

Shear thickening of corn starch suspensions: Does concentration matter?

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ABSTRACT

Suspensions of corn starch and water are the most common example of a shear thickening system. Investigations into the non-Newtonian flow behavior of corn starch slurries have ranged from simplistic elementary school demonstrations to in-depth rheological examinations that use corn starch to further elucidate the mechanisms that drive shear thickening. Here, we determine how much corn starch is required for the average person to “walk on water” (or in this case, run across a pool filled with corn starch and water). Steady shear rate rheological measurements were employed to monitor the thickening of corn starch slurries at concentrations ranging from 0 to 55 wt.% (0–44 vol.%). The steady state shear rate ramp experiments revealed a transition from continuous to discontinuous thickening behavior that exists at 52.5 wt.%. The rheological data was then compared to macroscopic (~5 gallon) pool experiments, in which thickening behavior was tested by dropping a 2.1 kg rock onto the suspension surface. Impact-induced thickening in the “rock drop” study was not observed until the corn starch concentration reached at least 50 wt.%. At 52.5 wt.%, the corn starch slurry displayed true solid-like behavior and the falling rock “bounced” as it impacted the surface. The corn starch pool studies were fortified by steady state stress ramps which were extrapolated out to a critical stress value of 67,000 Pa (i.e., the force generated by an 80 kg adult while running). Only the suspensions containing at least 52.5 wt.% (42 vol.%) thickened to high enough viscosities (50–250 Pa s) that could reasonably be believed to support the impact of a man’s foot while running. Therefore, we conclude that at least 52.5 wt.% corn starch is required to induce strong enough thickening behavior to safely allow the average person to “walk on water”.

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1. Introduction

The rheological behavior of corn starch and water suspensions is a popular topic found in many scientific domains: polymers, food science and technology, ceramics, cosmetics, ballistics, and others [1,2]. Aqueous slurries of corn starch, affectionately named “oobleck” after a children’s story by Dr. Seuss, transition from fluid-like to solid-like behavior under high shear forces. This transition, typically denoted by an abrupt increase in viscosity, is termed shear thickening (or dilatancy). Shear thickening fluids have been exploited for commercial use in shock absorbing and force damping applications such as skis, tennis rackets, and more recently, flexible body armor [3,4]. The unique ability of corn starch suspensions to shear thicken makes them an intriguing system for study.

Shear thickening was first examined in detail by Hoffman [5] over 40 years ago and was thought to be a shift in suspension

microstructure from an ordered, layered state to a disordered state with increased particle interactions (coined the order-to-disorder transition (ODT) theory) [6–8]. In the decades following Hoffman’s work, researchers discovered that the onset of shear thickening is actually a result of particle hydroclustering (clusters of particles held together solely by hydrodynamic lubrication) and an order-to-disorder transition is not a requirement for dilatant behavior [9–14]. At large shear rates and stresses, convective and hydrodynamic forces dominate over interparticle forces and cause hydroclustering (or clumping) of particles [15–17]. Hydroclusters create fluctuations in particle motion and make movement throughout the suspension more difficult. The restriction in particle motion is represented by a higher rate of energy dissipation and an increase in viscosity (i.e., shear thickening). Hydroclusters (by definition) are reversible and a decrease in applied shear will disband the shear-induced clusters. Hydrocluster formation has been thoroughly studied through rheo-optical experiments [18,19], neutron scattering [13,14], stress-jump rheological measurements [20,21], and *in situ* rheological small-angle neutron scattering (termed rheo-SANS) [22]. Currently, hydroclusters are regarded as the defining aspect of the shear thickened state [23].

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A suspension of corn starch particles in water is the most well-known example of a shear thickening system. The unparalleled combination of fluid and solid-like behavior displayed by corn starch suspensions has allowed people to perform the seemingly impossible feat of “walking on water”. Childlike curiosity and the yearning for divine aptitude has sparked numerous online videos in which people are able to “walk on water” by taking advantage of the thickening response. At low shear forces, a suspension of corn starch and water behaves as a liquid, where it will flow, take the shape of its container, and resist compression. Yet, when a person applies a strong force by either running or jumping on the mixture, the suspension solidifies and keeps anything (or anyone) from penetrating its surface. One of the most popular videos of this type is from the Discovery Channel’s show *MythBusters* (Fig. 1a) [24]. In this episode the famed duo takes turns running across a large storage tote (~5 ft deep) filled with over 200 gallons of water and 1000 lbs. of corn starch (~50/50 mix by weight). Another widely observed video is from a television show originating in Barcelona, Spain. The film makers created a ~15 foot long pool filled with corn starch and water and examined the thickening behavior by running and jumping on the mixture (the actors even swim around in the pool) [25]. In both videos, the performers were able to run across their respective pools as if they were running across a rigid, solid surface. However, once the person stood still, removing nearly all applied stress, they sank. The observed sinking action is a consequence of the reversible nature of shear thickening, once the applied force is released the suspension’s viscosity returns to its original liquid-like state. “Corn starch monsters” is yet another popular genre of online videos utilizing corn starch and water suspensions (Fig. 1b). In these films, a mixture of corn starch and water is placed upon a speaker amplifying music. The vibrations from the music apply a stress on the suspension and cause it to stand up, acoustically growing “monsters”. The corn starch globs stay intact until the music is terminated; again, displaying the reversibility of the shear thickening response. These online video sensations (both the corn starch pools and acoustic “monsters”),

although entertaining, provide little scientific insight into the shear thickening of corn starch suspensions.

Other studies used corn starch as a model suspension to further investigate the underlying mechanisms behind shear thickening [26–32]. Recently, Brown and Jaeger used corn starch slurries to help elucidate the jamming phenomenon [29] and to distinguish jamming from discontinuous shear thickening behavior [31]. While Fall et al. [26–28] show that corn starch shear thickening can be viewed as re-entrant solid transition, where the suspension’s viscosity changes from a solid to a liquid and then back to a solid with increasing shear stress. All of the above studies use corn starch slurries as a means to investigate a specific aspect of shear thickening, where thickening behavior is the focal point. The authors only operate at a finite starch concentration range (somewhere between 40 and 60 wt.%) where shear thickening is most prevalent. Although these previous examinations have provided a detailed insight into the shear thickening response, many questions still exist pertaining to the mysterious shear thickening behavior of corn starch. What happens at lower concentration regimes? Does shear thickening cease? If you apply a strong enough force can you get a low concentration (< 20 wt.%) corn starch slurry to shear thicken? What is the required amount of thickening in order for someone to “walk on water?” Is there a connection between bench scale rheological measurements and these online videos? The objective of this work is to perform a comprehensive investigation of corn starch shear thickening, where concentration is the focus. We examine the shear thickening behavior of aqueous corn starch slurries as a function of solids concentration, ranging from 0 to 55 wt.% (0–44 vol.%). More specifically, we determine the concentration at which a suspension of corn starch and water will thicken enough to allow the average person to “walk on water”. At last, we tie together bench-top rheological measurements and macroscopic corn starch “pool” experiments.

2. Experimental methods

2.1. Sample preparation

Suspensions of corn starch and water were prepared using both refined (Argo corn starch, ACH Food Companies, Inc., Memphis, TN) and bulk corn starch (Honeyville Food Products, Inc., Brigham City, UT) in ultrapure DI water at varying concentrations of: 10, 20, 25, 30, 40, 45, 47.5, 50, 52.5 and 55 wt.%. Measured weight fractions were converted to calculated volume fractions assuming a corn starch density of 1.55 g/cm³ [32]. Mixtures were thoroughly stirred and allowed to equilibrate for approximately 24 h at room temperature to ensure consistent hydration of the corn starch grains. Prior to experimentation, samples were re-stirred and then sonicated for 10 min to break up any aggregates, as well as to ensure sample homogeneity.

2.2. Rheological measurements

All rheological measurements were conducted using TA Instruments’ AR-G2 stress controlled rheometer (New Castle, DE). All rheology measurements were performed at 25 °C and repeated in triplicate (at a minimum) to quantify measurement error. Temperature control of ± 0.1 °C was provided by a Peltier heating jacket. Each sample was run through the following three-step experimental procedure to probe for shear thickening behavior: (1) a stress ramp from 0.01 to 100 Pa with a step termination greater than 100 s⁻¹ to quantify yield stress, and (2) a steady-state shear rate ramp from 0.01 to 1000 s⁻¹ and a steady-state shear rate reduction from 1000 to 0.01 s⁻¹ to confirm the reversible nature of any shear thickening event. Samples were initially sheared using a 40 mm

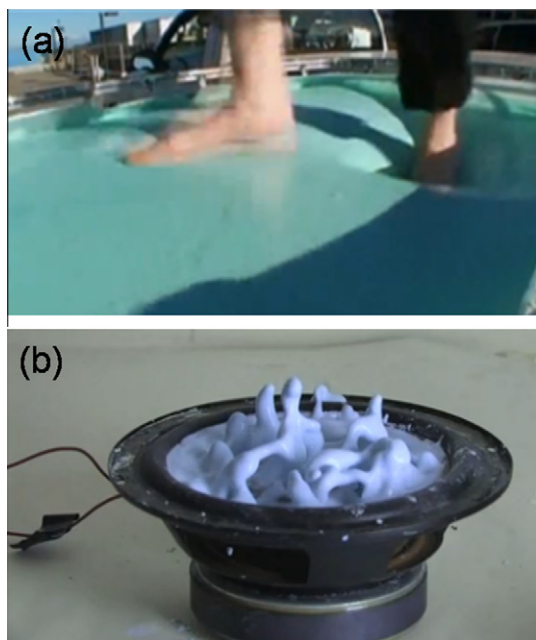


Fig. 1. (a) *MythBusters* walking on “water” YouTube video: *MythBusters – Walking on water – Ninja part 5/5* (http://www.youtube.com/watch?v=IhJE0VRh_zY) and (b) “Corn starch monsters” in YouTube video: *Non-Newtonian fluid on a speaker cone* (<http://www.youtube.com/watch?v=3zoTKXXNQIU>).

cone and plate geometry; however, the samples were found to phase separate during experimentation, making the collected data sporadic and irreproducible. Thus, yield stress and steady flow measurements were conducted using the vane and cup setup (diameter = 15 mm, gap = 1 mm, and height = 38 mm).

The four blade vane geometry was selected to combat the effects of phase separation and to help eliminate erratic data sets. Also, the vane setup is commonly employed for yield stress measurements of structured fluids [33–38] and measuring yield stress as a function of particle concentration is one way to eliminate the possibility of slip at the tool-suspension interface [33,37]. The average yield stress of the corn starch and water suspensions increased from ~ 0.01 to 10 Pa with increasing starch concentration from 30 to 55 wt.% (all samples were pre-sheared prior to the yield stress measurement to insure a consistent starting microstructure across all particle loadings). The exponential increase in yield stress as a function of suspension volume fraction agrees with theoretical predictions [39–41] which describe an infinitely increasing yield stress with increasing volume fraction. Therefore, we are confident that the rheological data presented in this study is devoid of phase separation and slip at the tool interface.

2.3. Microscopy

Samples were imaged on an inverted light microscope utilizing an Epix high speed camera (Buffalo Grove, IL) with a 40 \times Leica objective (headquartered Solms, Germany). Samples were allowed to rest for 24 h, re-stirred, and then imaged (Fig. 2a and b). Image post processing and data analysis were performed using MATLAB. 283 and 249 particles were evaluated for the refined and bulk corn starches, respectively. Image analysis shows that the refined and bulk corn starches, on average, are composed of similar sized particles (Fig. 2c). The average refined corn starch particle area is $191 \mu\text{m}^2$ with an average equivalent diameter of $15.0 \pm 4.2 \mu\text{m}$,

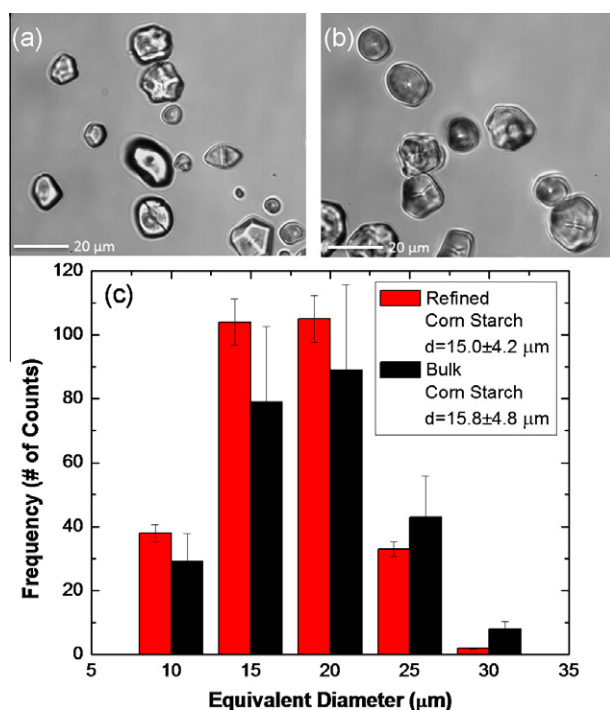


Fig. 2. (a) Microscope image of refined and (b) bulk corn starch particles suspended in water. (c) Particle size distribution of refined (red) and bulk (black) corn starches. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

while the mean bulk corn starch particle area is $213 \mu\text{m}^2$ with an average equivalent diameter of $15.8 \pm 4.7 \mu\text{m}$.

2.4. Corn starch pool preparation

Large pools containing ~ 5 gallon mixtures of water and corn starch were made using bulk corn starch and tap water. Corn starch was weighed in a plastic tub (~ 18 inches \times 15 inches \times 6 inches, length \times width \times height, respectively) ranging in concentration from 30–55 wt.% (in increments of 5 wt.%) and tap water was slowly added while stirring with a small garden rake. Stirring was continued until a uniform mixture was achieved through visual inspection. Corn starch pools were used for performing macroscopic stress measurements by running, jumping, and dropping objects onto the mixture. These macroscale experiments were then compared to rheological results.

3. Results and discussion

3.1. Steady shear experiments

Corn starch suspensions exhibit two distinct viscosity regimes with increasing shear rate: (1) at low shear rates (~ 0.01 – 1 s^{-1}), shear thinning behavior is witnessed and (2) at higher shear rates ($>1 \text{ s}^{-1}$), shear thickening behavior is observed (Fig. 3). Shear thinning is commonly observed in colloidal suspensions and historically, was characterized as particle layering with the direction of flow, where layers of particles can slide past one another more easily than if they were randomly distributed [6,23,42,43]. Recent work by Cheng et al. [44] and Brown et al. [30] argue that the degree of shear thinning displayed by suspensions cannot be attributed to particle rearrangement alone. The large decrease in viscosity during the shear thinning regime is a result of two contributing factors: (1) a constant, hydrodynamic viscosity contribution caused by viscous stresses and (2) an entropic contribution triggered by random particle collisions.

In the shear thickening regime, increases in viscosity are accredited to the formation of transient particle clusters (i.e., hydroclusters). The formation of hydroclusters is initiated when particles are convected into near contact with one another by strong shear forces. The particles are then held together by large lubrication forces stemming from the fluid that is entrained between the clusters. Both the shear thinning and thickening viscosity regimes agree in principle with previous data from a 55 wt.% corn starch

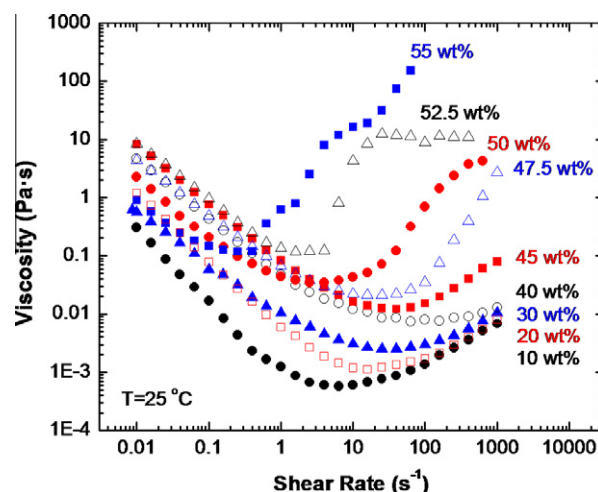


Fig. 3. Steady state shear rate ramp of corn starch and water suspensions ranging in concentration from 10 to 55 wt.%.

slurry published by White et al. [32]. The inflection point at which the transition from shear thinning to shear thickening behavior occurs is considered the critical thickening shear rate and a corresponding thickening shear stress can be extracted at this location. Previous studies have shown that shear thickening scales with applied stress rather than shear rate [14–16].

In general, as the corn starch concentration was increased from 10 wt.% to 55 wt.%, thickening behavior not only occurred at lower shear rates, but the degree of thickening became more prominent (Fig. 3). At the lower starch concentrations (10–30 wt.%), the suspensions exhibit relatively weak thickening behavior and an increasing critical thickening shear stress was observed with increased particle loading (Fig. 4). Conversely, once the corn starch concentration reached 40 wt.% the thickening shear stress remained constant at ~ 0.5 Pa with increasing weight fraction. In theory, at low particle loadings (<40 wt.%), shear thickening is governed solely by viscous stresses and thickening shear stress is reported to increase as a function of increasing particle loading [14,30]. However, at higher packing fractions (>40 wt.%), shear thickening is still driven by hydrodynamic (or viscous) stresses, but it also incorporates a non-viscous mechanism arising from the confining forces of the system boundaries [31]. The fixed stiffness of the boundaries leads to a thickening shear stress that is independent of the solids fraction. Other colloidal systems have been reported to shear thicken at a single critical stress value, regardless of the solids fraction [14–16,45].

Here, shear thickening became so strong that a transition from continuous to discontinuous thickening was observed at 52.5 wt.% (Fig. 3). A shift from mild (continuous) thickening to strong (commonly discontinuous) thickening has been reported in many systems [14,26,29,46–49]. Egres and Wagner [46] observed a transfer from continuous to discontinuous shear thickening at a volume fraction (ϕ) of 0.35 using precipitated calcium carbonate particles suspended in polyethylene glycol. Brown and Jaeger [29] witnessed a change in thickening behavior at $\phi = 0.56$ for a suspension of glass spheres and at $\phi = 0.48$ for a corn starch and water system (the water was density matched with corn starch using CsCl). The authors also noted that there was a high degree of uncertainty (± 0.1) amongst their reported corn starch volume fractions due to absorbed water from the atmosphere. In our study, the observed change in thickening behavior at 52.5 wt.% ($\phi = 0.42$) falls directly within the range of published critical concentrations and coincides, within experimental accuracy, with data presented by Brown and Jaeger [29]. Previous studies examining the shear thickening of corn starch and water slurries also witnessed this

discontinuous thickening behavior and even use these suspensions as a model system to further elucidate the jamming transition [26,32]. With this work, we want to develop a correlation between discontinuous thickening behavior and the ability to walk across an aqueous corn starch suspension. Is a “jammed” microstructure required in order for the average person to “walk on water” (in this case a mixture of corn starch and water)?

3.2. Rheological comparison of refined and bulk corn starches

Before examining the capability of a corn starch suspension to support the weight of an average adult human, we must first verify that the shear thickening behavior between refined and bulk corn starch slurries is similar (financially, it would be irrational to attempt to fill a ~ 5 gallon pool with corn starch that was not purchased in bulk quantity). Therefore, we compared the steady state flow curves of a 40, 45, and 52.5 wt.% corn starch suspension for both the refined and bulk starches (Fig. 5). At all three particle loadings, the bulk slurries had higher overall viscosities (throughout the shear thinning and thickening regimes) than the suspensions prepared with the more refined corn starch. Initially we thought the discrepancy in viscosity originated from differences in average grain size between the two types of corn starch. However, there is no statistical difference in the average particle size shown in Fig. 2c. The divergence in viscosity may stem from variations in surface chemistry, particle anisotropy, or degree of cross-linking within the microgel-like starch particles. Work by Dziechciarek et al. [50] witnessed a decrease in reduced viscosity of colloidal starch suspensions with increased levels of cross-linking (higher cross-linking within microgels generally leads to decreased swelling [51,52]). It is possible that the refined corn starch contains a higher degree of cross-linking than the bulk corn starch, however, water uptake studies were inconclusive.

Also, when focusing on the 52.5 wt.% samples, the discontinuous thickening behavior displayed by the refined corn starch slurry was absent in the flow curve of the bulk suspension. However, after the discontinuous thickening by the refined suspension and the continuous thickening of the bulk mixture, both samples thicken to the same end-point viscosity. As discussed by Barnes [7] the lack of discontinuous thickening behavior exhibited by the bulk sample may be due to the broader size distribution of the bulk starch particles (Fig. 2c).

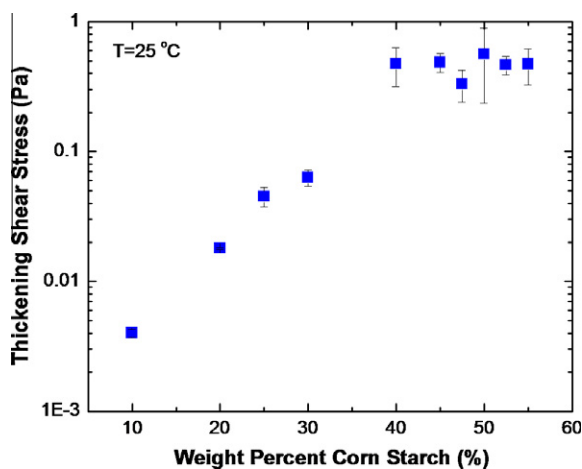


Fig. 4. Thickening shear stress as a function of corn starch concentration (wt.%). The critical thickening shear stress was extracted from the viscosity minima along the steady state flow curves (Fig. 3).

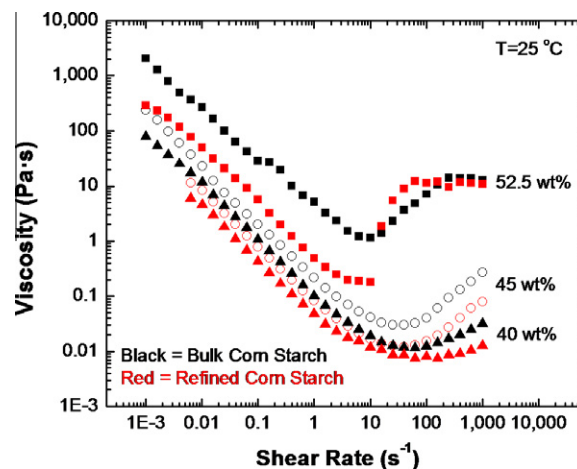


Fig. 5. Steady state shear rate ramp of the refined (red) and bulk (black) corn starches at 40 (triangles), 45 (circles), and 52.5 (squares) wt.%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Connecting rheology with corn starch pool experiments

Since the rheological behavior of the refined and bulk corn starches agreed, we proceeded to relate our rheological measurements to macroscopic “pool” experiments. To make this comparison, we filled a large plastic storage tub with ~5 gallons of corn starch slurry at concentrations ranging from 30 to 55 wt.%. A rock with a mass of 2.1 kg and an impact surface area of nearly 142 cm² (this was the largest and flattest face on the rock) was dropped from a height of 0.3 m onto the surface of the corn starch suspensions (the rock dropping experiment resulted in an applied shear stress of ~1500 Pa). Dropping the rock on the starch mixtures allowed us to predict the minimum concentration of corn starch required to support the stress generated from the foot of a person during walking (without the mess and safety concerns of someone actually attempting to walk across the samples).

From the “rock drop” experiments, it was observed that suspensions containing 45% corn starch by weight or less, were unable to support the force of the rock (Fig. 6a). The rock passed through the lower weight fraction suspensions with minimal resistance, creating a large splash and hitting the bottom of the pool almost instantly (see the “Rock Drop Experiments” video in the supplementary data). The suspensions with less than 45 wt.% corn starch were able to be mixed with little difficulty and for the most part, portrayed fluid-like behavior regardless of the applied stress. Conversely, suspensions containing 50 wt.% corn starch (or more), were able to support the force of the rock through an impact-induced thickening response (Fig. 6b). When the rock hit the surface of these highly concentrated slurries it “stuck” and was momentarily suspended on the surface of the suspension. At a corn starch concentration of 52.5 wt.% the rock hit the surface of the pool and was stopped (Fig. 6c) and then recoiled slightly upward (Fig. 6d) before slowly sinking to the bottom of the tub. The eventual sinking of the rock is a depiction of the reversible nature of shear thickening. Also, it is worth noting that the observed thickening response was independent of the “impact area” at which the rock contacted the corn starch mixture (i.e., dropping the rock on a “sharp” face did not lead to surface penetration). In addition to resisting the force of the rock, the mixtures containing ≥ 50 wt.%

were able to support the impact of an 80 kg adult male while running.

In order to make a direct comparison between our rheological measurements and corn starch pool experiments, an estimate of the force per area exerted by the foot of an average adult male while running must be calculated. Cross [53] measured the maximum applied force from the foot of an 80 kg person running at a speed of 6 m/s to be ~2000 N. We then approximated the surface area of a size 10 (US) men's shoe to be ~0.03 m². Using the measured applied force from Cross (2000 N) and our estimate of the surface area from a men's size ten shoe (0.03 m²), we calculated the applied stress from an average adult male while running to be ~67,000 Pa. In order for a man to “walk on water”, an aqueous corn starch slurry must thicken to a near solid-like viscosity under the critical applied stress of 67,000 Pa. Unfortunately, a stress of this magnitude (>10,000 Pa) is unmeasurable in a conventional rheometer; therefore, a direct comparison between our rheological data and observations from the corn starch pool experiments could not be made.

Instead, a steady state shear stress ramp from 0.01 to 1,000 Pa was conducted on corn starch suspensions of 40, 45, and 52.5 wt.% (for both the refined and bulk corn starches; Fig. 7). The shear thickening regime from the steady state stress data was fit to a trendline and then extrapolated out to the calculated critical applied stress value of 67,000 Pa (extrapolated data are represented by open symbols in Fig. 7). We are operating under the assumption that the viscosity of each suspension would rise in a continuous fashion and discontinuous jumps in viscosity are not witnessed at large shear stresses (≥ 1000 Pa). Thus, the extrapolation is a first approximation of each suspensions' viscosity at an immeasurable shear stress regime. From the extrapolation, an approximate viscosity at 67,000 Pa was obtained for each examined corn starch concentration (Table 1).

At the calculated critical shear stress (67,000 Pa) the 52.5 wt.% refined and bulk corn starch suspensions displayed viscosities that were respectively 180 and 18 times greater than their 45 wt.% counterpart (Table 1). The 52.5 wt.% corn starch slurries have viscosities that are comparable with the intrinsic viscosities of semisolids such as ketchup (50 Pa s) and peanut butter (250 Pa s).

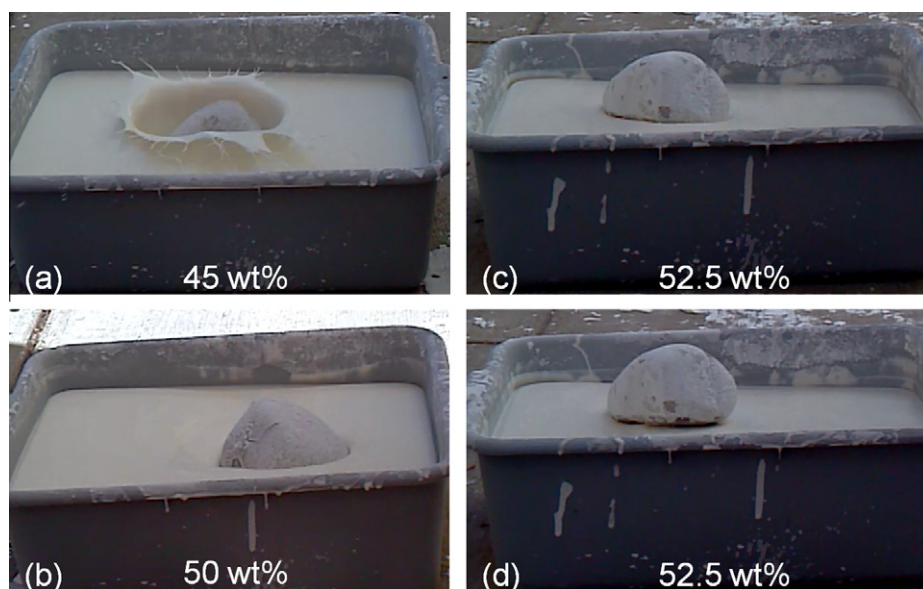


Fig. 6. Images of a 2.1 kg rock impacting the surface of corn starch slurries with concentrations of: (a) 45 wt.%, (b) 50 wt.%, (c) 52.5 wt.% at impact, and (d) 52.5 wt.% immediately after impact. See the real-time impact of the rock on the “Rock Drop Experiments” video in the supplementary material.

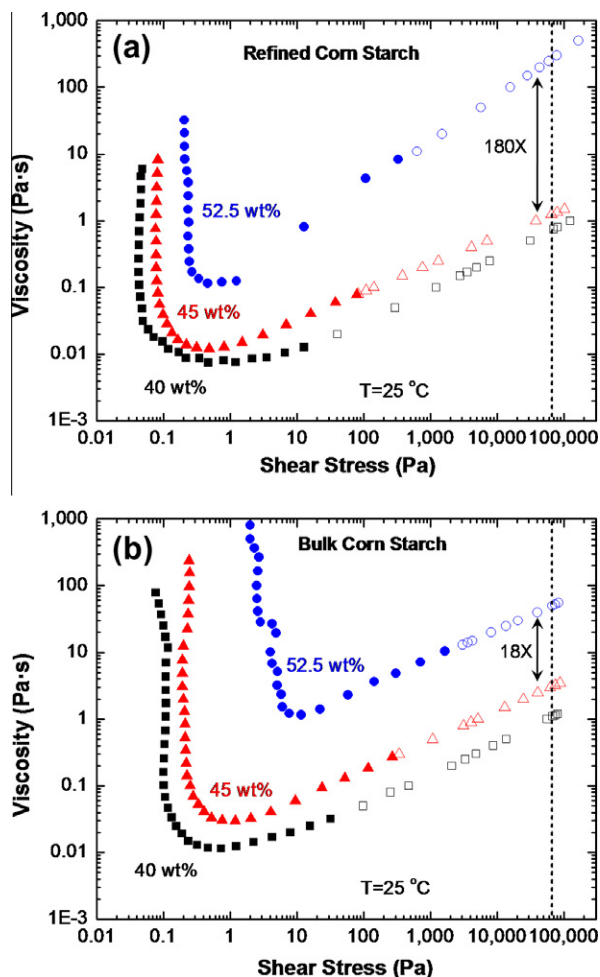


Fig. 7. Steady state shear stress ramp of (a) refined and (b) bulk corn starch slurries at 40 wt.% (black squares), 45 wt.% (red triangles), and 52.5 wt.% (blue circles). Filled symbols represent measured rheological data and open symbols are extrapolated data out beyond the calculated critical stress of 67,000 Pa. The vertical dashed line corresponds to the calculated applied stress from an average adult male while running (67,000 Pa). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Estimated viscosities for corn starch slurries at an applied shear stress of 67,000 Pa.

Corn starch concentration (wt.%)	Viscosity (Pa s)	
	Refined	Bulk
40	0.7	1.1
45	1.5	3.1
52.5	270	55

One could imagine running across a pool filled with peanut butter. However, the suspensions with 45 wt.% corn starch or less (both refined and bulk) exhibited viscosities that were lower than honey (≤ 3 Pa s). Even though honey is quite viscous relative to water, it is doubtful that a pool of honey could support the impact force from the foot of an adult male while running. Therefore, our extrapolated rheological data suggest that the corn starch concentration must be ≥ 52.5 wt.% (42 vol.%) in order to safely run across a pool filled with aqueous corn starch slurry.

It is likely that two separate mechanisms govern the thickening behavior observed in our rheological measurements and “rock drop” studies. The discontinuous thickening behavior witnessed in our rheological data is expected to be connected to a jammed

microstructure that generates a volume-spanning particle network, where the upper stress limit is set by the rigidity of the system walls. However, it is improbable that the impact-induced thickening observed in our “rock drop” experiments undergoes a similar jamming transition on such a macroscopic scale. Recent work by Waitukaitis and Jaeger [54] disputes the current mechanism that connects the jamming transition observed in shear thickening suspensions with the confining forces of the system walls or boundaries. Waitukaitis and Jaeger challenge the “boundary stiffness” argument on the basis that shear thickening can be observed locally in large containers, where the point of impact thickens to a solid-like state while the majority of sample volume remains as a liquid. To avoid confinement and boundary effects, Waitukaitis and Jaeger conducted dynamic stress tests by monitoring the impact of an aluminum rod on large volumes (25 l) of corn starch and water. The authors monitored local compression of the particle microstructure beyond the jamming transition and demonstrated that large thickening stresses can be observed without the requirement of a hard confining boundary. Waitukaitis and Jaeger conclude that the large normal forces created during impact-induced thickening are not a result of bounding conditions, but rather, a momentum transfer between the rapidly growing solid “plug” that is pushed through the surrounding suspension by the impacting object. We believe the thickening observed in our “rock drop” studies follows a similar impact-generated solidification front outlined by Waitukaitis and Jaeger [54] and is therefore, caused by a different mechanism than the shear-induced thickening observed in our rheological measurements.

Although the thickening reported in rheological and impact studies is likely caused by two separate driving forces, the extrapolation of shear data for comparison to our “rock drop” experiments is a conservative approximation of the true impact-induced viscosity and thus, remains relevant. Impact-solidification (as discussed by Waitukaitis and Jaeger [54]) occurs beyond the jamming transition in a region of shear stress (>5000 Pa) immeasurable by conventional rheological techniques (due to both mechanical and boundary limitations). The upper limit of measured shear stress during shear thickening is typically set by the rigidity of the suspension particles or system boundaries [26,31,55] and has been reported to arise between 5000 and 10,000 Pa [26,32,56,57]. The extrapolation of shear data is clearly an underestimation of the local viscosity generated at the point of impact. As a result, the extrapolation of our rheological data to a calculated critical stress of 67,000 Pa predicts semisolid viscosities (50–250 Pa s) for the 52.5 wt.% corn starch slurries instead of the solid-like impact viscosities observed in our “rock drop” experiments. Therefore, extrapolating shear data measured using a conventional rotating rheometer out to impact relevant stresses (>5000 Pa) should be used with restraint, anticipating that local impact-induced viscosities will be underestimated.

4. Conclusions

All employed investigative tools (steady shear rheology, “rock drop” pool experiments, and extrapolated shear stress data) indicate a transition in thickening behavior when the corn starch concentration reaches 52.5 wt.% (or a volume fraction of 0.42). The steady state shear rate ramps (Fig. 3) depict a shift from continuous to discontinuous shear thickening at 52.5 wt.%. Abrupt, discontinuous thickening is typically synonymous with a “jammed” microstructure that generates a particle network that spans the volume of the measurement device (i.e., the vane geometry) and is constrained by the boundary walls. At corn starch volume fractions below the critical value of 0.42, any shear-induced structures are not large enough (relative to the flow-gradient direction) to

fully disrupt the particle framework within the suspension. Simply, the starch particle concentration is too low.

The still images from the “rock drop” studies (Fig. 6) verify that suspensions of 45 wt.% corn starch and below, display liquid-like behavior at large applied stresses (>1000 Pa) and are unable to withstand the force of a man while running. Corn starch slurries at 50 wt.% were able to momentarily support the weight of the dropped rock (Fig. 6), but it was not until the starch concentration reached 52.5 wt.% when solid-like behavior was observed. At 52.5 wt.% corn starch, the falling rock impacted the suspension surface and then recoiled (before eventually sinking to the bottom of the pool) as if it were hitting a true solid interface. The corn starch pool experiments were further validated through the extrapolation of measured steady stress data. Only the 52.5 wt.% slurries demonstrated viscosities at the calculated critical stress of 67,000 Pa that were within the range of semisolid behavior (50–250 Pa s). The other corn starch suspensions (<45 wt.%) did not thicken to high enough viscosities, even under such a strong applied stress, to realistically suggest they were capable of supporting the weight of an adult man while running. Therefore, we conclude that the minimum required corn starch concentration for the average man to “run on water” (corn starch and water) is 52.5 wt.% (42 vol.%).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2013.01.024>.

References

- [1] M. Singh, J.A. Byars, *Journal of Food Science* 76 (2011) E530–E535.
- [2] D. Sabanis, C. Tzia, *Food Science and Technology International* 17 (2011) 279–291.
- [3] Y.S. Lee, N.J. Wagner, *Rheologica Acta* 42 (2003) 199–208.
- [4] C. Fischer, S.A. Braun, P.-E. Bourban, V. Michaud, C.J.G. Plummer, J.-A.E. Manson, *Smart Materials and Structures* 15 (2006) 1467–1475.
- [5] R.L. Hoffman, *Journal of Rheology* 16 (1972) 155–167.
- [6] R.L. Hoffman, *Journal of Colloid and Interface Science* 46 (1974) 491–506.
- [7] H.A. Barnes, *Journal of Rheology* 33 (1989) 329–366.
- [8] W.H. Boersma, J. Laven, H.N. Stein, *AIChE Journal* 36 (1990) 321–332.
- [9] J.F. Brady, G. Bossis, *Annual Review of Fluid Mechanics* 20 (1988) 111–157.
- [10] G. Bossis, J.F. Brady, *Journal of Chemical Physics* 91 (1989) 1866–1874.
- [11] T. Phung, J.F. Brady, *AIP Conf. Proc.* 256 (1992) 391.
- [12] H.M. Laun, R. Bung, F. Schmidt, *Journal of Rheology* 35 (1991) 999–1034.
- [13] H.M. Laun, R. Bung, S. Hess, W. Loose, O. Hess, K. Hahn, E. Hadicke, R. Hingmann, F. Schmidt, P. Lindner, *Journal of Rheology* 36 (1992) 743–787.
- [14] J.W. Bender, N.J. Wagner, *Journal of Rheology* 40 (1996) 899–916.
- [15] B.J. Maranzano, N.J. Wagner, *Journal of Rheology* 45 (2001) 1205–1222.
- [16] B.J. Maranzano, N.J. Wagner, *The Journal of Chemical Physics* 114 (2001) 10514–10527.
- [17] J. Vermant, M.J. Solomon, *Journal of Physics-Condensed Matter* 17 (2005) R187–R216.
- [18] P. D’Haene, J. Mewis, G.G. Fuller, *Journal of Colloid and Interface Science* 156 (1993) 350–358.
- [19] J.W. Bender, N.J. Wagner, *Journal of Colloid and Interface Science* 172 (1995) 171–184.
- [20] B. Kaffashi, V.T. O’Brien, M.E. Mackay, S.M. Underwood, *Journal of Colloid and Interface Science* 187 (1997) 22–28.
- [21] V.T. O’Brien, M.E. Mackay, *Langmuir* 16 (2000) 7931–7938.
- [22] B.J. Maranzano, N.J. Wagner, *Journal of Chemical Physics* 117 (2002) 10291–10302.
- [23] N.J. Wagner, J.F. Brady, *Physics Today* 62 (2009) 27–32.
- [24] T.D. Channel, *Walking on Water*, 2007. The United States of America.
- [25] Gestmusic, *El hormiguero*, 2006. Spain.
- [26] A. Fall, N. Huang, F. Bertrand, G. Ovarlez, D. Bonn, *Physical Review Letters* 100 (2008).
- [27] A. Fall, A. Lemaitre, F. Bertrand, D. Bonn, G. Ovarlez, *Physical Review Letters* 105 (2010).
- [28] A. Fall, F. Bertrand, G. Ovarlez, D. Bonn, *Journal of Rheology* 56 (2012) 575–591.
- [29] E. Brown, H.M. Jaeger, *Physical Review Letters* 103 (2009).
- [30] E. Brown, H. Zhang, N.A. Forman, B.W. Maynor, D.E. Betts, J.M. DeSimone, H.M. Jaeger, *Physical Review E* 84 (2011).
- [31] E. Brown, H.M. Jaeger, *Journal of Rheology* 56 (2012) 875–923.
- [32] E.B. White, M. Chellamuthu, J.P. Rothstein, *Rheologica Acta* 49 (2010) 119–129.
- [33] Q.D. Nguyen, D.V. Boger, *Annual Review of Fluid Mechanics* 24 (1992) 47–88.
- [34] B.R. Stanmore, D.W. Page, *Powder Technology* 72 (1992) 167–175.
- [35] L. Leongpoi, D.G. Allen, *Biotechnology and Bioengineering* 40 (1992) 403–412.
- [36] M. Mohseni, H. Kautola, D.G. Allen, *Journal of Fermentation and Bioengineering* 83 (1997) 281–286.
- [37] G.V. Franks, *Journal of Colloid and Interface Science* 249 (2002) 44–51.
- [38] J.S. Knutsen, M.W. Liberatore, *Journal of Rheology* 53 (2009) 877–892.
- [39] D.G. Thomas, *AIChE Journal* 7 (1961) 431–437.
- [40] Y.K. Leong, P.J. Scales, T.W. Healy, D.V. Boger, *Journal of the American Ceramic Society* 78 (1995) 2209–2212.
- [41] P.C. Kapur, P.J. Scales, D.V. Boger, T.W. Healy, *AIChE Journal* 43 (1997) 1171–1179.
- [42] J.J. Stickel, R.L. Powell, *Annual Review of Fluid Mechanics* 37 (2005) 129–149.
- [43] J.M. Brader, *Journal of Physics-Condensed Matter* 22 (2010).
- [44] X. Cheng, J.H. McCoy, J.N. Israelachvili, I. Cohen, *Science* 333 (2011) 1276–1279.
- [45] A.S. Lim, S.L. Lopatnikov, N.J. Wagner, J.W. Gillespie, *Rheologica Acta* 49 (2010) 879–890.
- [46] R.G. Egres, N.J. Wagner, *Journal of Rheology* 49 (2005) 719–746.
- [47] E. Bertrand, J. Bibette, V. Schmitt, *Physical Review E* 66 (2002).
- [48] R.L. Hoffman, *Advances in Colloid and Interface Science* 17 (1982) 161–184.
- [49] N.C. Crawford, S.K.R. Williams, D. Boldridge, M.W. Liberatore, *Rheologica Acta* 51 (2012) 637–647.
- [50] Y. Dziechciarek, J.J.G. van Soest, A.P. Philipse, *Journal of Colloid and Interface Science* 246 (2002) 48–59.
- [51] H. Senff, W. Richtering, *Colloid and Polymer Science* 278 (2000) 830–840.
- [52] Y. Li, R. de Vries, T. Slaghek, J. Timmermans, M.A.C. Stuart, W. Norde, *Biomacromolecules* 10 (2009) 1931–1938.
- [53] R. Cross, *American Journal of Physics* 67 (1999) 304–309.
- [54] S.R. Waitukaitis, H.M. Jaeger, *Nature* 487 (2012) 205–209.
- [55] M.E. Cates, M.D. Haw, C.B. Holmes, *Journal of Physics-Condensed Matter* 17 (2005) S2517–S2531.
- [56] E. Brown, N.A. Forman, C.S. Orellana, H. Zhang, B.W. Maynor, D.E. Betts, J.M. DeSimone, H.M. Jaeger, *Nature Materials* 9 (2010) 220–224.
- [57] M.I. Smith, R. Besseling, M.E. Cates, V. Bertola, *Nature Communications* 1 (2010).