Supporting Information

Emulsion Microgel Particles as High Performance Bio-Lubricants

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CONTENT

S1. Flow curves of 20 wt% starch emulsion microgel particles

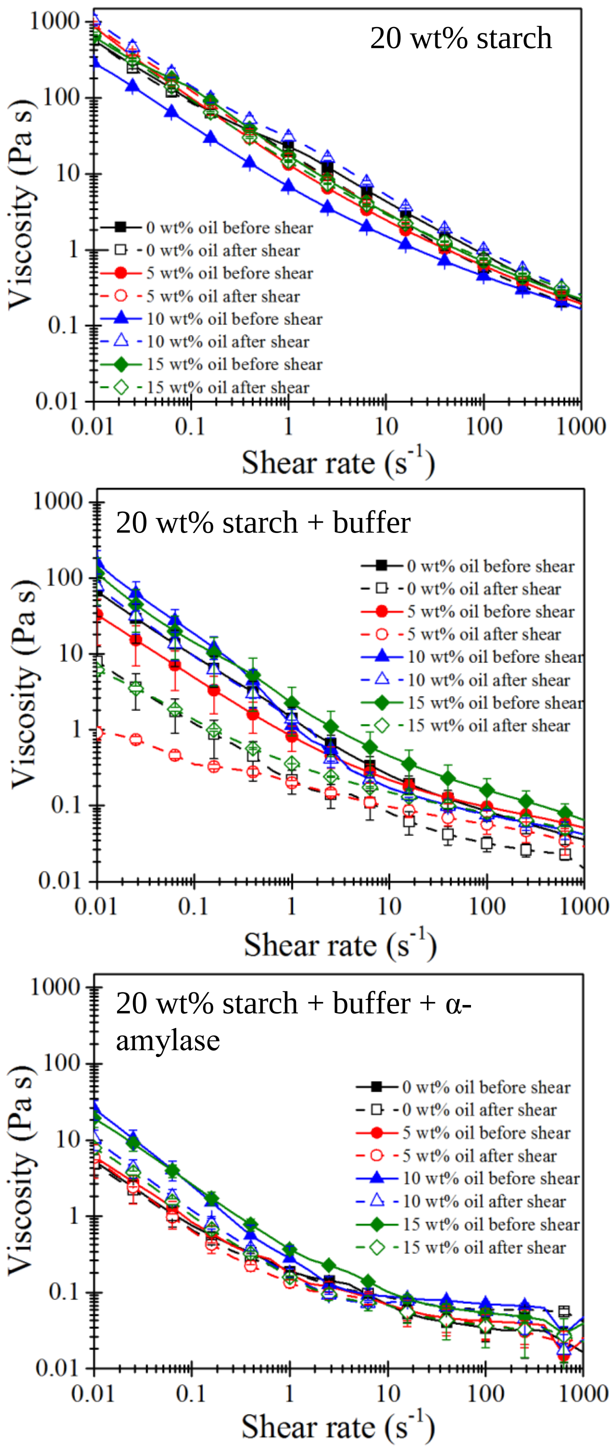

Figure S1. Flow curves of the emulsion microgel particles produced from 20 wt% starch.

S2. Friction coefficient of the emulsion at high entrainment speed

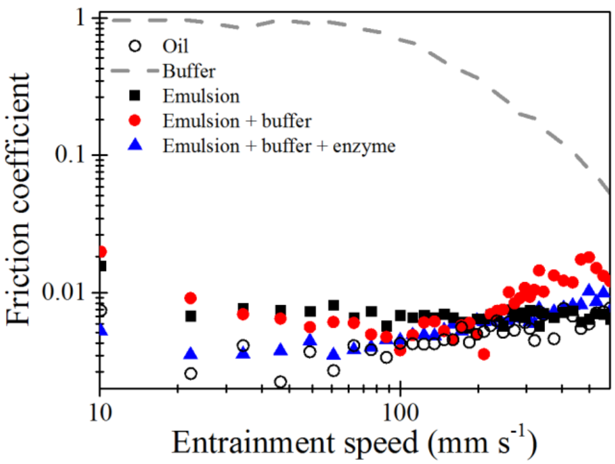

Figure S2. Coefficient of friction as function of entrainment speed ($10 < \overline{U} < 100$ mm s^{-1}) for sunflower oil, buffer with α-amylase and OSA starch stabilized emulsion in absence or presence of buffer and/or α-amylase subjected to an entrainment speed of 10 to 500 mm s^{-1}, a normal load of 2 N and at 37 °C

S3. Statistical analysis between the friction coefficients of buffer, sunflower oil and emulsion under different conditions and different entrainment speed

Table S3. Friction coefficient measured at 3 and 50 mm s^{-1}, 37 °C and 2 N of buffer, sunflower oil and emulsions under different conditions, column shown with means values ± standard deviations with same superscript letter are significantly different ($p < 0.05$).

Entrainment speed (mm s^{-1})	Coefficient of friction	
	3	50
Buffer	0.788 ±0.033 ^{a,b,c,d,e}	0.912 ±0.238 ^{a,b,c,d,e}
Sunflower oil	0.013 ±0.005 ^{b,a}	0.004 ±0.001 ^{b,a}
Emulsion (40 wt% oil)	0.043 ±0.016 ^{c,a}	0.007 ±0.004 ^{c,a}
Emulsion + buffer (20 wt% oil)	0.042 ±0.008 ^{d,a}	0.056 ±0.001 ^{d,a}
Emulsion + buffer + α-amylase (20 wt% oil)	0.006 ±0.001 ^{e,a}	0.004 ±0.001 ^{e,a}

S4. Friction coefficient of the emulsion microgel particles at high entrainment speed

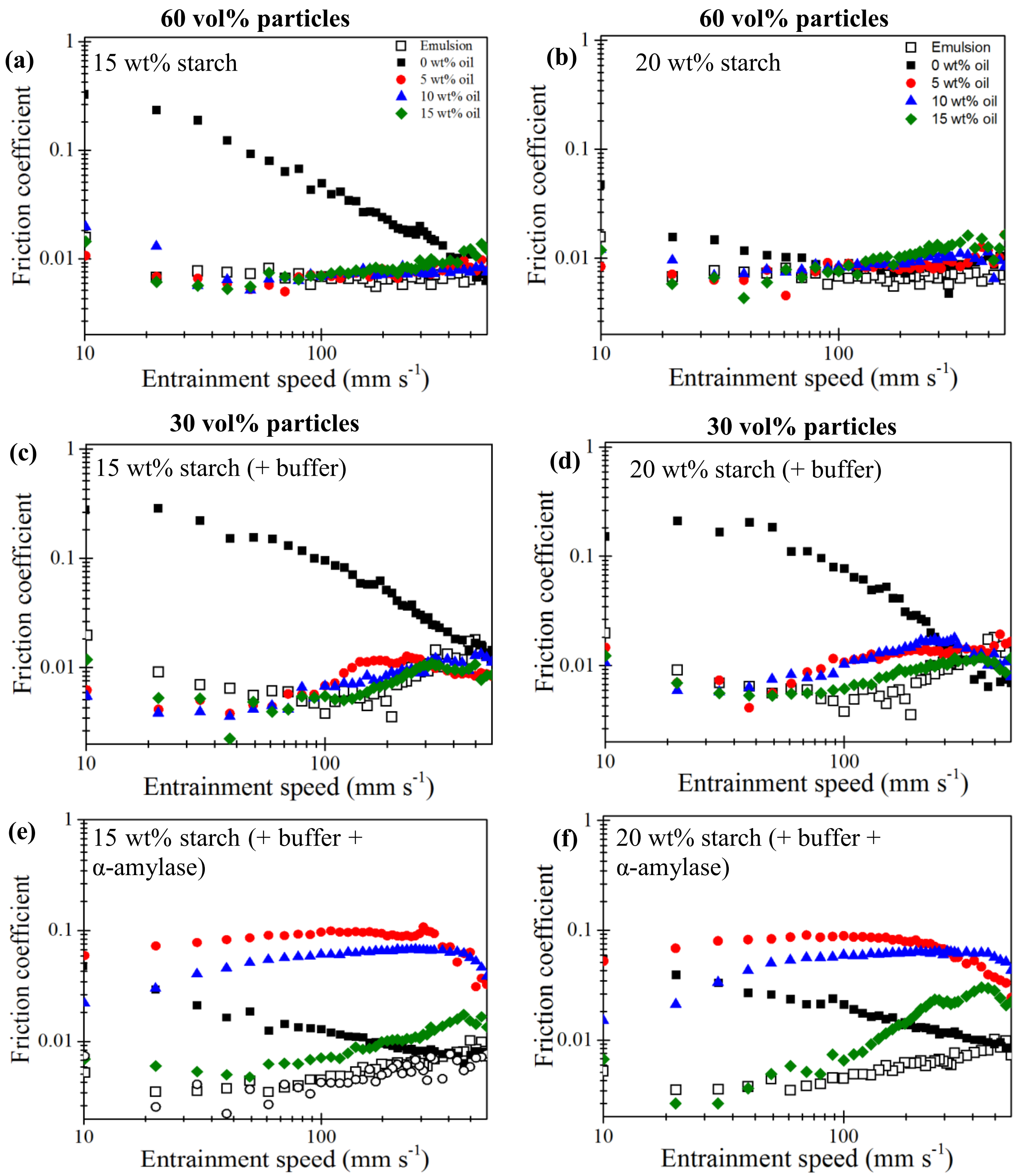

Figure S4. Coefficient of friction as function of entrainment speed of starch microgel particles encapsulating different oil content measured at 2 N and 37 °C in absence of buffer and α-amylase (a and b); in presence of buffer (50:50 w/w) without α-amylase (c and d); in presence of buffer (50:50 w/w) with α-amylase (e and f). Controls are the OSA stabilised-emulsion at the different conditions.

S5. Statistical analysis between the friction coefficients of buffer, sunflower oil, emulsion and emulsion microgel particles under different conditions at $\overline{U}$ = 3 mm s^{-1}

Table S5. Friction coefficient measured at 3 mm s^{-1}, 37 °C and 2 N of the starch based particles under different conditions, column shown with means values ± standard deviations with same superscript letter are significantly different ($p < 0.05$).

Physiological Condition	Coefficient of friction		
	No buffer + α-amylase	+ buffer	+ buffer + α-amylase
Buffer	0.788 ±0.033 ^{a,b,c,d,e,f,g,h,I,j,k}	0.788 ±0.033 ^{a,b,c,d,e,f,g,h,I,j,k}	0.788 ±0.033 ^{a,b,c,d,e,f,g,h,I,j,k}
Sunflower oil	0.013 ±0.005 ^{b,a,d,h}	0.013 ±0.005 ^{b,a,d,h}	0.013 ±0.005 ^{b,a,d,h}
Emulsion (40 wt% oil)	0.043 ±0.016 ^{c,a,d,h}	0.042 ±0.008 ^{c,a,d,h}	0.006 ±0.001 ^{c,a,d,h}
15 wt% starch + 0 wt% oil	0.428 ±0.107 ^{d,a,b,c,e,f,g,h,i,j,k}	0.287 ±0.077 ^{d,a,b,c,e,h,i,j,k}	0.054 ±0.005 ^{d,a,b,c,f,j,k}
15 wt% starch + 5 wt% oil	0.026 ±0.007 ^{e,a,d,h}	0.015 ±0.003 ^{e,a,d,h}	0.031 ±0.001 ^{e,a}
15 wt% starch + 10 wt% oil	0.101 ±0.009 ^{f,a,d}	0.014 ±0.017 ^{f,a,d,h}	0.012 ±0.001 ^{f,a,d,h}
15 wt% starch + 15 wt% oil	0.022 ±0.010 ^{g,a,d,h}	0.015 ±0.009 ^{g,a,d,h}	0.017 ±0.009 ^{g,a,h}
20 wt% starch + 0 wt% oil	0.166 ±0.028 ^{h,a,b,c,d,e,g,I,j}	0.188 ±0.110 ^{h,a,b,c,d,e,i,j,k}	0.026 ±0.007 ^{h,a,b,c,i,j,k}
20 wt% starch + 5 wt% oil	0.021 ±0.003 ^{i,a,d,h}	0.054 ±0.015 ^{i,a,d,h}	0.024 ±0.001 ^{i,a,h}
20 wt% starch + 10 wt% oil	0.022 ±0.016 ^{j,a,d,h}	0.032 ±0.021 ^{j,a,d,h}	0.012 ±0.000 ^{j,a,d,h}
20 wt% starch + 15 wt% oil	0.061 ±0.033 ^{k,a,d}	0.055 ±0.018 ^{k,a,d,h}	0.014 ±0.001 ^{k,a,d,h}

S6. Statistical analysis between the friction coefficients of buffer, sunflower oil, emulsion and emulsion microgel particles under different physiological conditions at $\overline{U}$ = 50 mm s^{-1}

Table S6. Friction coefficient measured at 50 mm s^{-1}, 37 °C and 2 N of the starch based particles under different conditions, column shown with means values ± standard deviations with same superscript letter are significantly different ($p < 0.05$).

Physiological Condition	Coefficient of friction		
	No buffer + α-amylase	+ buffer	+ buffer + α-amylase
Buffer	0.912 ±0.238 ^{a,b,c,d,e,f,g,h,I,j,k}	0.912 ±0.238 ^{a,b,c,d,e,f,g,h,I,j,k}	0.912 ±0.238 ^{a,b,c,d,e,f,g,h,I,j,k}
Sunflower oil	0.004 ±0.001 ^{b,a}	0.004 ±0.001 $^{b,a\ d,h}$	0.004 ±0.001 ^{b,a,}
Emulsion (40 wt% oil)	0.007 ±0.004 ^{c,a}	0.056 ±0.001 ^{c,a,h}	0.004 ±0.001 ^{c,a}
15 wt% starch + 0 wt% oil	0.093± 0.014 ^{d,a}	0.156 ±0.015 ^{d,a,b,e,f,g,I,j,k}	0.019 ±0.006 ^{d,a}
15 wt% starch + 5 wt% oil	0.005 ±0.001 ^{e,a}	0.005 ±0.001 ^{e,a,d,h}	0.086 ±0.006 ^{e,a}
15 wt% starch + 10 wt% oil	0.005 ±0.002 ^{f,a}	0.004 ±0.001 ^{f,a,d,h}	0.051 ±0.001 ^{f,a}
15 wt% starch + 15 wt% oil	0.006 ±0.001 ^{g,a}	0.005 ±0.001 ^{g,a,d,h}	0.005 ±0.001 ^{g,a}
20 wt% starch + 0 wt% oil	0.011 ±0.002 ^{h,a}	0.186 ±0.070 ^{h,a,b,c,e,f,g,i,j,k}	0.026 ±0.007 ^{h,a}
20 wt% starch + 5 wt% oil	0.086 ±0.006 ^{i,a}	0.006 ±0.001 ^{i,a,d,h}	0.083 ±0.003 ^{i,a}
20 wt% starch + 10 wt% oil	0.051 ±0.001 ^{j,a}	0.008 ±0.003 ^{j,a,d,h}	0.050 ±0.001 ^{j,a}
20 wt% starch + 15 wt% oil	0.005 ±0.001 ^{k,a}	0.005 ±0.001 ^{k,a,d,h}	0.005 ±0.001 ^{k,a}

S7. Statistical analysis between the friction coefficients of emulsion microgel particles containing different oil content under physiological degradation at $\overline{U}$ = 3 mm s^{-1}

Table S7. Friction coefficient measured at 3 mm s^{-1}, 37 °C and 2 N of the starch based particles with different oil contents, column shown with means values ± standard deviations with same superscript letter are significantly different ($p < 0.05$).

Oil content (wt%)	Coefficient of friction			
	0	5	10	15
15% Starch no buffer	0.428 ±0.107 $^{a, c, d, e, f}$	0.026 ±0.007 $^{a, e}$	0.101 ±0.009 $^{a, b, c, d, e, f}$	0.022 ±0.010 ^{a}
15% Starch + buffer	0.287 ±0.077 $^{b, a, c, f}$	0.015 ±0.003 $^{b, c, e}$	0.014 ±0.017 $^{b, a}$	0.015 ±0.009 $^{b, d}$
15% Starch + buffer + α-amylase	0.054 ±0.005 $^{c, a, b}$	0.031 ±0.001 $^{c, b, e}$	0.012 ±0.001 $^{c, a}$	0.017 ±0.009 ^{c}
20% Starch no buffer	0.166 ±0.028 $^{d, a}$	0.021 ±0.003 $^{d, e}$	0.022 ±0.016 $^{d, a}$	0.061 ±0.033 $^{d, b, f}$
20% Starch + buffer	0.188 ±0.110 $^{e, a}$	0.054 ±0.015 $^{e, a, b, c, d, f}$	0.032 ±0.021 $^{e, a}$	0.055 ±0.018 ^{e}
20% Starch + buffer + α-amylase	0.070 ±0.023 $^{f, a, b}$	0.024 ±0.001 $^{f, e}$	0.012 ±0.000 $^{f, a}$	0.014 ±0.001 $^{f, d}$

S8. Statistical analysis between the friction coefficients of emulsion microgel particles containing different oil content under physiological degradation at $\overline{U}$ = 50 mm s^{-1}

Table S8. Friction coefficient measured at 50 mm s^{-1}, 37 °C and 2 N of the starch based particles with different oil contents, column shown with means values ± standard deviations with same superscript letter are significantly different ($p < 0.05$).

Oil content (wt%)	Coefficient of friction			
	0	5	10	15
15% Starch no buffer	0.093 ±0.014 $^{a, e}$	0.005 ±0.001 $^{a, c, f}$	0.005 ±0.002 $^{a, c, f}$	0.006 ±0.001 ^{a}
15% Starch + buffer	0.156 ±0.015 $^{b, c, d, e}$	0.005 ±0.001 $^{b, c, f}$	0.004 ±0.001 $^{b, c, f}$	0.005 ±0.001 ^{b}
15% Starch + buffer + α-amylase	0.019 ±0.006 $^{c, b, e}$	0.086 ±0.006 $^{c, a, b, d, e}$	0.051 ±0.001 $^{c, a, b, d, e}$	0.005 ±0.001 ^{c}
20% Starch no buffer	0.011 ±0.002 $^{d, b, e}$	0.008 ±0.001 $^{d, c, f}$	0.008 ±0.000 $^{d, c, f}$	0.006 ±0.000 ^{d}
20% Starch + buffer	0.186 ±0.070 $^{e, a, c, d, f}$	0.006 ±0.001 $^{e, c, f}$	0.008 ±0.003 $^{e, c, f}$	0.005 ±0.001 ^{e}
20% Starch + buffer + α-amylase	0.026 ±0.007 $^{f, b, e}$	0.083 ±0.003 $^{f, a, b, d, e}$	0.050 ±0.001 $^{f, a, b, d, e}$	0.005 ±0.001 ^{f}

S9. Particle size distribution of 20 wt% starch emulsion microgel particles

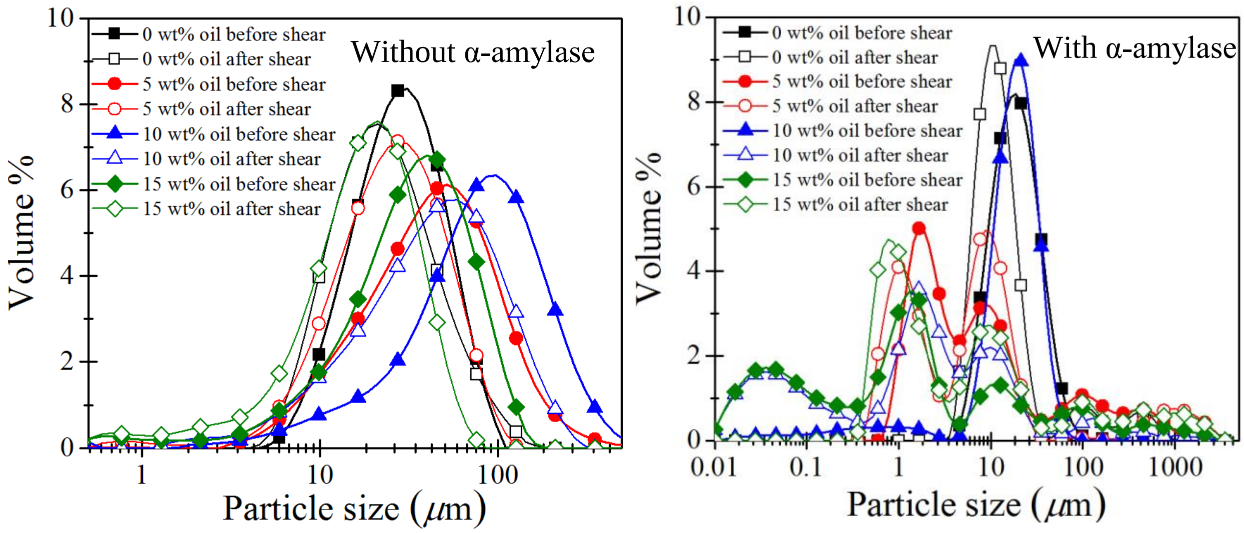

Figure S9. Particles size distribution of the emulsion microgel particles produced from 20 wt% starch before and after tribological shear.

S10. Theoretical analysis of the relative indentation and drag force of the different samples

In the mixed lubrication regime, the total load W_T is supported by both the asperity contact and the lubricant (i.e., emulsion or emulsion microgel particles) separating some regions of the surfaces. According to Otero, et al. [1] the friction coefficient μ, in the mixed regime, can be expressed in terms of the friction coefficient given by the lubricant μ_L and the one given by the asperities μ_B (Equation 1):

$$\mu = {f_\lambda}^{1.2}\mu_L + (1 - f_\lambda)\mu_B \quad (1)$$

where, $f\lambda$ is defined as the load carried by each component, $W_L = f\lambda\ W_T$ for the lubricant and $W_B = (1\text{-}f\lambda)W_T$ for the asperities. From Figure 3.a and Figure 5., it is noticeable that the friction coefficients of all lubricants (i.e., sunflower oil, emulsions, starch particles and emulsion microgel particles) (μ_L) are at least two order of magnitude lower compared to the ones obtained with the buffer (μ_B). Therefore, the term at the right side of Equation 1 can be neglected. Under this assumption, the load supported by the lubricant in terms of friction coefficients can be expressed by Equation 2:

$$W_L = \frac{\mu_B - \mu}{\mu_B} W_T \quad (2)$$

In order to understand the physical properties of the lubricant partially separating the contact surfaces a mechanical analysis of the emulsion droplets, starch and emulsion microgel particles in the contact area was introduced. From the Hertz theory at the contact point, the radius of contact a_H and the indentation of the contact δ can be obtained from Equation 3 and 4 for a point of contact supporting a load W, respectively:

$${a_H}^3 = \frac{3}{4}\frac{WR^*}{E^*} \quad (3)$$

and

$$\delta = \frac{{a_H}^2}{R^*} - f(\frac{a_H}{R})\frac{W}{\pi R^* E^*(1-\nu^2)} \quad , \tag{4}$$

with $f\left(\frac{a_H}{R}\right) = \frac{2(1+\upsilon)}{\left(4+\left(\frac{a_H}{R}\right)^2\right)^{3/2}} + \frac{(1-\upsilon^2)}{\left(4+\left(\frac{a_H}{R}\right)^2\right)^{1/2}}$

R^*, ν and E^* represent the reduced radius, Poisson ratio and reduced elastic modulus of the contacts formed by the particles and the PDMS contact surfaces, E^* was obtained from $E^* = \left(\frac{1-\upsilon^2}{E'} + \frac{1-\upsilon^2}{E''}\right)^{-1}$ where *E'* and *E''* are the reduced elastic modulus of PDMS and particles, respectively. *E''* was estimated from the elastic compression[2] $E'' = 2G'_f(1+\nu)$, where G'_f is the shear elastic modulus of the emulsion droplets or particles. In the case of the emulsion droplets [3-4], G'_f was obtained from: $G'_f = \frac{2\gamma}{R}$, where γ is the interfacial tension of the emulsion droplets stabilised by the OSA starch, measured previously at $\gamma = 27$ mN m^{-1} [5] and R is the radius of the particle. In the case of the particles, G'_f was obtained from measurements of the elastic modulus of the gels from which they were prepared [6].

The load (W_L) was assumed to be supported by the emulsion droplets or particles consequently, the load supported by each emulsion droplets (W_P) could also be estimated. This was achieved by relating the number of particles, forming a monolayer, inside the contact (N_p) with an effective fraction of particles ϕ_p covering the contact area:

$$N_p = \frac{\phi_p {a_{TP}}^2}{R^2}$$

where a_{TP} is the Hertz contact radius between the PDMS ball and disc, calculated at 2.07 mm, using Equation 3.

So the load per particles can be written as (Equation 5):

$$W_P = \frac{W_L}{N_P} = \frac{1}{\phi_p}\frac{W_T R^2}{{a_{TP}}^2} \tag{5}$$

Using this last expression and combining Equations 3 and 4, the relative indentation for a monolayer of particles in the contact can be expressed as (Equation 6):

$$\frac{\delta}{R} = \left(\frac{a_H}{R}\right)^2 - \frac{4}{3\pi(1-\upsilon^2)}\left(\frac{a_H}{R}\right)^3 f\left(\frac{a_H}{R}\right) \qquad (6)$$

where the ratio a_H/R is independent of R and relates the relative indentation to the fraction of surface covered by particles ϕ_p independently of the particle radius (Equation 7):

$$\frac{a_H}{R} = \left(\frac{3W_L}{4\phi_p E^* a_{TP}{}^2}\right)^{1/3} \qquad (7)$$

S11. References

(1) Otero, J. E.; Ochoa, E. d. l. G.; Tanarro, E. C.; López, B. d. R. Friction Coefficient in Mixed Lubrication: A Simplified Analytical Approach for Highly Loaded Non-Conformal Contacts. *Advances in Mechanical Engineering* **2017,** *9* (7), 1687814017706266, DOI: 10.1177/1687814017706266.
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(3) Torres, O.; Murray, B.; Sarkar, A. Emulsion Microgel Particles: Novel Encapsulation Strategy for Lipophilic Molecules. *Trends in Food Science & Technology* **2016,** *55*, 98-108, DOI: http://dx.doi.org/10.1016/j.tifs.2016.07.006.
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