

Compression testing and measurement of material properties
of a double network hydrogel

by

Diana Valero

Submitted to the Department of Mechanical Engineering in Partial Fulfillment of
the Requirements for the Degree of

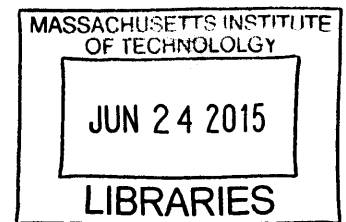
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Abstract

Double network hydrogel samples were synthesized and manufactured out of polyacrylamide (PAAm) and alginate solutions. They were casted into cube molds with each side measuring 20 mm. Samples were tested under compressive loads in cyclic compression tests and stress relaxation tests. A viscoelastic model was applied and material properties were calculated using the experimental data. The elastic modulus of these PAAm-alginate gels was found to be 35kPa, while the viscosity, η , was found to be 1.43 kPa·s. The viscous response was found to have a dependency on the strain rate by an exponential factor of 0.26. Using the applied theoretical model and the experimentally determined material properties, you can then characterize the mechanical response of the PAAm-alginate hydrogel when it undergoes small strains.

Thesis Supervisor: Lallit Anand

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Chapter 1

Introduction

Hydrogels are soft materials composed of water and a cross-linked, hydrophilic polymer network. Their mechanical behavior is known to exhibit elements of linearity and time dependency [1]. Due to their biocompatibility, hydrogels have a variety of biomedical applications and are currently used as drug delivery systems [4]. Their elastic properties, though, have made them very attractive in the field of tissue engineering. Unfortunately, their development into synthetic tissues, such as cartilage or skin, is limited. Tissues like cartilage, tendons and muscles not only possess a high mechanical strength, but they also possess a high fracture toughness. Most single network hydrogels, gels made of one type of polymer network, have fracture energies of about 10 Jm^{-2} , while cartilage has a fracture energy of about 1000 Jm^{-2} [5]. It has been difficult to, simultaneously, achieve fracture energies and mechanical strengths similar to these tissues using single network hydrogels. Single network hydrogels exhibit an inverse relationship between elastic modulus and fracture energy, therefore it has been difficult to create synthetic tissues that can mimic the the mechanical response of biological tissues and lead to the development of synthetic implantable tissues.

Unlike single network hydrogels, double network hydrogels are synthesized using two different polymer networks: a short chain network and a long chain network. It has been proven that combining two polymer networks improves both the mechanical strength and fracture toughness of hydrogels when compared to hydrogels synthesized from only one of it's individual components. Their favorable mechanical performance is a result of using a polymer that usually results in a brittle, rigid gel and using a second polymer that produces a very soft and ductile gel [4]. The enhanced mechanical properties of double network hydrogels makes them more similar to biological tissue and, therefore, more suitable for tissue engineering applications.

Biomedical devices and implants undergo many different loads in every day use. Before being able to use double network hydrogels as an implantable synthetic tis-

sue, it is of great importance to understand the mechanical response of these gels to different loads. Once implanted, this synthetic tissue would be expected to undergo compressive loads, therefore it is imperative to understand and characterize the mechanical behavior of these double network hydrogels under compression.

This thesis focuses on the the synthesis and testing of a double network hydrogel in order to apply a theoretical model and determine values of material properties and the relationship between the mechanical response and the strain rate under compressive loads. To complete the former I:

1. prepared molds and a pre-gel solution using two polymer networks, an ionically linked alginate network and a covalently linked polyacrylamide (PAAm) network, and manufactured testable structures by curing them using ultraviolet light;
2. conducted cyclic compression experiments on gel samples at different strain rates;
3. conducted experiments that applied a stepwise compressive load at different strain rates;
4. processed experimental data to observe elastic and viscous responses and extract their respective material property values

The following chapter describes the theoretical model used to determine the material properties of the PAAm-alginate hydrogel. Chapter 3 describes the procedure used to synthesize the double network hydrogel solution and the curing procedure used to create solid, testable structures, as well as, the process to manufacture the hydrogel molds. Chapter 4 describes the two types of experiments that were performed. The first part of Chapter 4 explains the cyclic compression tests that were performed at different strain rates. The second part of Chapter 4 describes the procedures and the experiments for the stepwise applied load. Chapter 5 presents the results and measured material property values. Lastly, Chapter 6 offers a conclusion and discusses future work that can be performed.

Chapter 2

Theoretical Model

Viscoelasticity refers to a response from a material that exhibits both an elastic mechanical response, and a viscous mechanical response. The mechanical response of a viscoelastic material is the summation of the elastic response and the viscous response. In this thesis, the Maxwell model, which consists of a spring and a dashpot in series, was applied to the experimental data in order to extract the material properties and the mechanical response's dependence on the strain rate at which the PAAm-alginate hydrogel samples were tested at. Figure 2.1 shows a schematic of model that was used.

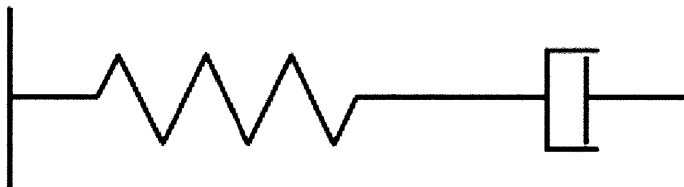


Figure 2.1: A pictorial representation of the Maxwell model which is composed of a spring and dashpot in series .

The spring portion of the model represents the solid linear elastic response of the material. Equation 2.1 shows the stress dependence on the strain. The stress, σ , and

strain, ϵ , are related by the elastic modulus, E , which is a material property of the hydrogel that this thesis sought to determine.

$$\sigma = E\epsilon \quad (2.1)$$

Upon applying a strain to the material and holding it at that strain level for any amount of time would not produce a change in the measured stress. Figure 2.2 shows a graph that exemplifies the expected mechanical behavior if the material were strained at a constant rate, as were the gel samples in these experiments, and that displacement was held by plotting the stress against the strain.

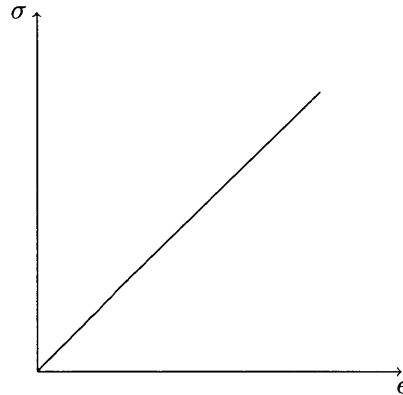


Figure 2.2: The stress versus strain for an elastic material. The slope of the line is the elastic modulus, E .

The dashpot portion of the model represents the viscous response of a material. Unlike the elastic response, the viscous response is dependent on time, in this case the strain rate, not the strain. Equation 2.2 shows the relationship between the stress, the viscosity, η and the strain rate of the load. The viscosity is another material property that this thesis sought to measure.

$$\sigma = \eta\dot{\epsilon}^m \quad (2.2)$$

Unlike the elastic model, the viscous model is not linearly dependent on the strain rate; it is dependent on the strain rate and the constant, m . This thesis

experimentally determined what this value of m is for this PAAm-alginate gel. From this model, upon applying a strain at a certain rate, we would observe a mechanical response, but if the material is held at a certain strain level we would expect to see the stress of the material drop to zero, since it is solely dependent on the strain rate not the strain. Figure 2.3 shows the expected mechanical response of a viscous material if the material were displaced to a certain point at a constant rate and then held by plotting the stress against the strain.

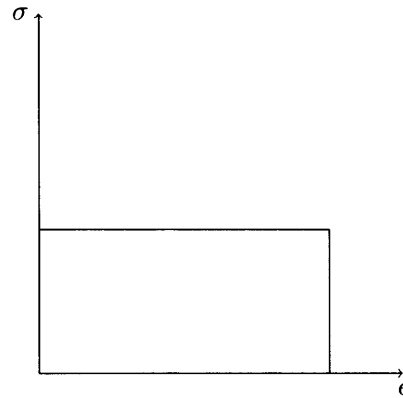


Figure 2.3: The stress versus strain for a viscous material.

A viscoelastic material exhibits an elastic response and a viscous response, and the entire mechanical response can be characterized by the summation of the elastic response and the viscous response. If a viscoelastic material is strained, at a constant rate, to a certain displacement and then held at that displacement we would first observe a linear relationship between the strain and the stress while the material is being displaced. Once the material is being held and no longer being displaced we would see a drop in the stress, although it would not drop to zero like a purely viscous material. The change in stress would come from the viscous component in the response and the stress that remains following the drop would be the stress produced by the elastic component of the mechanical response. Figure 2.4 shows the expected response of a viscoelastic material

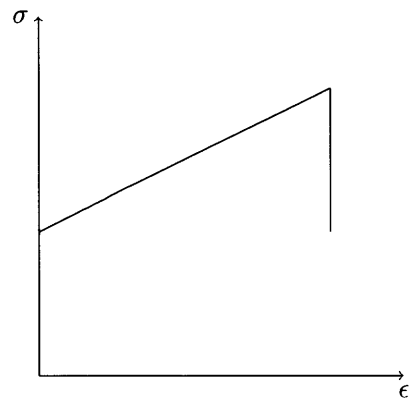


Figure 2.4: The stress versus strain for a viscoelastic material. The drop is a consequence of the viscosity.

Chapter 3

Manufacturing of Gel Samples

3.1 Gel Synthesis

The double network hydrogels used for this set of experiments were made of a short chain polymer network, alginate, and a long chain PAAm network. The gel was synthesized using the following solutions:

- (a) Acrylamide in deionized water (19% wt.)
- (b) Alginate in deionized water (4.8% wt.)
- (c) Ammonium Persulfate in deionized water (APS, 0.2 M)
- (d) N,N- methylenebisacrylamide in deionized water (Bis, 2% wt.)
- (e) Calcium sulfate in deionized water (1 M)
- (f) N,N,N9,N9- tetramethylenediamine (TMET)

The pre-gel solution was prepared and testable structures were manufactured using the following procedure:

1. Put 4.1 mL of alginate solution into a 20 mL syringe and add 102 μL APS and 900 μL Bis using a micropipette.
2. In a 10 mL syringe, put 5.5 mL PAAm solution.
3. Mix the contents of the two syringes using a coupler.
4. Degas the mixture in order to remove air bubbles.

5. Add 200 μL calcium sulfate and 8.2 μL TMET to empty syringe using a micropipette.
6. Quickly mix calcium and TMET with the degassed mixture using a coupler.
7. Add mixture to mold quickly, and cover.
8. Place mold in UV crosslinker for 1 hour to cure.
9. Remove mold from UV crosslinker, detach gel and store in refrigerator.

It was imperative that the mixture be carefully degassed, because air bubbles have a significant effect on the mechanical behavior of the gel samples. The TMET and calcium sulfate had to be mixed with the pre-gel solution and poured into the molds very quickly, because the TMET would accelerate cross-linking and gelation would quickly begin to occur.

3.2 Mold Fabrication

The desired test geometry for these samples were cubes so the gel samples were cured in cube shaped molds. Molds were made by laser cutting different layers of acrylic and then gluing them onto one another to obtain the necessary geometry. It was important that two slits also be included in the different layers, in order to allow for the insertion of glass slides. Figure 3.1 shows the top views of the different layers of acrylic that were glued on top of each other to create a mold. The bottom layer, the base of the mold, is shown on the far left of Figure 3.1. The next layer, the middle layer, was cut out a total of 3 times for each mold and all three layers were glued on top of each other. Lastly, the last figure was cut once and used as a cover for each mold while the gel samples were curing the UV crosslinker. The final structures had a cross sectional area of 400 mm^2 and were 20 mm tall. Figure 3.2 shows a completed mold used to create samples.

In order to ensure that the glass slides bonded to the gels, glass slides were first treated with plasma. Then, a glass cleaner solution was poured over the plasma treated side. Special care was taken to avoid touching or disrupting the treated sides of the glass slides, since that side was to be bonded to the cube structures to create testable samples. Glass slides were left the glass cleaner solution for 1 hour and then removed, rinsed off with deionized water and dried off using pressurized air prior to being placed in molds. The strongest bonding occurred if the glass slides were used immediately following this hour of treatment. If more time elapsed, and the solution dried onto the glass slides, the bond strength between the gel and the glass was weaker. Figure 3.3 shows an image of a completed gel sample following its removal from the mold.

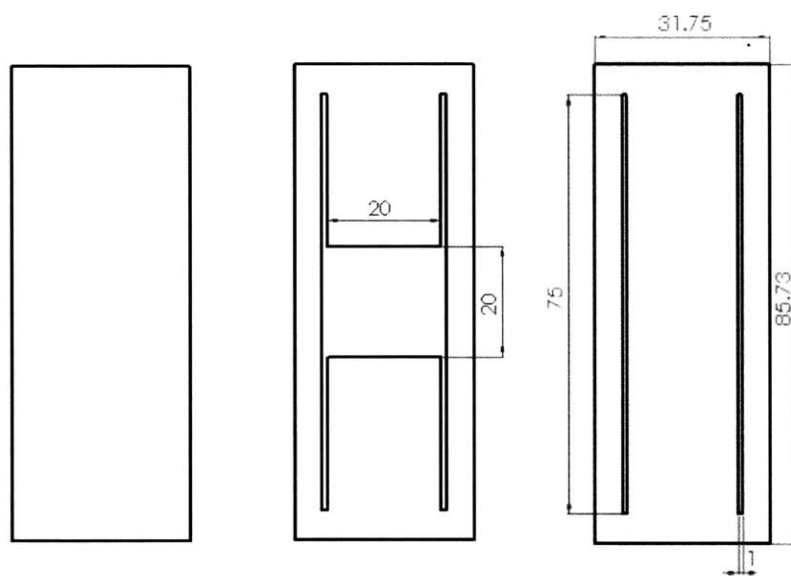
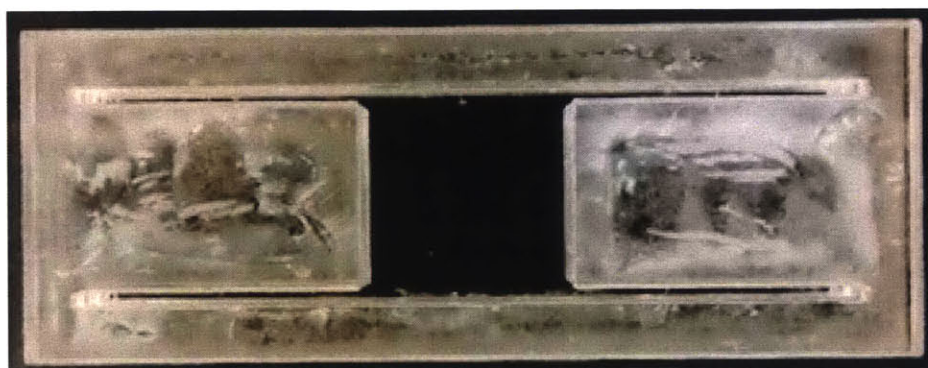
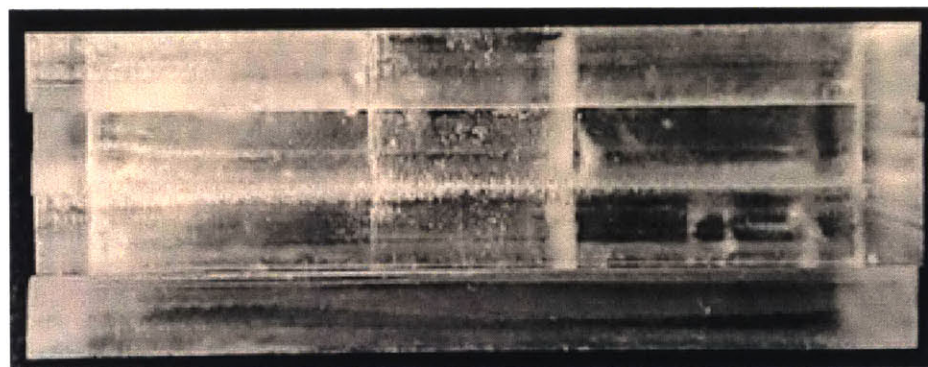


Figure 3.1: The layers used to fabricate the molds



(a)



(b)

Figure 3.2: Photographs of a typical mold used to create gel samples. (a) The top view of the acrylic mold, the glass slides were placed in the slits and the gel solution poured in the middle square. (b) The side view of a mold, that shows the four different layers that were glued on top of each other.

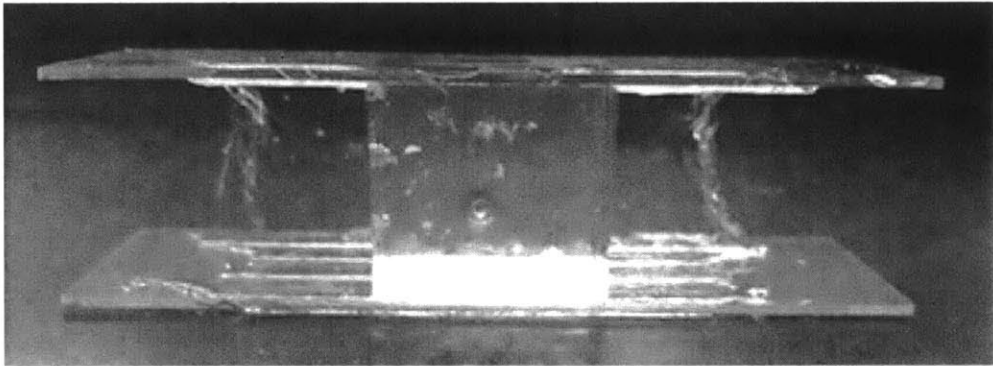


Figure 3.3: A gel sample prior to testing. The gel sample is bonded to two glass slides to allow for compression testing.

Chapter 4

Experiments

Two different types of tests were conducted in order to be able to observe the mechanical behavior and determine the material properties of the PAAm-alginate hydrogel. The experiments were on gel samples manufactured as described in Chapter 3. It was important that, after removal from the mold, and prior to testing, the samples not be deformed in any way, because applying any load would cause a change in the mechanical response that they exhibited. The following two tests were performed:

1. Cyclic compression tests were conducted at different strain rates. This was achieved by applying the same displacement to each gel sample at different displacement rates, and then unloading the sample at the same displacement rate. The load was then applied and removed again for a total of two cycles.
2. Stress relaxation tests were performed also using different strain rates, in order to observe the viscoelastic response of the material. A stepwise displacement was applied at different rates. The same stepwise displacement was used to unload and then reload the material.

4.1 Cyclic Compression Tests

This experiment was conducted on different gel samples on a Zwick Roell. This test consisted of two compressive cycles. In this experiment, the samples were first displaced 12 mm. Then the load was released and the sample was returned to its original height by displacing it in opposite direction at the same rate at which it was initially compressed. The same cycle was completed again, where there was loading and then unloading. The time, standard force and standard travel were all measured.

The four applied displacement rates were:

- (a) 10 mms/s

- (b) 50 mm/s
- (c) 100mm/s
- (d) 200 mm/s

For each displacement rate, the strain rate was calculated and the stress was plotted against the stretch ratio. The stress was calculated using the measured standard force during the experiment and dividing by the cross sectional area of the sample. The stretch was found by dividing the length by the original length, the length was found by subtracting the standard travel from the original length.

4.2 Stress Relaxation Tests

This experiment was also conducted on samples using a Zwick Roell. A stepwise displacement was applied until the sample was compressed 12 mm. The displacement was applied 2 mm at a time, at different displacement rates, and held for 100 s at each of the steps. After being compressed 12mm, the load was released by allowing the sample to return to it's initial height by applying the same stepwise displacement in the negative direction and holding each step for the same amount of time, 100 s. The sample was then, once more, compressed using a stepwise displacement. The time, standard force and standard travel were all recorded.

This test was conducted at seven different displacement rates:

- (a) 1 mm/s
- (b) 10 mm/s
- (c) 50 mm/s
- (d) 100 mm/s
- (e) 150 mm/s
- (f) 200 mm/s
- (g) 400 mm/s

Similarly, the stress of the material was measured by dividing the standard force by the cross sectional area of the gel sample.

Chapter 5

Experimental Predictions of Mechanical Properties

From the cyclic compression experiments, it was evident that the response of the material exhibits both strain and strain-rate dependency. Figure 5.1 shows the stress plotted against the stretch ratio for the four different strain rates that were tested in the cyclic compression experiments.

Figure 5.2 shows the maximum stress, the stress felt at the end of the loading cycle plotted against the strain rate. The hydrogels that were compressed at a larger strain rate, exhibited higher maximum stresses.

The stress relaxation experiments also were representative of the strain rate dependence of the hydrogel. Figure 5.3 shows the stress against the stretch during the first loading curve of the gel. At each point where the strain was held, the hydrogel relaxed and there was a drop in the amount of stress. This drop in the amount of stress depends on the viscosity of the material, the elasticity and the time that the material was held at that certain strain. From figure 5.4 we see that for each step in the loading cycle the mechanical response follows the a very similar trend across strain rates

From the data, the elastic modulus, E , the viscosity, η and the exponent, m , were determined fitting a Maxwell model to the data in order to characterize the stress relaxation response. The experimentally determined elastic modulus was calculated to be 35kPa., which is similar to the values reported for a poly2-acrylamido-2-methylpropanesulfonic acid (PAMPS), PAMPS-PAAm double network gel [2]. For the viscous response, m was calculated to be 0.26 and the viscosity of the material was found to be 1.43 kPa.s. Figure 5.5 shows the stress relaxation behavior by showing the data and the the fit created by the model, using the material properties that were measured for a strain of 0.1. From this example, it is evident that the Maxwell model captures the viscoelastic response at small strains.

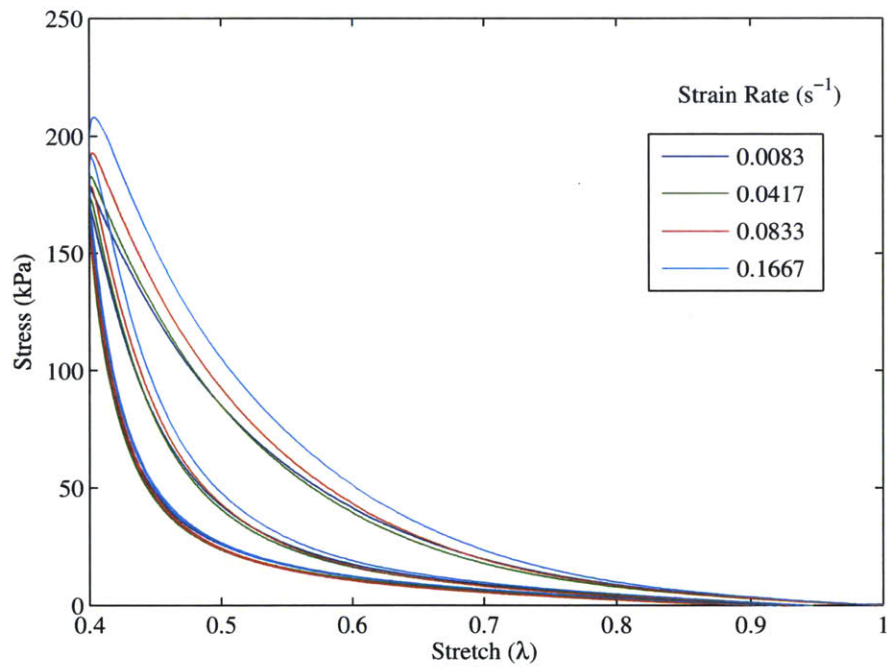


Figure 5.1: This shows the data from the two loading and unloading cycles that were performed on different strain rates

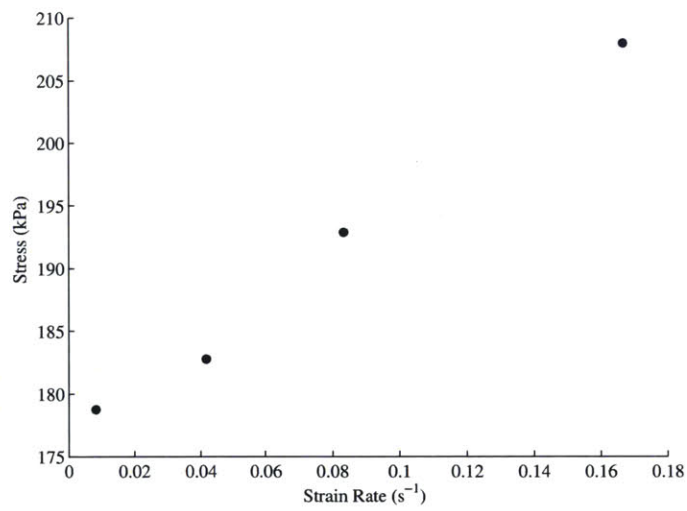
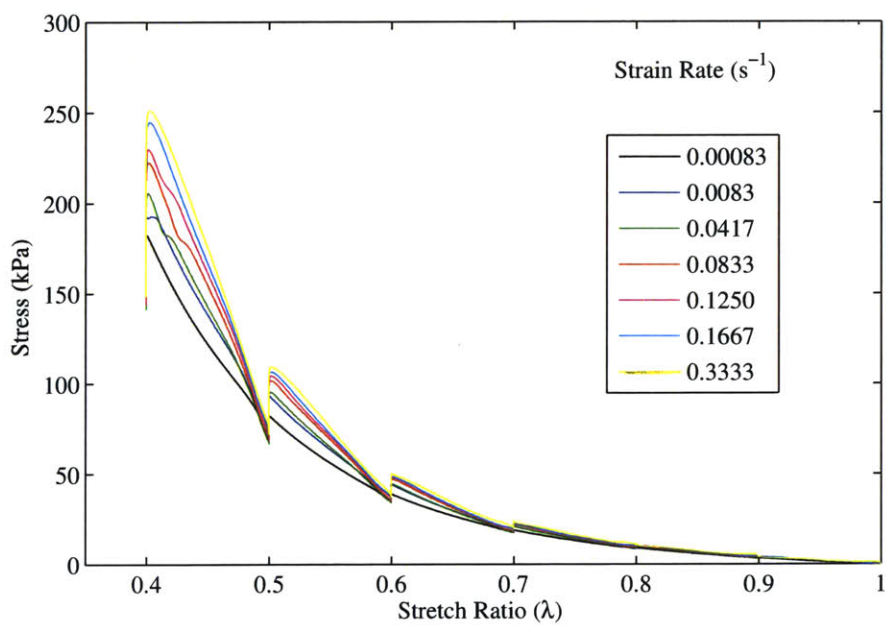


Figure 5.2: The maximum stress during loading during the cyclic compression experiments against the strain rate.



a

Figure 5.3: Data during loading during stress relaxation experiments at different strain rates.

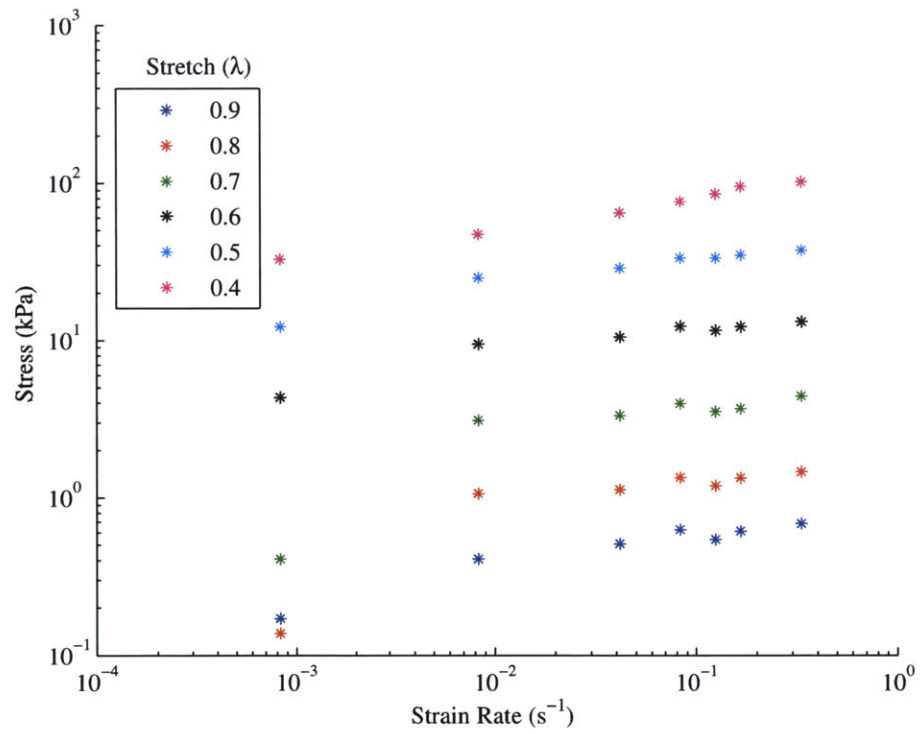


Figure 5.4: The amount that the material relaxes in kPa plotted against strain rate at each different stretch ratio.

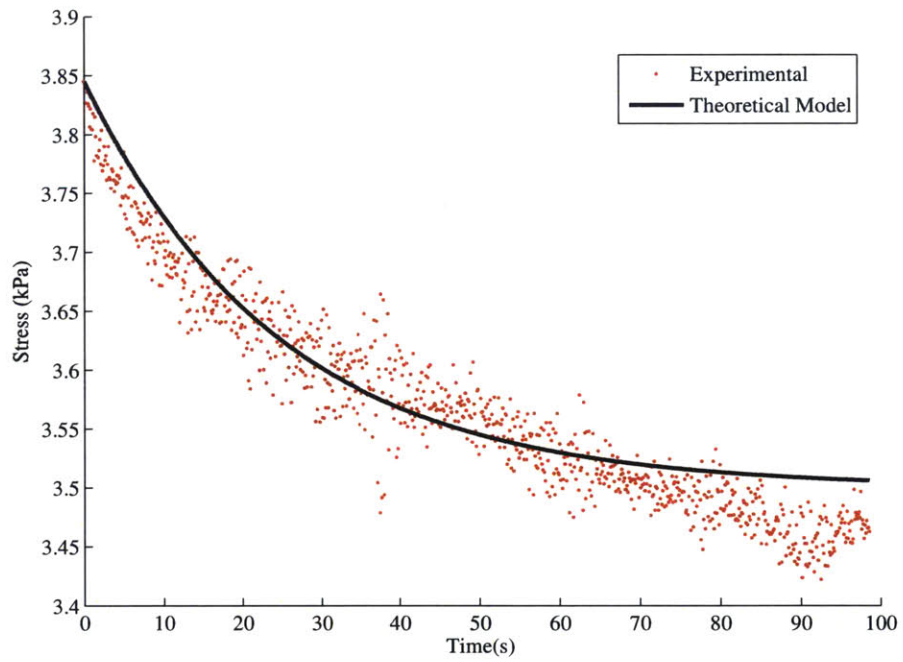


Figure 5.5: The stress is plotted against the time, while the material is relaxing. Both the experimental data and the theoretical model using the measured material properties are plotted.

Chapter 6

Conclusion and Future Work

Double network hydrogels synthesized from alginate and PAAm polymer networks were casted into cube shaped samples. The samples were tested under two different experimental tests using compressive loads. The first was a cyclic compression test and the second was a stress relaxation test. The gel samples exhibited viscous and elastic mechanical responses by their dependence on the strain and the strain rate. Their viscous and elastic material properties were experimentally determined by applying a Maxwell model to the mechanical responses. Then, the theoretical model was compared to the small strain experimental responses.

In the future, it would be useful to study the plastic response of the hydrogels. Following removal of the hydrogel samples after the stress relaxation experiments there was visible plastic deformation. This is partially attributed to the fact that the hydrogel samples were not confined in the directions orthogonal to the axes at which the load was applied. It would be of interest; to see the response of the material during compression in a confined environment, and study the three-dimensional mechanical response, instead of solely the one-dimensional response

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