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Pickering water-in-water emulsions: A review on their rheological and tribological performance

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Pickering water-in-water (W/W) emulsions have attracted renewed research attention owing to the recent discovery of their aqueous lubrication performance. We cover the current knowledge of Pickering W/W emulsions regarding their rheological and tribological performance. Particularly, we examine the recent advances that have surfaced in the literature in the last five years, highlighting how the two phases and the Pickering particles affect the rheological properties and microstructural evolution of W/W emulsions when subjected to various degrees of shear stresses. We postulate how biolubrication performance of Pickering W/W emulsions can be altered by formulation engineering of the water droplets to offer fluid film lubrication while the particles providing boundary lubrication. This review therefore offers a stepping stone in highlighting the requirement of systematic experimental studies and rational design of the next-generation Pickering W/W emulsions for them to act as effective aqueous lubricants for a range of biomedical and allied applications.

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Introduction

Designing aqueous lubricants that can significantly lower the boundary friction with friction coefficient (μ) values of <0.005 has attracted significant academic and industrial research interest, owing to their applications at biological tissue interfaces in particular [1]. Recent understanding of naturally evolved biolubricants such as saliva and synovial fluids reveals that these materials rely on synergistic interactions between various biomacromolecules in aqueous media and the native biological surfaces [2]. Some of these molecules tend to be strongly adsorbed to biological substrates to give a sufficiently thick surface layer, offering boundary lubrication, while other highly hydrated macromolecules have open, branched chain–type features that provide viscosity modification of the continuous phase that facilitates fluid film lubrication [3–5]. Other areas where aqueous lubrication needs to be improved are saliva substitutes in case of dry-mouth conditions, artificial tears in case of dry eyes, and food and cosmetic applications where a reduction in fat and/or hydrocarbon content is desired.

The use of water-in-water (W/W) emulsions as aqueous lubricants is a relatively recent proposal. Such emulsions are unique colloidal dispersions formed by phase separation of blends of biomacromolecules, where the droplet and the continuous phases are rich in one of the two polymers. As such, they may have a wide range of applications in food, biology, and biomedical sectors [6]. The emulsion structure can form spontaneously, without the requirement of any surfactant, typically on mixing different proteins and/or polysaccharides. Thus, the preparation process for these emulsions is notably straightforward and can be consistently replicated, requiring minimal input of mechanical energy [7–9]. Recently, several critical reviews have been published on W/W emulsions, covering their formation, stability, and various applications [6,10]. However, the rheological and tribological performance of such emulsions has attracted relatively little attention to date. W/W emulsions consisting of polyethylene glycol (PEG) and dextran (DEX) stabilized by methylene polyethylene glycol (mPEG)-collagen nanofibrils were reported to show ultralow μ (0.003–0.011) in soft contacts using a pin-on-disk reciprocating tribometer [11], but the

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Given the role as Guest Editor, Brent Murray had no involvement in the peer review of the article and has no access to information regarding its peer-review. Full responsibility for the editorial process of this article was delegated to Krassimir Velikov.

details of the underlying mechanisms of how this system reduces friction in the different tribological regimes, that is, boundary, mixed, elastohydrodynamic (EHL), and hydrodynamic, are not well understood.

Previous studies have investigated in detail the morphological changes of W/W emulsion droplets subjected to shear forces [12–14]. It is worth noting that the droplets of W/W emulsions tend to deform relatively easily under shearing conditions and that the degree of deformation from ‘droplets’ to ‘strings’ can be modulated by modest variation of the shear rate ($\dot{\gamma}$), for example, in the range of 5–120 s^{-1} [15]. Formation of strings is usually followed by their rupture and coalescence, although the strings can also rapidly break up into small droplets when the shear forces are terminated [15]. This special characteristic of W/W emulsion droplets provides the possibility that water-based domains in the form of droplets can enter the gap and transform into boundary tribofilms that may reduce friction further, though this mechanism remains poorly understood and explored in the literature.

Besides W/W emulsions in general, Pickering W/W emulsions, that is, those that are stabilized by particles present at the water–water (W-W) interface, have attracted further attention owing to their greater storage stability [16]. So far, a wide variety of particles have been reported as effective stabilizers of W/W emulsions, such as protein microgels (composed of β-lactoglobulin [β-lg] or whey protein) and cellulose nanocrystals (CNCs), as reviewed relatively recently [8,17]. Given the existing evidence for the role of microgels in the bulk phase in reducing friction, the presence of microgels in Pickering W/W emulsions is hypothesized to contribute significantly to their lubrication as well [18,19]. Unlike oil-in-water (O/W) emulsions stabilized by microgels, even at low microgel concentration, there are often excess unbound microgels in the aqueous phase [17]. It is suggested that these excess free microgels that are present in the continuous phase might act as ‘surface-separators’ to reduce friction [18]. On the other hand, if the microgels are adsorbed at the droplet surfaces, they might be expected to increase the droplet stability and also the viscosity of the droplet phase and so enhance their entrainment into the contact zone via higher drag forces. Additionally, adhesive microgels at the interface could potentially promote entrainment of water droplets to form a continuous surface-bound water layer providing fluid film lubrication. In a contrasting argument, the adhesive nature of the microgels at the interface of droplets may lead to jamming of droplets in the contact zone raising friction which needs further consideration.

This review therefore presents recent research on the rheology and tribology of Pickering W/W emulsions, with a particular focus on the morphological changes of the droplets under shear conditions. Literature focusing on the tribology and rheology of *non–phase separating* biopolymer mixtures or covalent conjugates is out of scope for this review [2,20]. We first summarize the stabilization aspects of Pickering W/W emulsions, with particular reference to tribological implications. We then summarize the factors influencing the formation of a ‘string’-like structure under shear and discuss how such string-like structures may affect the way Pickering W/W emulsions act as aqueous lubricants. Finally, we discuss the future perspective for these emulsions offering lubrication performance in food, health care, and allied

Table 1

List of abbreviations and symbols used in this article.

Abbreviations/symbols	Full form
AMP	Amylopectin
A-W	Air–water
aSNCs	Acetylated starch nanocrystals
β-lg	β-lactoglobulin
CLSM	Confocal laser scanning microscopy
CNCs	Cellulose nanocrystals
CNPs	Cellulose nanoparticles
CS CPs	Chitosan colloidal particles
cSNCs	Cross-linked starch nanocrystals
DEX	Dextran
EHL	Elastohydrodynamic
η_c	Viscosity of continuous phase
η_d	Viscosity of dispersed phase
HPMC	Hydroxypropyl methylcellulose
γ	Interfacial tension
$\dot{\gamma}$	Shear rate
GG	Guar gum
GS	Gelatinized corn starch
κC	κ-carrageenan
λ	Viscosity ratio
LMWS	LLow-molecular-weight surfactant
MD	Maltodextrin
mPEG	Methylene polyethylene glycol
μ	Friction coefficient
O/W	Oil-in-water
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
PEO	Polyethylene oxide
ϕ	Volume fraction
pI	Isoelectric point
pNIPAM	poly(N-isopropylacrylamide)
PUL	Pullulan
R	Particle radius
SA	Sodium alginate
SNCs	Starch nanocrystals
SPI	Soy protein isolate
θ	Contact angle
WPMs	Whey protein microgels
W/O	Water-in-oil
W/W	Water-in-water
W-W	Water–water
XG	Xyloglucan
ZPs	Zein-based nanoparticles

soft matter applications. Table 1 lists all the abbreviations that have been used in this review.

Timeline of key milestones in literature of W/W emulsions acting as aqueous lubricants

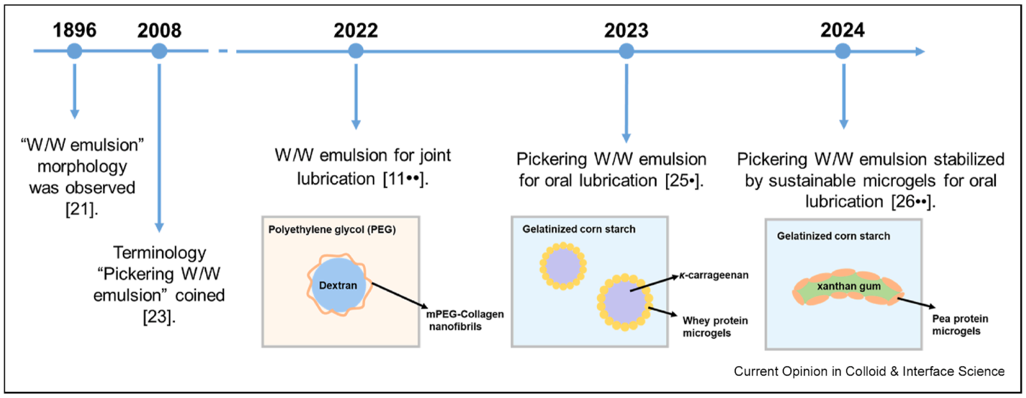
Figure 1 shows the timeline of key milestones in the progress of W/W emulsions particularly focusing on aqueous lubrication. In 1896, W/W emulsions were first described by Beijerinck, who observed the formation of droplets in the starch—gelatin aqueous mixture [21]. Following this, he investigated a second system composed of agar and gelatin [22]. This led to a significant body of literature in W/W emulsions formed using varying polymers and biopolymers and the effects of changing the environmental conditions. However, approximately a century passed before the next milestone when Poortinga reported the first *so-called* ultrastable Pickering W/W emulsions stabilized by particles [23]. Firoozmand et al. [24] in 2009 first demonstrated model particles accumulating at the W-W interface. Following these results, there has been a series of studies demonstrating a wide range of particles, including deformable microgels as stabilizers of W/W emulsions [17]. Exploration of the lubrication behavior of W/W emulsions is even more recent. In 2022, Wang et al. first reported the ultralubrication behavior of mPEG-collagen nanofibril-stabilized PEG/DEX W/W emulsions—showing a coefficient of friction μ in the range 0.003—0.011 [11]. Shortly after, You et al. [25] from our laboratory reported the first work on the lubrication performance of gelatinized corn starch-κ-carrageenan (κC) W/W systems stabilized by whey protein microgels (WPMs), that is, Pickering W/W emulsions [25]. The same system could also be stabilized by alternative protein-based microgels such as pea protein microgels (PPMs) [26]. It was also demonstrated that these PPM-stabilized droplets exhibited nonspherical flattened shapes that possibly explained the lower μ than the more spherical W/W droplets stabilized by WPMs. Thus, the morphology of droplets may influence the tribological properties, but it is clear that much more work needs to be done to fully understand and optimize such systems for maximum lubrication benefits.

Stabilization of Pickering W/W emulsions

Fabrication of W/W emulsions results from the phase separation of aqueous mixtures of two biopolymers. Broadly speaking, phase separation of aqueous biopolymer mixtures occurs in two possible ways: associative and segregative phase separation, which is determined by the specific molecular interactions between the different polymer molecules. Associative phase separation happens when the polymers have strong attractive interactions with each other and complexes can be formed that retain some 'solubility' in the bulk aqueous phase. Segregative phase separation happens when the macromolecules have unfavorable interactions with each other, resulting in their phase separating into, for example, two aqueous phases, each phase being rich in one of the polymers but deficient in the other. The regions of segregative phase separation are most easily visualized via a composition phase diagram, in which the binodal line represents the boundary separating the one-phase and two-phase regions, and the spinodal line, lying within the two-phase region, separates the metastable and the unstable regions of the two-phase system [27,28].

The *kinetics* of phase separation of biopolymers can proceed via two mechanisms: spinodal decomposition and nucleation and growth [29]. In a thermodynamically unstable system, if small-concentration fluctuations can reduce the free energy, these fluctuations will grow, leading to the formation of an interpenetrating

Figure 1



Timeline presenting the key milestones in the landscape of fabrication of W/W emulsions focusing particularly on the recent discovery of lubrication behavior of Pickering W/W emulsions. W/W, water-in-water.

continuous network that coarsens over time. This is the spinodal decomposition mechanism. On the other hand, when much larger and less frequent concentration fluctuations occur, these large fluctuations are manifested as phase-separated nuclei of a certain size that grow independently to form disconnected regions (often with a droplet-like appearance) of one type of aqueous phase dispersed in another. This nucleation and growth mechanism are the usual origins of the so-called W/W emulsions. Note that the ultimate destination of both mechanisms is the same—two completely separate macroscopic phases, each dominated in concentration by a different polymer.

One effective strategy for controlling phase separation in W/W emulsions is the incorporation of particles that strongly adsorb at the interface through Pickering stabilization mechanisms, which have been known for O/W emulsions for over a century. The classical understanding of Pickering stabilization for the oil—water (O-W) interface involves the irreversible adsorption of particles at the interface due to the high energy required for their desorption. However, recent studies have suggested that certain particles can also reduce interfacial tension (γ) in a manner like surfactants. This surfactant-like behavior complicates the distinction between conventional surfactant-stabilized and particle-stabilized emulsions [30].

In contrast, in the case of W/W emulsions, conventional low-molecular-weight surfactants (LMWSs) are completely ineffective at stabilizing the W-W interface. This is because the γ at W-W interfaces is extremely low (*e.g.* 0.01 μN m^{-1} or lower), making the spatial extent of the interface relatively larger in dimensions than typical LMWSs [17]. For instance, the γ of 2.4% DEX and 3.6% gelatin was reported as 0.008 μNm^{-1} and the estimated thickness of the interface 8—20 nm [31], which is at least one order of magnitude larger than the typical thickness for (O-W) or even air—water (A-W) interfaces. The adsorbed layer of colloidal particles at W-W interfaces can be very much larger than these dimensions, which is the key reason why they are one of the few entities that can stabilize W/W emulsions. Like any other Pickering emulsion, the adsorbed particles provide a steric barrier that inhibits both droplet coalescence and Ostwald ripening. As shown in Table 2, particles such as WPMs [25], β-lg particles [32], and CNCs [33] have been demonstrated as showing significant stabilizing capacity for W/W emulsions [16].

Particle stabilization of W/W emulsions still faces many challenges; these are summarized as follows: (i) There are no general particles (form or composition) that seem to work with all W/W eulsion systems—each class of W/W emulsion requires searching for a suitable type of particle for that particular biopolymer combination. (ii) Particles that are effective in stabilizing an emulsion of phase A dispersed in phase B may not necessarily stabilize the inverse emulsion of phase B dispersed in phase A, akin to the behavior often observed in O/W and W/O emulsions [34]. (iii) Particles appear to be able to stabilize W/W emulsions of one type only within a specific range of polymer compositions [35]. Thus, there remains a lack of universally applicable rules to predict the success of specific particles for stabilizing W/W emulsions. Therefore, before focusing on rheological and tribological aspects, it is worth summarizing the latest insights into the factors governing the stabilization of Pickering W/W emulsions.

General principles of the stabilization of Pickering W/W emulsions

A few general characteristics of W/W emulsions stabilized by particles can be noted as follows. (i) Particles do not seem to be able to inhibit the coalescence over very long timescales ($> \sim 1$ month). Neighboring droplets, once in contact, seem to be able to form channels that can expand and eject particles from the interface [36]. (ii) As with all Pickering emulsions, some degree of stabilization appears possible even when the particles do not ‘completely’ cover the surface of the droplets [37]. (iii) Frequently, particles exhibit varying degrees of stabilization depending on whether phase A is dispersed in phase B or vice versa, even though γ should be the same in both instances. Notably, in certain systems, it was demonstrated that emulsions were more stable when the particles favorably partitioned into the continuous phase [38], in-line with the general interpretation of the Bancroft or Finkle rule commonly applied to O-W emulsions [39]).

The adsorption of the particles into the interface containing biopolymeric phases A and B is related to the particle radius (R), interfacial tension (γ_{AB}) between the two aqueous phases, and the contact angle (θ). The latter is related to γ of each phase in the presence of the particle (γ_{PA}, γ_{PB}) given by the following equations [17,40]:

$$\Delta G = -\pi R^2 \gamma_{AB}(1 - |\cos\theta|) \tag{1}$$

$$\cos\theta = \frac{(\gamma_{PA} - \gamma_{PB})}{\gamma_{AB}} \tag{2}$$

Only when the $\gamma_{AB} > | \gamma_{PA} - \gamma_{PB} |$, should particles spontaneously adsorb at the interface [17]. For example, Machado et al. [41] added a third polysaccharide to modulate γ_{AB} to facilitate the adsorption of WPMs at the amylopectin (AMP)−pullulan (PUL) interface. Three anionic (alginate, low-methylated pectin, and κC) and one neutral (xyloglucan [XG]) polysaccharides were found to change the partitioning of the Pickering particles between the phases, even when only small amounts were added and the third polymer did not

Table 2

Preparation, physicochemical, and material properties of Pickering W/W emulsions in the last five years.

Components of W/W emulsions	Emulsion properties			Pickering particle properties				Viscosity	References
	Preparation conditions	Droplet size (μm)	Stability	Type	Size (nm)	Shape	Concentration		
Polyethylene oxide (PEO) and dextran (DEX)	5 wt% PEO + 8% DEX, pH 6.3	–	12 h	Oppositely charged latex particles	5×10^5	–	0.35 wt%	–	[35]
	16 wt% DEX+8 wt% PEO	–	3 weeks	poly(N-isopropylacrylamide) (pNIPAM) microgels with methacrylated DEX	About 50	Rough and irregular	–	–	[57]
	1.50–2.50 wt% + 5.0 wt% PEO 4.50–5.50 wt% PEO +2.00 wt% DEX	6.41 ± 2.69	At least 7 days	Cellulose nanocrystals (CNCs)	157.2	Needle-like	0.2 wt%	√	[54]
Polyethylene glycol (PEG) and DEX	PEG:DEX ratio of 1:3, 20 wt% polymer, pH 5.5	22	At least one week	Self-assembled chitosan colloidal particles (CS CPs)	–	Spherical	2.0 mg mL^{-1}	–	[53]
	8/2–2/8 w/w	–	–	Sodium hexametaphosphate crosslinking and acetylation modified starch nanocrystals (SNCs)	Around 370	Irregular puzzles	2–60 mg mL^{-1}	√	[48]
Amylopectin (AMP) and xyloglucan (XG)	1.023 wt% AMP +1.300 wt% XG, pH = 4.0	–	–	β-lg microgels	R_h = 184 ± 7	Spherical	–	–	[45]
	1.02 wt% AMP + 1.30 wt% XG	–	168 h	Sulfated CNCs	232 ± 51 236 ± 45 268 ± 52	Rod-like	0.15–0.50 wt%	–	[59]
				Phosphate CNCs	60 ± 11	Spherical	0.15–0.50 wt%		
DEX and maltodextrin (MD)	20 wt% DEX + 10 wt% MD	2.01 ± 0.40	At least one week	Bacterial cellulose nanofibrils	Width: 93.25 ± 9.68 Height: 9.37 ± 1.65	Fiber	0.16 wt%	√	[50]
Hydroxypropyl methylcellulose (HPMC) and MD	3 wt% HPMC + 4 wt% MD	4.69 ± 1.14	30 days	CNCs	Width: 105.11 ± 11.93 Height: 3.56 ± 1.62	–	0.025–0.1 wt%	√	[49]
DEX and HPMC	pH 3.0	–	At least one week	β-lg microgels	190–200	–	0.5 wt%	–	[52]
Soy protein isolate (SPI) and guar gum (GG)	3 wt% SPI + 0.60 wt% GG	–	–	Pectin modified zein nanoparticles	533 ± 5.7	Spherical	0.3 wt%	–	[58]
AMP and pullulan (PUL)	5.7 wt% PUL+ 8.5 wt% AMP	–	At least one week	Whey protein microgels (WPMs)	125	–	0.4 wt%	–	[62]

W/W, water-in-water.

interact directly with the WPM particles [41]. Similarly, the incorporation of anionic sodium alginate (SA) improved the stability of CNC-stabilized maltodextrin-in-hydroxypropyl methylcellulose (MD–HPMC) emulsions, which might be because the SA altered the distribution of the CNCs between the phases, favoring their adsorption from one side of the interface [42]. Another study reported that θ of the gelatin microgels at the DEX–polyethylene oxide (PEO) interface could be adjusted by pH changes. θ was measured from images obtained via confocal laser scanning microscopy (CLSM). The gelatin microgels bridged the neighboring droplets to form a continuous network in the interface and between the interfaces, inhibiting droplet coalescence and forming a fragile W/W emulsion gel [43].

Factors influencing the stability of Pickering W/W emulsions

Morphology and size of Pickering particles

According to equation (1), assuming γ_{AB} is fixed by the composition of the W–W systems, the stability of W/W emulsions can be enhanced by either increasing the R of a spherical Pickering particle or altering the particle geometry such that it occupies more area in the interface, that is, becoming nonspherical. However, the packing of irregular shaped colloidal particles at W/W interfaces often encounters geometric limitations, leading to relatively low overall coverage ratios, typically ranging between 20% and 40%, thereby contributing to restricted stability [44]. Hence, the selection of particles with appropriate morphology is of paramount importance. Across most studies listed in Table 2, the shape and size of the particles were found to be key factors influencing the stability. Disc-like and rod-like particles can cover larger interfacial areas per unit mass of material [45–47]. CNCs in the form of nanorods were reported as very effective Pickering stabilizers of PEO/DEX emulsions [33]. Biocompatible β-lg particles in forms of fibrils, microgels, and fractal aggregates can stabilize PEO/DEX emulsions. Fibrils have been shown to be the most effective at pH 7.0, but fractal aggregates were the most effective at pH 3.0 [38]. However, β-lg fibrils were reported to be able to stabilize AMP/XG emulsions under a wider pH range than β-lg microgels [45] (Table 2). Qian et al. [48] reported that by modifying starch nanocrystals via sodium hexametaphosphate crosslinking, the particle size increased from 110 nm to 370 nm (Table 2) and that these larger aggregated particles showed improved emulsifying ability. Kulkarni et al. [35] investigated the effect of particle charge. A mixture of oppositely charged polystyrene particles was more effective in stabilizing the DEX/PEO emulsions, even though both negatively and positively charged polystyrene particles preferred the continuous PEO phase. This seemed to be because the mixtures formed larger aggregates at the interface via electrostatic attraction [35].

Concentration of Pickering particles

The concentration of Pickering particles in either phase can obviously affect the kinetics of adsorption of particles to the interface and thereby its coverage and ultimately the stability of the droplets (Table 2) [49]. A higher concentration is expected, up to a limit, to give more rapid coverage and therefore possibly stabilize smaller droplets, by analogy with conventional surfactants. The limit may depend on the tendency of the particles to aggregate above a certain concentration, as well as the $\dot{\gamma}$ that can be applied to disperse the system. At the same time, an increased ‘bulk’ concentration of particles generally results in an increase in viscosity. This can slow down particle adsorption but increase the overall viscosity of the system (which in turn will have effects on the tribological performance of such a system—see later), retarding phase separation, creaming, and coalescence [50]. Xie et al. [49] used CNCs to stabilize W/W emulsions containing HPMC and MD with a dextrose equivalent of 12. As the CNCs content increased from 0.025 wt% to 0.1 wt% (see Table 2), the droplet size decreased, which was attributed to increased interfacial coverage. In addition, the Pickering emulsion system exhibited shear thinning which was attributed to deformation and alignment of droplets with the shear field, reducing the resistance to flow. The apparent viscosity increased with higher CNC concentrations, while the shear thinning behavior remained consistent, suggesting that the presence of the CNCs did not significantly affect the deformation of droplets in this particular case [49]. Such increased viscosity will contribute to increased drag forces to allow entrainment in the contact zone between two surfaces, resulting in enhanced lubrication. Thus, the rheological behavior as well as the stability of Pickering W/W systems is likely to vary considerably with particle concentration, and this is another factor that needs to be taken into account in future tribological assessment of them. Kibbelaar et al. [51] reported that in ethyl cellulose nanoparticle (CNP)–stabilized O/W emulsions, short-range interactions between particles at the surfaces of adjacent droplets could significantly influence the rheological properties, leading to the development of yield stress within the emulsion. This finding has potential implications for W/W emulsions, suggesting that particle–particle interactions between surrounding water droplets may similarly affect both their rheological and tribological behaviors.

In another study, the size of the droplets in HPMC/DEX emulsions decreased with increasing addition of β-lg microgels up to 0.3 wt%. A further increase in microgel concentration did not significantly alter the droplet size [52]. Cui et al. [53] also reported that the mean diameter of W/W droplets decreased from 83 μm to 22 μm when the concentration of self-assembled chitosan colloidal particles (CS CPs) was increased from

0.2 mg mL^{-1} to 2.0 mg mL^{-1} (Table 2). On increasing the concentration of CS CPs in PEG/DEX emulsions to higher than 2.0 mg mL^{-1}, macroscopic precipitation of CS CPs was observed in the PEG phase [53], and thus beyond this concentration, no benefits in terms of stabilization were perceived. In another study, the effect of CNC concentration on DEX/PEO emulsions was different—the droplet size changed only marginally (from 6.41 μm to 6.71 μm) on increasing concentration of CNCs from 0.05 to 0.15 wt%, possibly indicating that at 0.05 wt% the interface was already saturated with particles [54]. In general, more work needs to be done to understand the kinetics of interfacial coverage as a function of particle concentration in all these systems.

Wettability of particles

As already mentioned, the phase which forms the continuous phase is generally the one in which the particles have a greater preference, that is, are preferentially wetted [55,56]. The θ of sodium hexametaphosphate cross-linked starch nanocrystals (cSNCs) at the A-W interface of PEG and DEX solutions were 78° and 49°, respectively (Table 2). As a result, the DEX phase preferred to form the continuous phase even when the ϕ of the DEX phase was <0.5 [48]. A similar asymmetric capacity to stabilize PEO/DEX or DEX/PEO emulsions was also observed for rod-like CNCs [33]. In contrast, acetylated starch nanocrystals (aSNCs) exhibited higher θ at the A-W interface of both PEG and DEX solutions (87° and 55°, respectively), indicating a lower affinity for both phases. The reasons for these differences are not clear—undoubtedly the polymers themselves may have different affinities for the different particle surfaces. At the same time, the aSNC-stabilized emulsions showed better stability than the cSNC-stabilized systems at the same particle loading, in line with the predictions of equation (1) of higher desorption energy for higher θ. Furthermore, the cSNC-stabilized PEG−DEX emulsions exhibited higher viscosity and dynamic modulus than the aSNC-stabilized systems due to a greater retention of cSNCs in the DEX phase [48]. Thus, cross linking of the starch particles is one way of changing their wettability, stabilizing properties and also the viscosity of the different phases, which in turn may affect their tribological properties.

Merland et al. [57] also used manipulation of wettability to improve emulsion stability using 2 types of particles—where one particle preferred phase A and the other favored phase B. It became possible to optimize interfacial adsorption by fine-tuning the composition. In their system, poly(N-isopropylacrylamide) (pNIPAM) microgels had greater affinity for the PEO phase (Table 2). The wetting of the microgels by the DEX or PEO phase was adjusted by introducing a DEX component *into* the microgels: only microgels with the highest DEX content (27 wt%) were effective in stabilizing PEO/DEX emulsions. Temperature affects the stabilization behavior of the microgels—at room temperature, they effectively inhibit coalescence in DEX/PEO emulsions but not in the inverse. However, above 32 °C, the microgels only prevent coalescence in PEO/DEX emulsions [57].

In a similar fashion, Chen et al. [58] used pectin to modify zein-based nanoparticles (ZPs) to alter their wettability. ZPs were totally wetted by soy protein isolate (SPI), and as the amount of pectin in the ZPs was increased, particles tended to be wetted more by the guar gum (GG) phase (Table 2). A particular concentration of ZPs with a zein-to-pectin ratio of 2:1 showed the best capacity to stabilize the SPI/GG emulsions, while coalescence occurred in the emulsions stabilized by ZPs with a zein-topectin ratio of 1:2 due to the higher wettability of the latter for the GG phase [58].

In AMP-in-XG emulsions, there was no evidence of sulfated CNPs being present at the interface even at the highest concentration (0.50 wt%; see Table 2) because XG interacted with the particles [59]. However, these systems displayed stability (i.e. no macroscopic phase separation) for up to 168 h, but this was attributed to the high viscosity of the continuous phase due to the presence of the nanoparticles. In contrast, phosphated CNPs interacted much less with the XG phase, allowing them to migrate to the XG−AMP interface and partially stabilize emulsions via particle adsorption at the W-W interface, that is, *true* Pickering stabilization.

How all these instances of changing particle wettability and therefore W/W emulsion stability affect the lubrication performance of the systems is unknown—in particular, how the effects of changes in particle aggregation and adsorption to the tribological surfaces might be separated out from the effects of the W/W emulsions themselves. It is known from work from own laboratory [18] that even using the same particles (WPMs) at the same ϕ, changing a highly hydrophobic polydimethylsiloxane (PDMS) surface to a hydrophilic PDMS surface (via oxygen plasma treatment) significantly influences the tribological properties of the WPMs. We hypothesize that altering θ of the particles so that there are more particles in the continuous phase may diminish or enhance lubrication, via either particle jamming or entrainment, respectively.

Environmental factors

As shown in Table 2, only specific pH and ionic strength conditions enabled preparation of stable Pickering W/W emulsions. The adjustment of pH in the Pickering W/W emulsions influenced the distribution of protein microgels between the two phases by changing the wettability, like in the previous section. The isoelectric point (pI) of β-lg microgels is around pH 5.2. Soft and poorly cross-linked microgels can swell and display a flexible internal structure at pH values far from the pI, due to increasing internal charge density and therefore increasing strand/chain repulsion [60]. HPMC/DEX emulsions stabilized by β-lg microgels phase separated between pH 6 and 7, while no phase separation occurred at a pH value <5.0. The greater stability at a pH value <5 was attributed to the microgels being more aggregated in the interface (apparent from CLSM images) [52]. Gonzalez-Jordan et al. [61] reported that β-lg preferred the DEX phase for a pH level >4.0 while preferring the PEO phase at lower pH. By adjusting the pH between 4.5 and 5.5, close to the pI, distinct protein aggregates formed between droplets in PEO-in-DEX emulsions, forming weak gels that prevented creaming and coalescence [61].

Adjusting the pH has also been shown to change the affinity of WPMs for AMP–PUL phases [62] (Table 2). In AMP/PUL emulsions between pH 7.0 and 5.7 the WPMs showed strong affinity for the PUL phase and remained dispersed within it. Consequently, the emulsions rapidly destabilized. Decreasing the pH caused the WPMs to become more compatible with the AMP phase—they adsorbed more strongly to the W/W interface, and the emulsions were stable for at least 1 week. However, on further lowering the pH below 3.5, all WPMs accumulated in the AMP phase [62] and the systems were no longer stable. Hazt et al. [45] reported in a similar study that β-lg microgels showed distinct changes with pH for stabilizing AMP/XG emulsions. When the pH value was pH 4.0, 1.0 wt% β-lg microgels showed strong adsorption to the interface and good Pickering stabilization. As the pH value increased to 5.0, a thinner adsorbed layer was observed. At pH 6.0 and pH 7.0, the particles largely resulted in aggregation and gelling of the continuous phase [45].

Nguyen et al. [63] used charged bis-hydrophilic microgels formed from DEX and pNIPAM, where each component had a different affinity for different phases of DEX–PEO emulsions, to investigate the effect of particle charge on W/W emulsion stability. They found that more highly charged microgels gave less stability, primarily due to their reduced adsorption at the interface. Adding NaCl screened electrostatic repulsion between the charged microgels at pH 7, thereby increasing microgel adsorption at the interface and emulsions stability, especially in the case of PEO/DEX emulsions. However, at pH 3, where charge on the microgels was very low, adding NaCl gave little improvement in stability, even though adsorption *was* enhanced [63]. Many other studies have shown varying effects of ionic strength, which can be attributed to either changes in electrostatic repulsion and therefore aggregation between particles in the interface, in the bulk, and/or changes in their partitioning between the different aqueous phases [49,52,55,64].

Not surprisingly, temperature can also influence stability, particularly with microgel particles, since temperature affects their unfolding, swelling, and surface behavior [65]. Additionally, heating increases the Brownian motion of particles, causing their redistribution at the interface. Zhou et al. [54] reported that DEX/PEO emulsions stabilized by CNCs became unstable to coalescence when the temperature was increased to 70 °C because the redistribution of CNCs led to more exposure of the droplet surfaces [54]. There was no observable impact with strongly charged microgels (where a fraction of the pNIPAM units was replaced by acrylic acid). However, the effect was recovered upon neutralizing the microgels by reducing the pH [63]. Pedro et al. [64] reported that higher temperature (35 and 40 °C) led to a reduction in the viscosity of MD/PEG emulsions stabilized by lignin nanoparticles—the mobility of the droplets increased, causing coalescence [66]. Of course, changes in temperature will also change factors such as solubility, interfacial tension, viscosity, and the conformation of macromolecules, all of which can impact the stabilization of Pickering W/W emulsions.

Lubrication behavior of W/W emulsions

Tribology and rheology

The assessment of lubrication performance is conducted through tribological measurements, typically using Stribeck analysis, originally developed for engineering bearings [67]. The tribological behavior of this lubricated system was typically described by a Stribeck curve, which is plotted by μ as a function of Hersey number ($U\eta/W$, where U is the sliding speed, η is the dynamic viscosity of lubricant, and W is the load). The Stribeck curve was characterized by three distinct regimes: boundary, mixed, and hydrodynamic lubrication. (i) At low speeds (boundary regime), the two surfaces come into direct contact; most lubricants are excluded from the contact area. The surface properties (asperity and hydrophobicity) of the tribopairs significantly influence friction in boundary regime. For compliant PDMS–PDMS contacts, a lower μ is expected in rougher surface because some lubricant could be trapped within the rough contact and provide hydrodynamic effects. Aqueous lubricants show enhanced entrainment in the hydrophilic contact compared with hydrophobic one [68]. Additionally, the lubricant with capacity to adsorb onto the substrates can contribute to the boundary lubrication by forming a submicron-sized thick film and separate the surfaces, forming some sort of discontinuous lubricant layer [68]. (ii) At high speeds, the lubricant is entrained into the converging contact; the two interfaces where the generation hydrodynamic pressure separates surfaces apart generate fluid film lubrication. This is called hydrodynamic lubrication regime for rigid contacts. In the Stribeck curve for compliant contacts (soft tribology), however, EHL lubrication regimes replace traditional hydrodynamic regimes. In EHL, the elastic deformation of the substrate and the pressure-viscosity effects of the lubricant significantly influence lubrication performance due to the hydrodynamic pressure generated.

Within the hydrodynamic/EHL regime, μ relies on the hydrodynamics of the lubricants, that is, the speed, the viscosity of lubricants, as well as the applied load [69]. The increasing viscosity and/or speed increases the viscous drag, resulting in a higher μ [68]. (iii) In between these two regions is the mixed regime, for which the μ decreases with the increasing entrainment of lubricants to a minimum value. Within this regime, both surface properties and viscosity of the lubricants (particularly at high $\dot{\gamma}$) play critical roles in reducing friction and facilitating the onset of fluid film lubrication. Higher viscosity enables the formation of a thicker film at lower speeds, promoting a quicker transition to fluid film lubrication. It is found that as the surface roughness increases, the transition from mixed to EHL regimes shifts to larger values of Uη [68,70].

Classic Stribeck analysis involves Newtonian fluids with constant viscosity. However, W/W emulsions are non-Newtonian fluid (typically shear thinning), making it challenging to predict their hydrodynamic film-forming behavior. Andablo-Reyes et al. [71] from our laboratory also identified that lubrication in the mixed and EHL regimes scales with the extrapolated high $\dot{\gamma}$ viscosity in the second Newtonian plateau for microgel dispersions in Newtonian fluids, such as buffer and corn syrup. However, for the microgel dispersions in non-Newtonian xanthan gum, the estimated effective viscosity in the EHL regime is much larger than the extrapolated high $\dot{\gamma}$ viscosity [71]. Xu et al. [72] systematically investigated the influence of shear-thinning fluid rheology on soft tribology and found that the high-shear viscosity had a strong influence on the friction in the EHL regime, while low-shear viscosity may play a role in the mixed regimes, with complex fluid—asperity interactions [72].

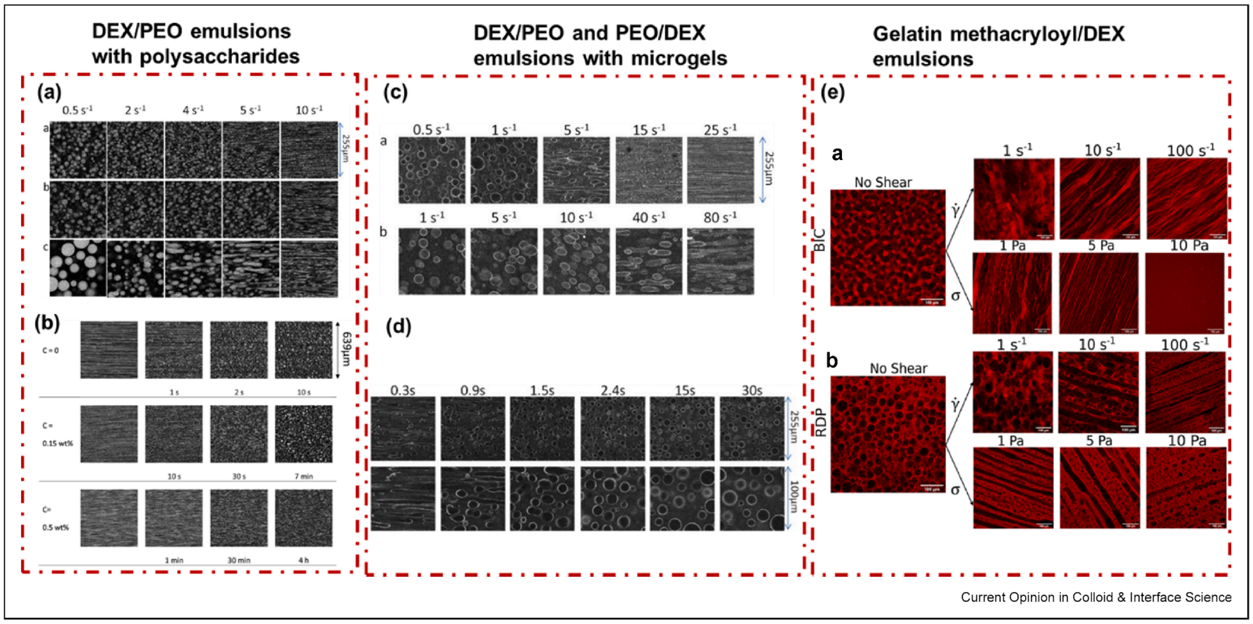
Theoretical frameworks are essential for understanding how the complex rheology of these systems influences their tribological performance across different lubrication regimes. While efforts have been made to extend conventional Stribeck analysis to include nonlinear rheology, these are still largely limited to single-phase lubricants—analytical solutions that fail to capture regime transitions with oversimplifications in contact mechanics and surface roughness [69]. Emerging concepts in the lubrication of ball-on-flat contacts by multiphase macromolecular fluids are providing fresh insights into possible mechanisms that depart from classical hydrodynamic or EHL theory and extend nonlinear rheology concepts. For multiphase lubricants, parallels can be drawn with active lubrication mechanisms of inlet aggregation [73] whereby large molecules/microstructures accumulate at the inlet of the contact, forming a concentrated plug that locally raises viscosity and enables much thicker lubricant films than would otherwise develop. As entrainment speed increases, this plug disperses more readily, so the film paradoxically thins with rising speed. In addition, friction reduction is likely achieved through entrainment of separated phases/adsorption of molecules onto the contact surfaces, in a similar fashion to synovial fluid. Because of the limited research on the tribology of W/W emulsions and the obvious importance of their rheological properties, we first discuss rheological studies carried out on W/W emulsions in this context.

String phase formation

The extremely low γ (between 10^{-7} to 10^{-5} N/m) in W/W emulsions facilitates easy deformation of droplets under relatively low $\dot{\gamma}$ [74]: the $\dot{\gamma}$ reported in existing studies generally ranges from 5 s^{-1} to 120 s^{-1} [15,75]. This γ imparts lower resistance to deformation of W/W droplets, making them easier to elongate into ellipsoidal droplets or even thread-like structures extending along the shear direction (Figure 2a, 2c, and 2e) [13,76]. Frith [27] reported that a balance between droplet breakup and coalescence could be achieved above a critical $\dot{\gamma}$, resulting in a steady-state structure. These morphologies have been termed ‘string phases’ by Hashimoto et al. [77] who first described the behavior in polymer blends. These thread-like droplets provide a possibility that they could enter the contact gap and provide fluid film lubrication. In addition, there is no literature to date on how much load these string-like droplets could support to prevent the two surfaces from touching, lowering boundary friction. One might hypothesize that such elongated structures might be easily entrained in a tribological contact zone. However, one should bear in mind that $\dot{\gamma}$ might be orders of magnitude higher than what has been typically tested to date. Under these conditions, phase separation might be induced, destroying string formation.

You et al. [26] reported droplets that are nonspherical in shape due to soft, adhesive PPMs present at the W/W interface, or in the interstices between the droplets, are better able to squeeze into the tribological gap, thus reducing the μ. Upon cessation of shear, these structures tend to break up into smaller droplets quickly (several seconds) due to Rayleigh—Plateau instabilities (Figures 2b and 2d) [15,78]. The viscosity of the system could influence the relaxation of the droplets. In W/W emulsions with higher viscosity obtained by adding

Figure 2



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Microstructure of DEX/PEO emulsion (**a**) with polysaccharides (DEX was labeled) when subjected to different shear rates [15] and (**b**) DEX/PEO emulsion with xanthan gum after cessation of the shear forces [33]; microstructure of DEX/PEO emulsions stabilized by 1 g/L whey protein isolate microgels (**c**) (microgels were labeled) at different shear rates and (**d**) after cessation of the shear forces [15]; microstructure of gelatin methacryloyl–DEX hydrogels obtained by photo-crosslinking of the solutions (**e**) during small amplitude oscillatory shear at different shear rates [13]. Images (**a**), (**c**), and (**d**) were reproduced with permission from ACS, while (**b**) and (**e**) are reproduced with permission from Elsevier and RSC, respectively. DEX, dextran; PEO, polyethylene oxide.

xanthan gum, the transition from the strand-like structure to spherical shape could take up to 4 h (Figure 2d) [34].

The flow morphology relationships of W/W emulsions have been relatively well studied in the literature in the last few years. String phase formation under steady shear is influenced by the $\dot{\gamma}$, ϕ of the dispersed phase, and the viscosity ratio ($\lambda = \eta_d / \eta_c$, where η_d is the viscosity of dispersed phase and η_c is that of the continuous phase [79]. String phases form above a critical $\dot{\gamma}$ which is a function of ϕ and λ [80]. Tromp and De Hoog [78] conducted a detailed investigation into the morphology of W/W emulsions composed of G and DEX under shear flow. They found that the strings tended to coalesce laterally into bands with time and the band formation in systems with higher ϕ of DEX-rich droplets occurred at lower $\dot{\gamma}$ (approximately 9 s^{-1} and 20 s^{-1} for $\phi = 0.50$ and 0.32, respectively). No band formation was observed for the systems with $\phi < 0.3$ [81]. Similarly, Tea et al. [15] investigated the effect of shear on the morphology of PEO–DEX emulsions. They reported that the critical $\dot{\gamma}$ at which droplets started to deform and form strings decreased with the increasing ϕ of dispersed phase. This was attributed to the larger size of the droplets in their resting state [15]. Once the strings had formed, ϕ influenced the thickness of the filaments. In gelatin–DEX mixtures, a coarse filament structure emerged when the ϕ of the gelatin phase was between 0.4 and 0.7. The filament structure was much finer above and below this range of ϕ. This result was attributed to the fact that coalescence significantly influenced the evolution of a particular morphological state during shear [80].

Regarding the influence of λ on the formation of strings, the efficiency of coalescence under shear is a function of the λ. As reported by Jeon and Hobbie, string phases exhibit a finer structure, that is, thinner filaments when the λ value was <1 (*i.e.* $\eta_c > \eta_d$), while a coarser string structure was observed for samples with $\lambda > 1$. The authors suggested that coarser strings phase formation for $\lambda > 1$ was driven by shear-induced coalescence, while it occurs spontaneously in systems with $\lambda \leq 1$ [82]. Wolf and Firth [80] investigated the gelatin–DEX system with a different λ and reported that string phase formation was favorable and that it occurs readily when λ measures <1, that is, the required $\dot{\gamma}$ was lower, while for $\lambda > 1$, a higher $\dot{\gamma}$ was required [80]. Tea et al. [15] observed that the critical $\dot{\gamma}$ was higher in PEO/DEX emulsions than in DEX/PEO systems. This phenomenon can be attributed to the lower viscosity of the DEX phase than that of the PEO phase since droplets of a less viscous dispersed phase are more susceptible to deformation [15].

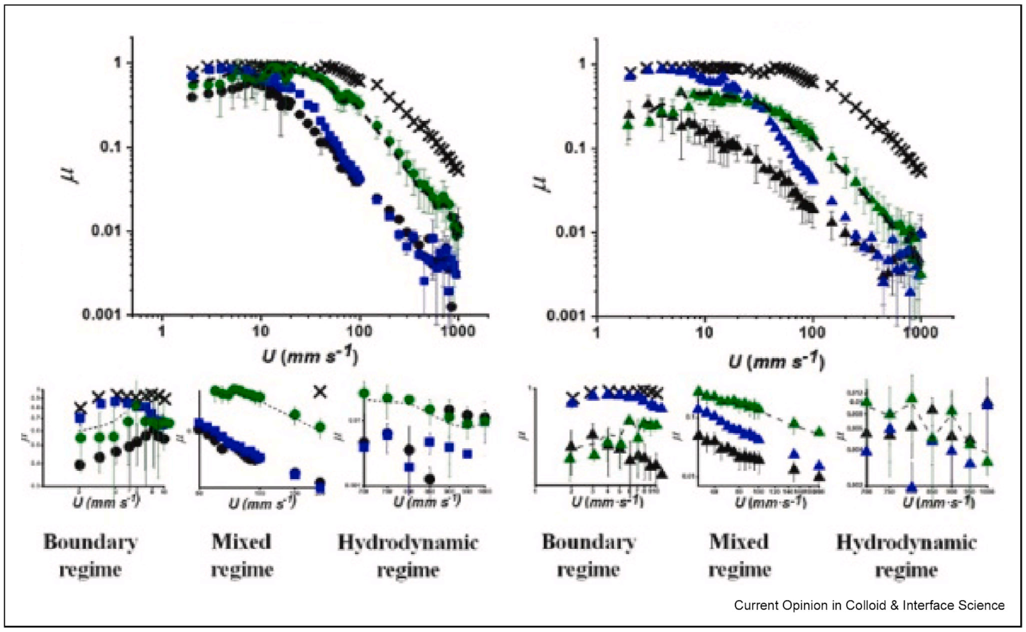
It is notable that researchers do not seem to agree on the behavior of systems when $\lambda \approx 1$. Tea et al. [15] observed that DEX/PEO emulsions with $\lambda \approx 1$ under shear presented the same string formation behaviors as the system with a $\lambda = 2.5$. In the case of G–DEX systems, Wolf and Firth indicated that string phases may form over a broad range of ϕ when $\lambda \approx 1$ [80]. In contrast, Tromp and De Hong [75] reported that when the $\lambda \rightarrow 1$ at $\phi = 0.5$, increasing shear led to progressively smaller droplets which did not develop long-range structures but were the result of a dynamic equilibrium of coalescence and break-up [75]. These results might be due to the limited range of $\dot{\gamma}$ applied, the maximum being 10.5 s^{-1}. This value may not have been below γ_{crit}.

Potential lubrication behavior of Pickering W/W emulsions

As highlighted previously, lubrication performance of DEX–PEG–based W/W emulsions stabilized by collagen nanofibrils was first reported a few years ago [11]. This system showed a μ in the range of 0.003–0.011. This superior lubrication performance was attributed to the following possible factors. (i) The collagen nanofibrils raised the viscosity of the system. (ii) Stable water droplets were trapped in the tribological gap instead of being squeezed out, providing aqueous lubrication. You et al. also reported that the W/W emulsion composed of gelatinized starch (G)-kappa-carageenan (κC) showed a lower friction coefficient than the corresponding individual components (Figure 3). The enhanced lubrication could be attributed to the emulsion structure, wherein the droplets could be entrained in the contact zone, flatten, forming a hydration layer to bear the surface load [25]. (iii) The collagen absorbed onto the contact surfaces, imparting boundary lubrication and also retaining the W/W droplets in the contact zone.

These potential factors are illustrated in Figure 4. In the boundary regime at low speeds/shear rates, for W/W emulsions containing microgels, the microgel particles could also enter the contact zone [18]. The adhesive properties of microgels therefore might not only ensure droplet stability but also boundary lubrication themselves. As the speed increases to reach the mixed and hydrodynamic regimes, string-like phases might be formed and contribute to the establishment of a viscous fluid film promoting surface separation and hydrodynamic lubrication [83,84]. It has been reported that W/W emulsions, formed by PEO and DEX with protein microgels as stabilizers, under shear showed filament formation (Figure 2b) [15]. Moreover, adhesive microgels at the interface not only ensure droplet stability but also exhibit the capability to adsorb onto surfaces.

Figure 3



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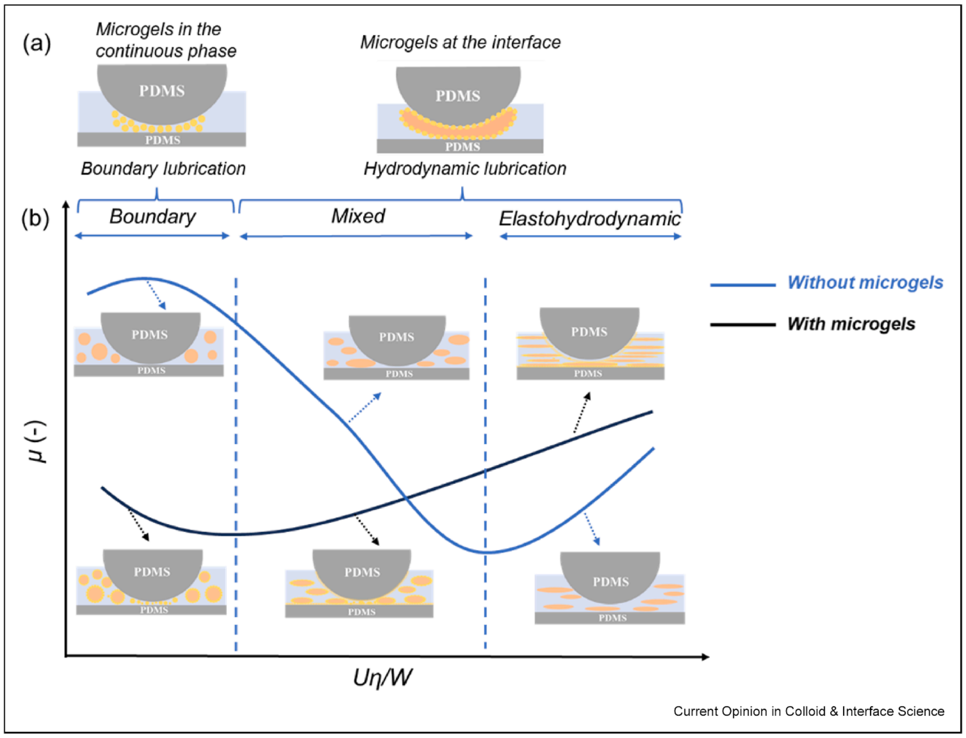
Friction coefficient (μ) as a function of entrainment speed (U) of W/W emulsions with low biopolymer concentration (●; 1.0 wt% gelatinized corn starch [GS] + 0.1 wt% kappa-carrageenan [κC]) and individual components: 1.0 wt% GS (●) and W/W emulsions with high biopolymer concentration (▲; 3.0 wt % GS + 0.3 wt% κC) and individual components: 3.0 wt% GS (▲), 0.3 wt% κC (▲). Permission taken from Wiley [25].

Figure 4



Lubrication performance of W/W emulsions in hydrophobic polydimethylsiloxane (PDMS) ball-on-disc contact. (**a**) Graphical depiction of hypothesized mechanism of microgels at interface versus microgels in the continuous phase in Pickering W/W emulsions for lubrication. (**b**) Possible Stribeck curve and schematic illustration of the lubrication performance of W/W emulsions with/without microgels.

You et al. [26] have demonstrated that both WPMs and PPMs exhibit effective adsorption onto hydrophobic PDMS surfaces. The study of Tea et al. [15] indicates that WPM can stay at the PEO—DEX interface during shear (Figures 2c and 2d), so the microgels might act as 'legs' to keep the droplet strings attached to the tribological surfaces, giving hydrodynamic lift and a decrease in friction.

To gain a deeper understanding of the mechanisms governing lubrication performance, advanced experimental techniques such as tribometry coupled with fluorescence microscopy [85—87] can be used to visualize droplet deformation and structural rearrangements during entrainment. When combined with white-light interferometry, these approaches also allow for measurement of film thickness, facilitating estimation of local shear rates within the contact region [88]. However, it is important to note that these techniques have not yet been widely applied to W/W emulsion systems. Their implementation holds great potential for uncovering how morphological evolution of the multiphasic systems correlates with their tribological properties in distinct lubrication regimes.

Conclusion and future perspectives

Pickering W/W emulsions have significant potential for controlling friction in various applications. However, for the stabilization of these emulsions, it is generally necessary to have a good level of particle coverage at the W/W interface, and the properties of these particles and environmental factors affecting their adsorption and aggregation will also affect the overall tribological performance. At the same time, excess particles present in either of the aqueous phases can significantly affect the rheology of these phases, which in turn affects hydrodynamic lubrication. If the water droplets are stable and small enough, they can also enter the tribological gap and influence friction or at high-enough shear rates distort into string-like structures. The effects of the latter on friction, and on admixture with stabilizing particles, for example, microgels, are far from clear. In addition, lots of other outstanding questions remain, such as do the tribological stresses affect particle desorption from the interface and coalescence of the water droplets? Also, does the adhesive nature of microgel improve entrainment in the contact zone or jam the droplets leading to increased friction? Consequently, although these systems may offer many advantages in terms of their biocompatibility for applications in medicines and foodstuffs, much more work needs to be done using systematic studies to understand and optimize Pickering W/W systems and develop theoretical framework to have meaningful application in the field of aqueous lubricants, for example, in biomedical, food, and allied soft matter sectors.

Declaration of competing interest

None.

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Data availability

No data was used for the research described in the article.

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