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Lubrication properties of model dairy beverages: Effect of the characteristics of protein dispersions and emulsions

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ABSTRACT

In this study we investigated the individual contribution of different ingredients to the lubrication properties of dairy-based model beverages containing whey protein (native or aggregated), micellar casein and emulsified oil in different combinations. In single-component systems, whey protein isolate (WPI) solutions showed the lowest friction coefficients of all protein samples. Whey protein aggregates (WPA, ~247 nm, irregular morphology) led to higher friction coefficients than micellar casein isolate (MCI) with comparable size (~207 nm, near spherical shape). When protein particles were combined, i.e. WPA and MCI, lubrication was not much affected. However, when WPI was added to either WPA or MCI, higher friction coefficients were observed compared to single-component systems. Emulsions (droplet size ~ 440 nm) provided better lubrication than the protein samples. Oil droplets stabilized by soy lecithin (SL) were more efficient at reducing friction than those stabilized by WPI. The friction coefficient of SE strongly increased in the presence of WPI. In comparison, lubrication of WE was less affected by the addition of WPI. These results show that different proteins affect the lubrication properties of emulsions stabilized with different emulsifiers in a different way. Our research also indicates that multicomponent systems are complex, and that control over the lubrication properties requires a better understanding of the contribution of individual components.

1. Introduction

Texture perception of beverages is an important factor contributing to consumer acceptance and palatability. It is of great interest for the food industry to understand the relationship between product composition and structure, rheological and tribological behavior, and sensory perception in order to optimize mouthfeel and after-feel attributes.

Food scientists have been exploring the link between sensorial attributes and food structure already for decades. A number of studies have unveiled correlations between physical properties of food and various sensory attributes. For instance, sensorial thickness of fluid foods have been correlated to the rheological parameter viscosity (Cutler, Morris, & Taylor, 1983; Richardson, Morris, Ross-Murphy, Taylor, & Dea, 1989; Shama & Sherman, 1973). Other sensory attributes, such as creaminess and smoothness, appear to be more complex and cannot be related to the rheological properties of the food only (Sonne, Busch-Stockfisch, Weiss, & Hinrichs, 2014). These complex and multidimensional sensory attributes are found to be more related to lubrication properties, and tribology has consequently gained interest as a tool to study food texture (Chojnicka, De Jong, De Kruif, & Visschers, 2008; Fan, Shewan, Smyth, Yakubov, & Stokes, 2021; Kokini, Kadane, & Cussler, 1977; Krop, Hetherington, Holmes, Miquel, & Sarkar, 2019; Malone, Appelqvist, & Norton, 2003; Rudge et al., 2021; Sarkar & Krop, 2019; Sonne et al., 2014; Stribiţcaia, Krop, Lewin, Holmes, & Sarkar, 2020; Upadhyay & Chen, 2019).

The friction coefficient is the main parameter obtained from tribological measurements and is normally presented as a function of a Hershey number (Chen & Stokes, 2012; De Vicente, Stokes, & Spikes, 2006; Sarkar, Andablo-Reyes, Bryant, Dowson, & Neville, 2019; Sarkar, Soltanahmadi, Chen, & Stokes, 2021; Selway & Stokes, 2013). In such a curve, three regimes can usually be identified: the boundary, the mixed and the hydrodynamic regime, which are used to describe the dynamic relationship between lubricant and interacting surfaces. During the first phase of oral processing, perception is more dominated by bulk properties, which is more related to the hydrodynamic regime (Dresselhuis et al., 2007; Nguyen, Bhandari, & Prakash, 2016; Zinoviadou, Janssen,

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Table 1

Composition of the studied binary systems. a) Protein solutions/ dispersions combined at different ratios; b) Protein solutions/ dispersions and emulsions combined at different ratios; c) Emulsions with a fixed oil concentration combined with protein solutions/ dispersions.

		MCI (%)				WPA (%)				WE (%)					SE (%)				
		1	2	3	4	1	2	3	4	1	2	3	4	5	1	2	3	4	5
WPI (%)	4	a				a				b				c	b				c
	3		a				a				b			c		b			c
	2			a				a				b		c			b		c
	1				a				a				b	c				b	c
WPA (%)	4	a								b				c	b				c
	3		a								b			c		b			c
	2			a								b		c			b		c
	1				a								b	c				b	c
MCI (%)	4									b				c	b				c
	3										b			c		b			c
	2											b		c			b		c
	1												b	c				b	c

& De Jongh, 2008). After oral manipulation, surface properties become more relevant as food gets trapped between the tongue and the palate, and thus, boundary and mixed lubrication properties become more relevant (Chen, 2014; Sarkar & Krop, 2019; Sarkar et al., 2021; Stokes, Boehm, & Baier, 2013).

The lubrication properties of food depend on their specific composition, structure and on their physical state, e.g. whether they are semi-solid or liquid, whether they are solutions, emulsions or colloidal dispersions (Pradal & Stokes, 2016). Many common liquid or semi-solid foods have been investigated to explore the link between composition and lubrication properties. For instance, milk systems with a higher fat content showed better lubrication properties (Chojnicka-Paszun, de Jongh, & de Kruif, 2012). However, for model emulsion systems, no effect of fat content on lubrication was found once the fat content was increased beyond a certain concentration (1%) (Dresselhuis et al., 2007). Next to the volume fraction of oil droplets, also the mechanical stability of oil droplets influence lubrication. In the case o/w emulsions were more prone to coalescence, friction coefficients were found to be lower than that of stable emulsions (Dresselhuis, de Hoog, Stuart, Vingerhoeds, & van Aken, 2008). This was attributed to shear-induced coalescence and the formation of an oil film. In the case of protein or protein particles, different characteristics have been shown to influence lubrication. Particles reduce friction due to particle lubrication, which is more commonly known as the ball-bearing mechanism. The rolling ability of particles depends on the shape, and therefore the morphology is considered an important factor in determining the lubrication properties. An effect of shape was also seen in a combined system of whey protein and casein, as the formation of protein clusters due to attractive interactions gave higher friction coefficients (Laiho, Williams, Poelman, Appelqvist, & Logan, 2017). These results suggest that different dispersed droplets or particles can lead to various changes in lubrication properties.

Most studies published up to now mainly focused on the lubrication properties of real foods or model systems containing a single component. Little information is known how individual ingredients influence the lubrication properties of multi-component systems. For instance, the effect of different proteins on the lubrication behavior of emulsions stabilized with different emulsifiers remains unclear. The aim of our study was to investigate the lubrication properties of multi-component liquid dairy systems consisting of different combinations of ingredients: whey proteins, whey protein aggregates, casein micelles and oil droplets stabilized with either protein or soy lecithin, to better understand the influence of these individual ingredients on the frictional behavior of more complex systems.

2. Materials and methods

2.1. *Materials*

Whey protein isolate powder (WPI, 90.5% w/w Protein Dry Basis, N × 6.38) was purchased from Davisco Foods International Inc. (Le Sueur, MN, USA). Micellar Casein Isolate (MCI, 86.5% w/w Protein Dry Basis, N × 6.38) was purchased from Royal Friesland Campina (Amersfoort, The Netherlands). Medium Chain Triglycerides (MCT) oil was purchased from CREMER OLEO GmbH & Co. KG (Hamburg, Germany). Soy lecithin (SL, Topcithin, HLB = 3) was purchased from Cargill (Wayzata, MN, USA). All materials were used without further purification. All samples were prepared with demineralized water (Milli-Q®) and concentration is expressed as the percentage content of individual ingredients.

2.2. *Sample preparation*

2.2.1. *Preparation of WPI solutions*

A WPI stock solution with an ingredient concentration of 10% (w/w) was prepared by dissolving WPI powder in Milli-Q® water and stirring overnight at 4 °C. Afterwards, the solution was homogenized 3 times at 200 bar with a homogenizer (Delta Instrument, Lab homogenizer, The Netherlands) to break possible agglomerates. Subsequently, the solution was filtered through a membrane filter (cellulose acetate membrane filter, Whatman, GmbH Germany) with a pore size of 1.2 μm to remove any remaining clusters. At the end, the solution was diluted with Milli-Q® water to obtain the desired final solutions that were stirred at room temperature (20 ± 0.1 °C) for 2 h.

2.2.2. *Preparation of WPI aggregate (WPA) dispersions*

The preparation of whey protein isolate aggregates (WPA) was based on a method described by de Vries and co-workers (de Vries, Wesseling, van der Linden, & Scholten, 2017). In short, a 7.5% WPI solution at pH 5.7 was heated at 85 °C for 15 min. The formed weak protein gel was then broken down and dispersed with a rotor stator homogenizer (Ultra turrax T25, IKA Werke, Germany) at 13000 rpm for 1 min to obtain ~ 200 nm aggregates. The aggregates were collected as the pellet by centrifugation at 4500 rpm for 20 min and re-dispersed and centrifuged twice with Milli-Q® water. To obtain a homogeneous dispersion, the pellet was then re-dispersed at 13000 rpm and homogenized (Delta Instrument, Lab homogenizer, The Netherlands) at 200 bar. The protein content of the dispersion was measured using Dumas (Dumas Flash EA 1112 Series, N Analyser, Thermo Scientific, N × 6.38). At the end, the dispersion was diluted with Milli-Q® water to achieve the final desired ingredient concentration, assuming that the samples contain only protein after the washing steps. The obtained dispersions were stirred at room temperature (20 ± 0.1 °C) for 2 h.

2.2.3. Preparation of casein micelle (MCI) dispersions

MCI stock dispersions with a concentration of 10% (w/w) were prepared by dissolving MCI powder in water and stirring overnight at 4 °C. Subsequently, the dispersions were stirred at room temperature (20 ± 0.1 °C) for 2 h and then homogenized for 3 times at 200 bars with a homogenizer (Delta Instrument, Lab homogenizer, The Netherlands) to disintegrate possible agglomerates of casein micelles.

2.2.4. Preparation of o/w emulsions

Oil-in-water stock emulsions (10% MCT oil, w/w) were prepared by using two different emulsifiers: WPI or SL. To minimize the amount of emulsifier and obtain stable emulsions, a 0.2% WPI and 0.6% SL were selected to stabilize 10% oil. A 0.2% (w/w) WPI solution was made by dissolving WPI powder in Milli-Q® water and stirring the solution at room temperature (20 ± 0.1 °C) for 2 h. Similarly, a 0.6% (w/w) SL dispersion was made by dispersing SL paste in Milli-Q® water. The oil-in-water emulsions were prepared by mixing MCT oil with the aqueous solutions. MCT oil was slowly added into the aqueous phase, and the mixture was pre-homogenized with a rotor stator homogenizer (Ultra turrax T25, IKA Werke, Germany) at 13000 rpm for 3 min. Afterwards, the pre-emulsion was homogenized with a homogenizer (Delta Instrument, Lab homogenizer, The Netherlands) at 200 bar for 10 cycles to produce the final emulsion.

2.2.5. Preparation of mixed systems

Mixed systems consisting of two components were prepared by mixing two of the single systems i.e. WPI solution, WPA dispersion, MCI dispersion, WPI-stabilized emulsion (WE), or SL-stabilized emulsion (SE) with a mini lab vortexer (VWR® Lab Dancer Mini Vortexer, VWR International Ltd, Waltham, USA) for 1 min and then stirred for 30 min to ensure good mixing of the systems. Compositions studied are summarized in Table 1: a) to obtain binary protein systems, two of the protein dispersions (WPI, WPA or MCI) with a total concentration of 5% were mixed at different ratios (1:4, 2:3, 3:2, 4:1), and is denoted as series a; and b) to obtain protein-emulsion binary systems, one of the emulsions (WE or SE) was mixed at different ratios (1:4, 2:3, 3:2, 4:1) with one of the protein dispersions (WPI, WPA or MCI) with a total concentration of 5%, denoted as series b. The total ingredient concentration of all these mixtures was 5%. A different series (denoted by c) was prepared using a fixed concentration (5%) of oil droplets and a varying concentration of proteins of 1%, 2%, 3%, and 4%. All percentages are weight-based.

2.3. Sample characterization

2.3.1. Particle size

The particle size distribution of the studied emulsion droplets was measured by static light scattering (MasterSizer2000, Malvern Instruments Ltd., Worcestershire, Malvern, UK). The refractive index of water was set to 1.33 and the particle size was reported as the volume mean (D[4,3]) and surface mean (D[3,2]). All the measurements were performed in triplicate and particle size is presented as mean ± standard deviation (SD).

The particle size of protein aggregates was measured by dynamic light scattering using Nano ZS (Zetasizer Ultra, Malvern Instruments Ltd., Worcestershire, Malvern, UK). The refractive index (RI) of samples was set at 1.0 for protein. All the measurements were performed in triplicate and particle size is presented as mean ± standard deviation (SD).

2.3.2. Zeta potential

The zeta potential of the samples was determined by dynamic light scattering using Nano ZS (Zetasizer Ultra, Malvern Instruments Ltd., Worcestershire, Malvern, UK). The refractive index (RI) of samples was set at 1.45 for MCT oil and 1.0 for protein. All the measurements were performed in triplicate and zeta potential is presented as mean ± SD of triplicate experiments.

2.3.3. Cryogenic-scanning electron microscopy (Cryo-SEM)

Cryo-SEM (FEI Magellan 400, USA) was used to visualize the morphology of WPA. The sample was filtered with paper and quickly cooled in liquid nitrogen. The cooled sample was then transferred to the preparation chamber by a vacuum transfer system for sublimation etching. After gilding, the sample was observed under scanning electron microscope.

2.3.4. Confocal laser scanning microscope (CLSM)

The structure of the different emulsions was assessed with a confocal laser scanning microscope (Nikon C2 CLSM, Tokyo, Japan). The samples were stained with a 0.05 w/w% BODIPY 505/515 solution (oil dye). Aliquots (20 μl) of each staining solution were added into a 200 μl sample and well mixed, and then stained for 10 min. Afterward, a volume of 60 μl was taken and added in hermetically sealed flat cuvettes that were glued on a microscopy slide in advance and sealed with coverslips (24 × 24 mm, # 1.5 mm, Thermo Fisher Scientific, MA, USA). The samples were analyzed using 60 × magnification (with immersion oil), and the excitation was performed using the laser beams at 488 nm.

2.3.5. Hydrophobicity determination

The hydrophobicity of protein dispersions (WPI, WPA, and MCI) was measured based on the method of Kato et al. (Kato & Nakai, 1980) with modifications. A series of protein concentrations (0.05, 0.1, 0.2, 0.5, 1, and 2 mg/mL) and a stock solution of the fluorescent marker 1-anilino-naphthalene-8-sulfonic acid (ANS, 8.0 mmol/L) were prepared. Each sample solution (5 ml) was mixed with 40 μl of ANS solution and incubated for 40 min. The fluorescence intensity (FI) was measured by a F-4600 fluorescence spectrophotometer (Hitachi, Japan) at wavelengths of 390 nm (excitation) and 470 nm (emission). The FI was plotted as a function of protein concentration and the slope was calculated by a linear regression analysis and used as the index of surface hydrophobicity (H_0).

2.3.6. Viscosity measurement

The viscosity of the samples was measured using a stress-controlled rheometer (MCR 302, Anton Paar, Austria) with a double gap geometry (probe DG.26.7/Ti; cup DG 26.7/T200/Ti). A sample of 3.8 ml was pipetted into the cup and equilibrated at 20 °C for 5 min before the measurement started. The shear rate was increased in 5 min with logarithmic steps from 0.1 s^{-1} to 1000 s^{-1}, and then decreased from 1000 s^{-1} to 0.1 s^{-1} in 5 min. All the measurements were performed in triplicate and the average value of the viscosity was determined.

2.3.7. Tribology measurement

Tribological measurements were performed with a stress-controlled rheometer (MCR 302, Anton Paar, Austria) equipped with a tribology accessory (T-PTD 200, BC 12.7, Anton Paar, Austria). The set-up was based on a glass ball-on-three-pins principle, consisting of a spherical glass ball (d = 12.7 mm) and three PDMS pins (d = 6 mm, roughness 0.2 μm ± 0.03). The temperature was kept at 20 °C and a normal force, F_N, of 1 N was applied. Samples with a volume of 0.6 ml were poured in the tribology cup, and the friction coefficient was measured as a function of sliding speed. One measurement consisted of 2 cycles, i.e. 4 runs in total with increasing and decreasing sliding speed, v_s, between 0.01 and 470 mm/s, in a period of 5 min per run. The data of the first run were disregarded as the results often deviated from those obtained in the other runs. The data of the third run were selected for further analysis. Each measurement was performed in triplicate with new samples. The averaged value of the friction coefficient (μ) was determined as a function of sliding speed. A power-law model was used to describe the decrease in

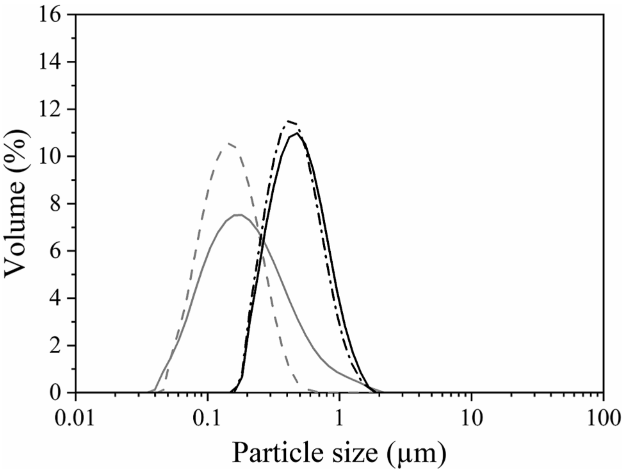

Fig. 1. Particle size distribution of dispersions with a concentration of colloidal particles of 5%: WPA dispersion (solid grey line), MCI dispersion (dashed grey line), WE (dotted dashed black line) and SE (solid black line).

Table 2
Physical parameters of samples with a concentration of colloidal particles of 5%.

Samples	D[4,3] (nm)	D[3,2] (nm)	Zeta-potential (mV)	Hydrophobicity (H_0)
WPI	–	–	−46.5 ± 1.3	9,657
WPA	247 ± 11	139 ± 3	−40.3 ± 2.7	66,844
MCI	207 ± 20	115 ± 7	−25.3 ± 0.6	10,241
WE	449 ± 39	360 ± 25	−37.3 ± 1.6	–
SE	434 ± 17	351 ± 17	−58.0 ± 0.9	–

the friction coefficient (slope of curve) in the mixed regime as

$$\mu \sim \text{speed}^{n} \tag{1}$$

2.3.8. *Statistical analysis*

Data were analyzed using SPSS (IBM SPSS statistics 25) to provide the average value and standard deviation (SD) of the triplicates.

3. Results and discussion

3.1. *Characterization of particle size, charge density and hydrophobicity*

The particle size distribution of protein particles and emulsified oil droplets was measured as it is an important factor influencing lubrication (Fig. 1, Table 2) (Giasson, Israelachvili, & Yoshizawa, 1997; Krzeminski, Großhable, & Hinrichs, 2011; Sonne et al., 2014). No large agglomerates, which could potentially affect the friction measurements, were observed in the different samples. The volume average diameter (D [4,3]) of the WPA was 247 ± 11 nm and that of the MCI 207 ± 20 nm. The oil droplets were larger than both WPA and MCI, with values of 449 ± 39 nm and 434 ± 17 nm for the droplets stabilized by SL and WPI, respectively. Thus, the size of the oil droplets stabilized with different emulsifiers was comparable.

The pH of all systems was around 7. At this pH, all samples displayed a negative zeta potential. Both WE and SE had a zeta potential value below −30 mV, which is often suggested to be sufficient to provide enough electrostatic repulsion to ensure emulsion stability (Mantovani, Cavallieri, Netto, & Cunha, 2013). For the protein particles, we also determined the hydrophobicity of the particles. Based on the results, WPA is most hydrophobic, whereas WPI is least hydrophobic. This was most likely due to more exposed hydrophobic regions as a result of heat-induced unfolding for the WPA (Moro, Gatti, & Delorenzi, 2001).

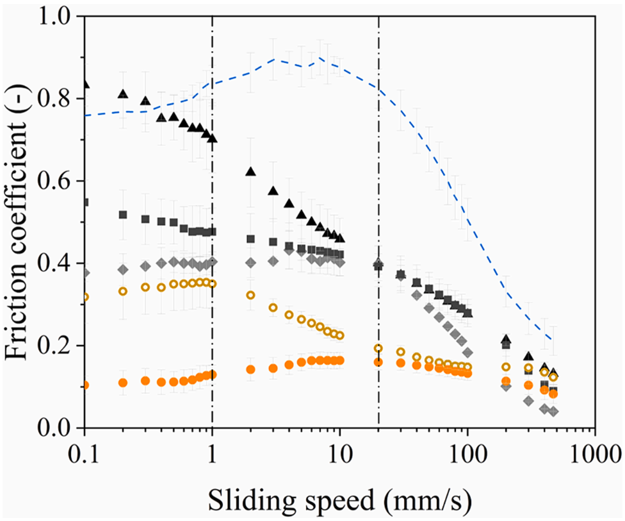

Fig. 2. Friction coefficient as a function of sliding speed for single-component dispersions and emulsions with a concentration of colloidal particles of 5%: WPI (grey diamond), WPA (black triangle), MCI (dark grey square), WE (yellow open cycle) and SE (orange circle). The friction coefficient of Milli-Q® water is shown as a reference (blue dashed line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. *Viscosity*

The viscosity of the different systems with a concentration of 5% was also measured, as this is an important parameter influencing friction behavior (Selway, Chan, & Stokes, 2017). The viscosities of the studied systems were within a range of 1–3 mPa·s and remained constant along a shear rate range of 1–500 s^{-1} (data shown in Figure A.1, supplementary information). Such narrow range in the viscosity is not expected to lead to differences in lubrication behavior. We expected differences in lubrication behavior to be due to the characteristics of the particles.

3.3. *Tribological behavior*

3.3.1. *Lubrication behavior of dispersions and emulsions with one component*

We first discuss the lubrication properties of single systems. The friction coefficients as a function of sliding speed measured for dispersions and emulsions with a concentration of 5% are shown in Fig. 2. Throughout the whole speed range the friction coefficient of SE was the lowest, and that of the WPA dispersion the highest. The shape of the friction curves for the different samples was quite different, indicating that the mechanisms responsible for the lubrication behavior were not the same. For SE and WPA, no evident boundary and mixed regime were observed. In other curves, a clear transition from a boundary to a mixed friction regime could be observed at a sliding speed of 1 mm/s (WE) or 20 mm/s (WPI and MCI), as indicated with a dotted dashed line in Fig. 2.

Among all protein samples, WPI molecules (<10 nm) showed better lubrication properties than the large protein particles MCI and WPA (~200 nm) at the same protein concentration. WPI had better boundary lubrication (<20 mm/s) and its friction coefficient decreased also faster ($n = -0.78$) in the mixed regime. With increasing sliding speed, WPI was able to lubricate the surfaces more efficiently. This was most likely due to the fact that WPI can adsorb on the PDMS surface to form a protein film, providing film formation, (Adamczyk, Nattich-Rak, Dąbkowska, & Kujda-Kruk, 2018; Vogler, 2012; Zembyla et al., 2021). In comparison, WPA, exhibited the highest initial friction coefficient (~0.83) at a low sliding speed of 0.1 mm/s that progressively decreased with increasing sliding speed ($n = -0.21$). If WPA would also provide film formation, we would expect better lubrication due to the higher hydrophobicity of

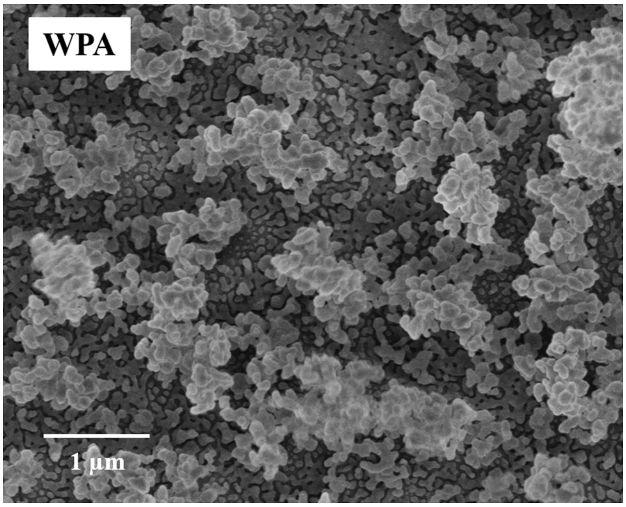

Fig. 3. Cryo-SEM image of WPA. The scale bar is 1 μm.

WPA compared to that of WPI (Table 2). As we observed the opposite result, it is more likely that WPA provides particle lubrication, also known as a ball-bearing mechanism. This mechanism is affected by the shape of the particles. As can be seen in Fig. 3, WPA has an irregular and random shape. This has also been reported by many others (de Vries et al., 2017; Nicolai, Britten, & Schmitt, 2011; Ryan & Foegeding, 2015; Sağlam, Venema, de Vries, van Aelst, & van der Linden, 2012; Sağlam, Venema, de Vries, & van der Linden, 2013). Due to this irregular shape, the moving or rolling efficiency of WPA is limited, and thus high friction coefficients were obtained. The low efficiency of WPA in decreasing friction has also been seen in another study (Chojnicka et al., 2008).

Compared to WPA, MCI showed a long boundary regime (<20 mm/s) with a much lower initial friction coefficient of 0.55, even though the particle size of these two ingredients was comparable (Table 2). The mixed regime of MCI started at around 20 mm/s, with a faster drop of the friction coefficient ($n = -0.48$). The superior lubrication properties of MCI are most likely related to the morphology of the particles. As discussed by Bouchoux and co-workers, casein micelles can be regarded as approximately spherical, and a relatively smooth surface was observed in microscopic images (Bouchoux et al., 2009; Dalgleish, Spagnuolo, & Douglas Goff, 2004).

Taking into account the ball-bearing mechanism, particles with a spherical shape and smooth surface, like MCI, will be able to roll better, providing less friction. This thus explains why MCI provided better lubrication. Therefore, the morphology and size of the proteins and protein particles had a large effect on the frictional behavior of single systems. These effects of particle properties on lubrication were larger in the boundary regime than in the mixed regime, where contact between the surfaces and the particles are more important. To give a better visualization of the described phenomena, a schematic representation is provided (Fig. 4a).

Compared to protein systems, the emulsions investigated in this study, i.e. SE and WE, showed better lubricating ability. Differences in lubrication properties between the two types of emulsions were observed: SE was more efficient in providing lubrication than WE. As the size of the oil droplets was similar, we deduced that the stability of the emulsified oil droplets and the hydrophobicity of the emulsifiers could explain these differences in lubrication (Cambiella et al., 2006; Wen & Huang, 2017). The soy lecithin (SL, HLB = 3) chosen for this research was more hydrophobic than whey protein, and the SL-stabilized oil droplets therefore had a higher affinity for the hydrophobic PDMS surface. In addition, small-molecule emulsifiers, such as lecithin, are expected to result in emulsion droplets more sensitive to coalescence than large-molecule emulsifiers like whey proteins (McClements & Gumus, 2016; McClements & Jafari, 2018; Pugnaloni, Dickinson, Ettelaie,

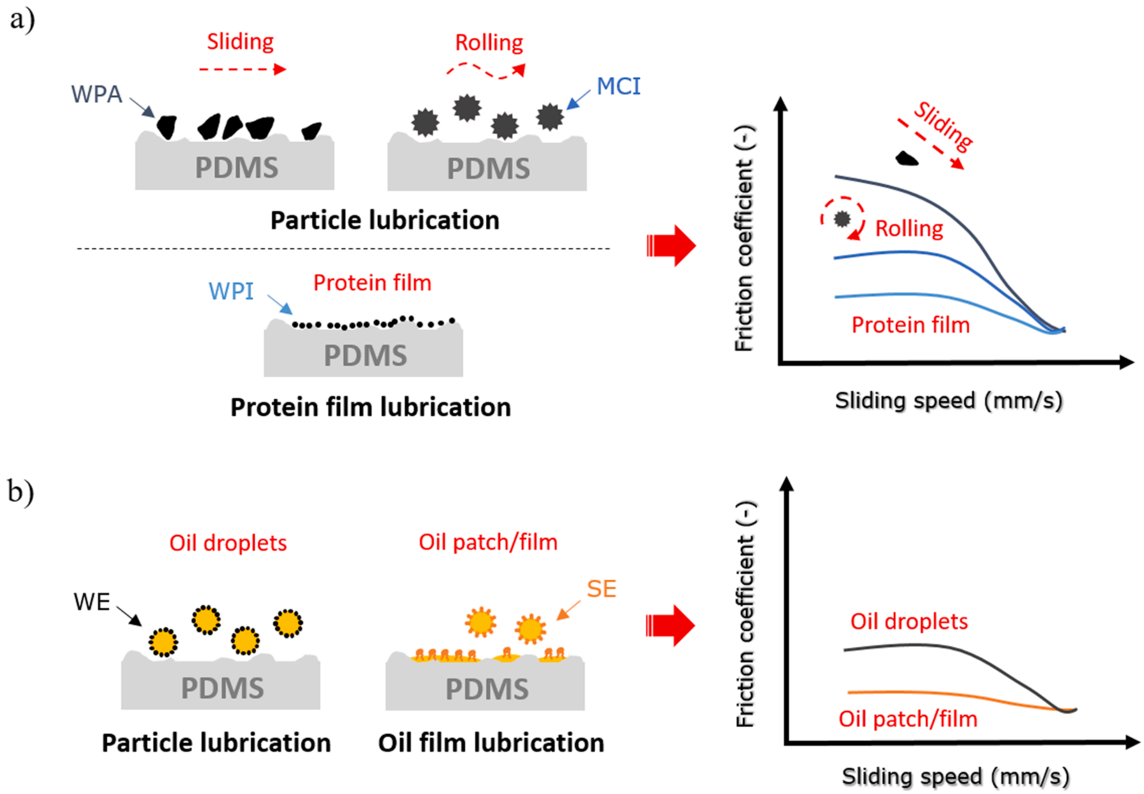

Fig. 4. Schematic representation of the particles used in our study within the tribometer measuring cell (glass ball on PDMS) and their effect on friction with expected mechanisms. a) Protein particles; b) Oil droplets stabilized with WPI or SL.

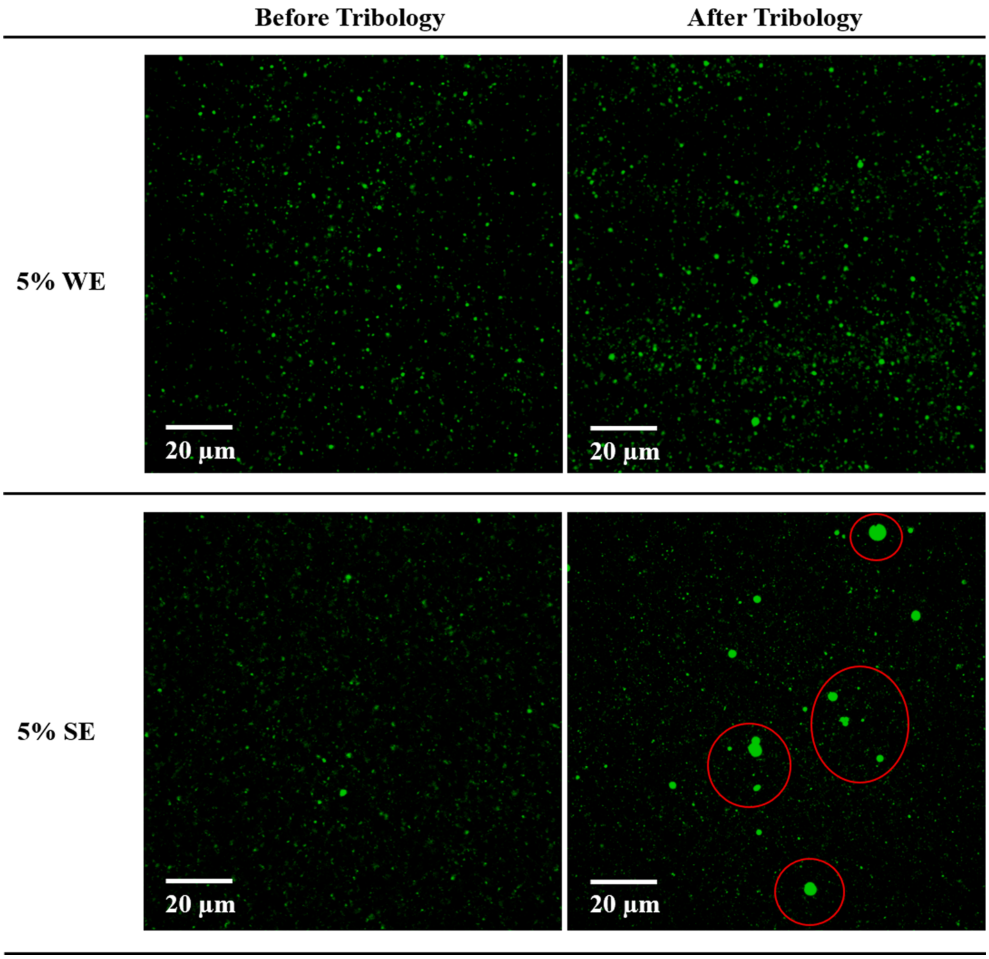

Fig. 5. CLSM images of WE and SE with a concentration of 5% before and after tribological measurements. The scale bar is 20 μm.

Mackie, & Wilde, 2004). The high affinity of the oil droplets for the PDMS surface and the higher degree of coalescence of the oil droplets would then lead to the formation of larger oil patches or an oil film on the PDMS surface, according to the so-called plate-out theory (Liu, Tian, Stieger, Van der Linden, & Van de Velde, 2016; Schmid & Wilson, 1996). In comparison, globular whey proteins are known to form a strong cross-linked layer at the o/w interface (McClements & Jafari, 2018; Pugnaloni et al., 2004). This strong protein layer at the o/w interface can provide a higher resistance against coalescence, limiting the formation of oil patches. WE, therefore, most likely induced lubrication through particle lubrication, i.e. a ball-bear mechanism. Our results are in line with those reported by Fuhrmann et al. (Fuhrmann, Sala, Stieger, & Scholten, 2019), who also observed that oil droplets stabilized by a more hydrophobic emulsifier (DATEM) lead to better lubrication than oil droplets stabilized by WPI.

To verify these effects, the samples were collected after the tribological measurement and the structure was visualized with CLSM. As shown in Fig. 5, large oil droplets were observed for SE (indicated with red circles), and this was not the case for WE. This confirms that indeed the oil droplets in SE coalesced and coalescence of oil droplets could promote oil patch or film formation on PDMS. In comparison, WE provided stable emulsion droplets, and thus contributed to lubrication via a ball bearing mechanism. These mechanisms are visually presented in Fig. 4b.

According to these results, film lubrication decreased friction coefficients more than particle lubrication in both boundary and mixed regime. Due to the higher hydrophobicity of the oil, oil film formation decreased friction coefficients more than protein film formation. Regarding particle lubrication, oil droplets (WE) generated the lowest friction in both boundary and mixed regime when compared to protein particles (WPA and MCI). The frictional curve of WE showed a transition from boundary to mixed regime at the sliding speed of 1 mm/s, which was earlier than that of MCI (20 mm/s), suggesting that spherical oil droplets enter the gap and separate the two contact surface more easily. Although large differences between components were observed in the boundary regime, these differences were limited in the mixed regime. In this regime, differences in friction coefficients were more related to the components (proteins or oil) than to the lubrication mechanism. Since both boundary regime and mixed regime are suggested to be linked to oral processing (Chen, 2014; Sarkar & Krop, 2019; Sarkar et al., 2021; Stokes, Boehm, & Baier, 2013), it can be expected that oil droplets will be more effective than protein particles in improving oral lubrication in such liquid systems, independently of the mechanism of lubrication.

3.3.2. Effect of concentration on tribological behavior

As discussed above, the lubrication properties of dairy protein systems are based on different mechanisms and different properties of the colloidal particles they contain. As these mechanisms may also be concentration-dependent, we investigated the influence of the concentration (1.25, 2.5, 3.75 and 5%) of the individual components on lubrication. For protein dispersions, the friction coefficient decreased with an increase in concentration (data not shown), suggesting that friction is related to the number of particles present in the system. A positive effect of particle number on lubrication has also been previously found for hydrogel particles (Rudge, van de Sande, Dijksman, & Scholten, 2020; Rudge, Scholten, & Dijksman, 2020). For emulsified systems, the progressive reduction of friction with increasing concentration was depending on the emulsifier type. In SE, a critical concentration was

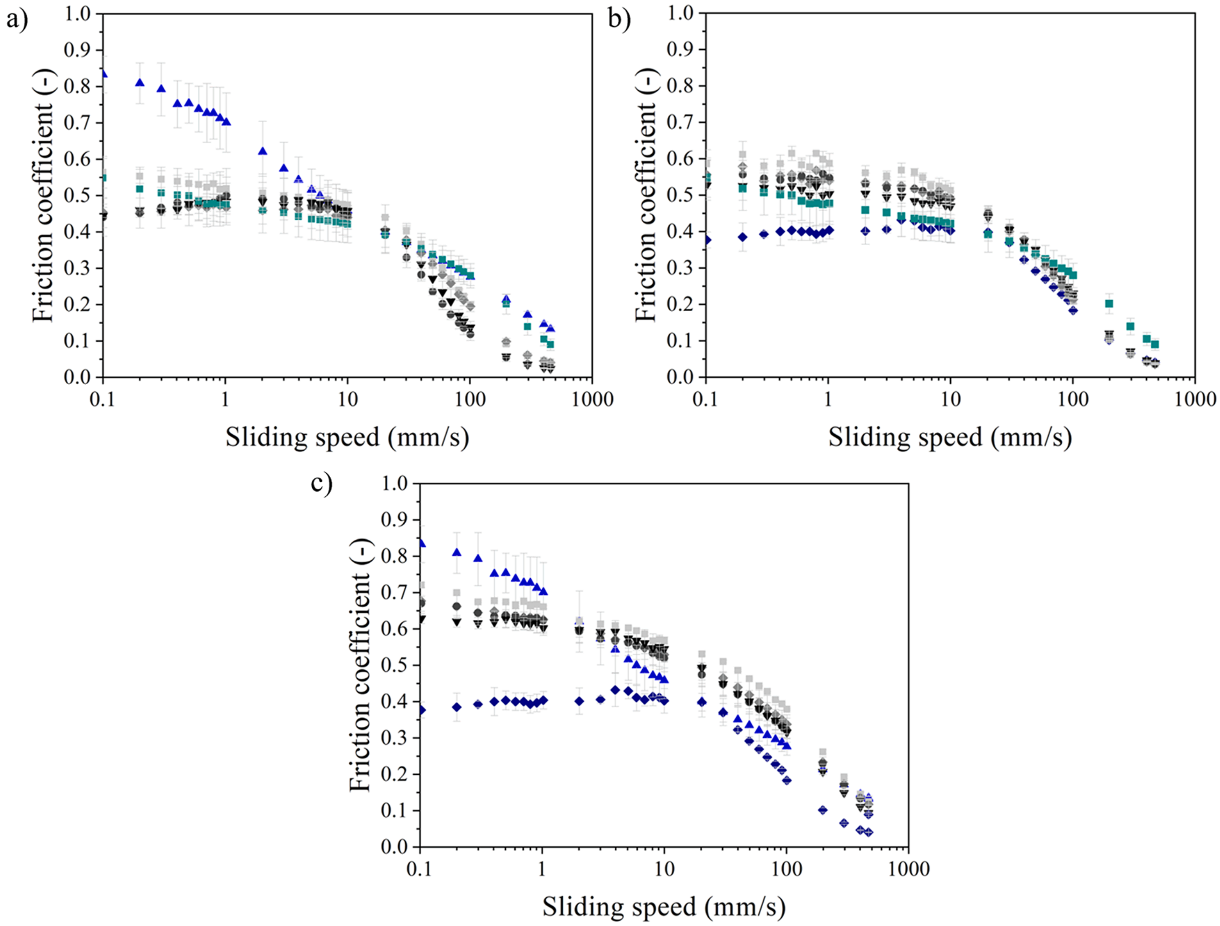

Fig. 6. Friction coefficient as a function of sliding speed for mixtures of a) WPA (blue triangle) and MCI (dark cyan square); b) WPI (navy diamond) and MCI (dark cyan square); c) WPA (blue triangle) and WPI (navy diamond): at ratios of 4:1 (light grey square), 3:2 (grey diamond), 2:3 (dark grey circle), and 1:4 (black triangle). The total concentration of all samples was 5%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

observed (2.5%) above which the friction coefficient became almost independent of concentration. This supports the hypothesis that for this sample lubrication was based on oil film formation due to a plate-out mechanism. Most likely, at the mentioned concentration the surfaces were already covered with oil patches. Additional oil droplets did not contribute to lubrication anymore. In contrast, WE showed a concentration dependence up to the highest measured concentration, indicating that the ball-bearing mechanism is indeed more relevant to explain friction.

The lubrication behavior of single systems was thus mainly determined by two mechanisms: film formation (WPI and SE) or ball-bearing (WPA, MCI and WE). Ingredients able to form a film on the surfaces provide good lubrication, whereas particle lubrication is less efficient, especially when particles are not round and smooth.

3.3.3. Mixed systems

3.3.3.1. Systems with multiple protein components. To investigate the role of the different ingredients in multi-component systems, the tribological behavior of different mixed systems was characterized. Binary systems were obtained by mixing different protein dispersions (WPI, WPA, MCI) at different ratios (1:4, 2:3, 3:2, 4:1) to achieve a total concentration of 5%.

When the two types of protein particles WPA and MCI were mixed, the friction coefficients of the mixtures were much lower than that of 5% WPA, and the shape of the friction curves resembled more that of 5% MCI (Fig. 6a). WPA itself did not show a clear transition from the boundary to the mixed regime (Fig. 2), but after mixing with MCI, a transition was observed at 20 mm/s, consistently with the behavior of MCI. In the mixed regime, the friction coefficients of the mixtures dropped faster with increased speed. These results indicate that a partial replacement of WPA with MCI (with particles size similar to WPA) can reduce the friction coefficient of the system. The MCI, which was able to reduce friction more efficiently, seemed to determine the lubrication behavior of the binary system.

When MCI was combined with WPI, the friction coefficients of the mixtures were higher than those of the two separate systems, mainly in the boundary regime (<20 mm/s), as shown in Fig. 6b. For these mixtures, dilution effects could not explain the high friction coefficient of the binary systems, indicating an antagonistic effect between WPI and MCI. The fact that the presence of WPI molecules negatively affected the lubrication of the MCI system was unexpected, since WPI showed better lubrication properties in the single system. Also no aggregation between MCI and WPI was observed from particle size measurements (data not shown), as both components were negatively charged. As the gap size between the surfaces is mostly determined by the large MCI particles, we expected that the MCI with good rolling ability would determine the lubrication behavior. However, we observed that WPI in the mixtures induced high friction and seemed to dominate the lubrication behavior. This may be related to the film formation of the protein molecules on PDMS, changing the hydrophobicity of the surface (Adamczyk et al., 2018; Vogler, 2012; Zembyla et al., 2021). Such protein film formation could have influenced the affinity for the large MCI particles for PDMS, which led to a decrease of the lubricating capacity of the MCI particles.

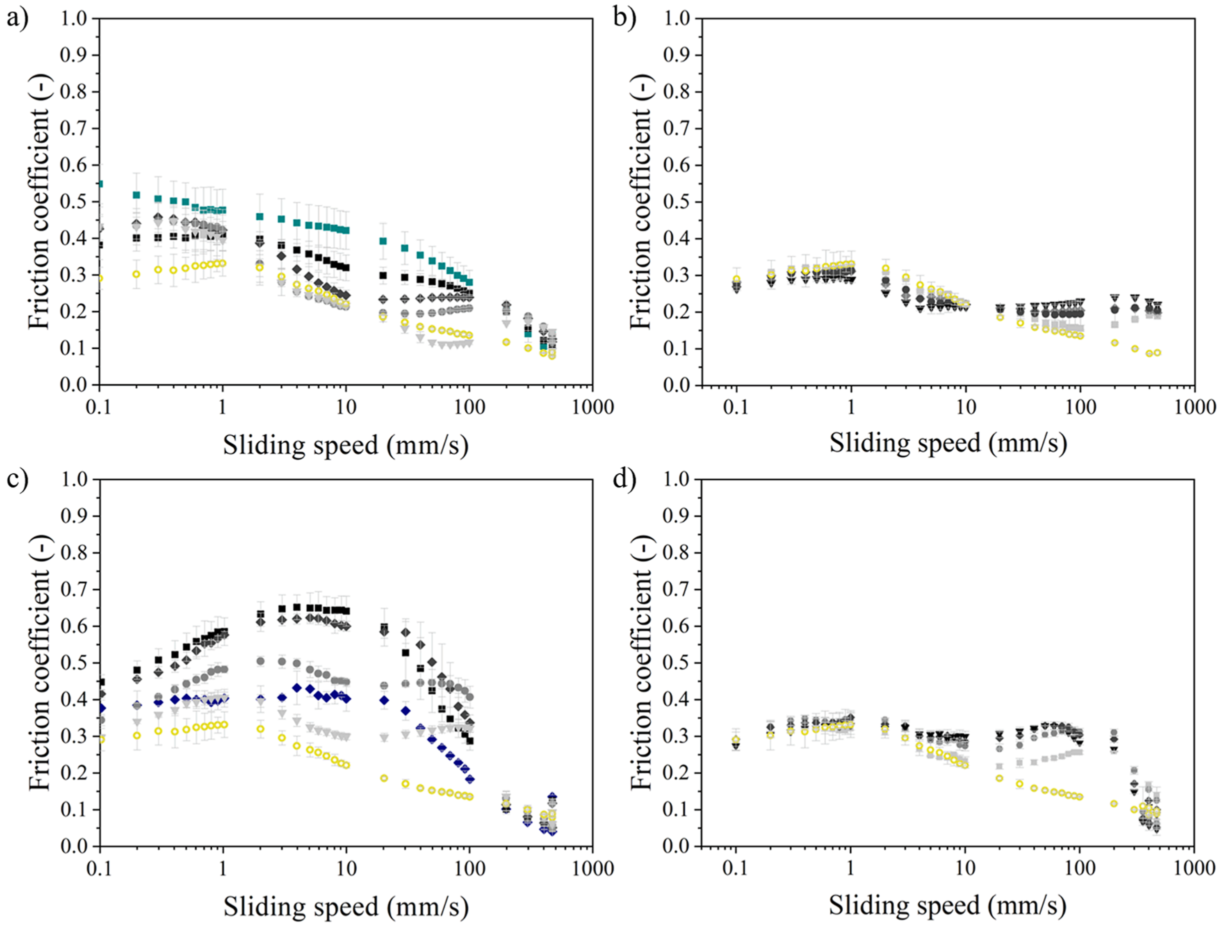

Fig. 7. Friction coefficient as a function of sliding speed for mixtures of a) MCI (dark cyan square) and WE (yellow open circle) at ratios of 1:4 (light grey triangle), 2:3 (grey circle), 3:2 (dark grey diamond), and 4:1 (black square); b) WE with a fixed concentration of 5% (yellow open circle), combined with 1% (light grey square), 2% (grey circle), 3% (dark grey diamond) and 4% (black triangle) MCI, respectively; c) 5% WPI (navy diamond) and 5% WE (yellow open circle) at ratios of 1:4 (light grey triangle), 2:3 (grey circle), 3:2 (dark grey diamond), and 4:1 (black square) d) 5% WE (yellow open circle), combined with 1% (light grey square), 2% (grey circle), 3% (dark grey diamond) and 4% (black triangle) native WPI solution, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

A higher friction coefficient of the mixtures compared to single systems was also observed for a combination of WPA and WPI, but only at sliding speed above 3 mm/s (Fig. 6c). At lower speeds (<3 mm/s), the friction coefficient was between those of WPI and WPA in single systems, and, therefore, could be explained by dilution effects. Again, at higher speeds, the adsorption of WPI of the surface affected the particle lubrication. Thus, for both particle systems, lubrication properties of large protein particles were negatively affected by the presence of small molecules. Systems that provide lubrication due to particle lubrication are thus sensitive to proteins that are able to form a film on the surface.

3.3.3.2. Combinations of protein dispersions and emulsions. Also the emulsion systems were mixed with different protein suspensions at different ratios (1:4, 2:3, 3:2, 4:1). Noticeably, proteins and protein particles affected the lubrication ability of WE in different ways (Fig. 7).

As shown in Fig. 7a, when MCI was mixed with WE, the friction coefficients of the mixtures were lower than that of the single MCI suspension, but higher than that of 5% WE, indicating the frictional behavior was an average of the two types of components. This phenomenon could be explained by dilution effects of the WE and MCI. To better understand the effect of MCI on the lubrication ability of WE, WE with a fixed concentration of 5% was mixed with MCI at increasing concentration (1%, 2%, 3%, and 4%). As shown in Fig. 7b, the measured friction curves of the mixtures overlapped with each other, resembling that of the individual emulsion, indicating that in these systems the emulsion dominated the lubrication behavior. WE consisted of oil droplets with an average size that was larger (449 nm) than the average size of MCI (207 nm) in the MCI dispersion. Thus, as WE and MCI both provided particle lubrication, the oil droplets with the largest size determined the gap size and the lubrication behavior. Similar results were obtained when WE was combined with WPA (data shown in Figure A.2, supplementary information). As the size of the oil droplets determined the lubrication behavior, the morphology of large protein particles, i.e. MCI or WPA, played a less important role in this case.

However, WPI seemed to increase the friction of mixed systems to a larger extent than protein particles. As shown in Fig. 7c, the shape of most friction curves resembled that of 5% WPI solutions, and the friction coefficients of most mixtures were higher than those of the two separate systems. WE with a fixed concentration of 5% was also mixed with increasing amounts of WPI (1%, 2%, 3%, and 4%). We observed that the effect of WPI at low speeds (<10 mm/s) was minimal, but WPI had a considerably negative influence on the lubrication of WE at higher speeds (Fig. 7d). These results imply that in this case the emulsion did not entirely dominate lubrication, but the system was also affected by the presence of WPI. These effects were similar to those seen in the systems with MCI and WPA, and show again that the presence of WPI decreased the efficiency of particle lubrication.

We also investigated the effect of protein particle addition for emulsions that provided lubrication due to oil film formation, i.e. SE. In comparison to WE, the addition of large protein particles affected the

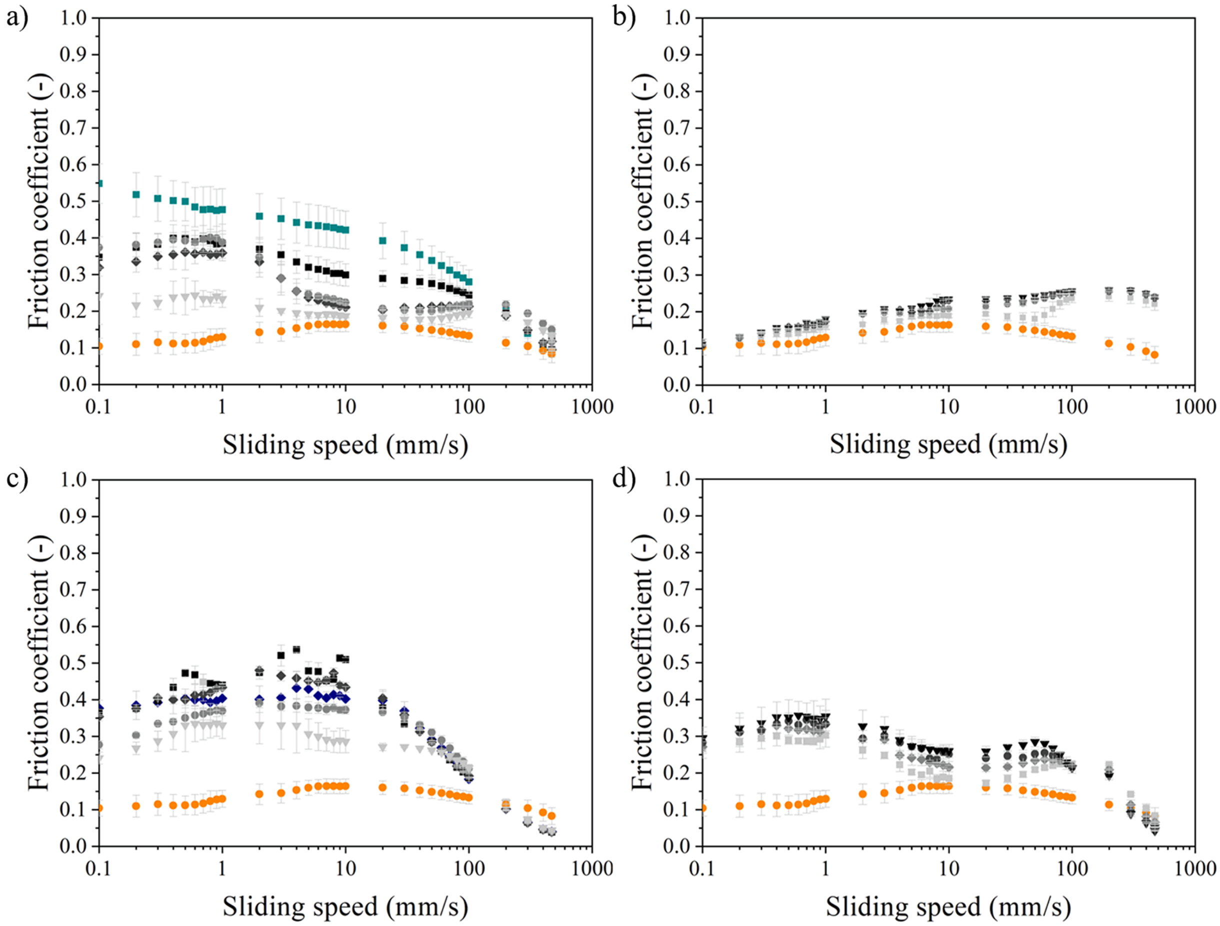

Fig. 8. Friction coefficient as a function of sliding speed for mixtures of a) MCI (dark cyan square) and SE (orange circle) at ratios of 1:4 (light grey triangle), 2:3 (grey circle), 3:2 (dark grey diamond), and 4:1 (black square); b) SE with a fixed concentration of 5% (orange circle) was combined with 1% (light grey square), 2% (grey circle), 3% (dark grey diamond) and 4% (black triangle) MCI, respectively; c) 5% WPI (navy diamond) and 5% SE (orange circle) at ratios of 1:4 (light grey triangle), 2:3 (grey circle), 3:2 (dark grey diamond), and 4:1 (black square) d) 5% SE (orange circle) was combined with 1% (light grey square), 2% (grey circle), 3% (dark grey diamond) and 4% (black triangle) native WPI solution, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lubrication of SE to a slightly larger extent (Fig. 8a).

Upon mixing SE with MCI, the shape of the curve for mixtures varied depending on the ratios, and the friction coefficients were lower than those of protein suspensions but higher than that of SE. As mentioned above, SE itself did not show clear boundary and mixed regimes (Fig. 2) as a single system, but after mixing with large protein particles, a clear transition from a boundary to a mixed friction regime was observed for ratios of 2:3 (MCI: SE) and 3:2 (MCI: SE) (Fig. 8a). SE with a fixed concentration of 5% was also mixed with MCI at increasing concentration (1%, 2%, 3%, and 4%), as shown in Fig. 8b. The friction coefficients of mixtures were still very low and close to that of 5% SE at low sliding speeds. It was noticed that with increasing sliding speeds, the friction coefficients of mixtures slightly increased and were higher than that of 5% SE at very high sliding speed (>100 mm/s). The presence of large MCI particles thus influenced the oil film lubrication only at high speeds. It could be that at high entrainment speeds, the presence of the large particles between the oil films led to a worse lubrication, as particle lubrication is less efficient than oil film lubrication. Similar results were observed when SE was combined with WPA (data shown in Figure A.2, supplementary information). So, compared with WE, SE was influenced by the presence of large particles to a larger extent. Protein particles thus influence emulsions providing lubrication though film formation, but have limited effect on emulsions providing lubrication through particle lubrication.

However, the presence of WPI showed an even larger negative effect on lubrication of SE. As shown in Fig. 8c, when SE was mixed with WPI at different ratios, the shape of the friction curve for mixtures resembled that of 5% WPI, indicating that WPI dominated the friction of the systems. To further investigate this effect, SE with a fixed concentration of 5% was also mixed with WPI at different concentrations (1%, 2%, 3%, and 4%) and the results are shown in Fig. 8d. The presence of WPI had a considerably negative influence on the lubrication of SE. The friction curves of the mixture were similar to each other, but very distinct from that of 5% SE. SE thus did not dominate the lubrication behavior of these mixed systems, and the presence of WPI influenced the lubrication properties and the lubrication mechanism of the emulsion. As we discussed in the single-component systems, SE provided lubrication most likely via forming of oil patches and oil film formation (plate-out mechanism). The increase in friction upon the addition of WPI indicated that the WPI molecules either changed the properties of the oil droplets themselves or changed the properties of the surface by WPI adsorption. We hypothesize that WPI adsorbed on the PDMS surface and reduced direct contact between the hydrophobic PDMS and SL-stabilized oil droplets and, thus, less oil patches formed on the PDMS surface. In addition, WPI in the continuous phase could adsorb on the o/w interface of the oil droplets and interact with SL, consequently affecting the interfacial properties of the droplets. Protein-lecithin complex formation has already been shown to strengthen the emulsifier film at the interface compared to a system with soy lecithin alone (McClements & Jafari, 2018; Rodríguez Patino, Navarro García, & Rodríguez Niño, 2001; Wang

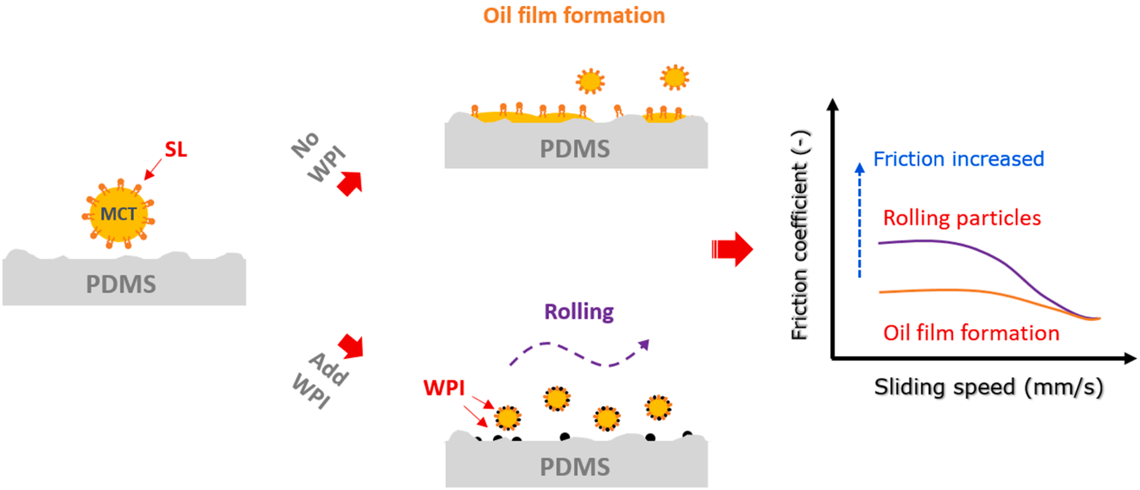

Fig. 9. Schematic representation of the influence of WPI addition on the coalescence of SL-stabilized oil droplets on PDMS surface and of the related effect on friction.

et al., 2017). A similar phenomenon could have occurred in our SE-WPI systems. The two described phenomena both result in a decreased droplet coalescence on the PDMS surface. Due to limited coalescence, the lubrication mechanism of SE could now change from plate out (film formation) to ball-bearing (rolling particles). As earlier discussed, particle lubrication is less efficient than film formation, so this change in mechanism leads to higher friction coefficients, as shown in the schematic representation of Fig. 9. Also, no coalescence of oil droplets (SE) was observed after adding WPI (images shown in Figure A.3, supplementary information), which confirms that the oil droplets indeed became more stable. The mechanisms described above may also explain why the lubrication of WE was less affected by WPI compared to that of SE at low sliding speeds. As these oil droplets were already stabilized by WPI, the interfacial properties of the oil droplets was less sensitive to the addition of WPI.

To summarize, changes in lubrication behavior of emulsions depended on the type of protein added. In the case of large protein particles that provide particle lubrication, their influence on the lubrication behavior of emulsions was minor, independently of the lubrication mechanism of the oil droplets. The lubrication behavior of the mixture was mainly determined by the emulsion. However, WPI had a considerably negative influence on the lubrication of the two emulsion types and in different ways. In the case of SE, WPI limited oil patch formation, whereas in WE, WPI limited the ball-bearing mechanism.

Our results show that different mechanisms play a role in the lubrication of single systems, and that the addition of specific ingredients can alter the lubrication behavior in different ways, i.e. influencing surface properties, changing interfacial properties, influencing particle rolling ability and oil film formation. The influence of certain ingredients and the competition of certain lubrication mechanisms thus needs to be considered to understand lubrication properties of more complex food systems.

4. Conclusion

We investigated the individual contribution of proteins and emulsified oil in model dairy beverages to lubrication behavior. We measured the friction coefficient for both single-component systems and binary systems. For single-component systems, oil droplets provided better lubrication than protein particles. The lubrication mechanism of the emulsions was determined by the emulsifier: a hydrophobic small molecular weight emulsifier seemed to favor oil patch or film formation on the surface, whereas protein-stabilized droplets were linked to ball bearing.

For mixed systems (protein combined with protein or emulsion), different effects were observed. The addition of large particles (whey protein aggregates and casein micelles) had limited effect on the lubrication properties of emulsions, independently of the lubrication mechanism. However, whey protein isolate (WPI) negatively affected the lubrication of both type of emulsions. WPI was able to limit the plate-out and ball bearing mechanism. This was probably due to a combination of the ability of proteins to adsorb onto the surface, and by changes in the interfacial structure of oil droplets. These results show that the lubrication properties of multi-component systems are quite complex and that several phenomena can influence lubrication properties. Ingredients exhibiting good lubrication properties in single systems may have a negative effect on the friction coefficient of mixed systems.

CRediT authorship contribution statement

Lei Ji: Investigation, Data curation, Methodology, Visualization, Writing – original draft. **Leonardo Cornacchia:** Writing – review & editing. **Guido Sala:** Methodology, Validation, Supervision, Writing – review & editing. **Elke Scholten:** Conceptualization, Methodology, Validation, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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