Interfacial instabilities in soft matter 3D printing

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I. INTRODUCTION

Microscale particles made from swelled cross-linked polymers are known as microgels (1, 2). When granular-sized (larger than 1 μm) microgels are so tightly packed together that they form a solid material, they are known to be in a jammed state (1). However, when a sufficient amount of stress is applied to the microgel, it transitions into an unjammed state in which the particles give way, locally fluidizing the gel where the stress is applied. The amount of stress applied to the gel needed to cause it to fluidize is called the yield stress (σ_y) and can be varied by changing the polymer concentration (1). When the stress is relieved from the gel, it quickly transitions back to the jammed state. The characteristic time it takes for the gel to shift between the jammed and unjammed states is called the thixotropic time and is about one second for the microgels investigated here (1). By leveraging this short thixotropic time and the jamming transition, the microgel offers an effective method of three-dimensional (3D) printing of soft matter materials (1, 2). When an object is printed into the microgel, the jamming/unjamming transition allows the needle to move around but traps the printed object in place, suspending it in space. The Soft Matter Engineering lab at the University of Florida has printed many intricate and complex structures with fluorescent polystyrene microspheres, polymers, and silicone elastomer inks that were not possible with traditional 3D printing methods (1,2). This lab has recently been printing cells using this method which could eventually lead to the printing of human organs (2).

3D printing with traditional methods or into microgels is a race against instabilities (1). The microgel may eliminate instabilities caused by gravity and interfacial tension when printing with miscible materials, but interfacial tensions between immiscible materials create a new source of instability (1). In order to understand the full capabilities of the microgel, it is important to understand all of its interfacial instabilities. This paper explores a new method of printing a sheet of silicone oil into an aqueous based microgel in order to understand how a highly anisotropic liquid shape behaves inside this soft solid. Predictions of the sheets stability were based on the stabilities of cylindrical shapes. These predictions, however, were unable to explain the observed behavior of the sheets.

II. MATERIALS AND METHODS

3D printing is an additive manufacturing technology (3). Unlike the traditional subtractive process that begins with a block of material and takes away undesired parts, 3D printing begins with nothing and creates something by adding a layer after layer. With these traditional 3D printing methods, a sheet is printed by layering lines (cylinders) on top of one another. However, interfacial instabilities between the ink and supporting microgel may arise during printing that can be detrimental to the sheet. Thus, a nozzle was developed to print the sheet in one pass. A thin cut 8.2 mm long and 0.5 mm wide was made to the side of a 1” 16 gauge McMaster-Carr needle with an outer diameter of 0.065” and an inner diameter of 0.053” using a Dremel grinding tool. The bottom of the needle was closed by filling it with epoxy (Figure 1).

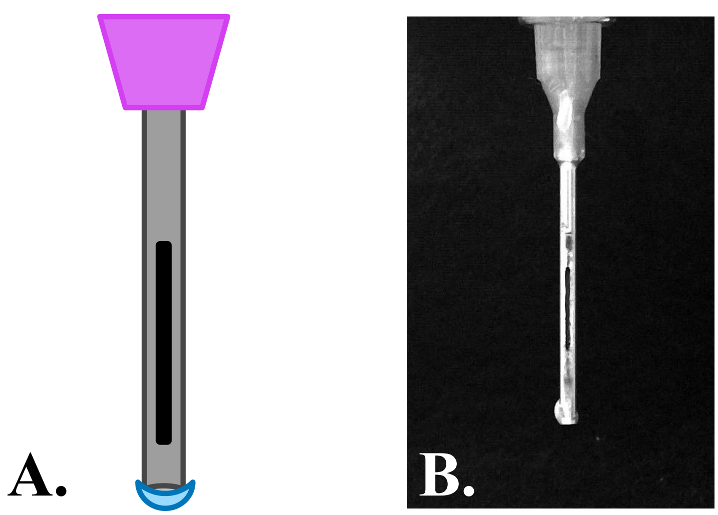

Figure 1. The custom made needle developed in order to print a sheet of oil into a microgel in one pass.

Five microgels of different polymer concentrations were made; 0.10%, 0.125%, 0.15%, 0.175%, and 0.20%. Based on the desired polymer concentration, a measured amount of Ashland 980 carbomer (Ashland Industries) was mixed with about 90 mL of UV Millipore water (Direct-Q 3). The mixture was put into a speed mixer (FlackTek Inc) for fifteen minutes in five minute intervals at 3000 RPM. Once combined, millipore water is added to the mixture until the desired concentration is reached. Five mL of 1 N NaOH (Fisher Chemical) per gram of carbomer is then added to reach a neutral pH. The gel is left to sit overnight to ensure all polymers have dispersed.

The sheets were printed using a syringe pump (Physik Intrumente) attached to a single linear stage (Physik Intrumente) that moved along the x-axis. In order to position the printer along the y and z axis, it was attached to two manual xy translation stages (Opto Sigma). The printer was controlled by custom written MATLAB scripts in which the length of the object, the flow rate at which the oil was pumped out, the velocity of the printer and the diameter of the needle could be varied. Two cameras (Imaging Source), controlled by MATLAB, took images of the objects being printed. A Nikon DX AF-S NIKKOR 12-24 mm lens was attached to one camera to record the side of the sheet while a Nikon AF NIKKOR 50 mm lens was attached to the other camera to record the sheet from the bottom. In order to record the sheet from the bottom, a printing stage with a 2” diameter hole in the middle was manufactured. The stage was mounted 5” from the table and a mirror, angled 45^{o}, was placed directly beneath the hole on an XY linear translation and rotation stage (Thor Labs).

To print, the microgel was placed in the speed mixer for 30 seconds at 2500 rpm to remove air bubbles. Glass boxes made from microscope slides were filled with the gel and placed on the printing stage. A 1mL syringe (BD 1 ml syringe luer-lok tip) with the self-made needle (McMaster-Carr) was filled with silicone oil viscosity 1,000 cst 25°C (Sigma-Aldrich) and attached to the pump. The syringe was lowered into the box, the MATLAB script was run, and a sheet was printed.

In each gel, 40 mm long sheets with a flow rate of 70,000 μl/hr, a print velocity of 2 mm/s, and a syringe diameter of 4.78 mm were printed. A timelapse video of each sheet was taken until the sheet became stable. In every gel, 40 mm long sheets with varying flow rates were printed in order to find the flow rate (sheet size) at which the sheets begin to separate. The time lapse videos were analyzed using ImageJ and Origin 6.1. The yield stress of each gel was found using a rheometer (Kinexus Pro+). The rheometer has two plates, a lower and an upper. The upper plate applies a unidirectional shear rate between 500 and 10^{-3} s^{-1} and measures the resulting shear stress of the gel (2). The yield stress can then be solved for by applying the Herschel-Bulkley model.

III. RESULTS AND DISCUSSION

Rheology is the study of the deformation and flow of matter which is used to characterize materials (4). The rheometer applies a unidirectional shear to the material at varying shear rates and measures the resulting shear stress. A Herschel-Bulkley fluid is a material that has a finite yield stress (5). If a stress below the yield stress is applied, the material behaves as a solid while an applied stress greater than the yield stress will cause the material to behave as a nonlinearly viscous fluid. This is the exact behavior observed with the microgels. We then use the Herschel-Bulkley model $\sigma = \sigma_y + k\dot{\gamma}^p$, where σ is the shear stress, σ_y is the yield stress, k is the consistency constant, $\dot{\gamma}$ is the shear rate, and p is some constant < 1, to calculate the yield stress of the microgel support materials (2,6). It has been found that yield stress can be controlled by varying the polymer concentration in the microgel (2). An increase in the polymer concentration results in an increase in the yield stress (Figure 2).

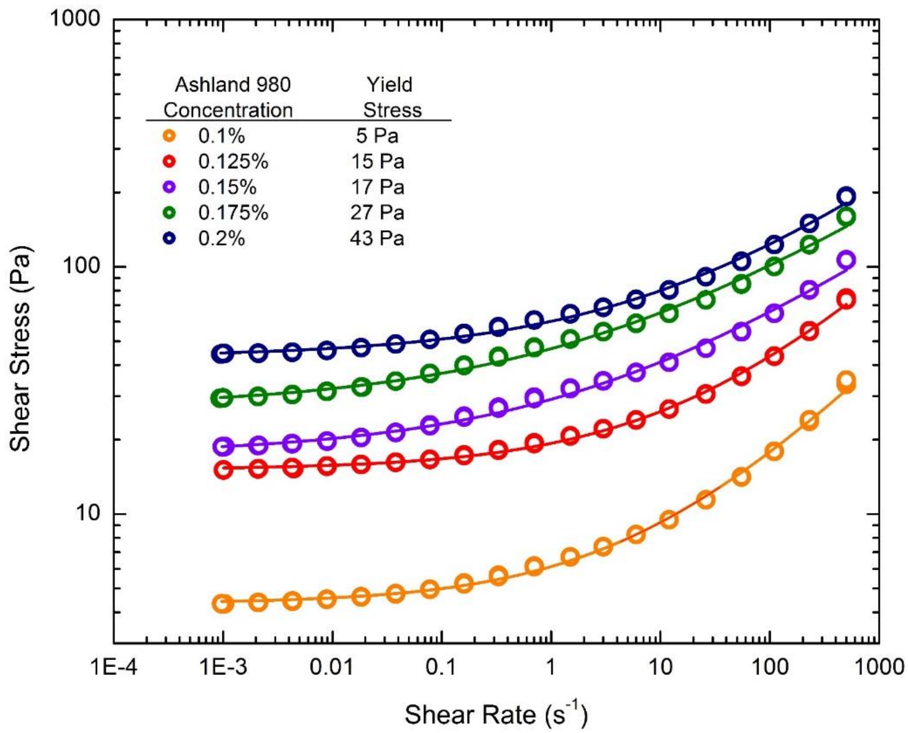

Figure 2. A unidirectional shear rate from 500 to 10^{-3} s $^{-1}$ was applied to each gel concentration. The resulting shear stress was then measured. The Herschel-Bulkley model was applied to find the yield stress. The yield stress increases as the polymer concentration increases.

A timelapse video of identical sheets (feature length of 40 mm, flow rate of 70,000 μl/hr, print velocity of 2 mm/s, and a syringe diameter of 4.78 mm) printed into each microgel was taken. A sheet was successfully printed into each microgel (Figure 3).

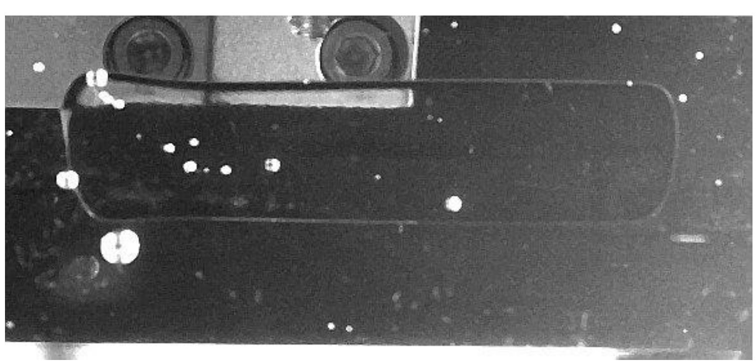

Figure 3. A typical sheet printed into a microgel. This sheet was printed with 1,000 cst silicone

The printed sheets would either be stable or they would shrink (Figure 4). Stability of the feature was determined by whether the sheet shrank or not. In Figure 4 A and B it is clear that there is deformation of the sheet in the bottom right corner. This is a result of the hydrostatic pressure of the microgel and unevenness in the sheet itself. The hydrostatic pressure on the sheet is greater at the bottom than at the top. Due to imperfections in the needle, the sheet was thinner, and therefore weaker, in the bottom right corner. As a result, the bottom corner of the sheet moved to a state in which there was a uniform thickness throughout the sheet. In Figure 4 C and D, the interfacial tension between the oil and microgel is greater than the yield stress of the microgel which causes the sheet to move towards a shape of minimum surface area.

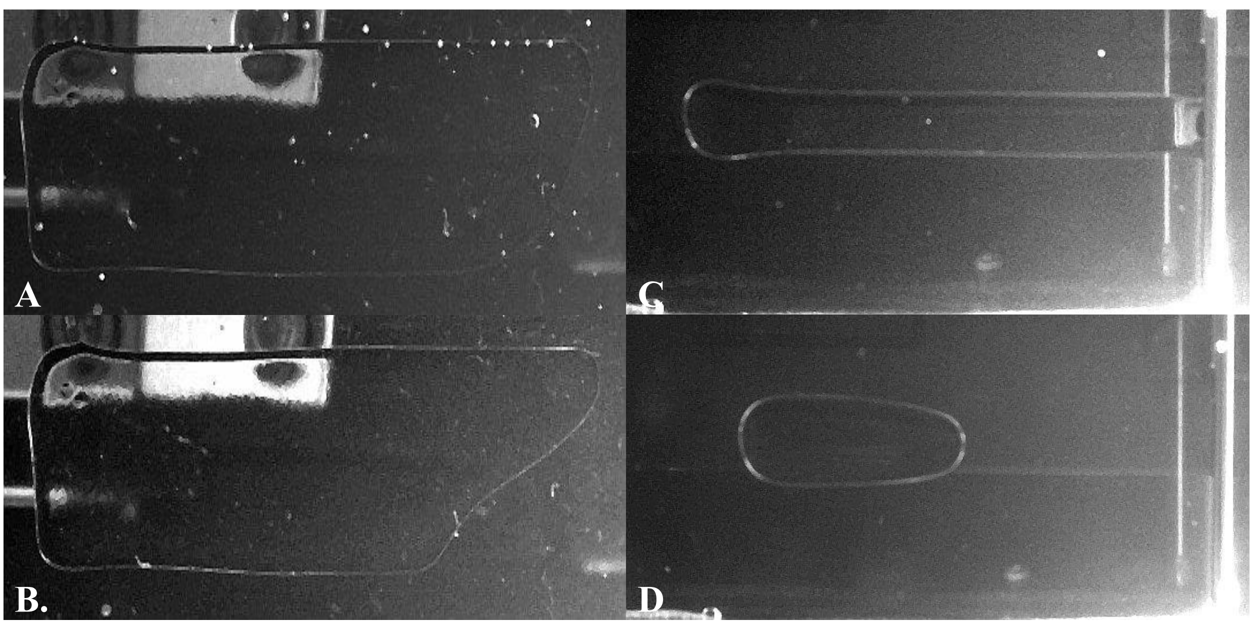

Figure 4. (A, B) A stable sheet printed into 0.2%. The deformation at the bottom is due to the hydrostatic pressure of the gel. The length of the sheet remained constant, so it can be said to be stable. (C, D) An unstable sheet printed into 0.1% microgel. This sheet began to shrink immediately after printing.

The change in the side and bottom cross sectional areas of the sheets were measured over time using ImageJ (Figure 5). Even though both the side area and bottom area of the sheet appear to be decreasing over time, the total volume of the sheet was conserved, confirmed with an aspect ratio. From this, it can also be seen that the feature size can be controlled by the yield stress in which it is printed. Higher yield stresses allow for taller and thinner sheets to be printed.

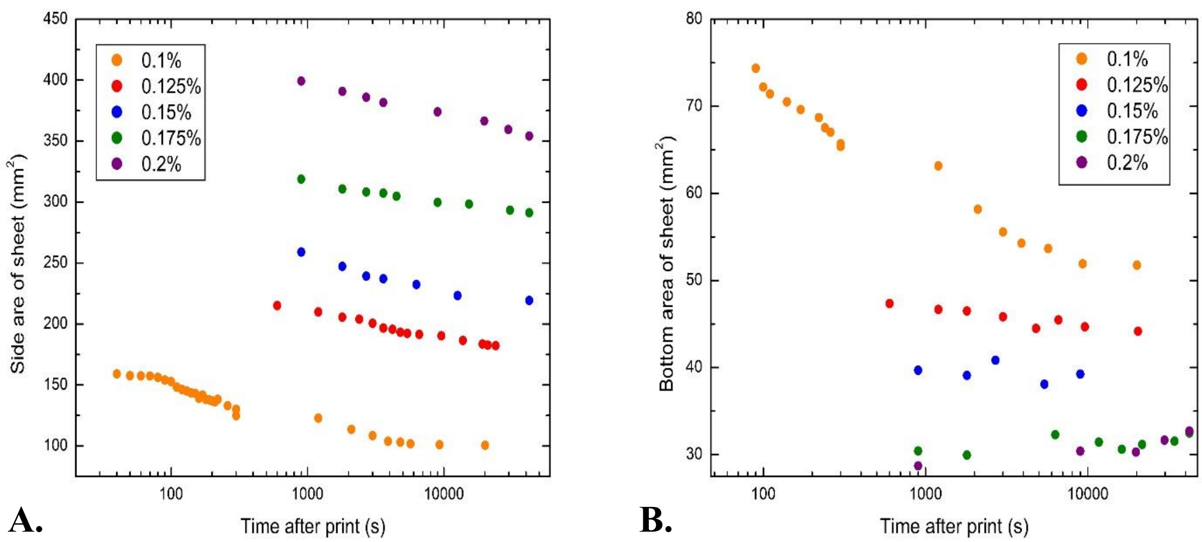

Figure 5. The cross sectional area of the sheet was measured using the freehand function of ImageJ. Even though both areas decreased, the total volume of the sheet remained the same, proven by dividing the side area by the bottom area for each sheet to find the aspect ratio. (A) The side area of the sheet was measured across various frames of the timelapse videos and plotted on a log time scale. (B) The bottom area of the sheet was measured from various frames of the timelapse videos and plotted on a log time scale.

A theory of droplet stability, based on cylindrical shapes, was used to predict that there would be a critical wavelength proportional to the interfacial tension divided by the yield stress of the material at which the sheets would break up. In order to find the dimensions of the sheet at which this wavelength was reached, different sized sheets were printed into each of the microgels. In order to change the feature size, the flow rate was adjusted. A variety of sheets were printed into the microgels and either shrank, broke up, or remained stable (Figure 6). These results, however, did not support what was expected (Figure 7). There is not a critical sheet size at which the sheet becomes unstable. This is because the predictions were based on how cylinders behave. Instead of a critical wavelength, there seems to be a critical surface curvature of the sheet at which it begins to become unstable. Due to the positioning of the cameras, the surface curvature of the sheet was not able to be measured and therefore a relation between unstable and stable sheets was not found.

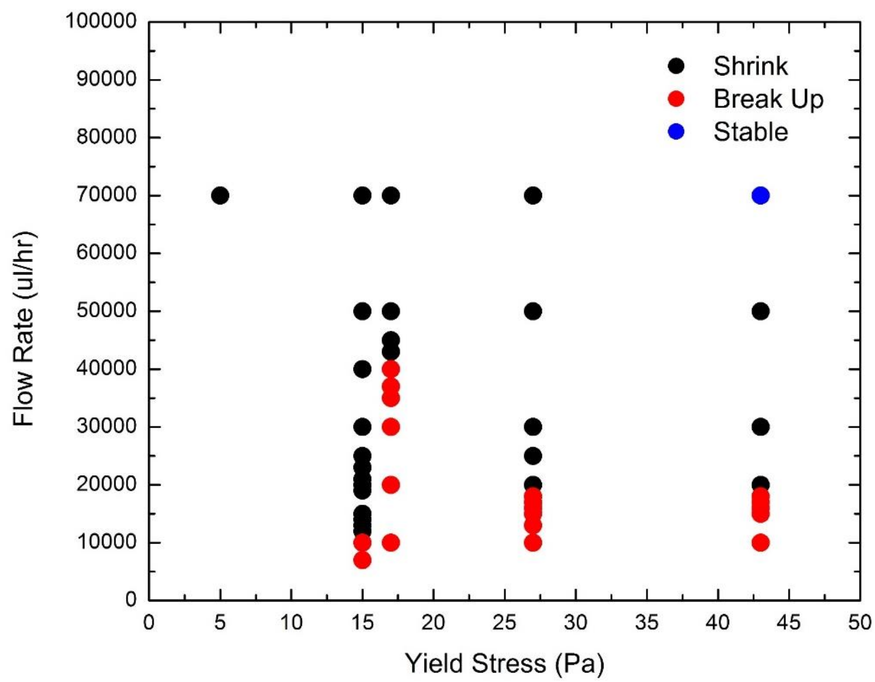

Figure 6. Sheets of varying flow rates were printed into each microgel concentration. Multiple sheets were printed into a gel at a time due to limited amounts of microgel. The sheets would shrink, break up, or remain stable.

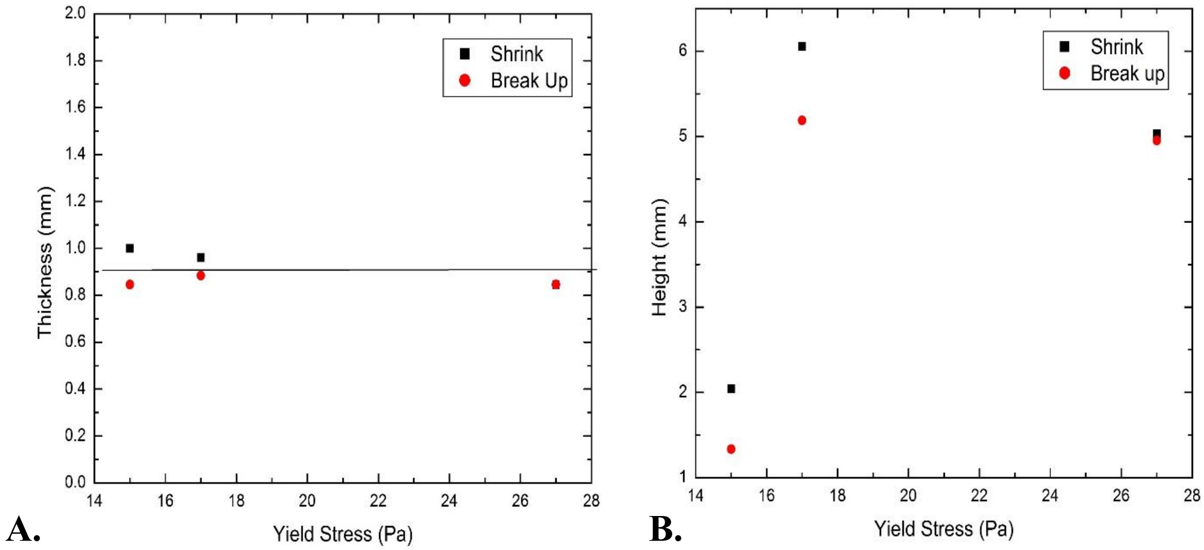

Figure 7. Images of sheets were taken at flow rates right before and right after break ups occurred. The height and thickness of these sheets were then measured using ImageJ. (A) The sheets have a relatively constant thickness despite their stability. (B) There does not appear to be any relation to the height of the sheet and whether or not the sheet breaks apart.

IV. CONCLUSION

This project has investigated the stability of liquid sheets, a highly anisotropic shape, printed into a soft granular gel support. The height and width of the sheet could be altered by varying the flow rate at which the silicone oil was printed and the yield stress of the microgel the sheet was printed in. The stability behavior of the sheet was unable to be predicted by a stability theory based on cylindrical shapes. Models accounting for the surface curvatures are needed to describe the highly anisotropic shapes explored here.

Unpredicted effects of hydrostatic pressure were also observed. When making the needle with which to print a sheet, it is important to make sure the hole is of uniform width. If it is not, the pressure of the gel will deform the sheet. The position of the sheet within the microgel was also shown to affect the stability of the sheet. The sheets were more stable when printed in the middle of the gel than when printed closer to the surface. Vertically printed sheets experience an uneven distribution of pressure because pressure increases as depth increases, so the bottom of the sheet experiences a greater pressure than the top of the sheet. Printing sheets horizontally would evenly distribute the pressure throughout the sheet, possibly eliminating some instability. In order to understand the unexpected behaviors of these sheets, further research must be done.

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