Development of a Smartphone App to Easily Measure Extensional Viscosity

by
Aleesha Swift

A THESIS

submitted to

Oregon State University

Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

Presented June 6, 2018
Commencement June 2019

AN ABSTRACT OF THE THESIS OF

Aleesha Swift for the degree of Honors Baccalaureate of Science in Chemical Engineering presented on June 6, 2018. Title: Development of a Smartphone App to Easily Measure Extensional Viscosity.

Abstract approved:____

Willie (Skip) Rochefort

The measurement of extensional viscosity is important in many chemical, biomedical, agricultural, and engineering applications. The determination of extensional viscosity is generally difficult, expensive, and inaccessible outside of research labs. The development of a smartphone application (app) that could use a phone's high-speed camera to measure this parameter could open doors for easy, cheap, mobile, and accessible measurements. In this study, a MATLAB script was developed to process and analyze videos taken by an Apple iPhone of a fluid being stretched between two surfaces then thinning until separation. The MATLAB script is used to extract information about the elasticity of various fluids. The materials chosen for use in this study were selected to represent materials that are easily accessible to most people. Ideal video-taking conditions were determined then used to take several videos of Newtonian and non-Newtonian fluids. When the extracted extensional relaxation time was compared to a recently developed technique called "optically-detected elastocapillary self-thinning dripping-onto-substrate" (ODES-DOS) the values were consistently higher by about 3 ms. However, both methods had similar extensional relaxation time vs PEO concentration trends with slopes of 0.67 for the ODES-DOS method and 0.62 for the smartphone video method. This shows that an iPhone app could be used in the field for rough measurements of the extensional viscosity of fluids which could also be used for precise qualitative comparisons given measurements of multiple samples. Neither the height the fluid was stretched, nor the amount of fluid stretched was found to significantly affect the values obtained.

Key Words: Extensional Viscosity, Smartphone Application, Rheology, Non-Newtonian Fluid Dynamics, Polymers

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I understand that my project will become part of the permanent collection of Oregon State University, Honors College. My signature below authorizes release of my project to any reader upon request.

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Aleesha Swift, Author

Table of Contents

Acknowledgments

I would like to thank the Walker Research Group for all the help and support throughout my time at Oregon State. The encouragement and advice I received from many of you kept me going during the difficult courses. Thank you specifically to Kristin Marshall for being a source of positivity and for helping me learn what it means to be a researcher. Working on this project with you was a great learning experience as well as a fun time.

Thank you to Travis Walker for taking me on as a small, scared freshman and teaching me how to be a confident engineer. You constantly believed in me and pushed me to think harder and work smarter.

Thank you to Skip Rochefort for all your many contributions to my education from classes, to outreach, to internships, to research. And thank you also for taking on mentorship of my thesis.

Thank you to Dr. Carlisle for serving on my thesis committee and supporting me as I complete a project I can be proud of. Your help and encouragement were a positive contribution to the committee.

Thank you to the University Honor's College and to the WME Grant for the opportunity to complete a thesis and for the funding to complete this project.

Thank you to my parents for everything you've provided for me. The sacrifices you've made throughout my life have helped me to become the woman I am today. You and Tyler have always believed in me and encouraged me to pursue my goals. I know I am loved by you and you are proud of me no matter what. That knowledge allows me to get back up when I fail and continue to work hard always. I love you all.

Thank you to my husband, Tristen, for believing in me and supporting me through all the difficult moments of my time at Oregon State University. I've never had to wonder if you are proud of me and rooting for me. I love you forever.

Introduction

The measurement of extensional viscosity is important in many chemical, biomedical, agricultural, and engineering applications. The determination of extensional viscosity is generally difficult, expensive, and inaccessible outside of research labs. The development of a smartphone application (app) that could use a phone's high-speed camera to measure this parameter could open doors for easy, cheap, mobile, and accessible measurements. In this study, a MATLAB script was developed to process and analyze videos taken by an Apple iPhone of a fluid being stretched between two surfaces then thinning until separation. The MATLAB script is used to extract information about the elasticity of various fluids. The materials chosen for use in this study were selected to represent materials that are easily accessible to most people. Ideal video-taking conditions were determined then used to take several videos of Newtonian and non-Newtonian fluids. When the extracted extensional relaxation time was compared to a recently developed technique called "optically-detected elastocapillary self-thinning dripping-onto-substrate" (ODES-DOS) the values were consistently higher by about 3 ms. However, both methods had similar extensional relaxation time vs PEO concentration trends with slopes of 0.67 for the ODES-DOS method and 0.62 for the smartphone video method. This shows that an iPhone app could be used in the field for rough measurements of the extensional viscosity of fluids which could also be used for precise qualitative comparisons given measurements of multiple samples. Neither the height the fluid was stretched, nor the amount of fluid stretched was found to significantly affect the values obtained.

Extensional Viscosity

Unlike Newtonian fluids, which have a constant viscosity, or ratio of stress to strain, non-Newtonian fluids do not behave consistently under flow. Specifically, their extensional viscosity, a measure of resistance to an extensional stress, is difficult to measure. The extensional viscosity of a fluid gives us insight into its elastic nature which is important to understand when using viscoelastic materials. Understanding elastic properties becomes important in such applications as ink jet printing, misting, or coating techniques. It can also be important when trying to understand or replicate the properties of biological fluids such as blood or synovial fluid.

Methods for mobile, qualitative measurements of various parameters are currently being developed in several studies. One study conducted by Kobori and colleagues aimed to detect male infertility by attaching a smartphone to a simple microscope to count sperm cells[1]. Many applications for smartphones have been developed for use in agriculture such as using the camera to determine plant diseases or using the GPS to share and find information about soil in an area. These applications, as well as several others, are outlined in a review by Pongnumkul and colleagues.[2] Collett et al. and Hallmark et al. have worked to develop techniques to measure extensional viscosity in the field.[3,4] The work already being done to develop mobile rheological measurement techniques shows the need for the further development of this technology. Being able to complete this task on a smartphone would allow for easy access to elasticity measurements to almost anyone in any location and would not require extra equipment to be created and carried to the site.

Background

CaBER

One current method to measure extensional viscosity is the use of an instrument called a Capillary Breakup Extensional Rheometer or CaBER. A small amount of the fluid of interest is stretched between two plates. Capillary forces in the filament created by this stretching attempt to move liquid to the two bulk regions on the plates, while viscoelastic forces work to hold the filament together (Figure 1). The competition

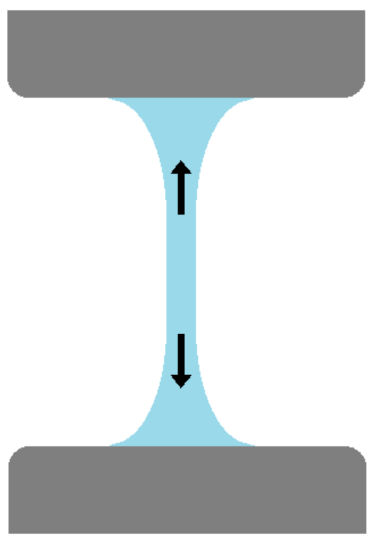

Figure 1. Schematic of capillary forces within a liquid bridge moving fluid to the bulk regions on each of the plates used to pull the fluid apart such as is done in a CaBER.

between these forces causes the diameter of the filament to exponentially decay over time. The CaBER uses a laser to measure the thinning of this filament as discussed in several papers.[5–10] The CaBER however has many practical limitations. It is expensive making it difficult to obtain, and it is also immobile making it impractical to use outside of the lab.

ODES-DOS

Dinic and coworkers described a new method to measure the extensional properties of viscoelastic fluids that was able to detect the presence of at concentrations below the detection limit of other methods including the CaBER.[8] This method is optically-detected elastocapillary self-thinning dripping-onto-substrate (ODES-DOS). This technique involves slowly dripping a small amount of a viscoelastic fluid out of a syringe tip a short height above a substrate. As the drop touches, then wets the surface, a liquid bridge is formed between the bulk drop on the surface and the syringe tip. A high-speed camera is used to capture video that is processed in a MATLAB script to track the diameter decay over time and thereby extract information about the fluid's elastic properties such as extensional viscosity and extensional relaxation time. With a powerful high-speed camera, two regimes can be detected, one showing power-law decay, and another displaying exponential decay. The balance of capillary and elastic forces causing the exponential decay of this fluid bridge can be described using an equation based on a theory developed by Entov and Hinch:[6]

$$\frac{D(t)}{D_0} = \left(\frac{GD_0}{4\sigma}\right)^{1/3} \exp\left(-\frac{t}{3\lambda_E}\right) \tag{1}$$

where $D(t)$ is the diameter at time t, D_0 is the initial diameter of the filament, G is the elastic modulus of the fluid, σ is the surface tension of the fluid, and λ_E is the extensional relaxation time. When linearized, this equation becomes:

$$\ln\left(\frac{D(t)}{D_0}\right) = \left(-\frac{1}{3\lambda_E}\right)t + \ln\left[\left(\frac{GD_0}{4\sigma}\right)^{1/3}\right] \tag{2}$$

the slope of which can be used to find the extensional relaxation time λ_E.

To find the extensional viscosity, the rate of decay is utilized in the following formula:

$$\eta_E = \frac{\sigma}{-2\left(\frac{dD(t)}{dt}\right)} \tag{3}$$

where η_E is the extensional viscosity. The Trouton ratio is defined as the ratio between a fluid's extensional and shear viscosities ($Tr = \eta_{E/}\,\eta$). For Newtonian fluids, the Trouton ratio is always 3. For non-Newtonian fluids however, the Trouton ratio can vary in magnitude from 10^1 to 10^5.

Methods and Materials

Sample Preparation

A stock polyethylene oxide (PEO) solution of 0.5 wt% was created by combining Dow Chemical Company PLOYOX WSR 303 (MW = 7×10^6) with deionized water (DIW). The solution was kept in an amber bottle under nitrogen. To create a series of Boger fluids, this PEO stock solution was combined in various amounts with glycerol and DIW and left in amber bottles in a slow-running shaker for 48 hours. The Boger fluids created had 0, 20, 40, 110, or 660 ppm PEO and each contained around 55.8 wt% glycerol and 44.2 wt% DIW. Boger fluids were used to study the elastic effects without disruption from a changing viscosity, a common method in rheology. Three silicone oil viscosity standards were also used to test the limitations of the smartphone technique with Newtonian fluids. A summary of fluids used and their properties can be found in Table 1.

The shear viscosity of each fluid was tested using a TA Instruments AR-G2 rotational rheometer with a titanium 60-mm cone upper geometry and a Peltier plate lower geometry. A flow sweep showed that each of the Boger fluids had similar shear viscosities, all of which remained constant under variable flow. A Krüss K10T tensiometer with a du Noüy ring was used to test the surface tension of each of the fluids.

Table 1. Fluid Properties

Fluid Sample	η_0 *mPa*s*	σ *mN/m*	Captured
0 ppm PEO	6.87	67.6	No
20 ppm PEO	9.17	58.7	Yes
40 ppm PEO	8.24	57.6	Yes
110 ppm PEO	9.03	57	Yes
660 ppm PEO	21.2	56.6	Yes
Silicone Oil	200	21.1	No
Silicone Oil	350	21.1	No
Silicone Oil	4870	21.4	Yes

Smartphone Video Analysis

To analyze the elastic properties of the fluids, videos were taken using the high-speed function on the camera of an Apple iPhone SE. This camera records 720p videos at 240 frames per second (fps). Each of the fluids was stretched between two surfaces over a short distance, then held in place as the filament thinned until breakage occurred. The video was then analyzed using a MATLAB script that tracked the edges of the filament to record the diameter over time.

A series of videos was taken changing video-taking parameters in order to optimize the video-taking process. Minor changes made include background color, background distance from sample, and camera distance from sample. Once adequate conditions regarding each of these minor parameters were determined, one major video-taking parameter persisted. The intent of this app is for it to be used quickly and easily without the need of extra equipment apart from the smartphone itself. Using a finger to separate the fluid resulted in unsteady separation with inconsistent pull distances. As a solution to this problem, a wooden clothespin, which is cheap and easily accessible to most people, was used as the pulling mechanism for the remainder of the trials.

To capture the videos of the samples in Table 1, the smartphone was placed on the table about 8 cm from the clothespin with the top of the phone resting on the table, and therefore the camera lens near the table surface (Figure 2). Before recording, 10-30 microliters of the fluid were pipetted onto the bottom piece of the naturally open end of a wooden clothespin. While recording at 240 fps, the clothespin was compressed until the two faces met, then released to quickly stretch the fluid to a final height of around 7-11 mm. The fluid filament was allowed to decay until breaking. The fluid was pulled 9 more times for a total of 10 trials per video.

Trials were also completed to test the effect of pull height and sample volume. Pull height was varied by securing small washers in the naturally-closed end of the clothes pin to keep it from stretching the full height. Heights of 6.61, 8.35, and 11.23 mm were tested. Sample volume was varied by using a pipette to measure out 10, 20, or 30 microliters of fluid onto the clothespin. All height and volume trials were completed using the 660 ppm Boger fluid.

A MATLAB script was developed to process the videos. Each video is cropped to only contain the frames from the time the fluid is fully stretched to the moment it breaks.

Each frame is also cropped to encompass only the region containing the filament. The video is then converted to black and white and cleaned to minimize noise. By observing a change in color in each horizontal line of pixels, the code can track the edges of the filament and plot the diameter as it decays over time.

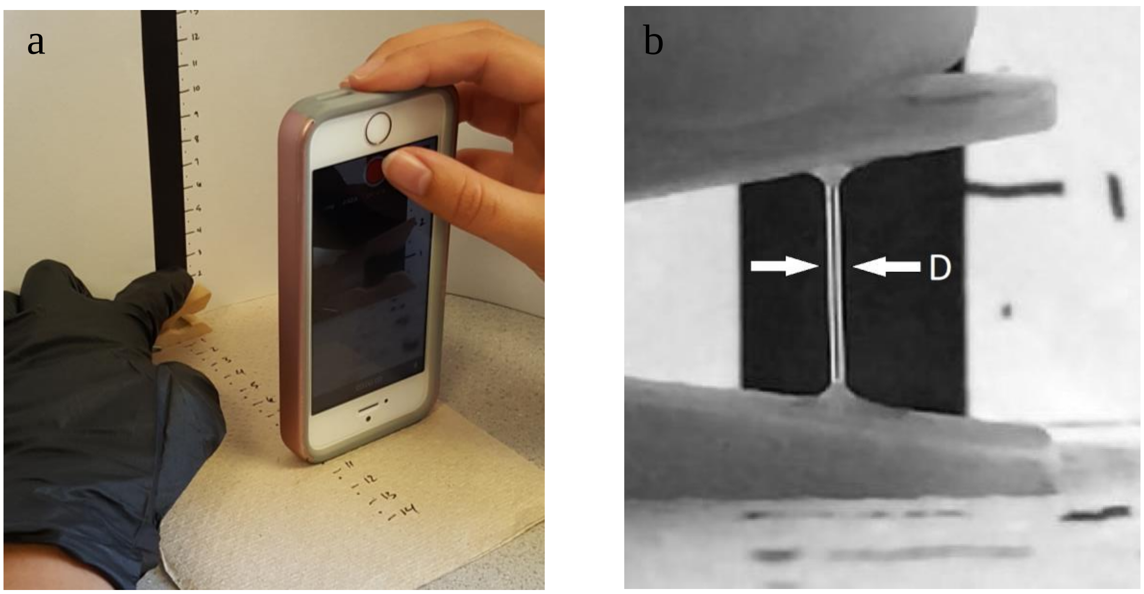

Figure 2. Experimental setup for filament thinning analysis using an iPhone SE. The phone is rested upside-down on the table to allow for close proximity of the camera lens to the sample (a). The high-speed camera is used to capture video of the liquid bridge decaying with time (b).

Verification Using ODES-DOS System

An ODES-DOS system was constructed in-house using several linear stages to facilitate movement of the syringe and the substrate. A 3D-printed scaffold was designed in AutoCAD to hold the syringe in place. Secured to the system was a Phantom V4.1 high-speed camera with a 130-mm extension tube and a 10x objective. Videos of each of the Boger fluids were captured at 1265 fps at a CCD array size of 800 x 600 pixels.

Videos from the ODES-DOS system were analyzed using a MATLAB script in a similar way as the smartphone videos.

Results

Stretching via Finger versus Clothespin

When stretching the fluid with a finger as opposed to using a clothespin, challenges arose such as the ability to stretch at a constant speed or to a constant height. The biggest challenge however was keeping the sample steady as the diameter decayed. Despite these challenges, the diameter decay profile between the two methods were very similar showing that either method is a valid choice for this application. However, as seen in Figure 3, the use of a clothespin led to less variability than using a finger. For that reason, a clothespin was chosen for the completion of the remaining trials. The ease of access to clothespins and their low price makes them a reasonable choice for making this smartphone app accessible to the public or to a researcher in the field.

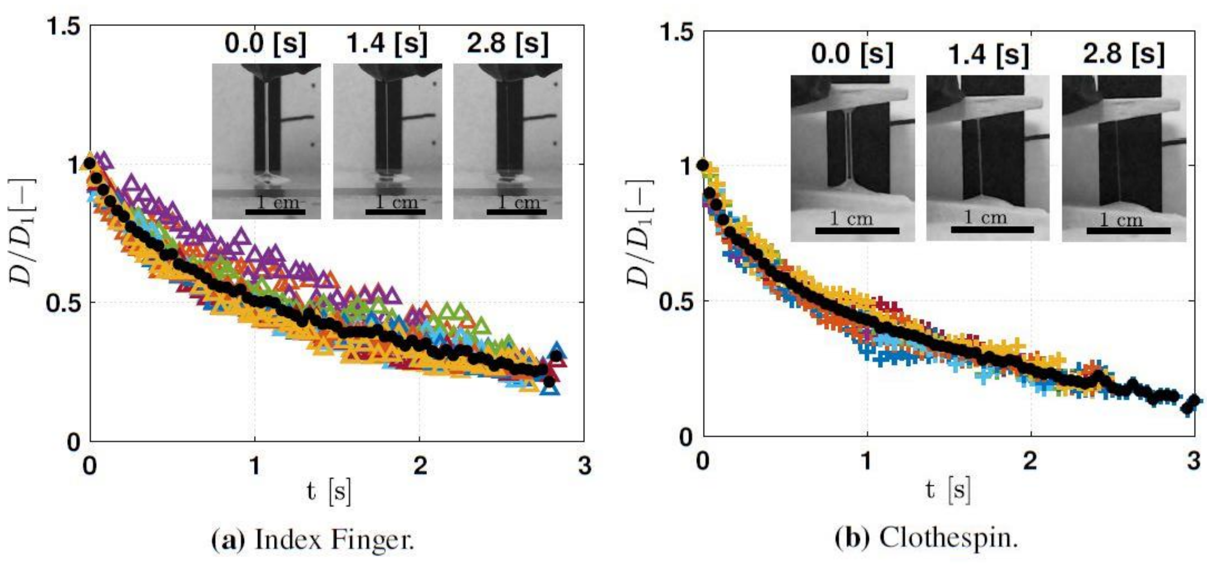

Figure 3. Profiles for diameter decay with time and the average of ten trials (black dots) for the finger method (a) and the clothespin method (b). Both methods show similar profiles but the noise, or variation, in the finger method is much greater.

Determination of Elastic Properties

Videos taken of the Boger fluids with varying PEO concentration were analyzed using the custom-made MATLAB script to find their elastic properties. Results from ten trials for each fluid were averaged to give a smoother profile with less noise.

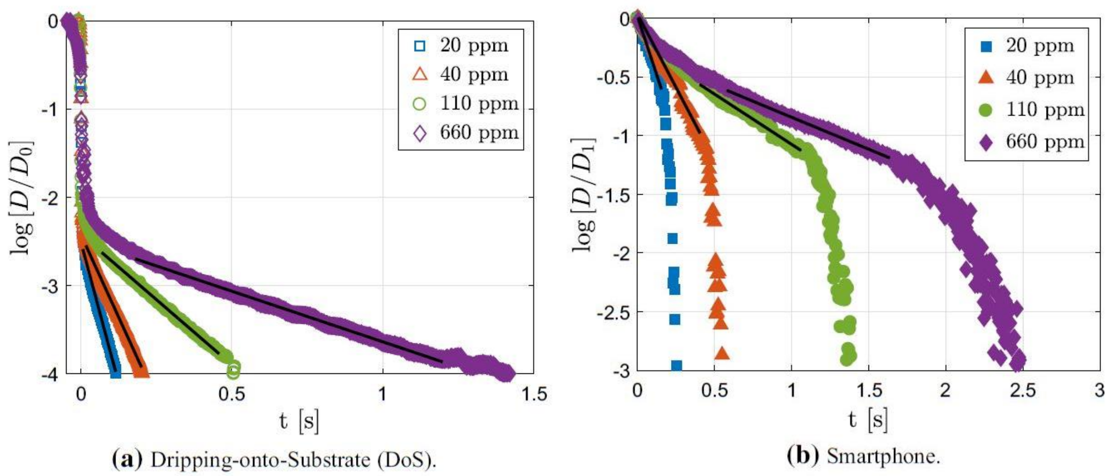

Figure 4. Log of diameter decay plotted at various concentrations of PEO according to Equation (2) for the ODES-DOS (a) and the smartphone (b). Data shown are averages of 10 trials for each fluid. Black lines show a linear fit for the exponential decay regime. Both methods are sensitive to small changes in polymer concentration.

The results of the smartphone method were compared to the results for the same fluids from the ODES-DOS system to determine the capability of the smartphone technique. As the ODES-DOS camera is capable of much higher fps than that of the smartphone, both the linear and exponential decay regimes were easily captured by the ODES-DOS camera. The smartphone on the other hand could not capture the linear regime but was able to collect ample frames containing the exponential decay of the filament (Figure 4). When the diameter decay is plotted on a log scale according to Equation (2), it can be seen that both methods are sensitive to small changes in elasticity.

The slopes of the exponential regime for each of the fluids were determined and are shown on the plots as black lines. The extensional relaxation time, λ_E, was plotted against PEO concentration, Φ, on a logscale for both methods (Figure 5). The slopes of these data are very similar showing that the smartphone method qualitatively gives similar results as the ODES-DOS. It also shows that this method follows the trends that were described by Dinic and colleagues who reported that the proportionality between λ_E and Φ should have a slope of $\alpha = 0.65$.[9] The orders of magnitude of the two methods were also very similar to each other and to the literature values presented by Hsu et al.[11] The smartphone values for the relaxation time however were consistently larger from those of the ODES-DOS by a little over 3 ms.

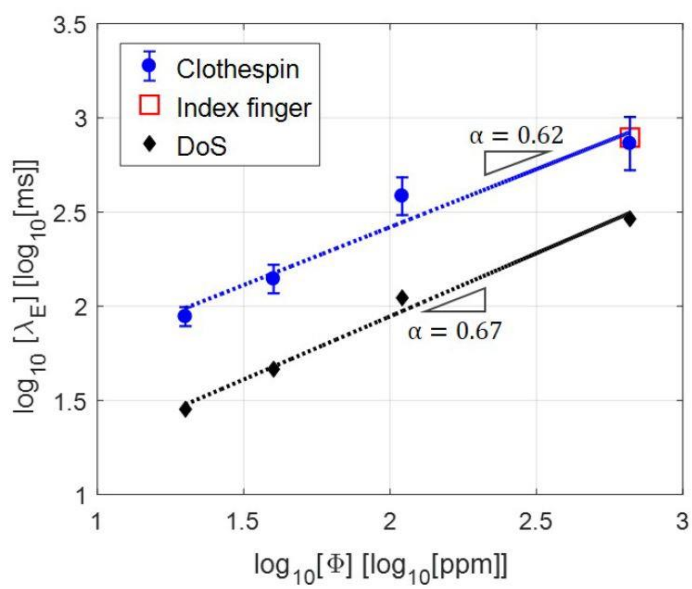

Figure 5. Extensional relaxation time, λ_E, plotted against PEO concentration, Φ, on a log-log scale for the smartphone method with a clothespin (blue circles) and the ODES-DOS method (black diamonds). The slope, α, for the smartphone analysis was similar to that of the ODES-DOS analysis. Error bars represent standard deviation with n=10. One point is shown for the finger method (red square) to show the similarity of results to the clothespin method.

Effect of Height and Volume

Trials with the smartphone app were completed with the intention to study the effect of height and volume of liquid stretched. Due to these trials being completed some time after the initial trials, the overall values for relaxation time are slightly lower than what was initially obtained, likely due to polymer chain scission that can occur over time. Regardless, the use of a single polymer sample at a single time can be used to look for trends in extensional relaxation time with varying height and volume. It was found that neither height nor volume had any significant impact on the results with p-values of 0.082 and 0.150 respectively for n=5 (Figure 6).

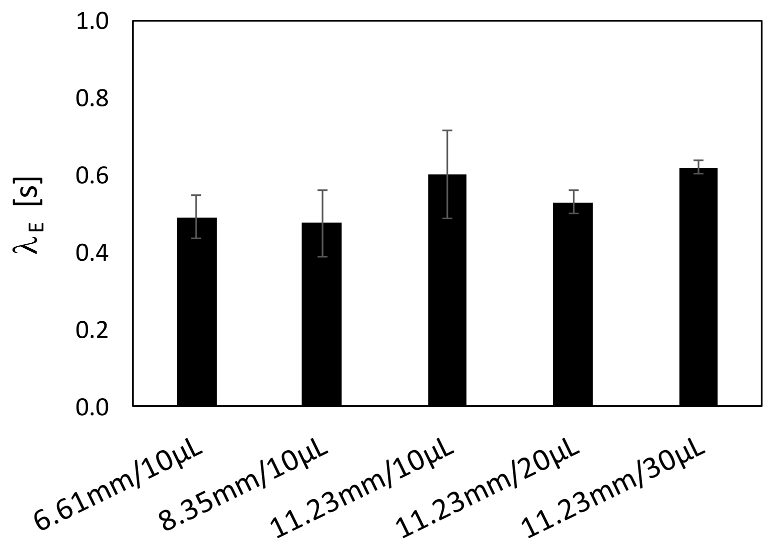

Figure 6. Comparison of relaxation time at various sample volumes and heights stretched. No significant difference was found between trials. Error bars represent standard deviation with n=5.

Newtonian Fluids

Of the three Newtonian fluids tested (η_0 = 200, 350, and 4870 mPa·s) only the 4870 mPa·s silicone oil had a decay slow enough to be captured by the 240-fps smartphone camera. While the non-Newtonian fluids tested only had a zero-shear

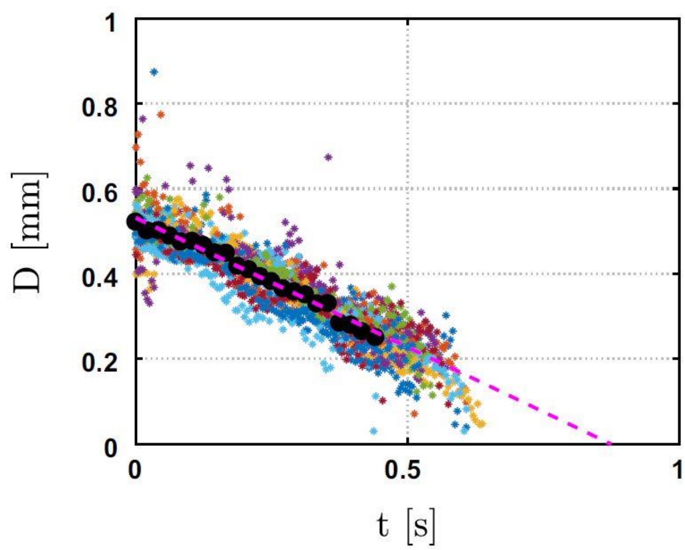

Figure 7. Diameter decay of Newtonian 4870 mPa·s silicone oil. Black points represent an average decay profile from 15 trials. Dashed line is the linear fit of the data used to represent Equation (4).

viscosity on the order of 10 mPa·s, the polymer added to the solution slowed the decay enough to be captured even at low concentrations. Figure 7 shows data for 15 trials with the 4870 mPa·s silicone oil. This data was fitted according to the equation from Papageorgiou:[12]

$$D(t) = D_1 - \frac{(2\beta - 1)}{3}\frac{\sigma}{\mu}t \qquad (4)$$

where β is determined to be 0.71 for a viscous filament as derived by Papageorgiou. Using this equation and the known surface tension of 21.4 mN/m, the shear viscosity was estimated to be 4540 mPa·s, giving about 7% error from the known viscosity of 4870 mPa·s. When Equation (4) is used in a similar manner to find the surface tension with known viscosity, the surface tension is found to be 22.9 mN/m.

Conclusion

As the elasticity of fluids plays a large role in many industries, it is important to be able to characterize this property. Many of the current methods for measuring extensional viscosity are expensive, inaccessible, and/or immobile. The development of a smartphone app that could measure the elastic properties of a fluid could make these measurements cheap, mobile, and more accessible to researchers and the public alike. The ability of the app to be used with simply a finger or something as cheap as a clothespin eliminates the need for large, expensive equipment. Using something steady like a clothespin reduces the noise in the measurements giving better results, however, simply using one's finger to pull the material works well enough to give adequate results. Height and volume stretched did not have a significant effect on the results showing that precise measurements are not necessary. A ruler was used in the experimental setup of these experiments, but it was found that this measurement is unnecessary since a normalized diameter is used for the analysis.

The values obtained by the smartphone for extensional relaxation time were larger than those obtained by the ODES-DOS method but were on the order of magnitude predicted by literature. The trends observed were also consistent with the ODES-DOS and with literature. These results imply that the smartphone app could be a sensitive and consistent tool for making qualitative observations about elastic fluids between a series of samples. The app could also be used to make approximate measurements of a fluid's elastic properties. Newtonian fluids must have a large shear viscosity for the filament breakup to be observed by the smartphone camera. As the capability of smartphone cameras increase, measurements using an app like the one proposed could become increasingly more accurate.

This study served as proof-of-concept for the development of a smartphone app for the measurement of extensional viscosity. A MATLAB script was used to analyze the data extracted, but the app is yet to be developed. A general app could be created that would measure the elastic properties of any type of fluid which could be used in research. Other apps could also be developed that would be more specific. For example, an app could be developed for public use that would allow a woman to track the elasticity of her cervical mucus over the course of her menstrual cycle. Since the elasticity of cervical mucus indicates the time of ovulation, an app like this could help with family planning.[13]

References

(1) Kobori, Y.; Pfanner, P.; Prins, G. S.; Niederberger, C. Novel Device for Male Infertility Screening with Single-Ball Lens Microscope and Smartphone. *Fertil. Steril.* 2016, *106* (3), 574–578.

(2) Pongnumkul, S.; Chaovalit, P.; Surasvadi, N. Applications of Smartphone-Based Sensors in Agriculture: A Systematic Review of Research https://www.hindawi.com/journals/js/2015/195308/ (accessed Apr 3, 2018).

(3) Collett, C.; Ardron, A.; Bauer, U.; Chapman, G.; Chaudan, E.; Hallmark, B.; Pratt, L.; Torres-Perez, M. D.; Wilson, D. I. A Portable Extensional Rheometer for Measuring the Viscoelasticity of Pitcher Plant and Other Sticky Liquids in the Field. *Plant Methods* 2015, *11*, 16.

(4) Hallmark, B.; Bryan, M.; Bosson, E.; Butler, S.; Hoier, T.; Magens, O.; Pistre, N.; Lee Pratt; Ward, B.-A.; Wibberley, S.; et al. A Portable and Affordable Extensional Rheometer for Field Testing. *Meas. Sci. Technol.* 2016, *27* (12), 125302.

(5) Bazilevsky, A.; Entov, V.; Rozhkov, A. Breakup of a Liquid Bridge as a Method of Rheological Testing of Biological Fluids. *Fluid Dyn.* 2011, *46* (4), 613–622.

(6) Entov, V. M.; Hinch, E. J. Effect of a Spectrum of Relaxation Times on the Capillary Thinning of a Filament of Elastic Liquid. *J. Non-Newton. Fluid Mech.* 1997, *72* (1), 31–53.

(7) Rodd, L. E.; Scott, T. P.; Cooper-White, J. J.; McKinley, G. H. Capillary Break-up Rheometry of Low-Viscosity Elastic Fluids. 2004.

(8) Dinic, J.; Zhang, Y.; Jimenez, L. N.; Sharma, V. Extensional Relaxation Times of Dilute, Aqueous Polymer Solutions. *ACS Macro Lett.* 2015, *4* (7), 804–808.

(9) Dinic, J.; Jimenez, L. N.; Sharma, V. Pinch-off Dynamics and Dripping-onto-Substrate (DoS) Rheometry of Complex Fluids. *Lab. Chip* 2017, *17* (3), 460–473.

(10) Sousa, P. C.; Vega, E. J.; Sousa, R. G.; Montanero, J. M.; Alves, M. A. Measurement of Relaxation Times in Extensional Flow of Weakly Viscoelastic Polymer Solutions. *Rheol. Acta* 2017, *56* (1), 11–20.

(11) Hsu, T. T.; Walker, T. W.; Frank, C. W.; Fuller, G. G. Instabilities and Elastic Recoil of the Two-Fluid Circular Hydraulic Jump. *Exp. Fluids* 2014, *55* (1), 1645.

(12) Papageorgiou, D. T. On the Breakup of Viscous Liquid Threads. *Phys. Fluids* 1995, *7* (7), 1529–1544.

(13) Wolf, D. P.; Blasco, L.; Khan, M. A.; Litt, M. Human Cervical Mucus. II. Changes in Viscoelasticity During the Ovulatory Menstrual Cycle *. *Fertil. Steril.* 1977, *28* (1), 47–52.