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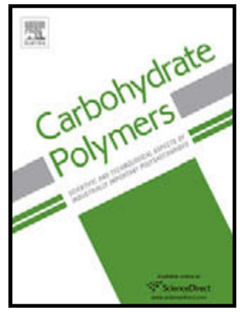

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Author: Bin Zhang Nichola Selway Kinnari J. Shelat Sushil Dhital Jason R. Stokes Michael J. Gidley

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Highlights

- tribology and rheology properties of cooked swollen starch granules (ghosts) characterised
- maize granule ghost suspensions reduce friction compared to water
- bell-shaped tribology curves due to particle entrainment for maize granule ghosts
- limited friction reduction for potato ghosts due to break-up under tribological contact
- potato granule ghost suspensions also break up under steady shear

Tribology of Swollen Starch Granule Suspensions from Maize and Potato

Bin Zhang[a, b, †], *Nichola Selway*[c], *Kinnari J. Shelat*[a, b, c], *Sushil Dhital*[a, b], *Jason R. Stokes*[b, c], *and Michael J. Gidley*[a, b, *]

[a] Centre for Nutrition and Food Sciences, Queensland Alliance for Agriculture and Food Innovation, The University of Queensland, St. Lucia, Brisbane, QLD 4072, Australia

[b] ARC Centre of Excellence in Plant Cell Walls, The University of Queensland, St. Lucia, Brisbane, QLD 4072, Australia

[c] School of Chemical Engineering, The University of Queensland, St. Lucia, Brisbane, QLD 4072, Australia

* Corresponding author.

Phone: +61 7 3365 2145; Fax: +61 7 3365 1177. Email address: m.gidley@uq.edu.au (M. J. Gidley)

† Current address: School of Food Science and Engineering, South China University of Technology, Guangzhou 510640, China, zhangb@scut.edu.cn

Abstract

The tribological properties of suspensions of cooked swollen starch granules are characterised for systems based on maize starch and potato starch. These systems are known as granule 'ghosts' due to the release (and removal) of polymer from their structure during cooking. Maize starch ghosts are less swollen than potato starch ghosts, resulting in a higher packing concentration and greater mechanical stability. In a soft-tribological contact, maize ghost suspensions reduce friction compared to the solvent (water), generate bell-shaped tribological profiles characteristic of particle entrainment and show a marked concentration dependence, whereas potato ghost suspensions exhibit lubrication behaviour similar to water. Microscopy analysis of the samples following tribological testing suggests that this is due to the rapid break-up of potato ghosts under the shear and rolling conditions within the tribological contact. A reduction in the small deformation moduli (associated with a weak gel structure) is also observed when the potato ghost suspensions are subjected to steady shear using parallel plate rheometry; both microscopy and particle size analysis show that this is accompanied by the partial shear-induced breakage of ghost particles. This interplay between particle microstructure and the resultant rheological and lubrication dynamics of starch ghost suspensions contributes to an enhanced mechanistic understanding of textural and other functional properties of cooked starches in food and other applications.

Keywords: starch; granule ghosts; maize; potato; tribology; rheology

1. Introduction

Although most carbohydrate energy in higher plants is stored as semi-crystalline starch granules, the desirable physical properties of starch in food and industrial applications occur following a granule gelatinization process associated with loss of crystalline order. After heating in excess water with limited shear, starch granules swell to several times their initial size and release some low molecular weight soluble polymers particularly amylose (an essentially linear glucose polymer). However, the granules do not dissolve completely and can persist in a highly swollen state that is effectively a 'ghost' of its original swollen form (termed granule ghosts) (Prentice, Stark, & Gidley, 1992). The major difference between a "gelatinized starch granule" and a "granule ghost" is that solubilised polymers are absent from the granule ghost. This difference is not often recognized in the starch literature. Whilst granule ghosts are not commonly referred to, a majority of studies on the rheology-structure of gelatinized starch pastes are in fact on starch ghost pastes (Evans & Haisman, 1980; Evans & Lips, 1992; Lagarrigue & Alvarez, 2001). Generally, these highly deformable ghost particles are thought to play an important role in many of the characteristic physical properties of starch pastes, solutions, or gel networks such as viscosity, texture, and rheology (Evans & Lips, 1992; Lagarrigue & Alvarez, 2001; Steeneken, 1989). For example, the presence of dilute or highly packed granule ghosts in some semi-solid starch-containing foods such as soups, dressing, custards and sauces leads to 'short' texture, thick appearance and sometimes creamy mouthfeel (Stokes, 2011).

Granule ghosts isolated from normal starches such as maize and potato are enriched in amylopectin (a highly branched glucose polymer) with less than 10% of amylose (Zhang, Dhital, Flanagan, & Gidley, 2014). Recently, we found that the ghost remnants after amylase digestion only contain less than 1% of single/double helices, and concluded that the ghost 'skin' originates from physical entanglements of highly branched and large molecular size amylopectin molecules (Zhang, Dhital, Flanagan, & Gidley, 2014). Fisher, Carrington, and Odell (1997) reported that the potato ghost skin could support about 4000 mN/m tensile stress, approximately 1000 times higher than the yield stress of a red blood cell membrane. Starch components other than amylopectin (e.g., amylose, surface lipids and proteins, minerals et al.) also play a role in restricting the extent of swelling (Debet & Gidley, 2006; Han & Hamaker, 2002), which varies depending on the botanical origins of the starch (Obanni & BeMiller, 1996). Shear and heat stability of ghost particles can be modified through certain chemical/physical methods, e.g., chemical cross-linking (to strengthen the wall structure and achieve high shear resistance) and pre-gelatinization (to increase the heat sensitivity).

Starch granule pastes/gels subjected to gelatinization and/or retrogradation exhibit a typical non-Newtonian and viscoelastic behavior, with a low yield stress and shear thinning behavior (Bagley & Christianson, 1982). The size, integrity and concentration (phase volume) of ghost particles within the matrix are important parameters which determine the viscosity and viscoelastic properties. Desse, Fraiseau, Mitchell, and Budtova (2010) reported strong deformation and solvent loss of individual swollen starch granules subjected to shear stress with the aid of a rheo-optical set-up. The morphological structure (e.g., size, shape and integrity) of starch ghost particles is influenced by their botanical origin, modification methods and processing conditions such as shear, cooking/storage temperature and time (Bagley & Christianson, 1982; Debet & Gidley, 2006). The viscosity of starch pastes is governed by the volume fraction of ghost particles in the dilute regime, whereas the particle rigidity (size, shape and deformability) is a decisive factor in the closely packed regime (Steeneken, 1989). Steeneken (1989) further suggested that both ghost particle rigidity and volume fraction within starch pastes are important in a broad concentration range between these two limiting behaviors.

While the rheological behavior of starch pastes/gels has been extensively investigated both experimentally and theoretically (Evans & Haisman, 1980; Evans & Lips, 1992; Lagarrigue & Alvarez, 2001), the lubrication properties of granule ghost suspensions have not been investigated. Lubrication has long been considered to play a critical role in oral perception of liquid and semi-solid foods, including textural and mouthfeel attributes such as smoothness and creaminess (Stokes, Boehm & Baier, 2013). However, only during the past decade have researchers attempted to quantify oral lubrication using soft-tribology as an in vitro technique, where elastomeric surfaces (e.g. polydimethylsiloxane, PDMS) are typically employed to mimic the low pressure contact between compliant oral surfaces (Bongaerts, Fourtouni, & Stokes, 2007). Lubrication behavior is inherently dependent on relative motion between the soft-contacts of the tribometer, which is classically presented as a Stribeck curve with three different regimes namely boundary, mixed and hydrodynamic lubrication. In the hydrodynamic regime, the high fluid (or hydrodynamic) pressure can fully support the applied load and separate the contacts. This normally occurs at higher speeds with increased friction coefficients and shear force, although not all fluids have a hydrodynamic regime. Boundary lubrication occurs at lower speeds, higher load or with a poor lubrication system, as the fluid is excluded from the contact area, resulting in insufficient fluid pressure to support the applied load. In the mixed lubrication regime, the load can be partially supported by fluid pressure and partially by contacting asperities, i.e. intermediate between boundary and hydrodynamic lubrication. The friction coefficient under boundary and mixed regime conditions is more associated with surface characteristics, whereas the hydrodynamic regime is controlled by bulk rheological properties (Stokes, Boehm, & Baier, 2013).

Using these soft-tribological contacts, Selway and Stokes (2013) found that semi-solid foods (yogurt and custard) with similar viscoelasticity and flow behavior exhibit different frictional responses; hence probing the physical dynamics of complex soft systems at multiple length scales may provide better insights into texture and mouthfeel perception. Textural attributes such as the grittiness and smoothness of microparticulate dispersions have been shown to depend on particle size, shape and elasticity (Guinard & Mazzucchelli, 1996; Singer & Dunn, 1990; Tyle, 1993). The lubrication behaviour of such systems is also strongly dependent on the particle size relative to the film thickness between tribological contacts (Wilson, Sakaguchi, & Schmid, 1994). It has been shown that soft hydrogel particles smaller than the film thickness or surface asperity height are entrained between the surfaces, whereas larger particles tend to be excluded from the contact zone (de Vicente, Stokes, & Spikes, 2006; Garrec & Norton, 2012). Particle elasticity and phase volume have also been shown to have a profound influence on the tribological properties of dispersions, where stiffer (less deformable) gelled particles and higher phase volumes generate lower friction coefficients due to a reduction in surface-surface contact (Garrec & Norton, 2013).

Using maize and potato starches as exemplars, the first objective of the present study is to probe the lubrication properties of starch ghost suspensions over a range of concentrations to determine the influence of particle mechanics. The second objective of this study is to understand the viscosity and viscoelastic properties of starch ghost suspensions in both dilute and concentrated regimes. We report the small deformation oscillatory rheological behavior before and after repeated large deformation steady shear tests, combined with light microscopy of ghost particles before and after the test. The particle properties are discussed in terms of the observed differences in soft-tribological response between maize and potato ghost suspensions.

2. Materials and Methods

2.1 Materials

Maize starch was purchased from Penford Australia Ltd. (Lane Cove, NSW, Australia), and potato starch was from Sigma-Aldrich. (St. Louis, MO, USA). Other chemicals used were obtained from

Sigma-Aldrich. All water used was deionized.

2.2 Preparation of granule ghosts

Granule ghosts were prepared by following a method reported previously (Debet & Gidley, 2007; Zhang, Dhital, Flanagan, & Gidley, 2014). Starch (200 mg) was suspended in a small amount of cold water and then poured into hot water (95 °C, 40 mL) with gentle mixing (250 rpm with magnetic stirrer bar) to prevent sedimentation. The dilute suspension (0.5% w/v starch) was cooked at 95 °C for 30 min to ensure the maximum swelling capacity was achieved and then centrifuged (30 °C, 2000 *g* for 15 min). The supernatant was removed, and the spun ghosts were washed twice by resuspension in hot water (90 °C, 100 mL) with gentle manual stirring followed by centrifugation. The fresh ghost particles were finally resuspended in water (room temperature) at weight concentrations of 0.01%, 0.1%; and 0.87% (close packing limit, recovered directly from centrifugation) for potato ghost (PG) suspensions, and 0.01%, 0.1%, 1%, 2%, and 3% (close packing limit, recovered directly from centrifugation) for maize ghost (MG) suspensions, for tribological and rheological measurements. Ghost particles were freshly prepared immediately prior to tribological and rheological measurements in order to minimize any retrogradation effects. The continuous phase of ghost suspensions was separated after centrifugation at 4000 g for 15 min.

2.3 Dry Weight Measurement

The solid content of ghost samples was determined in triplicate by drying the samples in a vacuum oven at 105 °C overnight. The solid content is calculated from the ratio of sample weight measured before and after drying.

2.4 Tribological / lubrication measurements

The friction measurements for all starch ghost suspensions and their continuous phases (20 mL) were obtained at a controlled temperature of 35 °C on a Mini Traction Machine (MTM2, PCS Instruments Ltd., UK), following the methods of Bongaerts, Rossetti, and Stokes (2007) and Selway and Stokes (2013). The tribometer was equipped with a PDMS smooth ball with a radius of 9.5 mm and a flat PDMS disc with a radius of 23 mm and a thickness of 4 mm (PCS Instruments Ltd., UK), which form the rubbing contact. PDMS was selected due to its well-defined mechanical properties and surface chemistry, and suitably low elastic modulus to mimic the low pressure contact typical in biolubrication processes. Prior to the experiments, the PDMS tribopairs were cleaned in an ultrasonic bath with 1% sodium dodecyl sulphate solution, followed by rinsing with de-ionized water. The friction force (F_f) was determined as a function of the applied entrainment speed (U) over a range between 1 and 1000 mm/s under the ball-on-disc configuration. The entrainment speed is defined as the average surface speed of ball and disc, i.e., $U = (U_{ball} - U_{disc})/2$, where U_{ball} and U_{disc} are the surface speeds of the ball and disc, respectively. The applied load (W) was set to 1 N for all tests, and the friction coefficient (μ) can be calculated as the friction force divided by applied load, i.e, $\mu = F_f / W$; the slide-to-roll ratio (SRR) was fixed at 50% to provide a mixed sliding and rolling motion. While the friction coefficient (μ) was measured both for decreasing speed from 1000 to 1 mm/s and followed by increasing speed from 1 to 1000 mm/s, only data obtained from the decreasing speed step are discussed in the main text for clarity. Results are expressed as means with standard deviations of at least five measurements.

2.5 Rheological measurements

The rheological measurements were carried out on an advanced controlled-stress rheometer (Haake Mars 3, Thermo Fisher Scientific, Karlsruhe, Germany) with a heat adjustable Peltier element and temperature controlled hood at a temperature of 35 °C. A 60 mm diameter parallel plate geometry was used to measure steady state flow and viscoelastic properties of aqueous starch ghost suspensions. The gap was set at 200 μm for all experiments in order to avoid any slip or artifact due to the larger particulates, as the sizes of starch ghost particles as estimated from light micrographs were 15 – 35 μm for maize ghosts and 50 – 150 μm for potato ghosts (Zhang, Dhital, Flanagan, & Gidley, 2014). The gap between parallel plates was always zeroed at a normal force of 4 N before each test, and gap error for this set of experiments was typically around 15 μm, calculated using the mathematical method of Davies and Stokes (2005). Prior to the tests, an oscillatory stress sweep test at a frequency of 1 rad/s was performed in order to determine the linear viscoelastic region of samples over a stress range from 0.001 to 100 Pa. To characterize the effect of shear force on the viscoelastic modulus of ghost suspensions (0.87% PG, 1%, 2% and 3% w/w MG), an oscillatory frequency sweep test was performed to determine storage (G') and loss moduli (G") (step 1), followed by a steady shear viscosity measurement (step 2). The sample was then subjected to another oscillatory frequency sweep test (step 3) followed by a steady shear viscosity measurement (step 4), and a final oscillatory frequency sweep test (step 5). The oscillatory frequency sweep test was run at a stress within the linear viscoelastic region in the range of 0.01 to 10 rad/s, and the steady shear measurements were performed for shear rates ranging from 1 to 10,000 s^{-1}. Results were expressed as means with standard deviations of at least duplicate measurements. For the ghost suspensions at dilute concentrations (0.01%, 0.1% w/w PG and MG), only steady shear measurements were performed for shear rates ranging from 1 to 10,000 s^{-1}.

2.6 Light microscopy

Light microscopy was performed using a Zeiss Axio microscope (Oberkochen, Germany). One drop of fresh ghost suspension was diluted and stained with 2% iodine solution, before being recorded by a Zeiss CCD camera (AxioCam ERc5s, Oberkochen, Germany).

2.7 Particle size distribution

Particle size analysis was performed on a Mastersizer Hydro 2000MU (Malvern Instruments Ltd., Malvern, UK) following the method of Zhang, Dhital, Flanagan, and Gidley (2014). A refractive index of 1.34 was used for size calculation of ghost particles. The starch samples were added to circulating water until an obscuration of >10% was recorded. Each measurement was repeated three times with an accuracy of about 0.5%.

3. Results and Discussion

3.1 Tribological characterization of starch ghost suspensions

The tribological properties of starch ghost suspensions and their corresponding continuous phases were investigated across a wide range of concentrations. For clarity, only data obtained from decreasing speed steps are plotted in Figure 1 (data for increasing speed steps are shown in Supporting Information Figure S1). The friction curves of all ghost suspensions (Figure 1 A, B) suggest that lubrication is occurring in the boundary and mixed regimes, with a thin film of lubricant and surface characteristics being dominant. Figure 1A shows that the lubrication properties of maize ghost suspensions are highly dependent on their particle concentration in the fluid. With decreasing values of entrainment speed from 1000 mm/s, all tribological profiles including the water control show a gradual increase in friction coefficient to a maximum occurring at a speed of 40 mm/s. It is observed that this maximum friction coefficient decreases to below that of water with increasing weight concentration (0.01%, 0.1% and 1% w/w) of maize ghost suspensions, indicating that ghost particles are entrained into the contact zone. These entrained particles provide a boundary layer which prevents direct contact between the opposing PDMS surfaces; hence increasing the number of particles entrained reduces the friction coefficient. However, no further reduction in friction coefficient is observed for higher concentrated maize ghost systems (i.e., 1%, 2%, and 3% w/w). This could be explained by considering that once a threshold concentration is reached, where a layer of particles provides a complete barrier to surface contact, further increasing the number of particles does not have a marked influence on the friction coefficient; this has been observed for hard glass-particle suspensions in soft tribological contacts (Yakubov, Branfield, Bongaerts, & Stokes, 2015). For the most dilute and concentrated (i.e., 0.01% and 3% w/w) maize ghost suspensions as well as water, there is a plateau in tribological profiles at low speeds between 1 and 40 mm/s. For other concentrations of maize ghost samples, an increase in friction coefficient with speed is observed in this region (1 – 40 mm/s), possibly due to the deformation or breakdown of the elastomeric ghost particles in the direct contact (Selway & Stokes, 2013). Furthermore, a hysteresis is observed between the decreasing speed steps and increasing speed steps, with the hysteresis extent being concentration dependent (Supporting Information Figure S1). This hysteresis phenomenon has been observed in other soft fluid gels such as agarose (Gabriele, Spyropoulos, & Norton, 2010).

In the case of potato ghosts with various weight concentrations, all tribological profiles (Figure 1 B) starting from high speeds show a gradually increasing friction coefficient in the mixed regime and then a boundary plateau at lower speeds (< 30 mm/s). Compared with the water control, only a slight reduction of friction coefficient is observed over the full range of entrainment speeds. It is noteworthy that the behavior of the potato ghost suspension is independent of weight concentration, suggesting that the potato ghost particles are excluded from or degraded by the soft-contacts. There is a negligible hysteresis observed for potato ghost suspensions and all continuous phase samples (data not shown). The continuous phase of all ghost suspensions (Figure 1 C, D) shows similar tribological profiles with friction coefficient being close to the water control, consistent with few starch polymers being present in the continuous phase.

Maize ghost particles have approximately spherical appearance with relatively small sizes (around 20 - 35 μm), whereas potato ghosts are ellipsoidal and have larger particle sizes (50 - 150 μm) with some apparent fragmentation occurring during the isolation process (Figure 2, before rheology or tribology test). In a previous study, we reported that potato ghosts expand about ca. 4 fold in diameter compared with the parent granule with skins being thinner, more fragile and sensitive to shear force, compared with maize ghosts which increase ca. 2 times in diameter cf. parent granules as estimated by microscopy (Zhang, Dhital, Flanagan, & Gidley, 2014). Maize ghosts subjected to the tribology test only resulted in slightly reduced integrity in morphology, whereas potato ghosts show a significant amount of granule fragments (Figure 2).

We also assessed the particle size of maize ghosts by laser light scattering, the results of which are presented in Figure 3 and Table 1. It is not appropriate to assess particle size of potato ghosts using the Mastersizer instrument, since microscopy analysis showed that shear degradation occurs during measurement at the circulating impellor speed of 2000 rpm (data not shown). Following tribology and rheology tests, the presence of an additional small particle component was seen by both light scattering (Figure 3) and microscopy (Figures 2 and 6). The laser scattering technique makes assumptions that granule ghosts are spherical and homogeneous in order to calculate particle sizes, resulting in an overestimate compared with apparent sizes from microscopy, particularly for the volume weighted mean diameter as shown in Table 1 which emphasizes larger particles within the distribution. Although the laser scatting technique overestimates the actual size of maize ghosts, the presence of a small size fraction led to a slight reduction in calculated values of volume weight mean diameter ($d_{4,3}$) for maize ghosts after tribology and rheology tests with greater effects at higher ghost concentrations (Table 1) in agreement with light microscopic measurements.

3.2 Rheological characterization of starch ghost suspensions after steady shear treatments

The rheology of the dilute starch ghost suspensions is shown in Figure 4. Steady shear viscosity measurements are performed at shear rates of up to 10,000 s^{-1}, which is of similar order to the shear rate present in the tribological contact (Selway & Stokes, 2013; Stokes, Macakova, Chojnicka-

Paszun, de Kruif, & de Jongh, 2011). Figure 4 shows that dilute (0.01% and 0.1%) maize ghost suspensions and 0.01% potato ghost suspension are Newtonian (relatively constant viscosity with shear rate) and measured to have a similar viscosity to the solvent, water, but a 0.1% w/w potato ghost suspension is shear thinning. As their viscosities are all similar, the observed differences in the tribological behavior shown in Figure 1 between the dilute suspensions (≤0.1 %w/w) of maize and potato starch ghost granules is likely to be associated with differences in ghost particle mechanics (e.g. particle modulus) and/or their surface properties. In more concentrated conditions, maize ghost suspensions exhibit a similar maximum friction coefficient (~0.5) at entrainment speeds of around 40 mm/s, presenting a clear particulate lubrication behavior. In contrast, potato ghost suspensions do not show this peak that is common to particle suspensions (Yakubov, Branfield, Bongaerts, & Stokes, 2015; G. E. Yakubov, Zhong, Li, Boehm, Xie, Beattie, et al., 2015). We propose that this is due to the disintegration of the potato ghosts which are entrained within the tribometer gap, as suggested by the observation in Figure 2 of potato ghost granule fragments after the tribology test, whereas maize ghosts were mostly intact.

To gain insight into how shear affects the structure and rheology of granule ghost suspensions, a series of dynamic and steady shear rheology experiments were performed. The viscoelastic moduli (G' and G") (step 1) and steady shear viscosity (step 2) of ghost suspensions at relatively high particle concentrations (i.e., 0.87% w/w potato ghost suspension (approximating to maximum volume occupancy), 1%, 2% and 3% w/w maize ghost suspensions) are presented in Figure 5 as average and standard deviation of duplicate measurements. For the first frequency sweep step (i.e. subjected to no pre-shear), the maize ghost suspensions behave as a weak gel with the storage modulus exceeding the loss modulus and relatively constant with frequency (Figure 5, A, C, E). As the weight concentrations of maize ghost suspensions increases, storage modulus increases. For the concentrations of ghost particles recovered directly from centrifugation (0.87% w/w potato ghost suspension and 3% w/w maize ghost suspension), maize ghosts (Figure 2) have higher storage modulus and viscosity values than the more swollen potato ghosts (Figure 5 E - H), consistent with a previous report on starch pastes (Steeneken, 1989). In contrast to ≤0.1% concentrations, it was found that all ghost suspensions at these higher concentrations have typical non-Newtonian shear thinning flow behavior (i.e., viscosity decreases as a function of increasing shear rate).

The second and third small-amplitude oscillatory shear measurements (step 3 and 5) characterize viscoelastic properties immediately after one and two shear rate sweeps (steps 2 and 4) respectively. After being sheared for one cycle, the ghost granule suspensions display a marked decrease in storage and loss modulus, but still behaved as a weak gel with storage modulus higher than loss modulus over the frequency range (Figure 5 A, C, E, F). In addition, the differences between the storage modulus and the loss modulus after steady shear rate sweep are smaller, especially for 1% w/w maize and 0.87% w/w potato ghost suspensions. After two cycles of steady state shear treatment, further decrease of viscoelastic moduli can be seen, but not as great as the differences caused by the first cycle (Figure 5 A, C, E).

After the five-step rheological measurements, maize ghosts at concentrated regimes show reduced integrity in morphology as judged by microscopy (Figure 6 A - C), consistent with small differences in the corresponding particle size distribution (Figure 3) and volume weight mean diameter ($d_{4,3}$) data (Table 1). Almost all potato ghost particles subjected to two-rounds of steady shear treatment show significant amounts of small rod-like fragments (Figure 6), consistent with rheoscope observations of elongated particles under high shear force (Desse, Fraiseau, Mitchell, & Budtova, 2010). It is interesting that the fragments from potato ghosts after steady shear treatment are different in morphology to potato ghosts after the tribology test (Figure 2); we suggest that the more rounded fragments in the latter result from both rolling and shear effects between soft-contacts in the tribometer.

4. Conclusions

This paper has reported for the first time the lubrication and rheology of aqueous suspensions of isolated swollen starch granule ghosts over a wide range of concentrations, using maize and potato starches as exemplars. Although all suspensions show boundary and mixed lubrication, there are clear differences in tribology and rheology between maize and potato starch swollen granule ghosts. Subjecting the smaller size and more robust maize ghosts to tribology or rheology tests only resulted in slightly reduced integrity in morphology, whereas large and fragile potato ghosts showed significant amounts of granule fragments after testing. A markedly decreased maximum friction coefficient point at an entrainment speed of 40 mm/s with increasing concentration (from 0.01% to 1% based on weight) of maize ghost suspensions was observed, while the apparent friction coefficient is concentration independent for potato ghosts although this is likely to be due to disintegration of fragile potato ghosts under tribological contact. We conclude that soft-tribological properties of starch ghost suspensions can be due to either particulate (e.g. maize ghosts) or polymeric (particularly for potato ghosts) forms, the balance between which could potentially contribute to the perception of starch-containing food in the mouth and the properties of starches as processed and used in a wide range of technological applications.

AUTHOR INFORMATION

Corresponding Author

Email: m.gidley@uq.edu.au (M. J. Gidley). Phone: +61 7 3365 2145; Fax: +61 7 3365 1177.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MG, maize ghost suspension; PG, potato ghost suspension;

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FIGURE CAPTIONS

Figure 1. Friction coefficient as a function of entrainment speed for starch granule ghost suspensions (A, B) and their continuous phases (C, D) at different concentrations. (MG, maize starch ghost suspension; PG, potato starch ghost suspension; CP, continuous phase)

Figure 2. Light micrographs of starch granule ghost suspensions before and after being subjected to tribology test. Arrows show starch ghost fragments present after tribology test. (MG, maize starch ghost suspension; PG, potato starch ghost suspension; tribo, tribology test)

Figure 3. Particle size distributions of 3% maize ghost suspension before and after being subjected to tribology or rheology test. (MG, maize starch ghost suspension; tribo, tribology test; rheo, rheology test)

Figure 4. Steady state viscosity of dilute starch granule ghost suspensions. (MG, maize starch ghost suspension; PG, potato starch ghost suspension)

Figure 5. Five-step rheology for concentrated starch granule ghost suspensions after sequential small amplitude oscillatory (Steps 1, 3 and 5) and steady shear (Steps 2 and 4) measurements: (A, C, E, G) storage modulus and loss modulus as a function of frequency (step1, 3 and 5); (B, D, F, H) steady state viscosity as a function of shear rate (step 2 and 4). (MG, maize starch ghost suspension; PG, potato starch ghost suspension)

Figure 6. Light micrographs of starch granule ghost suspensions after being subjected to five-step rheology test. Arrows show starch ghost fragments present after five-step rheology test. (MG, maize starch ghost suspension; PG, potato starch ghost suspension; rheo, rheology test)

Figure 1.

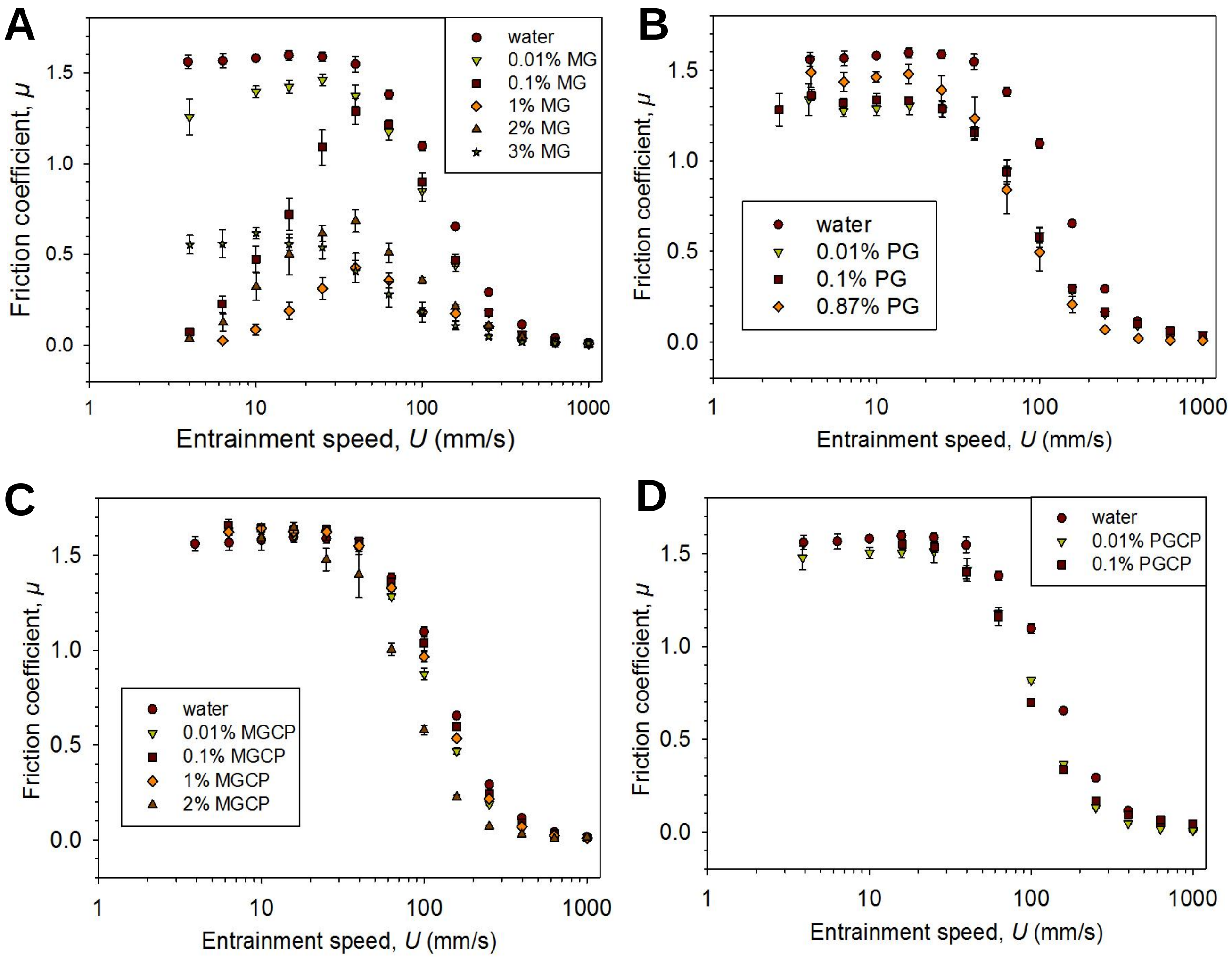

A
water
0.01% MG
0.1% MG
1% MG
2% MG
3% MG
Friction coefficient, μ
Entrainment speed, U (mm/s)
B
water
0.01% PG
0.1% PG
0.87% PG
Friction coefficient, μ
Entrainment speed, U (mm/s)
C
water
0.01% MGCP
0.1% MGCP
1% MGCP
2% MGCP
Friction coefficient, μ
Entrainment speed, U (mm/s)
D
water
0.01% PGCP
0.1% PGCP
Friction coefficient, μ
Entrainment speed, U (mm/s)

Figure 2.

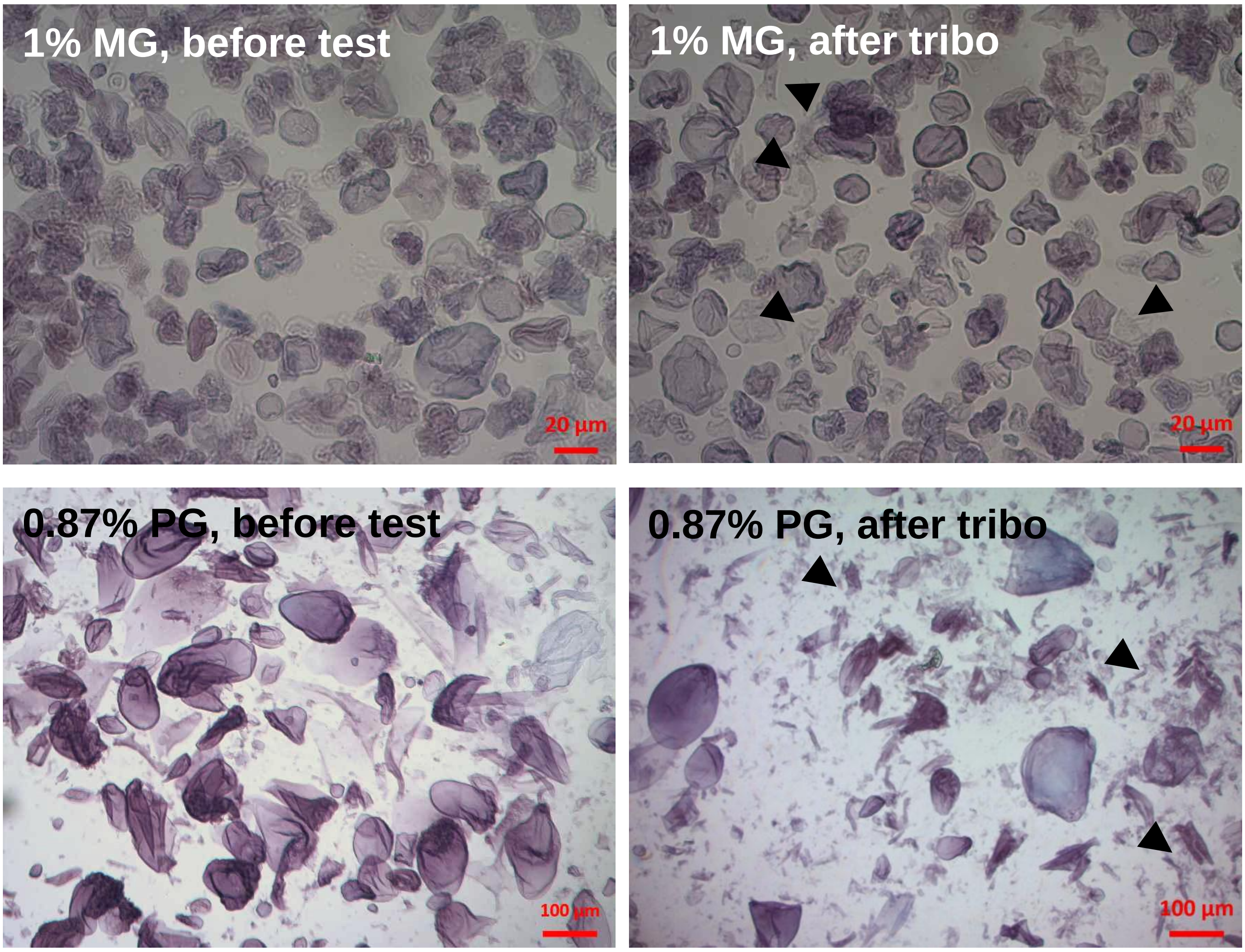
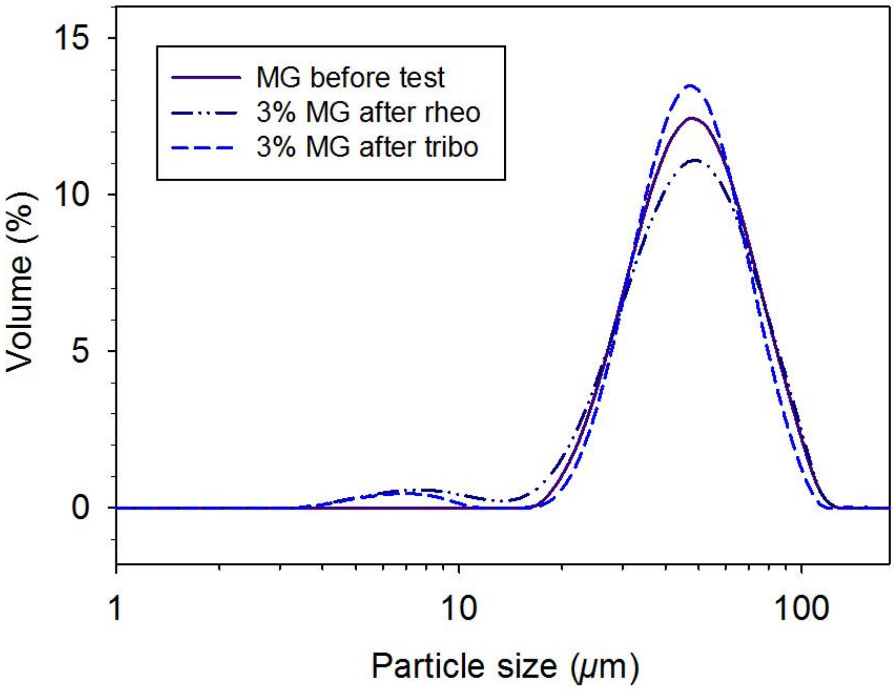
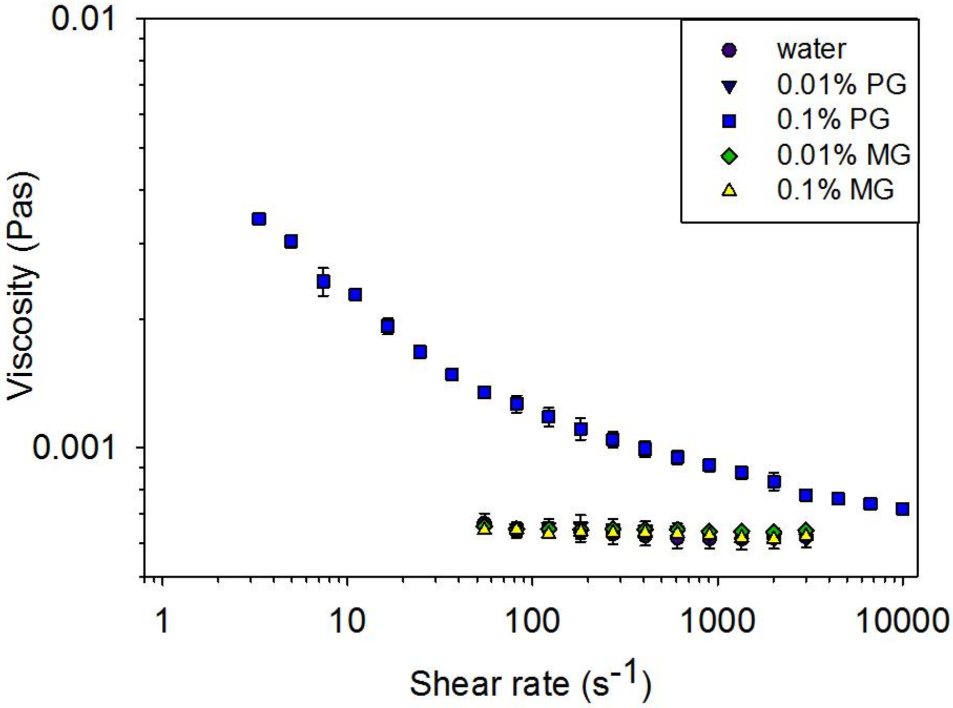

1% MG, before test
20 µm
1% MG, after tribo
20 µm
0.87% PG, before test
100 µm
0.87% PG, after tribo
100 µm

Figure 3.



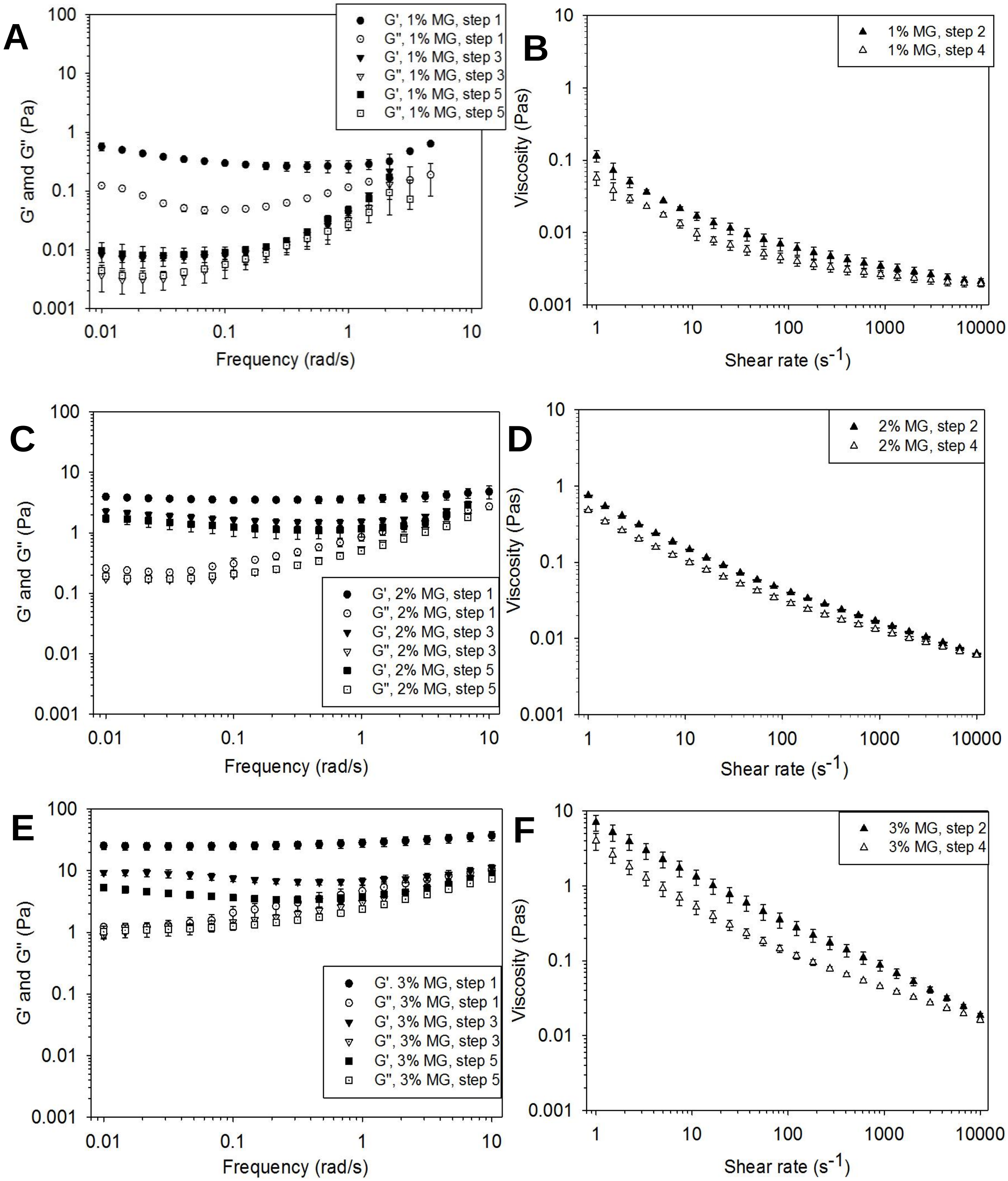
15
10
5
0
Volume (%)
MG before test
3% MG after rheo
3% MG after tribo
1
10
100
Particle size (μm)

Figure 4.



0.01
0.001
Viscosity (Pas)
1
10
100
1000
10000
Shear rate (s-1)
water
0.01% PG
0.1% PG
0.01% MG
0.1% MG

Figure 5.



A
G', 1% MG, step 1
G", 1% MG, step 1
G', 1% MG, step 3
G", 1% MG, step 3
G', 1% MG, step 5
G", 1% MG, step 5
G' amd G" (Pa)
Frequency (rad/s)
B
1% MG, step 2
1% MG, step 4
Viscosity (Pas)
Shear rate (s-1)
C
G', 2% MG, step 1
G", 2% MG, step 1
G', 2% MG, step 3
G", 2% MG, step 3
G', 2% MG, step 5
G", 2% MG, step 5
G' and G" (Pa)
Frequency (rad/s)
D
2% MG, step 2
2% MG, step 4
Viscosity (Pas)
Shear rate (s-1)
E
G'. 3% MG, step 1
G", 3% MG, step 1
G', 3% MG, step 3
G", 3% MG, step 3
G', 3% MG, step 5
G", 3% MG, step 5
G' and G" (Pa)
Frequency (rad/s)
F
3% MG, step 2
3% MG, step 4
Viscosity (Pas)
Shear rate (s-1)

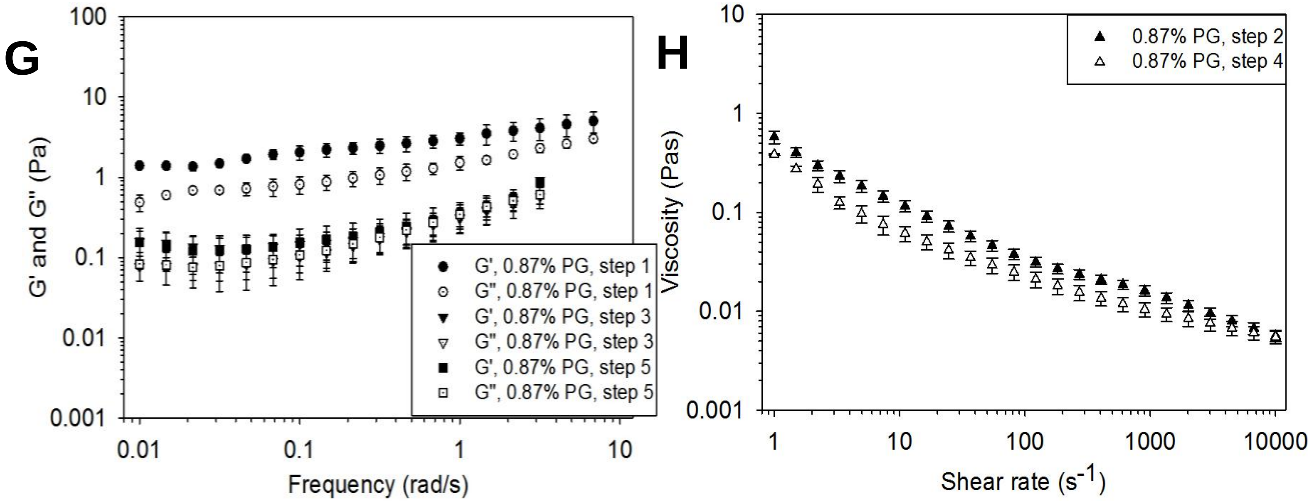
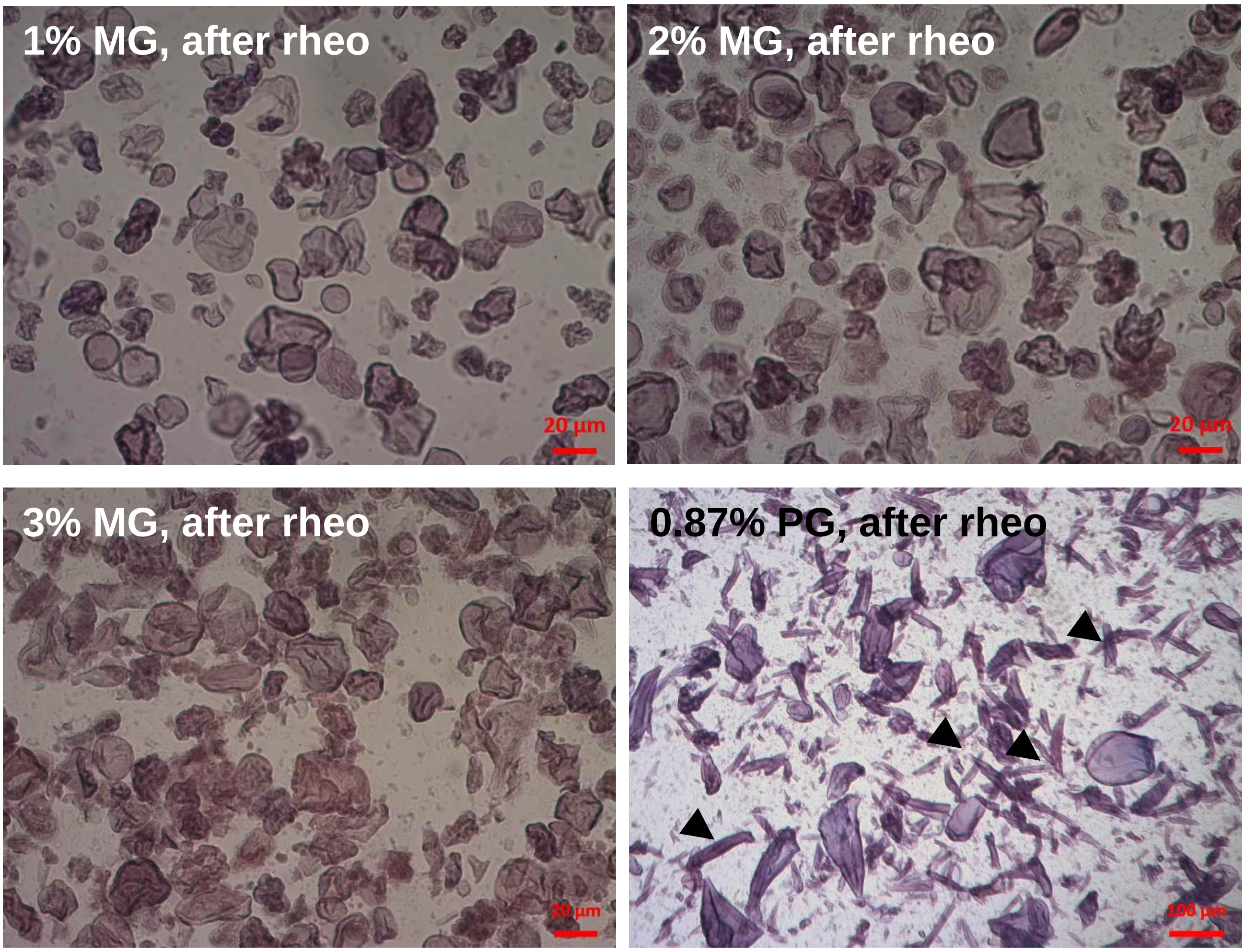

G
100
10
1
0.1
0.01
0.001
G' and G'' (Pa)
0.01
0.1
1
10
Frequency (rad/s)
G', 0.87% PG, step 1
G'', 0.87% PG, step 1
G', 0.87% PG, step 3
G'', 0.87% PG, step 3
G', 0.87% PG, step 5
G'', 0.87% PG, step 5
H
10
1
0.1
0.01
0.001
Viscosity (Pas)
1
10
100
1000
10000
Shear rate (s-1)
0.87% PG, step 2
0.87% PG, step 4

Figure 6.



1% MG, after rheo
20 µm
2% MG, after rheo
20 µm
3% MG, after rheo
20 µm
0.87% PG, after rheo
100 µm

Table 1. Calculated values for volume weighted mean diameter ($d_{4,3}$) in μm of maize starch granule ghost suspensions (MG) before and after being subjected to tribology and rheology tests.

sample	$d_{4,3}$	sample	$d_{4,3}$
MG	47.60 ± 0.12		
1% MG after tribo	47.36 ± 0.14	1% MG after rheo	46.50 ± 0.53
2% MG after tribo	46.71 ± 0.20	2% MG after rheo	46.23 ± 0.85
3% MG after tribo	46.14 ± 0.09	3% MG after rheo	45.84 ± 0.05