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Polyvinyl Alcohol Hydrogels

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Anisotropic Polyvinyl Alcohol Hydrogels

Fall 2019 Report

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Background

White matter in the brain is anisotropic, which means it has directionally dependent properties, and has a stiffness of 1-3 KPa. The objective of this project was to create PVA that mimicked these properties well. A hydrogel that mimicked the properties of the brain was to be created and the process had to be easily replicable. Polyvinyl Alcohol is a water soluble synthetic polymer and can be made into a hydrogel.

The protocol used was largely based on a paper from 2014 by Chatelin[i]. They made PVA and put it through freeze-thaw cycles to increase the stiffness and stretched it to induce anisotropy. The experiment done by Chatelin used 5% PVA and wt 1% cellulose. The cellulose functioned as a scattering agent. The PVA went through 5 total freeze thaw cycles, and the PVA was stretched to 180% after two freeze thaw cycles. The samples were frozen at -18ºC for 12 hours and thawed at 20ºC for 12 hours. To stretch, the samples were cut to 50mm x 50mm x 12 mm. The resulting storage modulus for Chatelin's experiments was between 2 and 5 KPa.

The other two papers used to develop the methods were Millon 2006[ii] and Hudson 2011[iii]. The procedures from all three papers were modified and utilized in this paper. The freeze-thaw cycles increased the stiffness of the gels while stretching the gels affected the crosslinking in them. This led to the gels exhibiting anisotropy when tested. A Dynamic Shear Tester was used find the shear moduli in different directions and a planar biaxial test was used to find the tensile moduli in different directions. The gels were fabricated and tested in collaboration with Alexa Panrudkevich.

Methods

Overview

For the PVA samples, the hydrogels were created by mixing PVA and distilled water in a beaker and then heating it up to 90°C and holding it at that temperature for fifteen minutes. Then, the samples were poured into containers and put into the freezer around 9am. Then, they would be taken out to thaw at 5pm on Sunday. Then, they would be frozen at 9am on Monday and these freeze thaw cycles continued until Wednesday when the gels had gone through 3 freeze thaw cycles. The PVA tested was 10% by weight. Previously, PVA of 8%, 6%, and 5% + Agar had been tested.

Gel Fabrication

The methods used to create the PVA were based on the Chatelin paper from 2014 and other sources. The procedure used in the lab was a modified version of the protocol from the previously mentioned papers. To create a 10% PVA hydrogel by weight, a solution was created by mixing 99+ % hydrolyzed PVA (Sigma-Aldrich, mw 89,000-98,000) with distilled water (10g PVA + 90g DI water). The solution was placed in a hot water bath, and held at 85 °C, and stirred for 15 minutes. The water that evaporated out was replaced with distilled water after being heated. Plastic containers of 6.5 cm x 6.5 cm x 2.5 mm were used to hold the PVA hydrogels. In order to prevent water loss, the containers were wrapped in parafilm. Each sample, (65x95 mm, ~5mm thick) was subjected to 2 freeze-thaw cycles of at least 8 hours. The samples were made on Friday and then put into the freezer Friday morning around 9am. Then, they were taken out Sunday at 5pm. The samples were then placed back in the freezer at 9am on Monday. After 1 freeze thaw cycle, the samples were stretched to 180%. The stretching was done after 1 freeze-thaw cycle in order to induce more anisotropy. This is also why the weight percentage of PVA was increased, so that the gels wouldn't tear during the stretching process. After being stretched, the samples were put through three more freeze thaw cycles. In order to stretch the sample 180%, the ends of the wide body samples were wrapped in a paper towel in order to prevent slipping. Parafilm was wrapped around the PVA sample to prevent evaporation during the freeze thaw cycles. There were unstretched control samples that went through the same amount of freeze thaw cycles. The stretchers used are shown in Fig. 1 and Fig. 2 below and were designed by Devin Williamson.

Figure 1: Stretching apparatus.

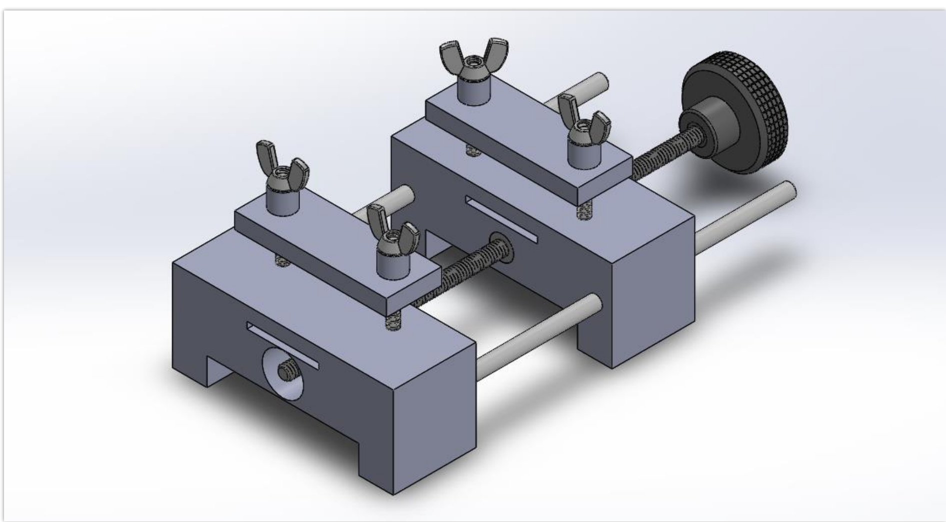


Figure 2: Design for the PVA puller

Mechanical Testing

The PVA was subject to two different types of mechanical testing.

Dynamic Shear Testing

The first type of testing was shear testing and the Dynamic Shear Tester (DST) was used. To test on this device, a sample fifteen millimeters in diameter was punched out. The test was done on both stretched and unstretched samples with different freeze thaw cycles and the results gave us a storage modulus, loss factor, and the ratios for both by putting direction one over direction two.

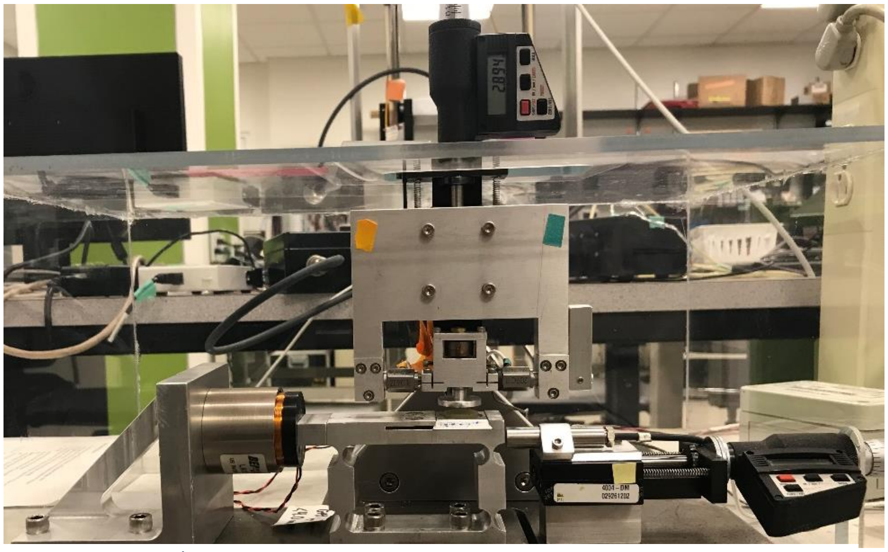


Figure 2: DST machine

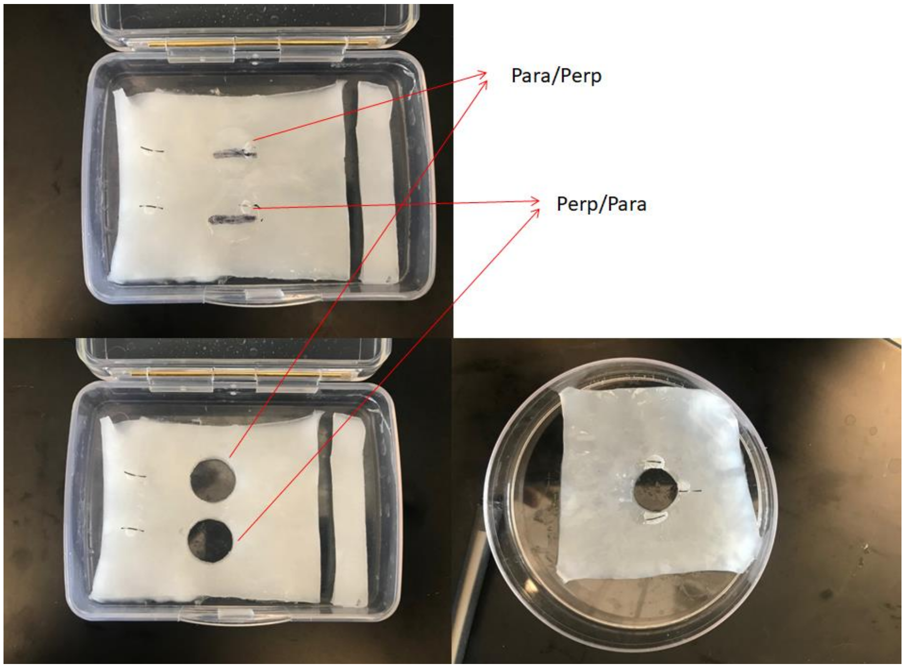


Figure 4: How samples were cut

Biaxial Tensile Testing

In Dr. Spencer Lakes's Musculoskeletal Soft Tissue Lab, planar biaxial tension tests were performed using the procedure described in Deeken 2014. The PVA was held in place using long metal clamps and needles. The samples were cut out to be 50×50 mm and about 4 mm thick. The green needle shows edge number 1 and a 20N load cell is placed on edges three and four of the biaxial testing machine. All biaxial testing was done by Alexa Panrudkevich.

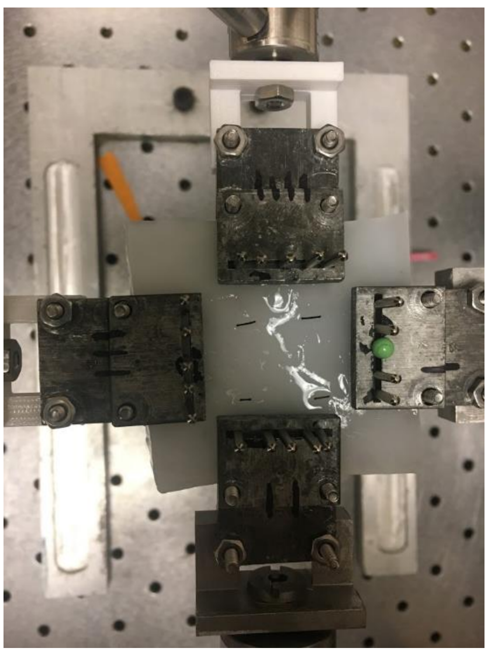


Figure 5: Unstretched Sample Loaded into Planar Biaxial Testing Machine

Results

Dynamic Shear Testing

Table 1, displayed below, displays the average values for the storage modulus for various tests as well as the storage modulus ratios for those tests. Fig. 6 displays the loss factor ratio for all tests done in the fall semester and Fig. 7 displays the storage modulus ratio for those same tests. The data shows that PVA has a higher storage modulus in the direction it is stretched but there is a lot of deviation within the values for each test. Thus, it can be concluded that PVA is slightly anisotropic.

Table 1: Storage Modulus Averages

Test	Average Value	Number of Samples	Standard Deviation
Para/Perp Storage Modulus for 2nd 12% Test	4.31 KPa	11	0.9373
Perp/Para Storage Modulus for 2nd 12% Test	4.93 KPa	10	1.4896
Unstretched Storage Modulus for 2nd 12% Test	4.27 KPa	6	3.1917
Para/Perp Storage Modulus Ratio	0.901	11	0.1673
Perp/Para Storage Modulus Ratio	1.144	10	0.2429
Unstretched Storage Modulus Ratio	1.106	6	0.1310

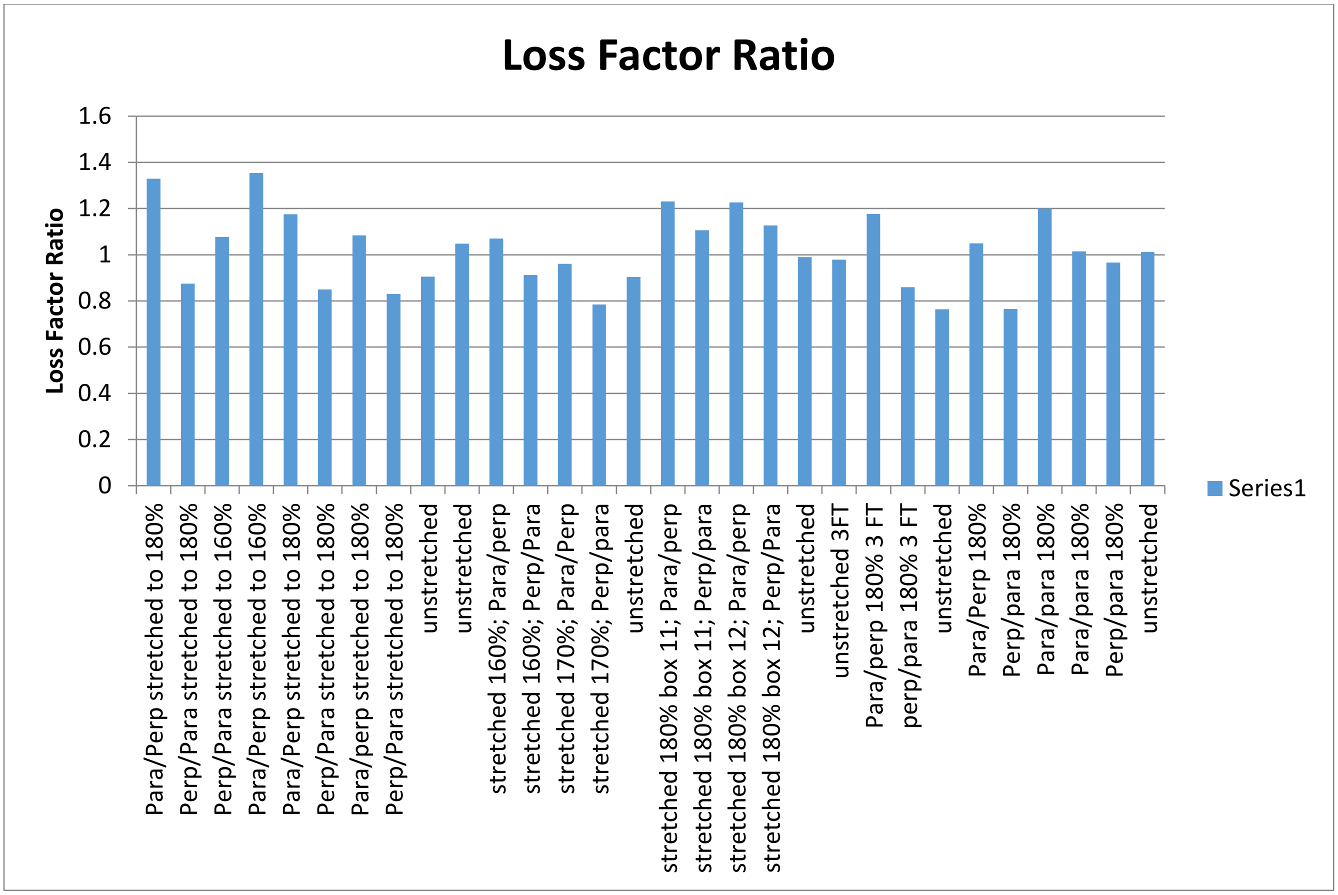


Figure 6: Loss Factor Ratio Graph

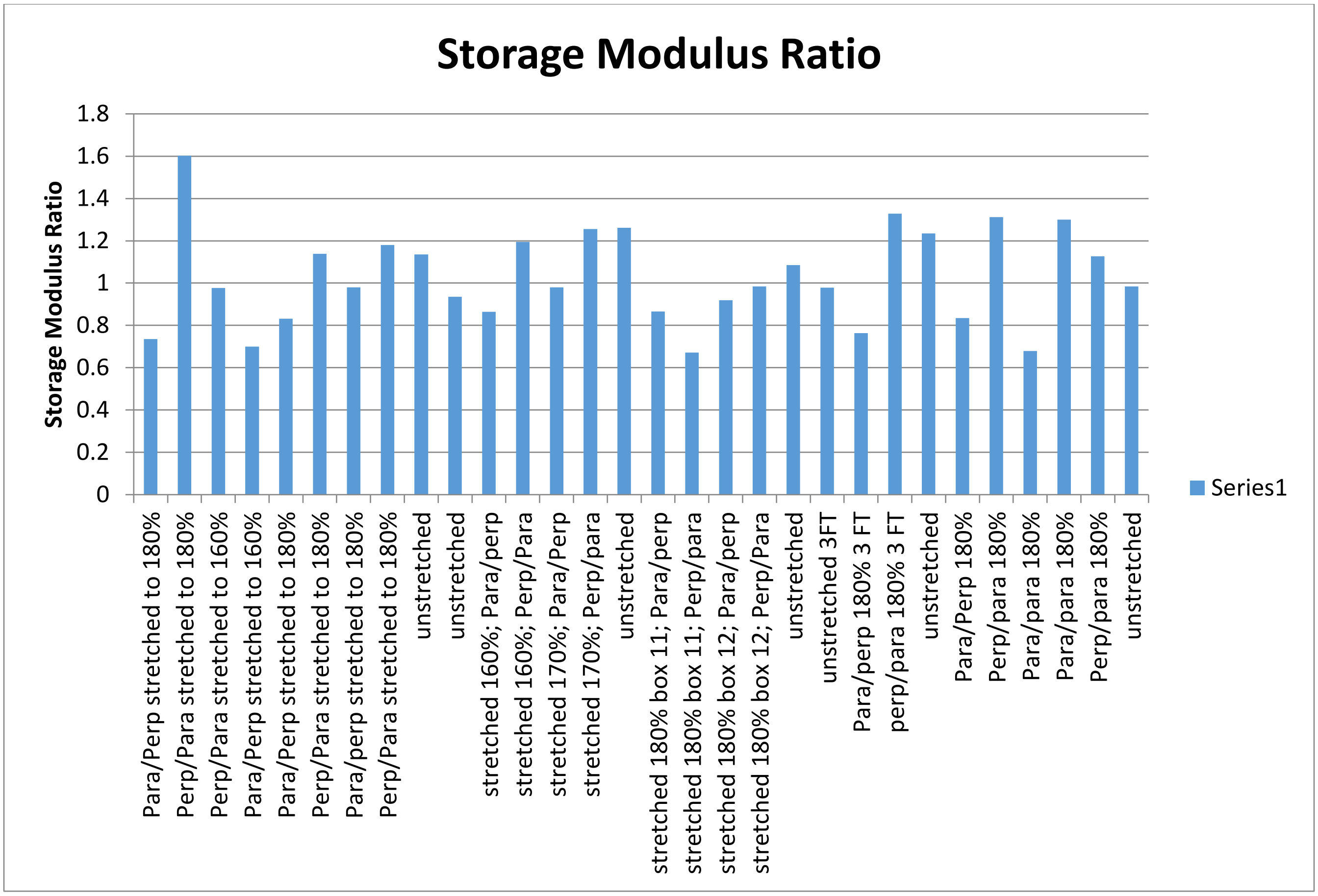


Figure 7: Storage Modulus Ratio Graph

Biaxial Tensile Testing

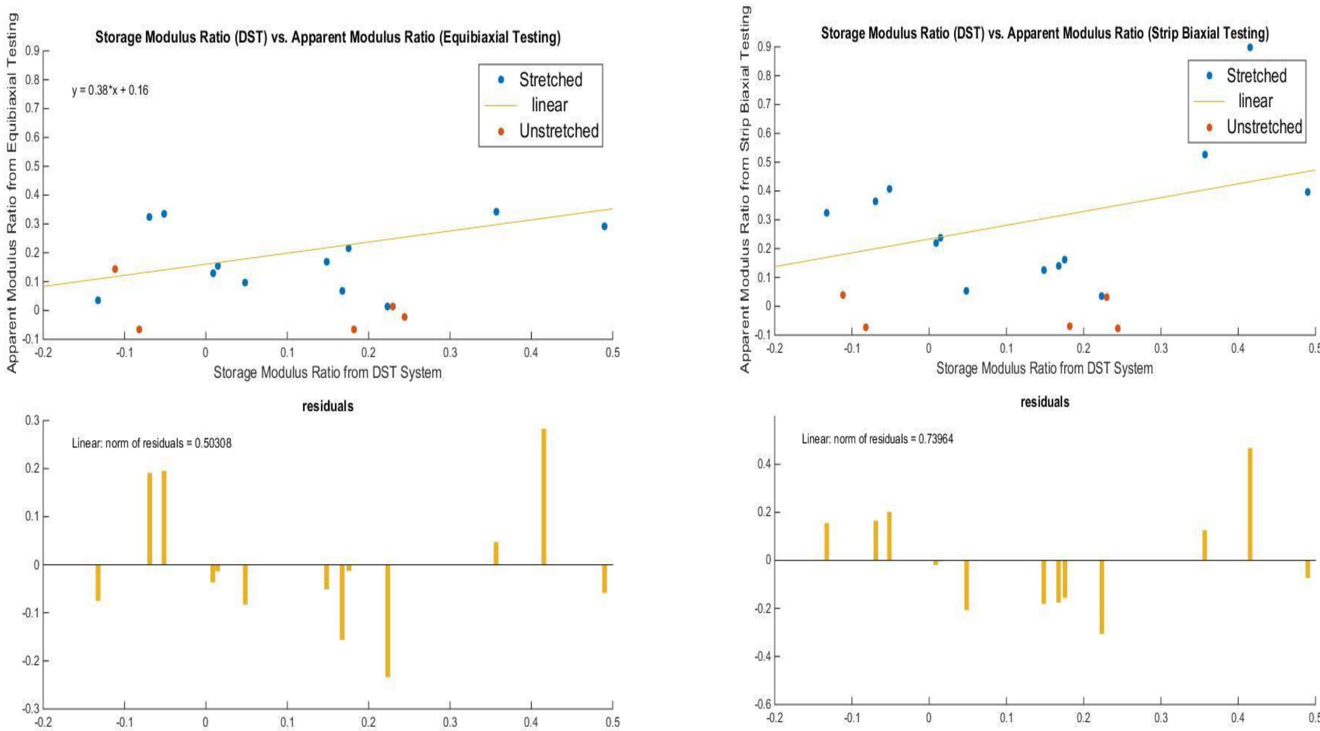
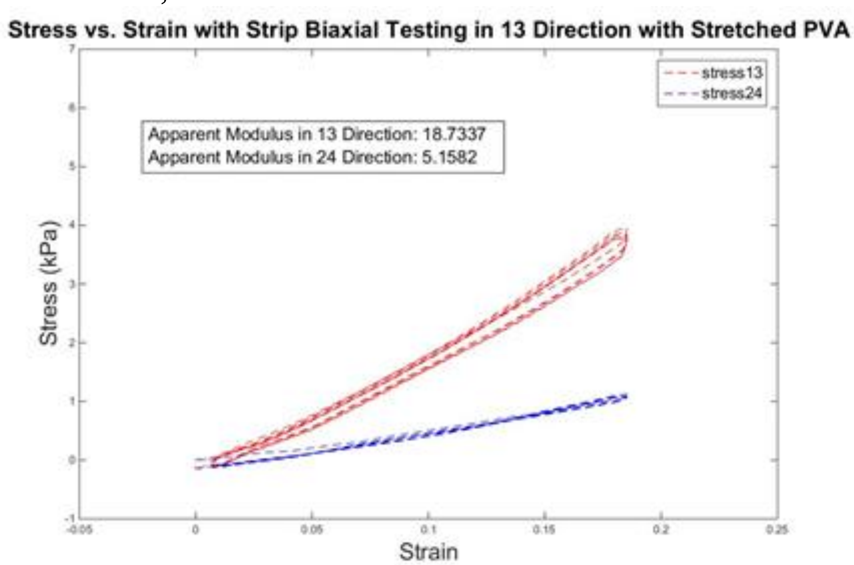


Figure 8: Biaxial test results compared to DST results

180% stretched; 10% PVA made 10/18/19



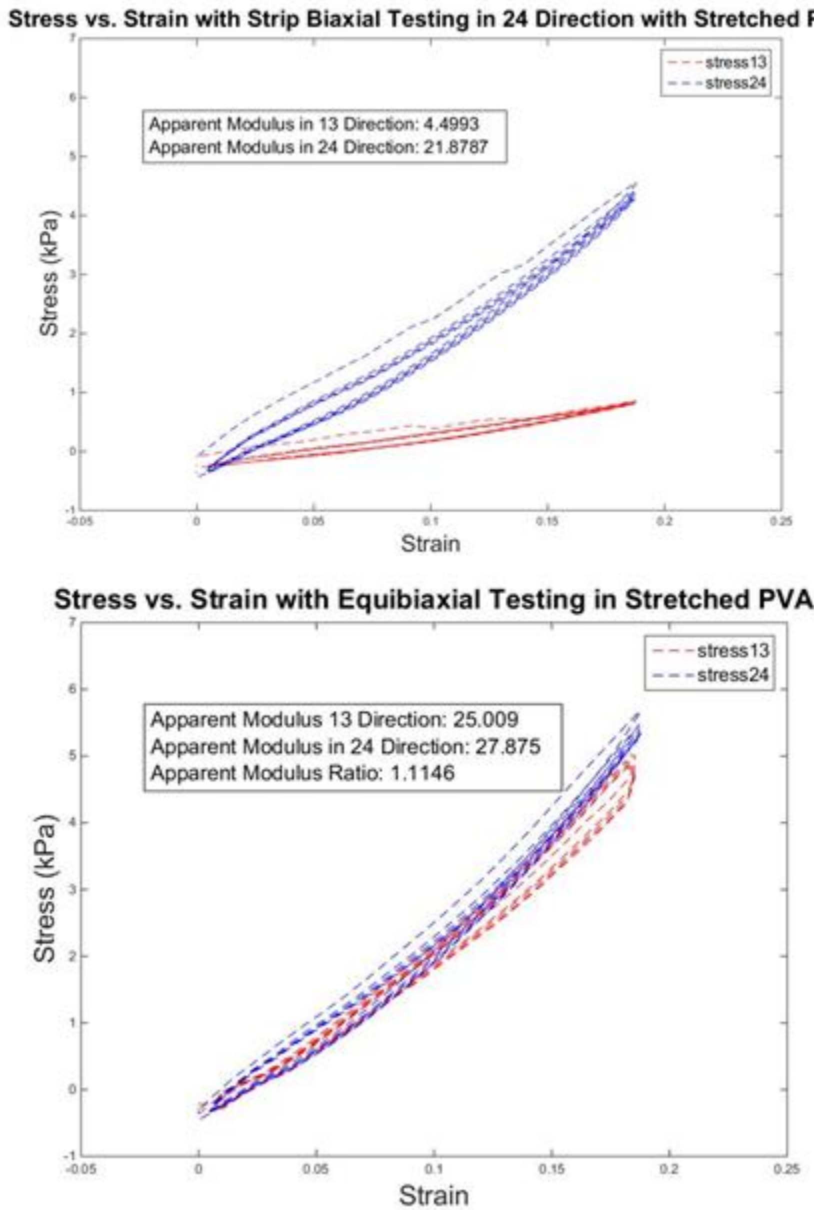


Figure 9: Biaxial results for 180% stretched PVA

The results in Fig. 8 display the biaxial testing results compared to the DST results from the Summer of 2019. Fig. 9 displays what the typical biaxial results from a stretched sample look like. The data shows that the DST and Biaxial tests both indicate that PVA hydrogels are slightly anisotropic.

Discussion

From the results of the PVA testing from the Fall 2019 semester and previous semesters, it can be concluded that while PVA can mimic some of the material properties of brain tissue, the results are too inconsistent. This semester, the weight percentage of the PVA was increased to 10% in order to be able to stretch the material after 1 freeze-thaw cycles. Stretching after 1 freeze-thaw cycle increased the anisotropy in the material. However, this resulted in the Shear Modulus of the material ranging from 4-5 KPa which is too stiff to mimic brain tissue. The material also has an average shear modulus ratio of .901 when tested in the Para/Perp direction and 1.144 in the Perp/Para direction. While this does indicate that the material is anisotropic when stretched, it is not anisotropic enough.

Limitations

Although PVA does mimic some of the properties of brain tissue, it does have many limitations. The main problem is that the PVA is only slightly anisotropic. Another problem is that the results are highly inconsistent. In Table 1, the standard deviations for the storage modulus ratios and averages can be seen. Some of this inconsistency can be attributed to human error as the gel is very soft and slippery which makes it difficult to test.

Conclusions and Future Work

From the DST and Biaxial testing that was completed this semester, as well as the Uniaxial and Rheometry testing completed in previous semester, the mechanical properties of PVA have been well established. The gels, at a 10% concentration, have a shear modulus between 4 and 5 KPa, which is too stiff, and the gels are slightly anisotropic. In the future, 3D printed soft gels will be tested to see if they are a good material for this project. The same testing methods will be used to characterize the gels.

Appendix A: Spreadsheets and data files

DST summary: brainlab/Shear_tester_data/PVA_Data/PVA DST_Results_Summary_V5

- The DST summary spreadsheet contains all the DST done on PVA and includes all the data about the PVA sample as well as the results

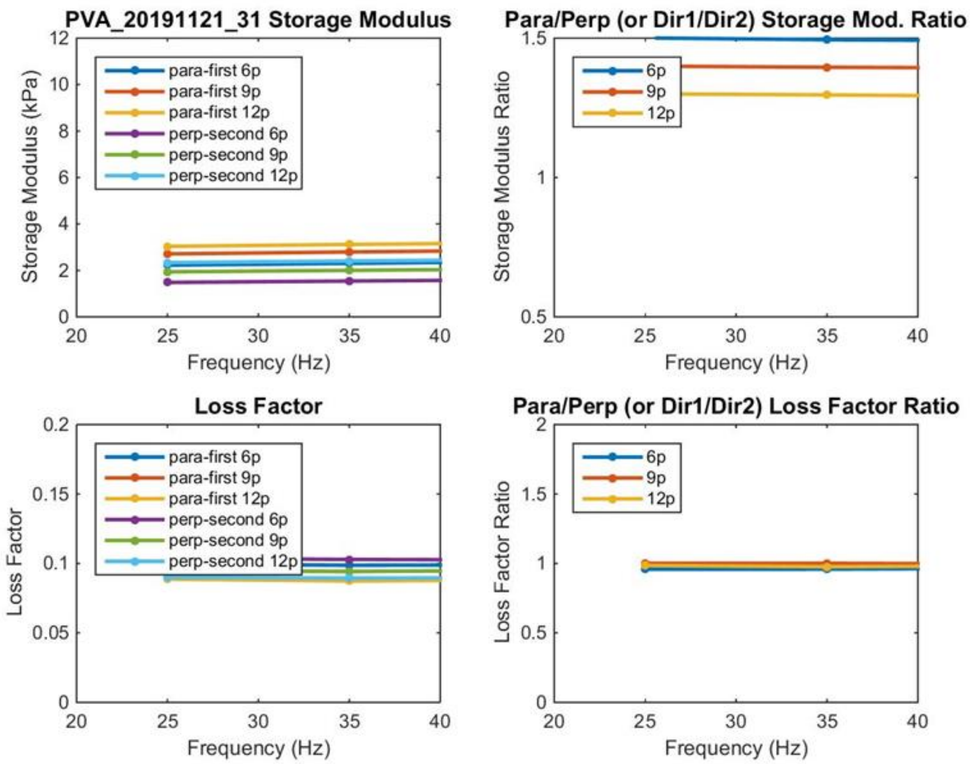
DST Data files: brainlab/Shear_tester_data/PVA_Data/Fall_2019

Biaxial Data files: brainlab/Shear_tester_data/PVA_Data/Fall_2019

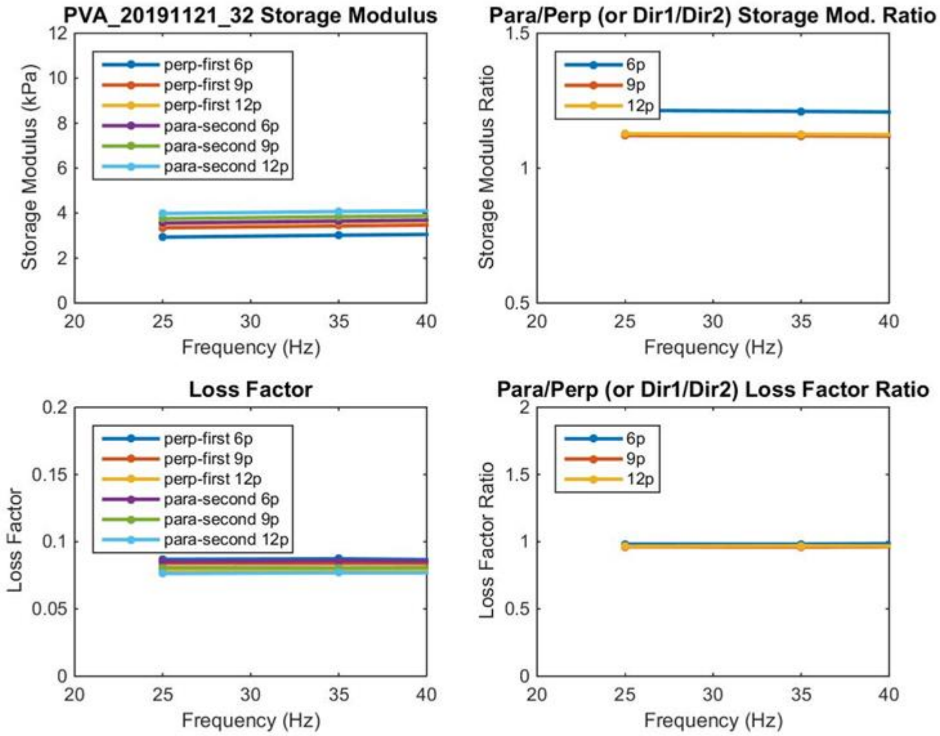
Appendix B: Raw Data

DST Raw Data

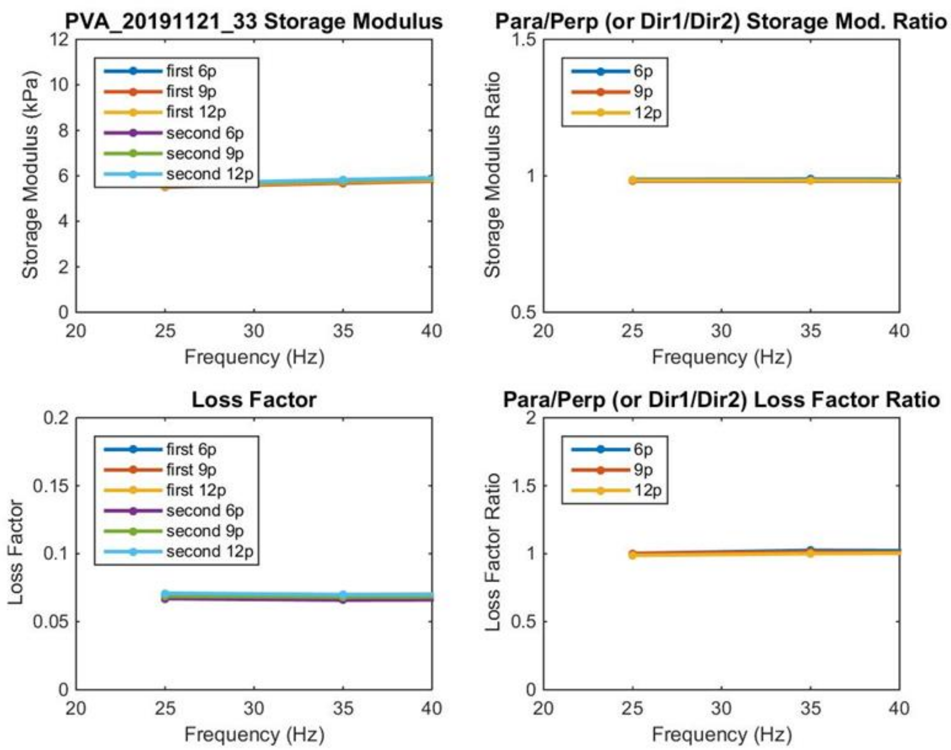
180% stretched; 10% PVA made 11/15/2019 Para/perp



180% stretched; 10% PVA made 11/15/2019 Perp/para

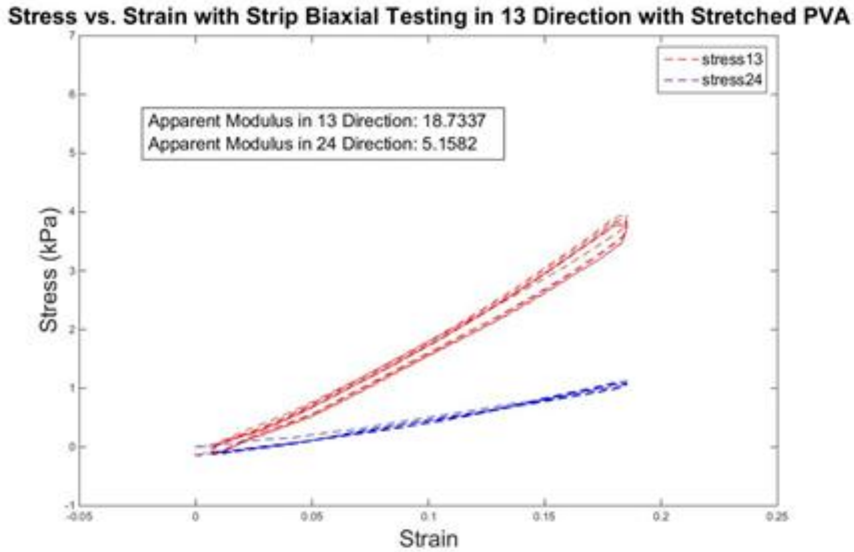


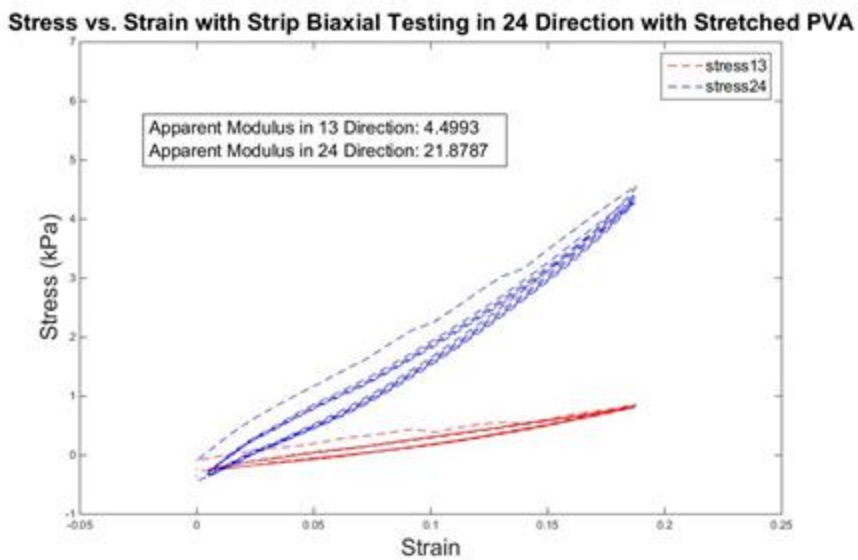
Unstretched 10% PVA made 11/15/2019

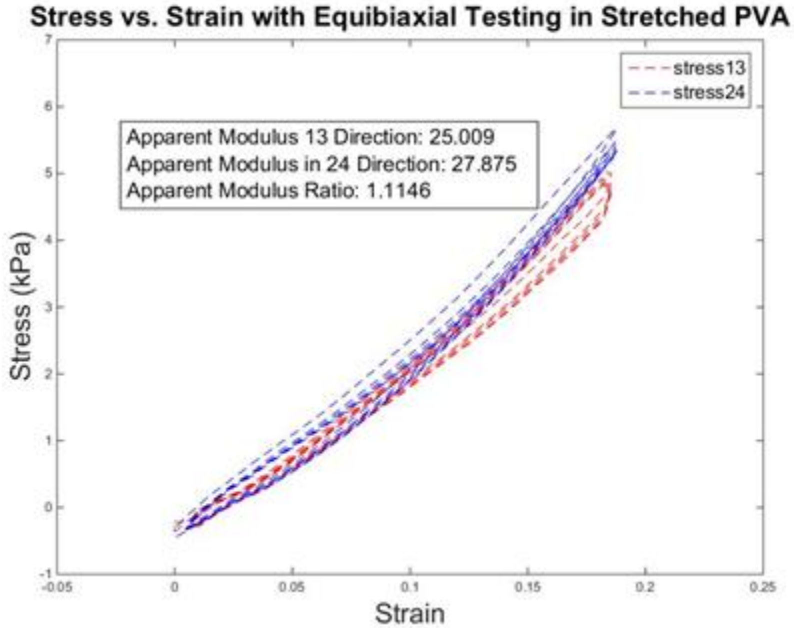


Biaxial Raw Data

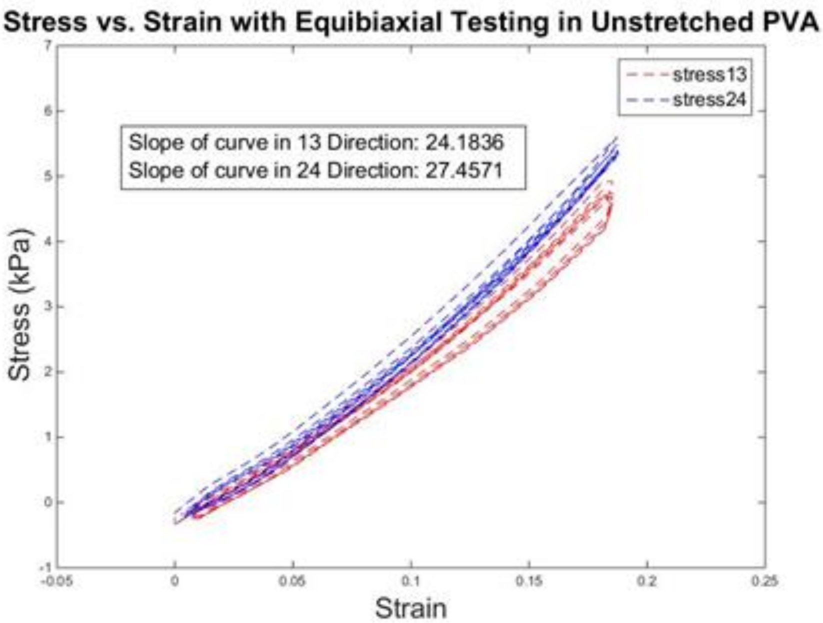
180% stretched; 10% PVA made 10/18/19

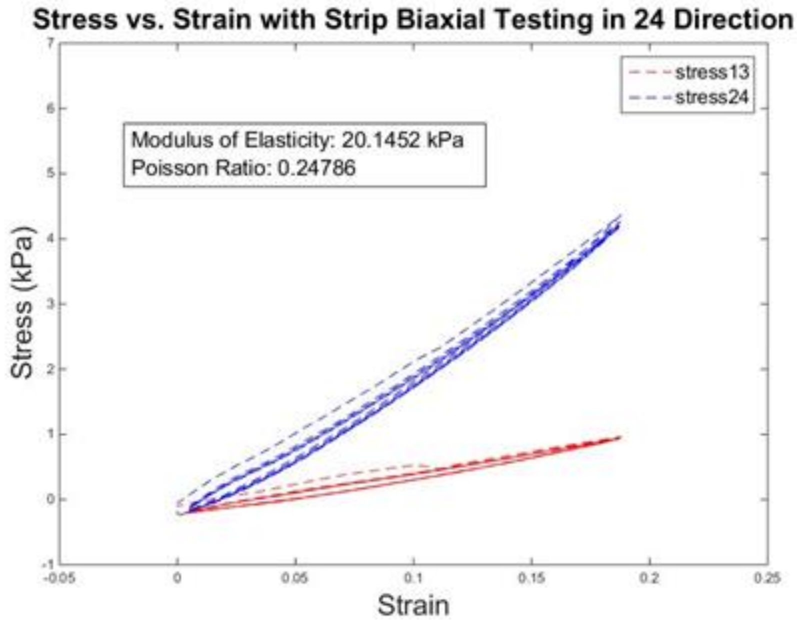


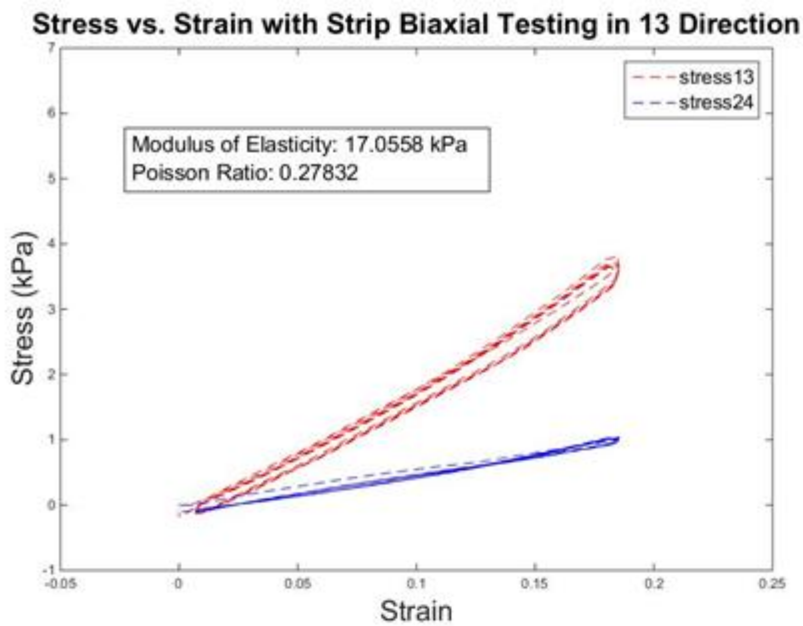




Unstretched 10% PVA made 10/18/2019




Stress vs. Strain with Strip Biaxial Testing in 24 Direction
stress13
stress24
Modulus of Elasticity: 20.1452 kPa
Poisson Ratio: 0.24786
Stress (kPa)
Strain
7
6
5
4
3
2
1
0
-1
-0.05
0
0.05
0.1
0.15
0.2
0.25


Stress vs. Strain with Strip Biaxial Testing in 13 Direction
stress13
stress24
Modulus of Elasticity: 17.0558 kPa
Poisson Ratio: 0.27832
Stress (kPa)
Strain
7
6
5
4
3
2
1
0
-1
-0.05
0
0.05
0.1
0.15
0.2
0.25

Appendix C: References

[i] Chatelin S et al. Anisotropic polyvinyl alcohol hydrogel phantom for shear wave elastography in fibrous biological soft tissue: a multimodality characterization. Phys Med Biol. 2014 Nov 21

[ii] Millon LE, Mohammadi H, Wan WK. Anisotropic polyvinyl alcohol hydrogel for cardiovascular applications. *J Biomed Mater Res B Appl Biomater*. 2006

[iii] Hudson SD, Hutter JL, Nieh MP, Pencer J, Millon LE, Wan W. Characterization of anisotropic poly(vinyl alcohol) hydrogel by small- and ultra-small-angle neutron scattering. *J Chem Phys*. 2009