity | 0.001Pa s, 0.013Pa s and 0.5Pa s and a gel | 20% aqueous phase 40% aqueous phase The viscosity was varied by adding sodium alginate (1% or 2%), gelling of the aqueous phase with 1% κ-carrageenan For each set of emulsions, the emulsification time and energy were adjusted to keep droplet size constant, with a fixed PGPR/water ratio of 0.1. |
| Emulsifier type | PGPR, Span 80 and pickering particles | 40% water emulsions For each set of emulsions, the emulsification time and energy were adjusted to keep droplet size constant, with a fixed PGPR/water or span 80/water ratio of 0.1 |
| Emulsifier concentration | 1%, 2%, 4% and 7% | 20% water emulsions with PGPR as an emulsifier For each set of emulsions, the emulsification time and energy were adjusted to keep droplet size constant |



Fig. 2. Stribeck curve for 40% water in oil emulsion at various ball loads.

7N load. These findings are in accordance with the results of Bongaerts et al. (2007), which showed the lubrication of aqueous polymer solutions in the boundary and mixed regime decreasing for increasing loads.

3.2. Phase volume

Fig. 3a shows measured friction coefficients as a function of entrainment speed for oil continuous systems containing 0%, 20%, 40% and 60% water. All samples and emulsions contain 4% PGPR (w/w). There is a clear difference in boundary lubrication between sunflower oil and emulsions, demonstrating that the incorporation of a dispersed water phase significantly decreases the friction coefficient in the boundary regime. For the emulsions, the lubrication behaviour in this regime seems to be independent of the water content. At each sliding speed measured, the standard error bars for emulsions overlap. However, taken as whole at low entrainment speeds, water content shows a consistent pattern with respect to friction. As the water content increases, the hydrodynamic lubrication regime is attained at lower entrainment speeds. Concentrated emulsions (60% water) exhibit mixed-lubrication at the lowest speed, leading to a decreased friction compared to other



Fig. 3a. Stribeck curve for 4% PGPR in sunflower oil systems, containing 0%, 20%, 40% and 60% water.

systems, and full film lubrication (hydrodynamic lubrication) at higher speed. These results are in accordance with predictions from hydrodynamic lubrication theory, where higher viscosities lead to increased friction coefficients.

Similar experiments have been carried out with the PGPR/water ratio fixed to 0.1 to fix the proportion of "excess" PGPR for all systems (Fig. 3b). As expected, a similar trend can be observed, with a stronger differentiation for 60% water emulsions. This is most certainly due to an increase in effective viscosity of concentrated emulsions and will be discussed later on.

3.3. Droplet size

Fig. 4 shows the lubrication behaviour of emulsions containing 40% or 60% water, each realised so that their average droplet size is around 10 μ m or 0.5 μ m. There is no significant effect of water droplet size on lubrication behaviour, regardless of the phase volume considered. Checks on the sample were performed to ensure that the findings were not a result of further droplet break-up during the experiment. The average droplet size was unchanged and for the largest droplets used (~10 μ m) shown to decrease by one micron. Reducing the droplet size would result in a slight increase



Fig. 3b. Stribeck curve for sunflower oil systems, containing 0%, 20%, 40% and 60% water with a fixed PRPG/water ratio of 0.1%.

in viscosity, however not enough to induce significantly different lubrication behaviour.

Previous studies report that droplet size of an emulsion would affect the film thickness (Wan et al., 1984) and the resulting lubrication in the elastohydrodynamic regime: when droplets are entrained in the contact zone, the film thickness increases. Other studies suggest that, for water in oil emulsions, entrainment film can be only oil, leaving the water droplet at the pool at the entrance. This is sometimes used to explain why oil continuous emulsions behave in the same way as oil only (Benner et al., 2006).

The result presented here shows no significant effect of emulsion droplet size on lubrication properties: smaller droplets do not seem to be preferably entrained. This tends to imply that water is excluded from the contact zone regardless the droplet size. However, we have shown that the tribological behaviour depends on the phase volume of the emulsions, excluding this hypothesis. In order to observe the phase volume effect, some water must be entrained in the contact zone, probably due to the high viscosity of the oil. The amount of water entrained depends on the total water content rather than the water droplet size and result in increased viscosity within the contact zone, thus resulting in the differences in lubrication behaviour.

3.4. Dispersed aqueous phase: viscosity ratio

In order to test the effect of aqueous phase flowing properties in flow, alginate (1% and 2% w/w of the water phase) and κ -carrageenan (1%) were added to the water phase (Fig. 5a, 20% water emulsions and Fig. 5b, 40% water emulsions). The κ -carrageenan and potassium chloride concentrations were chosen so that the



Fig. 4. Stribeck curve for sunflower oil systems, 40% and 60% water with average droplet size (D3,2) of ${\sim}10$ and ${\sim}0.2~\mu m.$



Fig. 5a. Stribeck curve for 20% water in oil emulsion, the water phase containing 0%, 1% or 2% alginate.



Fig. 5b. Stribeck curve for 40% water in oil emulsion, the water phase containing 0%, 1% or 2% alginate, or 1% κ -carrageenan.

resulting aqueous phase would be gelled. The alginate solutions exhibited Newtonian behaviour over the range of shear rates studied $(1-100 \text{ s}^{-1})$ and the resulting viscosities were 0.001 Pa s, 0.013 Pa s and 0.55 Pa s respectively for solutions containing 0%, 1% and 2% alginate. The average droplet size for all emulsions considered here was between 0.2 and 0.5 μ m. Increasing the aqueous phase viscosity does not affect the lubrication behaviour of systems containing low quantities of aqueous phase (Fig. 5a). However, when the phase volume is increased to 40%, the viscosity of the aqueous phase affects the lubrication behaviour in the boundary and mixed regime (Fig. 5b), implying that the friction coefficient increases with the addition of alginate. Surprisingly, no further increase is observed when the aqueous phase is gelled with κ -carrageenan.

3.5. Emulsion stability: emulsifier type (incl. pickering particles)

Emulsions stabilised with PGPR (a large surfactant), Span 80 (a small molecular emulsifier) and hydrophobic Pickering particles were tested in order to verify the effect of emulsifier type on overall lubrication behaviour. The results presented in Fig. 6 show the friction coefficient of 40% water in oil emulsions as a function of entrainment speed. All emulsions had an average droplet size of 10–15 µm. Emulsions stabilised with silica particles do not exhibit boundary lubrication for the entrainment speed range tested and, at low entrainment speed, result in higher friction than the two molecular emulsifiers. In the near mixed regime, Span 80 stabilised



Fig. 6. Stribeck curve for 40% water in oil emulsions stabilised by PGPR, Pickering particles and Span 80.

emulsions present slightly reduced friction compared to PGPR. However, all three emulsions form a hydrodynamic layer above a similar entrainment speed (about 100 mm s⁻¹); with similar lubrication properties.

3.6. Emulsifier concentration

The emulsifier concentration is expected to affect the elasticity of the interface and the ability to further reduce the droplet size by stabilising smaller droplets produced when the emulsion is subjected to forces inducing droplet break up. Fig. 7 presents the lubrication behaviour of 20% water in oil emulsions stabilised by 1–7% PGPR. The resulting droplet sizes are comparable for every formulation (approx. 0.3 μ m in diameter). Again, all emulsions tested present the same lubrication behaviour, regardless the emulsifier concentration. However, there looks like a consistent pattern at low sliding speeds where higher PGPR concentration lead to lower friction coefficient.

4. Discussion

4.1. Load effect and film thickness

The friction coefficient is proportional to the applied load and these experiments show a decrease in friction with applied load, as described by friction theory. Water in oil emulsions, despite exhibiting higher viscosities than oil alone, often form thinner films compared to those formed by oil only, affecting their lubrication behaviour in the EHL regime (Liu et al., 1994). Kimura et al. (1996) describe a 2-phase model for emulsions between the two surfaces of the tribopair. This can be summarised as a "patch theory" where, in their studies, water droplets with a diameter smaller than the film thickness (h_c) create patches of deformed droplets. As a consequence of this new configuration of the lubricating fluid, its effective viscosity decreases. The film thickness is given by Eq. (1) (de Vicente et al., 2005), where R is the ball radius (m), η is the effective viscosity (Pa s), U the entrainment speed (m s⁻¹), W is the applied load (N) and E' is the reduced elastic modulus (5.45 MPa s in this configuration).

$$h_c = 4.37 R^{0.76} (\eta U)^{0.66} W^{-0.21} E^{\prime - 0.45}$$
⁽¹⁾

The film thickness is expected to decrease with increasing load and decreasing viscosity. More droplets are then flattened, contributing to the lowering of the effective viscosity according to the 'patch theory'. However, past the transition to EH regime the



Fig. 7. Stribeck curve for 20% water in oil emulsion containing 1%, 2%, 4% and 7% PGPR.

slopes are similar regardless of the applied load, indicating that once a hydrodynamic film has been created, the lubrication performance is independent of the load.

In the configuration used in this study, the elastohydrodynamic film thickness calculated for a load of 3N and a viscosity corresponding to that of the continuous oil phase varies between 14 μ m and 66 μ m for entrainment speeds of 100 and 1000 mm s⁻¹, respectively. The maximum droplet diameter obtained in our study is around 10 μ m. Interestingly, emulsions with average droplet size in the same order of magnitude as the film thickness do not exhibit different behaviour to emulsions with droplet sizes 10 times smaller. This tends to indicate that the bigger droplets are either easily deformed rather than being excluded from the contact area. Indeed, the exclusion of the contact area would lead to lubrication behaviour similar to oil only, which does not occur in this case.

4.2. Collapse of Stribeck curves

The friction coefficient vs entrainment speed curves for emulsions shown in Fig. 3 represent the typical sequence of liquid lubrication, i.e. boundary, mixed and hydrodynamic. This type of behaviour is observed when a film of liquid is entrained. In steel ball on glass disk experiments, under loads two orders of magnitude greater than those chosen here, (Benner et al., 2006) observed that the lubrication behaviour of systems containing up to 30% water was essentially similar to that of pure oil systems. However, the effect of dispersed phase viscosity on overall lubrication behaviour observed here seems to be specific to the choice of tribopairs and load chosen, as in the current study inclusion of a dispersed phase induced a lubrication behaviour different from pure oil systems.

The rate of entrainment of the lubricant depends on both the entrainment speed and the effective dynamic viscosity (K, in Pa s) of the fluid considered. Emulsions are typically non-Newtonian. Therefore, as the shear rate experienced during tribological experiments is far above the capabilities of standard rheometers, an estimated value of the effective viscosity have been obtained accordingly to de Vicente et al. (2005). This corresponds to a value for which friction coefficient vs ($K \times U$) curves are collapsed (Fig. 8). The effective dynamic viscosity of sunflower oil was set to 0.026 Pa s, corresponding to its measured viscosity at 20 °C. The obtained values are summarised in Table 2.

de Vicente et al. (2005) applied a coefficient *K* to the entrainment speed, which resulted in the collapse of all curves in the hydrodynamic regime. In these experiments however, applying a coefficient to the entrainment speed results in a superimposition of Stribeck curves for not just this regime, but all lubrication regimes visualised. This indicates that one single effective viscosity



Fig. 8. Friction coefficient vs (K·U), where K is the effective dynamic viscosity.

Table 2Effective dynamic viscosity and measured viscosity for sunflower oil containing 4%PGPR and up to 60% water.

| _ | Water content (%) | Estimated effective dynamic viscosity <i>K</i> (Pa s) | Measured dynamic viscosity at 100 s ⁻¹ (Pa s) |
|---|----------------------|---|--|
| | 0 | 0.026 | 0.026 |
| | 20 | 0.020 | 0.098 |
| | 40 | 0.036 | 0.245 |
| | 60 | 0.112 | 1.050 |
| | | | |

value is valid for the range of shear rate experienced under mixed lubrication conditions. All systems exhibit a significant shift in friction coefficient for $(K \cdot U) > \sim 3$, the value above which fluid film lubrication occurs.

4.3. Viscosity ratio

De Vicente and co-workers showed that overall lubrication behaviour of O/W emulsions is strongly dependent on the viscosity ratio between the two phases (de Vicente et al., 2006b). For dispersed phase viscosities at least four times greater than the continuous phase viscosity, the dispersed phase determines the friction properties. The authors argue that at such a high viscosity ratio, the droplets are less deformable, and can thus enter the contact zone instead of forming a pool of dispersed phase at the inlet. In the case of this current set of experiments however, the viscosity of the aqueous phase show very little effect, probably because the droplets are too small to either be excluded or create a patch that will be in the contact zone. Given the range of film thicknesses expected and the high viscosity ratio, it is unreasonable to assume droplets are excluded from the contact phase. Furthermore, previous studies of lubrication behaviour of water in oil systems have shown that a larger film thickness is obtained when the droplet diameter is similar in size to the film thickness corresponding to pure continuous phase (Wan et al., 1984). For all these reasons, it can be concluded that the change of lubrication behaviour compared to pure oil is due to the increase of effective viscosity of the liquid phase in the contact zone, independent of the composition of the dispersed phase. Significantly different behaviour can be observed in the boundary lubrication regime, where highly viscous or gelled particles act as impurities and increase the friction coefficient at low speed.

4.4. Interface and particle rigidity: drop deformation

For dispersed droplets entering the contact zone, their behaviour is expected to depend on the elasticity of the oil-water interface. The latter is affected by several factors:

- the emulsifier concentration; i.e. the amount of surface active molecule able to stabilise an increased surface area when the drop is deformed,
- the type of surfactant, which will determine the elasticity of the interface, i.e. its ability to deform,
- the viscosity or structure of the inner phase.

Lubrication behaviour appears to be independent of the PGPR concentration emulsifier used. It is expected that higher PGPR concentration leads to a thicker interface. However, in this case where the droplets are smaller than the lubricating film, no effect of the interface rigidity was to be expected.

The results presented in Fig. 6 were obtained with dispersed droplets of size similar to the estimated film thickness. Their lubrication behaviour significantly differs from that of oil only, which implies that the dispersed phase is not excluded from the contact zone. However, the type of surface active molecule used (Pickering particle, Tween 80 or PGPR) does not affect the lubrication behaviour in the elastohydrodynamic lubrication regime. The two molecular surfactants considered here provide a stable interface, yet sufficiently elastic to allow the droplets to enter and deform in the contact zone. Pickering stabilised droplets are expected to result in a more rigid interface, preventing droplet deformation and favouring emulsion breakup (Frelichowska et al., 2009), without however interfering with the lubrication ability of the emulsion.

4.5. Boundary lubrication

Boundary lubrication was observed to be very limited over the speed range tested in this study. Interestingly, higher loads lead to slightly decreased friction (Fig. 2). This observation which is slightly counter-intuitive, arises from the nature of the emulsion systems. With increased loading, the fluid thickness between the tribopairs is decreased and consequently fewer droplets enter this region and interact with each other.

Emulsions with greater phase volume tend to lubricate slightly better in this regime; due to their higher viscosities, they support the load better and prevent excessive friction between the tribopairs. The effect of phase volume on boundary lubrication behaviour is masked for sub-micron droplets, where typically much more droplets are present, which contributes to an increase in emulsion viscosity, regardless of the composition of the aqueous phase (Figs. 4 and 5a). Conversely, for emulsions with droplet sizes similar to that of the film thickness, structuring the aqueous phase leads to improved boundary lubrication (Fig. 5b). This is because highly viscous or gelled droplets limit friction, whereas hard Pickering particles inhibit lubrication (Fig. 6).

5. Conclusions

All the emulsions considered here exhibit the same trends in terms of lubrication behaviour: at the entrainment speed considered, very little boundary lubrication is observed and the friction coefficient is load dependant. The volume of dispersed aqueous phase affects overall tribology of oil continuous emulsions via an increase in their dynamic viscosity. Increasing the phase volume leads to an increase in friction in the elastohydrodynamic regime whereas the lubrication in the boundary regime is improved. This suggests that there would be a significant impact on sensory perception, e.g. a pure liquid fat system would be expected to generate lower lubrication than its reduced fat emulsion counterpart. In summary, the composition of the aqueous phase and the resulting droplet size have been shown to have the following effects:

- When the droplet size is much smaller than the expected film thickness, the composition of the aqueous phase and its structure has no effect on lubrication behaviour.
- Unlike water continuous systems, the viscosity ratio between dispersed and aqueous phases in water in oil emulsions has no effect on the tribology in the elastohydrodynamic regime. However, this ratio significantly affects boundary and mixed lubrication, and can lead to friction levels similar to that of pure oil when a highly viscous phase included. This is expected to have a significant impact on the design of low fat emulsions that match the lubrication properties of their full fat version.
- For slightly bigger droplets entering the contact zone, there appear to be a large window of interface properties for which the overall behaviour is not compromised. Here, effective dynamic viscosity is the main parameter controlling the lubrication behaviour of emulsions.

As sensory perception has previously been shown to be linked to soft lubrication behaviour, these finding are expected to provide guidelines for the design of low fat food emulsions systems.

Acknowledgement

The authors of this article wish to acknowledge Izabela Gladkowska for carrying out part of the experiments.

References

- Benner, James J. et al., 2006. Lubricating properties of water in oil emulsions. J. Tribol. 128 (2), 296–311.
- Bongaerts, J., Rossetti, D., Stokes, J., 2007. The lubricating properties of human whole saliva. Tribol. Lett. 27 (3), 277–287.
- Cassin, G., Heinrich, E., Spikes, H.A., 2001. The influence of surface roughness on the lubrication properties of adsorbing and non-adsorbing biopolymers. Tribol. Lett. 11 (2), 95–102.
- Chen, J., Stokes, J.R., 2012. Rheology and tribology: two distinctive regimes of food texture sensation. Trends FoodSci. Technol. 25 (1), 4–12.

- Chojnicka, Agnieszka et al., 2008. Lubrication properties of protein aggregate dispersions in a soft contact. J. Agric. Food Chem. 56 (4), 1274–1282.
- de Vicente, J., Stokes, J.R., Spikes, H.A., 2005. Lubrication properties of nonadsorbing polymer solutions in soft elastohydrodynamic (EHD) contacts. Tribol. Int. 38 (5), 515–526.
- de Vicente, J., Stokes, J.R., Spikes, H.A., 2006a. Soft lubrication of model hydrocolloids. Food Hydrocolloids 20 (4), 483–491.
- de Vicente, J., Spikes, H.A., Stokes, J.R., 2006b. Viscosity ratio effect in the emulsion lubrication of soft EHL contact. J. Tribol.-Trans. Asme 128 (4), 795–800.
- de Wijk, René A., Prinz, Jon F., 2005. The role of friction in perceived oral texture. Food Qual. Prefer. 16 (2), 121–129.
- Dresselhuis, Diane et al., 2007. Tribology of o/w emulsions under mouth-like conditions: determinants of friction. Food Biophys. 2 (4), 158–171.
- Fernández Farrés, I., Douaire, M., Norton, I.T., 2013. Rheology and tribological properties of Ca-alginate fluid gels produced by diffusion-controlled method. Food Hydrocolloids 32 (1), 115–122.
- Frelichowska, Justyna et al., 2009. Pickering w/o emulsions: drug release and topical delivery. Int. J. Pharm. 368 (1–2), 7–15.
- Gabriele, A., Spyropoulos, F., Norton, I.T., 2010. A conceptual model for fluid gel lubrication. Soft Matter 6 (17), 4205–4213.
- Garrec, D.A., Norton, I.T., 2012. The influence of hydrocolloid hydrodynamics on lubrication. Food Hydrocolloids 26 (2), 389–397.
- Giasson, Suzanne, Israelachvili, Jacob, Yoshizawa, Hisae, 1997. Thin film morphology and tribology study of mayonnaise. J. Food Sci. 62 (4), 640–652.
- Kimura, Yoshitsugu, Okada, Kazumi, Liu, Wenyi, 1996. Elastohydrodynamic films with emulsions. In: Taylor, C.M., Childs, T.H.C., Dalmaz, G., Berthier, Y., Flamand, L., Georges, J.M., Dowson, D., Lubrecht, A.A. (Eds.), Tribology Series, vol. 31. Elsevier, pp. 563–572.
- Liu, Wenyi et al., 1994. Elastohydrodynamic lubrication with water-in-oil emulsions. Wear 179 (1-2), 17-21.
- Luengo, Gustavo et al., 1997. Thin film rheology and tribology of chocolate. J. Food Sci. 62 (4), 767–812.
- Malone, M.E., Appelqvist, I.A.M., Norton, I.T., 2003. Oral behaviour of food hydrocolloids and emulsions. Part 1. Lubrication and deposition considerations. Food Hydrocolloids 17 (6), 763–773.
- Mills, Tom, Koay, Adeline, Norton, Ian T., 2013. Fluid gel lubrication as a function of solvent quality. Food Hydrocolloids 32 (1), 172–177.
- Selvway, N., Stokes, J.R., 2013. Insights into the dynamics of oral lubrication and mouthfeel using soft tribology: differentiating semi-fluid foods with similar rheology. Food Res. Int. 54 (2013), 423–431.
- van Aken, George A., Vingerhoeds, Monique H., de Hoog, Els H.A., 2007. Food colloids under oral conditions. Curr. Opin. Colloid Interface Sci. 12 (4–5), 251– 262.
- Wan, G.T.Y., Kenny, P., Spikes, H.A., 1984. Elastohydrodynamic properties of waterbased fire-resistant hydraulic fluids. Tribol. Int. 17 (6), 309–315.