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**Article:**

Sarkar, A [orcid.org/0000-0003-1742-2122](https://orcid.org/0000-0003-1742-2122), Kanti, F, Gulotta, A et al. (2 more authors) (2017) *Aqueous Lubrication, Structure and Rheological Properties of Whey Protein Microgel Particles*. *Langmuir*, 33 (51). pp. 14699-14708. ISSN 0743-7463

<https://doi.org/10.1021/acs.langmuir.7b03627>

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1 **Aqueous lubrication, structure and rheological properties of**  
2 **whey protein microgel particles**

3

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16

17

## 18 **Abstract**

19 Aqueous lubrication has emerged as an active research area in recent years due to its prevalence  
20 in nature in biotribological contacts and its enormous technological soft-matter applications. In  
21 this study, we designed aqueous dispersions of biocompatible whey-protein microgel particles  
22 (WPM) (10-80 vol%) cross-linked via disulfide bonding and focused on understanding their  
23 rheological, structural and biotribological properties (smooth polydimethyl siloxane (PDMS)  
24 contacts,  $R_a < 50$  nm, ball-on-disk set up). The WPM particles ( $D_h = 380$  nm) displayed shear-  
25 thinning behavior and good lubricating performance in the plateau boundary as well as the mixed  
26 lubrication regimes. The WPM particles facilitated lubrication between bare hydrophobic PDMS  
27 surfaces (water contact angle  $108^\circ$ ), leading to a 10-fold reduction in boundary friction force with  
28 increased volume fraction ( $\phi \geq 65\%$ ), largely attributed to the close packing-mediated layer of  
29 particles between the asperity contacts acting as ‘true surface-separators’, hydrophobic moieties  
30 of WPM binding to the non-polar surfaces and particles employing a rolling mechanism analogous  
31 to ‘ball bearings’, the latter supported by negligible change in size and microstructure of the WPM  
32 particles after tribology. An ultra-low boundary friction coefficient,  $\mu \leq 0.03$  was achieved using  
33 WPM between  $O_2$  plasma-treated hydrophilic PDMS contacts coated with bovine submaxillary  
34 mucin (water contact angle  $47^\circ$ ), and electron micrographs revealed that the WPM particles spread  
35 effectively as a layer of particles even at low  $\phi \sim 10\%$ , forming a lubricating load-bearing film  
36 that prevented the two surfaces from true adhesive contact. However, above an optimum volume  
37 fraction,  $\mu$  increased in HL+BSM surfaces due to the interpenetration of particles that possibly  
38 impeded effective rolling, explaining the slight increase in friction. These effects are reflected in  
39 the highly shear thinning nature of the WPM dispersions themselves plus the tendency for the  
40 apparent viscosity to fall as dispersions are forced to very high volume fractions. The present work

41 demonstrates a novel approach for providing ultra-low friction in soft polymeric surfaces using  
42 proteinaceous microgel particles that satisfy both load bearing and kinematic requirements. These  
43 findings hold great potential for designing biocompatible particles for aqueous lubrication in  
44 numerous soft matter applications.

## 45 **Introduction**

46 Microgel dispersions form an important class of sub-micron to micron-sized, gel-like colloidal  
47 particles that essentially consist of a cross-linked network of polymer molecules.<sup>1</sup> The particles  
48 are swollen by the solvent (e.g., water), and have the ability to swell or de-swell depending upon  
49 the properties of the solvent, the cross-linking density of the polymer and other environmental  
50 conditions. Microgel suspensions have attracted a lot of fundamental and practical research  
51 attention owing to their unique rheological properties, which share the classical signature of both  
52 polymer solutions and ‘hard’ colloidal spheres.<sup>2</sup> These characteristics, together with their high  
53 responsiveness to environmental conditions, high surface area-to-volume ratio as compared to bulk  
54 hydrogel, and surface properties have led to a wide range of technological applications, such as  
55 surface coatings, oil recovery, foods, pharmaceutical and personal care, advanced biomaterials,  
56 lubrication and colloidal stabilizers.<sup>3-13</sup>

57 Recently, tribological characterization has also been employed to assess the application of  
58 microgels for aqueous lubrication.<sup>14</sup> In nature, most biological lubrication systems use an aqueous  
59 medium. Soft biological interfaces, such as the oral cavity, hip joints, respiratory tracts and eyes  
60 rely on aqueous lubricants, such as saliva or food-saliva mixture, synovial fluids, mucosal layer,  
61 or tears, respectively, to reduce sliding friction. However, water on its own is a poor lubricant and  
62 key approaches used in aqueous lubrication have involved grafting of certain amphiphilic block  
63 copolymers,<sup>15, 16</sup> such as polyethylene glycol (PEG) or polyethylene oxide (PEO) and adsorption  
64 of mucin<sup>17</sup> onto bare hydrophobic or plasma-treated hydrophilic polydimethyl siloxane (PDMS  
65 substrates). These materials have demonstrated effective aqueous lubrication, particularly under  
66 solvent conditions where the polymer was stretched out and highly solvated, creating an effective  
67 barrier layer against the bare surfaces to ensure effective boundary lubrication.

68           There have been efforts to understand the aqueous lubrication properties of fluid gels, i.e.,  
69 concentrated dispersions of microgels made up of polysaccharides, such as, agarose,<sup>18, 19</sup> alginate,<sup>20</sup>  
70  $\kappa$ -carrageenan.<sup>21</sup> These studies suggest that particle entrainment was a key determining factor,  
71 which reduced or increased the friction coefficient between the contacting surfaces depending  
72 upon the elasticity of the particles, their size, volume fraction, as well as the surface roughness of  
73 the tribopairs. On the other hand, surfactant-functionalized carbon microspheres of ~450 nm  
74 diameter have demonstrated their efficacy in reducing the friction between two silica surfaces via  
75 a “ball-bearing mechanism” and generating extremely low friction coefficients ( $\mu \approx 0.03$ ) if the  
76 particles are somehow trapped and not squeezed out of the confinement.<sup>22</sup>

77           Thus, aqueous dispersions of microgels could be particularly promising, combining the  
78 lubrication behaviour of the solvent, i.e., taking advantage of the efficiency of the aqueous phase  
79 as lubricant for potential fluid film formation as “surface separator”, as well as the particles, the  
80 latter providing potential “ball-bearing” effects. From a practical viewpoint, aqueous lubrication  
81 properties can be particularly important when considering interactions of microgel particles with  
82 biological environments, such as the oral cavity, where boundary- and mixed-lubrication regimes  
83 come into play and rheological measurements alone cannot completely describe the behaviour of  
84 these particles between the sliding surfaces. To our knowledge, there have been no studies on the  
85 effectiveness of sub-micron sized biopolymeric microgel particles as aqueous lubricants between  
86 soft surfaces that also evaluate the rheological behaviour of such dispersions.

87           In the work described here, biocompatible whey-protein microgel (WPM) particles were  
88 prepared for tribological studies via thermally induced disulphide crosslinking. The size and  
89 structure of the microgels, as well as their bulk shear rheological behaviour as a function of volume  
90 fraction were investigated. To comprehensively compare the lubricating mechanisms and

91 efficiency of the microgel particles at different volume fractions, two tribological contacts based  
92 on hydrophilic and hydrophobic surfaces were considered. Bare hydrophobic and O<sub>2</sub>-plasma-  
93 treated hydrophilic PDMS/PDMS contacts at 37 °C were employed for their resemblance to  
94 wettability of external human skin surfaces (water contact angle > 100 °)<sup>23</sup> and internal mucosa-  
95 coated surfaces (water contact angle ≤ 70 °)<sup>24</sup>, respectively. In the case of the O<sub>2</sub>-plasma-treated  
96 PDMS, the substrate was coated with bovine submaxillary mucin to enhance its relevance to  
97 human oral conditions, where mucin-mediated aqueous lubrication has a crucial impact on oral  
98 health, swallowing, mouthfeel, etc. We hypothesize that the sub-micron sized WPM particles will  
99 act as aqueous “ball bearings” and the lubrication behaviour will be strongly dictated by the  
100 volume fraction of these particles entrained within the tribological contacts, thus contributing to  
101 both kinematic and load bearing properties, respectively. Although there has been one study that  
102 investigated the tribological properties of sub-micron sized poly(N-isopropylacrylamide)-graft-  
103 poly(ethylene glycol) (PNIPAAm-g-PEG) microgels,<sup>14</sup> to the best of our knowledge, this is the  
104 first study that reports the aqueous lubrication behaviour of biocompatible protein-based microgel  
105 particles between soft tribological contacts.

106

## 107 **Experimental Section**

108 **Materials.** Whey protein isolate powder (WPI) containing with ≥90% protein was donated by  
109 Fonterra Limited (Auckland, New Zealand). Phosphate buffer was purchased from Fisher  
110 Chemicals (Loughborough, UK). Analytical grade sodium azide was purchased from Sigma  
111 Aldrich, Gillingham, UK. Bovine submaxillary mucin BSM (Type I-S, M3895) was purchased  
112 from Sigma Aldrich, Dorset, UK. As described by the supplier, BSM contained 9-24% bound  
113 sialic acids and ≤ 2.5% free sialic acids. For the purification, BSM (30 mg/mL) was dispersed in

114 Milli-Q water and dialyzed in a 100 kDa molecular weight cut-off membrane followed by  
115 lyophilization, as described previously.<sup>25</sup> Polydimethylsiloxane (PDMS, trade name Sylgard 184  
116 elastomer kit) was obtained from Dow Corning, Midland, MI, USA. Milli-Q water (water purified  
117 to a resistivity of 18 M Ω.cm by Milli-Q apparatus, Millipore Corp., Bedford, MA, USA) was used  
118 as a solvent unless otherwise specified.

119 **Preparation of aqueous dispersion of whey protein microgel (WPM) particles.** An aqueous  
120 dispersion of whey-protein microgel (WPM) particles was prepared based on a slight  
121 modification of the methods previously described by Sarkar et al.,<sup>4</sup> and Murray and  
122 Phisarnchananan<sup>13</sup> via the disulphide bond-mediated covalent crosslinking of WPI followed  
123 by controlled shearing. Whey protein solution (10 wt%) was prepared by dissolving WPI  
124 powder in 20 mM phosphate buffer at pH 7.0 for 2 hours to ensure complete solubilization.  
125 The WPI solution was heated at 95 °C for 10 minutes and cooled at room temperature for 30  
126 minutes followed by storage at 4 °C overnight to form a WPI gel. The gel was broken into  
127 fragments using a hand blender (HB711M, Kenwood, UK) for 10 minutes before  
128 homogenization using two passes through the Leeds Jet Homogenizer<sup>6</sup> operating at pressure  
129 of 300 ± 20 bar. In the Jet Homogenizer, the ratio of the gel to buffer was adjusted using two  
130 chambers of the jet homogenizer to obtain 80 vol% of WPM particles using equation (1):

131 
$$vol\% = \frac{wt\%}{\rho} = \frac{x}{(x+y)\rho} \times 100\% \quad (1)$$

132 where,  $\rho$  is the density of the gel,  $x$  is the weight of the gel, and  $y$  is the weight of the buffer at pH  
133 7.0. To obtain aqueous dispersions with lower volume fractions of WPM (10-75 vol%), 80 vol%  
134 WPM was diluted with buffer at pH 7.0.

135 **Rheology.** A modular compact rheometer, MCR-302 (Anton Paar, Austria) was used to measure  
136 the viscosity of WPM aqueous dispersions (volume fraction, 10-80 vol%). A cone-and-plate



137 geometry (CP50-2, diameter: 50 mm cone angle: 2°) was used for all measurements at 25 °C. The  
138 rheometer was initialized with 0.208 mm gap between the cone and plate. The shear rate was set  
139 in the range of 0.1 s<sup>-1</sup> to 50 s<sup>-1</sup>, except for the extreme volume fractions (10 and 80 vol%), where  
140 the shear rate ranged from 10<sup>-4</sup> to 10<sup>3</sup> s<sup>-1</sup> at both 25 and 37 °C. For each measurement, a small  
141 amount of sample was pipetted onto the top of the plate, excluding any air bubbles. Silicone oil  
142 was used to prevent evaporation during the measurements. Samples were left in the rheometer for  
143 approximately 5 minutes to achieve a steady state, after which the viscosity was measured. Then,  
144 after a 2 min interval, hysteresis was checked for by measurement at shear rates 50 s<sup>-1</sup> to 0.1 s<sup>-1</sup>.  
145 Although the normal force was nominal set to zero, during measurements it typically fluctuated  
146 between 0.3 and 0.5 N. Viscosity at each concentration was measured three times on separate  
147 samples. Viscosity values for each sample were exported from Anton Paar RheoCompass 1.13  
148 software and analyzed using OriginPro 9.1.

149 **Tribology.** Tribological measurements of the WPM dispersions at different volume fractions (10-  
150 80 vol%) at pH 7 were performed in a Mini Traction Machine (MTM2, PCS instruments, UK)  
151 using a ball-on-disk set up to facilitate a mixed rolling and sliding contact.<sup>26</sup> Smooth hydrophobic  
152 polydimethylsiloxane (PDMS) balls (Ø 19 mm) and discs (Ø 46 mm) with surface roughness (R<sub>a</sub>)  
153 < 50 nm were prepared by mixing base fluid and cross linker (10:1 w/w), as described in the  
154 specification of the Sylgard 184 kit, vacuuming to remove the entrapped air, casting using smooth  
155 stainless steel moulds and subsequently curing overnight at 70 °C.<sup>27</sup>

156 In order to investigate the effect of the surface chemistry on the lubrication properties, two  
157 types of PDMS disks were used that differed in their hydrophobicity. Bare PDMS balls and disk  
158 without any treatment were hydrophobic in nature, reported as HB hereafter. For the preparation  
159 of hydrophilic surfaces, some of the PDMS balls and disks were subjected to oxygen plasma

160 treatment (Zepto, Diener Electronic) at a vapor pressure of 0.4 mbar for 1 min. To avoid loss of  
161 hydrophilicity on storage, these substrates were stored immersed in Milli-Q water and used for  
162 tribology experiments within 4 days. These balls and disk are hereafter referred to as hydrophilic  
163 (HL). The HL balls and disks were coated with 100  $\mu\text{L}$  of BSM solution (30 mg/mL) for 30  
164 minutes followed by drying in  $\text{N}_2$ , as a model to represent a thin film of saliva on the substrate as  
165 observed in oral environments.<sup>28-30</sup> This system is hereafter reported as HL+BSM. A normal load  
166 of 2 N was used, which is equivalent to a maximum Hertzian contact pressure ( $P_{\text{max}}$ ) of 100 kPa.  
167 According to Amontons' rule (1699), the coefficient of friction,  $\mu = F/W$ , where F is friction force  
168 and W is the normal load was measured as a function of sliding speeds starting from high (2000  
169 mm/s) to low (1 mm/s) as well as from low-to-high, at a sliding-to-rolling ratio (SRR) of 50% and  
170 at a fixed load ( $W=2$  N). We only report the data obtained from high-to-low speeds, as the Stribeck  
171 curves showed negligible hysteresis. The entrainment speed of the contact between the surfaces  
172 was calculated according to the following equation (2):

$$173 \quad \bar{U} = \frac{1}{2}(U' + U'') \quad (2)$$

174 where,  $\bar{U}$  is the entrainment speed,  $U'$  is the rolling speed of the ball and  $U''$  is the sliding speed  
175 of the discs. Prior to each test, the surfaces were cleaned with acetone and rinsed with MilliQ water  
176 for the HB balls and disks. One ball-and-disk pair was used each time for an individual experiment  
177 and then discarded. The temperature used for all the tribological tests was  $37\text{ }^\circ\text{C} \pm 1$ , aiming to  
178 mimic human oral conditions. All the experiments were carried out at pH 7 where BSM and WPM  
179 are negatively charged. The mean value of three measurements for each sample was used to plot  
180 the Stribeck curve.

181 **Contact angle of the PDMS disks.** The contact angle ( $\theta$ ) of MilliQ water on the PDMS disks  
182 (hydrophobic, HB; hydrophobic coated with BSM, oxygen plasma treated, HL and oxygen plasma

183 treated coated with BSM, HL+BSM) was measured using a drop-shape analysis device (OCA 25,  
184 Dataphysics UK), which consisted of a computer-controlled automatic liquid deposition system  
185 and a computer-based image processing system. The measuring range of the apparatus for contact  
186 angle was 0-180° with a resolution of  $\pm 0.1^\circ$  and each reported value is an average of more than  
187 five independent measurements. Typical measurement error was less than 2°. A 500  $\mu\text{L}$  volume  
188 of MilliQ water was used, produced via a straight needle of 0.52 mm outer diameter and 0.26 mm  
189 internal diameter, to form a sessile drop. The temperature of the chamber during the tests was at  
190 20 °C to reduce evaporation of the liquid.

191 **Particle size.** The mean hydrodynamic diameter ( $D_h$ ) of the WPM particles before (25 °C) and  
192 after subjecting 10 vol% to tribological stress (at 37 °C) was measured via dynamic light scattering  
193 (Zetasizer, Nano ZS series, Malvern Instruments, Worcestershire, UK), equipped with a 4 mW  
194 He/Ne laser (wavelength = 633 nm). Sizing was performed (at 25 °C) at 10 s intervals in disposable  
195 plastic cuvettes (ZEN 0040) using non-invasive backscattering at a detection angle of 173 °.  
196 Measurements of the WPM particle size were based on a relative refractive index of 1.150, i.e.  
197 assuming a refractive index of WPI (1.53) to 1.33 for the aqueous phase. The absorbance value of  
198 the WPM particles was set at 0.001.

199 **Confocal scanning laser microscopy (CLSM).** The microstructure of 10 vol% dispersions of  
200 WPM particles before and after subjecting to tribological stress (at 37 °C) was studied using a  
201 Zeiss LSM 700 confocal microscope (Carl Zeiss MicroImaging GmbH, Jena, Germany). Fast  
202 Green (1 mg  $\text{mL}^{-1}$  in Milli-Q water, 1:100, v/v) was used to stain WPM (He-Ne laser with an  
203 excitation line at 633 nm). About 10  $\mu\text{L}$  of WPM before and after the tribology experiment was  
204 mixed with 10  $\mu\text{L}$  of Fast Green for 15 min and imaged using a concave slide at a 63×  
205 magnification.

206 **Scanning electron microscopy (SEM).** In order to directly visualize the interaction of PDMS  
207 surfaces with WPM particles, SEM observations were carried out using a FEI Quanta 200F FEG  
208 microscope (FEI Company, Eindhoven, Netherlands). A small portion of the PDMS disk (HB or  
209 HL+BSM coated) in the presence and absence of WPM particles (10 vol%), before and after being  
210 subjected to tribological shear at 37 °C, were cut and mounted on 13 mm diameter pin stubs and  
211 coated with platinum (5 nm thick) in a Cressington 208HR sputter coater. The samples were  
212 imaged at 5 kV at 50,000 and 5,000 × magnification.

213

## 214 **Results and Discussion**

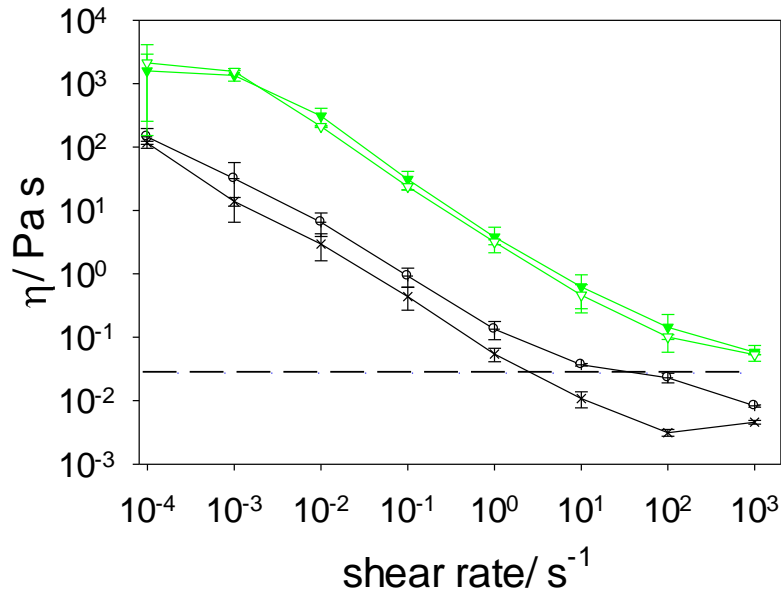
215 **Rheology of aqueous dispersions of WPM particles.** Figure 1 shows the viscosity versus shear  
216 rate for WPM dispersions at 10 and 80 vol%, with the mean and standard deviation plotted for  
217 measurements on 3 separate aliquots of the same dispersion, at 25 and 37 °C. At both temperatures  
218 and volume fractions ( $\phi$ ), extreme shear thinning behavior was observed, with suggestions of  
219 plateau values being reached only at the low and high shear rate limits ( $10^{-4}$  and  $10^3$  s $^{-1}$ ) for  $\phi =$   
220 80% and 10 vol%, respectively. These shear rates represent the lowest and highest values at which  
221 reproducible data could be obtained for these samples with the rheometer used. Despite the data  
222 at  $\phi = 80\%$  apparently suggesting definite low and high shear rate limiting viscosities, it was not  
223 possible to obtain a satisfactory fit of the Cross equation:

$$224 \quad \frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + K\dot{\gamma}^m} \quad (3)$$

225 to the data across the full shear rate range; where  $\eta_{\infty}$  and  $\eta_0$  are the ‘infinite’ and ‘zero’ shear rate  
226 limiting viscosities,  $\dot{\gamma}$  the shear rate,  $K$  and  $m$  arbitrary constants. Flocculated particle networks or  
227 solutions of entangled or weakly cross-linked polymers typically follow this equation and other

228 workers<sup>30</sup> have managed to fit data of other microgels to such models, suggesting that the WPM  
229 rheology is more complex than this. However, the errors in the data at the low shear rates in  
230 particular should be noted, so that it would be unwise to interpret this much further. Of more  
231 relevance here is the fact that the viscosities at such low shear rates are unlikely to be of much  
232 relevance to conditions of the lubrication measurements (most of which will be at much higher  
233 shear rates) or the shear rates operating in the mouth, the latter being generally accepted to lie in  
234 the range of approximately  $0.1$  to  $50 \text{ s}^{-1}$ .<sup>31</sup>

235         It may also be noted that the viscosity curves at  $25$  and  $37$  °C are almost indistinguishable  
236 at  $\phi = 80\%$ , whereas at  $\phi = 10\%$  the viscosities at  $37$  °C are significantly higher than at  $25$  °C for  
237 shear rates  $> 10^3 \text{ s}^{-1}$ . The reasons for this are not clear, but possibly the WPI gel particles swell  
238 slightly at the slightly higher temperature, giving rise to slightly higher viscosities that are more  
239 noticeable at lower  $\phi$ . Viscosity as a function of  $\phi$  at  $25$  °C was measured in more detail. Because  
240 of the difficulties in obtaining reproducible data at very high and low shear rates, plus the limited  
241 relevance of measurements in this range to lubrication, we restricted ourselves to the shear-rate  
242 range of  $0.1$  to  $50 \text{ s}^{-1}$  and did not attempt to find low or high shear-rate limiting viscosities at each  
243  $\phi$ , i.e., viscosities independent of shear rate in the low and high shear rate regions. In addition,  
244 hysteresis effects turned out to be significant – as explained below. Figure 2 compares the viscosity  
245 versus shear rate data in Figure 1 with data obtained for a completely separate preparation of WPI  
246 particle dispersions, over a wider range of  $\phi$ , but probed over a narrower range of shear rate.



247

248 **Figure 1.** Viscosity ( $\eta$ ) of WPM dispersions versus shear rate at vol% ( $\phi$ ) = 10 %, 25 °C (grey +);

249 80 %, 25 °C (green filled triangle); 10 vol%, 37 °C (black ×); 80 vol%, 37 °C (green open triangle).

250 Error bars are shown for repeat sets of measurements on 3 different aliquots the same dispersion.

251 The dashed line shows the viscosity of 70 wt.% glycerol at 25 °C, for comparison with tribological

252 data later.

253

254 The data for the second dispersion at  $\phi = 10$  vol% show very good agreement with the data

255 described in Figure 1 for the first dispersion at the same  $\phi$ , but the viscosities are considerably

256 higher for the second dispersion  $\phi = 80\%$ , for example (error bars have been omitted for clarity,

257 but they are of the same order as in Figure 2 for both sets of dispersions). In this shear-rate range,

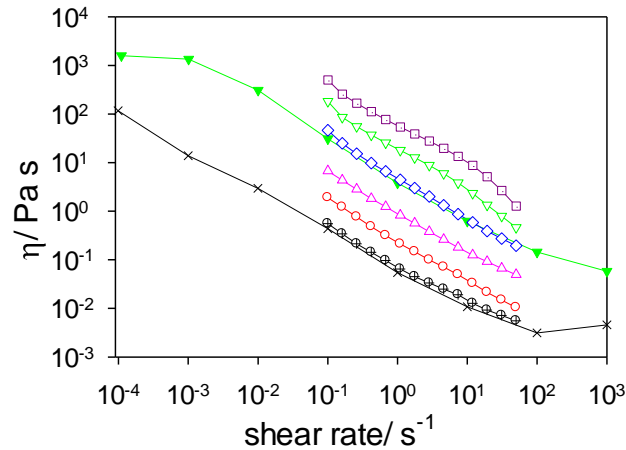
258 the plots of  $\log \eta$  versus  $\log$  shear rate are practically linear (and parallel), enabling fitting each

259 set of data between  $\phi = 10$  to 80 vol% to a simple power law model:

260

$$\eta = K \left( \frac{d\gamma}{dt} \right)^{n-1} \quad (4)$$

261 Equation 4 gave values of  $n$  between 0.73 and 0.90, with all linear regression coefficients  
 262  $> 0.99$  at each  $\phi$ .



263  
 264 **Figure 2.** Comparison of viscosity ( $\eta$ ) versus shear rate at different apparent volume fractions ( $\phi$ )  
 265 for two different preparations of WPM dispersions. Data at  $\phi = 10$  and 80 vol% are for the first  
 266 preparation shown in Figure 1 (grey  $\times$  and green filled triangle, respectively). Data for the second  
 267 preparation (open symbols) are shown at  $\phi = 10$  % (black cross); 20 % (red circle); 50 % (pink  
 268 triangle); 60% (blue diamond); 75% (purple square); 80% (green triangle).

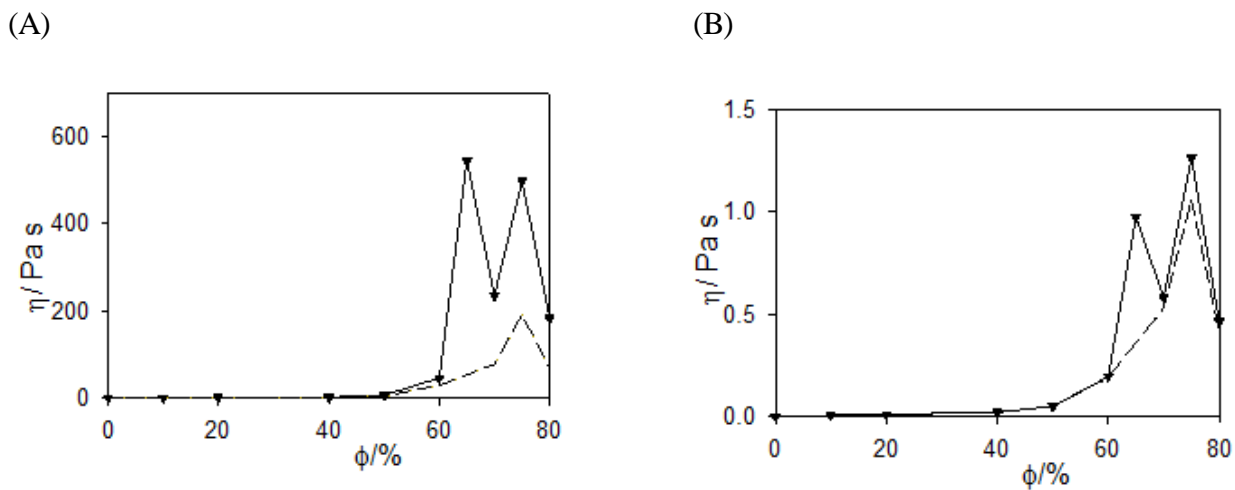
269  
 270 The data of Senff & Richtering<sup>32</sup> for poly (N-isopropylacrylamide) (PNiPAM) microgels  
 271 show a similar value of  $n$  (approximately 0.6) for the most viscous ( $\eta = 3$  Pa s at  $0.1$  s<sup>-1</sup>) system  
 272 they studied, although all their systems showed lower viscosities than the WPM at equivalent  
 273 effective volume fractions and shear rates, giving definite zero shear rate limiting viscosities ( $\eta_0$ )  
 274 at much higher shear rates. This may be a reflection of a greater contribution of microgel particle  
 275 aggregation to  $\eta$  in the case of the WPM particles. We note that in earlier work<sup>13</sup> on WPM  
 276 rheology, a strong dependence of WPM dispersion rheology on pH was noted, attributed to

277 changes in the protein charge as a function of pH, which resulted in changes in their state of  
278 aggregation. One other curious feature to note in Figure 2 for the second dispersion, is that  $\eta$  at  $\phi$   
279 = 75% is apparently higher than at  $\phi = 80\%$ . Microgel particles are generally accepted as being  
280 compressible to some extent and the maximum packing fractions that can be reached are generally  
281 much higher than for model hard spheres.<sup>33</sup> Such a reversal in viscosity with  $\phi$  is not predicted for  
282 any hard-sphere models. At least part of the reason is explained in Figures 3A and 3B, which  
283 show viscosities measured at  $0.1 \text{ s}^{-1}$  and  $50 \text{ s}^{-1}$ , respectively, at each  $\phi$  where the shear rate was  
284 ramped up (full lines on the Figure 3) and then ramped down (dashed lines in Figure 3), as  
285 described in the Methods section. For clarity, the data points are only shown for the shear rate  
286 ‘up’ curves. It is seen that, at the ‘low’ ( $0.1 \text{ s}^{-1}$ , Figure 3A) or ‘high’ ( $50 \text{ s}^{-1}$ , Figure 3B) shear rates  
287 the viscosity increases extremely steeply with  $\phi$  as  $\phi > 50\%$ , as might be expected as the particles  
288 become more closely packed.

289 Although the viscosities plotted in Figure 3 are not in the Newtonian regime (i.e. shear  
290 thinning), the large increase in  $\eta$  occurs in the region of an assumed volume fraction that is typical  
291 of the effective volume fraction seen in other studies – close to the random close packing limit (64  
292 vol%) of truly hard spheres. However, between  $\phi = 65$  and  $70\%$ , on the viscosity up curves, i.e.,  
293 where the shear rate was being increased, there is a fall in apparent viscosity, followed by an  
294 increase in apparent viscosity at  $\phi = 75\%$  and then another fall at  $\phi = 80\%$ . The latter explains  
295 why the viscosity at 75 vol% is higher than at 80 vol% as discussed above with reference to Figure  
296 2. As discussed by Senff & Richtering<sup>32</sup> and many others, the bulk rheology of microgel particles  
297 as a function of  $\phi$  is a complex and controversial subject, since the spheres are not hard or indeed  
298 have a true surface in the usual sense, since they are particles of a gel network. Thus the surface



299 is expected to be porous and ‘fuzzy’ to some extent, whilst the particles may be deformable, as  
300 already noted, or even be able to interpenetrate to some extent.



301 **Figure 3.** Detailed viscosity ( $\eta$ ) versus apparent volume fraction ( $\phi$ ) at pH 7 (black symbols and/or  
302 lines) at shear rates of (A)  $0.1 \text{ s}^{-1}$  and (B)  $50 \text{ s}^{-1}$ , for the second dispersion referred to in Figure 2.  
303 Data are shown for the shear rate increasing from  $0.1$  to  $50 \text{ s}^{-1}$  (full lines) and the shear rate  
304 decreasing from  $50$  to  $0.1 \text{ s}^{-1}$  (dashed lines).

305  
306 In our case, the calculated  $\phi$  was based on the volume of gel broken up into particles and  
307 the volume of extra added buffer. This completely ignores the possibility of release of aqueous  
308 phase from the gel to the bulk during its disruption into microgel particles, or during the rheology  
309 measurement itself, or any swelling or shrinkage of the particles after their formation. Therefore,  
310 in line with many other studies, it is difficult to be certain of the effective volume fraction of the  
311 particles. However, it is not the purpose here to try and place the rheology of the WPM particles  
312 in the context of all detailed prior work in this area, but just to point out that the particles have  
313 similar characteristics to the behavior observed with other microgel particles.

314 Thus, the apparent increase and decrease in  $\eta$  with  $\phi$  suggest some sort of collapse or  
315 interpenetration of the WPM particles as they are forced and sheared together at these very high  
316 volume fractions, effectively decreasing the  $\phi$ , in other words decreasing the  $\eta$  and/or enhancing  
317 particle aggregation i.e. increasing the  $\eta$ , which might have an influence on their lubrication  
318 behavior. Upon decreasing the shear rate, (the shear down curves) all viscosities are lower than on  
319 the up curve, indicating some irreversible change (at least on the time scale of the measurements).  
320 The up and down shear rates values gradually converge at low  $\phi$ . On the other hand, higher  $\eta$  is  
321 still seen at  $\phi$  at 75 % than 80 % on the shear ‘down’ curve, making the collapse followed by  
322 recovery of  $\eta$  as a function of  $\phi$  even more convincing. It should also be noted that we attempted  
323 to fit each  $\eta$  versus  $\phi$  curve, up to the first fall in  $\eta$ , to the Krieger-Dougherty model of viscosity,  
324 but no value of a maximum volume packing fraction could be found for each curve that would  
325 give convergence. This is perhaps not surprising, given the hysteresis just described, which  
326 emphasizes the fact that the particles cannot be treated as hard spheres, aggregating or not.

327 What the detailed rheology measurements show is that the particles can give very wide  
328 ranging  $\eta$  values as a function of shear and shear history. In addition, high values of  $\eta$  persist after  
329 subjection to fairly high shear rates ( $50 \text{ s}^{-1}$ ) even though the systems are highly shear thinning.  
330 Thus, the particles may aggregate or interpenetrate as a function of shear and volume fraction, but  
331 they are certainly not destroyed completely by subjecting them to these conditions, so this must  
332 occur reversibly to some extent, suggesting the particles are more resilient under the conditions of  
333 shear than suggested by the moduli of the WPI gels from which they are prepared (see  
334 Supplementary Figure 1 for modulus of the whey protein gels from which WPM was prepared).

335

336 **Surface properties and tribology.** To gain insight into the ability of the aqueous dispersions of  
 337 WPM to wet the PDMS surfaces, the water contact angle of PDMS surfaces with and without O<sub>2</sub>-  
 338 plasma treatment was determined. In general, the surface of PDMS is widely accepted as highly  
 339 hydrophobic, with water contact angles reported to lie in the range of 95–110°. <sup>30,34</sup> As shown in  
 340 Table 1, the measured water contact angle of the HB PDMS remained fairly constant, at 108°  
 341 (Table 1). Immediately after plasma treatment, the PDMS substrates became hydrophilic (30°, data  
 342 not shown) due to the conversion of the methyl groups to hydroxyl and carboxyl groups at the  
 343 exposed surface of PDMS, but had a rapid rate of hydrophobic recovery, as reported previously. <sup>34,</sup>  
 344 <sup>35</sup> In about 3 days, the contact angle reached 63° (Table 1) and remained at the same value for up  
 345 to a week.

346 A marked decrease in contact angle ( $p < 0.01$ ) was observed upon coating with BSM in  
 347 the case of HL PDMS, i.e., the coated HL surfaces were significantly more hydrophilic than the  
 348 uncoated HL surfaces (Table 1) suggesting adsorption by mucin. The contact angle was in a similar  
 349 range to previously reported values of PDMS modified with mucin of porcine origin. <sup>30</sup> We  
 350 hypothesize that such low contact angles ( $< 50^\circ$ ) might result in easier wetting of the HL disk  
 351 surfaces by the WPM dispersions. The aqueous dispersions of WPM with high viscosities (Figure  
 352 2), might spread and enable the formation of a lubricating film on the substrate.

353

354 **Table 1.** Contact angles of water droplets measured with the sessile drop method on the different  
 355 PDMS disks with or without plasma treatment and BSM coating.

PDMS Surfaces	Contact angle ( $\theta$ )
HB	108.0 ± 3.0
HL	63 ± 1.0
HL+BSM	47 ± 2.0

356

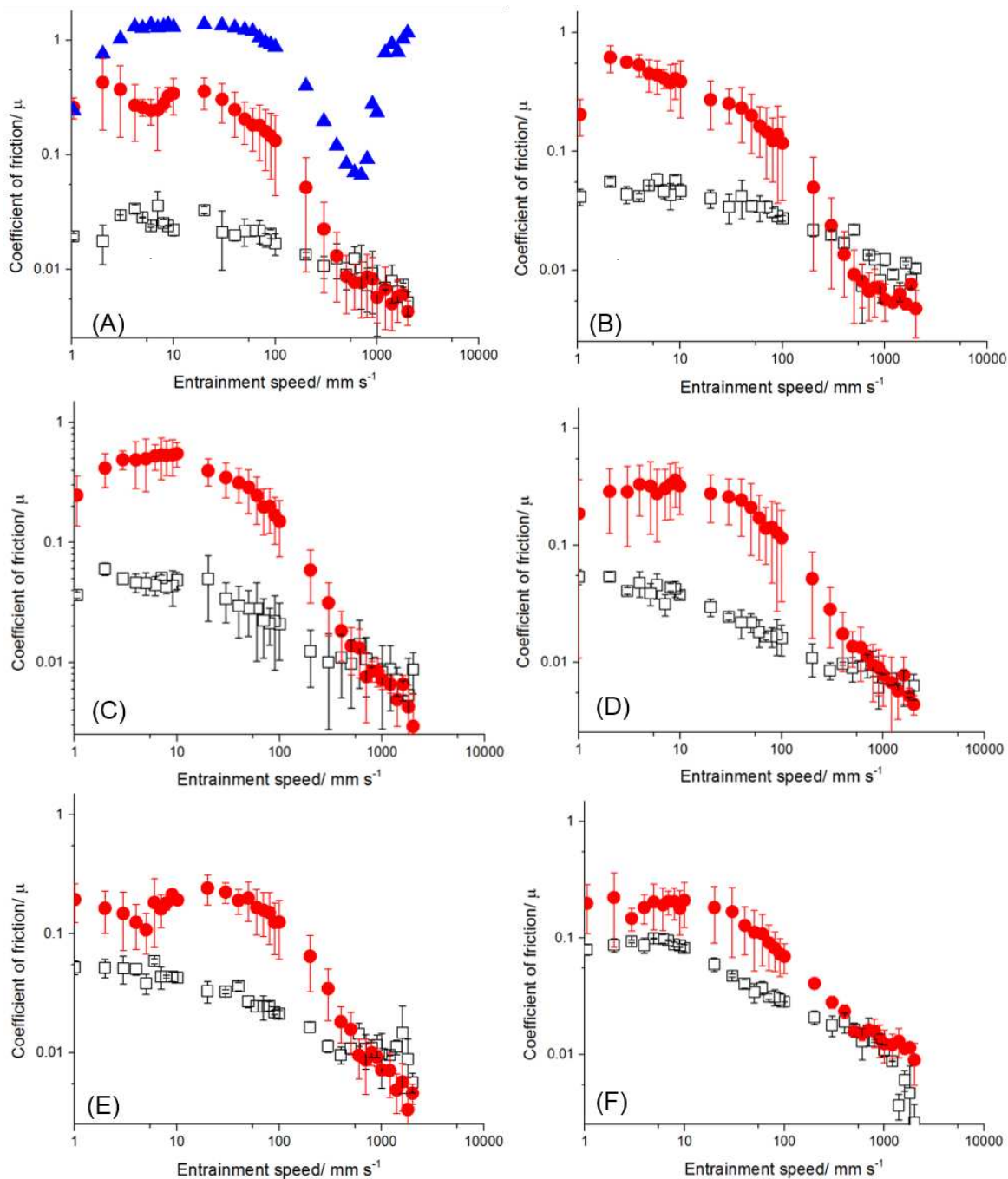
357 To understand the influence of surface hydrophobicity on lubrication properties, HB (108°)  
358 and HL+BSM (47°) disks were used for tribological measurements of aqueous dispersions of  
359 WPM particles (10-80 vol%) at pH 7. Figure 4 shows the lubricating properties of the WPM  
360 particle dispersions with a range of volume fractions as a function of the entrainment speeds with  
361 HB and HL+BSM balls and disks forming the tribological contact surfaces. Based on classical  
362 tribological behavior,<sup>36, 37</sup> one might expect that at the boundary condition, the PDMS ball and the  
363 disk are in dry contact where both the continuous phase and/or the particles are excluded from the  
364 dry contact area. As the disk speed starts to increase, friction is expected to decrease due the  
365 dispersion material filling the gap between the surface asperities in the mixed regime. The  
366 inclusion or exclusion of WPM particles in the gaps between the contacting surfaces will largely  
367 depend on the size of the particles compared to the size of the gaps. As the speed increases further,  
368 the pressure of entrained multilayers of particles plus continuous phase should further push the  
369 two contacting surfaces apart, reducing the friction up to the beginning of hydrodynamic  
370 lubrication regime, where bulk rather than surface properties dominate.

371 The plateau boundary ( $\bar{U} \leq 10$  mm/s) and mixed regime ( $10 < \bar{U} \leq 300$  mm/s) of lubrication  
372 could be clearly identified in all the Stribeck curves (Figure 4). In case of the buffer, the  
373 elastohydrodynamic lubrication regime was also evident ( $300 < \bar{U} \leq 2000$  mm/s). At  $\bar{U} \geq 500$  mm/s,  
374 the friction coefficient ranged between 0.006 to 0.012, irrespective of the WPM concentration and  
375 the hydrophobicity of the substrates used. Considering the relevance to biologically relevant  
376 speeds (e.g., tongue speed), we have only focused on the boundary and mixed lubrication regimes  
377 ( $\bar{U} \leq 300$  mm/s). The Stribeck curve of the phosphate buffer alone resulted in much higher friction  
378 coefficients ( $\mu \geq 1.0$ ) in the boundary and mixed lubrication regimes. Such high interfacial friction  
379 might be due to the buffer being squeezed out from the tribo-contacts as well as the adhesive nature

380 of the PDMS–PDMS interface in the absence of any load-bearing lubricating film.<sup>38</sup> Interestingly,  
381 native whey protein solution (data not shown) gave similar friction coefficients as phosphate  
382 buffer, suggesting no formation of hydration layer between the surfaces. However, the presence of  
383 WPM particles significantly reduced the friction coefficient by up to one decade, especially in  
384 mixed lubrication regime, that is for sliding speeds 10-300 mm/s, even for extremely low volume  
385 fractions (10 vol%) (Figure 4A). The difference in lubrication properties between native whey  
386 protein/ buffer and WPM particles might be attributed to the presence of exposed hydrophobic  
387 moieties in the latter,<sup>6</sup> which possibly conferred adsorption and lubricity on the hydrophobic  
388 PDMS surfaces. Although WPM particles showed fairly effective lubricating properties in the  
389 mixed regime, a sharp loss in the lubricity was seen with decreasing entrainment speed (Figure  
390 4A). This suggests that at the low volume fractions WPM particles were squeezed out from the  
391 contact region at low speeds due to low numbers of hydrophobic moieties anchored to the HB  
392 PDMS surfaces, resulting in partial direct contacts between the HB PDMS surfaces. However,  
393 such boundary friction was reduced at higher volume fractions, which is discussed in more detail  
394 below.

395 Focusing on the lubrication behavior of WPM particles for the bare HB PDMS surfaces  
396 (Figure 4A-F), all the aqueous dispersions of WPM particles (10-80 vol%) showed superior  
397 lubrication properties as compared to the buffer. In particular, a significant ( $p < 0.05$ ) fall in  $\mu$   
398 values to ca. 0.06-0.4 was seen in the low-to-mid speed range ( $p < 0.05$ ).

399



400

401 **Figure 4.** Stribeck curves of aqueous dispersions of WPM particles (10 vol%) (a), 40 vol% (b), 60  
 402 vol% (c), 65 vol % (d), 70 vol% (e) and 80 vol% (f) between smooth HB PDMS tribopairs (●) and  
 403 HL+BSM-coated PDMS tribopairs (□), showing apparent coefficient of friction measured as a  
 404 function of the entrainment speed. Stribeck curve of phosphate buffer is represented by ▲. Error  
 405 bars indicate standard deviation as obtained from three independent measurements.

406 The plateau boundary friction coefficient was almost 6-times lower with WPM,  
407 particularly for  $\phi \geq 65$  vol% WPM (Figure 4 D-F), reaching very low  $\mu$  values (ca. 0.08) compared  
408 to  $\mu \approx 0.5$  at lower  $\phi$  (10-60 vol%) (see Figures 4 A-C).

409 Since the PDMS surface had a  $R_a$  surface roughness of 50 nm, whilst the WPM particles  
410 had diameters 100-500 nm (discussed later), the particles could act as third body filling the gap  
411 between the asperities and result in a rolling motion, i.e., act as sub-micron scale 'ball bearings',  
412 as reported previously by St.Dennis et al.<sup>22</sup> and Alazemi et al.<sup>39</sup> with carbon microspheres of  
413 similar size range ( $450 \pm 20$  nm). Having said this, carbon microspheres are expected to be much  
414 stiffer than WPM particles. Excellent lubricity with higher volume fractions of WPM (Fig. 4D-F)  
415 was also observed in the mixed regime,  $\mu$  reaching values as low as 0.02 at 100 mm/s, i.e., more  
416 than 1 order of magnitude lower than that with 10-40 vol% WPM ( $\mu = 0.4$ ) (Fig. 4A-C). A clear  
417 trend of the dependence of friction force on  $\phi$  ( $>1$  N, 10 to 40 vol%; 0.69 N, 60 vol% and  $\leq 0.3$  N,  
418 65 to 80 vol%) is seen (Figure 5A) in both boundary and mixed lubrication regimes ( $p < 0.05$ ).  
419 Interestingly, the magnitude of the friction forces were fairly similar ( $p > 0.05$ ) in both the mixed  
420 and boundary regimes for higher  $\phi$  samples ( $\geq 65$  vol%).

421 The higher lubricity of 65-80 vol% WPM might be attributed to the higher viscosity of the  
422 dispersions and the higher number of hydrophobic moieties adsorbing to hydrophobic PDMS  
423 surfaces, inhibiting the dispersion from being squeezed out of the gap. Furthermore, the WPM  
424 particles apparently rolled easily between the HB contacts without any jamming even at high  
425 volume fractions of 80 vol%. Thus, the WPM at higher  $\phi$  must replenish the contact region creating  
426 effective hydrated 'monolayer' of particles, filling asperity contacts (of the order of a few hundreds  
427 of nanometers). Figure 5A indicates this schematically, explaining the higher effective lubrication  
428 with PDMS-PDMS.<sup>38</sup> It is noteworthy that the appearance of tribological differences in the two

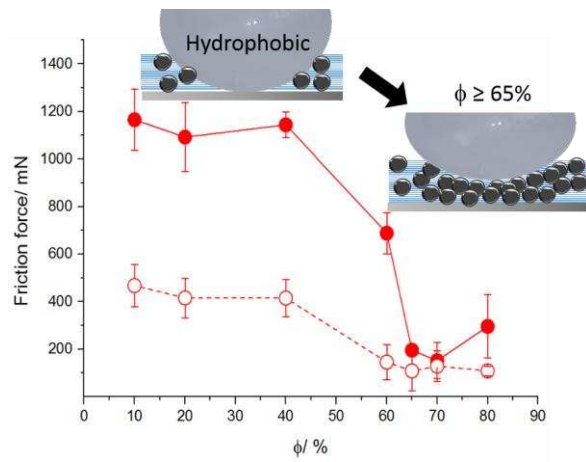
429 volume fraction regions ( $\phi \geq 65\%$  and  $< 65 \text{ vol}\%$ ) is highly congruent with the regions of most  
430 significant increase in  $\eta$  (Figure 2). As close packing is approached, the microgel particles might  
431 associate with each other and/or have some degree of interpenetration, helping to fill in the surface  
432 asperities more effectively, preventing surfaces from coming into contact even in the boundary  
433 condition region.

434 Low volume fractions of WPM showed relatively poor lubricity, with high friction forces  
435 in the mixed lubrication regime, possibly due to insufficient numbers of WPM particles  
436 replenishing the contact region (Figure 5A), as well as lower numbers of particles sticking to the  
437 surfaces. At this point it is also worth comparing the effectiveness of the WPM in reducing friction  
438 with that of a high viscosity Newtonian aqueous solution – namely 70% glycerol. Supplementary  
439 Figure 2 shows the Stribeck curve for 70% glycerol solution and the dashed line on Figure 1 shows  
440 the corresponding viscosity ( $\eta = 27 \text{ mPa s}$ ) of this solution (at  $25 \text{ }^\circ\text{C}$ ) over the same shear rate  
441 range as measured for the WPM dispersions. So at  $\phi = 10 \text{ vol}\%$ , for example, the viscosity of  
442 microgel dispersion is lower than for 70% glycerol above a shear rate of ca.  $1 \text{ s}^{-1}$ , whereas the  
443 viscosity of  $\phi = 80 \text{ vol}\%$  is higher than that of 70% glycerol until ca.  $10^3 \text{ s}^{-1}$ , notwithstanding the  
444 hysteresis observed in Figure 3. Once again, it is hard to compare entrainment speed with shear  
445 rate, but the fact that even the 10 vol% WPM dispersion reduces the friction even more than the  
446 70% glycerol at the highest entrainment speed (see Supplementary Figure 2), whilst the 80 vol%  
447 gives lower friction at all entrainment speeds, points to a combined mechanism with the microgel  
448 particles, i.e., it is not just the viscosity of the dispersion that is important.

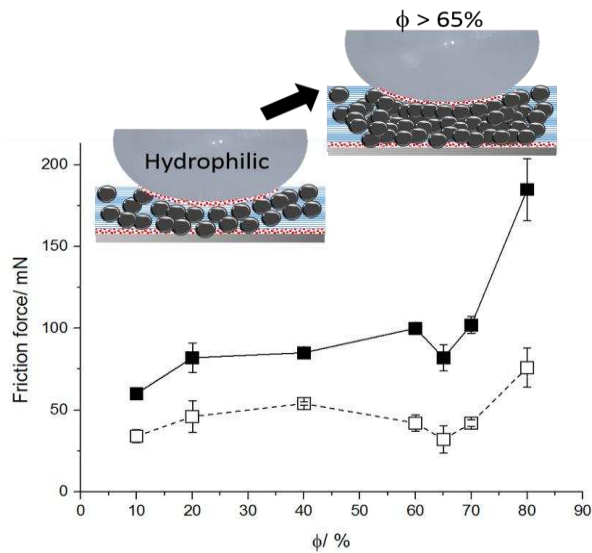
449



(A)



(B)



451 Figure 5. Effect of microgel volume fraction on the friction force of HB PDMS ( $\circ$ ) (A) and  
 452 HL+BSM-coated PDMS ( $\square$ ) (B) in the boundary,  $U=3$  mm/s (closed symbols, solid line) and  
 453 mixed lubrication regimes,  $U=100$  mm/s (open symbols, dashed line) with insets of schematic  
 454 representation of the proposed mechanism of microgel lubrication. Balls and disks are represented  
 455 in grey, microgel particles are presented by small gray spheres, the continuous phase is represented  
 456 by blue lines, BSM is represented by red solid dots in case of HL+BSM PDMS surfaces.

457 Turning to the HL+BSM surfaces in detail, the data in Figure 4 show clear differences in  
458 the Stribeck curves between the bare HB and HL+BSM surfaces, independent of the WPM volume  
459 fraction (Figure 4A-F). In the case of HL+BSM + WPM particles, the friction coefficient was  
460 reduced by more than one order of magnitude as compared to the HB surfaces at entrainment  
461 speeds (1-300 mm/s) for 10-65 vol%. At higher volume fractions (70-80 vol%), the differences in  
462 lubricity between HB and HL+BSM were not significant ( $p > 0.05$ ) in the boundary regime. Thus,  
463 at high volume fractions WPM particles were excellent lubricants independent of hydrophobicity  
464 of the PDMS substrate.

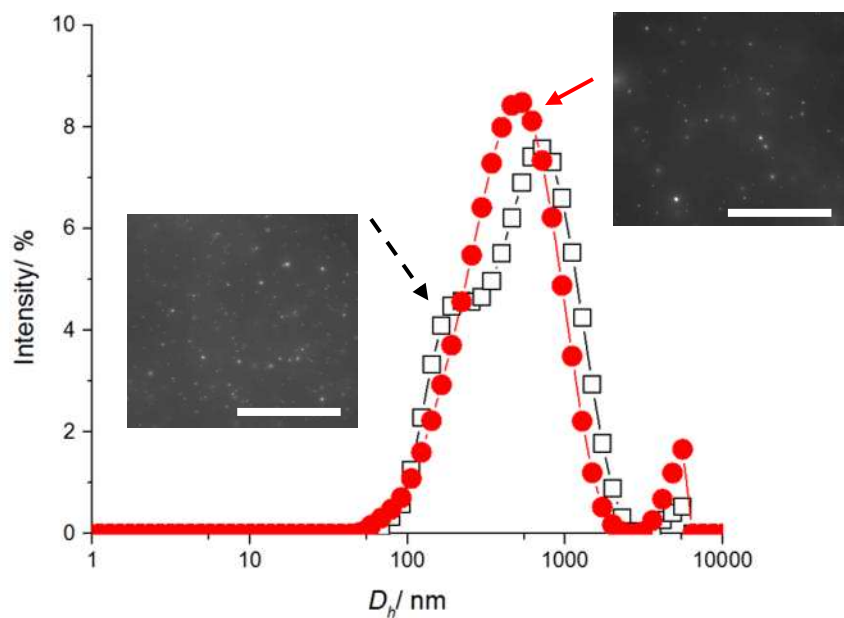
465 It is noteworthy that, irrespective of WPM volume fraction, ultra-low boundary friction  
466 coefficients ( $\mu \leq 0.01$ ) were achieved with HL+BSM. This suggests that with this surface WPM  
467 perhaps formed a monolayer preventing true adhesive contact completely and continuously flowed  
468 into the contact region with particles even at low volume fractions (10 vol%), due to effective  
469 wetting of the surfaces, as schematically illustrated in Figure 5B. Interestingly, the trend of friction  
470 force with  $\phi$  was markedly different in case of the hydrophilic PDMS as compared to hydrophobic  
471 PDMS. It appears that there is an optimal  $\phi$  ( $\leq 65$  vol% WPM) for effective lubrication with  
472 HL+BSM surfaces where the contact region is saturated with microgel particles. Above this  
473 volume fraction, the friction force starts to increase again, possibly due to particle close packing  
474 and aggregation/interpenetration that impedes their rolling motion rather than shear thickening due  
475 to friction between particles as seen in close packed hard sphere suspensions.

476 Together, these findings are in agreement with our hypothesis that the volume fraction of  
477 WPM particles play an important role in the lubricity in both HB and HL+BSM PDMS surfaces.  
478 The experiments also demonstrate for the first time that proteinaceous microgel particles can

479 generate ultralow friction forces  $\leq 100$  mN between HB PDMS and HL+BSM surfaces at higher  
480 ( $\phi \geq 65$  vol%) and lower ( $\phi < 65$  vol%) volume fractions respectively, respectively.

481 **Size of WPM particles before and after friction measurements.** The WPM particles had  $D_h$  of  
482  $380 \pm 26$  nm with a relatively prominent peak in the region 100-1000 nm and a small peak above  
483 1000 nm, the latter ascribed to their aggregation (Figure 6). The 380 nm size is  $\sim 7.5$  times larger  
484 than the surface mean roughness of the PDMS surfaces, i.e., it is worth re-stating that it is unlikely  
485 that the particles would get trapped between the surface asperities of the PDMS.<sup>22</sup> This would  
486 facilitate the ability of the particles to reduce friction by a rolling mechanism.

487



488

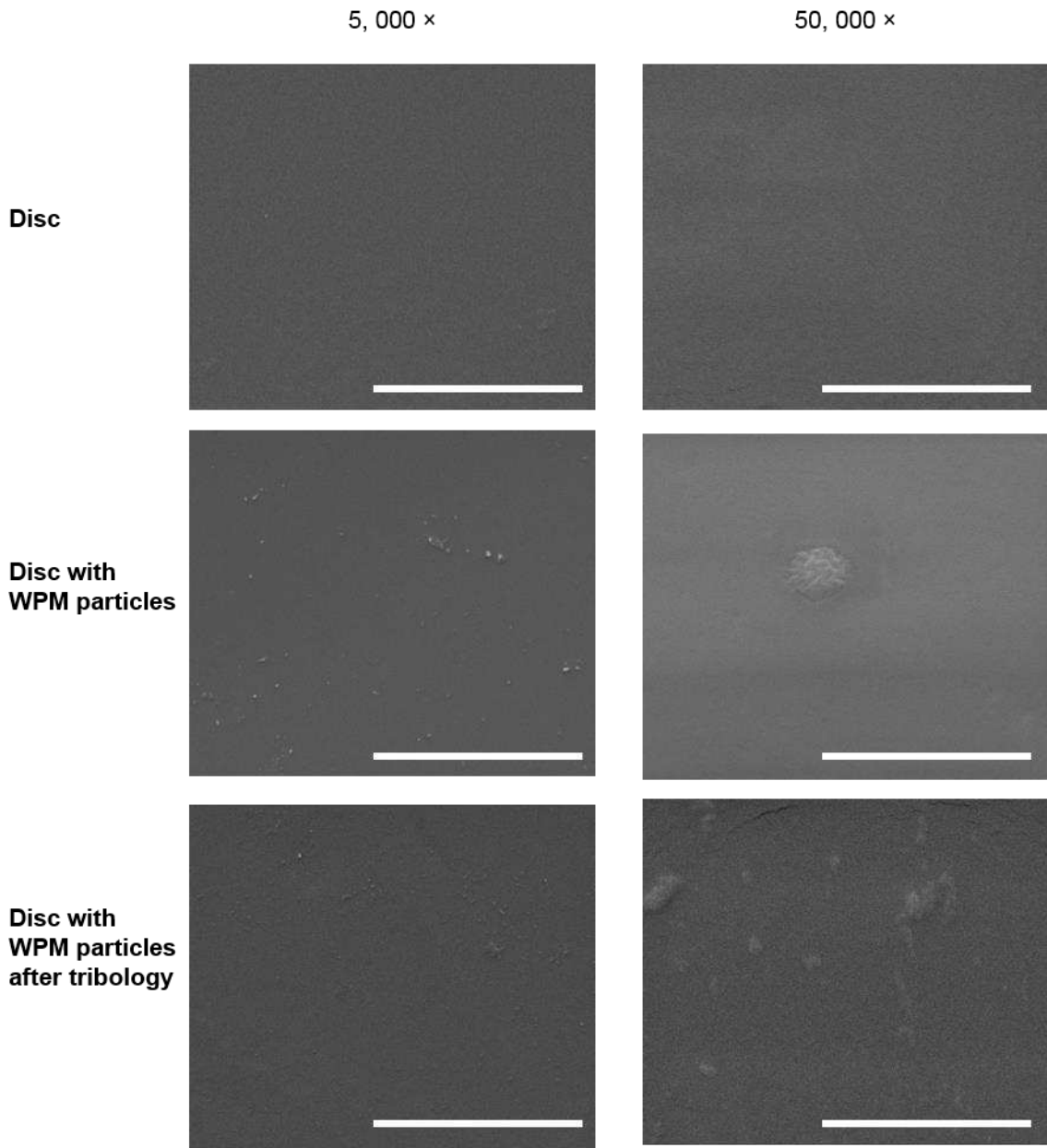
489 Figure 6. DLS measurements (A) of WPM particles (10 vol%) at 25.0 °C ( $\square$ , dashed line), after  
490 subjecting to tribological shear at 37.0 °C ( $\bullet$ , solid line), plotted as hydrodynamic size vs intensity,  
491 with insets representing the corresponding confocal laser microscopy images. Scale bars  
492 correspond to 50  $\mu$ m, respectively.

493

494 Furthermore, there was no significant change in this  $D_h$  after subjecting the particles to tribological  
495 shear between the HB contacts surfaces, as can also be observed in the confocal images. A  
496 slight increase in the peak in the region of 1000-10000 was observed (Figure 6), suggesting the  
497 tribological measurement induced some slight aggregation of the WPM particles, as might be  
498 expected due to the entrainment stresses. However, overall the particle size was largely preserved  
499 under the extreme boundary lubrication conditions, further supporting the suggestion of a rolling  
500 lubrication mechanism. This is also consistent with the fact that the pressure applied (2 N normal  
501 load) was almost 2-3 orders of magnitude lower than the yield stress of the WPM gels from which  
502 particles were formed (Supplementary Figure 1).

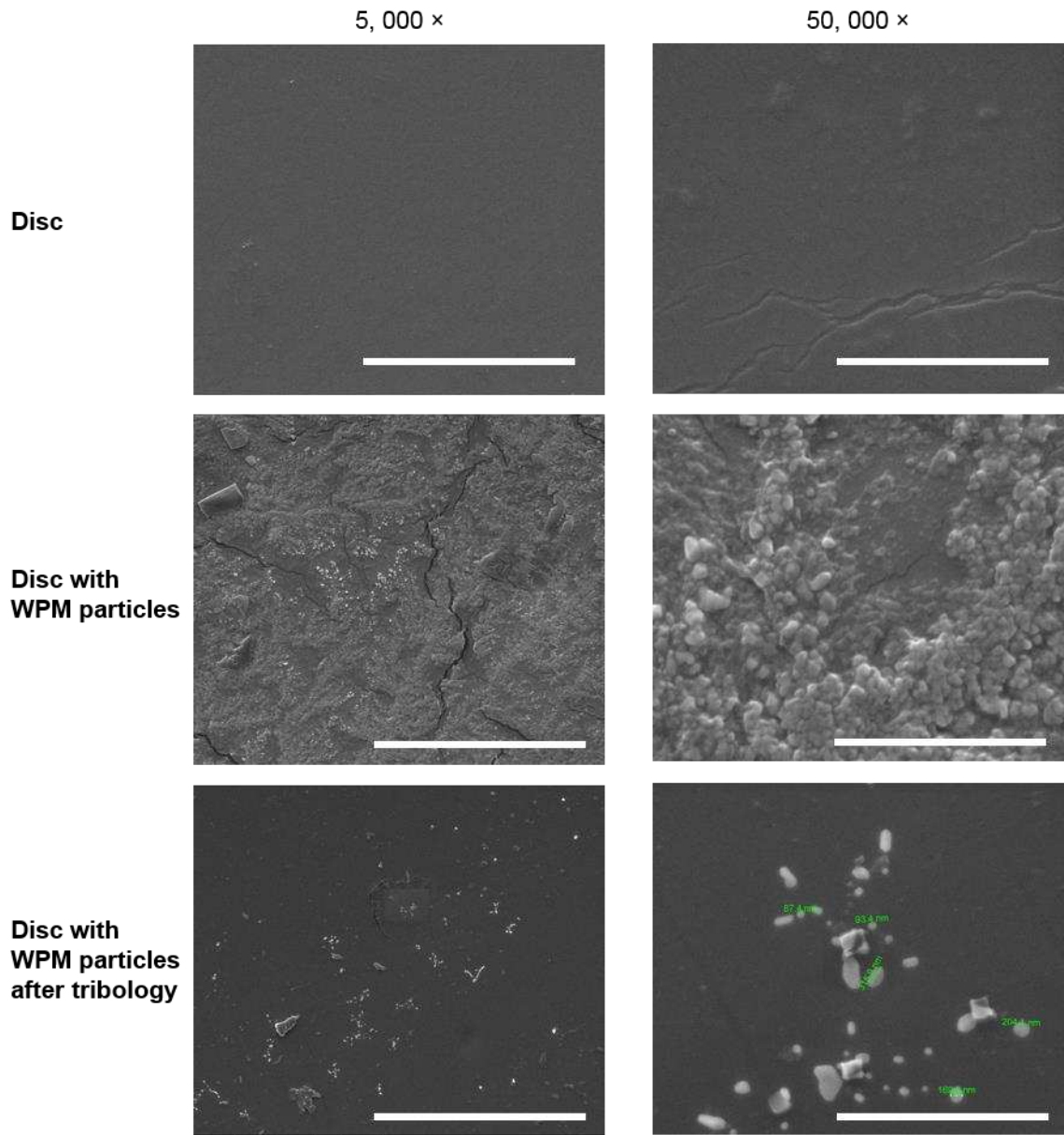
503 **Morphology of WPM particles and surfaces before and after friction measurements.** Figures  
504 7 and 8 show the SEM images of the HB, and HL+BSM surfaces used, before and after tribology  
505 measurements. The HB disks had the smoothest surfaces (Figure 7), whereas some scratches and  
506 channels were visible in HL+ BSM surface (Figure 8). The imperfections in the latter are probably  
507 due to the plasma treatment, as reported previously.<sup>40</sup> The HB PDMS disks with WPM particles  
508 showed a rather sparse distribution of particles on the surface, suggesting that there was limited  
509 retention of the hydrophilic particles on the hydrophobic substrate (Figure 4), which might be  
510 expected, especially with 10 vol% particles. After the tribological measurements, there were some  
511 visible remnants of particles, which might indicate some particle abrasion while still maintaining  
512 some degree of lubricity, as observed in Figure 4a. In contrast, Figure 8 shows that the HL+BSM  
513 surfaces were almost completely covered by a jammed layer of WPM particles, indicating better  
514 binding of the WPM particles to the hydrophilic substrates, congruent with the findings of reduced  
515  $\mu$  (see Figure 4) irrespective of the volume fraction. Figure 8 shows that, after application of the  
516 tribological stresses, a significant proportion of particles remained intact and appeared to wet the

517 surfaces more evenly. Compared to the HB surfaces, this seems to fit in with the much lower  
518 friction forces as observed with the HL surfaces (see Figure 4a) and the suggested rolling  
519 mechanism of WPM particles.



520

521 **Figure 7.** SEM images of HB PDMS disks in absence or presence WPM particles (10 vol%)  
522 before and after subjecting to tribological shear. Scale bars in 5,000 × and 50,000 × correspond to  
523 30 and 3 μm, respectively.



524

525

526 **Figure 8.** SEM images of HL+BSM PDMS disks in absence or presence WPM particles (10 vol%)

527 before and after subjecting to tribological shear. Scale bars in 5,000 × and 50,000 × correspond to

528 30 and 3 μm, respectively.

529

530 Interestingly, the particles also did not show any apparent change in particle morphology  
531 on exposure to tribological shear when examined at higher magnification (Figure 8) and consistent  
532 with the only slight change observed in the DLS data. The latter (see Figure 6) showed a change  
533 in the size distribution of particles on the surface, but no significant change in mean  $D_h$ . The WPM  
534 particles in the SEM images before and after shear appeared to be rather smaller compared with  
535 the DLS data, but this is probably due to the inevitable shrinking during sample preparation for  
536 SEM. The HL+BSM surfaces with WPM showed the presence of some degree of inter-connected  
537 WPM particles. This might be due to depletion flocculation of the weakly negatively charged  
538 WPM with the BSM at pH 7<sup>29</sup> or the shearing processes in the narrow gap between the surfaces.  
539 The SEM micrographs of the WPM particles on the PDMS surfaces before and after tribology are  
540 also consistent with the rheology results, which inferred possible interpenetration of particles as a  
541 function of shear whilst they did not irreversibly collapse.

542 It is also worth noting that some WPM particles showed some sharp facets (almost like  
543 crystals), which might be expected to impede rolling, although, such particles would favour a 'flip-  
544 flop' mechanism of particle faces between surfaces. These flat sided objects appear more prevalent  
545 after shearing, but there are far more particles visible on the surfaces before shearing, and the  
546 densely packed layer makes it difficult to determine the fraction of more flat sided particles over  
547 more rounded ones. It is possible that some separation of the two types of particles occurs during  
548 shearing and that the flat-sided type sticks better to the surfaces and so are apparently more  
549 prevalent than the round ones in the SEM images. However, it is difficult to compare with certainty  
550 the sphericity of the WPM particles embedded on the PDMS surfaces before and after tribology  
551 because of the possible effects of preparation for SEM on particle morphology, as already  
552 mentioned. Also, it is important to understand the change (if any) of the sphericity of the particles

553 after rheological measurements. Hence, additional high-resolution characterization, before and  
554 after rheology as well as shearing in confinement between the surfaces, is needed in order to clarify  
555 if one type of WPM particle morphology is more important than another in providing the ultra-  
556 low friction observed.

557

## 558 **Conclusions**

559 The aqueous dispersions of WPM particles have been shown to be efficient boundary lubricants  
560 in PDMS-PDMS contacts. The coefficient of friction  $\mu$  varied as a function of volume fraction of  
561 WPM used, closely associated with the packing fraction when confined between the HB PDMS ( $\phi$   
562  $\geq 65\%$ ) or HL+BSM ( $\phi < 65\%$ ) contact surfaces. The key mechanism proposed to prevent adhesion  
563 and lower friction between the sliding contacts was probably a rolling mechanism, analogous to  
564 that provided by ball-bearings as well as load bearing ability attributed to the viscosity of closely  
565 packed WPM particles. The motion of the top surface causes the WPM particles to roll, while the  
566 confined region was continuously replenished from the surrounding medium with WPM particles  
567 at higher volume fraction. In addition, the hydrophobic moieties of the WPM particles ensured  
568 effective adsorption to the hydrophobic PDMS surfaces while the hydrophilic moieties of WPM  
569 formed a true hydration layer, in other words a 'surface-separator'. In the case of the hydrophilic  
570 PDMS surfaces, the effective wetting by WPM allowed reduction of boundary friction even at low  
571 volume fractions ( $\phi = 10-40$  vol%), supported by electron microscopy observations. However,  
572 above an optimum volume fraction, the interpenetration of particles possibly impeded effective  
573 rolling, explaining the slight increase in friction. These findings provide a fundamental  
574 understanding of the rheological and aqueous lubrication properties of proteinaceous microgel  
575 particles and may lead to innovative strategies for the development of food, drugs, personal care,



576 biological and biomaterial applications, exploiting their excellent aqueous lubrication and shear  
577 thinning properties.

578

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585

### 586 **Notes**

587 The authors declare no competing financial interests

588

### 589 **Acknowledgements**

590 The European Research Council is acknowledged for its financial support (Funding scheme, ERC

591 Starting Grant 2017, Project number 757993) for this work. Author (AS) is grateful to Prof.

592 Nicholas Spencer (Dept. of Material Science, ETH Zurich, Switzerland) for the useful discussion

593 and would like to thank Dr. Simon Connell for allowing us to use the plasma chamber in School

594 of Physics and Astronomy at University of Leeds, UK. Authors would like to gratefully

595 acknowledge the contributions of Martin Fuller for his technical support in electron microscopy

596 imaging at Bio-imaging Facility within the Faculty of Biological Sciences of the University of

597 Leeds.

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