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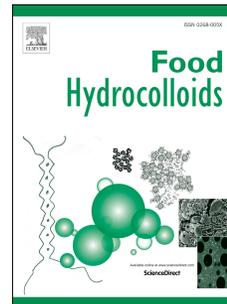
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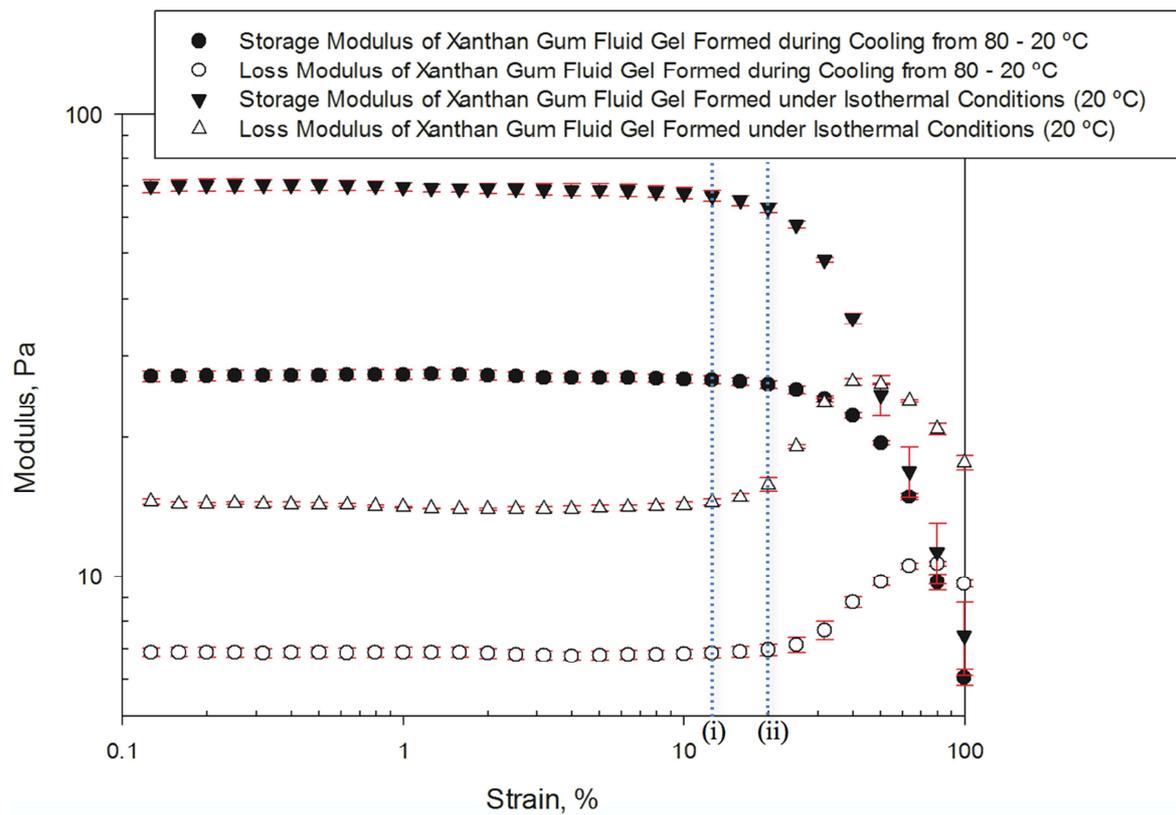
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1 **Modification to the Lubrication Properties of Xanthan Gum Fluid Gels as a Result of Sunflower** 2 **Oil and Triglyceride Stabilised Water in Oil Emulsion Addition**

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11 **Abstract**

12 A range of xanthan gum fluid gels and fluid gel emulsion mixtures have been constructed and their
13 lubrication behaviour compared to high oleic sunflower oil. In addition, the lubrication properties have
14 been measured after the addition of oil to the fluid gel, along with the effect of dispersing 10 %
15 (wt/wt) of a stabilised and un-stabilised oil continuous emulsion into the fluid gel postproduction.

16 This study has highlighted a method of producing xanthan gum fluid gels as well as a fat mimetic
17 formulation based on a xanthan gum fluid gel/oil formulation, which has lubrication properties
18 equivalent to that of standard sunflower oil during soft tribology experiments. The final formulation
19 was shown to have similar initial lubrication behaviour as sunflower oil with a 93 % oil reduction.
20

21 **Keywords:**

22 Fluid gel, Fat replacement, Lubrication, Sunflower oil, Xanthan gum, Fat mimetic
23
24

25 **1. Introduction**

26 The presence of fats is a vital component in foodstuffs due to its contribution to oral properties
27 such as flavour, palatability, mouth feel and lubrication. (de Wijk, Terpstra, Janssen, & Prinz, 2006;
28 O'Quinn, et al., 2012) The consumption of excessive quantities of dietary fat has been shown to
29 increase the risk of medical conditions such as obesity, high blood pressure and coronary heart
30 disease. (Willett, 2012) The food industry in an attempt to facilitate healthier diets has adopted several
31 methods of fat replacement. One such method is the use of hydrogels with lipid-like properties.
32 Hydrocolloids are increasingly becoming key components in food industry formulations and have
33 been widely discussed as potential systems in fat reduction/replacement applications. (Farres, Moakes,
34 & Norton, 2014; Gidley, 2013) In order to be successful in emulating the attributes of fat systems, it is

1 important to gain an understanding of the lubrication behaviour of these systems so that the impact of
2 fat reduction on oral perception is minimised. (Selway & Stokes, 2013)
3 The disruption of the molecular ordering of a biopolymer during its gelation is the primary method of
4 forming fluid gel systems. (Cassin, Appelqvist, Normand, & Norton, 2000; Garrec, Frasc-Melnik,
5 Henry, Spyropoulos, & Norton, 2012) A method commonly used is the application of shear forces to
6 the gelling mixture leading to the separation of gel nuclei's, limiting aggregation. (Farres, Douaire, &
7 Norton, 2013; Garrec & Norton, 2012) Xanthan gum is a naturally occurring polysaccharide widely
8 used as a thickening/stabilisation agent in the food, cosmetic and pharmaceutical industries due to its
9 highly pseudoplastic behaviour. (Fitzpatrick, Meadows, Ratcliffe, & Williams, 2013; Sworn, 2009)
10 The production of fluid gels that possess properties similar to that of oil emulsion systems is a viable
11 method of fat replacement but unfortunately, the vastly different oral perception of water/gels to that
12 of oil means that fat replacement systems of this type can be easily distinguished from their full fat
13 counterparts, necessitating the inclusion oil into formulations. (Chojnicka-Paszun, de Jongh, & de
14 Kruif, 2012; Nishinari, 2006; van Aken, Vingerhoeds, & de Wijk, 2011)
15 This study aims to investigate the production of xanthan gum fluid gels and how the rheological
16 behaviour differs from xanthan gum hydrated and sheared at room temperature. Once produced the
17 effect of the addition of sunflower oil on the lubrication behaviour of the xanthan gum fluid gels is
18 shown. Comparisons between sunflower oil and xanthan gum formulations where oil dispersed around
19 the particles have been measured by ball on disk tribology. Finally, the effect on lubrication the
20 mixing of a 30 % water in oil (w/o) triglyceride stabilised emulsion system into the fluid gel
21 postproduction was assessed.

22 **2. Materials and methods**

23 **2.1. Materials**

24 The sodium form of xanthan gum was obtained from MH Foods, Nile red was purchased from
25 Sigma-Aldrich, and sunflower oil was obtained from a generic source. Glyceryl monostearate
26 (Dimodan HP Kosher), Tri-palmitate (Edenor C16-98 MY), and Polyglycerol Polyricinoleate were
27 provided from Danisco, Emery Oleochemicals, and Palsgaard, respectively. All materials were used
28 as received and without further purification.

29 **2.2. Methods**

30 **2.2.1. Xanthan gum fluid gel production.**

31 Dry pre-weighted xanthan gum powder (1.5 % wt/wt) was added slowly and under constant
32 agitation to heated distilled water (approximately 80 ± 5 °C). The pre gel solution was kept isothermal
33 (above the literature ordered-disordered transition temperature) until complete hydration was achieved,
34 then stirred for a further 30 minutes under cover to prevent evaporative losses. (Mannion, et al., 1992)
35

1 Xanthan gum fluid gels were produced by flowing the pre-gel solution through a thermally controlled
2 pin stirrer set to a shaft rotation speed of 2000 rpm (schematic shown in **Fig. 1.**)

3
4 The pin stirrer consists of a rotor shaft with evenly distributed pins along its length, which is
5 inserted into a thermally controlled jacket with stators running the length of the inside wall. The
6 arrangement is such that when assembled the rotor pins are positioned between the stator pin of the
7 jacket. In operation, areas of high shear are developed in the gaps between the pins when the centre
8 shaft is rotated. Further details of the construction of the pin stirrer is described in Garrec *et al.* (Garrec
9 & Norton, 2012) For fluid gel production, prior to being subjected to the shear field the fluid
10 temperature remained at ~ 80 °C and was reduced to 20 °C during transit through the unit. The
11 reduction in temperature provided the driving force for ordering whilst the shear between pins limited
12 overall gelation of the solution volume as a whole.

14 **2.2.2 Water /Oil Emulsion Production (w/o)**

15 As described by Frasc-Melnik *et al.* and Garrec *et al.* particulate emulsions were produced by
16 pumping the pre-emulsion (at a flow rate of 150 ml min^{-1}) through a jacketed scraped surface heat
17 exchanger, followed by a pin stirrer, both of which were set to a shaft rotation speed of 2000 rpm and
18 cooled to 5 °C with water. (Frasch-Melnik, Norton, & Spyropoulos, 2010; Frasc-Melnik,
19 Spyropoulos, & Norton, 2010; Garrec, Frasc-Melnik, et al., 2012) Prior to production, a mixture of
20 nucleation agent (Glyceryl monostearate, 1%), solid fat (Tri-palmitate, 3 %) and emulsifier (PGPR, 1
21 %) were added to the oil phase, and the bulk temperature raised to ca. 95 °C. Once the oil reached the
22 required temperature and a homogeneous dissolution was obtained, water (heated to 60 °C) was added
23 to the stirring oil mixture to produce a pre-emulsion that was 30 % w/o (by mass). This pre-emulsion
24 was maintained at 80 °C, before being pumped firstly through both the units, collected then passed
25 through the system a second time at the same rate, in order to induce fat network break-up and reduce
26 the particle size of the final emulsion.

28 **2.2.3. Characterisation**

29 *Optical light microscopy*, Light microscopy was performed using a Brunel SP300-fl (Brunel
30 Microscopes Ltd, UK) fitted with a DSLR camera (Cannon EOS Rebel XS, DS126 191). For the
31 purpose of imaging particles 20x or 40x objective lens were used. Post image processing was made
32 using the software package ImageJ.

33
34 *Confocal scanning laser microscopy (CLSM)*, CLSM was performed using a Leica TCS-SPE
35 (Leica DM2500, Leica Microsystems Ltd, UK) fitted with an argon laser. Lipid based particles and
36 sunflower oil were dyed with Nile red. Dyes were excited at 488 nm and detected between 500-550
37 nm, and image slices were collected at 1 μm intervals through the samples under 40x magnification.

1 UV transparent/fluorescence free immersion oil (Sigma-Aldrich, UK) was placed between the lenses
2 and coverslip of the sample slide during imaging. Image processing was made using the software
3 package ImageJ.

4 5 **2.2.4 Rheology measurements**

6
7 *Oscillatory measurements*, Storage and loss modulus measurements were made at 20 °C using
8 a Kinexus pro rotational rheometer (Malvern instrument, UK) with a parallel plate geometry (diameter
9 60 mm, gap set to 1 mm) calibrated with pure water (at 20 °C). Solution of xanthan gum fluid gel and
10 gels hydrated at 20 °C were transferred to the geometries, and the temperature allowed to equilibrate
11 for 5 minutes. The percentage strain on the sample was varied between 0.1 and 100 %. All
12 measurements were made at 1 Hz in triplicate and the average reported on a plot of modulus versus
13 strain percent.

14
15 *Viscosity measurements during production of fluid gel and gels hydrated at 20 °C*, Single
16 shear viscosity measurements during fluid gel production were made using a Kinexus pro rotational
17 rheometer (Malvern instrument, UK) with a vane geometry (internal cup diameter 27 mm, vane rotor
18 25 mm) calibrated with water (at 20 °C). The required mass of deionised water was added to the vane
19 and the temperature allowed to isotherm either at 20 °C or 80 °C depending on experiment type. Dry
20 powdered xanthan gum was added slowly to the vane under shear (500 s^{-1}) and allowed to mix for 60
21 minutes. In experiments where the temperature was set to 20 °C, shearing continued for a further 30
22 minutes. Where the temperature was reduced for 80 °C, the gel temperature was reduced at a cooling
23 rate of 2 °C min^{-1} to 20 °C over a period of 30 minutes under the same shearing rate (500 s^{-1}). All
24 measurements were made in triplicate and the average reported on a plot of viscosity versus time.

25 *Viscosity measurements of final fluid gels and gels hydrated at 20 °C*, Viscosity measurements
26 as a result of shear rate were made at 20 °C using a parallel plate geometry (diameter 60 mm, gap set
27 to 1 mm) calibrated with water (at 20 °C). Finished samples were prepared in a pin stirrer either by
28 shearing isothermally or during cooling and tested 48 hours after production. Measurements were
29 made between 0.01 and 500 s^{-1} . All measurements were made in triplicate and the average reported on
30 a plot of viscosity versus shear rate.

31 32 **2.2.5 Soft tribology**

33 As in Garrec *et al.* (2012) lubrication (expressed as friction coefficient, μ) was recorded as the
34 result of the normal and tangential forces ($\mu = F/W$) using a Mini Traction Machine (MTM, PCS
35 Instruments, UK). (Garrec, Frasc-Melnik, et al., 2012) In order to give results more representative of
36 lubrication in oral processing between a hard and soft surface, similar to the work of Malone *et al.*
37 (2003) typical hard surface was represented using a $\frac{3}{4}$ inch stainless steel ball (AISI 400) (PCS

1 instruments, UK) coupled with a Polydimethylsiloxane (PDMS) (Samco Silicone Products, UK) disk
2 used for the soft surface. (Malone, Appelqvist, & Norton, 2003) Stribeck curves were obtained when
3 $W =$ between 0.5 and 6N, and measurements taken as the average of the entrainment speed (U) shown
4 in **Eq. 1**, being raised from 1 to 1000 mm s⁻¹ three times. During these experiments the slide-to-roll
5 ratio (SRR) calculated by **Eq. 2** was equal 50 % and defined as:

$$6 \quad U = \frac{(V_{Ball} - V_{Disk})}{2} \quad (1)$$

$$7 \quad SRR = \frac{V_{Ball} - V_{Disk}}{U} \quad (2)$$

8
9 Each measurement reported was plotted from triplicate measurements of each sample type.

10 11 12 **3. Results and discussion**

13 14 **3.1 Gel Particle production**

15 A combination of optical and confocal microscopy (CLSM) was used to confirm, that fluid gel
16 particles had been formed. Microscopy of xanthan gum gels formed after hydration then shearing in
17 the pin stirrer at room temperatures (20 °C) and those hydrated at 80 °C then sheared in the pin stirrer
18 whilst cooling from 80 – 20 °C highlighted a significant difference in the particle shapes and sizes of
19 the final gels (**Fig. 2.**).

20
21 When gels were sheared at 20 °C the resultant gel particles were shown to be angular and strongly
22 resembled broken quiescent gel fragments (**Fig. 2a**). When sheared during cooling the fluid gel
23 particles were rounded (**Fig. 2b**). This change in particle shape is probably the result of the application
24 of shear confining the xanthan gum polymer whilst undergone a conformational transition from a
25 disordered coil to a ordered helix. (Garcia-Ochoa, Santos, Casas, & Gomez, 2000; Milas & Rinaudo,
26 1986; Morris, Lanson, & Turner, 1982) In the samples made at 20 °C the helical xanthan gum chains
27 appeared to be too ridged and “rod-like” to be able to be manipulated into particles by the shear forces
28 alone, on cooling while shearing the more flexible single coiled chains present above the transition
29 temperature was shown to be far more susceptible to manipulation.

30 The mechanism for 1.5 % (wt/wt) xanthan gum fluid gel production and stabilisation proposed is
31 highlighted below:

- 32
33 1. Hydration of the xanthan gum occurs in the heated solution to bring about the helix-coil
34 transition of the biopolymer

- 1 2. The denatured xanthan is then able to align to a greater extent, exposing a greater number of
2 small segments where junction zones can be formed. At these junctions, interaction between
3 the glucose and mannose side chains and the sterically compatible cellulose backbone of other
4 xanthan chains can occur to form discrete xanthan aggregates as reported by Southwick *et al.*
5 (1980). A similar methodology of biopolymer compatibility to that reported in the works of
6 Carins *et al.* (1986) for xanthan gum carob gum mixtures. (Cairns, Miles, & Morris, 1986;
7 Southwick, Lee, Jamieson, & Blackwell, 1980)
- 8 3. The size and concentration of xanthan gum in the particle can then grow to the maximum
9 size permitted by the turbulent shear environment, and the excess biopolymer is redispersed to
10 polymer deficient areas
- 11 4. Stabilisation of the particles is thought to occur whilst the biopolymer backbone still has
12 flexibility, the negatively charged side chains undergo electrostatic repulsions. The process
13 can then lead to increased packing and/or hindering the remaining small junction zones
14 preventing further entanglement. (Southwick, Jamieson, & Blackwell, 1982) Once back in the
15 ordered conformation, the particle formation is complete and weak interactions between
16 particles is reduced due to potentially a greater number of negatively side chains being
17 exposed, leading to the reduction in storage modulus observed in **Fig 3**.

18
19 Investigations are still on going to understand, if the mechanism is the same for xanthan gum as
20 reported by Frith *et al.* (2002) and Garrec *et al.* (2012) in kappa-carrageenan systems were the
21 production temperature and biopolymer concentration could be used to control and tailor properties
22 like particle stiffness and stability during fluid gels production.

23
24 *Changes in storage and loss modulus of xanthan gum as a result of formation temperatures*, Changes
25 in storage and loss modulus of xanthan gum gels that had been formed at 20 °C and those formed
26 whilst cooling from 80 – 20 °C were measured. The comparison is shown in **Fig. 3**.

27
28 A significant difference was recorded in both the storage and loss modulus between gels formed under
29 shear isothermally at 20 °C (**Fig. 3**, triangles) and those formed whilst shearing as the temperature was
30 reduced from 80 °C to 20 °C (**Fig. 3**, circles). Under isothermal conditions a bulk storage modulus of
31 69.7 ± 1.5 Pa, was measured compared to 27.84 ± 0.2 Pa when the gels were prepared as the
32 temperature was reduced (value taken at 1 % strain). A similar difference was noticed in the loss
33 modulus where isothermally hydrated gels of 14.07 ± 0.06 Pa compared to those formed during
34 cooling of 6.9 ± 0.17 Pa (value taken at 1 % strain). Results showed a 60 % reduction in the gel
35 strength for gels prepared during temperature reduction compared to those prepared under isothermal
36 conditions, indicating a reduction in the particle-particle interactions as a consequence of stabilisation
37 brought about by the shearing processes. A 7 % decrease in the gels resistance to deformation was also

1 recorded for the fluid gel formed during cooling in respect to the isothermal formation (**Fig. 3.** ii and i,
2 respectively), further indicating the reduction in molecular ordering of the biopolymer. The
3 rheological properties developed by the production of the fluid gel, rather than those of gels
4 hydrated and sheared at 20 °C meant that the xanthan gum sheared as the temperature was reduced
5 exhibited more emulsion like behaviour, thought to be vital for mimetic materials
6

7 Changes in the viscosity of xanthan gum gels were measured during the hydration at 20 °C under shear
8 (500 s^{-1}) and during the hydration at 80 °C then cooling to 20 °C whilst being subjected to shear (500 s^{-1}).
9 The comparison is shown in **Fig. 4.**

10
11 A constant rise in viscosity was observed as xanthan gum powder was hydrated at 80 °C (**Fig. 4.** open
12 triangles). As the temperature was reduced after 3600 minutes and the literature helix-coil temperature
13 of the polymer (Mannion, et al., 1992) was reached (shown by the red arrow in **Fig. 4.**) the viscosity
14 increase ceased and a reduction in the viscosity occurred, this reduction being a result of the formation
15 of discrete particles (fluid gels). Once formed the particle–particle interaction of the xanthan gum gel
16 was reduced resulting in the constant viscosity values (0.0325 ± 0.001) seen at the end of the test in the
17 fluid gel trace (**Fig.4.** open triangles). The reduction in viscosity in fluid gel systems seen below the
18 transition temperature of gels produced under shear has been described previously in the work of
19 Gabriele *et al.* (2009) in kappa-carrageenan systems as a result of demixing caused by polymer rich
20 and polymer poor regions. (Gabriele, Spyropoulos, & Norton, 2009) These observations are in
21 agreement with the fluid gel formation method proposed earlier in this paper where once xanthan
22 chains have been entangled at the exposed junctions zones in the flexible coil state and repulsive
23 forces have led to the biopolymer adopting the most thermodynamic stable arrangement, the return to
24 the ridge helix conformation then restricts further mobility in the backbone isolating the negative side
25 chains, resulting in repulsion between the newly formed gel particles, and aiding demixing of the un-
26 entangled polymer chains.

27 The continual gain in viscosity seen when the xanthan gum was formed at 20 °C under shear at 500 s^{-1}
28 (shown by solid circles in **Fig. 4.**) showed the hydration and subsequent interaction by hydrated
29 particles was unaffected by the shear field whilst the biopolymer was in the ridged form, necessitating
30 the need for the thermal treatment in the production of the fluid gel.

31
32 Measurement of the fluid gels viscosity as a result of the applied shear rate after a period of 48 hours
33 had past is shown in **Fig. 5.**

34
35 The fluid gels formed whilst cooling thought the transition temperature were shown to have lower
36 values of bulk viscosity compared to those formed isothermally. Both gels exhibited shear-thinning
37 behaviour although the overall reduced bulk viscosity values at all shear rates in the fluid gels formed

1 during cooling were in agreement with the increased stabilisation as a result of forming a xanthan gum
2 fluid gel. The sustained difference in viscosity values (after 48 hours) also gave evidence that the
3 production method did not form a state in which rheological properties of the fluid gel were only
4 temporary, although the length of stability of these gel structures is still under investigation.

6 *Fluid gels particulate w/o emulsion mixtures*

7 The addition of 10 % wt/wt of triglyceride stabilised emulsion to the fluid gel was investigated. In
8 other published work by the authors, the use of the stabilised emulsion (30/70 water in oil) was shown
9 to give values of friction close to those of sunflower oil alone during rolling friction tests. (Akash Beri,
10 2015) The benefit of using emulsions as lubrication modifiers as opposed to oil alone was shown to be
11 that these microstructures could use water to replace the overall oil content by 30 % (by mass).
12 Emulsion droplets were dispersed in the fluid gel mixture postproduction CSLM was then used to
13 identify the composition of the dispersed phase of the fluid gel. Upon emulsification it was evident
14 (from the resultant images – **Fig. 6.**) that higher concentration of the Nile red were incorporated into
15 the triglyceride during solidification and in turn resulted in a distinctive contrast between fat shell
16 particles, oil in the system, and the non-stained fluid gel particles. The confocal images of the
17 composite mixtures can be seen in **Fig. 6.**

18
19 It was evident by the dyed areas that the oil and emulsion droplets were well dispersed in the aqueous
20 continuous phase and may aid in the overall reduction of friction by lubricating particle-particle
21 interactions or facilitating the separation of the ball and disk surfaces.

23 **3.2 Measurements of lubrication of fluid gels by tribology**

24
25 Friction measurements were made of water and sunflower oil as a comparison to fluid gels and fluid
26 gel/emulsion mixed systems. **Fig. 7.** Shows the comparison of sunflower oil and water to the fluid gel
27 alone, and when 10 % sunflower oil had been dispersed into the continuous phase of the fluid gel
28 (labelled “Fluid gel – 10 % oil suspension” in the figure).

29
30 Aside from sunflower oil there was no evidence that the systems reached hydrodynamic conditions
31 before 1000 mm s^{-1} (shown by the increase in traction at high entrainment speeds), due to the
32 entrainment speed being insufficient to fully suspend particles of the fluid gel particles in the entrained
33 fluid. All formulations showed reduced overall friction in comparison to that of water, with the
34 friction values of the fluid gel only systems all exhibited values higher than sunflower oil for all
35 entrainment speeds. Differences in the limit of boundary lubrication (taken at a point where the values
36 of friction are no longer constant) were also evident in the different formulations. Sunflower oil was
37 shown to overcome boundary conditions at entrainment speeds around 1.5 mm s^{-1} , in comparison,

1 fluid gel only systems were shown to exhibit lower friction than water and to enter the mixed regime
2 at entrainment speeds above 7 mm s^{-1} , whereas fluid gel oil suspensions were shown to overcome
3 boundary conditions at 4.5 mm s^{-1} (**Fig. 7 blue arrows**). The measured friction values of the fluid gel
4 being significantly lower than water suggesting that the entrained continuous phase of the fluid gel
5 may also contain some hydrated/partially hydrated unassociated rigid polymer chains, which provide
6 some lubrication by preventing contact between the ball and disk surfaces.

7 The friction coefficient of the fluid gels ran parallel to that of water until 200 mm s^{-1} when friction
8 drastically reduced. Above this entrainment speed it is likely a layer of mono particles is established
9 between the ball and PDMS disk surfaces aiding lubrication. This behaviour has been previously
10 described by De Vicente *et al.* (2010) for confinement of neutralised carbopol particles to a reduced
11 friction layer. (de Vicente, Stokes, & Spikes, 2006)

12 When 10 % sunflower oil was added to the continuous phase of the fluid gels, a reduction in the
13 boundary friction was evident at low speeds, friction values similar to sunflower oil were observed, as
14 a result of the additional lubricant in the continuous phase. Once in the mixed regime the friction
15 values tended towards those of the sunflower oil, strongly indicating that the addition of low amounts
16 of sunflower oil gave oil like friction properties to the fluid gel both in the boundary and mixed
17 sections of the experiment (**Fig. 7 inverted triangles**). The measurement of friction coefficient
18 showed that if oil was added to the continuous phase of the fluid gel, the system closely resembled an
19 oil in water emulsion (Shown in **Fig. 8** for comparisons) and the presence of the fluid gel particle
20 became negligible as equivalent levels of friction could be obtained without the need to exceed the
21 sunflower oil content of the formulation by more than 10 %.

22 The comparison of the friction coefficient when the fluid gels continuous phase had the addition of 10
23 % sunflower oil and when 10 % of a water in oil emulsion (stabilised using triglyceride) is shown in
24 **Fig. 8**.

25

26 The low values of boundary friction shown for both the w/o emulsion (**Fig. 8** inverted triangles) and
27 stabilised emulsion/fluid gel mixtures (**Fig. 8** triangles), highlighted that a fluid gel mixed with a w/o
28 emulsion could be used to reduce friction to a point close to sunflower oil. The stabilisation of w/o
29 emulsions with a triglyceride shell around the dispersed water phase can be used to encapsulate water
30 and allow formulations to be more suitable in moisture sensitive applications. The reduction in friction
31 coefficient exhibited in fluid gel with 10 % triglyceride stabilised emulsion added to the continuous
32 phase was the result of particles of emulsion and fluid gel with varying levels of deformability. The
33 rigidity of the triglyceride-stabilised particles is thought to allow them to be rapidly entrained in the
34 contact between the ball and disk (illustrated in **Fig. 9**) at low entrainment speeds. The result of the
35 particles entrainment being a decrease in deformation of the more compressible xanthan particles,
36 reducing the contact area and lowering the measured friction. The importance of deformability of the
37 fluid gels particles was in agreement with the work of Garrec *et al.* (2013) who in kappa carrageenan

1 systems reported an increase in friction coefficient when particles become more deformable as a result
2 of reducing surface separation. (Garrec & Norton, 2013) The entrainment of ridged particles aids the
3 system in quickly overcoming initial boundary friction, resulting in lubrication behaviour, which
4 mimics that of sunflower oil.

5 In order to verify the proposed mechanism of particle entrainment, both xanthan gum fluid gels and
6 the fluid gel mixed with 10 % (wt/wt) of the stabilised w/o emulsion, were subjected to rolling
7 lubrication under loads between 0.5 and 6 N. The results are shown in **Fig. 10**.

8 The friction coefficient in xanthan gum fluid gels systems were seen to rise as the entrainment speed
9 increased under all loads (shown by the closed symbols in **Fig. 10**). This rise was likely due to
10 initially the particles of the fluid gel being excluded from the contact point until the accumulation of
11 excluded particles became sufficient to overcome the load on the ball. **Fig. 10** shows that the
12 entrainment speed needed to overcome this exclusion was reduced from 2.3 mm s⁻¹ to 1.5 mm s⁻¹
13 when the load was reduced from 6 N to 3 N (indicated by the blue arrows in **Fig. 10**). Under very low
14 loads (0.5 N) the increase in friction and overall lubrication was seen to be much lower as the fluids
15 and particles easily overcame the resistance to entrainment between the ball and the disk. The increase
16 in lubrication as a result of the addition of the stabilised emulsion particles was also evident from the
17 results, where it can be seen that overall lubrication was increased at all levels of load tested. The
18 initial increase in friction when the load on the ball was equal to 6 N was as result of the exclusion of
19 both the fluid gel and emulsion particles at low speeds. Under lower loads (3 N) the absence of the
20 earlier increase in friction is in agreement with the proposed entrainment method. Under rolling
21 conditions the deformable xanthan particles may initially be separated from the continuous phase as
22 the continuous phase is entrained between the ball and PDMS disk, preventing the particles from
23 having an effect on lubrication. On the other hand the smaller size and increased uniformity and
24 hardness of the stabilized emulsion particles increased the likelihood of entrainment and subsequent
25 lubrication as the contact point could be quickly parted. A similar dependence of the particle size on
26 the friction as well as the resultant perceived fatty mouth feel has also been reported previously by de
27 Wijk *et al.* (2005) for custard/starch desserts under similar rolling condition. (de Wijk & Prinz, 2005)
28 Beyond the boundary regime the lubrication properties of the fluid gel with stabilised emulsions/fluid
29 gel mixtures became equivalent to those of a sunflower oil/water mixture, strongly indicating that the
30 system behaved like an oil in water emulsion with the added benefit of 30 % (by mass) of the
31 additional oil being replaced with low calorie water.

33 **4. Conclusion**

34
35 This investigation has shown that xanthan gum fluid gels are formed by the application of shear forces
36 during cooling through the conformational transition. The addition of 10 % (wt/wt) sunflower oil to
37 the continuous phase of the xanthan gum fluid gels was shown to reduce the measured friction

1 coefficient, and the values of friction were similarly reduced by the addition of 10 % of an w/o
2 emulsion stabilised by triglycerides to the continuous phase. The increased lubrication was a result of
3 ridged emulsion particles parting the surface and limiting deformation of the fluid gel particles, and
4 confirmed by studying the dependence of the friction coefficient on the load exerted on the surfaces.
5 Overall composite mixtures of fluid gels and triglyceride stabilised w/o emulsions have been shown to
6 be a viable route to obtaining lubrication behavior similar to sunflower oil at 7 % sunflower oil
7 content.
8

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Figure 1. Schematic representation of the pin stirrer unit (a) sample inlet (b) sample outlet (c) inlet for thermal jacket (d) thermal jacket outlet

Figure 2. Bright field images of xanthan gums produced under shear (a) after hydration at 20 °C (b) by hydrating at 80 °C and sheared whilst cooling. * denotes the xanthan particle.

Figure 3. Storage and loss modulus of xanthan gum gels produced under shear conditions as the temperature is reduced from 80 °C to 20 °C (circles) and isothermally at 20 °C (triangles). All measurements made at 20 °C.

Figure 4. Gel viscosity formation curves of xanthan gum formed under shear (500 s^{-1}) at 20 °C (solid circles) and as the temperature was reduced from 80 °C to 20 °C (open triangles).

Figure 5. Viscosity response as a function of shear rate for gels formed whilst cooling from 80 °C (filled circles) and gels formed isothermally at 20 °C (open circles). All measurements made at 20 °C.

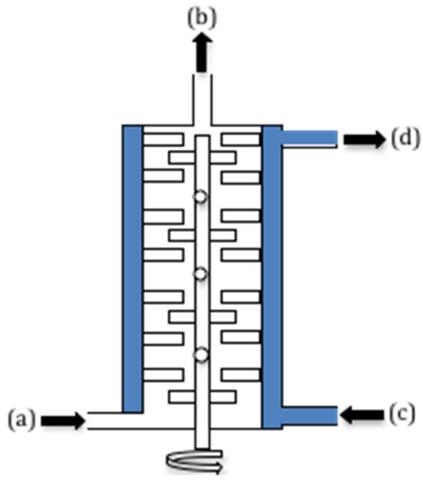
Figure 6. Confocal imaging of (a) Triglyceride fat shell emulsion dyed with Nile red (b) Sunflower oil (green) oil and water emulsion, (c) and Xanthan gum fluid gel particles (black voids)

Figure 7. Comparison of Stribeck curves for xanthan gum fluid gels and fluid gel oil suspension, limit of boundary friction highlighted by blue arrows.

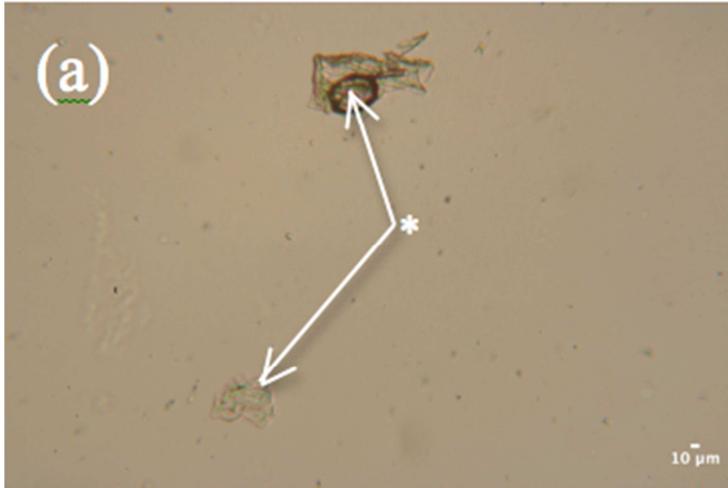
Figure 8. Comparison of Stribeck curves for xanthan gum fluid gels and fluid gel particulate emulsion suspension

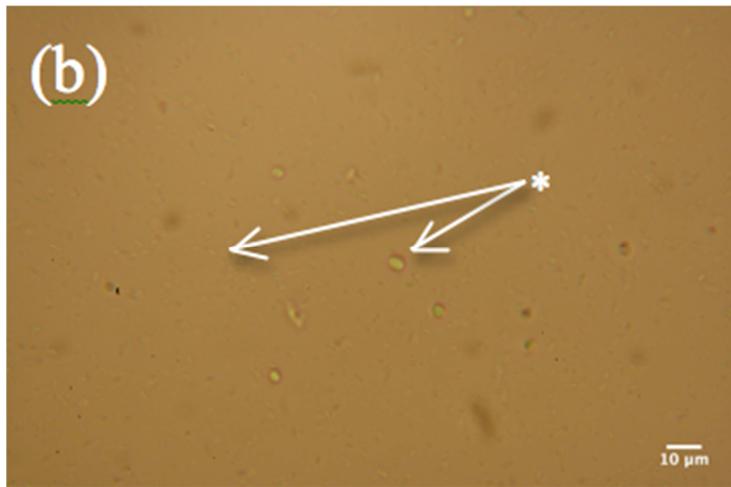
Figure 9. Schematic of the behaviour of fat replacement fluid gels under increased entrainment speeds (a) fluid gels (b) 10 % triglyceride stabilised emulsion added to the continuous phase of the fluid gel

Figure 10. Comparison of the lubrication behaviour under varying loads of xanthan gum (closed symbols) and xanthan gum/triglyceride stabilised emulsion mixtures (open symbols)

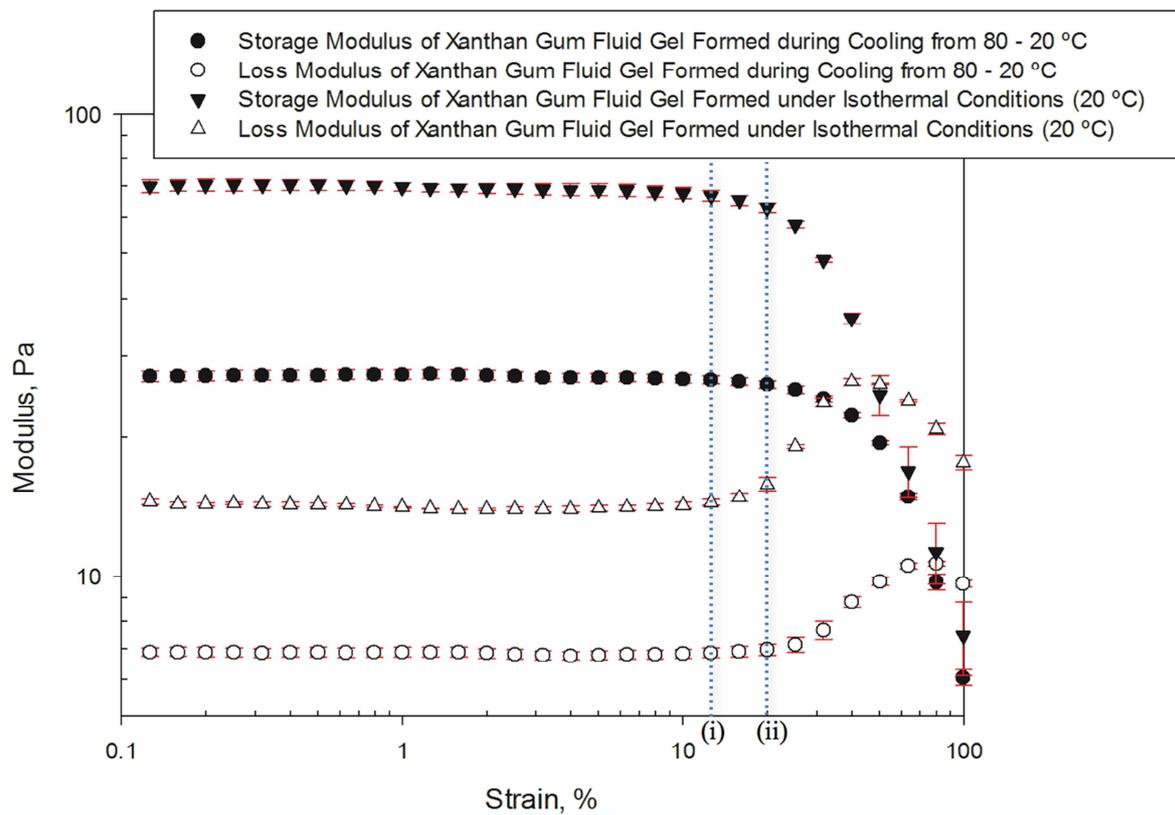


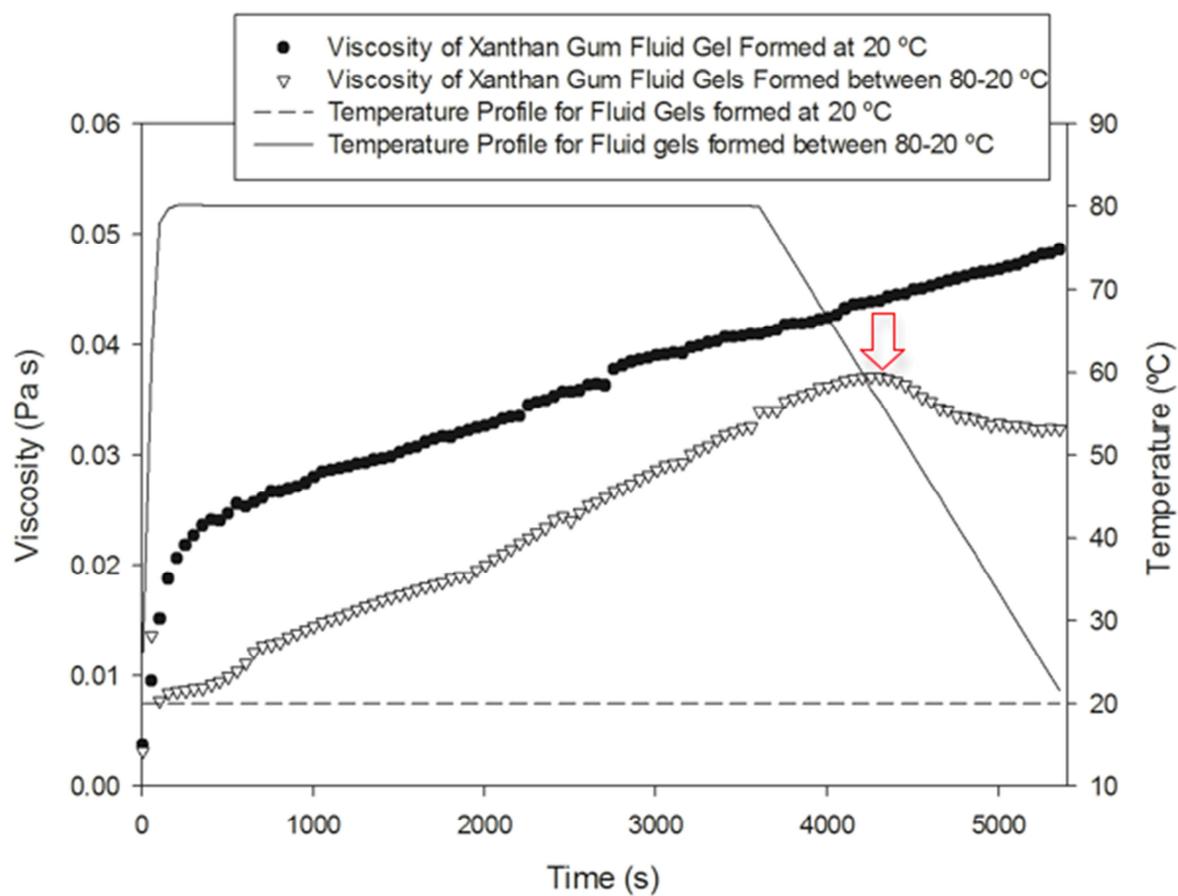
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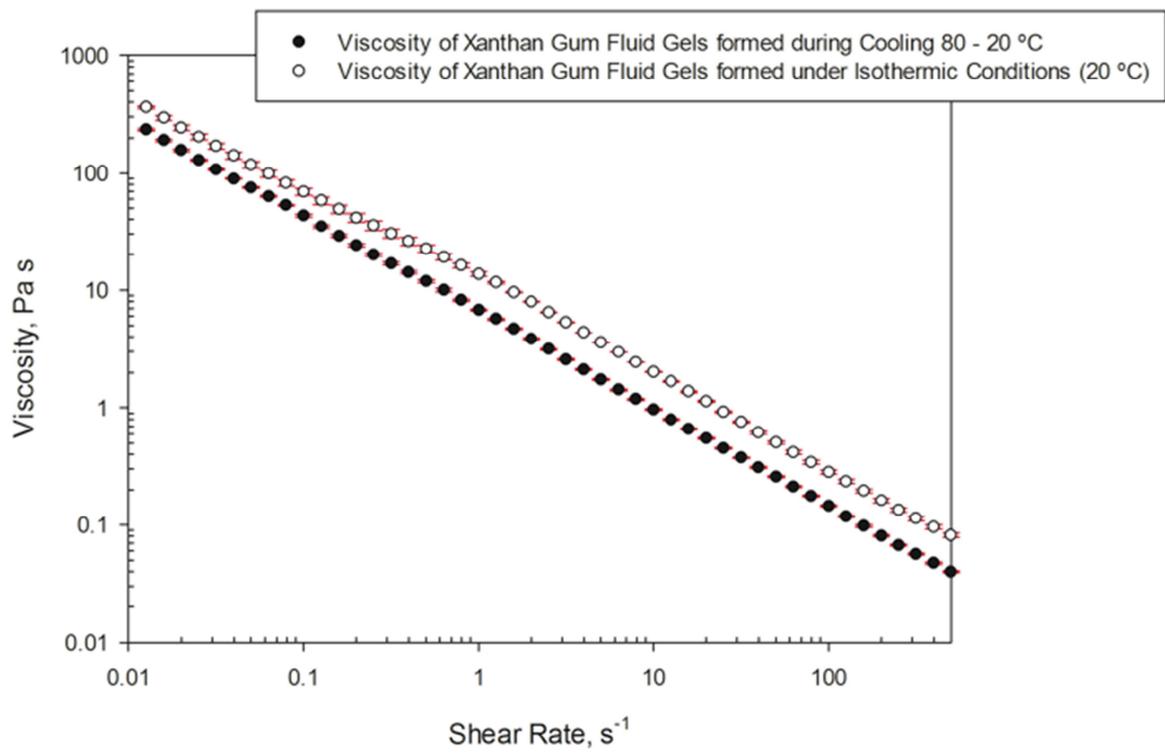




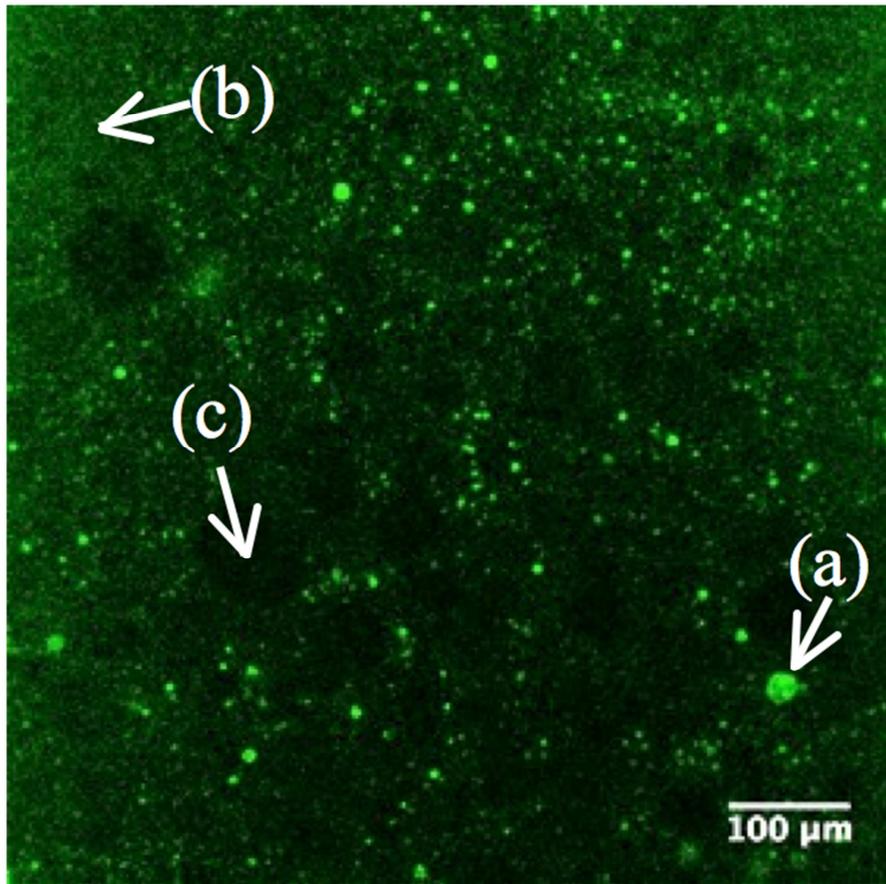
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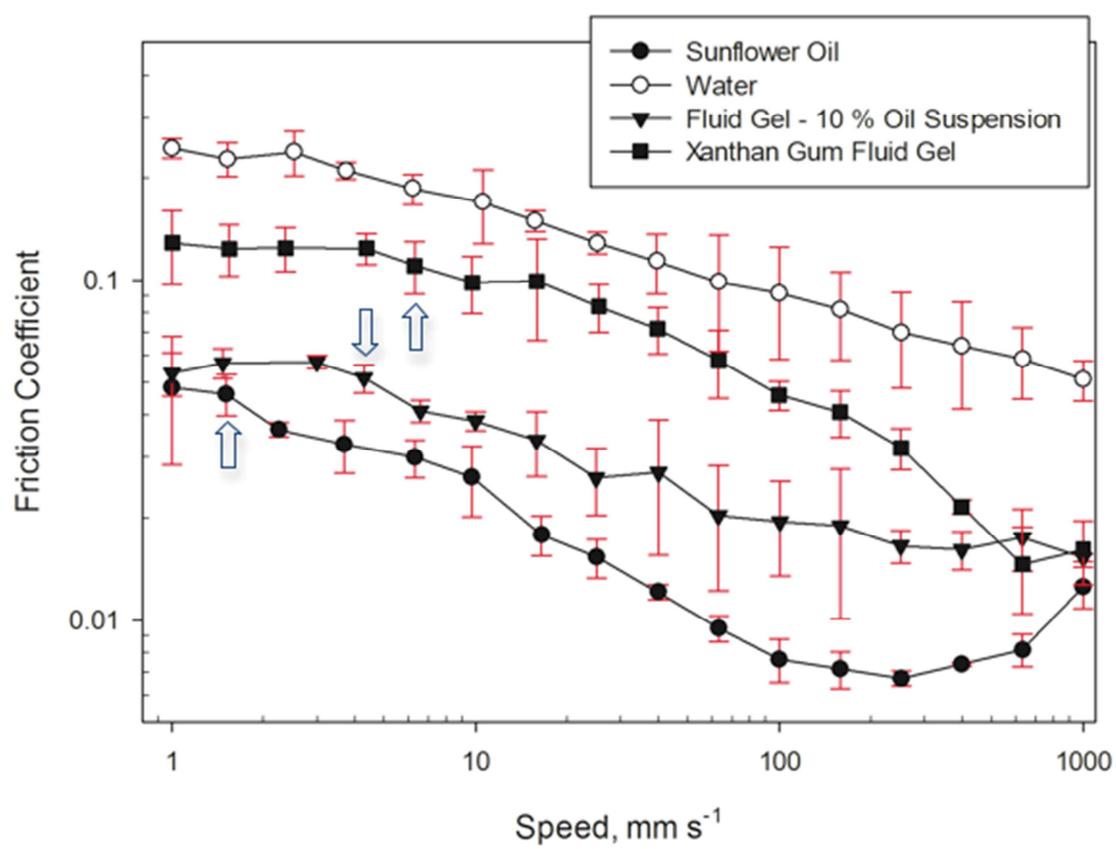


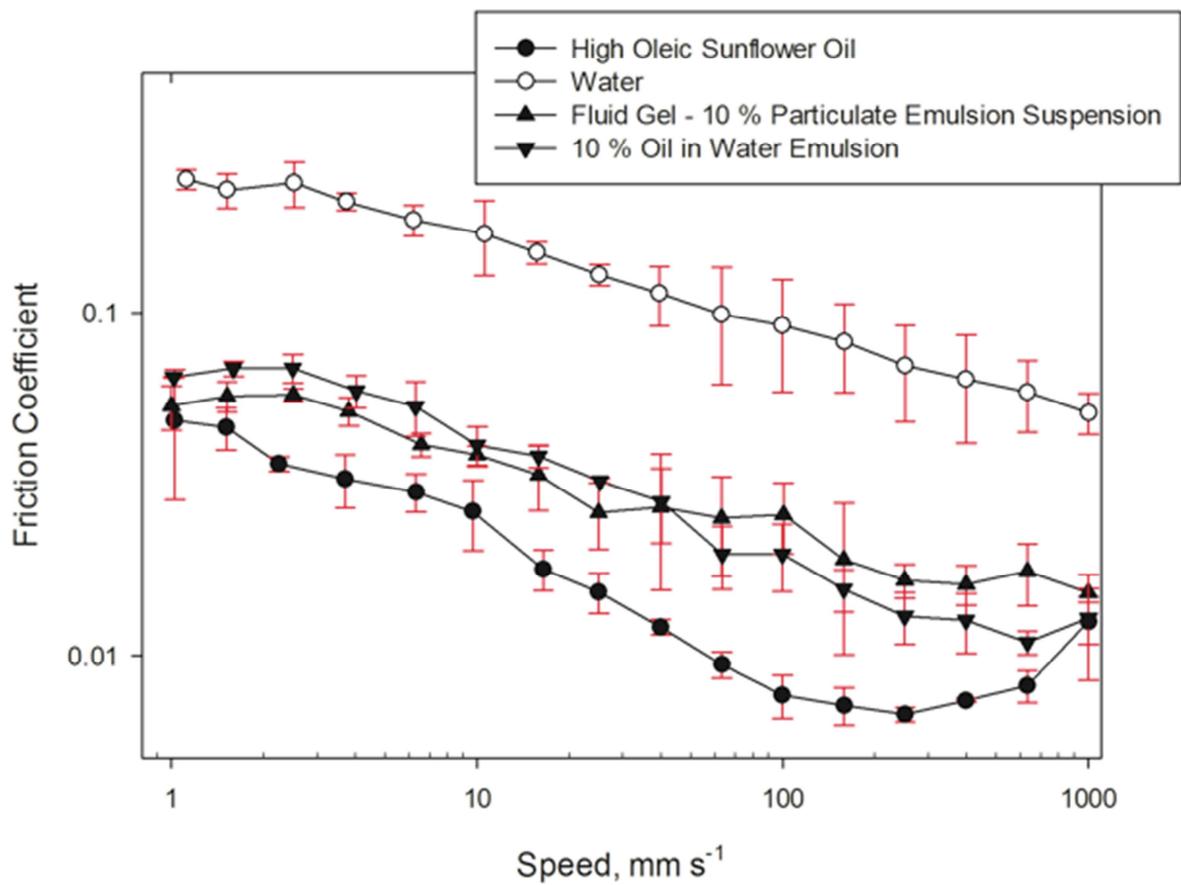


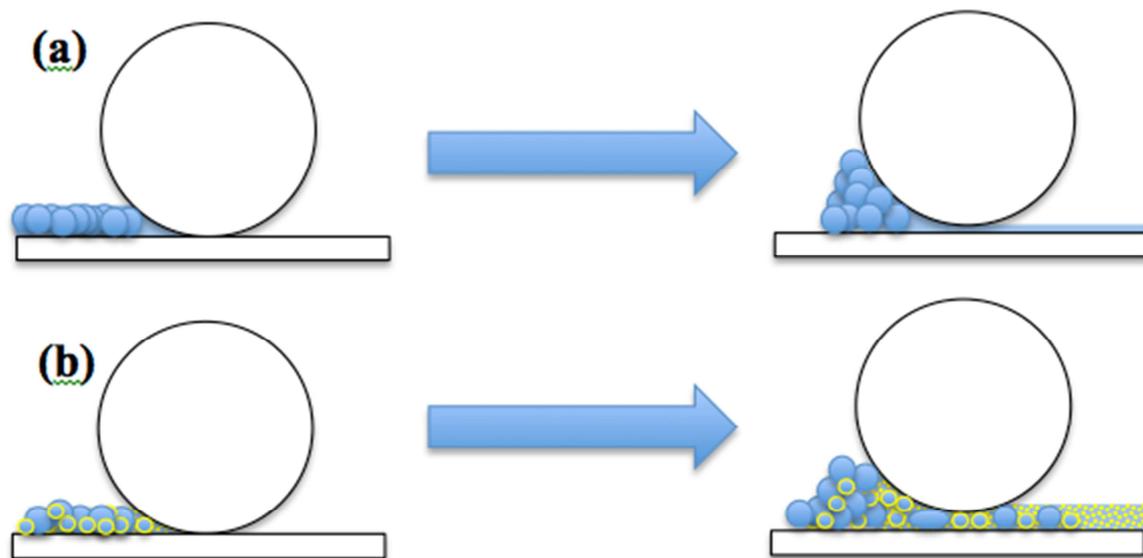


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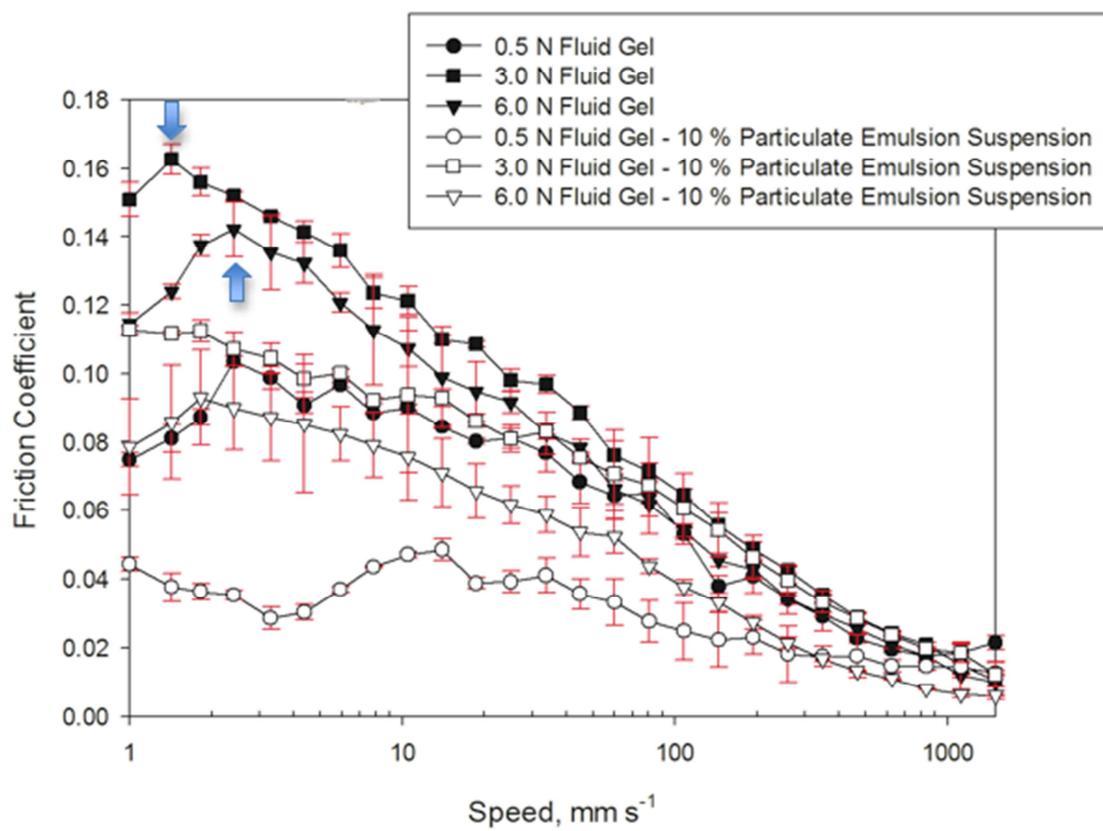








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Highlights

- Xanthan Gum fluid gels have been produced
- Inclusion of sunflower oil in fluid gel particles increase friction
- Addition of triglyceride stabilised water in oil emulsions to the continuous phase lower friction

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