THE DEVELOPMENT OF TRIBOLOGICAL TECHNIQUES FOR MODEL FOOD FORMULATIONS

By

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ABSTRACT

The aim of this thesis was to develop tribological testing techniques in order to make them more closely relatable to oral processing and for those to be more accessible to researchers in academia and industry. An exploration of available tribological testing equipment, processing parameters and configurations were carried out to determine optimum testing conditions which could be related to oral processing. Two tribological testing systems were compared and model food systems analysed; one purpose built and commercially available for tribology and the other an attachment for a rheometer. Surfaces used in oral tribology experiments were also developed in two ways. The first being the surface chemistry of a polymer commonly used in oral processing tribology (PDMS) to more closely resemble the chemistry of oral surfaces. The second being textured surfaces to more closely resemble the texture of tongue. Lastly, all experiments aimed to investigate complex food systems, in particular particulate suspensions including agar fluid gels and astringent compound solutions including tannins found in wine and catechins found in tea. Both particulate suspensions and astringent compounds are commonly found in food systems and have been linked to affecting friction properties, sensory perception and consumer acceptance. The work presented in this thesis has shown the properties of the testing surfaces greatly affected the lubrication response. This information could then be used to develop tribological testing further in order to more closely resemble to oral cavity and allow accurate *in-vitro* assessment of food products to determine their lubricating performance when consumed.

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NOMENCLATURE

A_r	Contact radius
d	Arm length
E	Elastic modulus
E*	Reduced elastic modulus
F	Friction force
F_N	Normal force
M	Torque
P_{max}	Maximum contact pressure
R	Radius of contact
R*	Reduced radius
R_a	Average surface roughness
U/U_m	Entrainment speed
U_{ball}	Disc speed
U_{disc}	Ball speed
W	Normal load
η	Viscosity
μ	Friction coefficient
ν	Poissons ratio

ABBREVIATIONS

AFM	Atomic force microscopy
ATR	Attenuated total reflection
β-LG	Beta-lactoglobulin
DSA	Drop shape analyser
EGCG	Epigallocatechin gallate
EHL	Elastohydrodynamic lubrication
FTIR	Fourier transform anfrared
MCC	Microcrystalline cellulose
MTM	Mini Traction Machine
PBS	Phosphorus buffered saline
PDMS	Polydimethylsiloxane
PVA	Polyvinvyl alcohol
SRR	Slide-roll ratio $[(U_{disc} – U_{ball})/U]$
TA	Tribology attachment for TA systems rheometer
UDA	Undecyclenic acid
WCA	Water contact angle

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1. INTRODUCTION

1.1. Motivation and background

Tribology is the science and engineering of relative surfaces in relative motion. It consists of the study of friction, lubrication and wear between interacting surfaces. It is considered an interdisciplinary subject spanning engineering, chemistry, physics and mathematics. Tribology is traditionally associated with mechanical engineering where applications typically include improving the lifetime of tools, studying greases or the efficiency of machinery. More recently, tribology has been identified as a useful technique when trying to understand the material and mechanical behaviour of food products used by consumers, particularly when coupled with other techniques like rheology, texture analysis and sensory studies (A Chojnicka-Paszun, De Jongh, & De Kruif, 2012; De Vicente, Stokes, & Spikes, 2006; Diane M Dresselhuis et al., 2007; Foster et al., 2011; Krop et al., 2019; Liu et al., 2016; Malone, Appelqvist, & Norton, 2003, Stribitcaia et al., 2020). This thesis will cover the aims and objectives of the project entitled ‘Development of tribological techniques for model food products’, a relevant critical literature survey, completed work and future plans. A number of studies use smooth, hydrophobic surfaces which are of little relevance to the oral cavity, whereby surfaces are covered in a hydrophilic coating of saliva and surfaces such as the tongue are covered in structures like papillae (Laguna & Sarkar, 2017; Sarkar et al., 2019). As surfaces are not representative, tribological measurements may have less correlation with sensory evaluation (Pradal & Stokes, 2016; Sarkar & Krop, 2019). This project hopes to address this and move towards alternative testing surfaces including textured pillared surfaces and chemically modified hydrophilic surfaces in order to more closely resemble surfaces found in the mouth. The friction and lubrication properties of complex, multiphase and multicomponent foods are difficult to measure. This work looks at developing testing techniques with focus on investigating model versions of these systems including particulate suspensions and astringent compound solutions. These are both relatively under investigated yet are present in a wide range of foods. Foods that contain particulates or are particulate in nature are often associated with negative sensory perceptions, such as grittiness or graininess (Stokes, Boehm, & Baier, 2013). There are few studies which investigate small particles and how these affect friction, but in comparison there are few studies to date which look at large particles (< 500 µm). Astringency is a complex phenomena and has been linked to a physical interactions including friction between astringent compounds and oral surfaces, as well as a chemical interaction (Stokes, Boehm, & Baier, 2013). It is hoped through examining these, a better understanding of the behaviour and mechanisms involved as food is consumed can be developed. This would benefit scientists and researchers in academia and the food industry.

1.2. Aims and objectives

The aim of the work presented in this thesis is to develop tribological techniques in order to better understand oral processing when analysing multicomponent, complex systems, like foods. The overall aims and objectives of this project are to:

- Develop tribology equipment
    - Comparison of two tribological testing instruments: one purpose built and commercially available for tribology and the other an attachment for a rheometer
- Develop tribological surfaces
    - Design, fabricate and investigate textured surfaces to resemble the tongue
    - Identify and modify chemical properties of polymer testing surfaces to resemble the chemistry of oral surfaces
- Investigate complex food systems; specifically, particulate suspensions and astringent compounds

1.3. Layout of thesis

This thesis follows the alternative thesis format of the University of Birmingham where results chapters (Chapters 3-5) are presented in a form published in peer-reviewed journals.

Chapter 2 – This chapter consists of a critical and comprehensive literature review of relevant published literature covering fundamental tribology, oral processing, tribological testing techniques and tribological studies relating to foods to gain a better understanding in order to develop new and better food products.

Chapter 3 – This is the first of the results chapters and compares two different tribological testing techniques, one frequently used in oral tribology measurements (a mini traction machine) and a three-ball-on-plate tribology attachment for rheometer. The aim of this chapter was to understand the scope for the tribology attachment in comparison to the well-used mini traction machine, including pros and cons. A range of model food systems were investigated in including Newtonian fluids, guar gum solutions, oil in water emulsions and agar fluid gels. Techniques used in this chapter include tribology and shear rheology. This chapter was published as "Using a three-ball-on-plate geometry for soft tribology applications" (Taylor, B. L and Mills, T. B., *Journal of Food Engineering*, 2019).

Chapter 4 – This is the second results chapter which follows on from the first, using a three-ball-on-plate tribology attachment for rheometer and chemically modified polydimethylsiloxane (PDMS) surfaces. Surfaces were modified to be hydrophilic and various model polymer samples were examined to probe the role of the surface chemistry in measuring their friction properties. The aim of this chapter was to understand how these chemically modified surfaces performed in tribological experiments: whether they would be suitable as an analogue to oral surfaces by probing how they interacted with aqueous food systems, including astringent compounds which are said to increase friction in the oral cavity. A range of model food systems were examined including aqueous polymer solutions (xanthan, guar gum, Carbopol and chitosan) and astringent compound solutions (alum, tannic acid and epigallocatechin gallate) in order to investigate how these interact with the modified surfaces. Techniques used in this chapter include tribology, shear rheology, contact angle measurements, FTIR and AFM). This chapter was prepared as “The lubrication of aqueous polymer solutions using chemically modified PDMS substrates” (Taylor, B. L, Norton, I.T. and Mills, T. B.).

Chapter 5 - This is the third results chapter and addresses the use of surface textures in oral tribology, using a moulding and casting technique to impart texture into soft surfaces. Particulate systems and their interactions with the textured surfaces were examined. This chapter used a mini traction machine (MTM) for tribology measurements, instead of the tribology attachment for rheometer, as a larger contact area was required. Compared to the tribology attachment, more textures would be present in the contact between ball and disc. The aim of this chapter was to understand how large surfaces textures (>500 μm) affected friction, and whether particles affected friction when examined using these surfaces compared to a smooth surface, which is not representative of the oral cavity. A range of model food systems were examined including Newtonian fluids, hard particulate suspensions and agar fluid gels in order to investigate how the particles interact with the surface textures. Techniques used in this chapter include tribology, shear rheology and 3D printing. This chapter has been submitted to Biotribology as “Surface texture modifications for oral processing applications” (Taylor, B. L. and Mills, T. B., *Biotribology*, November 2019).

Chapter 6 - In this final chapter, the conclusions of this work are summarised, together with suggestions for future work to improve, continue and further utilise the developed techniques and test methods.

1.4. Publications and presentations

1.4.1. Publications

- Taylor, B. L and Mills, T. B., Using a three-ball-on-plate geometry for soft tribology applications, *Journal of Food Engineer*ing, 2019.
- Taylor, B. L and Mills, T. B., Surface texture modifications for oral processing applications, *Biotribology*, 2019.

1.4.2. Presentations

- Taylor, B. L., Mills, T. B., Norton, I. T, The influence of surface chemistry on the aqueous lubrication of polydimethylsiloxane (PDMS) substrates, *RSC International Conference on Materials Chemistry (MC14)*, Birmingham, UK, 2019.
- Taylor, B. L., Mills, T. B., Norton, I. T, Using a three-ball-on-plate configuration for soft tribology applications, *8th International Symposium of Food Structure and Rheology*, Zurich, Switzerland, 2019.

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Stribitcaia, E, Krop, E. M., Lewin, R., Holmes, M., Sarkar, A. Tribology and rheology of bead-layered hydrogels: Influence of bead size on sensory perception. *Food Hydrocolloids*, 104 (2020) 105692

2. LITERATURE REVIEW

Abstract

The development of oral tribology testing techniques to more closely resemble eating and the oral cavity *in-vitro* is beneficial for both academics and researchers in the food industry. To achieve this, an understanding of the work completed relevant to this area was needed. This review includes topics of oral processing, tribology, soft tribology and oral processing in tribology. It is evident from the review that there is a need for the development of understanding and techniques to replicate *in vivo* conditions (i.e. mouth feel). One crucial aspect is the surface properties including surface topography and surface chemistry. Food systems themselves are also incredibly complex as is there interaction with the oral surfaces, so a greater understanding of model systems relating to more complex systems is required in order to understand how a food would behave in use. It would be ideal if *in-vitro* experiments could be used to help formulate products accepted by consumers, without the need for extensive sensory testing. Tribology shows great potential towards achieving this.

2.1.Introduction

Developing tribological test methods in order to better understand behavior of food materials in the mouth is beneficial for academics and researchers in the food industry. To achieve this, an understanding of the work completed relevant to this area was needed. This chapter presents a critical literature survey in the work of soft tribology relating to oral processing, mouth-feel and complex food systems covering relevant experiments and theories to date in the area of food formulation science and engineering. The aim of this chapter was to summarize, compare and critically evaluate existing literature whilst also identifying any gaps in the literature. This review includes topics of oral processing, tribology, soft tribology and oral processing in tribology. Focus was given to equipment and techniques used in tribology, as well as the surfaces used.

2.2. Food products

This section identifies structural and formulation properties of foods and model foods in more detail. A series of food-based systems were identified in this work to provide a range of food material behaviours. The following section discusses these and reviews publications which have previously studied them.

2.2.1. Biopolymers in food products

Biopolymers are natural polymeric substances of plant, animal or microbial origin and cover a wide range of materials. They are commonly used as ingredients in a wide range of food products and provide a range of structural and functional properties for food formulations. The main application is as thickeners, emulsifiers, rheology modifiers and gelling agents which impart structure (Dickinson 2003). Of particular relevance to this thesis, the following biopolymers which can be used as rheology modifiers are covered in more detail: agar, guar gum and xanthan gum.

Agar

Agar is a hydrocolloid extracted from red algae composed of D-galactose and 3-6-anhydrogalactose. Commercial agar is made up of two components: a linear polysaccharide agarose which is the gelling component, and a mixture of smaller molecules called agaropectin. Agar is commonly used in biological applications (culture media) and foods to create gelled structures, for example desserts or sweets.

Guar gum

Guar gum is a galactomannan polysaccharide extracted from seeds of the guar bean consisting of a series of mannose units with galactose side chains. Guar gum is widely used as a thickener or stabiliser in food products. It is frequently used in in ice cream to modify the texture and mouthfeel to feel ‘smooth’ (Clarke 2004).

Xanthan gum

Xanthan gum is a high molecular weight polysaccharide created by fermentation of bacteria *Xanthomonas campestris*. Xanthan gum’s structure consists of a linear chain of β-D-glucose with trisaccharide side groups. It is used in food products as a thickener or stabiliser, often to prevent phases from separating or to retain structure. In solution, xanthan is shear thinning at low concentrations which is useful in many food products to maintain structure at rest but to pour or dispense under force (García-Ochoa, Santos, Casas, & Gómez, 2000).

2.2.2. Emulsions in food products

Emulsion use in food is widespread, both in natural and processed foods, such as milk, mayonnaise and soups. The basic structure of an emulsion generally contains two immiscible liquids, typically oil and water, where one is dispersed in the form of droplets (dispersed/internal phase) within the other (continuous/external phase). This dispersion can be achieved using a number of techniques. A relatively simple method involves mixing the two liquids together under high shear where the stability and properties of the resulting dispersion depends upon the liquids used and the amount of energy put into the system. Usually in this case the emulsion produced has a limited lifespan, so will start to separate, as droplets of the dispersed phase collide and aggregate into clusters of droplets (flocculation or coalescence) or form a discrete layer (creaming or sedimentation). To prevent this, a stabiliser can be added either in the form of an emulsifier or texture modifier or in some cases a mixture of the two.

However, food products are often more complex than just two immiscible liquids. For example, ingredients can be complex or phases can exist in different states (i.e. frozen, gelled, foamed etc.).

2.2.3. Particulates in food products

Particulate suspensions

Many food products contain particles of different sizes, shapes and mechanical properties. Particles in food are extremely important when relating to consumer acceptance and sensory properties as the presence of particles is said to affect sensory attributes such as creaminess, roughness, dryness and grittiness (Prakash et al. 2013; de Wijk & Prinz 2004; Krzeminski et al. 2013). Large and irregularly shaped particles in foods are often associated with typically negative sensory attributes, whereas small, smooth particles are often accepted by a consumer (Malone et al. 2003; de Wijk & Prinz 2004). The perception of these attributes is caused by friction between the particles and the oral mucosa whereby the physical properties of the particles, such as size, concentration, shape and hardness, as well as properties of the matrix in which the particles are dispersed, affect friction (Heath & Prinz 1999; de Wijk & Prinz 2004; De Wijk & Prinz 2006; Verhagen & Engelen 2006).

Carbopol

Carbopol, a synthetic polymer which produces microgels in suspension, is used in this thesis. There are several Carbopol grades which are chemically similar in that they are all high molecular weight, crosslinked polyacrylic acid polymers. However, these gel-forming polymers differ by their chemical crosslinking. It is widely used as a gelling agent in cosmetics and toiletries, including gels, creams and lotions and detergents.

Fluid gels

Hydrocolloid fluid gels are increasing being used as fat replacements in liquid and semi solid food products (Cassin, Appelqvist, Normand, & Norton, 2000). Fluid gels are concentrated suspensions of micro-gel particles dispersed in a continuous medium, typically water, and are produced by applying a shear field to the hydrocolloid solution while the sol-gel transition is taking place (Norton, Frith, & Ablett, 2006; Norton, Jarvis, & Foster, 1999). The use of fluid gels is of increasing interest to the food industry because not only are they a natural and affordable fat replacement, they potentially impart desirable mouthfeel and texture attributes (e.g. smoothness) (Malone, Appelqvist, & Norton, 2003). Typical fluid gels include agar, whey protein or kappa carrageenan (Ellis et al, 2017; Fernández Farrés & Norton, 2015; Garrec, 2013; Lazidis et al, 2016). Agar fluid gels are examined in this thesis.

2.3. Oral processing

Oral processing describes the intake of food and/or drink into the mouth as the tongue, palate, teeth and saliva mechanically and physically interact with it before it is swallowed. As the mouth provides first contact with a food product, it is highly important in oral processing. A diagram of the mouth is shown in *Figure 2.1*. The processes involved during eating are complex consisting of mechanical manipulation by movement of the oral surfaces (teeth, tongue, lips, cheeks and palate), chemical changes and wetting by saliva with constant assessment and feedback by the tongue and oral surfaces. This involves multiple stages. The first stage can be described as the processing stage that allows the perception of hardness, brittleness and viscosity of a substance. For liquid products, the oral processing stage is relatively short with low shear rates experienced, meaning there is a limited amount of mixing experienced. For solid products, this stage is longer and the mechanical process of mastication contributes to breaking the product down further. Mastication involves the entire oral cavity, utilising teeth, lips, cheeks, tongue, palate and saliva. It begins with appropriate compressive, shearing and tensile forces brought about by the intermittent separation and closing movements of the mandible. As food is broken down further and a sense in change of properties including particle size, hardness, strength and elasticity are detected, mastication evolves to continue manipulating and processing the food (Heath & Prinz 1999). With continuous incorporation of saliva and mechanical processing, the surface area of food increases as size of particles decreases, leading to the formation of a soft bolus. The next stage is oral propulsion where mastication continues and the tongue moves upwards towards the palate of the mouth, introducing flow to the back of the mouth ready for the bolus to be swallowed. Here, the bolus experiences high shear and force, along with further mixing. From the first two processes, sensory attributes such as sliminess, chewiness, creaminess and grittiness are determined by the consumer. The concluding stage is swallowing, where the bolus is cleared from the mouth. There can be some residual material retained by oral surfaces which can continue to play a role in the sensory experience, for example flavour and physiochemical sensations.

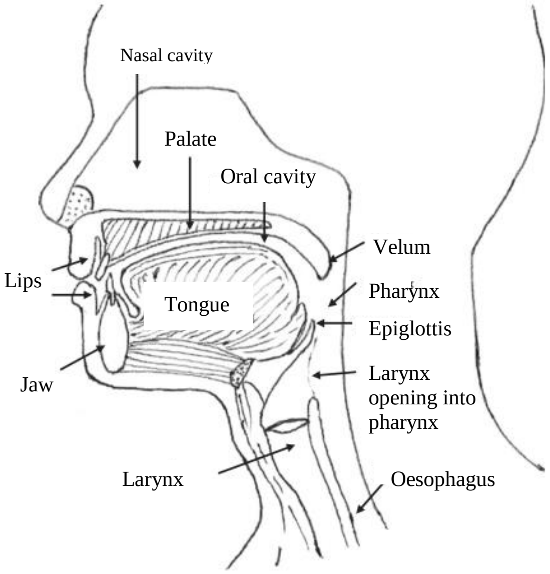

Figure 2.1 – An anatomical illustration of the oral cavity (adapted from Chen (2009)).

Aside from mechanical manipulation, the incorporation of saliva produces material and environmental changes. Saliva despite consisting of over 99% water is shown to be a highly lubricating complex fluid with a large number of components. It contains salts, enzymes and proteins which interact with the food in order to break it down (Humphrey & Williamson 2001). It is secreted into the mouth to lubricate the oral cavity, to protect to the oral surfaces and to dilute food as it enters the mouth. The composition and therefore lubricity of saliva varies among populations, with factors like age, nationality, gender and health affecting its ability to lubricate. The material being processed also influences saliva properties through interactions leading to the formation of new compounds, complexes and microstructures.

To develop new, functional, food products, there is a need for better understanding of the processes involved as they are consumed as well as their material properties. In order to understand oral perception, the following factors need to be determined (Malone et al. 2003):

1. The rheological and mechanical failure properties and the mechanisms of oral sensation
2. The eating processes and the breakdown of food in the mouth
3. The physiology of the mouth environment particularly the oral surfaces
4. Interactions between food and the oral cavity
5. The influence of microstructure on perception, taste and flavour release

Verhagen & Engelen (2006) stated that there are multiple factors that affect the ‘feel’ of a food product. This makes it challenging for industries to predict how a consumer may respond to innovations without gathering feedback from sensory panels. Oral perception of texture depends on the bulk food response to initial deformation between the teeth (early stage of the eating process) as well as the manipulations of softened and/or thinned food between the saliva lubricated tongue and palate (later stages of the eating process). Experimental tests of texture profile analysis and rheology measurements are most widely used to assess structural and textural properties of food products. A texture analyser is able to cater for measurements of specific textural attributes and imitate some processes (e.g. first bite). These results can then be directly linked to sensory perception. The rheometer allows fundamental physical and structural characteristics to be determined including viscosity, stress, strain, storage modulus and loss modulus. Well-defined geometries and testing parameters allow for qualitative and quantitative measurements. This allows the behaviour of foods to be described as they are squeezed and flow through the mouth. However, both of these measurements are only able to understand the early stages of oral processes as the food is deformed with the teeth or tongue. It does not allow for the assessment of food at the later stages of oral processing, where food continues to be broken down and a bolus forms as the process is dominated by a combination of fluid flow and surface properties. Rheological and textural properties become less relevant but surface friction and lubrication become more suitable for the analysis of texture and sensory perception. During processing, textural properties that are related to food rheology are detected relatively quickly and are related to large-scale deformation (e.g. viscosity, particulates, roughness, dryness), whereas those associated with tribology (e.g. mouthfeel attributes including creaminess, smoothness, stickiness, astringency, etc.) are sensed relatively slowly (Chen & Stokes, 2012; Krop et al., 2019; Stribitcaia et al. 2020). This is described in *Figure 2.2*.

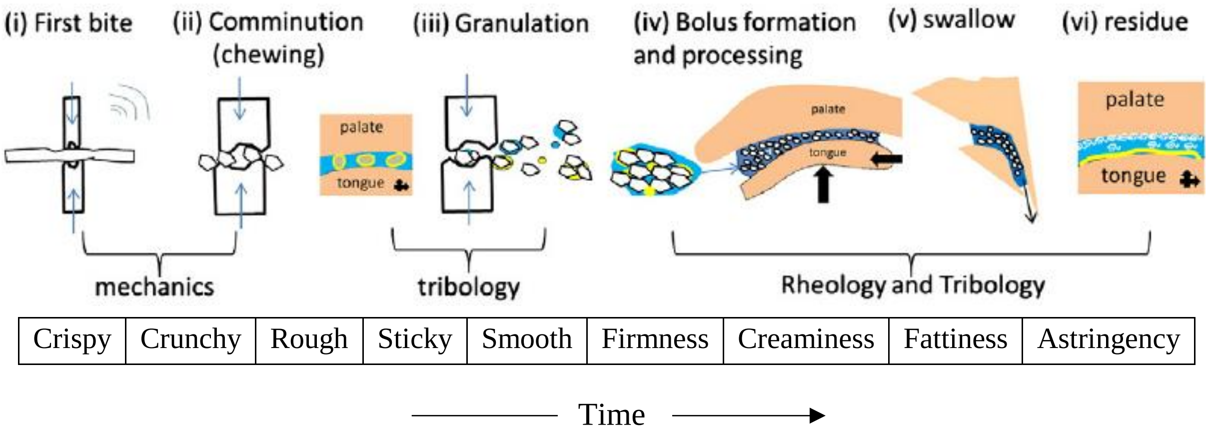

Figure 2.2 - Visualisation of the six stages Stoke et al propose occur during oral processing of solid food (adapted from Fig 3. from Stokes et al. (2013))

Oral processing is complicated, involving many components. It also differs between populations and depends on the type of food that is consumed. It is easy to see why this process is difficult to replicate experimentally with so many factors involved. This also highlights why there is a need to replicate the process experimentally, as it is important in food consumption and therefore the perception of food.

2.4. Tribology

Tribology is the study of friction, lubrication and wear between interacting surfaces in relative motion. It has been used as a research tool for many years where the traditional and primary application for knowledge gained in this area is in the field of mechanical engineering. This typically concerns lubrication and friction effects relating to contacting, rubbing and rotating surfaces that are susceptible to wear. Lubricants are key to reducing the friction experienced, therefore improving processes as well as the efficiency and lifetime of equipment (Hailing, 1991).

Friction is defined as the force resisting the motion of interacting surfaces when sliding against one another. One of the most important parameter in tribological testing is the friction coefficient, expressed in *Equation 2.1*:

$$\mu = F/W \qquad (Equation\ 2.1)$$

where μ is the friction coefficient, F is friction force, and W is the normal load perpendicular to the direction of friction. The friction coefficient is often used to represent the friction characteristics of a system allowing ease of comparison between different systems. This equation, known as Amontons' equation, is considered as the most basic rule of sliding friction (Amontons 1699). Amontons is regarded as the founder of the first and second laws of friction. The third law of friction regarding dynamic friction was added by Coulomb (1875). The findings of Amontons and Coulomb are as follows:

1. The force of friction is directly proportional to the applied load.
2. The force of friction is independent of the apparent area of contact.
3. The force of dynamic friction is independent of sliding speed.

These laws only apply to elastic deformation without lubricant. As friction involves the interaction of two materials, the friction coefficient is dependent on the properties of both materials. Friction is a system property so is dependent on a number of factors including normal force, temperature, surface topography, surface chemistry, material elasticity and relative speeds. When there is a fluid lubricant present in between the two surfaces, friction is also influenced by the properties of this lubricant and the interaction of the lubricant with the surfaces. Entrainment of the lubricant between the surfaces is influenced by the relative speed of the surfaces in motion. The friction behavior of lubricants can be represented by a Stribeck curve (*Figure 2.3*). The Stribeck curve shows the friction coefficient plotted as a function of the friction parameter, also known as Hersey number (defined as speed × viscosity/load). For a given viscosity and load, the Stribeck curve shows how friction changes with increasing speed.

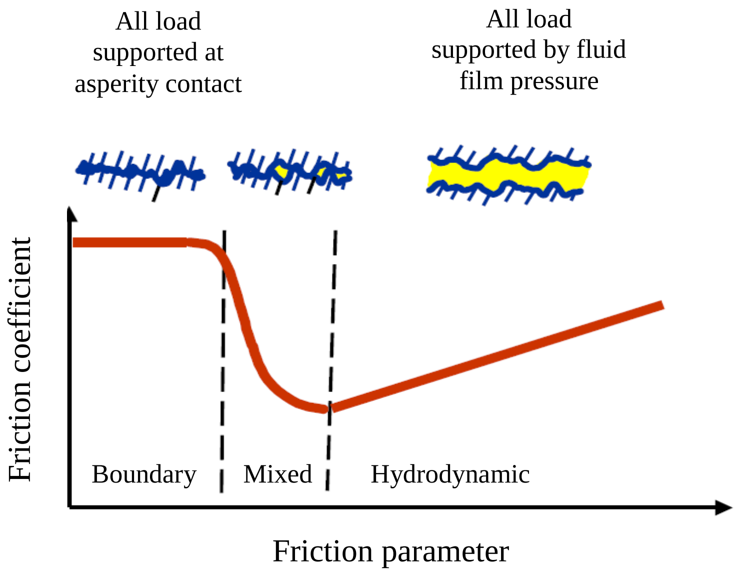

Figure 2.3 - Figure showing typical Stribeck curve with boundary lubrication regime (BL), mixed regime and the hydrodynamic regime (adapted Fig.1 from De Vicente et al. 2006).

The Stribeck curve depicts three lubrication regimes: the boundary lubrication regime, the mixed regime and the hydrodynamic lubrication regime (also known as elastohydrodynamic regime (EHL) if deformable surfaces are used). The boundary lubrication regime is observed when the speed of the surfaces in relative motion is small and the lubricant has a low viscosity. In these conditions, there is little/no lubricant between the two surfaces as separation between them is small and asperities are in direct contact. In the boundary regime, the friction force can be correlated to surface roughness (asperity interactions). With increasing surface roughness, more asperity contact will occur. The boundary regime largely depends on the physicochemical properties of the surfaces and the chemical composition of the thin lubricant film that covers the surfaces. The mixed lubrication regime is observed when further lubricant becomes entrained between the surfaces. Through the increase in speed, only large asperities are in contact, therefore reducing friction. This behavior continues with increasing speed, which is reflected in the Stribeck curve decreasing in friction. In the mixed regime, both the properties of contact surfaces and the bulk properties of the lubricant are important for friction. Once the entrainment of lubricant is sufficient (either due to increasing speed or bulk viscosity) the surfaces separate and the Stribeck curve enters the hydrodynamic (or elastohydrodynamic if elastic surfaces are used) lubrication regime. In this regime, friction between the surfaces is mainly determined by the lubricant’s bulk properties including rheology (Hailing, 1991).

2.5.Tribological techniques in oral processing

Although tribology is suited for the analysis of foods, there has been little progress using the technique due to a lack of fundamental understanding of its relevance to oral processing and oral perception. The oral cavity and food systems are both complex, and need to be developed in order to better understand oral processing.

When assessing friction in this area, there are two factors to be considered when designing or choosing tribological equipment. These are the control of the sliding and/or rotation and the material properties of the contacting surfaces. There are many interchangeable parameters concerning tribology test equipment and test methods, discussed below. An ideal surface material for oral processing and food studies would be the one that imitates the tongue, palate or teeth in the oral cavity. However, as discussed previously in Section 2.1, this would be very difficult given the complex nature of these surfaces and variation between populations. Therefore, it would be required to work towards imitating elasticity, surface chemistry and surface topography of these surfaces in order to find a universal equivalent.

2.5.1. Tribology equipment

Friction has been measured in a variety of ways, where either one or both surfaces are in motion. Typically, for the food industry, both surfaces rotate in order to mimic the complex nature of consuming foods where there are at least two surfaces in relative motion. A range of instruments have been used to examine friction and lubrication, from lab-made testers to more commercially available tribometers.

Many researchers choose to developed friction testers in house as they can be made relatively simply and inexpensively. One of the earliest studies investigating oral processing was by Kokini et al. (1977) who investigated friction properties of a range of food products using a test sample (in this case chamois leather) pressed against a rotating, variable speed turntable. This is counterbalanced with pivot-mounted lever arm where the opposite end a hemispherical polymer slider is attached. As the table rotates, friction between film and slider induces a torque in the arm which is measured by a strain gage and recording system. The friction measurements obtained were directly correlated to rheological and oral perception measurements, finding smoothness is related to frictional force between tongue and palate and slipperiness related to a combination of viscous and friction factors. Years after this, Prinz & Lucas (2000) studied the effects of tannins in the lubrication of saliva using a similar friction system. They used a Boothroyd friction tester that consisted of one end of a rubber band looped round the steel shaft of a small electric motor and the other end connected to a universal testing machine (*Figure 2.4*). The friction coefficient between the shaft and the rubber band was calculated using the fundamental friction assumptions, comparing the force at the load cell whilst the motor is run clockwise and then anti-clockwise.

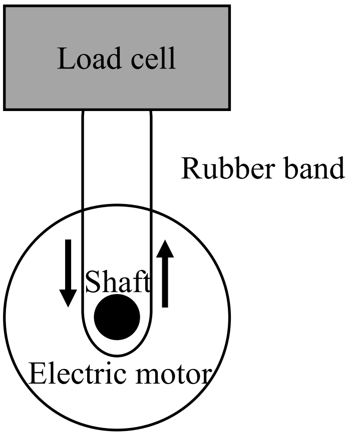

Figure 2.4 – Schematic of a Boothroyd friction tester which consists of a rubber band around the shaft of an electric motor.

They found tannins, known to be astringent, increased the friction coefficient when added to saliva, suggesting astringency was a tactile phenomenon as mentioned previously. The studies have been able to provide fundamental insights into food perception, linking them with physical measurements and are simple to set up. However, the lack of baseline studies and continuity when using lab made devices makes it difficult to analyse measurements and compare data easily. The materials are relatively restrictive, as a rubber band is required. This does not resemble the oral cavity well, and does not allow defined sliding and rolling speeds or temperature control. This limits the conclusions that can be made from them.

Other researchers have developed test methods on existing equipment which primarily has another purpose. This would be useful to researchers who already have these equipment and do not wish to purchase specialist, expensive tribology equipment. One example of this is friction measurements using a Texture Analyser (Stable Microsystems, UK) a piece of equipment well used in the food industry. Chen et al. (2014) developed and built a device to attach to this instrument to measure friction (*Figure 2.5*). Accessories were fabricated in house, consisting of stainless steel base with temperature control and a moving probe with three stainless steel balls attaching to the moving probe of the Texture Analyser.

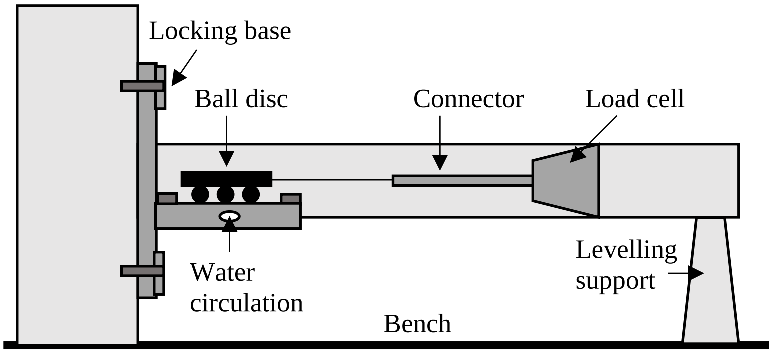

Figure 2.5 – Illustration of experimental set-up of Texture Analyser with friction device (replicated from Chen et al. (2014)*).*

The authors examined samples resembling Newtonian and non-Newtonian fluids and found results were reproducible and comparable to literature. Brossard et al. (2016) later used the same setup to measure the friction coefficient of saliva when mixed with wines obtaining significant differences, indicating that the friction between oral surfaces increases in the mouth with the presence of wine. Again, these studies provided developments in oral processing and insights into oral perception using friction measurements. The modification to the texture analyser was simple, reproducible and relatively low-cost method to measure friction. However, there are limitations. The design only allows for sliding friction, with no way to measure rolling friction, which may be relevant in oral processing studies. The speeds were limited and relatively low compared to those observed in oral processing (Malone et al. 2003).

Another example of this is the Atomic Force Microscope (AFM), although this is used to examine forces and interactions at the nanoscale rather than the macroscale due to the small contact area. In the study of contacting mechanics, AFM performs universally in surface characterization and force determination. The AFM has wide applications as it has a high precision and resolution, and it is non-destructive. The key component in AFM is the sensor for measuring the force on the tip due to its interaction with the sample. Alongside other measurements, this can be used to measure friction force. It has played an important role in evaluating surface properties, especially for nano- and bio- materials. A study by Pettersson & Dedinaite (2008) involved using a colloidal probe AFM technique to investigate friction forces between flat mica surfaces and silica particles coated with mucin, a highly lubricating protein group found in saliva. They show forces between the mucin layers show a low effective friction coefficients. Whilst this technique allows for smaller samples to be analysed, even cells, and fundamental aspects of tribological interactions to be studied, it is not that reprsentative of the oral cavity. As mentioned previously, rolling contributions are not considered and this equipment is expensive and surfaces with high roughness cannot be easily examined.

Many rheometers now manufacturer tribology attachments for their instruments. These systems are easily tailorable and vary between instrument manufacturers, but generally consist of a rotating aspect and a stationary aspect. These contacts can be plates, balls, discs or rings and can consist of single or multiple contacting surfaces. Rheometer based tribological measurements are increasing in popularity for food applications, as many food scientists already own a rheometer. For example Joyner (Melito) et al. (2014) investigates two tribological apparatus: ball-on-three-plate and double-ball-on-plate, shown below in *Figure 2.6.*

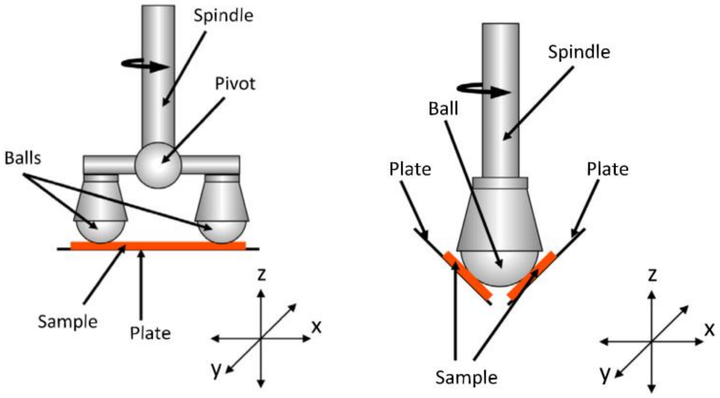

Figure 2.6 - Schematic of double-ball (left) and ball-on-three plate tribology apparatus (right) for Physica MCR 302 Anton Parr rheometer from Joyner (Melito) et al. (2014).

The authors found the tribological measurement system did not affect friction regimes observed for each material, but did affect the magnitude of friction coefficient. The difference in these results were attributed to the set-up of the contacting surfaces. For the ball-on-three-plate system, the lubricant flowed to the bottom of the plates and collect under the ball since the plates are tilted. In the double-ball system, the plate is flat, allowing for the formation of a continuous film of lubricant on the plate surface. Researchers Kim et al. (2015) use the same rheometers ball-on-three-plate system to examine how the mixing ratios of curing agent to base agent of the soft-elastomer surface affect mechanical properties and so the collection and consistency of tribological data. They found the equipment effective in doing so, allowing for all lubrication regimes to be examined. Using a rheometer for tribological applications is advantageous as a range of normal forces, speeds and testing surfaces can be examined with ease.

Using the different testing equipment that primarily has another purpose have their advantages. However, using instruments like the Texture Analyser, AFM and rheometer would only be low cost to someone who already owned these instruments, but if the sole purpose were to measure friction it would be more useful to purchase an instrument dedicated to tribological measurements.

One of the most commonly used commercially available tribometers is the Mini Traction Machine (MTM) by PCS Instruments. In this machine, there are two independently driven, rotating surfaces consisting of a ball, pin or ring on a shaft and a disc. The shaft is lowered to achieve a 45° angle to the horizontal disc to create a contact point between ball and disc (see *Figure 2.7*). A force transducer is attached to the ball arm allowing measurement of the friction force.

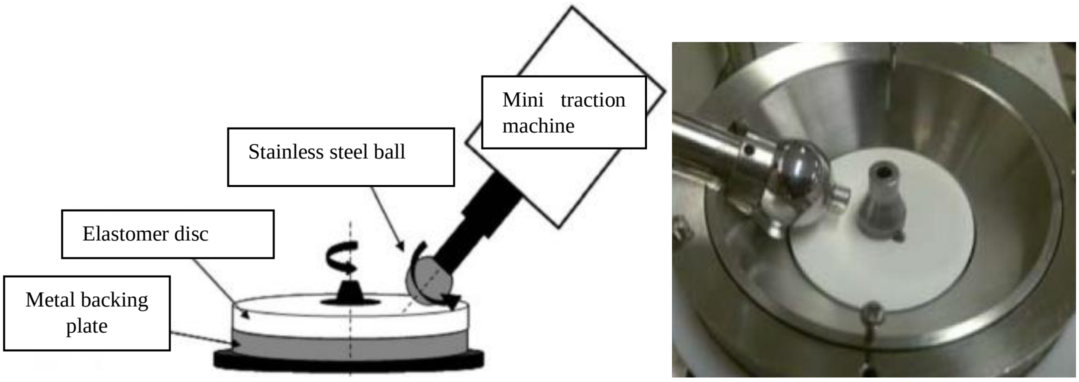

Figure 2.7 – Schematic of MTM (left) adapted from De Vicente et al. (2004) *and photograph of set up (right) for use with soft contacts.*

Normal load, entrainment speed (U) and slide-roll ratio (SRR) are parameters easily defined by the user. U is the mean value of the ball (U_{ball}) and disc speeds (U_{disc}). The SRR is the ratio of sliding to rolling speeds at the contact, described in *Equation 2.2.*:

$$SRR = \frac{U_{ball}-U_{disc}}{U}$$ (*Equation 2.2.*)

The configuration of ball and disc allows friction, lubrication and wear measurements to be obtained for a variety of surfaces and samples, including foods. The ball and disk are enclosed in an insulated chamber and temperature controlled chamber, where sufficient sample to cover ball and disc is placed. The measurements obtained from the MTM are used to understand a range of different lubrication behaviour, from boundary, lubrication and mixed regimes, to rolling, sliding or reciprocating friction which is beneficial when looking to assess oral processing. As the instrument allows the use of one or both contacting surfaces being ‘soft’, contact pressures can be tailored. One of the most common test methods performed using the MTM is the Stribeck test where the friction coefficient (μ) is measured at a desired range of speeds and normal force. At each specified speed, the ball and disc are travelling at different speeds in order to give the desired SRR. A number of studies use the MTM to correlate friction measurement to mouthfeel attributes like slipperiness, fattiness, and astringency (Chojnicka-Paszun et al. 2012; Chojnicka-Paszun et al. 2014; Laguna et al. 2017; Rodrigues et al. 2017; Rossetti et al. 2009).

The advantages of using the MTM are that it is sensitive and designed to give accurate frictional results over a wide range of sliding speeds, sliding and rolling conditions and normal forces. The enclosure of the ball and disk allows complete excellent temperature control whilst there are also a range of accessories available to measure film thickness, electrical contact resistance and various soft contact adaptations. One major drawback of this equipment is the expense, and for researchers who cannot warrant this specialist piece of equipment it may not be the most cost effective instrument of choice.

Although the theory and fundamental knowledge about tribological instruments such as the MTM are well established, a limited number of studies use the MTM to link friction measurements to consumer sensory data. Greater effort is required to develop relevant testing techniques. There is a need to properly design sensory and tribological studies that uncover the tribological basis for perception so it may be possible to obtain predictive capabilities.

2.5.2. Test method development in oral tribology

In order to obtain accurate and reproducible tribological measures, appropriate selection of tribological testing equipment and parameters is critical. An understanding of the measurement process is required in order to be able to assess friction behaviour between the contacting surfaces and the lubricant. As there are so many factors that can impact tribological data, careful consideration should be employed when comparing studies that use different parameters. In an ideal situation, a standard measurement protocol should be employed that allows ease of comparison of tribological studies and a database to be built. A fundamental approach to study the oral tribology of foods is to use well-defined test surfaces, configurations and testing conditions, as well as model lubricants that allow deeper understanding of the tribology measurements. One of the main things that differs between researchers is the equipment and the testing surfaces themselves. The ball-on-disk in a mixed rolling and sliding conditions using at least one PDMS contact is the most widely used set up for oral tribology studies, mainly using the mini-traction machine from PCS Instruments. But, even this differs between researchers. For example, a study by Kim et al (2015) emphasizes that there are multiple degrees of freedom e.g. mixing ratio, curing temperature, curing time, mould finishing, etc. of the PDMS substrate. Further developments are needed in this area in order to improve tribology testing relating to oral processing.

2.5.3. Surfaces in tribology

For traditional tribology, stainless steel contacting surfaces are used. This is of little relevance to the food industry as the surfaces are rigid and do not deform, thus are not representative of softer oral surfaces like the tongue or palate. Tribological studies in the food industry use a combination of soft surfaces (typically a rubber, elastomer or PDMS disc or ball) or a soft surface paired with a steel ball (Dresselhuis et al. 2007; Timm et al. 2011; Garrec & Norton

2012; Sarkar et al. 2019). For soft surfaces, PDMS is most commonly used because of its tailorable properties and low elastic modulus compared to existing tribological surfaces. This allows flexibility in contact area and pressures, although the contact pressures exhibited using PDMS in tribological studies are still of an order of magnitude higher than those found in the mouth (Sarkar et al., 2019). It is easily modified to be hydrophobic, hydrophilic, rough, smooth, etc and can be used to engineer specific topographies to emulate the tongue surface. It is relatively easy to functionalise and it is widely available. Mills (2011) compared the characteristics of different combinations of ball and disc tribopairs (*Table 2.1*).

Table 2.1 - The surface characteristics comparing various ball and disc combinations (Mills 2011).

Surfaces (ball/disc)	**Curve definition across regimes**	**Overall friction values**	**Surface properties**
PDMS/Elastomer	Good	High	Two deformable surfaces, but variability between elastomer discs
PDMS/PDMS	Good	Medium	Two deformable surfaces, consistent surface properties
Steel/Elastomer	Good	Medium	One deformable surface, variability between elastomer discs
Steel/PDMS	Poor	Low	One deformable surface

Mills found the PDMS/Elastomer pair produced curves with good definition across the regimes over the speed range 1-1000 mm/s. PDMS/PDMS and steel/elastomer surfaces provided midrange friction values with good definition across the speed range. Steel/PDMS were two smooth surfaces so showed low friction values but also poor curve definition. The author highlighted issues associated with using commercially supplied elastomer discs as the surface roughness is varied compared to the PDMS fabricated in a laboratory setting where the surface properties can be controlled. Roughness has been shown to play a key role in the friction properties of surfaces in contact. Scaraggi et al. (2011) showed how anisotropic surface roughness strongly influenced the transition from the boundary lubrication regime to the EHL regime. Experiments were carried out using a ball-on-disc configuration to measure the friction coefficient at the contact between a smooth steel ball and a rough PDMS disc as a function of sliding speed. The PDMS discs were made by casting them against two aluminium plates, one of which had an anisotropic rough surface. The results of this study showed the rough PDMS gave rise to a local micro-EHL regime at the contact interface. This can be seen in the Stribeck curves in *Figure 2.8*.

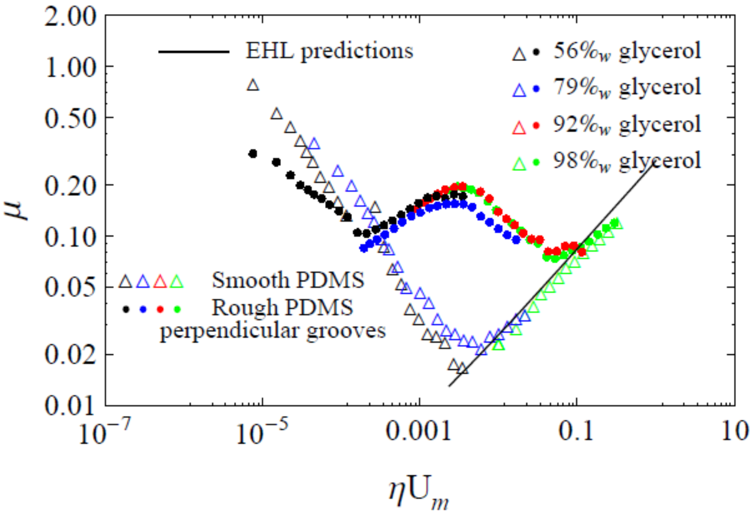

Figure 2.8 – A graph to show the friction coefficient μ as function of the product dynamic viscosity η & mean velocity Um, for the rough surface with grooves perpendicular to the sliding direction, and for smooth rubber for different %w of glycerol (Fig. 4 from Scaraggi et al. 2011).

The author suggests a micro-EHL occurs locally at the individual asperities, each of them having their own local hydrodynamic regime, affording the observed data. As sliding velocity increased, the micro-EHL regime disappeared, being replaced by the EHL regime determined by the macroscopic properties of the system.

Krzeminski *et al.* (2012) studied the effect of stiffness and surface roughness of elastic discs that emulate human tongue properties in order to investigate their frictional behaviour. The authors found lubricating performance was strongly affected by patterning on the tribological testing surface, where the roughness indices were more crucial for lubricating properties in a tribosystem than the stiffness parameters. Nguyen *et al.* (2016) studied three solid substrates (surgical tape, silicone rubber and ethylene propylene diene monomer rubber) which are commonly used in tribological measurement. It was observed that surgical tape best discriminated dairy solutions of different compositions compared to the rubber substrates; the authors attributing this to the surfaces being similar to that of the tongue. None of these surfaces were as representative of the tongue's architecture as the study by Dresselhuis *et al.* (2008) who used oral tissue in the form of a cross section of pig tongue *ex vivo*. However, using a biological sample may cause issues in reproducibility, and samples may not be available or accessible to all researchers, so designing textures in a similar order of magnitude of the tongue is of interest. Ranc *et al.* (2006) investigated a range of hemispherical surface structure in the sub-millimetre range, corresponding to typical tongue roughness. They found the textures critically affect the frictional behaviour of the systems tested. Under dry conditions, the coefficient of friction decreased significantly with an increase in density of hemispherical pillars. In lubricated systems, a structure of high pillar density yielded higher coefficients of friction. This effect was attributed to the protruding structures disturbing the homogeneity of the lubricant film.

The hydrophobicity of the surfaces as well as the lubricant used can also influence friction (Bongaerts *et al.* 2007; Vardhanabhuti *et al.* 2011). Studies acknowledge the importance of using hydrophilic surfaces to more closely represent the oral environment, surfaces are typically modified to be hydrophilic by exposing PDMS to oxygen plasma or ultraviolet-ozone irradiation (Bongaerts et al. 2007; De Vicente et al. 2004; Yakubov et al. 2015). Unfortunately, these methods of treating the surface of PDMS are not permanent as it begins to revert to its previous hydrophobicity within hours; ultimately proving impractical. Coatings have also been applied to PDMS, but these are often not permanent and are able to wash off surfaces, which may be of little use in tribology experiments using a lubricant (Lee & Spencer, 2005; Macakova et al, 2010; Stokes et al, 2011; Vardhanabhuti et al, 2011; Wong & Ho, 2009). Polymer brushes have also been explored, whereby hydrophilic polymers are covalently grafted to the PDMS surface (Bongaerts et al, 2009; Lee & Spencer, 2005; Muller et al, 2003). This method often involves complex techniques, often not accessible to all researchers. Surface modifications need to be stable, relatively simple to achieve and not time consuming in the hope to be as widely accessible as possible to researchers. These attributes remain undeveloped so is of interest to further study.

2.6. Oral processing and tribology

Oral textural sensation is a dynamic process involving food and the interacting surfaces (palate and tongue) in relative motion as they interact with one another. This process incorporates the oral physiological aspects discussed earlier, coupled with the physical (viscosity, temperature, stability) and chemical properties (pH, flavour) of the food. During consumption, food coupled with saliva act as a lubricant between the contacting surfaces, thus the frictional forces will directly depend on the properties of the food. The roughness of the interacting surfaces, the speed and direction of relative motion coupled with the force exerted from the muscles all contribute to the lubrication of food and therefore, oral perception. Alongside this, personal attributes such as saliva quality and quantity, temperature and residence time will affect friction properties (Dowson, 2012; Lilienthal, 1955; Prinz & Lucas, 2000). All of these factors make oral tribology so complex to replicate *in-vitro*. Despite this, tribological measurements have successfully shown to relate lubrication properties with mouthfeel (Malone et al. 2003). Malone related the frictional values of varying fat contents (measured using a tribometer) with 'fattiness' scores obtained from a sensory panel. Dresselhuis et al. (2007) utilised two rotating surfaces in a tribometer to show the effect of oil in water emulsions in mouth-like conditions. Several studies suggest the tribological behavior of foods during oral processing are in the mixed lubrication regime (Chojnicka-Paszun et al. 2012; Dresselhuis et al. 2007; Dresselhuis et al. 2008; Malone et al. 2003). These studies have meant tribology is increasingly being used in the food industry in order to relate friction to how a formulation will behave in the mouth (de Wijk & Prinz 2004). Many well established studies on tribology in food research have focused on liquid foods or liquid food model systems, such as milk (Nguyen et al. 2016; Chojnicka-Paszun et al. 2012), cream (Kokini & Cussler 1983), protein dispersions (Chojnicka et al. 2008) and emulsions (Dresselhuis et al. 2008; Malone et al. 2003). In general, these studies indicate that the individual components, interaction between the components, as well as the bulk properties of the food systems affect lubrication properties and sensory perception. In summary, food tribology is an incredibly useful technique in this area and alongside rheology and texture analysis, it contributes towards understanding the relationship between food structure, texture and mouthfeel.

2.6.1. Saliva in oral tribology

Alongside mechanical manipulation of food as it processed in the oral cavity, there are also chemical manipulations from saliva and the oral surfaces. Saliva has been studied tribologically, as a whole, in components and synthetically (Morell et al. 2017; MacAkova et al. 2011; Prinz & Lucas 2000; Reeh et al. 1996) but despite saliva playing such a crucial role in the processing food and drink, most food tribology work does not consider saliva or salivary substitutes during *in-vitro* tests. This is due to the variability and limited availability of saliva to researchers and lack of an agreed upon standard for artificial saliva. Physiological buffer, phosphate buffered saline (PBS), is commonly used as an artificial saliva due to its wide availability and chemical composition offering similar buffer capabilities to saliva (Mystkowska et al. 2018; Lilienthal 1955). However, Rodrigues et al. (2017) compared using PBS buffer and human saliva tribologically, and found saliva to be significantly more lubricating than PBS showing it may not be that representative as a model saliva in tribology studies. They also showed the quantity of saliva and subsequent mixing with the sample before testing affects *in-vitro* friction.

Whilst saliva was shown to be highly lubricating, it is not straightforward to use tribologically and there are discrepancies in its format and preparation before testing. For example, Bongaerts, Rossetti, & Stokes (2007) compared the tribological performance of fresh and air-dried whole human saliva. They found that fresh saliva lowered the friction of the soft contacts by an order of magnitude compared to air dried saliva. The lubrication property of saliva is also different between stimulated (e.g. chewing or acidic conditions) and unstimulated saliva, with high coefficients of friction in the former. Joyner et al. (2014) found when using whole human saliva there was poor discrimination when saliva was added to samples, regardless of friction behaviour of samples alone. Whilst the saliva was found to be highly lubricating, this measurement is not anticipated this to be an accurate reflection of the lubricating properties of the food whilst they are in the oral cavity.

Some researchers use saliva in *in-vitro* tribology measurements to compare to oral perception. A key oral sensation, astringency, is often examined relating to saliva. Astringency refers to the puckering or drying sensation in oral cavity caused by specific compounds in food and drink. The mechanism for astringency is not yet fully understood as there are no conclusive results which correlate well with sensory perception, but it has been attributed to chemical interactions as well as physical perception caused by diminished lubrication due to interaction of oral surfaces with astringent compounds (Brossard et al. 2016). Though the formation of complexes with saliva and astringent compounds is believed to play a role in the development of astringency, an understanding of the friction behaviour of astringent compounds is not well reported. The effect of β-lactoglobulin (β -LG) at pH 3.5 and 7.0 on the lubricating property of saliva was investigated using tribology (Bongaerts et al. 2007). Saliva was adsorbed onto a polydimethylsiloxane (PDMS) ball and disc to mimic conditions in the oral cavity and the lubricity of saliva films upon exposure to astringent compounds was measured. While addition of non-astringent β -LG at pH 7.0 slowly increased friction of saliva film between tribopair surfaces, β -LG at pH 3.5 rapidly increased the friction coefficients of saliva, which was observed for other well-known astringent compounds epigallocatechin gallate and alum (Vardhanabhuti et al. 2011; Rossetti et al. 2009). This supports the hypothesis that the method of astringency arises from the loss of lubrication of saliva. However, a simple relationship between friction and sensory astringency cannot be found for all conditions, not all astringency compounds cause salivary protein precipitation and not all agents that cause salivary protein precipitation cause astringency (Gibbins & Carpenter 2013).

These studies highlight the incredibly complex role saliva plays in lubricating the oral cavity. Continued studies are necessary in order to understand mechanism behind salivary lubrication during oral processing and also to develop testing conditions akin to saliva lubricated oral surfaces. Such developments are needed to not only accurately assess, understand and quantify food-saliva interactions but also to allow uniformity of food tribological measurements across researchers and industry. As saliva use in tribological measurements is not yet agreed upon, in this thesis saliva or saliva analogues were not used so as to not complicate measurements and complications further.

2.6.2. Tribology and food formulations

Oral tribology studies typically examine food-based samples. However, as foods are complex, often with multiple components and/or with multiple phases, these present a challenge to examine tribologically due to their chemical, structural and physical properties. A table summarising food tribology studies, the equipment and surfaces used is described below (Table 2.2), followed by an overview discussion of studies of particular relevance to this thesis. The majority of these studies use a mini traction machine (MTM) with PDMS surfaces which are smooth and hydrophobic. It is clear more research into modified surfaces is needed, with both model and actual foods.

Table 2.2 – A summary of relevant food tribology studies, the equipment and surfaces used.

Food type	**Lubricant**	**Tribological measurement**	**Type of surfaces used**	**References**
Biopolymer and plant based solutions	Hydrogels of κ-carrageenan, locust bean gum, sodium alginate and calcium alginate beads	MTM	PDMS ball and disc	Krop et al (2019)
	Guar gum solutions	MTM	Stainless steel ball and disc	Malone et al (2003)
	Tea catechins	MTM	PDMS ball and disc	Rossetti et al (2009)
	Hydrogel beads of κ-carrageenan, sodium alginate calcium alginate beads	MTM	PDMS ball and disc	Torres et al (2019)
	Starch granule suspensions of maize and potato	MTM	PDMS ball and disc	Rongkaumpan et al (2019)
	Mango and banana plant cells	MTM	PDMS ball and disc	Zhang et al (2016)
Emulsions and microgels	O/w emulsions	MTM	Stainless steel ball and disc	Malone et al (2003)
	O/w emulsions	MTM	Stainless steel ball and silicone disc	Douaire, Stephenson and Norton (2005)
	O/w emulsions	Optical tribology configuration	Smooth glass, PDMS and pig's tongue	Dresselhuis et al (2008)
	O/w emulsions and emulsions filled gels	Optical tribology configuration	Glass and PDMS	Liu et al (2016)
	Mayonnaise	Friction tester developed in house	Metal cylinder rotating against rubber band	deWijk and Prinz (2005)
	Agar fluid gels	MTM	Silicone disc and stainless steel ball	Fernández Farrés & Norton (2015)
Foods	Milk	Tribo-rheology attachment	Double polypropylene ball on PDMS disc	Li et al (2018), Li et al (2018)
	Yoghurt	Lab-modified texture analyser	Silicone elastomer surface and steel ball	Morell et al (2017)
	Custard dessert	Ring on plate tribology attachment for rheometer	Steel ring and rough surgical tape	Godoi et al (2017)
	Wine	Lab-modified texture analyser	Stainless steel balls and disc	Brossard et al (2016)

Hydrocolloids in food and tribology

Hydrocolloids are commonly used as ingredients in a wide range of food products in order to provide a range of structural properties. These form rheologically complex fluids in aqueous solution and have been used to model food systems in previous tribological studies to probe how friction behaviour is affected by their physical properties (Stokes et al. 2011; De Vicente et al. 2006; Malone et al. 2003). Studies seek to probe the influence of the hydrocolloid polymers on the three tribological regimes to infer their potential relevance on the behaviour of foods during oral processing. For example, in studying sensory properties of foods, Malone (2003) considered that ‘oral slipperiness’ perception of guar gum solutions was related to the mixed lubrication regime friction when using a steel ball and rough-elastomeric plate. Using the same tribopair, Cassin et al. (2001) showed that increasing concentrations of guar gum and pig gastric mucin glycoprotein decreased the friction coefficient in the mixed regime due to adsorption and viscous effects. The measured friction coefficient was related to the adsorption properties of the polymers investigated with evanescence wave spectroscopy, whereby mucins showed a lower boundary friction coefficient compared to water, attributed to a thin film forming on the surface. Whereas guar gum showed similar boundary lubrication to water because it did not adsorb to the surface. Stokes et al. (2011) probed the lubrication properties of polysaccharide solutions with smooth and rough soft contacts. Their results showed that while the polysaccharides demonstrated a similar rheology at low shear rates ($<100\ s^{-1}$), due to their differences in viscosity at high shear rates, their hydrodynamic friction differed. The boundary and mixed lubrication regimes were found to depend on the conditions in the contact, in particular the adsorbed film properties. For smooth contacts, the boundary and mixed lubrication regimes were dependent on the wet mass of absorbed polymer and the adsorbed film storage modulus. Whereas for the rough surfaces, the actual amount of polymer adsorbed to the substrate was the main contributing factor on the friction coefficient in the boundary regime.

Emulsions in food and tribology

Emulsions are common in foods and often provide unique mouthfeel properties due to have at least two phases. The stability of emulsions during processing has attracted a lot of research attention, but of particular interest to food tribologists is the destabilization of emulsions once they have been consumed and orally processed. Chen (2015) and Sarkar & Singh (2012) discuss possible routes of destabilisation of food emulsions as a result of saliva mixing and shear during mastication. Four mechanisms are identified and presented in schematically in *Figure 2.9*: salt induced aggregation, depletion flocculation, bridging flocculation and coalescence.

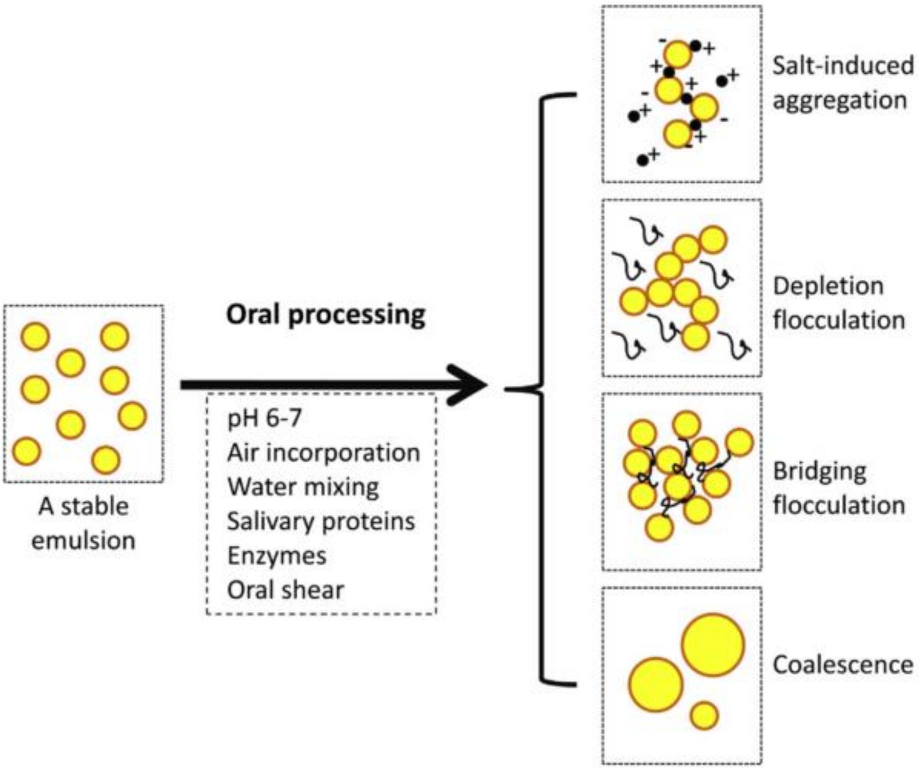

Figure 2.9 – Proposed methods of emulsion destabilisation (schematic from Chen (2015)).

Emulsions generally reside for a relatively short period of time in the mouth as they are processed but are subjected to a broad range of environmental conditions, such as exposure to body temperature, incorporation with saliva, ions, high shear and squeezing between oral contacting surfaces, such as grinding teeth, tongue–teeth and tongue–oral palate (Sarkar et al. 2017). The coalescence of fat droplets in emulsions that can occur during oral processing is suggested to decrease the coefficient of friction and to increase of perception of fat-related sensory attributes, such as creaminess (Chojnicka-Paszun et al. 2012; Dresselhuis et al. 2008).

Complex food products

Food systems are rarely ‘simple’. This presents a challenge for food tribologists – as tribology is so complex the testing of these substances means additional research and understanding is necessary. It is often hard to interpret given the difference in testing parameters between food tribologists (as mentioned previously). Nonetheless, researchers continue to make inroads in examining complex systems and as more research is disseminated, more research follows. In a study by Selway & Stokes (2013) complex commercial soft-food systems (custards, yogurts and thickened creams) were characterized. It was shown that despite generating similar bulk rheological properties, foods within each product series exhibit unique tribological properties, attributed to the preferential entrainment of different phases and components in the contact. This study highlights the importance of this research, but also the gaps in understanding complex systems.

Particles are often found in food products, giving rise to positive food experiences such as creaminess and smoothness but also to negative experiences like grittiness and roughness. Yakubov et al. (2015) investigated the lubrication of microsphere suspensions between compliant substrates (PDMS) to represent oral substrates. The study is thorough; investigating all aspects of possible interest including the influence of matrix viscosity, particle phase volume, surface roughness, wetting and the effect of slide-roll ratio. Generally, the suspensions behaved as expected in EHL regime, where the friction coefficient is dependent on bulk properties. The EHL regime was observed if the film thickness was greater than the particle diameter. Below this critical film thickness, the friction coefficient was characteristic of the mixed and boundary lubrication regimes. In the boundary regime, it was found particles of greater than 5% phase volume were entrained, even at low sliding speeds, due to the deformation of the soft, compliant substrates. In this regime, particles lowered friction due to ball bearing behaviour providing surface roughness was low enough to prevent surface-asperity interactions. A study by Liu *et al.* (2016) reported a similar ball bearing lubrication mechanism from the presence of micro-particulated whey protein particles reduced friction. Chojnicka-Paszun & De Jongh (2014) investigated suspensions of microcrystalline cellulose particles. The researchers found the particles may not fit into surface asperities, so enhanced surface roughness affording an extended boundary regime.

A study by Gabriele et al (2010) studied soft deformable particulate systems (fluid gels) and proposed a mechanism of their lubrication in tribological testing. A fluid gel is formed when shear is applied to a hydrocolloid during gelation, forming a suspension of gelled particles dispersed in a non-gelled continuous medium. Schematic representation of the proposed mechanism of fluid gel lubrication is presented in *Figure 2.10* below (Gabriele et al. 2010). Zone A shows the disc speed is not sufficient to induce entrainment of the particles whereby only the fluid medium can access the gap between the ball and the disk (inset images a and b). For Zone B, the gap between the ball and disc is similar to the size of the particles (inset image c), including their entrainment resulting in an increase in friction. For Zone C, a further increase in speed results in the gap between the surfaces being larger than the particles allowing more particles to be entrained, resulting in increased lubrication and a decrease in friction coefficient with speed (inset image d). Ideally, more work on particulate suspensions should be completed to understand how they lubricate between the contacting surfaces.

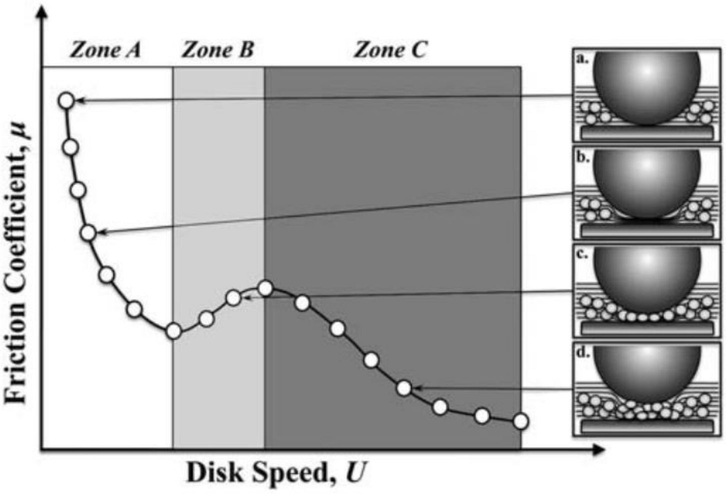

Figure 2.10 – Mechanism of fluid gel lubrication from Gabriele et al. (2010).

2.7. Conclusions

There is a wide range of existing and ongoing tribological studies relating to oral processing. Experiments performed using a wide range of lab-made or commercially available tribology devices show that the friction and lubrication properties of food samples can be measured. These can be related to mouth-feel attributes experienced by a consumer including fatty feel, astringency, smoothness, roughness, and slipperiness. It is important that appropriate testing conditions are employed (normal force, sliding and rolling conditions, relevant and appropriate materials of the contacting surface) in order to achieve accurate and representative tribological measurements. It is evident there is a need for the development of understanding and techniques to replicate *in vivo* conditions (i.e. mouth feel). One crucial aspect is the surface properties including surface topography and surface chemistry. There is scope to investigate different material properties including surface structure, where there is little investigation into how specific surface textures affect friction coefficient in soft contacts. Existing studies tend to use hydrophobic contacts, which have little relevance to the oral cavity which is hydrophilic due to a coating in saliva. Whilst there are studies available examining hydrophilic surfaces, few focus on examining a range of accessible, permanent techniques. The food systems themselves are also incredibly complex as is there interaction with the oral surfaces, so a greater understanding of model systems relating to more complex systems is required in order to understand how a food would behave in use. It would be ideal if *in-vitro* experiments could be used to help formulate products accepted by consumers, without the need for extensive sensory testing. Tribology shows great potential towards achieving this. Although there are limited studies concerning tribology and in food systems, the research to date shows great potential of the approach in establishing relationship between researchers using tribological measurements to design and formulate foods.

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3. USING A THREE-BALL-ON-PLATE GEOMETRY FOR SOFT TRIBOLOGY APPLICATIONS

Using a three-ball-on-plate geometry for soft tribology applications

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Keywords: friction coefficient, measurement, rheometer, soft tribology.

Abstract

Friction tests are a valuable tool for the analysis of food formulations to understand how they may behave during oral processing. Generally, food laboratories do not own specialist tribological testing equipment. It is more common for them to own or use a rheometer for which most commercially available instruments now offer an attachment to measure friction. The objective of this study was to examine the effect of using a three-ball-on-plate rheometer attachment for soft tribology measurements by assessing the friction properties of various model food-like systems. In addition, results were compared to an existing tribological instrument frequently used in oral processing applications (a mini traction machine) under pure sliding conditions. Results show similarities between the two techniques for simple systems, showing friction results depend less on the specific geometry compared to complex systems. The three-ball-on-plate geometry for the rheometer allowed detailed measurement of the boundary lubrication regime due to achieving low speeds unavailable when using the mini traction machine. Going forward, the three-ball-on-plate tribology attachment will be an incredibly useful tool in oral processing applications.

3.1. Introduction

Traditionally tribology, the study of friction, lubrication and wear, has been used to determine the properties of systems concerning contacting surfaces like machine components and bearings (Hailing, 1991). More recently, tribology has been used with focus on oral processing to study the frictional properties of food systems, for example oil-in-water emulsions (Chojnicka et al., 2008; Dresselhuis et al., 2007), dairy products (Chojnicka-Paszun et al., 2012; Joyner et al., 2014) and chocolate (Rodrigues et al., 2017). Tribological measurements of foods are generally performed on soft surfaces, such as rubbers, silicones and biological tissues as these more closely resemble oral surfaces than typical steel-steel contacts (Bongaerts et al., 2007; Chen and Stokes, 2012; Dresselhuis et al., 2008; Sarkar et al., 2019). Tribometers, like the Mini-Traction Machine (MTM) by PCS Instruments (Garrec and Norton, 2012; Myant et al., 2010), custom-made laboratory apparatus (de Wijk & Prinz, 2004; Dresselhuis et al., 2008) or rheometers with tribological attachments (Kieserling et al., 2018; Krzeminski et al., 2012) have all been used to understand the tribological properties of foods. Many rheometer manufacturers now offer tribology attachments for their instruments. These systems vary between instrument manufacturers but generally consist of a rotating aspect and a stationary aspect. The contacts can be plates, balls, discs or rings and can consist of two or more contacting surfaces. For example Joyner (Melito) et al. (2014) investigates two tribological apparatus: ball-on-three-plate and double-ball-on-plate. The authors found the tribological measurement system did not affect friction regimes observed for each material, but did affect the magnitude of friction coefficient. The difference in these results were attributed to the set-up of the contacting surfaces as the double-ball system had a horizontal plate; whereas the ball-on-three-plate system had angled plates meaning lubricant flowed off them and measurements were not accurate.

Using a rheometer for tribological applications is advantageous as a range of normal forces, speeds and testing surfaces can be examined with ease suggesting this method can provide similar information to other commercially available tribometers. The advantage of using the rheometer attachment for tribology measurements would be reduced cost and advanced measurement techniques for institutions that own or have use of a rheometer, but cannot warrant the purchase of a specialist piece of equipment for tribology. Rheometer based tribological measurements are relevant for food applications as many food scientists already own a rheometer. In this study, a three-ball-on-plate rheometer attachment is compared to a Mini Traction Machine (MTM), which is well established for use in soft surface tribology. The MTM consists of a disc mounted in a sample pot onto which a ball on a shaft is lowered to be in contact with at a 45° angle. Entrainment occurs between these surfaces as they rotate. Entrainment for the rheometer relies on the mounting plate repelling from the rotating geometry; separating to allow lubricant in between. The plate/disc surface in the rheometer is stationary giving only pure sliding friction measurements, whereas for the MTM a mixture of sliding and rolling friction can be used as both surfaces are able to rotate independently. During oral processing, the tongue moves up and down, pressing the food against the palate in order to process it. Since the palate does not move, it can be assumed that sliding motions likely dominate in the mouth. However, in practice this process is more complex as mastication, saliva incorporation and tongue motion mean food experiences both sliding and rolling motions (Chojnicka et al., 2008).

This study aims to use a range of previously tribologically examined model food systems. These include Newtonian fluids, a shear-thinning hydrocolloid solution, a simple emulsion and a soft particulate system. Hydrocolloids cover a wide range of materials, including a variety of polysaccharides and gums. These are widely used in food formulations as thickeners, rheology modifiers and gelling agents which give structure and specific textural properties to the product (Dickinson, 2003). Guar gum is frequently reported in literature due to its extensive use in foods and Non-Newtonian shear thinning behaviour. Malone previously studied guar gum tribologically finding correlation between concentration and oral perceived slipperiness (Malone et al., 2003). The use of emulsions in food is commonplace; both in manufactured and processed foods, and natural products like milk. Emulsions give textural (for example creaminess, oiliness) and taste to a product. The basic structure of an emulsion consists of two immiscible liquids, typically an oil phase and an aqueous phase. One is dispersed in the form of droplets within the other. Food based emulsions have been well examined tribologically (Anvari and Joyner (Melito), 2017; Douaire et al., 2014; Dresselhuis et al., 2007; Malone et al., 2003). A range of gels are used in food applications where the gelation process leads to a quiescent gel. The gelation process can be modified by applying shear during the cooling process, allowing discrete gel particles to form in suspensions. The resultant material, a fluid gel, is both solid-like and liquid-like. These gels are increasingly being used as fat replacement, due to being able to impart structural properties whilst comprising of mostly water. These show non-typical Stribeck behaviour so will be of interest to compare in this work (Fernández Farrés and Norton, 2015; Gabriele et al., 2010).

The MTM has long been the most widely used instrument in food tribology, however researchers are increasingly using rheometers with tribology attachments to study friction (Pradal and Stokes, 2016). To the author’s knowledge, a comparative and evaluative study of rheological apparatus for the application of oral processing has not been performed. Therefore, the objective of this study was to examine the effect of using a three-ball-on-plate rheometer attachment for soft tribology measurements by assessing the magnitude and variation of friction coefficient as well as comparing data to that obtained from the MTM in as close conditions as possible. A range of model food systems were used to compare measurements: Newtonian fluids, a shear-thinning hydrocolloid solution, an oil in water emulsion and a soft particulate fluid gel.

3.2. Materials and methods

Polydimethylsiloxane (PDMS) (Sylgard 184 Silicone Elastomer kit) was purchased from Dow Corning, US. Guar Gum, Agar and Tween 20 were obtained from Sigma Aldrich, UK. Vegetable oil for use in emulsions was purchased from Sainsbury's, UK. Materials were used with no further modifications or purification.

3.2.1. Disc preparation

Discs were fabricated using a two-part kit (Sylgard 184) consisting of silicone elastomer and curing agent which were mixed in the manufacturers recommended 10:1 ratio. The binary mixture was poured into a sheet of 4 mm thickness, degassed and placed in an oven at 70°C for 2 hours. The sheet was left to cool for at least 24 hours and discs were cut out for use in the tribometer using a 46 mm diameter disc cutter. Before all tests, PDMS discs and steel balls were sonically cleaned in isopropanol followed by distilled water for 6 minutes each. They were dried in air and fitted into the tribometer cell. Each disc was used for one experiment and then discarded.

3.2.2. Guar gum solutions

Samples were prepared by adding the desired concentration (wt%) of guar gum to distilled water and stirring for ~30 minutes. Whilst still stirring, samples were hydrated by heating for a further 30 minutes at 80°C. In this study, solutions of 0.2%, 0.4% and 0.6% guar were examined. Samples were produced on the same day as testing and tested three times to obtain an average.

3.2.3. Oil in water emulsions

Oil in water emulsions were prepared using required w/w% of vegetable oil, 1% Tween 20 and distilled water. The samples used in this study contained 20%, 30% and 50% vegetable oil in addition to pure water and pure oil samples. The samples were sheared for three minutes in a Silverson high shear mixer at 10000 rpm. Droplet sizes for all emulsions ranged from 5-10 µm (measured using an optical laser particle size analyser (Mastersizer 2000, Malvern Instruments, UK)). Samples were produced on the same day of testing and tested three times to obtain an average.

3.2.4. Soft particulate gels

Agar fluid gels were prepared in a lab-scale continuous process pin-stirrer (method replicated from Ellis, Norton, Mills, & Norton (2017)). The required mass of agar was dispersed in deionised water and heated to 90°C whilst stirring. The resultant hot solution was fed into the jacketed pin-stirrer cooled to 5°C via a peristaltic pump, set to a speed of 25 mL min^{-1}. The inlet temperature was controlled to ~ 70°C and the outlet to 5°C to ensure gelation occurred under shear (gelation temperatures ~ 30°C). The shaft rotation speed was set to 2000 rpm. Fluid gels were tested after 48 hours to ensure post-production particle ordering completion and stored at 5°C until use. Particle sizes were measured using an optical laser particle size analyser (Mastersizer, Malvern Instruments, UK). Agar fluid gels of concentration 1%, 2%, 3% and 4% agar were found to have average particle diameters of 188 ± 11 µm, 132 ± 9 µm, 112 ± 14 µm and 125 ± 5 µm respectively.

3.2.5. Shear rheology

Rheological measurements were performed using a Kinexus Pro rheometer (Malvern Instruments, UK). For the agar fluid gels, viscosity curves were obtained by recording shear viscosity through a range of applied shear rates at equilibrium (0.001–500 s^{-1}). Measurements were performed at room temperature (25°C). To avoid slip a serrated parallel plate geometry was used (60 mm serrated parallel plate) with 1 mm gap. Experiments were carried out in three replicates.

3.2.6. Tribology

Two different tribological set ups were investigated and compared. A rheometer with three-ball-on-plate tribo-geometry attached and a mini traction machine were used to determine friction properties. A tribo-pair of stainless steel ball and lab-made PDMS discs were investigated for both systems; materials previously used to represent of oral surfaces due to similar mechanical properties to that of the tongue (Bongaerts et al., 2007; Dresselhuis et al., 2007). The stainless steel balls were provided by the manufacturer of the instrument used.

3.2.7. Mini-traction machine

A mini traction machine (MTM) manufactured by PCS Instruments, UK was used to perform tribological measurements to compare data obtained from the rheometers. The MTM consists of a ball loaded onto a disc producing a small point of contact where material can be assessed. The ball and disc are independently driven which gives precise control over speeds and direction of rotation of the contacting surfaces as well as ratio of speeds of the contacts. The MTM also allows for control over applied normal force. As the rheometer only has sliding functionality, pure sliding conditions of 200% SRR was used. Three tests of ascending sliding speed 1 to 1000 mm/s were completed and the average reported. A volume reducing insert was used allowing for a sample size of 15 ml. Experiments were performed at room temperature (25°C). A normal force of 1 N was used (unless stated otherwise) as in mouth friction was reported to be between 0.1 N and 10 N (Miller and Watkin, 1996). 1 N would allow low contact pressure, which is of relevance in oral processing applications.

3.2.8. Tribology attachment for rheometer

A three ball-on-plate tribology attachment (TA) for Discovery HR-2 rheometer by TA Instruments, UK was used. The geometry consists of 3 x ¼ inch diameter stainless steel hemispheres, which screw onto a flat plate (*Figure 3.1*). The geometry head where the hemispheres were attached is flexible due to a spring-like beam coupling.

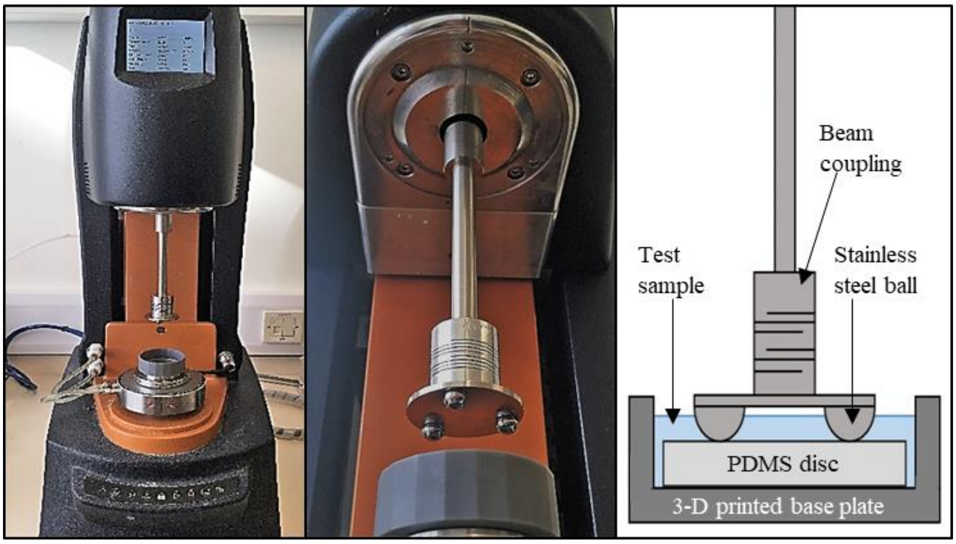

Figure 3.1 – Three-ball-on-plate tribology attachment for the Discovery HR-2 rheometer by TA Instruments.

The torque was the independent variable which enabled calculation of friction coefficient. The friction coefficient, μ, was calculated by *Equation 3.1*:

$$\mu = \frac{M}{dF_N} \qquad \text{(\textit{Equation 3.1})}$$

where M = torque (Nm), d = arm length at 0.015 m and F_N = normal force (N).

Flow sweeps were performed measuring torque through a range of applied velocities at equilibrium (0.0001 to 10 radians/s where the linear speed equates to ~ 0.002 to 150 mm/s sliding speed) with ten measurements per decade (50 measurements total) at room temperature

(25°C) and normal force of 1 N, unless stated otherwise. During testing, the PDMS disc was secured using a custom 3-D printed base plate seen in *Figure 3.2* and visible in *Figure 3.1*. A sample volume of 15 mL was used. Each sample was tested three times and an average obtained.

Figure 3.2 – Photographs of 3-D printed base plate (tribometer cell) for holding the PDMS disc.

The contact area and average contact pressure at 1 N normal force were calculated for both systems and are displayed in *Table 3.1* below where total contact area was calculated using equations from Gabriele (2011). The TA system has a smaller contact area, but a larger contact pressure when comparing the same applied normal force.

Table 3.1 – The ball diameter, contact area and average contact pressure at 1 N for the stainless steel ball and PDMS tribo-pair for each tribological set up.

Instrument	**Ball diameter (radius, m)**	**Total contact area 1 N (m^2)**	**Avg contact pressure 1 N (kPa)**
MTM	¾ inch (0.0095)	5.4×10^{-6}	185
TA	¼ inch (0.003175)	3.7×10^{-6}	270

3.3. Results and discussion

A series of Stribeck curves were investigated to compare and evaluate the tribological systems with different test samples: Newtonian fluids (vegetable oil and water), shear thinning polymer solutions of varying guar concentration, oil in water emulsions with varying oil concentration and particulate suspensions (agar fluid gels) with varying agar concentration are reported. These samples were chosen as they cover a range of formulations found in food products. They have also been well investigated tribologically and will be used to allow for comparison between data collected in this study and existing data from literature.

3.3.1. Newtonian fluids

The tribological behaviour of a Newtonian fluid, vegetable oil, was examined and shown in *Figure 3.3* comparing the MTM and tribology attachment (TA) for rheometer measurement systems. The TA system showed typical Newtonian behaviour, with a full Stribeck constructed over the speed range tested. Above 1 mm/s, the MTM and TA systems show similar behaviour to one another. For the MTM, it is clear only the hydrodynamic regime is present under these testing conditions as friction coefficient increases with increasing speed.

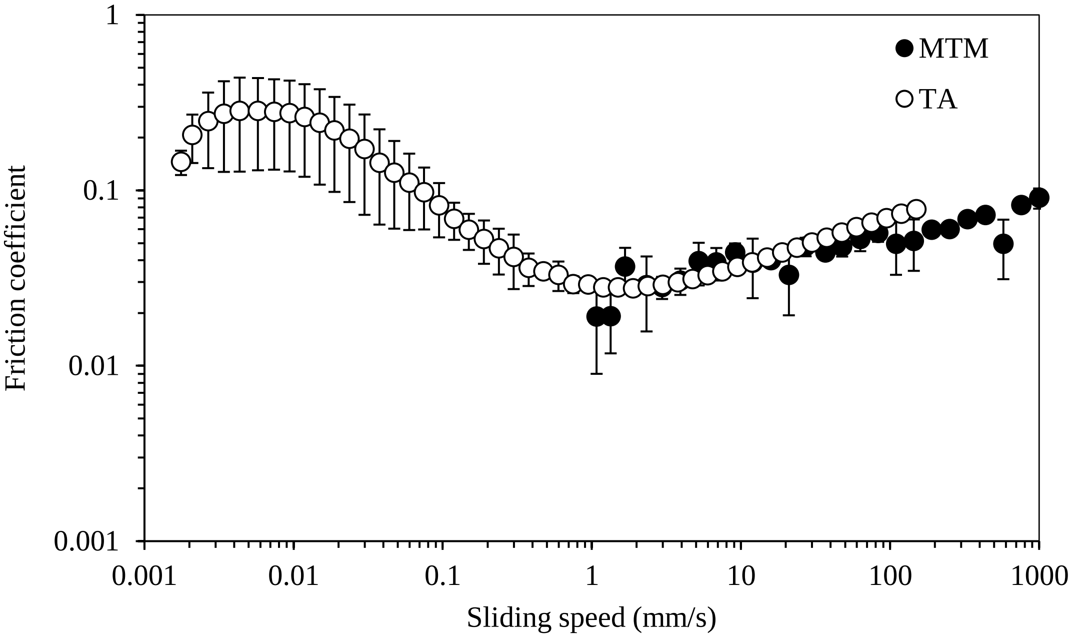

Figure 3.3 – Friction coefficient vs sliding speed of vegetable oil with the two different tribological measurement systems at normal force 1 N.

The tribological behaviour of water, a lower viscosity Newtonian fluid, was examined and shown in *Figure 3.4* comparing the MTM and TA systems.

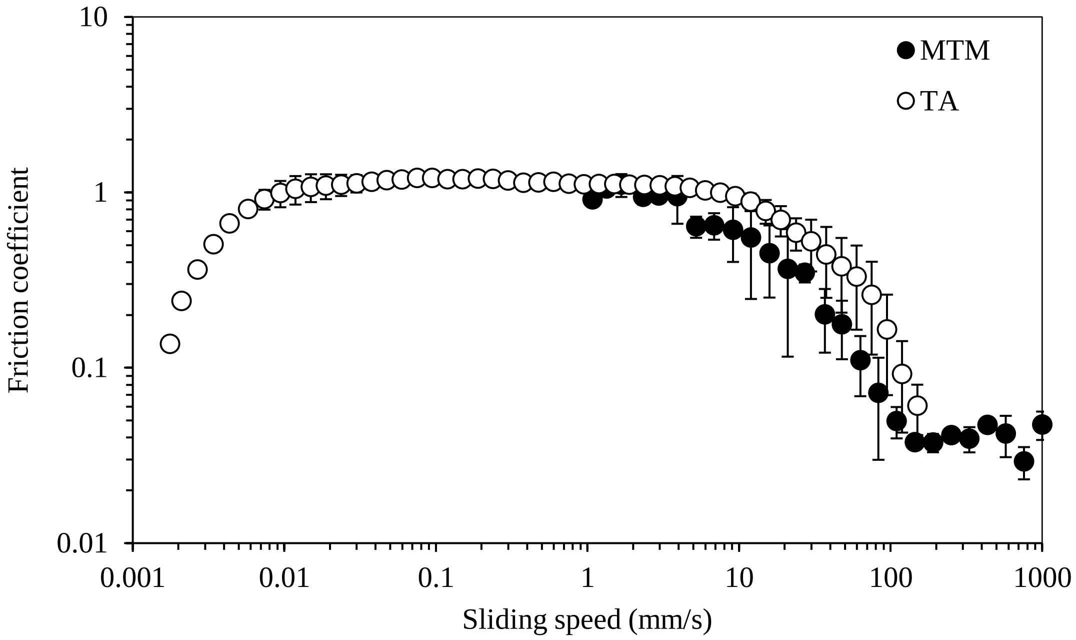

Figure 3.4 – Friction coefficient vs sliding speed of water with the two different tribological measurement systems at normal force 1 N.

The data presented here is different to that of the more viscous vegetable oil, with an extended boundary regime observed for the TA system. The TA system shows boundary and mixed lubrication, whereas the MTM system shows a small amount of boundary, mixed and initial hydrodynamic lubrication behaviour. Again, the systems show a similar trend in friction behaviour where the speeds overlap. The initial increase in friction coefficient below 0.01 mm/s is typical of static friction, due to low sliding speeds (Kieserling et al., 2018).

The correlation coefficient was calculated to show similarities between friction response between comparable sliding speeds (1 mm/s-150 mm/s). When comparing MTM and TA systems, a strong positive correlation coefficient was observed of 0.85 for vegetable oil and 0.96 for water confirming a good agreement with the trend of data for the overlapping speeds for both measurement systems.

3.3.2. Normal force comparison

Further experiments were performed to examine a range of normal forces (*Figure 3.5*). Test parameters (speed, SRR, test substrates) were the same as previous experiments but the normal force was changed. Normal forces examined were 0.1 N - 5 N, to explore the range of normal forces reported to be experience in the mouth (Miller and Watkin, 1996). The test lubricant was vegetable oil.

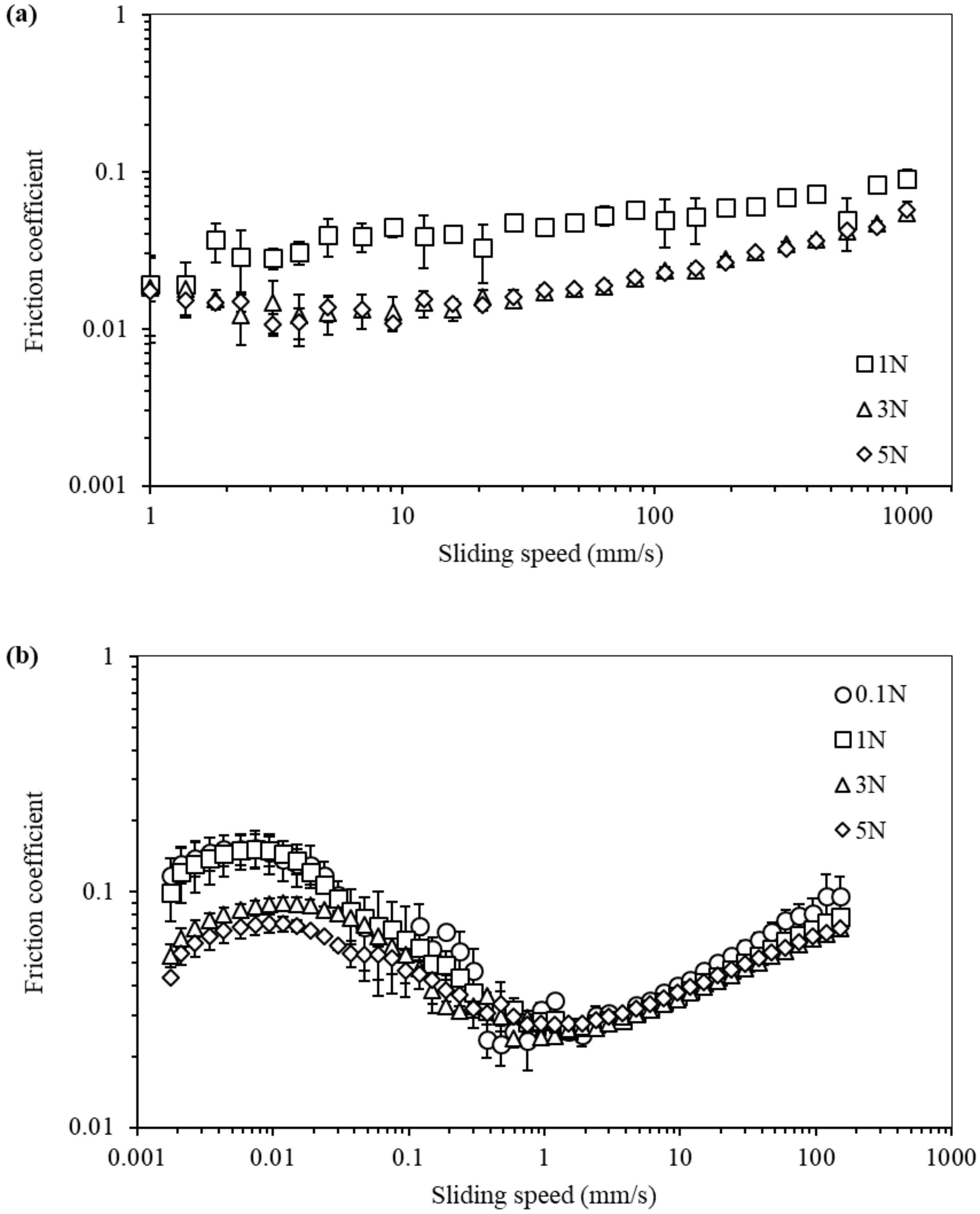

Figure 3.5 - A comparison of normal force for pure vegetable oil performed by (a) MTM by PCS Instruments and (b) Discovery HR-2 rheometer by TA Instruments with three-ball-on-plate tribology attachment.

For the MTM, the results at 1 N, 3 N and 5 N normal forces are presented, showing the same lubrication regimes over the speed range tested (*Figure 3.5a*). The MTM system showed a reduction in friction coefficient with increasing load which can be explained by smoothing of the surfaces due to deformation of the asperities (Prinz et al., 2007). 0.1 N showed high variation due to limitations in normal force control of the equipment so is not presented in this work.

The TA system allowed the measurement of friction at low normal force and speed (*Figure 3.5b*) as a full Stribeck curve was obtained for the range of normal forces. 0.1 N and 1 N behaved similarly, with a greater friction coefficient at low sliding speeds compared to 3 N and 5 N, which also behaved similarly at these speeds. As with the MTM system, the TA system showed a reduction in friction coefficient with increasing load. A greater reduction in friction coefficient was observed for the MTM system compared to the TA system.

The normal force capability of both instruments was examined further by comparing the average applied normal force to assess accuracy. *Table 3.2* shows the variation in the control of normal force for both instruments at a range of speeds where they both showed values close to 1 N with overlapping standard deviations.

Table 3.2 – A comparison of normal force (1 N applied) at different fixed speeds for pure vegetable oil for two different tribological measurement systems (mean ± 1 standard deviation).

Speed (mm/s)	**Measured normal force (N)**	
	MTM	**TA**
1	1.03 ± 0.02	1.00 ± 0.04
10	1.03 ± 0.01	0.97 ± 0.04
100	1.01 ± 0.01	1.03 ± 0.06

3.3.3. Guar gum solutions

The aim of these particular studies were to investigate the friction behaviour of a shear thinning polymer solution. Guar gum solutions of 0.2, 0.4 and 0.6 wt% were tribologically investigated using the MTM and TA systems (*Figure 3.6*).

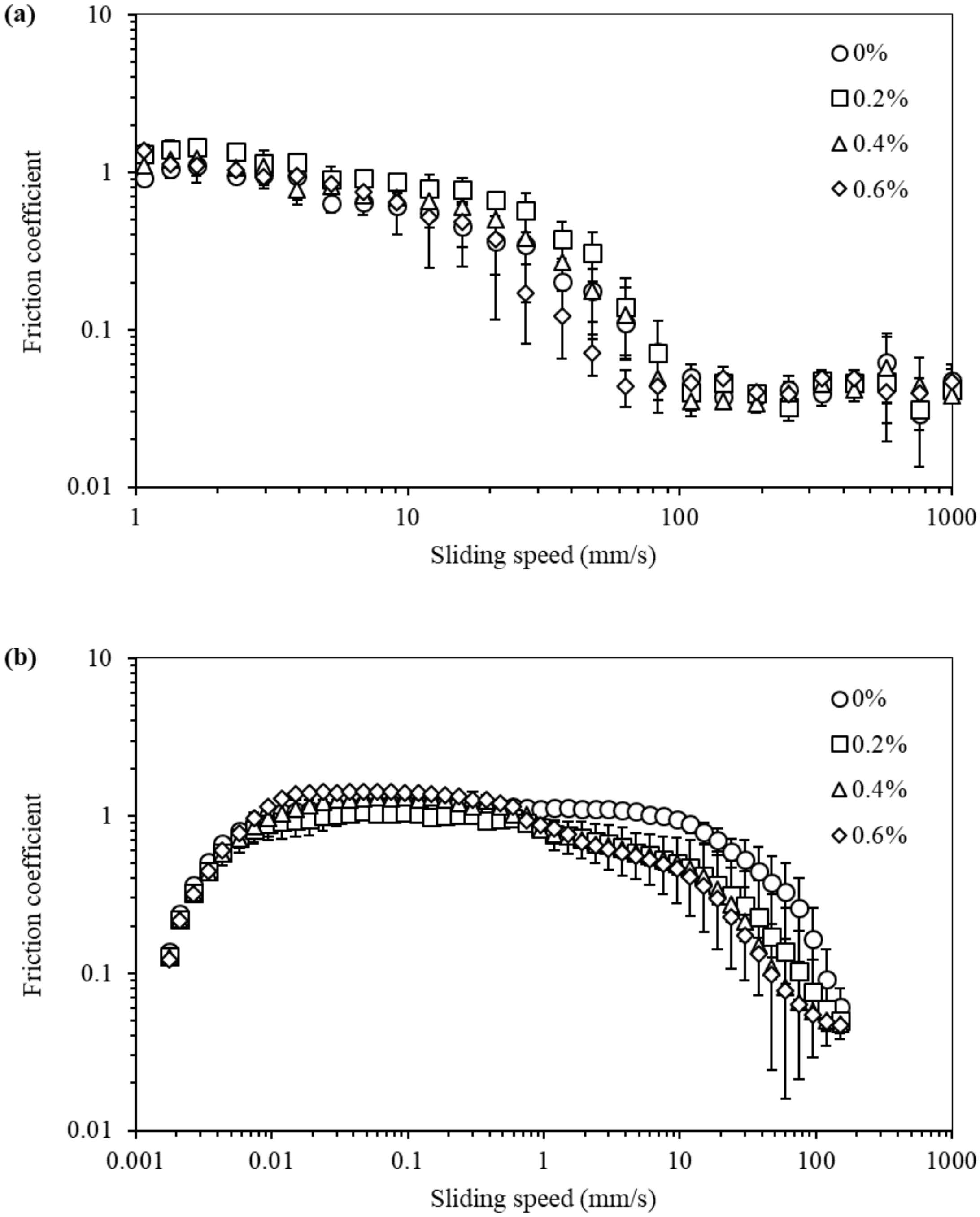

Figure 3.6 – Friction coefficient vs sliding speed of guar gum solutions of varying concentration measured using (a) MTM by PCS Instruments and (b) Discovery HR-2 rheometer by TA Instruments with three-ball-on-plate tribology attachment at normal force 1 N.

There is smooth progression between regimes of all samples tested on the MTM (*Figure 3.6a*), although only a small section of the hydrodynamic regime was observed for the speed range tested. The friction behaviour transitions from boundary lubrication where the ball and PDMS are in contact, to mixed lubrication as the guar gum solutions begins to be entrained; to the hydrodynamic regime (>100 mm/s) when the guar solutions are fully entrained. Overall for the MTM, there was little difference observed between concentrations of guar gum tested under these conditions and the solutions showed a similar response to water. The TA system showed boundary lubrication and mixed lubrication over at the speed range tested (*Figure 3.6b*). Below 0.1 mm/s, static friction is observed. The data generally followed the same trend until the speed reached 10 mm/s where definition between the different samples becomes clearer. Above this speed, the mixed regime is entered and guar gum solutions with increasing concentration lubricate more effectively. Below speeds of 0.5 mm/s, greater concentrations of guar gum exhibited the highest friction coefficient. This is likely due to the increased amount of polymer chains of guar gum which have been suggested to block the contact inlet, limiting lubrication of the contacting surfaces (Garrec and Norton, 2012).

For 0.4% guar gum solution, the data from each instrument was compared (*Figure 3.7*). Above 1 mm/s, friction coefficient decreases as the mixed regime is entered. The MTM and TA data show a similar trend in friction behaviour across the overlapping speed range.

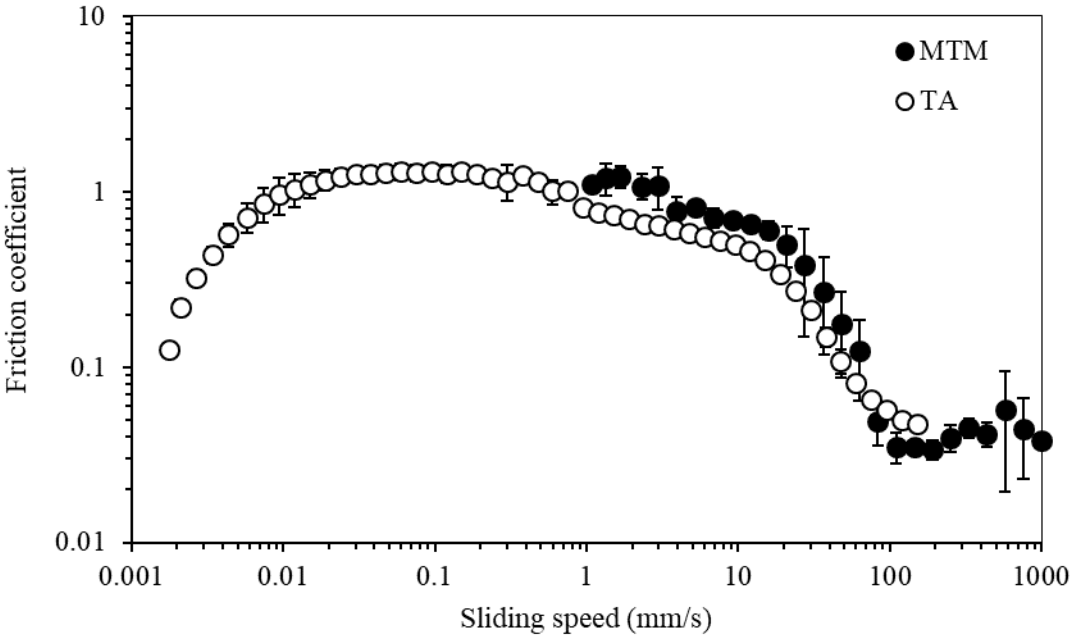

Figure 3.7 - Friction coefficient vs sliding speed of 0.4% guar gum solution with the two different tribological measurement systems at normal force 1 N.

The MTM system shows mixed and hydrodynamic lubrication, but little boundary lubrication. The TA system shows static, boundary and mixed, with little/no hydrodynamic lubrication behaviour at the sliding speed range examined. Both systems observed the main differences between increasing concentrations of guar gum solutions in the mixed regime, as friction coefficient is decreasing with increasing sliding speed. When comparing these results to literature, similar mixed lubrication behaviour has been previously reported by De Vicente, Stokes & Spikes (2004) and Garrec & Norton (2012) who also used an MTM to examine their samples. However, unlike the MTM system, the TA system shows differences between the samples in boundary lubrication where with increasing guar gum concentration, the friction coefficient increases. The MTM does not show the same degree of differentiation in the boundary regime where all samples behave similarly. This could be attributed to only using pure sliding conditions (200% SRR) whereas the studies by De Vicente, Stokes & Spikes (2004) and Garrec & Norton (2012) use a mixture of sliding and rolling conditions; SRR has been shown to affect tribological measurements (Yakubov et al., 2015). It may be of interest to complete further research in order to understand the importance of sliding and rolling conditions to oral processing applications.

3.3.4. Oil in water emulsions

Oil in water emulsions with 20%, 50% oil as well as pure water (0%) and pure oil (100%) were investigated using the MTM and TA systems (*Figure 3.8*).

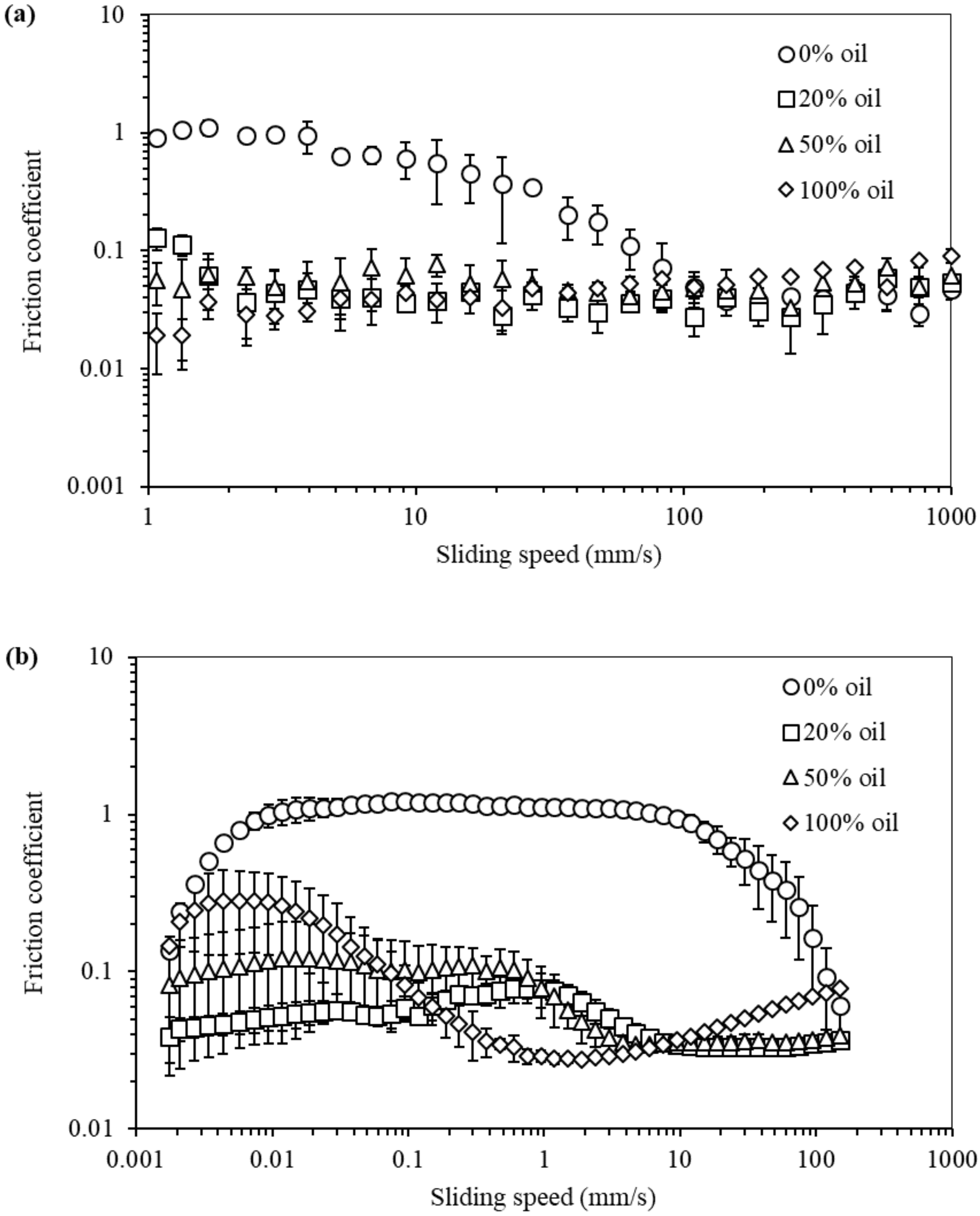

Figure 3.8 - Friction coefficient vs sliding speed of oil in water emulsions of varying oil concentration measured using (a) MTM by PCS Instruments and (b) Discovery HR-2 rheometer by TA Instruments with three-ball-on-plate tribology attachment at normal force 1 N.

The results for the MTM system do not follow a typical Stribeck curve, there is little distinction between the different samples (*Figure 3.8a*) with the exception of the 0% oil (pure water) sample discussed previously. The oil is highly lubricating; all oil samples show similar lubrication properties as 100% oil with friction coefficients less than 0.1 across the speeds tested. Results from the TA system for the speed range studied showed with a greater oil content providing greater lubrication (*Figure 3.8b*). The data observed for 100% oil as previously discussed shows a near perfect Stribeck curve with clear definition of regimes and smooth transition between them. The emulsions demonstrated similar friction response, with boundary lubrication present until around 1 mm/s, where as speed increased mixed lubrication and initial hydrodynamic lubrication were observed.

Whilst the behaviours for both systems are not similar, generally, the MTM showed poor distinction between all samples containing oil whereas the TA system showed distinction between 100% oil and the emulsions. Over the speed range tested, the TA system was successful in showing as much of the Stribeck as possible allowing better comparison of the samples. For the 20% oil emulsion, the data from each instrument was compared (*Figure 3.9*). Above 10 mm/s, the MTM and TA systems showed similar trends in friction behaviour where the mixed lubrication progresses into hydrodynamic lubrication with increasing speed.

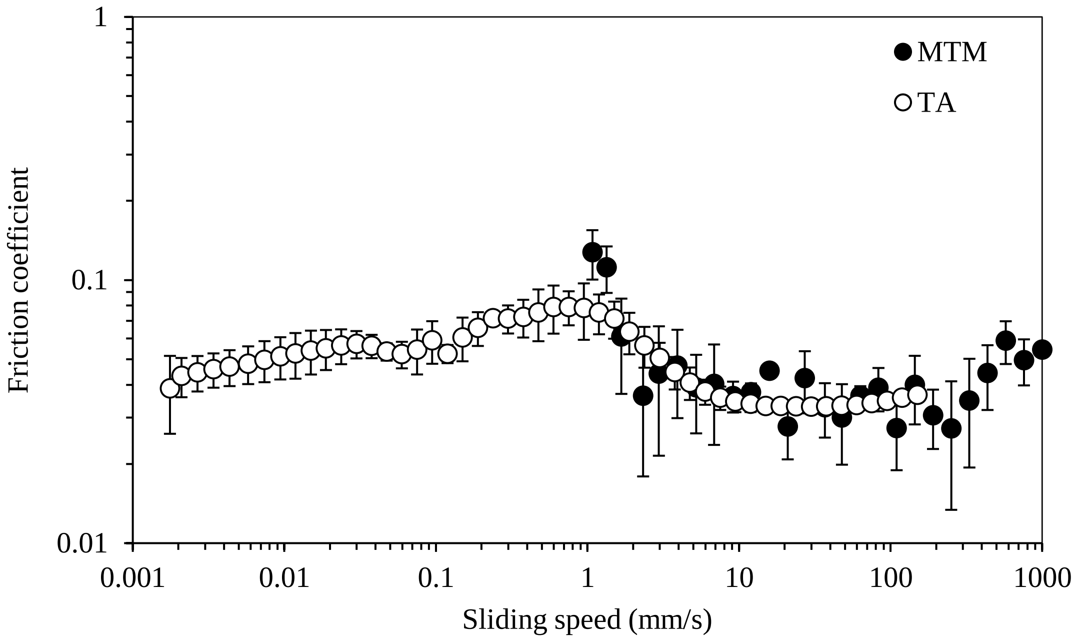

Figure 3.9 - Friction coefficient vs sliding speed of 20% oil emulsion with the two different tribological measurement systems at normal force 1 N.

Existing tribological data in literature by Malone et al. (2003) examining emulsions closely resembles the results obtained using the TA system, where boundary and mixed lubrication was observed for oil emulsions and mixed and hydrodynamic lubrication was observed for pure oil. The MTM system demonstrated similar results to Dresselhuis et al. (2007) who reported emulsions exhibiting similar friction coefficient values to pure oil. Friction is determined by oil covering the contact points and/or film formation due to oil release from droplets.

3.3.5. Soft particulate gels

Agar fluid gel particulate systems of varying concentrations of agar (1, 2, 3 and 4 wt%) were investigated using the MTM and TA systems. The viscosity profiles of agar fluid gels at various agar concentrations were measured (*Figure 3.10*). All systems showed shear thinning behaviour as expected for interacting particulate systems (Saha and Bhattacharya, 2010). As agar concentration increases, the steady shear viscosity increases across the shear rates examined.

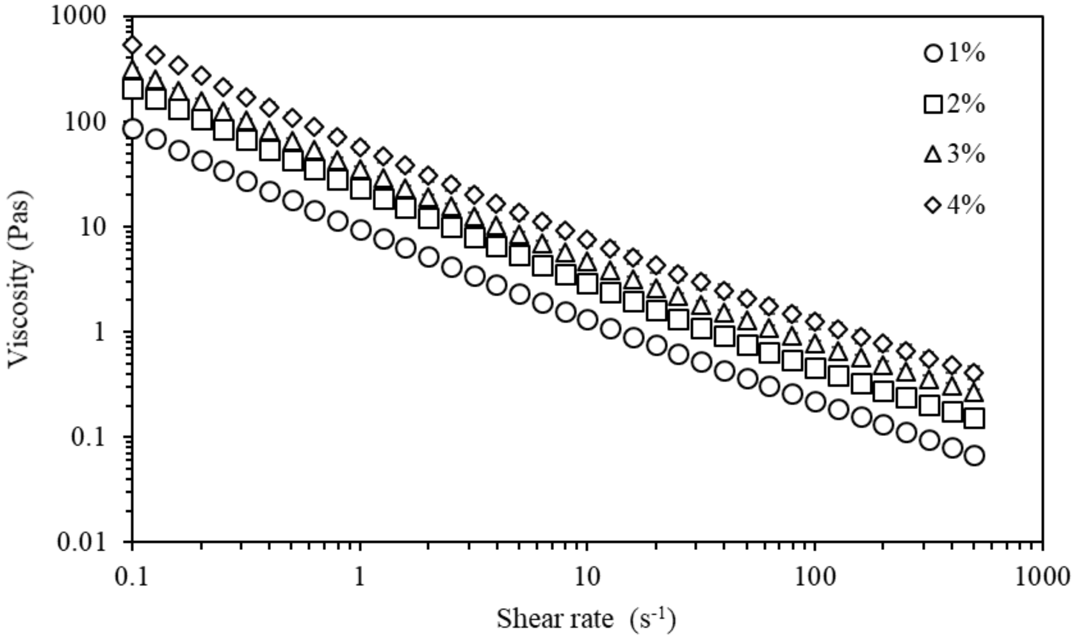

Figure 3.10 – The shear rheology for agar fluid gels of varying concentrations.

The friction measurements for the MTM system showed some mixed and hydrodynamic lubrication (*Figure 3.11a*). As speed was increased to 100 mm/s, friction coefficient decreases for all samples. As speed increased above 100 mm/s, friction coefficient gradually increases. Above 100 mm/s, the agar fluid gels show with greater increase in concentration of agar the poorer the lubrication. Increasing concentration of agar is said to increase particle rigidity (Gabriele, 2011). For the less rigid fluid gel systems with lower concentrations of agar, it is likely particles are able to be entrained by squeezing into the gap. For the more rigid particles at higher concentration, where the friction coefficient changes very little over the speed range tested, it could be possible only few particles are able enter the gap so the remainder are building up around the contact area thus increasing friction. For the speed range studied, the TA system exhibited static, boundary and mixed lubrication with increasing speed (*Figure 3.11b*). Above 0.05 mm/s, clear distinction between agar concentrations becomes apparent; where with a greater concentration of agar, there was a lower friction coefficient.

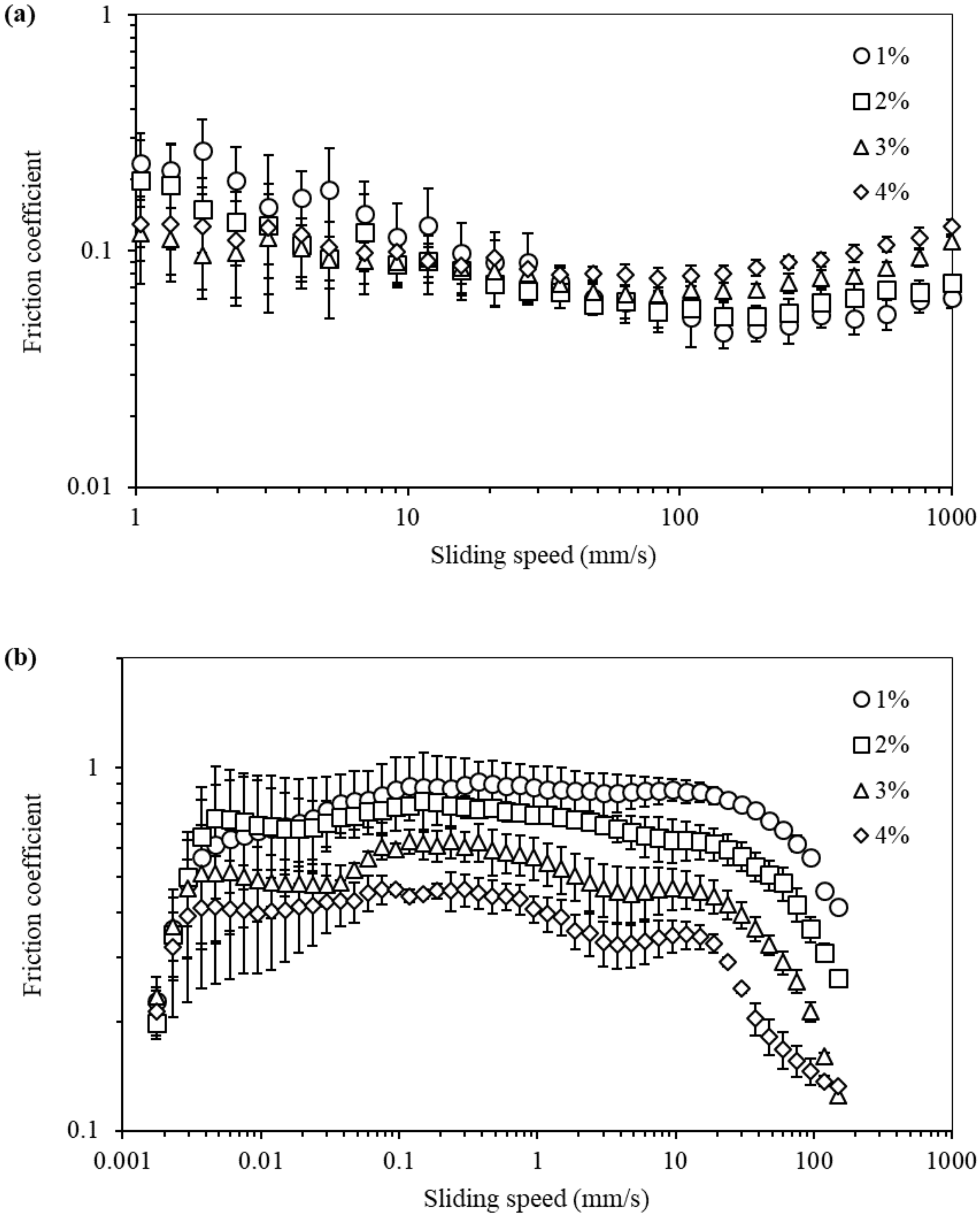

Figure 3.11 - Friction coefficient vs sliding speed of agar fluid gels of varying concentration measured using (a) MTM by PCS Instruments and (b) Discovery HR-2 rheometer by TA Instruments with three-ball-on-plate tribology attachment at normal force 1 N.

For 4% agar fluid gel, the data from each instrument were compared (*Figure 3.12*). A difference in friction behaviour can be seen between the systems, where the TA systems shows an unusual increase in friction coefficeint around 10 mm/s. This can be described as a micro-EHL regime, also observed by A Gabriele, Spyropoulos, & Norton (2010). This regime describes how at low sliding speeds only the fluid medium can access the gap between the ball and the disk, and as speed increases particle entrainment begins which results in an increase in the values of the friction coefficient as gap size is similar to particle size. As speed increases further, more particles are entrained and this decreases the friction coefficient. This is not present with the MTM; possibly due to the limited amount of mixed lubrication observed in the speed range tested. If lower speeds could be achieved, it may be possible this behaviour is present under these conditions. The differences in friction coefficient between the two systems with the agar fluid gel may be due to differences in contact area and pressures. The smaller contact area and greater contact pressure may act to limit the amount of particles in the contact, increasing friction coefficient for the TA system compared to the MTM system. Futher research is required to understand how contact area and pressures affect entrainment of particulate systems like agar fluid gels.

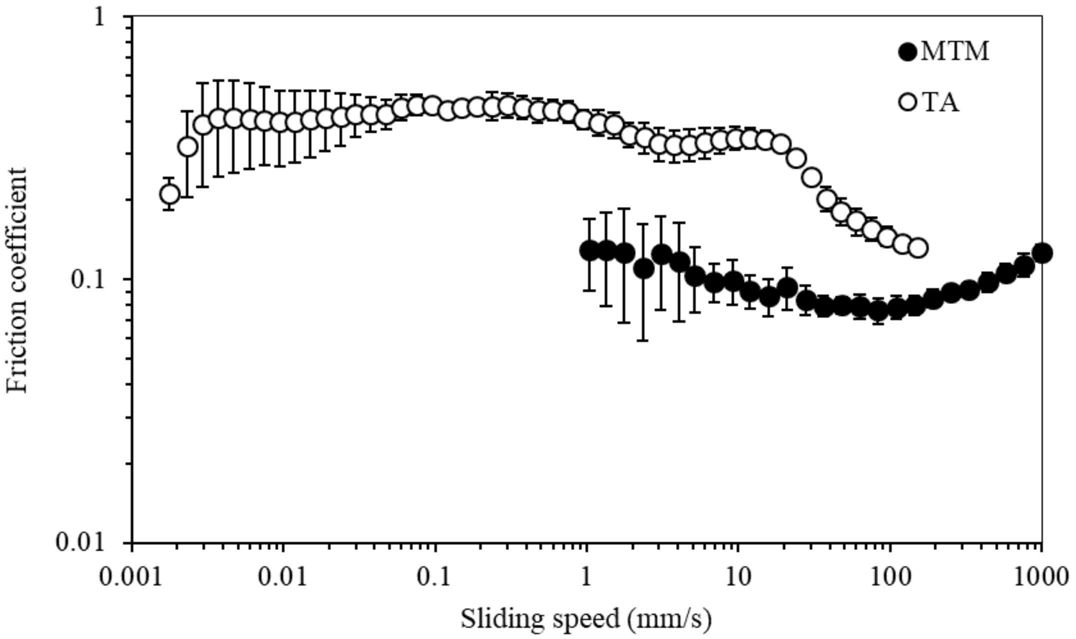

Figure 3.12 - Friction coefficient vs sliding speed of 4% agar fluid gel with the two different tribological measurement systems at normal force 1 N.

Measurements performed using the TA system was able to demonstrate similarities in friction response to the established MTM system for some model food-based formulations. These results indicate that friction measurements of simple systems depend less on the specific geometry compared to more complex systems. The TA and MTM systems showed agreement and similar trends in the Newtonian fluids, guar gum and oil in water emulsions when the speeds overlapped. Differences were observed between the TA and MTM systems for soft gel particles; although, it has been previously reported particulate systems are difficult to measure tribologically (Yakubov et al., 2015). Both systems were comparable to similar studies in literature. The TA system afforded boundary lubrication features of the Stribeck curve due to achieving lower speeds compared to the MTM. This finding is useful for researchers interested in boundary lubrication where surfaces are in contact. However, at very low speeds there is a larger associated error between measurements; likely due to stick-slip behaviour between the contacting surfaces (Goh et al., 2010; Zhang and Meng, 2015). The Discovery HR-2 three-ball-on-plate tribology geometry is flexible but the contact area is small, meaning for a given normal force a high pressure is applied when compared to the MTM system. This may be good for some applications where high pressures are representative of a process, like mimicking joints. However, it is also possible to examine samples at low contact pressures, as normal forces lower than 1 N can be used successfully with soft surfaces unlike the MTM, which may be relevant to some biological, soft tribology applications.

3.4. Conclusions and future work

The friction properties of a range of model food like systems were measured using a three-ball-on-plate rheometer attachment and compared to measurements obtained from an MTM. Testing using a soft surface showed similarities between the two different testing equipment for simple systems, showing the friction results depend less on the specific geometry compared to complex systems. The data yielded was also comparable to existing studies in literature. The TA system allowed the boundary lubrication regime to be examined for all samples due to achieving lower speeds compared to the MTM; speeds as low as 0.02 mm/s are able to be tested using the Discovery HR-2 rheometer. However, it is likely this measurement is related to static friction as little differences were observed between samples at these low speeds. The rheometer however, is limited to sliding friction only. For the guar gum solutions and oil in water emulsions, the three-ball-on plate friction data showed similar trends when compared to MTM data, with relative distinctions between the different samples. However, for the soft particulate system, discrepancies were observed likely as a result of particle entrainment being affected by difference in contact area. As there are many parameters that can affect tribological measurements, including the testing equipment, it is clear more work needs to be done to determine ideal testing conditions to be able to successfully analyse food products, which are often particulate in nature. Ideally, a standard protocol for measurements using a rheometer with tribology attachment should be determined and adopted. It is recommended further studies are completed to compare friction data obtained using a rheometer to sensory data with the intent of finding relationships between quantitative measurements and texture perception.

3.5. Acknowledgements

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4. THE LUBRICATION OF AQUEOUS POLYMER SOLUTIONS USING CHEMICALLY MODIFIED POLYDIMETHYLSILOXANE SUBSTRATES

The lubrication of aqueous polymer solutions using chemically modified polydimethylsiloxane (PDMS) substrates

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Abstract

Methods for measuring the properties of food tribologically typically involve using soft surfaces with similar properties to that of the tongue in order to somewhat mimic the oral cavity experimentally. The soft surfaces match the mechanical properties of oral surfaces, but rarely match the chemical properties. This work employs relatively simple chemical surface modifications to a commercially available polymer (polydimethylsiloxane (PDMS)) to create hydrophilic testing substrates, more closely resembling oral surfaces which are hydrophilic due to a coating in saliva. The lubrication properties of aqueous polymer solutions with the modified PDMS surfaces was studied using a three-ball-on-plate testing configuration for a rheometer. Modified surfaces were shown to affect the friction properties, demonstrating the importance of choosing suitable testing parameters with full consideration of surface chemical properties. Of the modifications examined, PDMS modified using non-ionic surfactant Triton X-100 was identified to be a useful surface modification to employ relating to oral processing applications. Future tribological studies relating to oral processing should take into consideration the surface chemistry of the testing surface.

4.1. Introduction

The selection and consideration of testing conditions is critical to obtain reproducible tribological data representative of oral processing conditions. Surfaces used should mimic those found in the mouth with a similar surface chemistry, topography and elasticity; however, these conditions are difficult to replicate and vary from person to person. Therefore, friction measurements of food are generally performed on soft surfaces such as silicone elastomers, rubbers, hydrogels or even biological tissues (Chojnicka-Paszun, De Jongh, & De Kruif, 2012; Dresselhuis, de Hoog, Cohen Stuart, & van Aken, 2008; D. A. Garrec & Norton, 2012; Joyner, Pernell, & Daubert, 2014; Krzeminski, Wohlhüter, Heyer, Utz, & Hinrichs, 2012). Typically, the oral surfaces are hydrophobic, however due to a coating of saliva they are rendered hydrophilic (Bongaerts, Rossetti, & Stokes, 2007; Ranc, Servais, Chauvy, Debaud, & Mischler, 2006). As the hydrophobicity of a surface affects how aqueous substances interact with it, it is expected to influence friction and lubrication properties. Whilst oral tribology researchers have examined hydrophilic surfaces tribologically before, there is not one surface that is considered standard (Joyner et al., 2014; Tsui, Tandy, Myant, Masen, & Cann, 2016; Yakubov, Branfield, Bongaerts, & Stokes, 2015).

A common substrate used in oral tribology applications is polydimethylsiloxane (PDMS) as it has tailorable mechanical and physical properties. As PDMS is natively hydrophobic (water contact angle >90°), and studies acknowledge the importance of using hydrophilic surfaces to more closely represent the oral environment, surfaces are typically modified to be hydrophilic by exposing PDMS to oxygen plasma or ultraviolet-ozone irradiation (Bongaerts, Fourtouni, & Stokes, 2007; De Vicente, Stokes, & Spikes, 2004; Yakubov et al., 2015). Unfortunately, these methods of treating the surface of PDMS are not permanent as it begins to revert to its previous hydrophobicity within hours; ultimately proving unsuitable for friction measurements which are often over periods of time. Surface modifications need to be stable, relatively simple to achieve and not time consuming in the hope to be as widely accessible as possible to researchers. These kind of permanent surface modification of PDMS have been achieved; however, they have not been studied in detail tribologically. In this study, a selection of techniques are employed to fabricate hydrophilic PDMS surfaces. Adding a non-ionic surfactant has been shown to enhance wettability of PDMS (Kim, Kim, Kim, Park, & Park, 2010; Madadi & Casals-Terré, 2012). This technique has been used previously in a tribological application, where a non-ionic siloxane surfactant was added to the pre-cured PDMS base and curing agent mixture during preparation (Garrec, 2013). This showed the one-step modification was successful in permanently rendering the PDMS surface hydrophilic as well as enhancing the entrainment of water to form a lubricating film analogous to saliva on a standard PDMS surface. The structures of PDMS and the surfactant suggest that the non-polar chains physically entangle with the PDMS whilst the polar head migrates towards the surface of the bulk material which increases the hydrophilicity of PDMS surface (Garrec, 2013). Another relatively simple method identified involves coating PDMS substrates with polyvinyl alcohol (PVA; a hydrophilic polymer) after treatment with ozone to give hydrophilic functionality on the PDMS surface (Trantidou, Elani, Parsons, & Ces, 2017). The contact angle of a water drop on modified substrates was successfully reduced compared to native PDMS and found to be stable for over 1 month. A similar surface modification technique for modifying the surface of PDMS involves coating the PDMS substrate with a thin film of undecyclenic acid (UDA) followed by heat treatment in order to induce hydrosilylation. This introduces the permanent functionality of a carboxylic acid to the surface reducing the contact angle to ~ 75° that was stable for over 1 month (Zhou, 2012).

This work aims to probe the importance of surface chemical properties of testing substrates when assessing the friction and lubrication behaviour of food systems. A rheometer with a three-ball-on-plate tribology attachment was used to assess the friction and lubrication behaviour of aqueous polymer solutions with chemically modified PDMS substrates. Three different commercially available polysaccharides (xanthan gum, guar gum and chitosan) and Carbopol microgel suspensions were assessed. These form rheologically complex fluids in aqueous solution and have been used to model food systems in previous tribological studies to probe how friction behaviour is affected by their physical properties (De Vicente, Stokes, & Spikes, 2006; Malone, Appelqvist, & Norton, 2003; Stokes, Macakova, Chojnicka-Paszun, De Kruif, & De Jongh, 2011). To further examine the suitability of the modified PDMS surfaces, astringent compounds were examined. Astringency refers to the puckering or drying sensation in the mouth and throat caused by specific compounds in food and drink. The mechanism for astringency has been attributed to a physical perception caused by diminished lubrication due to interaction of oral surfaces and with astringent compounds (Brossard, Cai, Osorio, Bordeu, & Chen, 2016; Laguna & Sarkar, 2017). Though the formation of complexes with saliva and the astringent compounds is believed to play a role in the development of astringency, an understanding of the friction behaviour of astringent compounds is not well reported. This study examines how astringent solutions affect the friction and lubrication behaviour when assessed using hydrophilic PDMS compared to hydrophobic PDMS surface.

4.2. Materials and methods

4.2.1. Materials

Polydimethylsiloxane (PDMS) (Sylgard 184 Silicone Elastomer kit) was purchased from Dow Corning, US. Polyvinyl alcohol (PVA) (87-90% hydrolysed, MW 30000-70000 gmol^{-1}), undecyclenic acid (UDA), Triton X-100, xanthan gum, guar gum, chitosan, potassium alum, tannic acid and epigallocatechin gallate (EGCG) were obtained from Sigma Aldrich, UK. Carbopol (Carbopol 974P NF) was kindly provided by Lubrizol, supplied by IMCD, UK. Materials were used with no further modifications or purification.

4.2.2. Methods

Fabrication of PDMS substrates

PDMS was prepared using the two-part kit consisting of silicone elastomer and curing agent mixed in the recommended 10:1 ratio. The binary mixture was poured into A4 stainless steel mould of 4 mm thickness, degassed and placed in an oven at 70°C for 2 hours. The sheet was removed from the mould and allowed to cool at room temperature for at least 24 hours. For testing, discs of 46 mm diameter were cut from the sheet. Before modification and testing, all discs were cleaned by sonication in ethanol followed by distilled water for 6 minutes each and allowed to dry in air.

For polyvinylalcohol (PVA) grafted PDMS, a method was followed outlined in a study by Trantidou, Elani, Parsons, & Ces (2017). Firstly, PVA was dissolved in water at 1 wt% and stirred at room temperature for 40 minutes until fully dispersed. The temperature was then increased to 100°C whilst the solution was stirred for 40 minutes. Finally, the temperature was reduced to 65°C and left to stir overnight. PDMS, as prepared above, was treated by oxygen plasma (using a handheld oxygen plasma treatment device (Oplasma surface treatment, SisoMM.com) then placed into the PVA solution for 10 minutes. The samples were dried in air and cleaned before use as described above.

For undecylenic acid (UDA) grafted PDMS, a method was followed outlined in a study by Zhou (2012). Native PDMS was placed in a sealed glass container with sufficient UDA to thinly coat the bottom surface of the PDMS. The UDA coated PDMS was kept in an oven at 70°C overnight. After this, the sample was removed from the oven and cleaned as described above to remove any excess UDA.

For non-ionic surfactant added PDMS, Triton X-100 was added to the pre-cured liquid mixture of silicone elastomer and curing agent at 3 wt%. The non-ionic surfactant added PDMS was poured into the stainless steel mould, degassed and cured in an oven overnight at 50°C. The sheet was removed from the mould and allowed to cool at room temperature for at least 24 hours. Discs of 46 mm diameter were then cut from the sheet to use in testing.

Contact angle measurements

Sessile drop contact angle measurements were performed using a goniometer (Krüss Drop Shape Analyser, Germany). A symmetrical drop of volume of 10 μL was deposited on the surface material using a syringe. All surfaces were cleaned with ethanol, distilled water and dried in air prior to testing. The contact angles were determined at room temperature from image analysis via the Laplace-Young method using DSA Software provided with the equipment. Reported contact angles are the average of three measurements.

Mechanical analysis

Compression tests were performed using a Texture Analyser (Stable Micro Systems, UK). Young’s moduli were calculated using software provided with the equipment using the gradient of the initial slope. A 40 mm cylindrical probe was used in conjunction with 30 kg testing arm. Polymer samples were cut into 20 mm diameter with 4 mm thickness cylindrical discs. Measurements were repeated in triplicate and an average obtained.

FTIR analysis

Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra were obtained on a FT/IR-6300 (Jasco, UK). A total of 64 scans were taken at room temperature with a resolution of 2 cm^{-1}. Data was collected in the range 4000 Hz - 800 Hz with a scan speed of 2 mm/s.

AFM analysis

The surface topography and roughness of the PDMS and modified PDMS surfaces were studied using a JPK Nanowizard Atomic Force Microscope (AFM), Germany. The surface analysis was performed in tapping mode, with a Bruker NCHV-A probe tip with a spring constant of 42 N/m and frequency 320 kHz. For each surface, scan sizes of 20 µm × 20 µm and 10 µm × 10 µm were probed. Various scan rates ranging from 0.4 Hz to 1 Hz were used with a resolution of 512 lines per sample. Analysis was completed using Gwyddion software.

Preparation of samples

To examine the effect of the surface modifications, aqueous polymer solutions with varying properties were examined. These were xanthan (shear thinning and anionic), guar gum (neutral), chitosan (cationic, mucoadhesive) and Carbopol (microparticulate, also negatively charged). Xanthan was prepared by dispersing 0.05% w/w in distilled water. Guar gum was prepared by dispersing 0.5% w/w in distilled water. Chitosan was prepared by dispersing 0.5% w/w in 0.2 M acetic acid. Carobopol was prepared by dispersing 0.05% in distilled water, then netralised with 18% volume NaOH to a pH of ~7.5 as recommended by the manufacturer. To further probe surfaces, known astringent compounds were examined. These were dispersed in distilled water at room temperature. Potassium alum (also know as alum) was prepared at a concentration of 1.5 g/L, tannic acid prepared at 2 g/L and EGCG 0.138 g/L. These concentrations were chosen as these have previously been described in literature as the limits of detection for astringent response (Ross & Weller, 2008; Rossetti, Bongaerts, Wantling, Stokes, & Williamson, 2009; Schiffman, Suggs, & Simon, 1992). All samples were preapred at room temperature (~20°C), dispersed by stirring for at least 2 hours and used within 2 days.

Shear rheology

The shear viscosity of polymer solutions (xanthan, guar gum, chitosan and neutralised Carbopol) were analysed using a Kinexus Pro rotational rheometer by Malvern Instruments, UK with cup and bob geometry over shear rates 1-1000 s^{-1} allowing equilibrium to be reached. Samples were repeated in triplicate and an average obtained.

Friction measurements

Friction measurements were performed using a three-ball-on-plate tribology geometry for the Discovery HR-2 rotational rheometer (TA Instruments, UK). The geometry consists of 3 × ¼ inch diameter stainless steel hemispheres fixed onto a flat plate. Surfaces were analysed dry, with distilled water and viscosity matched polymer solutions of xanthan, guar, chitosan and neutralised Carbopol as well as with astringent compound solutions. A normal force of 1 N was used with speed range of 0.002-150 mm/s under pure sliding conditions. The sweeps were run with ten measurements per decade (50 measurements total) at room temperature (25°C). Measurements were repeated in triplicate and an average obtained.

4.3. Results and discussion

PDMS and modified PDMS surfaces were characterised to assess their suitability in friction testing.

4.3.1. Characterisation of surfaces

Water contact angle

A symmetrical drop of distilled water of volume 10 µL was deposited on PDMS surfaces. All modified surfaces were found to be hydrophilic (water contact angle < 90°) whereas the native

PDMS was hydrophobic (water contact angle > 90°) (*Table 4.1*). The contact angle of the tongue has been reported to be between 50-80° (Ranc et al. 2006; Sarkar et al. 2019)

Table 4.1 – Mean (± 1 standard deviation) static water contact angle measurements (WCA) after 60 s for PDMS and modified PDMS substrates.

	WCA after 60 s (°)
PDMS	102 ± 3
PVA	72 ± 7
UDA	73 ± 4
Triton X-100	70 ± 2

Mechanical analysis

PDMS samples were assessed to investigate if modifications affected their mechanical properties, which in turn would affect friction measurements and need to be considered. Compression tests showed comparable values of Young's modulus for all surface modifications tested compared to native PDMS (*Table 4.2*).

Table 4.2 - Mean (± 1 standard deviation) Young's Modulus values for PDMS and modified PDMS substrates.

	Young's Modulus (MPa)
PDMS	1.3 ± 0.2
PVA	1.4 ± 0.1
UDA	1.1 ± 0.1
Triton X-100	1.1 ± 0.1

FTIR analysis

ATR-FTIR provided additional information on the chemical functionalities of the PDMS surface upon modification and verified the modifications had changed the surface chemistry. *Figure 4.1* shows the absorption spectra of native and modified PDMS samples between 800 - 1300 cm^{-1}. All surfaces showed the characteristic peaks of PDMS with absorbance peaks around 845, 1050, 1258 and 1412 cm^{-1} due to Si-CH bonds and peaks around 910 cm^{-1} due to Si-OH (I.-J. Chen & Lindner, 2006). When comparing PVA modified PDMS to native PDMS, there is an increase in the absorbance intensity of Si-O-Si bonds doublet at 1012 and 1060 cm^{-1}. This is attributed to the increase in bonding between silicon and the hydroxyl groups on PVA (Berdichevsky, Khandurina, Guttman, & Lo, 2004). When examining the UDA modified PDMS spectra, there was a decrease in intensity of Si-O-Si bonds. This suggests this is where the vinyl terminated carboxylic acid bonds to the PDMS. For the UDA modfied PDMS surface, a peak at 1720 cm^{-1} is observed due to stretching of the C=O in the carboxylic acid (Zhou, 2012). This is not present in other the samples tested. Non-ionic surfactant added PDMS with Triton X-100 showed similar absorption values with a small decrease in intensity of the Si-O-Si bond at 1060 cm^{-1} and the Si-C bond at 845 cm^{-1}. The degree of crosslinking is restricted by the presence of surfactant in the pre-cured PDMS mixture.

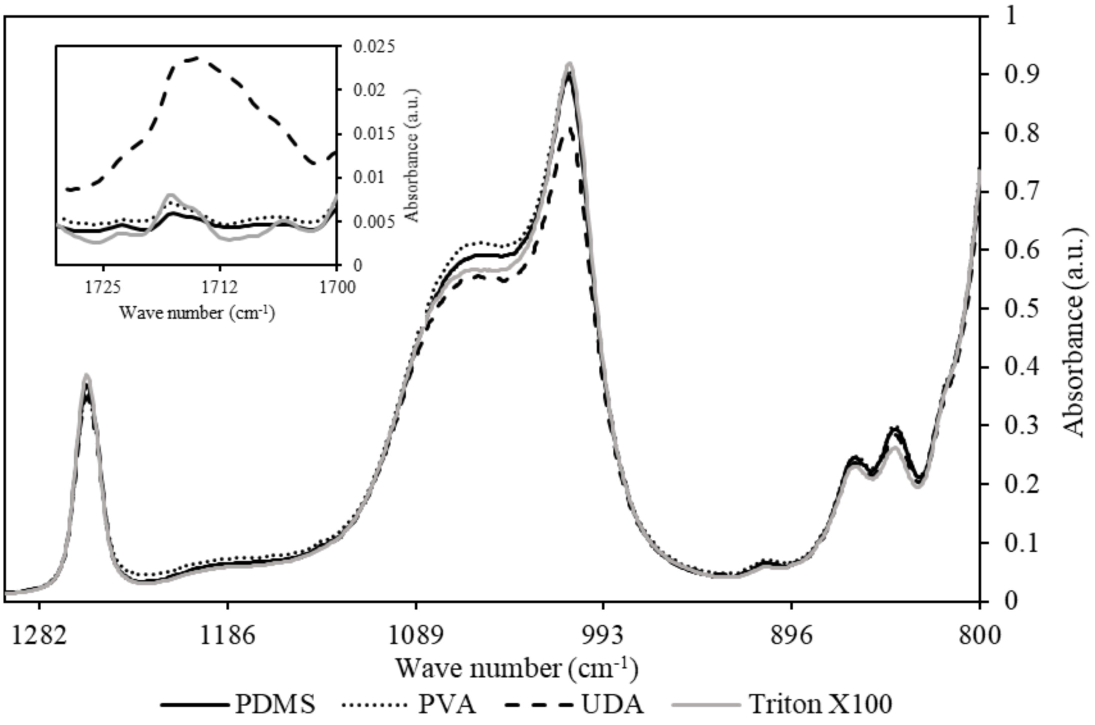


Figure 4.1 – Measured absorbance of PDMS substrates for 800-1300 cm^{-1}. Inset, absorbance for PDMS substrates for 1700-1730 cm^{-1}.

AFM analysis

AFM surface analysis provided additional information to how the chemical functionality of the PDMS surface upon modification changed the surface roughness. *Table 4.3* below shows the measured roughness values for the PDMS surfaces.

Table 4.3 - Mean (± 1 standard deviation) Average Surface Roughness (R_a) for PDMS and modified PDMS substrates.

	Average surface roughness R_a (nm)
PDMS	6 ± 1
PVA	8 ± 2
UDA	5 ± 2
Triton X-100	16 ± 6

It was found that UDA and PVA modified PDMS had comparable roughness values to native PDMS, attributed to being cast in the same steel mould. However, Triton X-100 modified PDMS showed an increase in average surface roughness, with a value of 16 ± 6 nm. The surface was visibly ‘pitted’ showing cavities of air which were unable to be removed during fabrication (*Figure 4.2*) compared to native PDMS. The pre-cured binary PDMS mixture is transparent, however the surfactant added PDMS is opaque due to the amount of trapped air in the mixture, also reported by (Madadi & Casals-Terré, 2012). Despite degassing over long periods, the air remained and affected the surfaces roughness, in the form of small, trapped air bubbles at the surface < 3 µm in diameter. It is important to consider how this difference in surface roughness will affect the friction properties.

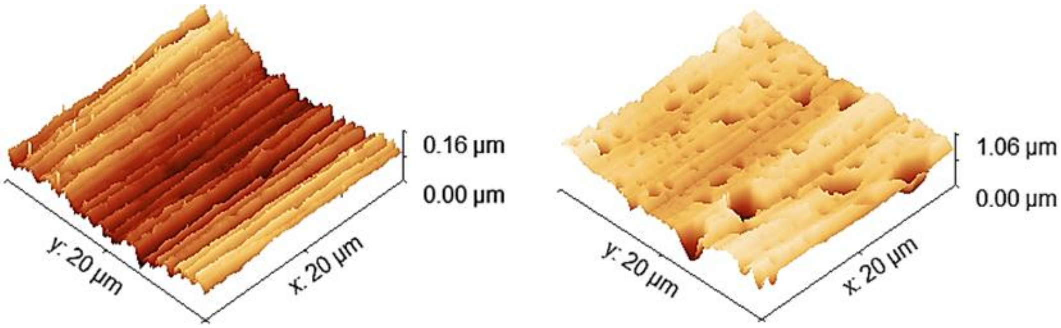


Figure 4.2 – 20 µm × 20 µm 3D AFM images of native PDMS (left) and Triton X-100 modified PDMS (right) surfaces.

4.3.2. Friction measurements

Dry friction

Dry friction between ball and disc was examined for all surfaces (*Figure 4.3*). All surfaces demonstrated an increase in friction coefficient as sliding speed increased. Besides Triton X-100 below 0.003 mm/s, both native and modified PDMS surfaces demonstrated a similar friction response suggesting the chemical attributes associated with each surface does not affect dry friction under these testing conditions. Below 0.003 mm/s, the Triton X-100 modified PDMS surface exhibited a slightly lower friction coefficient which could be due to the increased surface roughness yielding a reduced contact area.

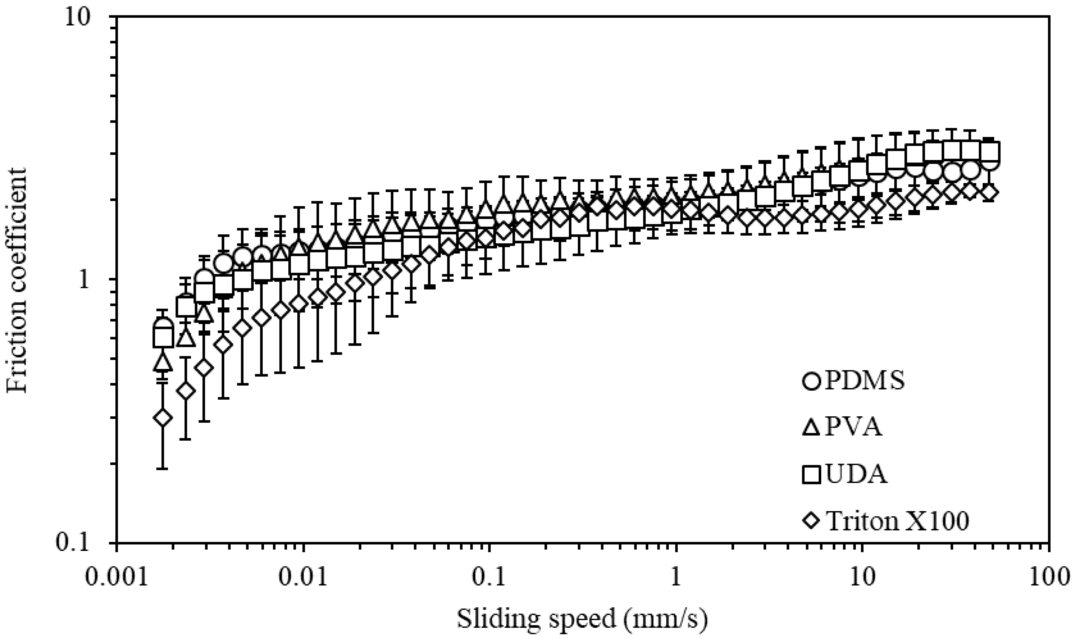


Figure 4.3 – Dry friction of native (hydrophobic) and modified (hydrophilic) PDMS substrates.

Water lubricated friction

Friction was assessed using water as a lubricant (*Figure 4.4*). PDMS, the only hydrophobic surface, showed the greatest friction across the speed range tested. For PDMS, as speed increased to 0.01 mm/s, static friction is observed. Above this, water influences the friction coefficient until speed reaches 10 mm/s, as friction coefficient does not increase with increasing speed as it did with dry contacts. Above 10 mm/s, the mixed regime begins as the coefficient of friction decreases with increasing speed.

Entrainment of water with native PDMS begins at the highest speed in comparison to other surfaces tested. Given the modified surfaces are comparable to native PDMS for Young’s Modulus (*Table 4.2*), but the hydrophilicity is changed (*Table 4.1*), this study demonstrates the chemical surface properties play a crucial role in friction behaviour. Initially, PVA modified PDMS behaves similarly to native PDMS, below 0.01 mm/s, where static friction can be observed. As water becomes entrained at around 0.01 mm/s, friction coefficient decreases as speed increases. Water molecules are able to interact with the hydrophilic surface to facilitate lubrication (Lee & Spencer, 2005). For PVA, the entrainment of water occurs at a lower speed compared to other surfaces tested, this can be explained by the formation of a solvated boundary layer enhancing lubrication where the normal load forces are supported by steric repulsions of the large polymer chains of the PVA (Chen, Briscoe, Armes, & Klein, 2009). Surface-surface contact is minimised once solvated, providing high lubricity. UDA modified substrates with water behaved similarly to dry UDA surface, although with lower friction coefficient, showing an increase in friction as speed increases until the transition to the mixed regime above 10 mm/s. PDMS modified with Triton X-100 showed an increase in friction coefficient until 0.01 mm/s, followed by a decrease in friction coefficient until 0.3 mm/s, then an increase again in friction coefficient before 10 mm/s when the mixed regime was entered. This observed friction behaviour has been observed for other rough surfaces and can be explained by the inherent roughness of the surface, giving rise to a micro-elastohydrodynamic lubrication (EHL) regime (Scaraggi, Carbone, & Dini, 2011).

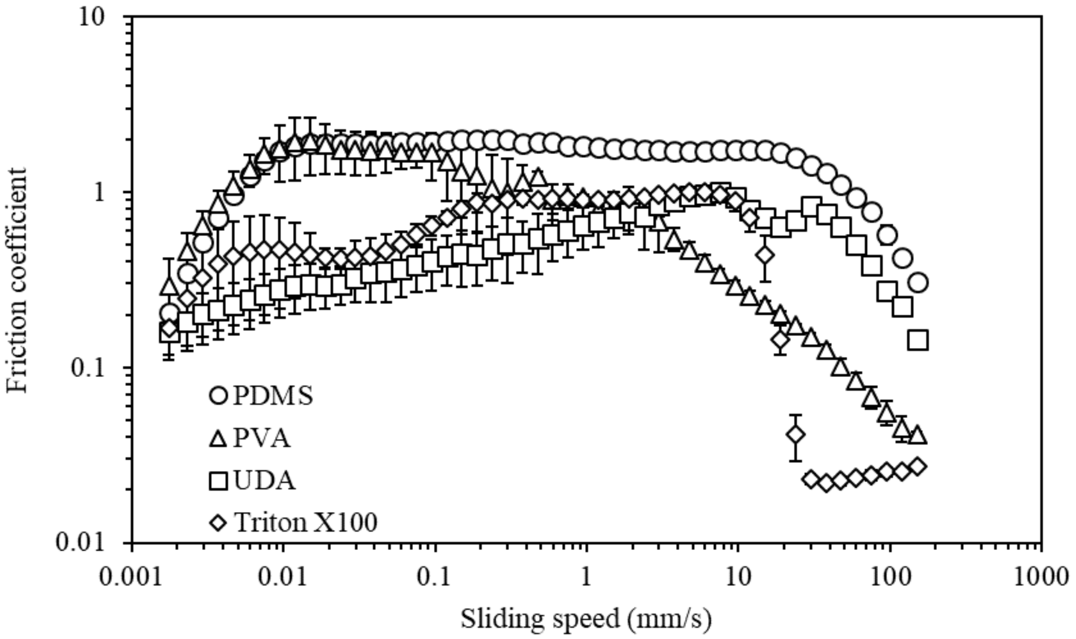


Figure 4.4 – Water lubricated friction properties of native (hydrophobic) and modified (hydrophilic) PDMS substrates.

Polymer solutions friction

To take into consideration the effect of viscosity on friction, the viscosity of the samples were matched at high shear rates as these are said to be experienced during oral processing (Stokes, Boehm, & Baier, 2013). *Figure 4.5* shows viscosity curves for the final sample concentrations used in this study with approximate overlaps in viscosity at shear rates greater than 50 s^{-1}.

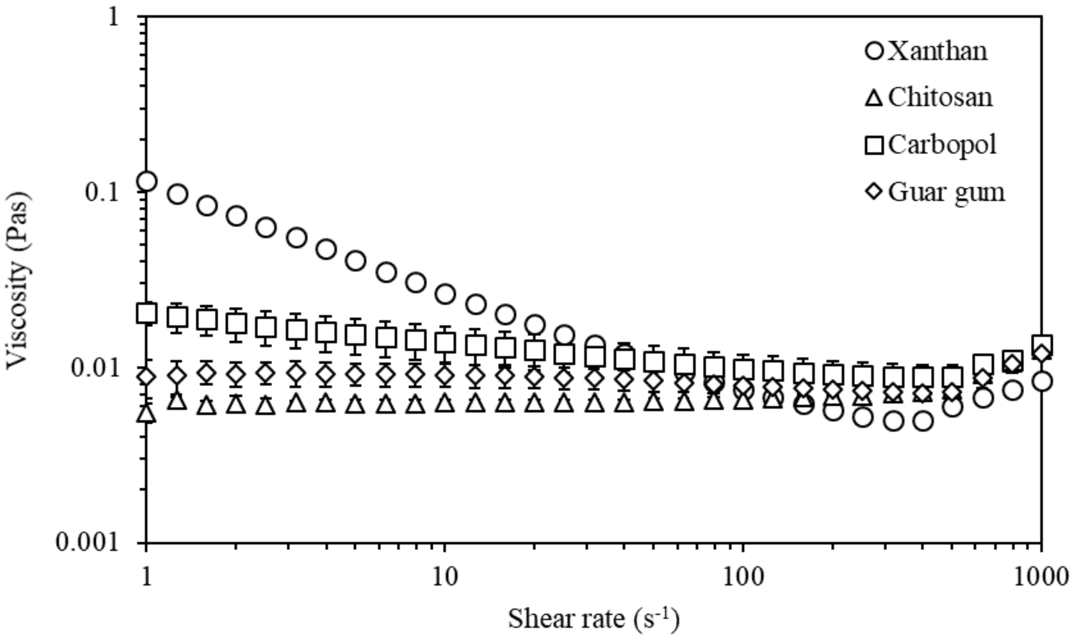


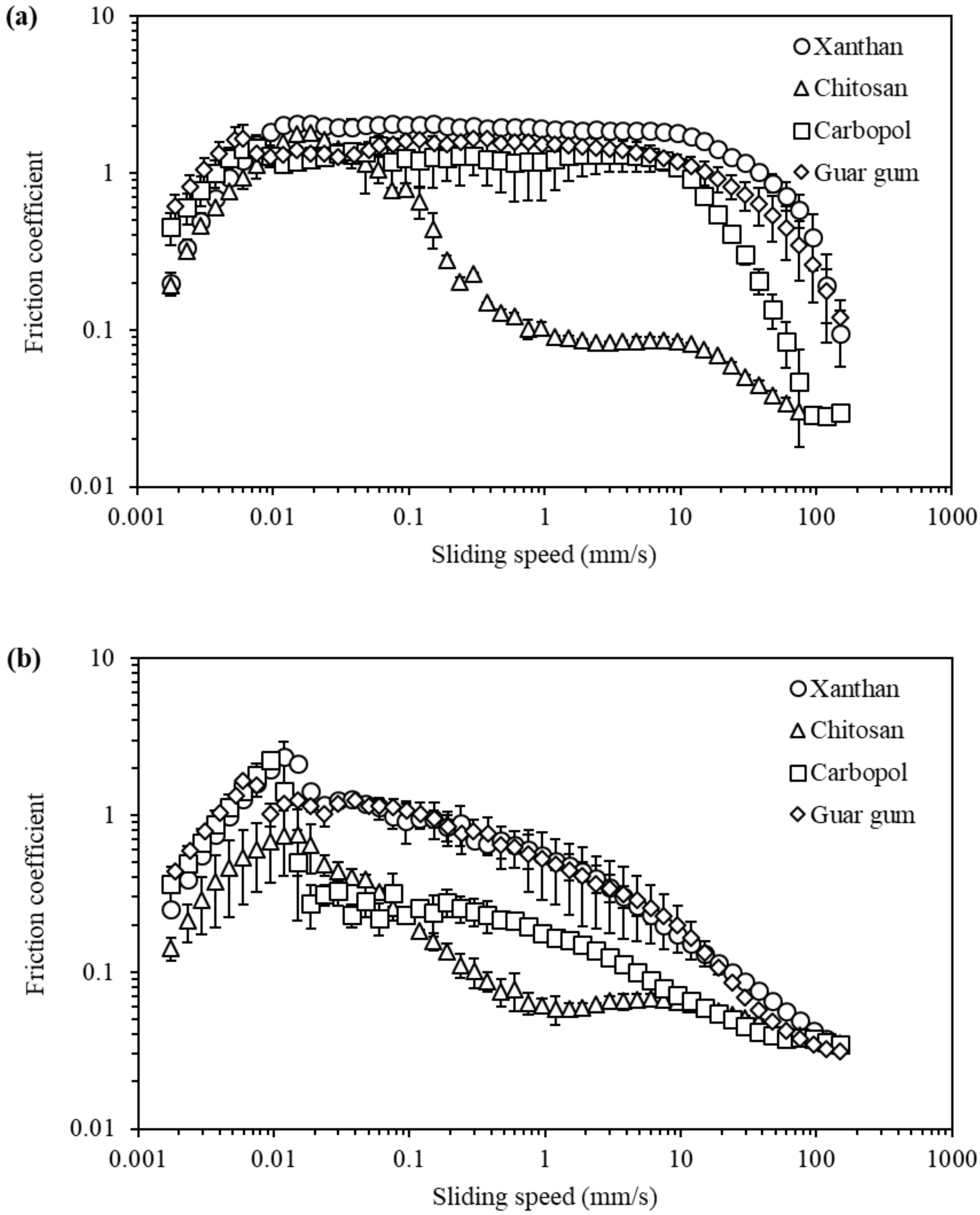
Figure 4.5 – Shear viscosity of polymer solutions with approximate overlap at high shear rates.

Native PDMS showed boundary and mixed lubrication for all samples as well as the beginning of hydrodynamic lubrication regime for Carbopol and chitosan above 75 mm/s (*Figure 4.6a*). Xanthan, Carbopol and guar gum solutions showed similar friction behaviour until speed reached 10 mm/s, whereby the mixed regime was entered and friction coefficient decreased. Chitosan entered the mixed regime at the lowest speed of 0.05 mm/s. Chitosan was highly lubricating between the PDMS and steel contacts cmpared to the other polymer solutions examined. Above 100/s, xanthan demonstrates the greatest friction coefficient.

The PDMS modified with PVA showed a different response to hydrophobic PDMS, with all samples entering the mixed lubrication from around 0.01 mm/s (*Figure 4.6b*). Until this speed, chitosan demonstrated the lowest friction coefficient. Guar and xanthan exhibited a similar frictional response until 20 mm/s, where above this speed xanthan demonstrated a greater friction response.

PDMS modified with UDA showed an extended boundary lubrication regime for all samples (*Figure 4.6c*). As speed increased above 20 mm/s, xanthan showed the highest coefficient of friction.

The non-ionic surfactant modified PDMS with Triton X-100 showed aspects of all lubrication regimes for all samples tested (*Figure 4.6d*). Hydrodynamic regime is observed for Chitosan from 0.03 mm/s, Carbopol from 20 mm/s, guar gum from 50 mm/s and xanthan from 90 mm/s. For chitosan, mixed lubrication occurs from ~ 0.004 mm/s, where a low friction coefficient (< 0.1) was observed as speed increased until the hydrodynamic regime was entered. For Carbopol, there was a friction decrease around 0.02 mm/s, then an increase in friction as speed continued to increase until ~ 4 mm/s.


(a)
Friction coefficient
10
1
0.1
0.01
0.001
0.01
0.1
1
10
100
1000
Sliding speed (mm/s)
Xanthan
Chitosan
Carbopol
Guar gum
(b)
Friction coefficient
10
1
0.1
0.01
0.001
0.01
0.1
1
10
100
1000
Sliding speed (mm/s)
Xanthan
Chitosan
Carbopol
Guar gum

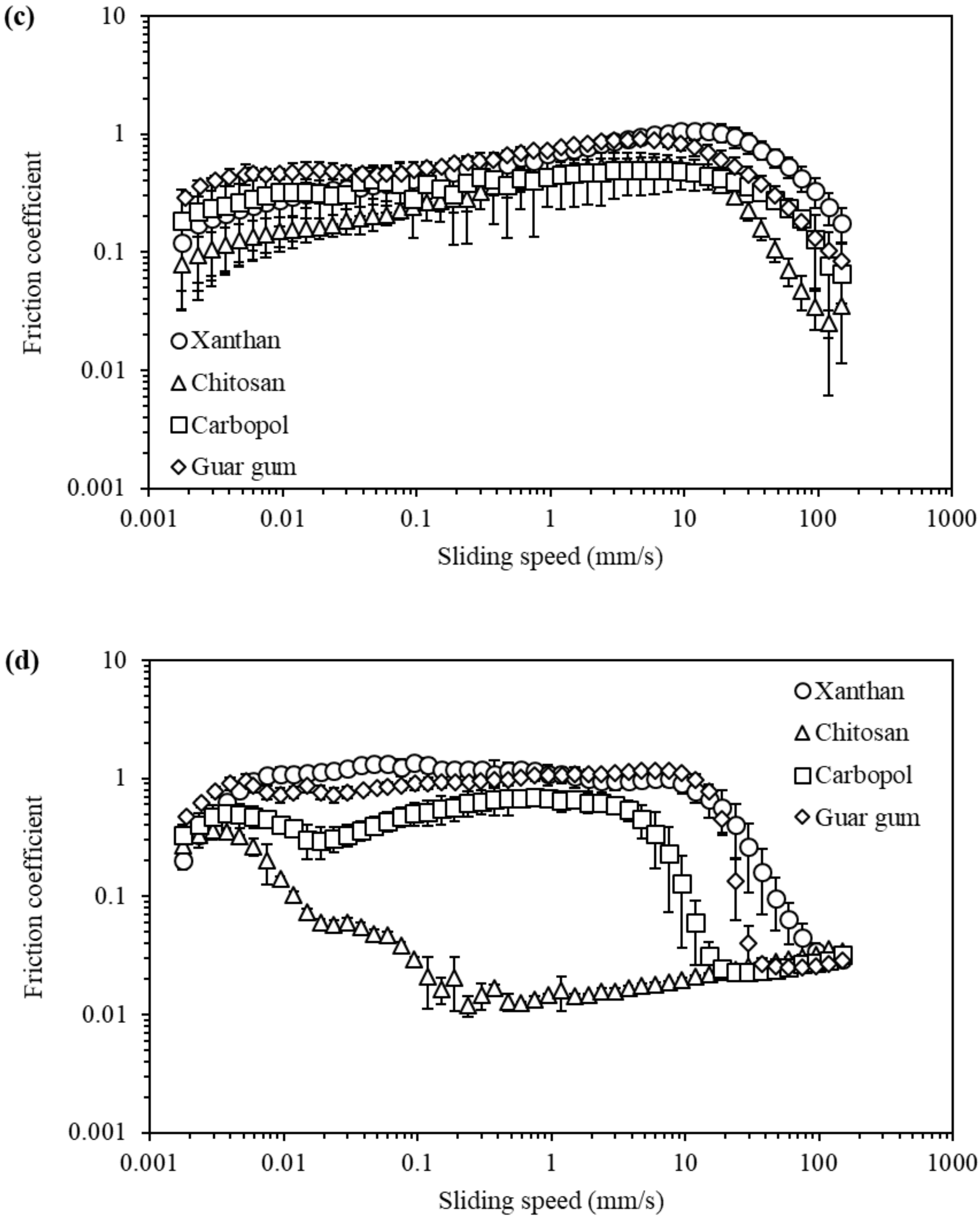


Figure 4.6 – Measured tribological properties of aqueous polymer solutions with (a) PDMS, (b) PDMS modified with PVA, (c) PDMS modified with UDA and (d) PDMS Modified with Triton X-100 disc and steel ball tribopair using a three ball on plate system at 1 N, showing the friction coefficient as a function of sliding speed.

From these experiments using aqueous polymer solutions with hydrophobic and hydrophilic PDMS surfaces, it is clear the surface modifciations have a strong impact on friction response, particularly friction relating to the boundary and mixed lubrication regimes where the surfaces are likely to be in contact. PDMS modified with PVA showed similar initial friction to hydrophobic PDMS, but the boundary regime is shorter as all samples were entrained at a lower speed. This could be due to the bulky nature of the PVA molecule on the PDMS surface, facilitating lubrication by solvation (shown when water alone is used as a lubricant, *Figure 4.4*). This is magnified when polymer samples are used and they are also be entrained, supporting the normal load further. PDMS modified with UDA showed an extended boundary regime with lower initial friction values compared to other surfaces. The measured friction for water lubricated and polymer lubricated PDMS modified with UDA was lower than in dry conditions; suggesting some entrainment of sample occurs but the contacting surfaces dominate the friction properties. PDMS modified with Triton X-100 allowed all regimes to be examined with this testing configuration in the speed range tested, showing a shortened boundary regime (in comparison to native PDMS) as well as mixed and hydrodynamic regimes. Once entrainment occurs, full film lubrication was achieved in a short speed range. This has been observed when using rough surfaces in previous studies (Bongaerts, Fourtouni, et al., 2007).

In general, for all surfaces across the speeds tested, xanthan showed poorest lubrication. As xanthan solutions are highly shear thinning, this would influence the lubrication properties as shear is occuring in the contact (Cassin, Heinrich, & Spikes, 2001). Previous research examining the friction properties of Carbopol microgel suspensions found a similar response to this study, where for boundary lubrication there was an increase, decrease and subsequent increase in friction with increasing speed until sufficient entrainment and the mixed regime is entered (De Vicente et al., 2006). This behaviour can be attributed to the confinement of the microgel particles in the interfacial film instead of bulk properties suggesting the response may be a reflection of the microrheology of the confined microstructure (Cassin et al., 2001). As speed increases, and separation between surfaces as hydrodynamic pressure increases, more particles are able to facilitate lubrication and bulk rheology then dominates the friction response as is the case with the other samples. Chitosan, which appears to facilitate lubrication, transitions to the mixed regime for UDA at 10 mm/s, PDMS at 0.05 mm/s, Triton X-100 at 0.03 mm/s and PVA at 0.01 mm/s. This facilitation of lubrication has been previously shown in an AFM set-up where chitosan formed ‘cushion-like’ layers of trapped water resulting in reduced friction (Nordgren, Eronen, Sterberg, Laine, & Rutland, 2009). Chitosan entrains at the lowest speed for PDMS modified with PVA. As all samples are entrained around the same speed (0.01 mm/s) regardless of lubrication properties of the sample, it is clear the surface modification dominates friction here. In this case, PDMS modified with UDA does not faciliate the entrainment of chitosan, a greater speed is required to achieve suffecient hydrodynamic pressure to allow polymer between the surfaces. This again, is a similar pattern across all samples for this surface, showing high speeds are required to be able to examine and differentiate between the lubrication properties of the aqueous polymer solutions. PDMS modified with Triton X-100 allowed all regimes to be examined and showed differentation between samples in the speed range tested.

As the wetting of the surface plays an important role in determining friction, the contact angle of the polymer solutions on the PDMS surfaces were measured. All modified surfaces showed a lower water contact angle when compared to natively hydrophobic PDMS (*Table 4.1*). The influence of surface wetting can further be explored and comapred to the friction measurements when examining the contact angle of water and each of the polymer solutions (xanthan, Carbopol, chitosan and guar gum) on each surface in order to assess their lubricant-substrate contact angle versus the measured friction coefficient (*Figure 4.7*).

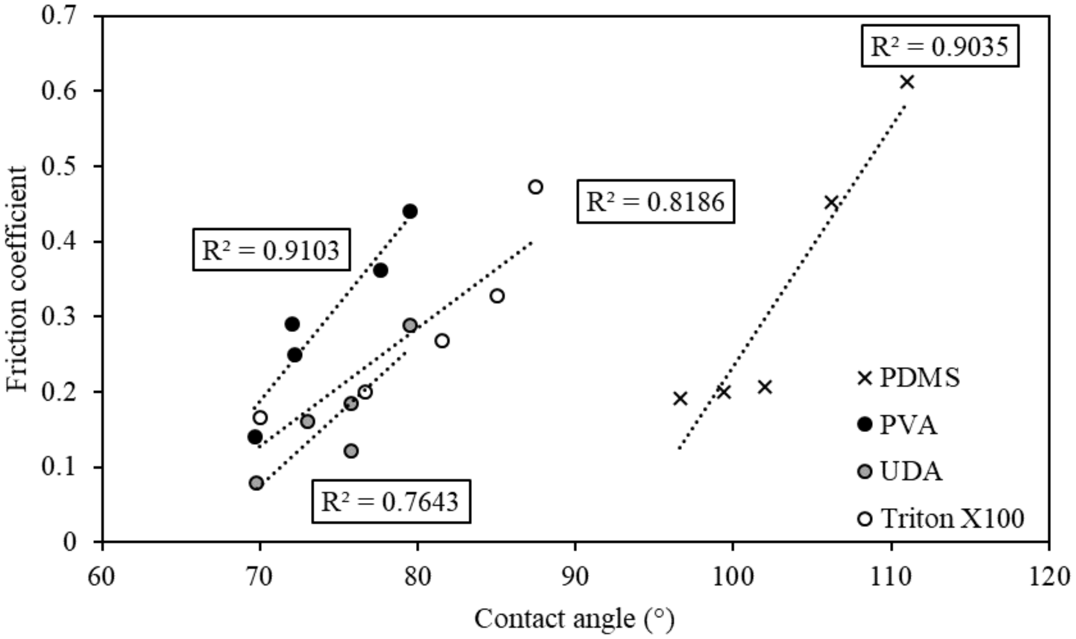


Figure 4.7 – Measured friction coefficient at 0.002 mm/s versus average contact angle of 10 µL droplet of water and polymer solutions (xanthan, Carbopol, chitosan and guar gum) on surfaces measured after 60 s. Line of best fit added labelled with R^2 value.

Hydrophobic PDMS demonstrated the greatest contact angle for all solutions tested. For the contact angle measurements of each polymer sample and water, there is a strong correlation between initial friction coefficient (when surfaces are in contact) and contact angle, with an R^2 value of 0.90. For example, for PVA modified PDMS chitosan had a low contact angle, and demonstrated the lowest friction coefficients at speeds below 0.01 mm/s. Conversely, the measured contact angle for UDA modified PDMS and guar gum was higher than with xanthan which is mirrored with higher initial fricton coefficient measurements below 0.1 mm/s. It is clear the surface chemistry of the PDMS substrates affect the friction measurement of aqueous samples.

Astringent solutions friction

Astringent compounds have been reported to directly affect the surface properties of the oral surfaces where studies have shown astringency is a tactile sensation (Brossard et al., 2016; C. A. Lee, Ismail, & Vickers, 2012; Ma, Lee, Liang, & Zhou, 2016; Rossetti et al., 2009). Known astringent compounds were assessed to investigate the role they play in lubrication when using hydrophilic surfaces, as surfaces in the oral cavity are hydrophilic. Tribological measurements were completed using native PDMS and PDMS modified non-ionic surfactant Triton X-100 examining aqueous solutions of astringent alum (frequently used as a preservative in foods), tannic acid (commonly found in alcoholic beverages) and EGCG (a polyphenol found in tea).

At speeds lower than 0.01 mm/s, friction values for astringent compounds exhibit higher friction compared to water on PDMS without modifications (*Figure 4.8*). Tannic acid began mixed lubrication first around ~0.02 mm/s, followed by alum from ~2 mm/s, which showed friction decreased with increasing speed at a greater rate than the other samples. For EGCG, there was a decrease in friction coefficient compared to water alone; this lubrication pattern continues as speed increased. The mixed regime for EGCG is entered around 60 mm/s and water around 20 mm/s.

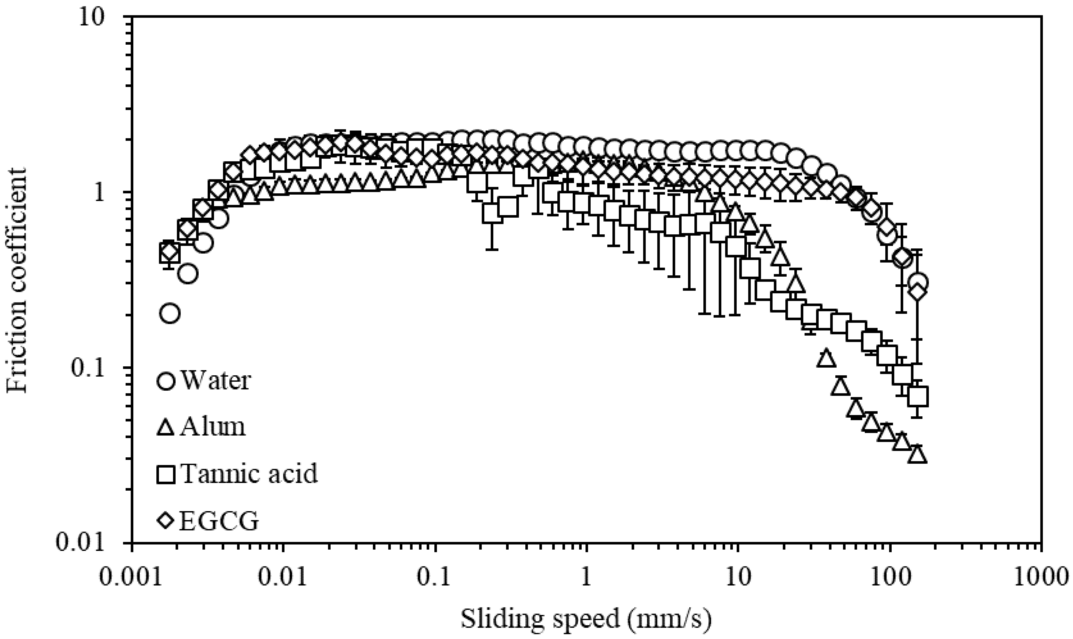


Figure 4.8 - Measured tribological properties of astringent solutions with PDMS disc and steel ball tribopair using a three ball on plate system at 1 N, showing the friction coefficient as a function of sliding speed.

PDMS modified with Triton X-100 showed different friction behaviour to native PDMS with astringent compound solutions (*Figure 4.9*). EGCG is entrained at the highest speed and shows greatest friction coefficient above 20 mm/s. Water enters hydrodynamic regime at the lowest speed compared to the astringent compounds suggesting the astringent compounds are decreasing the lubricity with the hydrophilic surface. Above 120 mm/s, all samples showed a similar friction coefficient value due to onset of hydrodynamic lubrication.

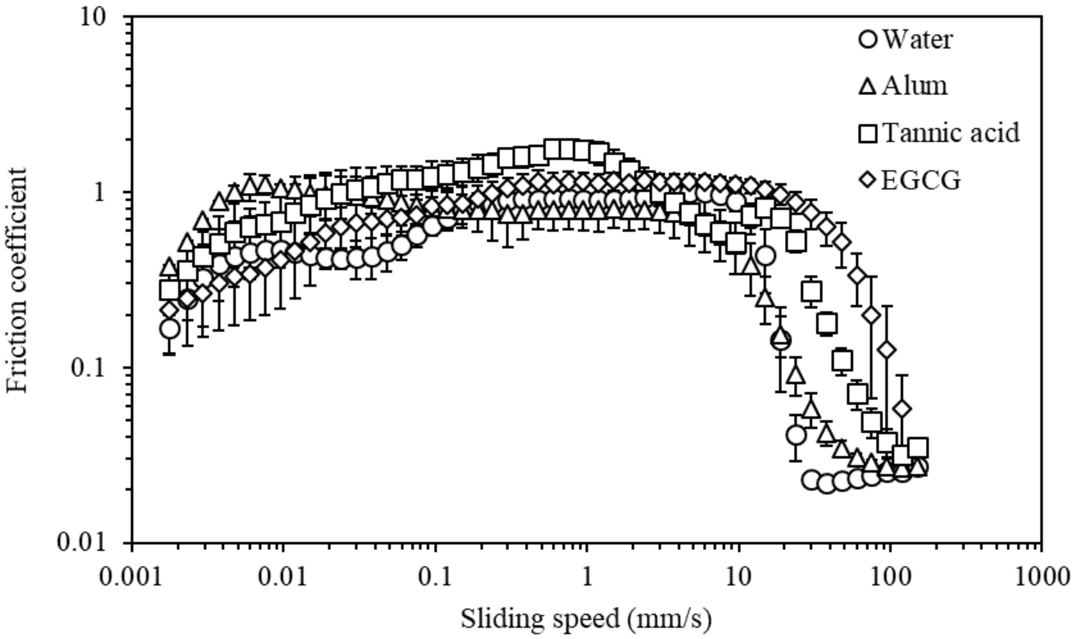


Figure 4.9 - Measured tribological properties of astringent solutions with PDMS modified with Triton X-100 disc and steel ball tribopair using a three ball on plate system at 1 N, showing the friction coefficient as a function of sliding speed.

PDMS modified with Triton X-100 showed differentiation between samples, with all regimes present under the conditions tested. Water was highly lubricating across the regimes, whereas astringent solutions showed an increase in boundary friction compared to water and an extended mixed regime, suggesting the astringent solutions are interacting with the surfaces to increase friction. Interestingly, for PDMS and tannic acid, once the mixed regime was entered around 0.1 mm/s, the tannic acid was found to be highly lubricating. A study by De Wijk & Prinz (2006) found when using a custom-made friction tester, there was a decrease in friction when tannic acid was mixed with saliva, suggesting the lubricity of saliva was increased by the tannic acid. EGCG was observed to be a poor lubricant, with friction properties similar to water. When using PDMS modified with Triton X-100, EGCG was the least lubricating solution tested when in the mixed regime above speeds of 20 mm/s. This correlates well with a study by Rossetti, Yakubov, Stokes, Williamson, & Fuller (2008) who found that EGCG diminished salivary lubricity due to interactions with an adsorbed salivary layer and the astringent molecule.

4.4. Conclusions

Chemical surface modification techniques were applied to PDMS surfaces enabling permanent hydrophilicity. The ability to impart hydrophilicity provides an avenue to better mimic the in-mouth conditions with quantitative physical measurements. The lubrication properties of these surfaces were studied using a three-ball-on-plate testing configuration for rheometer where friction coefficient was measured as a function of sliding speed. The modified PDMS surfaces were examined with a range of aqueous polymer and astringent solutions. Surfaces were shown to affect the friction properties, demonstrating the importance of choosing suitable testing parameters with full consideration of surface chemical properties in order to accurately assess samples. The simple surface modification of PDMS via non-ionic surfactant Triton X-100 showed good distinction between samples and allowed all lubrication regimes to be examined in the speed range tested. Data also compared well to existing data in literature. However, further research is needed examining a range of testing conditions and a wider range of samples where it would be useful to identify how friction data obtained using this surfaces relates to sensory perception data. Film thickness measurements (not achieveable with the configuration used in this study) could elucidate the exact role of the lubricating layers provided by the chemically modfied, hydrophilic PDMS substrates. These findings hold great potential for designing biocompatible surfaces for aqueous lubrication in numerous soft tribology applications. However, these studies have again highlighted the oral environment is complex and more research is needed to identify suitable and relevant testing conditions. Continued research is required to develop a method by which correlation between laboratory experiments and oral perception can be conclusively inferred without introducing variability and over complexity.

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5. SURFACE TEXTURE MODIFICATIONS FOR ORAL PROCESSING APPLICATIONS

Surface texture modifications for oral processing applications

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Key words: oral processing; particulate suspensions; surface texture; biotribology.

Abstract

The surfaces currently used in soft tribology when assessing oral processing *in-vitro* are not yet fully representative of the oral cavity. Surface topography, among other physical and chemical qualities, plays a key role in determining friction properties. This work examines the friction properties of pillar textures of 500 µm and 1000 µm in polydimethylsiloxane that resemble papillae found on the human tongue. Initially a system with Newtonian fluids was investigated using these textured discs. It was found the area density of pillars affected hydrodynamic lubrication, with a greater area density promoting full film lubrication. Model hard, spherical particulate suspensions were also examined showing a reduction in friction coefficient so long as particles were smaller than the pillars; particles that were too large for the cavities increased friction. Soft, deformable particulate gels, commonly used in food products, demonstrated different behaviour to the hard particulate systems. The findings show great potential for a more realistic analysis of complex food formulations and understanding of their behaviour as they are processed in the mouth, although a number of other factors still need to developed.

5.1.Introduction

As food enters the mouth and is consumed, it is subjected to a series of mechanical processes by the lips, tongue, teeth and palate in order to facilitate digestion. The surface of the tongue comprises of macroscale pits and grooves due to the presence of papillae. This design increases the contact area between surfaces and food allowing control of processing in the oral cavity. Papillae on the human tongue are commonly divided into four types: the folate and vallate which are located in the posterior of the tongue, and the fungiform and filiform papillae; located on the anterior. Papillae range in size and shape but typically have a height and diameter under 1 mm (Kullaa-Mikkonen and Sorvari, 1985; Sarkar et al., 2019; Spielman et al., 2010). Mechanoreceptors found on the interface of oral surfaces, including the tongue, allow the perception of friction of the food. Friction in the mouth is believed to contribute to mouthfeel attributes including creaminess, roughness and detecting the presence of particles (Malone et al., 2003). The friction properties depend on many factors including the lubrication properties of saliva, the oral surfaces involved (which differ between individuals depending on age, sex, health etc.) and the food itself. Studies have shown tribology to be a promising technique for correlations with oral behaviour and sensory perception, specifically relating to squeeze flow between the tongue and palate (De Vicente et al., 2006). Quantitative friction and lubrication properties combined with other physical measurements such as rheology and texture analysis as well as sensory perception measurements give an increased understanding of oral processing (Malone et al., 2003). Researchers continue to study and link rheology, sensory properties and tribology as investigations continue into understanding and relating tribological measurement to the oral perception of food and drink products (Godoi et al., 2017; Laguna et al., 2017; Miao and Lin, 2019; Sarkar et al., 2019; Sonne et al., 2014; Stokes et al., 2013).

A range of soft materials have been used in tribological oral processing applications including rubbers, silicones and biological tissues (Bongaerts et al., 2007; Dresselhuis et al., 2008). These materials typically fail to represent the inherent structural intricacies and topography of the tongue which are expected to affect friction. A number of studies address this by investigating rough soft contacts (Bongaerts et al., 2007; Bongaerts et al., 2007; Cassin et al., 2001; Yakubov et al., 2015; Yashima et al., 2014). Krzeminski *et al.* found lubricating performance was strongly affected by patterning on the tribological testing surface, where the roughness indices were more crucial for lubricating properties in a tribosystem than the stiffness of the material (Krzeminski et al., 2012). A study by Selway, Chan, & Stokes proposes the mechanism of lubrication within a smooth contact is governed by localised fluid entrapment and interfacial viscoelastic effects, whereas a different mechanism occurs for rough contacts whereby the lubricant properties have less effect on the interfacial friction (Selway et al., 2017). Other studies look to more closely resemble the tongues surface including Nguyen *et al.* who studied three solid substrates: surgical tape, silicone rubber and ethylene propylene diene monomer rubber (Nguyen et al., 2016). It was observed that surgical tape best discriminated dairy solutions of different compositions compared to the rubber substrates. The authors attribute this to the surfaces being similar to that of the tongue. None of these surfaces were as representative of the tongue's architecture as the study by Dresselhuis *et al.* who used oral tissue in the form of a cross section of pig tongue *ex vivo* (Dresselhuis et al., 2008). However, using a biological sample may cause issues in reproducibility, and samples may not be available or accessible to all researchers, so the design of textures using a non-biological material that are of the same order of magnitude of the tongue is of interest. Ranc *et al.* investigated a range of hemispherical surface structure in the sub-millimetre range, corresponding to typical tongue roughness (Ranc et al., 2006). They found the textures critically affected the frictional behaviour of the systems tested. Under dry conditions, the coefficient of friction decreased significantly with an increase in the density of hemispherical pillars. In lubricated systems, a structure of high pillar density yielded higher coefficients of friction. This effect was attributed to the protruding structures disturbing the homogeneity of the lubricant film.

Whilst considering the complexity of replicating the human tongue, it is also important to consider that foods products are structurally complex, comprising of multiple components, systems and phases. Food products are often particulate in nature but few tribological studies examine particulate samples directly. One example of these is Yakubov *et al.* who investigated glass spheres in glycerol (Yakubov et al., 2015). In this study, the authors varied the viscosity of the matrix in order to probe the influence of particles across all lubrication regimes. In the boundary regime, particles lowered friction due to ball bearing behaviour providing surface roughness was low enough to prevent surface-asperity interactions. A study by Liu *et al.* reported a similar ball bearing lubrication mechanism from the presence of micro-particulated whey protein particles reduced friction (Liu et al., 2016b). Chojnicka-Paszun & De Jongh investigated suspensions of microcrystalline cellulose particles (Chojnicka-Paszun and De Jongh, 2014). The researchers found the particles may not fit into surface asperities, so enhanced surface roughness affording an extended boundary regime. Ideally, more work on particulate suspensions should be completed to understand how they lubricate between contacting soft surfaces in relative motion.

This study aims to examine the influence of surface texture on the lubrication properties of particulate suspensions relevant to oral processing applications. Soft-surface textures and particles have been investigated tribologically, but very few studies examine these together, despite it being known particles interact with oral surfaces to affect sensory perception (Chojnicka-Paszun et al., 2014; Kim et al., 2015; Morell et al., 2017). It is clear from existing research that lubrication mechanisms for soft contacts are affected by surface roughness or textures and continued research in this area is necessary to understand the relevance to oral processing (Kieserling et al., 2018; Nguyen et al., 2016; Selway et al., 2017). Existing texture studies are typically on the micro- or nano-scale, whereas this study aims to more closely resemble the tongue structure by investigating larger (>500 µm) textures. Model hard spherical particles are investigated as well as soft, deformable particulate systems in order to examine a range of particle systems that may occur in food products. Typically, protein or polysaccharide suspensions are investigated; in this study agar fluid gels were used as these form relatively large particles and are more frequently being used in food products as fat replacement (Fernández Farrés and Norton, 2015; Lazidis et al., 2016; Sarkar et al., 2017; Sarkar and Singh, 2012).

5.2.Materials and methods

5.2.1. Materials

Glycerol >99% and agar were obtained from Sigma Aldrich, UK. Microcrystalline cellulose (Viva Pur MCC Spheres range) was kindly provided by JRS Pharma, Germany. Sylgard 184 Silicone Elastomer kit was purchased from Dow Corning. Materials were used with no further modifications or purification.

5.2.2. Glycerol solutions

Glycerol solutions of 25%, 50% and 75% glycerol were prepared by dispersing the desired wt% of glycerol in distilled water under stirring. Solutions were stirred for at least one hour to ensure thorough dispersion.

5.2.3. Hard particle suspensions

Hard spherical, microcrystalline cellulose particles (MCC) were added to glycerol under stirring at a phase volume of 10% w/v (unless stated otherwise). Suspensions were stirred for at least one hour to ensure uniform dispersion. Two discrete particle sizes with a bulk density of 0.8 gcm^{-3} were used for this study: 100-200 µm (Viva Pur MCC Spheres 100) and 500-700 µm (Viva Pur MCC Spheres 500).

Particle size distribution was measured using an optical laser particle size analyser (Mastersizer, Malvern Instruments, UK) and are summarised in *Table 5.1*, below. Measurements were carried out in triplicate.

Table 5.1 - A table showing median diameter of microcrystalline cellulose particles.

Particle type	**Median diameter of particle (µm)**
100-200 µm	158 ± 1
500-700 µm	536 ± 3

5.2.4. Soft particle suspensions

Agar fluid gels were prepared in a lab-scale continuous process pin-stirrer. The required mass of agar was dispersed in deionised water and heated to 90°C whilst stirring. The resultant hot solution was fed through a peristaltic pump into a jacketed pin-stirrer cooled to 5°C. The inlet temperature was controlled to ~ 70°C and the outlet to 5°C to ensure gelation occurred under shear (gelation temperatures ~ 30°C). The speed of the pump was set to 25 mL min^{-1}. The shaft rotation speed was set to 2000 rpm. Fluid gels were stored at 5°C until use.

To determine the diameter of the agar fluid gel particles, particles were analysed using an optical laser particle size analyser (Mastersizer, Malvern Instruments, UK) and are summarised in *Table 5.2*, below. Measurements were carried out in triplicate.

Table 5.2 – A table showing median diameter of agar fluid gel particles.

Concentration of agar (wt%)	**Median diameter of particle (µm)**
2	135 ± 5
4	121 ± 2

5.3.Methods

5.3.1. Shear rheology

Rheological measurements were performed using a Kinexus Pro rheometer (Malvern Instruments, UK). For glycerol suspensions, viscosity curves were obtained through a range of applied shear rates at equilibrium (1–100 s^{-1}) using a cup and bob geometry at 25°C. For MCC particulate suspensions, viscosity curves were obtained by recording shear viscosity through a range of applied shear rates at equilibrium (1–100 s^{-1}) using a spiralled cup and bob geometry at 25°C. For agar fluid gels, measurements were completed at 25°C, 48 hours after production, to ensure sufficient post-production particle ordering. Viscosity curves were obtained by recording shear viscosity through a range of applied shear rates at equilibrium (0.001–500 s^{-1}) using a serrated parallel plate geometry (60 mm serrated parallel plate) with 1 mm gap at 25°C. Experiments were carried out in triplicate.

5.3.2. General tribological set up

A mini traction machine (MTM) manufactured by PCS Instruments, UK was used to perform tribological measurements. A sample size of 15 ml with volume reducing insert fitted was used in all cases. For each experiment, the tribopair consisted of a ¾ inch (0.019 m diameter) stainless steel ball (supplied by PCS Instruments, UK) and polydimethylsiloxane (PDMS) disc. PDMS was chosen as the disc material due to its wide use in soft-contact tribology and its surface properties can be easily tailored (surface topography and hydrophobicity) (Bongaerts et al., 2007; Chojnicka-Paszun and De Jongh, 2014; Pradal and Stokes, 2016; Sarkar et al., 2017). Prior to testing, surfaces were sonically cleaned in isopropanol followed by distilled water for 6 minutes each.

5.3.3. Mould preparation

A moulding-casting technique was used to create the PDMS discs. Moulds were created using AutoCAD software and the Form Labs Form2 3D printer. The advantages of using this method to create moulds are that it is efficient for time and resources. Most importantly, however, the moulds are easily designed on the software allowing for a range of surface structures to be explored. Moulds to cast discs of 46 mm diameter, 4 mm thickness suitable for use in the MTM were printed using Grey Resin V3 supplied by Formlabs. Once printed, moulds were sonically cleaned in isopropanol to remove any excess uncured resin. The first PDMS disc was disposed of to ensure any uncured resin did not affect the disc surface.Six surfaces were investigated: S0, a smooth disc with no textures added to the mould (average roughness, $S_a \approx 2$ µm, characterised using a KLA Tencor MicroXAM2 Interferometer), and E1, E2, E3, E4 and E5 each with cylindrical pillar cavities of varying diameter, height and density, summarized in *Table 5.3*, that are a similar size range to papillae found on the human tongue (Spielman et al., 2010). Classical Hertz contact theory was used to calculate the contact area and maximum contact pressure (Hertz, 1881). The contact radius (A_r) subject to load (W) is given in *Equation 5.1*:

$$A_r = \left(\frac{3WR^*}{4E^*}\right)^{\frac{1}{3}} \quad \text{(\textit{Equation 5.1})}$$

$$R^* = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1} \quad \text{(\textit{Equation 5.2})}$$

$$E^* = \left(\frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}\right)^{-1} \quad \text{(\textit{Equation 5.3})}$$

$$P_{max} = \frac{3}{2\pi A_r^2} \quad \text{(\textit{Equation} 5.4)}$$

R* and E* are the reduced radius and reduced elastic modulus, given by *Equation 5.2 and 5.3*, where the subscript numbers 1 and 2 denote the two contacting surfaces e.g. 1 = ball and 2 = disc. R_1 and R_2 are the radii of the contacting surfaces, E_1 and E_2 represent elastic moduli and ν_1 and ν_2 are the Poisson‘s ratios. The maximum pressure in the contact can be calculated by *Equation 5.4*. In the case of this set up, E* = 170 MPa, R* = 0.0095 m, Ar = 2.3 mm, W = 3 N, and the maximum contact pressure = 270 kPa. The maximum pressure in the contact is an order of magnitude higher than the pressure of the oral-palate contact of healthy adults (typically around 30 kPa). For these pressures to be achieved, the tribological set-up would require using loads lower than 0.1 N, which is not possible when using a MTM (Sarkar et al., 2019).

Water contact angle measurements were performed to assess wettability of the PDMS substrates (*Table 5.3*). Sessile drop contact angle measurements were performed using a goniometer (Krüss Drop Shape Analyser, Germany). A symmetrical drop of volume of 10 µL was deposited on the surface material using a syringe. All surfaces were cleaned with ethanol, distilled water and dried in air prior to testing. The contact angles were determined at room temperature from image analysis via the Laplace-Young method using DSA Software provided with the equipment. Reported contact angles are the average of three measurements. All textured surfaces (E1-E5) show similar hydrophobicity.

Table 5.3 – A table showing surface properties the four fabricated PDMS discs: S0, E1, E2, E3, E4 and E5 with varying cylinder diameter, height and area density.

	Cylinder diameter (μm)	**Cylinder height (μm)**	**Cylinder density (mm^{-2})**	**Area coverage of cylinders (%)**	**Theoretical no. of cylinders in the contact**	**Water contact angle (°)**
S0	-	-	0	0	0	102 ± 3
E1	500	500	0.5	10	8	142 ± 5
E2	500	500	1	20	16	146 ± 2
E3	1000	1000	0.25	20	4	151 ± 6
E4	500	500	2	40	32	147 ± 6
E5	1000	1000	0.5	40	8	146 ± 6

5.3.4. Disc fabrication

The discs were made from PDMS, using Sylgard 184 Silicone Elastomer kit. The two components (silicone elastomer and curing agent) were mixed in the recommended 10:1 ratio. The binary liquid mixture was poured into the 3D printed mould, degassed and placed in an oven at 60°C for 3 hours. Without removing the disc, the moulds were left to cool for at least 24 hours. The discs were the removed and stored in an airtight container before use. The Young’s Modulus of the discs was 1.3 ± 0.2 MPa. Each disc was used once before disposal. The outcome is shown in *Figure 5.1*.

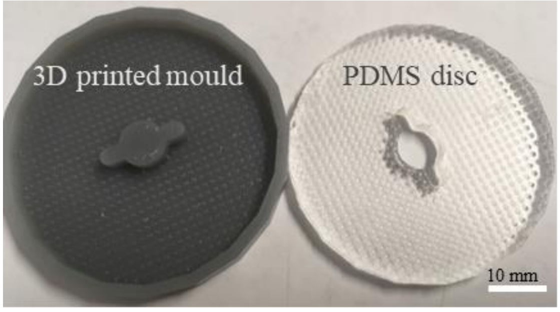


Figure 5.1 – 3D printed mould in Grey Resin (Formlabs), left, and PDMS disc (46 mm diameter, 4 mm thickness), right, cast from the mould for use in a mini traction machine.

Surfaces were analysed before and after testing where cylinders remain intact and no visible damage to the structure or shape was observed, as can be seen in optical microscopy images (obtained using Leica Microsystems, UK with objective lens up to 4× magnification) shown below in *Figure 5.2*.

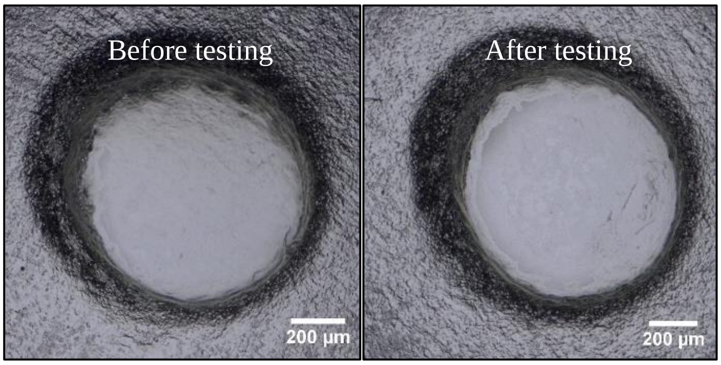


Figure 5.2 – light microscopy images of 1mm cylindrical pillars before (left) and after (right) testing.

5.3.5. Newtonian systems

Glycerol was used as the lubricant due to its Newtonian behaviour and aqueous glycerol solutions were used to probe the effect of viscosity and fluid substrate-interactions. Tribopairs of PDMS disc and stainless steel ball were used with six different surfaces: S0, E1, E2, E3, E4 and E5. The testing conditions used were 50% SRR and entrainment speed 1 to 1000 mm/s. Six Stribeck sweeps were performed alternating between ascending and descending speed without unloading for each step at room temperature (25°C) at normal force 3 N. Tests were performed in triplicate to obtain an average.

5.3.6. Particulate systems

Glycerol and MCC particle dispersions and agar fluid gel particles were studied. A PDMS disc with textured surface and steel ball were used. The testing conditions used were 50% SRR and entrainment speed 1 to 750 mm/s. Six Stribeck sweeps were performed alternating between ascending and descending without unloading for each step at room temperature (25°C) with normal force 3 N. Tests were performed in triplicate to obtain an average.

5.4.Results and discussion

5.4.1. Influence of surface texture with Newtonian systems

Aqueous solutions of glycerol were used to assess textured PDMS surfaces. *Table 5.4* lists the glycerol solutions used in this study and their measured viscosities at 25°C. All samples demonstrated Newtonian behaviour across the shear rates tested. The lubricating properties were measured using steel ball and textured PDMS discs: S0, E1, E2, E3, E4 and E5 at 3 N normal force, 50% SRR.

Table 5.4 – Table showing measured viscosity with cup and bob geometry averaged across 1-100 s^{-1} for glycerol solutions at 25°C.

Glycerol (wt%)	**Viscosity at 25°C (Pa s)**
25	0.0016 ± 0.0002
50	0.0038 ± 0.0003
75	0.0249 ± 0.0004
100	0.90 ± 0.01

Stribeck curves were constructed (*Figure 5.3)* for surfaces and the glycerol solutions to examine fluid substrate interactions, with data for overlapping speeds omitted for clarity. At 0.1 Pa mm, the boundary regime is generally observed for all surfaces. As speed increases, the onset of the mixed regime occurs first for E5, E2, E4 and S0 and then E1 and E3. For boundary and the onset of the mixed regime, surfaces E2 and E5 showed a lower friction coefficient. The textured surfaces transition into the elastohydrodynamic (EHL) lubrication regime at a lower speed compared to S0, with the greater area density of pillar cavities transitioning earlier. S0 transitions over a short speed range from boundary lubrication as speed increased to mixed and EHL lubrication. In comparison, the textured surfaces show extended mixed lubrication regimes. S0 also shows the lowest friction coefficient above 1 Pa mm as the transition to EHL occurs, with all textured surfaces demonstrating a higher friction coefficient at higher speeds. At 1000 Pa mm, S0, E1, E2 and E3 tend to similar friction coefficient values; whereas E4 and E5 tend to a similar, greater friction coefficient.

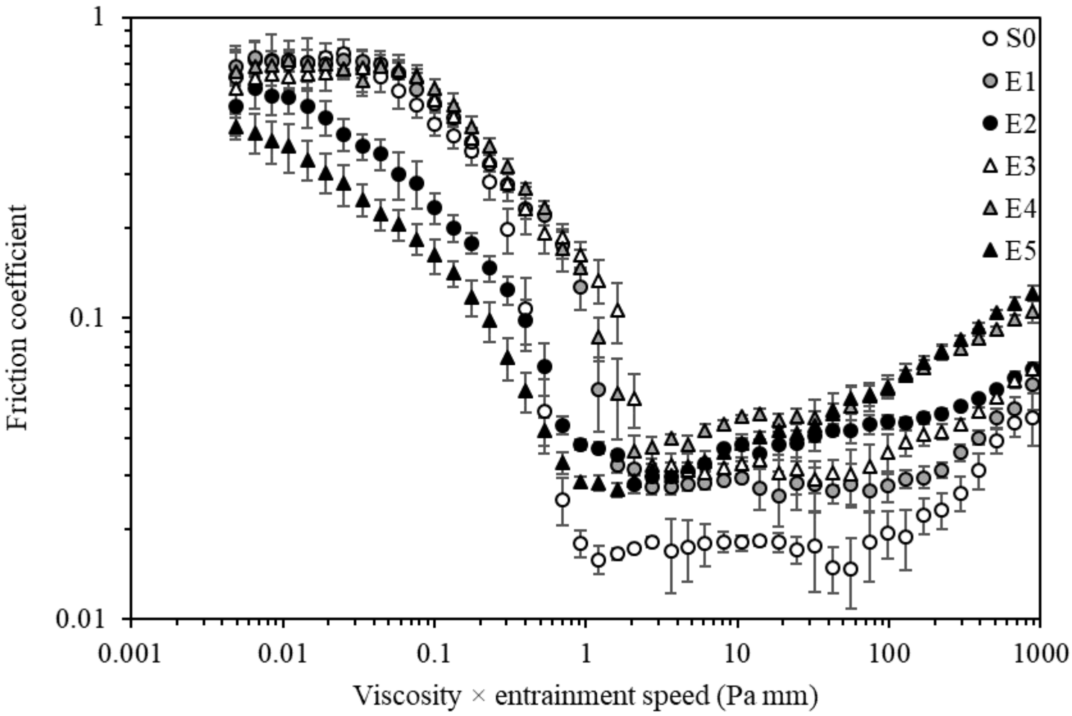


Figure 5.3 – Stribeck curves showing friction coefficient versus entrainment speed as a function of viscosity for glycerol suspensions with non-textured (S0) and textured PDMS surfaces (E1, E2, E3, E4 & E5).

It is clear the textured surfaces affect friction across all regimes. As the textured surfaces transition to the EHL earlier than S0, the pillar cavities are proposed to act as wells or reservoirs of lubricant which are able to facilitate lubrication at high speeds by providing a continuous supply of lubricant even as greater hydrodynamic pressure is applied as speeds increases (Mourier et al., 2006; Wang et al., 2009). Therefore, at high speeds the viscous drag from the lubricant is greater for the textured surfaces with the higher area density and a higher friction coefficient is observed (*Figure 5.4*).

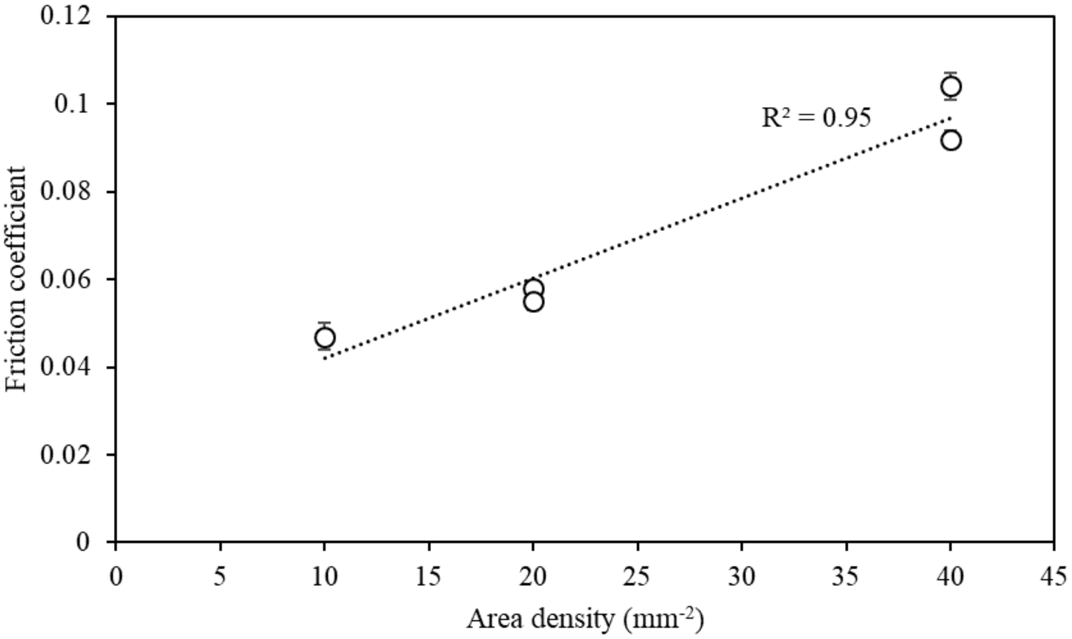


Figure 5.4 – Friction coefficient versus area density of pillars at 500 Pa mm.

5.4.2. Influence of surface texture with particulate suspensions

Food formulations are often particulate in nature therefore the aim of these experiments was to investigate the friction properties of particulate suspensions on the textured PDMS surfaces.

Hard particle dispersions

Model particulate suspensions of glycerol containing 10% phase volume of rigid, spherical MCC particles were examined. The shear rheology was measured and frictional behaviour assessed using the MTM, as described in Section 2.2. A tribopair of stainless steel ball and PDMS discs were used. Three surface textures were investigated: S0, E2 and E3. All particle dispersions showed Newtonian behaviour over the speed range tested, with measured viscosities described in *Table 5.5*.

Table 5.5 - Table showing measured viscosity with spiral cup and bob geometry averaged across 1-100 s^{-1} for glycerol solutions at 25°C.

Glycerol and particle dispersion	**Viscosity at 25°C (Pas)**
No particles	0.90 ± 0.01
100-200 µm	0.91 ± 0.01
500-700 µm	0.92 ± 0.02

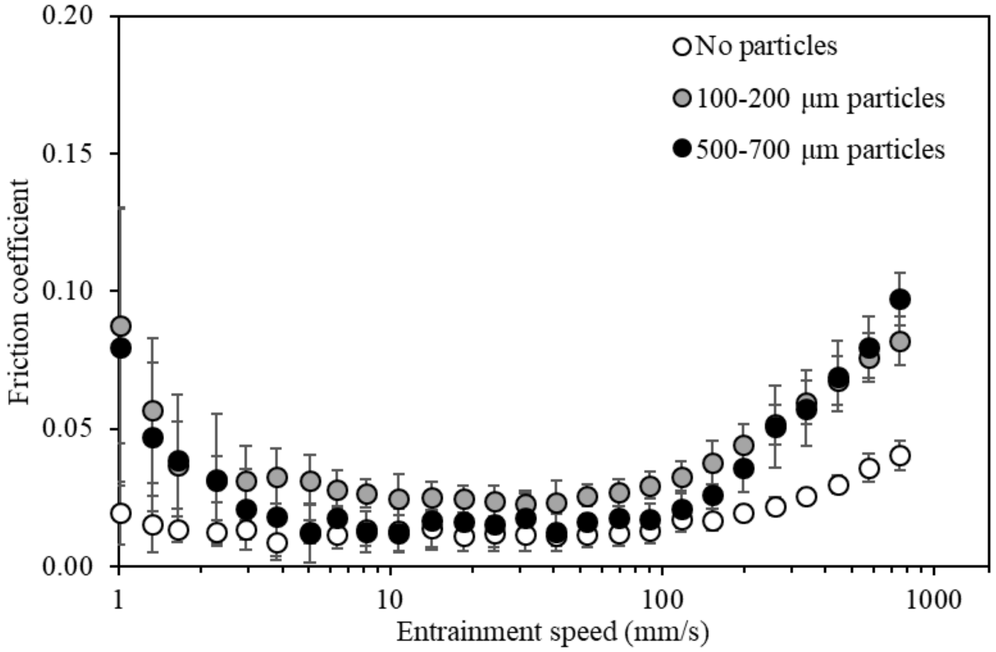
Figure 5.5a shows the friction coefficients of the glycerol suspensions measured using the non-textured PDMS disc, S0. At the initial stages of the lubrication process (for entrainment speeds up to 10 mm/s) the friction coefficient of the three systems decreased with increasing speed indicating mixed lubrication. The particulate systems showed greater friction coefficient below 10 mm/s compared to glycerol alone showing particles are influencing the friction response at low speeds when surfaces are likely to be in contact. As speed increases, clear distinction between no particle and particle suspensions was observed. Both the particle suspensions showed a similar, greater friction coefficient in EHL regime.

Figure 5.5b shows the friction coefficients measured from glycerol suspensions with textured surface E2 with cylindrical pillars of 500 µm height and diameter. For speeds lower than 10 mm/s, the addition of particles increased the friction coefficient as with surface S0. As speed increases and mixed lubrication transitions to EHL, the friction behaviour of the particulate suspensions differs. The particles sized 100-200 µm show a lower friction coefficient, with values closer to glycerol alone, compared to larger 500-700 µm particles.

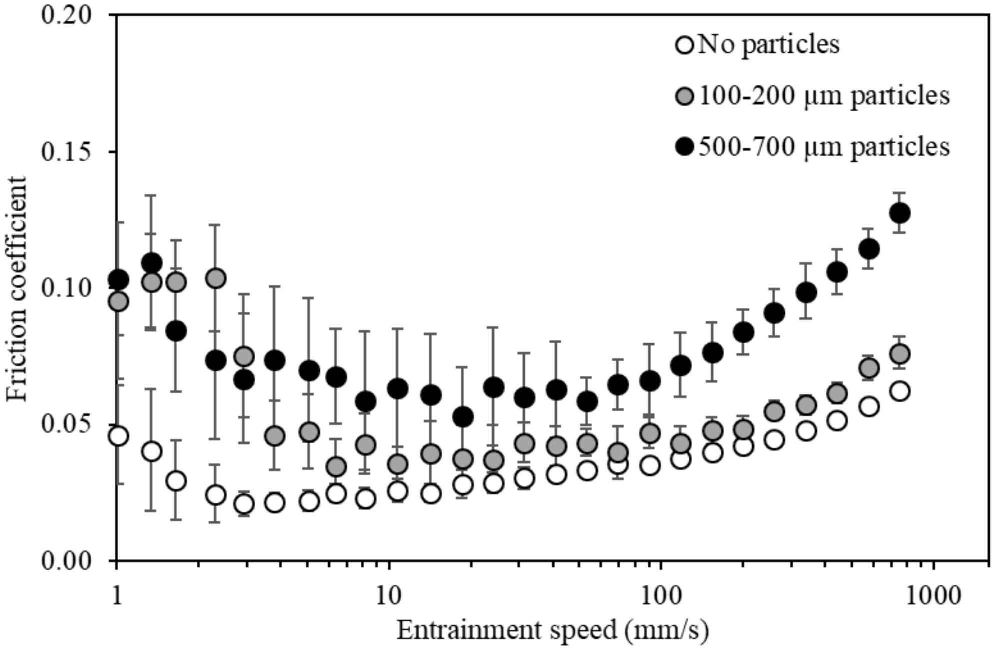
Figure 5.5c shows the friction coefficients measured from glycerol and glycerol particulate suspensions with textured surface E3 with cylindrical pillars of 1000 µm height and diameter.

For particles suspensions at speeds lower than 10 mm/s, the friction coefficient was higher than glycerol without particles, observed with surfaces S0 and E2. As speed increases, the friction response for all samples was similar and a smaller difference between the samples was observed compared to surfaces S0 and E2.

(a)



(b)



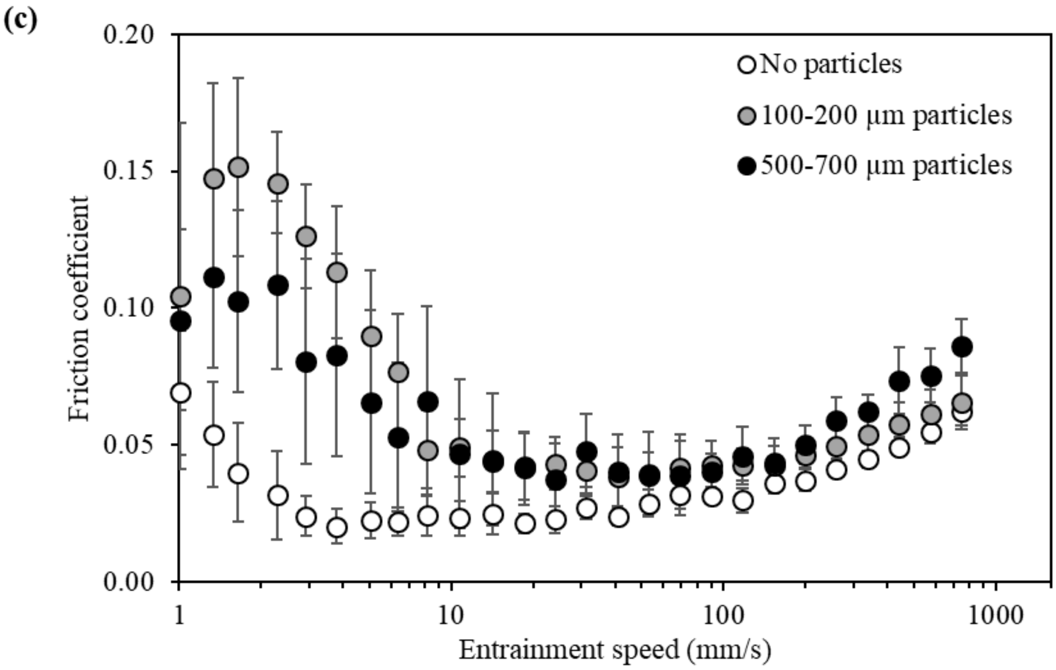
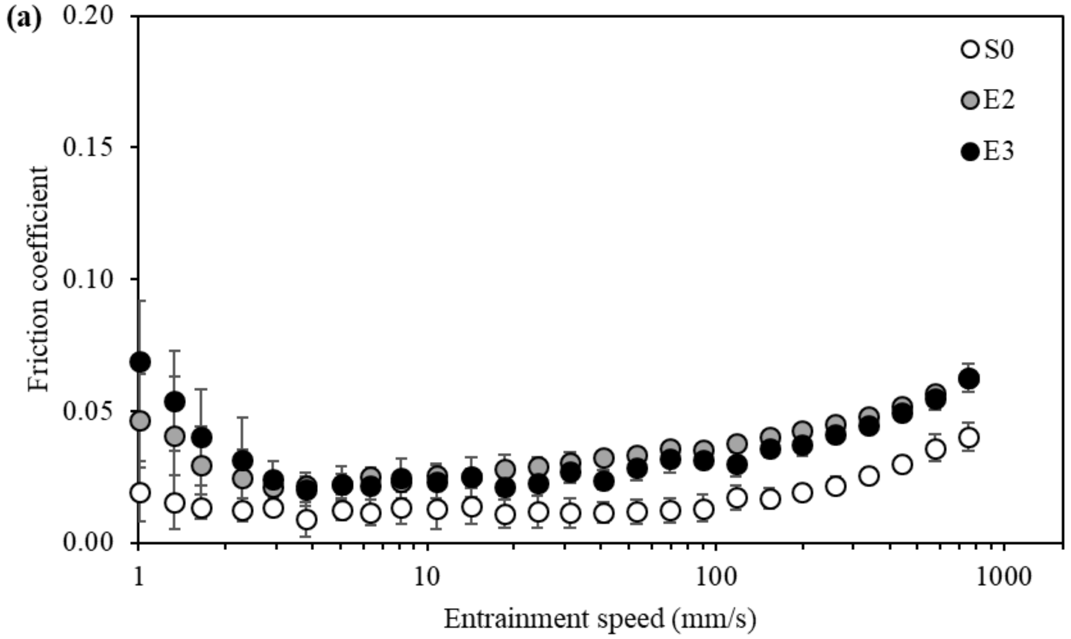


Figure 5.5 - friction coefficient versus entrainment speed for glycerol suspensions containing 10% MCC particles, with pure glycerol for comparison with surfaces S0 (a), E2 (b) and E3 (c).

To compare how the particulate systems behave across different surfaces, the surfaces were compared for a given particle size. For no particles, the results are presented in *Figure 5.6a*.

For the 100-200 µm MCC particles in the boundary regime (< ~10 mm/s) (*Figure 5.6b*), smooth surface S0 has the lowest coefficient of friction and surface E3 has the highest. As speed increases and the mixed and EHL regimes are entered, the surfaces behave similarly, however, the particulate systems show a lower friction coefficient with the textured surfaces E2 and E3 compared to smooth surfaces S0. The textured surfaces act to elongate the mixed lubrication regime as surface S0 enters the EHL regime around 100 mm/s, E2 around 200 mm/s, and E3 around 300 mm/s.

For MCC particles sized 500-700 µm (*Figure 5.6c*), S0 also has the lowest coefficient of friction below speeds of 8 mm/s and the textured surfaces showed a higher friction response. As speed increased above 75 mm/s, surface E2 shows the highest friction response. Here, 500-700 µm particles are too large to fit into the 500 µm features in the surface. However, as the EHL regime is entered above 100 mm/s, S0 and E3 show similar friction behaviour. Particles are expected to fit into 1000 µm cavities on surface E3 which in turn has shown a reduced friction coefficient in this system compared to E2.



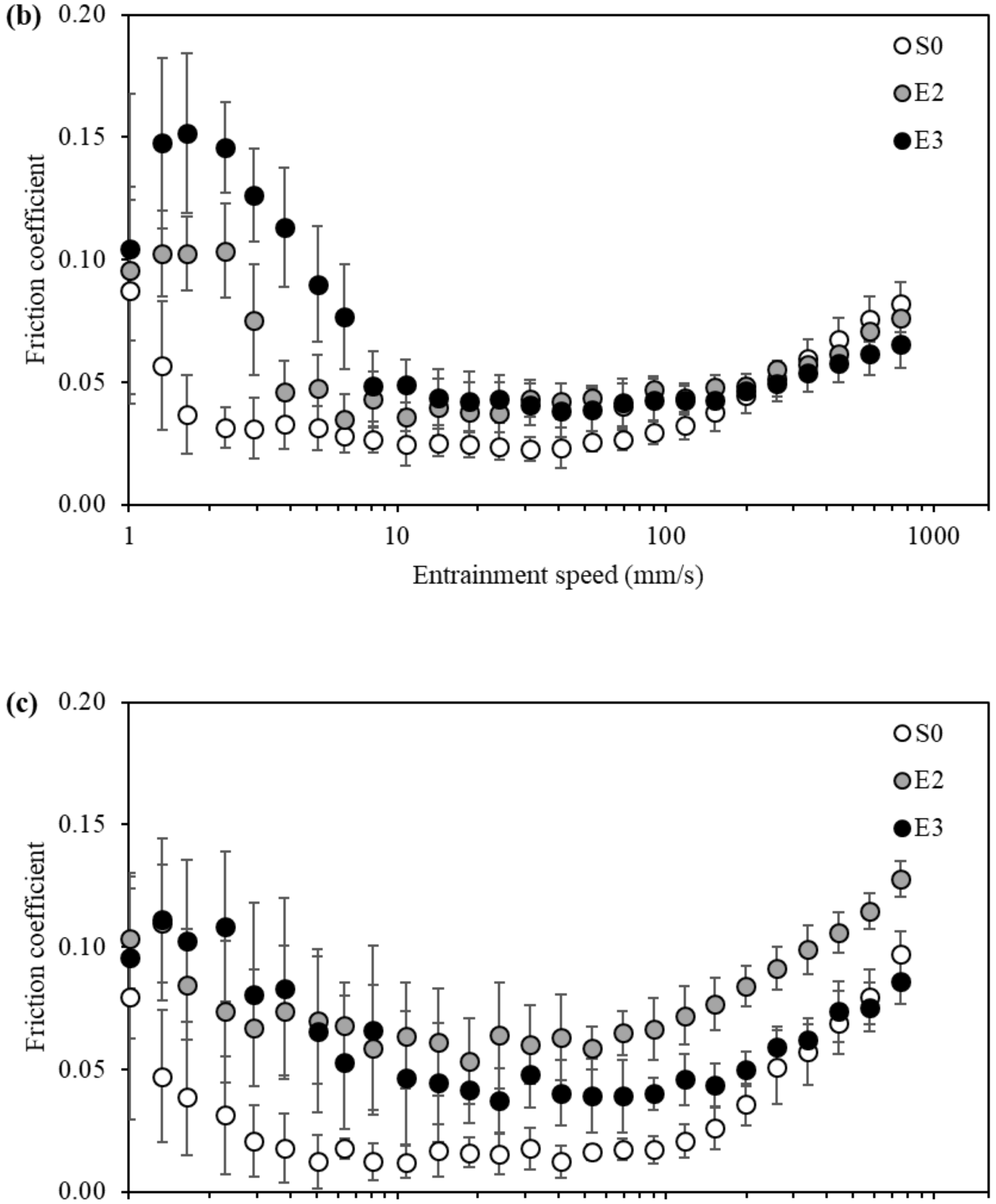


Figure 5.6 - friction coefficient versus entrainment speed for textured surfaces with glycerol suspensions without particles (a), with particles sized 100-200 µm (b) and with particles sized 500-700 µm (c).

In general, these results show the addition of particles results in higher friction. In this study, the particles used are relatively large and it is expected they are larger than the gap between the contacting PDMS and steel surfaces. However, due to the deformable nature of the soft PDMS surface and the consequential large contact area, it is clear from the data (independent of surface texture) particle suspensions are entrained between the contacting surfaces and influence friction, even at low speeds when the gap between contacting surfaces is expected to be small. This agrees with a previous study which showed hard particles directly interacted with the surface and were present even at low entrainment speeds attributing this to the deformable nature of the contact (Chojnicka-Paszun and De Jongh, 2014). When surfaces are compared for a given particle size, it becomes clear particles act to reduce the friction coefficient with the textured surfaces in the EHL regime, so long as they are able to 'fit' inside cavities. This reduction in friction has also been observed at the smaller length scale when particles were able to fit inside asperities (Chojnicka-Paszun and De Jongh, 2014; Liu et al., 2016a; Sarkar et al., 2017).

To understand the lubrication of the particles further, the role of phase volume was examined as both particles and the continuous phase are expected to affect friction and lubrication properties (Andablo-Reyes et al., 2019; Fernández Farrés and Norton, 2015). *Figure 5.7a* shows friction coefficient versus particle phase volume of MCC particles sized 100-200 µm at 750 mm/s where friction properties are expected to be dependent on the bulk properties of the lubricant (EHL regime). As phase volume of particles increases, friction coefficient increases for all surfaces investigated. The surface has little impact on friction coefficient at phase volumes greater than 10% with overlap of standard deviations showing similar friction response. Below 5% phase volume of particles for surface S0, the friction coefficients are lower than for the textured surfaces E2 and E3. It is likely due to a continuous film lubricating between the ball and the smooth surface that is not interrupted by surface textures or particles in the contact (as there are fewer particles in suspensions) (Andablo-Reyes et al., 2019; Fernández Farrés and Norton, 2015). Above 10% particle phase volume, the friction response of the surfaces is similar showing the particles are dictating friction response.

Figure 5.7b shows friction coefficient versus particle phase volume of MCC particles sized 500-700 µm at 750 mm/s. As phase volume increases, the friction coefficient increases for all surfaces increased. Surfaces S0 and E3 behaved similarly, whereas the friction coefficients for surface E2, with cylindrical pillars of 500 µm height and diameter, are consistently greater than E3, regardless of the amount of particles added. The particles are not able to fit into the pillars of surface E2 unlike surface E3 demonstrating that if the particles are able to fit inside the pillar cavities, a lower in friction coefficient can be observed.

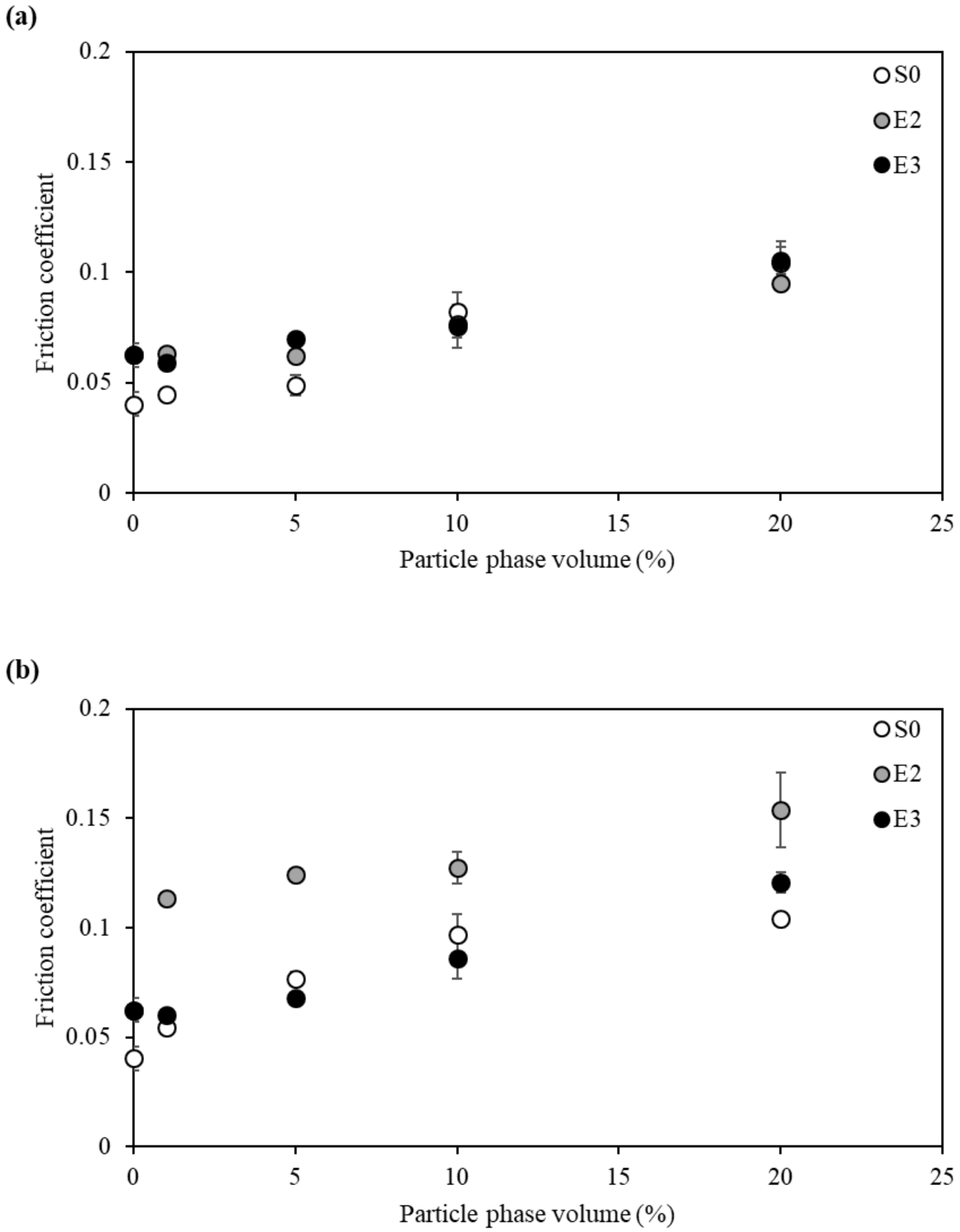


Figure 5.7 - friction coefficient at 750 mm/s versus particle phase volume for glycerol suspensions containing MCC particles sized 100-200 µm (a) and 500-700 µm (b) with surfaces S0, E2 and E3.

Soft particulate dispersions

The aim of these particular experiments was to further investigate the textured surfaces by examining agar fluid gels, which are deformable particulate suspensions irregular in shape. Agar concentrations of 2 and 4 wt% were examined. A tribopair of steel ball and PDMS discs were used with textures S0, E2 and E3 investigated.

The viscosity profiles of the agar fluid gels were measured (*Figure 5.8*). Shear viscosity increased upon raising agar concentration and both systems showed shear thinning behaviour as expected for particulate systems (Saha & Bhattacharya 2010).

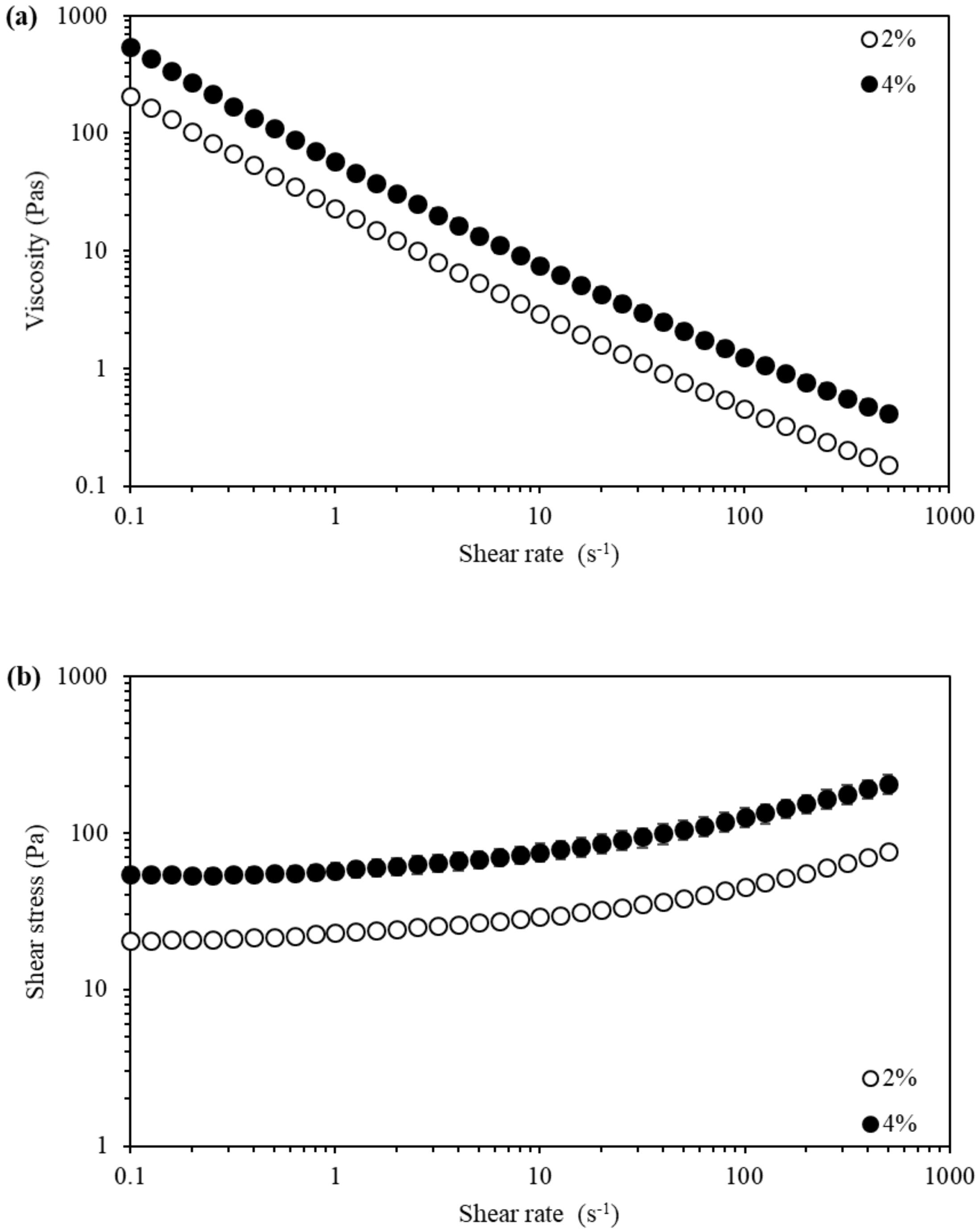


Figure 5.8 – shear rheology showing viscosity (a) and shear stress (b) as a function of shear rate for agar fluid gels of 2 and 4 wt%.

The friction coefficient of the agar fluid gels were measured (*Figure 5.9)* with surfaces S0, E2 and E3. The data collected from the agar fluid gel systems do not exhibit typical Stribeck behaviour. For all concentrations of agar, as speed increases to ~5 mm/s there was an increase in friction coefficient. This behaviour has been reported by Gabriele *et al.* where they attributed their observed increase in friction coefficient with entrainment speed due to particle exclusion of agarose fluid gel particles from the ball and disc contact with the continuous phase providing lubrication at low speeds (Gabriele et al., 2010). These were larger than the magnitude of the roughness of soft surfaces used meaning the mixed regime passed a maximum friction coefficient before the speeds were great enough to generate a film thickness that exceeds particle diameter, allowing entrainment and reducing friction. An alternative explanation is that at low speeds the agar fluid gels are entrained more efficiently and maintain a high viscosity film in the inlet region. Both of these explanations would need further study, and as suggested in other fluid gel studies, experiments using Surface Force Apparatus technique where the interaction forces between the two contacting surfaces are measured would help to elucidate the processes involved (Fernández Farrés and Norton, 2015; Israelachvili and McGuiggan, 1990).

A lower maximum friction coefficient for textured surfaces E2 and E3 for 2% agar fluid gel was observed (*Figure 5.9a*). Here, particles are smaller than the cavities in E2 and E3. At low speeds, S0 shows the highest friction until speed increased and the mixed regime begins to transition to the EHL, during which the amount of particles entrained is expected to increase. It is proposed for these fluid gel systems, particles are able to fit inside the surfaces textures to reduce friction when the surfaces are in contact in the boundary and mixed regimes - which are said to be most relevant for oral processing (Stokes et al., 2013). Whereas for the smooth surface, particles were excluded from the contact until sufficient hydrodynamic pressure was achieved at higher speeds. At this point, for all surfaces, friction is similar and bulk properties of the fluid gel system dominate. For 4% agar fluid gel (*Figure 5.9b*), initially, S0 shows a greater friction coefficient compared to E2 and E3. As speed increases the surfaces behave similarly to one another whilst also exhibiting a lower friction coefficient compared to 2% agar, showing the contact is better lubricated by the more concentrated, more viscous fluid gel system, which is expected. The maximum friction coefficient for the surfaces was reduced for S0 from 0.6 to 0.45 and E3 from 0.5 to 0.4 as the concentration of agar increased. For surface E2, the maximum values were similar. With the greater concentration of agar, particle rigidity is expected to increase (Gabriele, 2011). Greater lubrication by more rigid particles has been shown previously in Kappa-Carrageenan, agarose and alginate fluid gel systems where studies demonstrate that more rigid particles are able to support the normal load in the contact (Fernández Farrés and Norton, 2015; Gabriele et al., 2010; Garrec and Norton, 2012).

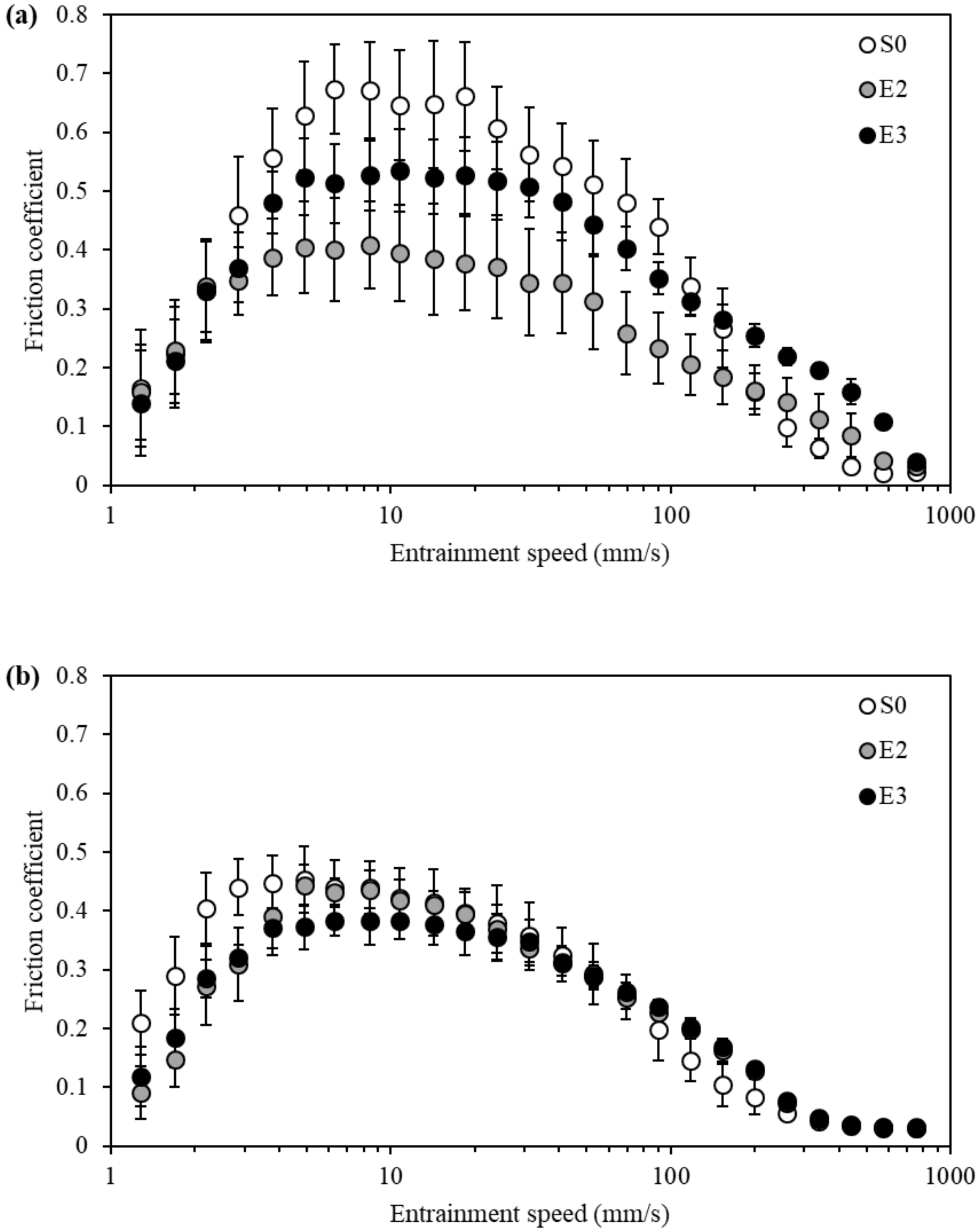


Figure 5.9 - friction coefficient versus entrainment speed for agar fluid gels at 2% (a) and 4% (b) agar concentrations with surfaces S0, E2 and E3.

5.5.Conclusions and future work

Textured surfaces were created by moulding and casting PDMS allowing the fabrication of a disc with cylindrical pillar cavities of a similar size to papillae found on the human tongue. Initially a system with Newtonian fluids was investigated using these textured discs. It was found the area density of pillars affected hydrodynamic lubrication, with a greater area density promoting full film lubrication. With a greater area density of pillars at high speeds, a higher friction coefficient is observed. Specifically how the asperities alter the fluid hydrodynamics would require more work to visualise flow in the measurement gap. Furthermore, the textured discs were used to investigate particulate systems as it is common for food products to contain particles. Model hard, spherical particles showed lower friction coefficients in the EHL regime so long as particles were smaller than the textures. Particles that were too large for the cavities increased friction. Soft, deformable particulate gels, commonly used in food products, demonstrated different behaviour to the ‘model’ particulate systems investigated where they showed lower friction in the mixed lubrication regime, which is suggested to be most relevant to oral processing. These results provide an insight into how particulate systems lubricate and interact with the surface in soft tribological contacts; which has relevance to oral processing applications as the tongue is not smooth like typical testing surfaces used in oral tribology. To understand particle and surface interactions further, a method allowing imaging and mapping of the soft contacts would be incredibly useful. Continued research is needed to link food formulations to physical properties, like friction, where closer resemblance to oral surfaces needs to be considered during experimental testing including surface chemistry and saliva effects.

5.6.References

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6. CONCLUSIONS AND FUTURE RECOMMENDATIONS

Detailed conclusions were given at the end of each of the results chapters. This current chapter summarises the overall outcomes of the thesis and proposes recommendations to build upon the work presented.

6.1. Conclusions

The aim of this research was to develop tribological techniques in order to better understand oral processing when analysing multicomponent, complex systems, like foods. Two tribological testing systems were compared and model food systems analysed; one purpose built and commercially available for tribology and the other an attachment for a rheometer. Surfaces used in oral tribology experiments were also developed in two ways. The first being the surface chemistry of a polymer commonly used in oral processing tribology (PDMS) to more closely resemble the chemistry of oral surfaces. The second being textured surfaces to more closely resemble the texture of tongue. Lastly, all experiments aimed to investigate complex food systems, in particular suspensions and astringent compounds, both of which are commonly found in food systems and have been linked to affecting friction properties, sensory perception and consumer acceptance. The main conclusions from the results chapters are summarised in the following sections.

6.1.1. Comparing tribological testing systems

- **Two different tribological testing systems were examined and compared.**

The friction properties of a range of model food like systems were measured using a three-ball-on-plate rheometer attachment and compared to measurements obtained from an MTM. These had different contact areas and pressure due to a different amount of and different sized stainless steel balls. The TA system had a smaller contact area and higher contact pressure, whereas the MTM had a greater contact area and lower contact pressure.

- **When analysing simple systems, the friction results depended less on the specific test geometry used to perform the tribological measurement.**

Testing using a soft surface showed similarities between the two different testing equipment for simple systems, showing the friction results depend less on the specific geometry compared to complex systems, despite the differences in contact area and pressure. The data yielded was also comparable to existing studies in literature. The TA system allowed the boundary lubrication regime to be examined for all samples due to achieving lower speeds compared to the MTM; speeds as low as 0.02 mm/s are able to be tested using the Discovery HR-2 rheometer. The rheometer however, is limited to sliding friction only. For the guar gum solutions and oil in water emulsions, the three-ball-on plate friction data showed similar trends when compared to MTM data, with relative distinctions between the different samples.

- **The complex system of soft particulate systems showed disagreement between the two systems.**

For the soft particulate system (agar fluid gels) discrepancies were observed likely as a result of particle entrainment being affected by difference in contact area and contact pressure. As there are many parameters that can affect tribological measurements, including the testing equipment, it is clear more work needs to be done to determine ideal testing conditions to be able to successfully analyse food products, which are often particulate in nature.

6.1.2. Surface chemistry modification of PDMS

- **Chemical surface modification techniques were applied to PDMS surfaces enabling permanent hydrophilicity.**

Two techniques involving grafting to a PDMS surface were examined (using UDA or PVA), as well as a surfactant incorporated PDMS, whereby a non-ionic surfactant (Triton X-100) was added to the procured PDMS matrix. The UDA modified and surfactant incorporated PDMS were one-step modifications, whereas the PVA modified PDMS required two steps as the PDMS required surface activation by ozone before exposing to the PVA polymer. These surfaces were compared to non-modified PDMS. The water contact angle of these was reportedly similar to that of the hydrophilic tongue. The ability to impart hydrophilicity provides an avenue to better mimic the in-mouth conditions with quantitative physical measurements. The lubrication properties of these surfaces were studied using a three-ball-on-plate testing configuration for rheometer where friction coefficient was measured as a function of sliding speed.

- **The modified PDMS surfaces were examined with a range of aqueous polymer and astringent solutions. Surfaces modified with non-ionic surfactant Triton X-100 performed best.**

Surfaces were shown to affect the friction properties, demonstrating the importance of choosing suitable testing parameters with full consideration of surface chemical properties in order to accurately assess samples. UDA modified PDMS showed strong interactions between the contacting PDMS and steel surfaces, regardless of lubricant used. PVA modified PDMS was shown to be highly lubricating, facilitating lubrication at low speeds compared to native PDMS and the other modified PDMS surfaces. The simple surface modification of PDMS via non-ionic surfactant Triton X-100 showed good distinction between a wide range samples examined and allowed all lubrication regimes to be examined in the speed range tested. Data also compared well to existing data in literature. These findings hold great potential for designing biocompatible surfaces for aqueous lubrication in numerous soft tribology applications.

6.1.3. Surface texture modification of PDMS

- **Pillar textures were imparted into the surface of PDMS using 3D printed moulds.**

Textured surfaces were created by moulding and casting PDMS allowing the fabrication of a disc with cylindrical pillar cavities of a similar size to papillae found on the human tongue. These were examined using the MTM, as this system has a larger contact area. If the surface textures were examined using the TA system, it is likely the pillar sizes and density would need to be altered in order to get more representative measurements, as it is likely the pillar sizes are too large for contact. It is possible the tribology attachment could be modified to have larger stainless steel balls, therefore a larger contact area.

- **A greater area density of textures promoted the onset of hydrodynamic lubrication.**

It was found the area density of pillars affected hydrodynamic lubrication, with a greater area density promoting full film lubrication whereas the number of pillars from the textures in the contact affected friction in the boundary and mixed regimes.

- **Particles that were able to fit inside the pillar textures reduced friction.**

The textured discs were used to investigate particulate systems as it is common for food products to contain particles. Model hard, spherical particles showed lower friction coefficients in the EHL regime so long as particles were smaller than the textures. Particles that were too large for the cavities increased friction. Soft, deformable particulate gels, commonly used in food products, demonstrated different behaviour to the model particulate systems investigated where they showed lower friction in the mixed lubrication regime, which is suggested to be most relevant to oral processing. These results provide an insight into how particulate systems lubricate and interact with the surface in soft tribological contacts; which has relevance to oral processing applications as the tongue is not smooth like typical testing surfaces used in oral tribology.

6.1.4. Model food systems in tribology

Shear thinning solutions including xanthan, guar gum, chitosan and Carbopol suspensions were examined and shown to be comparable to existing studies in literature. Chitosan was found to be highly lubricating independent of surfaces examined. Particulate suspensions, including model, hard spherical particulate suspensions and agar fluid gels were examined. Results show particle suspensions are entrained between the contacting surfaces and influence friction, even at low speeds when the gap between contacting surfaces is expected to be small. The hard, spherical particles reduced the friction coefficient with the textured surfaces in the EHL regime, so long as they were able to ‘fit’ inside cavities. Agar fluid gels were shown to produce a micro-EHL regime, observed in existing studies. It is proposed for the fluid gel systems, particles were able to reduce friction when the surfaces are in contact in the boundary and mixed regimes for textured surfaces. Whereas for the smooth surface, particles were excluded from the contact until sufficient hydrodynamic pressure was achieved at higher speeds. Solutions containing astringent compounds were examined in order to probe their friction response. Water was highly lubricating across the regimes, whereas the astringent solutions showed an increase in boundary friction compared to water and an extended mixed regime, suggesting the astringent solutions are interacting with the surfaces to increase friction.

6.1.5. Overall conclusions

Overall, this thesis presents a range of alternative techniques for tribological testing with oral processing applications with focus on examining model food systems. Both surface textures and hydrophilic surfaces were developed and examined tribologically. It was found these affected friction measurements and further research is needed in order to elucidate the exact mechanisms behind lubrication. Existing test methods and conditions are not standardised or representative, therefore a standard protocol for measurements should be determined and adopted. This thesis highlights the need for this whilst contributing towards this goal. Continued research is required to develop a method by which correlation between laboratory experiments and oral perception can be conclusively inferred without introducing variability and over complexity. It is recommended further studies are completed to compare friction data obtained to sensory data with the intent of finding relationships between quantitative measurements and texture perception.

6.2. Recommendations for future work

- **Examine a range of food and other model complex food systems.**

During this study, a range of model food-like systems were analysed; these have been analysed in literature and allowed for relatively simple experiments. In order to continue to develop tribological techniques and understanding of complex food products, future work would include analysing complete food systems, like yoghurt, milks and chocolate for example. This would determine if the techniques and methods are suitable and effective for the analysis of complex systems, and to develop understanding of both the test methods, test surfaces and the foods.

- **Perform sensory studies and link to tribological and rheological data**

Further research is needed examining how friction data obtained using these surfaces relates to sensory perception data. Ideally, these experiments should be run alongside and correlated to sensory studies, in order to relate experimental *in-vitro* results to sensory perception (Pradal & Stokes, 2016). This would help towards achieving accurate and representative techniques, and develop understanding of oral processing further. In the future, there is potential for these tests to be capable of predicting oral perception. For example, many existing studies correlate rheological and tribological experimental data to consumer panel test data (Cai, Li, & Chen, 2017; Chojnicka-Paszun, Doussinault, & De Jongh, 2014; Godoi, Bhandari, & Prakash, 2017; Laguna, Farrell, Bryant, Morina, & Sarkar, 2017; Morell, Chen, & Fiszman, 2017).

- **Examine surfaces with both surface texture and chemical modifications.**

A logical next step would be to combine both Chapter 4 and Chapter 5, by applying chemical surface modifications to textured PDMS surfaces. Further testing is required with both textured and chemically modified PDMS surfaces in order to understand how the surfaces affect friction. As both surfaces affected friction in this thesis, it would be highly interesting to examine the friction and lubrication effect of both.

- **Examine surfaces with saliva.**

Saliva is a key component of oral lubrication and should be incorporated in tribological measurements in order to closely resemble oral conditions. Some tribological studies already use saliva in friction experiments as it is extremely relevant to the oral processing of foods, however it is a biological sample so is complex and varies from person to person. It would be useful to examine both textured and chemically modified surfaces with saliva to probe how it affects the friction and how this compares to existing studies completed in this thesis and in literature. The development of salivary mimetics in friction studies may also lead to advanced molecular level knowledge interactions between food, oral surfaces and saliva.

- **Utilise advances made in imaging to further understand how particulate systems behave with tribological contacts.**

From Chapters 3 and 5, it is clear particulate systems affect friction properties. Visualization and mapping of particles in the contacts of both the rheometer and the MTM would help to further understand the mechanism in which both the hard and soft particulate systems lubricate and interact with the surfaces. There are a range of add-ons for rheometers and the MTM now, as well as new pieces of equipment that are for tribology and imaging available from PCS Instruments for example which allow a camera to visualize the contact during live experiments. Whilst this is relatively underused in tribological research, I am confident this will develop in the future and more researchers will use imaging techniques to understand friction and lubrication properties.

- **Understand interactions between chemically modified surfaces and test samples.**

It would be incredibly interesting to understand the role of in which modified PDMS surfaces interact with test samples, and if that can be linked to friction and lubrication. This could be achieved by using a combination of instruments such as atomic force microscopy, Quartz crystal microbalance, ellipsometry and tribology.

- **Identify and develop standard testing conditions for oral tribology.**

Ideally, a standard tribological test method would exist for oral tribology. Unfortunately this does not exist as of yet, as there are many factors involved when performing tribological tests such as instrument costs, experience of user, analysis and understanding of results, accessibility and usability. An ideal test method would be accessible in both industry and academia. It would allow fast and simple interpretation of results, allow analysis of a wide range of samples, and develop a database of known samples.

6.3.References

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