# NOVEL METHOD FOR ADDITIVE MANUFACTURE OF RUBBER WITH EXPLORATION IN SUPPORT STRUCTURE AND MATERIAL PERFORMANCE

by

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A THESIS

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# An Abstract of the Thesis of

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Approved: ________________________________________

Elizabeth Esponnette

3D printing is a rapidly growing additive manufacturing process that offers advantages in customizability, sustainability, cost reduction, precision, and accessibility over traditional processes. The limitation of printable materials, however, is still a major barrier preventing 3D printing moving from creating prototypes to producing final products. My work addresses the need to 3D print with thermosets, specifically focusing on rubber. Initially printing proof of concept tests by hand informed the selection of a 3D printer machine to order for further tests. To showcase this new manufacturing process for rubber, I designed a new insulation material for wetsuits that would not have been possible before. I developed a method to print natural liquid latex by hand, and identified poly(tetrahydrofuran) as a compatible support material. The 3D printer will print rubber alone with minimal difficulties, however introducing support material into the same print has proved much more challenging due to additional complex coding. Moving forward print head obstruction, support material temperature, and gcode adjustments must be addressed to improve the resolution and consistency of the prints.

# Acknowledgements

I would like to thank Beth Esponnette and Casey Check for helping me to fully examine the scope of this project from the perspective of different disciplines, and offering unwavering support and excitement throughout this process. This thesis would not have been possible without Beth's vision and guidance, and Casey's generous contributions of lab space and bright ideas. I want to appreciate Julie Haack for first inspiring me to pursue green chemistry in design, and for being a wealth of resources and connections for this project. I would also like to express my sincerest gratitude to Dan Rosenberg, for joining my thesis committee and serving as an exceptional professor and role model for the last five years. Thank you to everyone who got roped into helping with various aspects of this project, specifically Davo from Hyrel who provided us with endless printer tech support, and Trevor Petach for helping us develop a conductivity test. To my parents, your dedication to ensuring I always received the best education possible has meant the world to me; I cannot imagine being where I am today without a lifetime of your love and encouragement.

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# Prologue

As a designer with a passion for sustainability, I intend to spend my future working alongside chemists and designers to create products and processes that are safer for people and the environment. My thesis has allowed me to take the first steps in pursuing this goal through bringing together people from Product Design and Chemistry to collaborate on a project that aims to improve the future of manufacturing and material performance. Design carries with it a great responsibility of introducing new things into the world, and I hope this project and my work to come can serve as inspiration for others to recognize the potential of interdisciplinary collaboration and to take advantage of its innovative power for good.

# Introduction

*"Recognizing the need is the primary condition for design"* -Charles Eames

This project began when Beth Esponnette recognized a need, and I jumped at the chance to help work towards a solution. Designers are trained to invent and explore; to be agents of change as we envision a brighter future. Our job goes far beyond making things beautiful; we must immerse ourselves in the research process, be able to authentically empathize with our users, ideate, build, fail, and reassess over and over again. Before we ever make it to a final design, we must collaborate with those around us: engineers, manufacturers, scientists, users. Eventually (or more likely very quickly), we are expected to produce something that on some level has never been done before. My thesis addresses the need for a new system that overcomes manufacturing limitations by bridging the gap between currently incompatible materials and production methods. The main objectives of this project were to develop a new system of 3D printing to allow for *additive manufacturing* with *thermoset* rubbers, and to design a product dependent on this method for production that would utilize the resultant ability to manufacture new complex structures in rubber.

Design is everywhere. Everything that people interact with on a daily basis outside of nature has been designed, however, despite the familiarity with final products, people do not often stop to consider the design, engineering, and manufacturing behind these items. Without understanding the story of how things came to be, it is nearly impossible to understand the limitations that prevent the development of products from keeping up with creative imaginations.

To understand the need for 3D printing, it is important to first look at traditional manufacturing techniques, especially in the case of rubber. When it comes to plastics and polymers, common forms of manufacturing are: blow molding, thermoforming, rotation molding, vacuum casting, compression molding, injection molding, reaction injection molding, and dip molding (Thompson 97). Rubber specifically, is usually manufactured using either compression molding, or injection molding, which each include their own set of design considerations. Compression molding shapes either plastic or rubber by “compressing them into a preheated die cavity,” (Thomas 44). This process is low to moderate in cost and can produce high strength, well finished parts in medium to high volume production. When creating products for compression molding, designers must consider that the draft angles of the product should be about 0.5 degrees, but could be less depending on the quality of the tool and ejector system. While the part can be 0.1 kg - 8 kg, “the overall dimensions are limited by the pressure that can be applied across the surface area, which is affected by part geometry and design,” (Thomas 97). Wall size is also dependent on “the method by which gases are vented from the thermosetting material as it cures and heats up,” (Thomas 97). Wall thickness can be less than 1 mm up to 50 mm, but are generally determined by the nature of the thermosetting reaction that can cause blistering in thicker wall sections. Injection molding “is one of the leading processes used for manufacturing plastic products, and is ideal for high volume production of identical products,” (Thomas 50). First polymer granules are heated, stirred, and moved toward the die cavity. The melted polymer is then injected into the die at which point it sets, and is then forced out of the die by ejector pins. Ejected parts are usually dispensed onto a conveyor belt, ready for finishing work. This process has a very high tooling cost, but in turn a very low product cost. The injection cycle time is between 30 and 60 seconds, and can produce very high surface finish. “Designing for injection molding is a complex and demanding task that involves designers, polymer specialists, engineers, toolmakers and molders,” (Thomas 52). Two of the most common problems to account for are shrinkage and stress build-up.  Shrinkage can lead to warping, distortion, cracking and sink marks, while stress build-up can prevent even flow of material throughout the mold. Draft angles must be at least 0.5 degrees, and wall thicknesses should be equal or within 10%. Smaller draft angles will introduce too much stress when the part is ejected, while uneven wall thicknesses will warp due to variations in cooling times. Ribs are added to increase strength, decrease wall thickness, and aid in the flow of material through the mold. Although these manufacturing methods are very dependable, they are only practical for mass production. Creating custom dies is so expensive that producing models or small runs of products is not economically worth the tooling costs. The design constraints are also limiting enough that the prospects of a new manufacturing technique that give designers more freedom is highly sought after.

While new studies on 3D printing methods are being published all the time, it is a common misconception that the concept of 3D printing is a new technology; in fact the first patent application for 3D printing was filed by Dr. Hideo Kodama of Nagoya Municipal Industrial Research Institute in Japan in 1980. Dr. Kodama published a paper on his work creating an additive manufacturing method using photosensitive resin polymerized by an UV light, however he failed to submit the follow up full patent specification requirement before the deadline (Bensoussan). Although Dr. Kodama may not have received the first additive manufacturing patent, he was responsible for the earliest version of *Stereolithography* (SLA). In 1986, the first patent was granted for SLA to Charles HUll, followed by patents for *Selective Laser Sintering* (SLS) to Carl Deckard in 1989, and for *Fused Deposition Modeling* (FDM) to Stratasys in 1992 (3D Printing Industry). All the recent hype is understandable though as 3D printing has been a rapidly growing field since 2011 when FDM patents expired, expanding its focus beyond just being a rapid prototyping tool for professionals. As Rick Smith from Forbes says:

> For those of you who believe that 3D printing is just a fringe technology overhyped by an enthusiastic maker community, or that its impact is limited to headline grabbing futuristic experiments like 3D printed organs, think again. Industrial 3D printing, also referred to as additive manufacturing, is poised to significantly and permanently disrupt global production. No longer just a tool for rapid prototyping, 3D printing is now being used for end-use part production and adoption is growing exponentially. (Hyrel 3D)

While on one end of the spectrum 3D printers are becoming simpler for the sake of new at home users, the technological advancements of the professional side have taken off as 3D printers are being adapted for even more specialized applications with cutting edge materials and new printing processes. Some of these innovations include printing products such as carbon fiber bicycles, steel bridges, working organs, and other biomatter. The benefits of 3D printing come down to efficiency, cost reduction, sustainability, and customizability. Although the market is expanding, currently 3D printing is most often used for prototyping. This method of fabrication has a quick turnaround time and a lower cost because it serves as an alternative for creating expensive molds that will get very limited use. 3D printing also eliminates excess waste materials that result from using molds, as well as reduces the need for excess tooling and finishing processes. Finally, the customizability factor allows special parts to be custom made and easily refined and reprinted to fit the user's specifications.

3D printing begins with a digital file, which is then transformed into a physical object through an additive manufacturing process involving many thin layers of a material laid on top of one another. While the digital file is usually created in a *CAD* program, it can also be made from a composite of photographs from every angle of an object, or by scanning an object to recreate a digital representation. As for the printing process, there are currently three main types: Fused Deposition Modeling (FDM), Stereolithography (SLA), and Selective Laser Sintering (SLS). One thing that these methods all have in common is that they use *thermoplastics*, which are printed by changing the phase of the material. While these processes are typically successful for prototyping, there are certain manufacturing limitations especially when it comes to creating functional long lasting products. In theory, many of these limitations could be alleviated by using a different family of plastics known as thermoset plastics, however the only printable thermosets are UV curable polymers and silicone, whose printing methods are still being developed. For my thesis, I have worked alongside Beth Esponnette and Casey Check to create a new method of 3D printing that will allow printing thermoset rubber to become a reality.

Although 3D printing with thermoplastics can create a versatile range of products, there are additional benefits that come with printing thermoset polymers, such as rubber. Benefits of thermosets include:

- Corrosion and Steam Resistant
- Excellent *Chemical and Dimensional Stability*
- Excellent *Thermal Properties*
- Heat Resistant
- High *Dielectric Strength*
- High *Strength-to-Weight Ratio*
- Low *Creep/Shrink*
- Superior Thermal Insulation

(Woodland Plastics Corporation)

This means that there are large markets of products that cannot currently be 3D printed because the products demand attributes such as being chemically inert, heat resistant, and extremely durable, to an extent that thermoplastics cannot offer. While these additional material attributes combined with the other benefits of 3D printing hold great potential in many fields, I chose to focus on their advantages in insulation, for which I designed a wetsuit insulation material to physically showcase the importance and future of the new method.

# Placement Within Existing Work

While thermoplastics are the standard 3D printing material of choice, there has been increasing work in recent years to develop printing with thermosets. This work falls into two main material categories: UV curable polymers and silicone. One exception to these materials is a case documented in the Journal of Applied Polymer Science that dealt with liquid latex, however this method is even less developed.

## UV Curable Polymers

The first method of printing with thermoset elastomeric materials that currently exists, is printing with UV curable polymers, such as polyurethane and acrylic based polymers. These polymers can be printed in two ways, either using SLA or inkjet printing. When they are inkjet printed, a UV light attached to the print head cures the material after deposition. There is a lot of potential for innovative products using this method due to the precision and range of materials that can be printed, however further development is needed to be able to print with more substantial materials (Lukic).

## Silicone

The second option for printing with thermosets is to use silicone. Many companies such as Wacker, Hyrel 3D, and Structur3D Printing have experimented with printing silicone and now offer silicone 3D printing services or machines. While these methods rely on printing with syringes and avoiding shapes that require support material, Fripp developed a revolutionary method that earned them a patent. Fripp's process begins with an unpolymerized silicone bath, to which they add a cross linker whose ratio determines the Shore hardness of the print. A catalyst is then forced through the 0.2mm aperture of the injector at 2 BAR and polymerizes silicone sub-surface. Pieces are formed only where the catalyst is placed by the injector, and the remaining uncured silicone around the pieces serves as their support structure. After ten to thirty minutes the polymerization of the part is complete. Uncured silicone can be reused for another print. This method uses off the shelf two part RTV silicone, and has successfully printed from 20 Shore 00 to 40 Shore A (The PICSIMA Method). As Scott Grunewald describes this process in his article on 3Dprint.com, “the concept is almost a hybrid process between a powder bed 3D printer and a stereolithography 3D printer,” (Grunewald 2016).

### Printability of Elastomer Latex for Additive Manufacturing or 3D Printing

The research for Printability of Elastomer Latex for Additive Manufacturing or 3D Printing was completed at Loughborough University in the UK, and was published in 2016. This study analyzed the particle size, viscosity and surface tension of five latex materials to determine printability, and then carried out printing trials with the XSBR as the ink. While printing was moderately successful, “technical problems of agglomeration and print head clogging need to be addressed and both the material and process need to be optimized for consistent printing to be achieved,” (Lukic).

### Remaining Limitations

While printing techniques for photocurable polymers and silicone are slowly becoming more developed, it is easier for other companies to build off and further refine these successful processes than to create a process from the ground up. Due to the lack of research in printing other materials, the need for methods to accommodate 3D printing thermosets is still great. The only study that has attempted to print with liquid latex still encountered problems preventing them from developing a consistent printing method. We have the opportunity to explore an alternative printing method using a syringe, opposed to using an inkjet printer, and can hopefully work through some of the issues the other study ran into.

## Round 1: Printing by Hand (Spring 2016-Winter 2017)

We began our research by conducting Proof of Concept (POC) experiments to test if our ideas could work at all, opposed to diving into specific details and scientific procedures. The first round of POCs were various forms of 3D printing conducted by hand to prepare us for ordering the right kind of 3D printer, which we would work with to create final prints. The process and outcomes of each POC informed the plan for the next, which made for a constantly evolving direction for the whole project. We began with the intention of developing a method to print with thermoset polymers, focusing more specifically on printing synthetic rubber. We ended up working to develop a method to print with natural rubber, which is a thermoplastic, but can be crosslinked post printing to become a thermoset.

### First Silicone POC Experiment

*May 2016*

*Materials:*

- Silicone Part A (SORTA-Clear 40)
- Silicone Part B (SORTA-Clear 40)
- Nitrile gloves
- Safety Glasses
- Aprons
- Popsicle sticks
- Toothpicks
- Pouring/mixing cups

- Syringe
- Measuring scale
- Ease release 200
- Shallow containers (square, glass)
- Masking tape
- Pen
- Ruler
- Scissors
- Plastic tarp

*Setup and General Procedure*

We began by gathering our materials, labeling our containers, and donning gloves, eye protection, and aprons (Figure 1, 2, and 3). We completed Test #1 before we remembered to use the ease release spray, so we only used it on the containers for Test #2, #3, and #4. Every time we measured out more silicone we used a plastic cup that we cut to be roughly 2 inches high to minimize the material stuck to the walls between transfers. After placing the cup on the scale, we tared the scale, and added the silicone. In the cases where both Part A and Part B were mixed together, we weighed out Part A first and then re-tarred the scale and slowly added Part B to the same cup.

Figure 1: General Set Up

*Test #1: Control Without Sulphur*

For this test, we calculated the amount of parts A and B that we would need in grams to mix together in the right ratio in order to fill our container 20mm high, and immediately poured the premixed parts of silicone into our container (Figure 2). Part A was much more viscous than Part B.

*Calculations:*

Specific Gravity → 1.08 (g/cm3)

Mix Ratio → 100A:10B

Length/Width of Square Glass Container → 8.3cm

Goal → fill the container 20mm (depth)

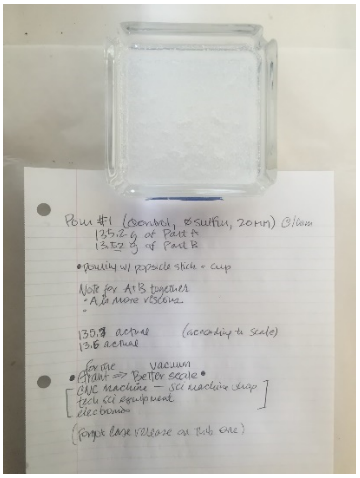
Area of glass dish: 8.3cm x 8.3cm = 68.89cm2

Volume to fill glass dish: 68.89cm2 x 2cm = 137.78cm3

Grams of silicone needed to fill that desired volume: 137.78cm3 x 1.08g/cm3= 148.80g

Grams of Part B needed: 148.80g / 11 =13.527g

Grams of Part A needed: 13.527g x 10 = 135.27g



Pour #1 (Control, ∅ sulfur, 20mm) @11am
135.2 g of Part A
13.52 g of Part B

• pouring w/ popsicle stick + cup

Note for A+B together
• A is more viscous
•

135.8 actual (according to scale)
13.6 actual

for the vacuum
• Grant => Better scale •
[CNC machine — sci machine shop
tech sci equipment
electronics]

(forgot base release on this one)

Figure 2: Test #1, Control Without Sulfur

*Test #2: AB Mixture + Part A*

For this test, we used a syringe of Part A to fill in the bottom of the container around the outside of the center circle (Figure 3). We then mixed appropriate amounts of Part A and B together and filled in just the center circle. To see the center circle better we placed an identically sized wooden circle under the glass tray to create more contrast (Figure 4). This process was repeated for 5 layers, each of which were roughly 2mm thick, and given about 7 minutes of setting time before the application of the next layer (Figure 5).

*Calculations:*

Specific Gravity → 1.08 (g/cm3)

Mix Ratio → 100A:10B

Length/Width of Square Glass Container → 8.3cm

Diameter of Circle in the bottom on the Square Glass Container → 5cm

Radius of Circle → 2.5cm

Goal → fill the container 20mm (depth)

Area of Circle: π(2.5cm)2= 19.63cm2

Volume of Circle: 19.63cm2 x 0.1cm = 1.96cm3

Grams of Silicone Needed to Fill the Circle: 1.96cm3 x 1.08g/cm3 = 2.12g

Grams of Part B Needed: 5.30g / 11 = 0.19g

Grams of Part A Needed: 0.482g x 10 = 1.92g

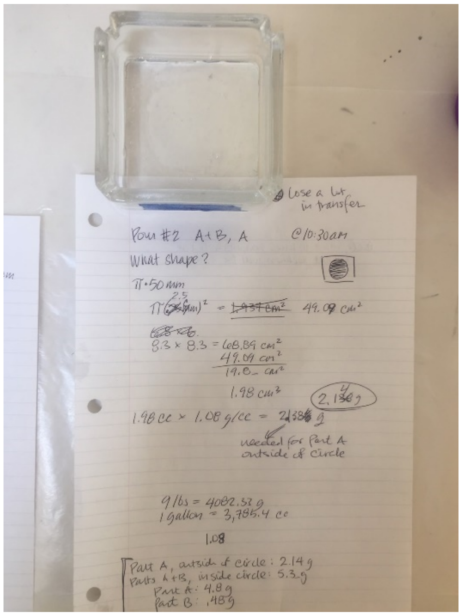
Area Outside the Circle: 68.89cm2-19.63cm2 =49.26cm2

Volume Outside the Circle:19.8cm2 x 0.1cm = 1.98cm3

Grams of Part A Needed for Outside the Circle: 1.98cm x 1.08g/cm3 =2.14g

Figure 3: Printing Test #2

Figure 4: Circle to trace under print bed



Lose a lot in transfer

Pour #2 A+B, A @10:30am

What shape?

$\pi \cdot 50$ mm

$\pi(2.5\ \mathrm{cm})^2$ = ~~[illegible]~~ 49.09 $\mathrm{cm}^2$

~~[illegible]~~

8.3 × 8.3 = 68.89 $\mathrm{cm}^2$

49.09 $\mathrm{cm}^2$

19.8 $\mathrm{cm}^2$

1.98 $\mathrm{cm}^3$

1.98 cc × 1.08 g/cc = 2.138 g

2.14 g

needed for Part A outside of circle

9 lbs = 4082.33 g

1 gallon = 3,785.4 cc

1.08

Part A, outside of circle: 2.14 g
Parts A+B, inside circle: 5.3 g
  Part A: 4.8 g
  Part B: .48 g

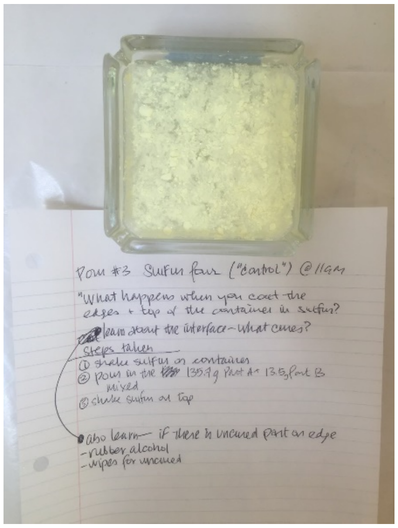
Figure 5: Test #2, AB Mixture + Part A

*Test #3: Control with Sulphur*

For this test, we coated the walls of the container with Sulphur, poured in a pre-measured mixture of parts A and B (same volume as Test 1), and coated the top surface with Sulphur (FIG. 8). This helped us to determine how deep the Sulphur inhibited the silicone from curing.

*Calculations:*

See Pour #1



Pour #3 Sulfur Pour ("control") @11AM

"What happens when you coat the edges + top of the container in sulfur?

learn about the interface–what cures?

Steps taken

① shake sulfur on container
② pour in the 135.7g Part A + 13.5g Part B mixed
③ shake sulfur on top

also learn— if there is uncured part on edge
- rubber alcohol
- wipes for uncured

Figure 6: Test #3, Control with Sulphur

*Test #4: AB Mixture + Sulphur*

For this test, we began with a solid 1mm layer of AB mixture on the bottom of our container. We then used a toothpick to spread Sulphur around the outside of the center circle up to the container walls (Figure 7). We added another full layer of AB mixture on top of the Sulphur layer. We repeated these layers 5 times (Figure 8). The

Sulphur was clumpy, which made it challenging to evenly distribute across the surface of the silicone.

*Calculations:*

Specific Gravity → 1.08 (g/cm3)

Mix Ratio → 100A:10B

Length/Width of Square Glass Container → 8.3cm

Goal → fill the container 1mm (depth) layer at a time

Area of Glass Dish: 8.3cm x 8.3cm = 68.89cm2

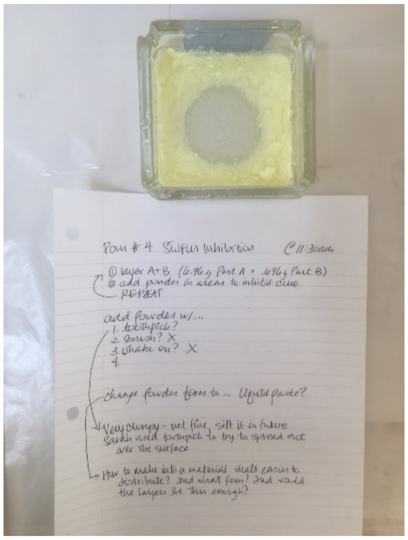
Volume to Fill Glass Dish per Layer: 68.89cm2 x 0.1cm = 6.89cm3

Grams of Silicone Needed per Layer: 6.89cm3 x 1.08g/cm3 = 7.44g

Grams of Part B Needed per Layer: 7.44g / 11 = 0.676g

Grams of Part A Needed per Layer: 0.676g x 10 = 6.76g

Figure 7: Spreading Sulphur



Pour # 4 Sulfur Inhibition @11:30am

① layer A+B (6.76g Part A + .676g Part B)
② add powder in areas to inhibit cure
REPEAT

add powder w/...
1. toothpick?
2. brush? X
3. shake on? X
4.

change powder form to... liquid paste?

Very clumpy - not fine, sift it in future
Sarah used toothpick to try to spread out over the surface

How to make into a material that's easier to distribute? and what form? and would the layers be thin enough?

Figure 8: Test #4, AB Mixture + Sulphur

## *General Notes*

We discovered that the scale was not as accurate as we had anticipated. Sometimes it stopped registering that more weight was still being added and then would make big jumps to catch up, which often resulted in having to take more material out of the cup again. Having a precise level of accuracy was not essential for our proof of concept tests, however we will be investing in a better scale for future experiments. Another issue to note is that even when we did measure out the correct amount of silicone and did our best to scrape all of it from the plastic cup to the final glass container, we still lost some of it in the transfer. When we mixed Part A and B we used them immediately, which resulted in bubbles getting trapped in the silicone. In the future, we plan to use some of our grant money to buy a small vacuum chamber to remove the bubbles before we pour the silicone mixture.

### First Silicone POC Results

*May 2016*

#### *Test #1: Control Without Sulphur*

The AB mixture in this container set evenly into a solid semi-flexible block of silicone with little bubbles that got trapped when we initially vigorously mixed the two parts together (Figure 9).

Figure 9: Test #1, Control Without Sulphur Results

### *Test #2: AB Mixture + Part A*

This test gave promising results to build off of in future POC tests. The circle in the center of the container made of layers of the AB mixture set into a single solid (Figure 10). The AB mixture crept slightly outside the circular pattern, especially in the layers closest to the surface (Figure 11 & 12). This may be because the amount of setting time between the application of new layers decreased as the test progressed. The uncured Part A surrounding the circle was slightly more viscous than when it was initially laid down, however it remained sticky and settled back to a flat surface if poked (Figure 13).

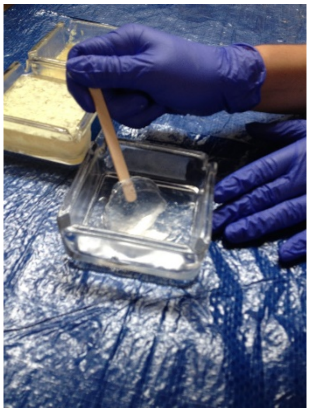


Figure 10: Removing Cured Silicone

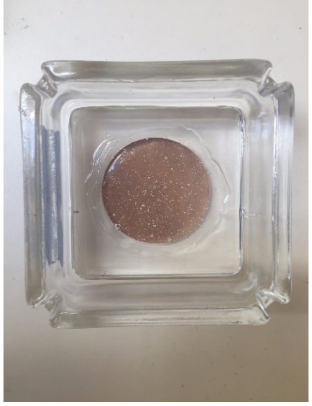


Figure 11: Spread of Cured Silicone Compared to Initial Shape

Figure 12: Cured Silicone Circle

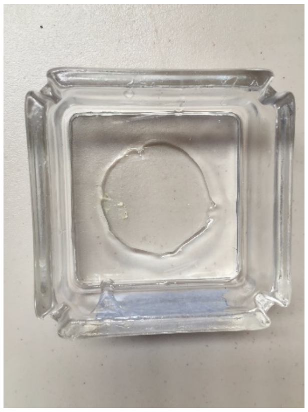


Figure 13: Part A Support Material

*Test #3: Control with Sulphur*

This test helped us to see how deep the Sulphur would inhibit the silicone from curing (Figure 14). The block ended up still setting up enough to remove it from the container in one solid piece. The Sulphur exhibited very shallow inhibiting properties, barely preventing the top layer from fully curing. The final block of silicone turned out to be a slightly more flexible version of the results of Test #2 opposed to being less viscous and completely uncured like Part A alone. The Sulphur on the surface remained a light-yellow color, however the Sulphur on the edges and bottom of the container darkened.

Figure 14: Test #3, Control with Sulphur Results

### *Test #4: AB Mixture + Sulphur*

This test turned out differently than anticipated and will have to be modified to possibly be of use in the future. The circle set up evenly, however the edges were not acutely defined and they ended up bonding to the Sulphur/AB mixture layers surrounding the circle (Figure 15). The layers of Sulphur and the AB mixture also set in layers that could be pulled apart, instead of the Sulphur entirely inhibiting the silicone from curing (Figure 16). Similarly to Test #3, despite the silicone setting, it was still much more flexible than the silicone without Sulphur. Due to the thinner layers of the AB mixture in between the layers of Sulphur, the edges of this test were even more flexible than the block from Test #3 (Figure 17). This test showed the same color change as in Test #3 where the Sulphur exposed to the air remained light yellow and the rest became darker.

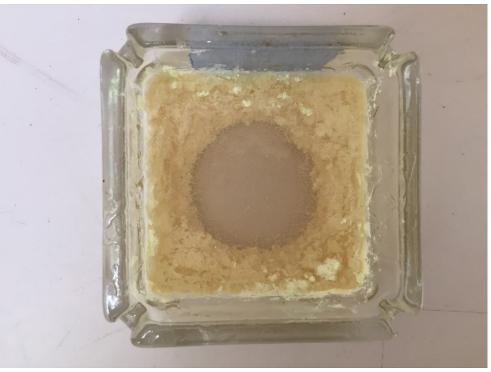


Figure 15: Test #4, AB Mixture + Sulphur Results

Figure 16: Layers of Sulphur and AB Mixture

Figure 17: Examining the Failure of Sulfur as an Inhibitor

## First Polyurethane POC Experiment

*September 2016*

After starting with silicone and finding some success in printing the AB mixture while using part A as support material, we decided to apply this method to printing with a two-part polyurethane rubber. Our goal for this experiment was to build on a method that held promise by printing with something closer to our final material.

*Materials:*

- Polyurethane Rubber Part A (PMC 770)
- Polyurethane Rubber Part B (PMC 770)
- Silicone Part A (SORTA-Clear 40)
- Nitrile gloves
- Safety Glasses
- Aprons
- Popsicle sticks
- Toothpicks
- Pouring/mixing cups
- Syringe
- Measuring scale
- Commercial-grade sulfur (inhibiting agent)
- Ease release 200
- Shallow containers (square, glass)

- Masking tape
- Pen
- Ruler
- Scissors
- Plastic tarp
- Thickening agent for silicone (not yet)

### *Setup and General Procedure*

The set up for this experiment was very similar to our first proof of concept test, however this time we used PMC-770 Polyurethane. Again we began by gathering our materials, labeling our containers, and donning gloves, eye protection, and aprons. This time we used ease release spray on all of our containers prior to beginning our experiments. Every time we measured out more silicone we used a plastic cup that we cut to be roughly two inches high in order to minimize the material stuck to the walls between transfers. After placing the cup on the scale, we tared the scale, and added the rubber. In the cases where both Part A and Part B were mixed together, we weighed out Part A first and then re-tarred the scale and slowly added Part B to the same cup.

### *Test #1: Control*

For this test, we calculated the amount of parts A and B that we would need in grams to mix together in the right ratio in order to fill our container 20mm high, and immediately poured the premixed parts of rubber into our container (Figure 18). Part A was much more viscous than Part B, but still less so than the silicone Part A.

*Calculations:*

Specific Gravity → 1.04 (g/cm3)

Mix Ratio → 2A:1B

Length/Width of Square Glass Container → 8.3cm

Goal → fill the container 20mm (depth)

Area of glass dish: 8.3cm x 8.3cm = 68.89cm2

Volume to fill glass dish: 68.89cm2 x 2cm = 137.78cm3

Grams of rubber needed to fill that desired volume: 137.78cm3 x 1.04g/cm3= 143.29g

Grams of Part B needed: 143.29g / 3 =47.76g

Grams of Part A needed: 47.76g x 2 = 95.53g

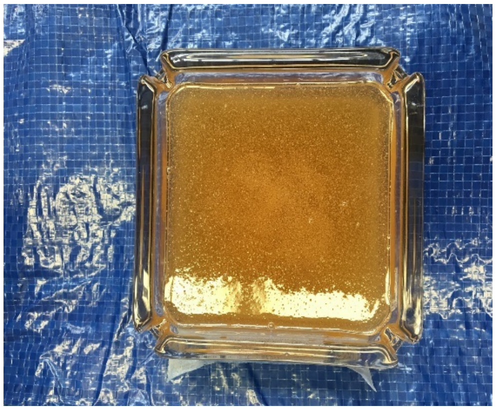


Figure 18: Test #1, Control

### *Test #2: PMC 770 AB Mixture + Part A*

For this test, we used a syringe of part A to fill in the bottom of the container around the outside of the center circle. We then mixed appropriate amounts of Part A and B together and filled in just the center circle. Again, we continued to use an identically sized wooden circle under the glass tray to create more contrast. This process was repeated for 5 layers, each of which were roughly 2mm thick, and given about 7 minutes of setting time before the application of the next layer (Figure 19).

*Calculations:*

Specific Gravity → 1.04 (g/cm3)

Mix Ratio → 2A:1B

Length/Width of Square Glass Container → 8.3cm

Diameter of Circle in the bottom on the Square Glass Container → 5cm

Radius of Circle → 2.5cm

Goal → fill the container with 5 layers 4mm each (total 20mm deep)

Area of Circle: π(2.5cm)2= 19.63cm2

Volume of Circle: 19.63cm2 x 0.4cm = 7.85cm3

Grams of Rubber Needed to Fill the Circle: 7.85cm3 x 1.04g/cm3 = 8.16g

Grams of Part B Needed: 8.16g / 3 = 2.72g

Grams of Part A Needed: 2.72g x 2 = 5.44g

Area Outside the Circle: 68.89cm2-19.63cm2 =49.26cm2

Volume Outside the Circle:49.26cm2 x 0.4cm =19.70 cm3

Grams of Part A Needed for Outside the Circle: 19.70cm x 1.04g/cm3 =20.49g

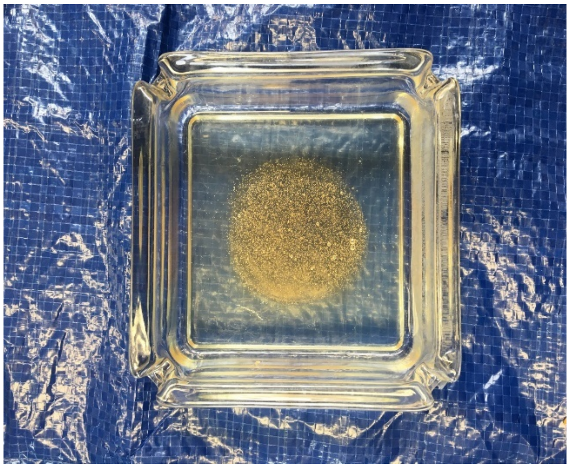


Figure 19: Test #2, PMC 770 AB Mixture + Part A

*Test #3: PMC 770 AB Mixture + SORTA-Clear 40 Part A*

For this test, we decided to take advantage of the high viscosity of the silicone part A, and repeat the method of Pour #2 using that as our support material (Figure 20). Upon depositing SORTA-Clear 40 Part A, the material retained its shape and was less prone to spreading out of place.

*Calculations:*

Specific Gravity PMC 770 → 1.04 (g/cm3)

Specific Gravity SORTA-Clear 40 Part A → 1.08 (g/cm3)

Mix Ratio → 2A:1B

Length/Width of Square Glass Container → 8.3cm

Diameter of Circle in the bottom on the Square Glass Container → 5cm

Radius of Circle → 2.5cm

Goal → fill the container with 5 layers 4mm each (total 20mm deep)

Area of Circle: π(2.5cm)2= 19.63cm2

Volume of Circle: 19.63cm2 x 0.4cm = 7.85cm3

Grams of Rubber Needed to Fill the Circle: 7.85cm3 x 1.04g/cm3 = 8.16g

Grams of Part B Needed: 8.16g / 3 = 2.72g

Grams of Part A Needed: 2.72g x 2 = 5.44g

Area Outside the Circle: 68.89cm2-19.63cm2 =49.26cm2

Volume Outside the Circle:49.26cm2 x 0.4cm = 19.70cm3

Grams of Part A Needed for Outside the Circle:19.70cm x 1.08g/cm3 =21.28g

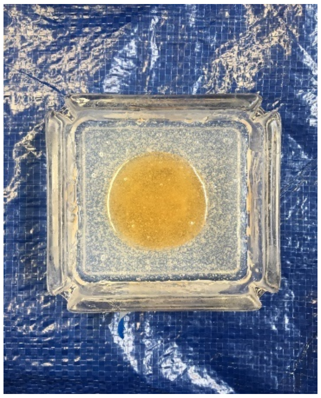


Figure 20: Test #3, PMC 770 AB Mixture + SORTA-Clear 40 Part A

### *General Notes*

Working with the polyurethane was similar to the silicone in many ways including the AB mixture viscosity, the curing time, and accidentally trapping bubbles.

## First Polyurethane POC Results

*September 2016*

### *Test #1: Control*

The polyurethane set into a dense, barely flexible block that was very difficult to remove from its glass dish (Figure 21).

Figure 21: Test #1 Polyurethane Control

### *Test #2: PMC 770 AB Mixture + Part A*

This test was mostly successful in that the resulting polyurethane piece is recognizable as being a circle, however there was still some seepage. The material that did seep beyond the circle was toward the bottom of the piece, so it is possible that a couple layers were not given enough time to cure before the next layers was added, and the additional weight on top of them pushed them out to the sides. The material outside the circle is thin, so most stayed within the boundaries. The uneven edges (even of the main circular shape) also indicate that the support material around the circle moved, allowing the polyurethane to flow out of place (Figure 22 ).

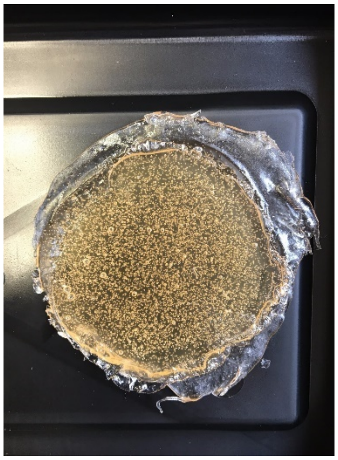


Figure 22: Test #2, PMC 770 AB Mixture + Part A

*Test #3: PMC 770 AB Mixture + SORTA-Clear 40 Part A*

This was the most successful test yet, which can be seen in the smooth edges and primarily uniform circular shape (Figure 23). Using the SORTA-Clear 40 Part A as the support material provided a stronger barrier and in turn worked much better. Moving forward we will build on this test.

Figure 23: Test #3, PMC 770 AB Mixture + SORTA-Clear 40 Part A

## Second Polyurethane POC Experiment

*September 2016*

Two of the drawbacks of the previous polyurethane experiments were how long we had to wait in between putting down layers, and the large amounts of support material required. In this second round of polyurethane POCs we addressed these two issues, and tried to replicate a printing methods used by Fripp, the only company to patent a 3D printing method with silicone.

*Materials:*

- Polyurethane Rubber Part A (PMC 770)
- Polyurethane Rubber Part B (PMC 770)
- Silicone Part A (SORTA-Clear 40)
- Nitrile gloves
- Safety Glasses
- Aprons
- Popsicle sticks
- Toothpicks
- Pouring/mixing cups
- Syringe
- Measuring scale
- Ease release 200
- Shallow containers (square, glass)
- Masking tape
- Pen
- Ruler
- Scissors

- Plastic tarp

*Test #1: PMC 770 AB Mixture + Accelerator + SORTA-Clear 40 Part A (just in a ring)*

For this test, instead of using SORTA-Clear 40 Part A to fill in the entire layer outside the circle, it was only printed in a single ring. The PMC 770 AB mixture was then deposited as it was before, layer by layer in a circle inside the support material. After the first couple layers it became apparent that the single ring of support material was not strong enough to contain the polyurethane as it continued to spread outward (Figure 24).

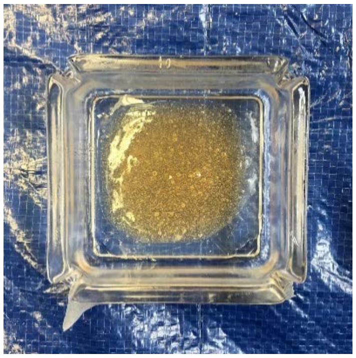


Figure 24: Test #1, PMC 770 AB Mixture + Accelerator +SORTA-Clear 40 Part A (just in a ring)

*Test #2: PMC 770 AB Mixture + Accelerator + SORTA-Clear 40 Part A (in a full exterior layer)*

This test repeated the same methods as Silicone Test #2 and Polyurethane Test # 2 and #3, with the addition of accelerator to the PMC 770 AB Mixture (Figure 25). By adding accelerator, the goal was to have the polyurethane set in place before it had time to seep. Due to faster setting time, less time was waited in between depositing new layers.

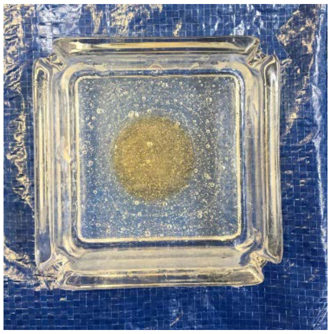


Figure 25: Test #2, PMC 770 AB Mixture + Accelerator + SORTA-Clear 40 Part A

### *Test #3: PMC 770 AB Mixture + SORTA-Clear 40 Part A (simulating Fripp method)*

This test was performed to better understand the silicone printing method used by Fripp (Fripp, Frewer, & Green). Instead of printing on a clean bed, a nozzle is inserted into a tank of support material, and the 3D print is created suspended in the support material. Instead of printing with silicone, this test printed polyurethane suspended in SORTA-Clear 40 Part A (Figure 26).

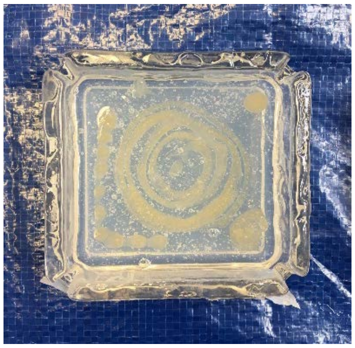


Figure 26: Test #3, PMC 770 AB Mixture + SORTA-Clear 40 Part A (simulating Fripp method)

### *General Notes*

It was immediately clear that Test #1 was not working, however we needed more time to see if Test #2 and Test #3 would be successful in reducing creepage.

### Second Polyurethane POC Results

*September 2016*

*Test #1: PMC 770 AB Mixture + Accelerator + SORTA-Clear 40 Part A (just in a ring)*

As observed earlier, the polyurethane pushed the support material out as it was being printed, and continued to move even after the last layer was added (Figure 27). The accelerator that was added in hopes of preventing the polyurethane from spreading did not act fast enough.

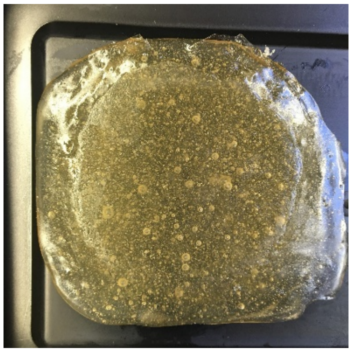


Figure 27: Test #1, PMC 770 AB Mixture + Accelerator + SORTA-Clear 40 Part A (just in a ring) Results

*Test #2: PMC 770 AB Mixture + Accelerator + SORTA-Clear 40 Part A (in a full exterior layer)*

Despite the addition of accelerator, the reduced rest time in between the application of new layers caused some seepage of lower layers (Figure 28). This method could have been improved by the addition of more accelerator and/or the addition of more time between printing each layer.

Figure 28: Test #2, PMC 770 AB Mixture + Accelerator + SORTA-Clear 40 Part A (in a full exterior layer) Results

*Test #3: PMC 770 AB Mixture + SORTA-Clear 40 Part A (simulating Fripp method)*

The layers that were printed on top of each other, did in fact adhere to one another (Figure 29). All the material that was printed also stayed exactly where it was deposited. One downside to this method was having to clean the silicone part A off all sides of every piece. While this method worked as it had been described in Fripp's patent (despite a slightly different method), this was not a direction that we intended to follow.

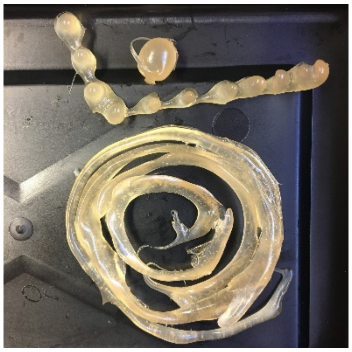


Figure 29: Test #3, PMC 770 AB Mixture + SORTA-Clear 40 Part A (Simulating Fripp Method) Results

## First Natural Rubber POC Experiment & Results

*January 2017*

The next step of our POC experiments was to try printing with natural rubber. Natural rubber is not a thermoset when it is harvested, however it can be vulcanized to crosslink its polymer chains and convert it into a thermoset. For our first natural latex test, we followed instructions in the lab handout to make a ball of latex in a cup (Katz). In addition, we tried a more experimental method of printing with one part (latex/water or vinegar) in a “bed” of the other part.

*Materials:*

- Liquid Latex (fun world)
- Mold Builder - Liquid Latex Rubber (Castin’ Craft)
- Vinegar
- Deionized water
- Nitrile gloves
- Safety Glasses
- Lab Coats
- Popsicle sticks
- Paper pouring/mixing cups
- Two 5 mL syringes
- Shallow containers (square, glass)
- Masking tape
- Pen

### *Setup and General Procedure*

For these POC tests we experimented with manual 3D printing techniques using two different kinds of rubber latex: *Fun World Liquid Latex* and *Castin' Craft Mold Builder*.

### *Test #1: Rubber Ball – Fun World Liquid Latex*

For this test, 15 mL of latex and 15 mL of deionized water were mixed in a paper cup. The cream-colored latex became slightly lighter, and remained a very low viscosity. While stirring with a toothpick, 15 mL of vinegar was slowly added to the original cup. The addition of vinegar evaporates the stabilizer in the latex and causes the mixture to coagulate almost instantaneously. The mass was removed from the cup, squeezed, and rinsed with water over a small bucket.

### *Test #2: Rubber Ball – Castin' Craft Mold Builder (Liquid Latex)*

The same method for Test #1 was also used for Test #2 with the substitution of Castin' Craft Mold Builder for Fun World Liquid Latex. This latex began as a more viscous consistency closer to honey than water. When mixing in the vinegar to the water/latex solution, small clumps developed slowly and consistently until they eventually stated binding together after about a minute. Once one mass was present in the cup, it took a couple more minutes of mixing for the ball to absorb the rest of the liquid in the cup.

### *Test #3: Printing in a Bed of Liquid Latex + Water*

Due to the quick coagulation in Test #1, we decided to move forward with Fun World Liquid Latex. To print with the latex rubber, we decided to mix the latex and the vinegar as we laid it down, opposed to combining them ahead of time. Again, we combined equal parts latex and water, this time enough to cover the bottom of our shallow square plastic tray, and poured it in (Figure 30). We filled a syringe with vinegar and attempted to draw a circle with dots (Figure 31). Once the circle was complete, we drew another circle on top of it. The solidifying material kept catching on the end of the syringe, which made it difficult to move to disperse the next dot without dragging along the previous dot. Some of the vinegar dots also rolled off the previous “printed” layer and reacted with surrounding latex/water (Figure 32).

We drew another circle with vinegar dots in the latex/water solution, however this time we covered the circle with excess latex/water solution before going back over the circle with a second layer of vinegar dots. Our hope was that by ensuring that the first layer was fully reacted before building on it, we could prevent excess vinegar from reacting in unwanted areas.

In trying to remove the pieces from the dishes that we created them in, the prints continued to react with the bed material around them (Figure 33).

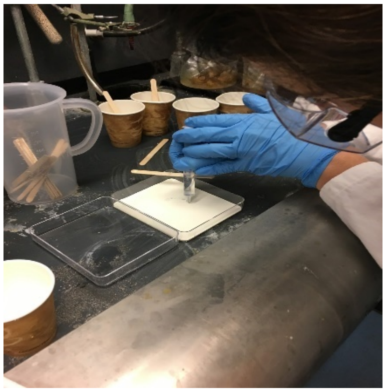


Figure 30: Test #3, Printing in a Bed of Liquid Latex + Water

Figure 31: Test #3, Two Layers Printed in a Bed of Liquid Latex + Water

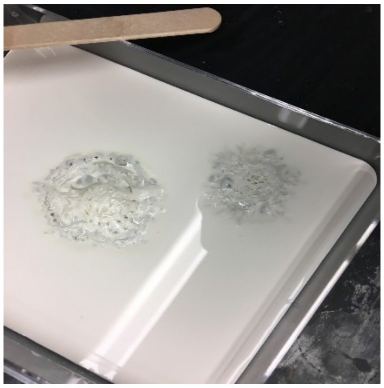


Figure 32: Test #3, Final Print

Figure 33: Test #3, Removing the Print

### *Test #4: Printing in a Bed of Vinegar*

We used the same method as Test #3, except printing with a syringe of latex/water in a bed of vinegar (Figure 34). This strategy proved more challenging for several reasons. Firstly, the latex was more difficult to push through the syringe, especially at a consistent rate. The latex also wanted to float on top of the vinegar rather than immediately reacting (Figure 35). By the end of the print, the latex had seeped into the vinegar and spread throughout the whole tray (Figure 36). The print had to be separated from the rest of the print bed with a popsicle stick because it continued to react with the surrounding vinegar (Figure 37).

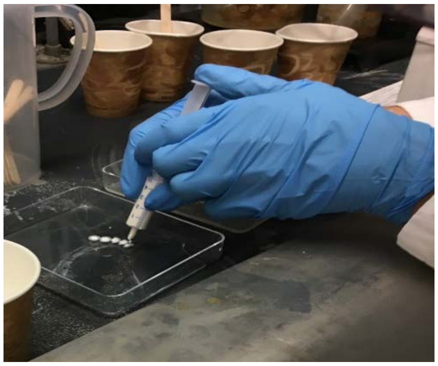


Figure 34: Test #4, Printing in a Bed of Vinegar

Figure 35: Test #4, Half way Through the Print

Figure 36: Test #4, Final Print

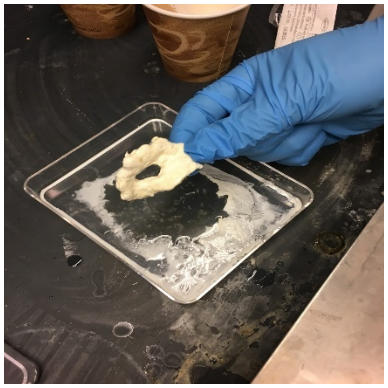


Figure 37: Test #4, Removing the Print

### Second Natural Rubber POC Experiment & Results

*January 2017*

In order to force the aqueous rubber solution to interact with the vinegar when and where we needed it to, we tried combining syringes in order to print with both parts at the same time in a dry bed.

*Materials:*

- Liquid Latex (fun world)
- Vinegar
- Deionized water
- Nitrile gloves
- Safety Glasses
- Lab Coats
- Popsicle sticks
- Paper pouring/mixing cups
- Six 5 mL syringes
- One 20 mL syringe
- Six 18 gauge syringe tips
- Shallow containers (square, glass)
- Masking tape
- Pen

### *Setup and General Procedure*

For these POC tests we continued experimenting with manual 3D printing techniques using *Fun World Liquid Latex*. This time our goal was to develop ways in which we could combine the latex/water mixture and the vinegar as they were being laid down in an empty dish.

### *Test #1: Two Syringes with One Bent Tip*

For this model, we bent one of the 18 gauge syringe tips end of a 15 mL syringe so that it would touch the end of another syringe when taped parallel to it. We then filled the bent syringe with 5 mL of vinegar and the unaltered syringe with 5 mL of the latex/water mixture. We taped a section of popsicle stick to the top of both syringes to give one surface to depress so that both liquids would be dispensed equally (Figure 38). Unfortunately, it was really difficult to apply even pressure to both syringes at the same time, so one material often bursted out at a time (Figure 39).

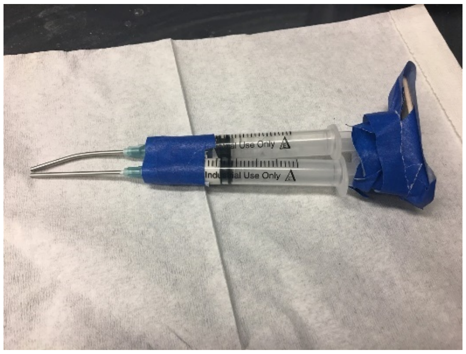


Figure 38: Test #1, Two Syringes with One Bent Tip

Figure 39: Test #1, Irregular Deposition

### *Test #2: Two Small Syringes Inside a Larger Syringe*

For this test, we fit two 5 mL syringes inside of a 20 mL syringe that we cut down to the 45 mL mark (Figure 40). The two inner syringes had 18 gauge tips. We intended this device to allow us to combine the two parts before they touched the "printing bed." Instead of printing latex rubber as it was coagulating, the two parts set inside the 20 mL syringe, clogged the tip, and started filling the space sideways and up instead of being pushed down and out.

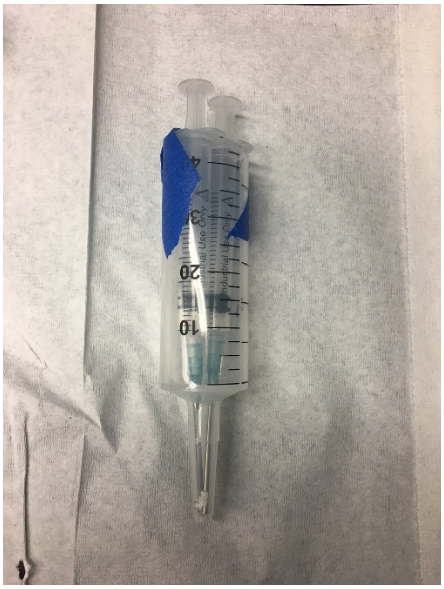


Figure 40: Test #2, Two Small Syringes Inside a Larger Syringe

### *Test #3: Two Syringes Feeding into a Small Tube*

We attempted to join two syringes into a small tube, but the 18 gauge syringe tips and tubing that we had were not properly sized, so we decided to try this again next time.

### *General Notes*

While we had trouble achieving and maintaining a consistent flow rate of the rubber, these experiments helped us to generate more ideas about what to try next time. We found out that the rubber mixture should make contact with the vinegar as it is being printed (like Test #1), not before (like Test #2). One of the issues we had was that only the rubber and vinegar that made full contact would react right away, and there would be excess unreacted material left in the dish.

### Third Natural Rubber POC Experiment & Results

*January 2017*

*Materials:*

- Liquid Latex (fun world)
- Vinegar
- Spray Bottle
- Nitrile gloves
- Safety Glasses
- Lab Coats
- Popsicle stick
- One 5 mL syringe
- Two 10 mL syringes
- One 2 oz. syringe
- Four 18 gauge syringe tips
- One 20 gauge syringe tip
- Shallow containers (square, plastic)
- Masking tape
- Pen

*Setup and General Procedure*

This time we continued our experiments with double syringes, building on our previous observations, and worked to select the best for our purposes moving forward

(Figure 41). Based on our experience having unreacted materials left over, we also decided to try using a spray bottle of vinegar to react with the surplus latex. We also tried printing the rubber without the addition of water as the initial instruction on the bottle had called for.

Figure 41: Third natural Rubber POC Syringes

*Test #1: Two Syringes Feeding into a Small Tube*

This tool was built using a 10 mL and a 5 mL syringe whose 18 and 20 gauge tips were inserted and came together inside plastic tubing (Figure 42). The most challenging part about using this tool was applying equal pressure to the popsicle stick taped across the top of the plungers, so that the rubber would be dispensed at the same rate as the vinegar (Figure 43). The vinegar had a lower viscosity, which made it easier to push through, resulting in puddles of vinegar on the printing surface (Figure 44).

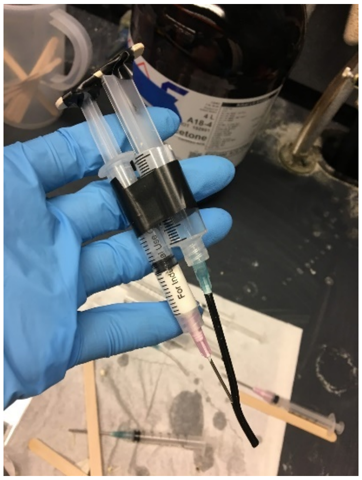


Figure 42: Test #1, Two Syringes Feeding into a Small Tube

Figure 43: Test #1, Depositing Latex Through Double Syringe Tube

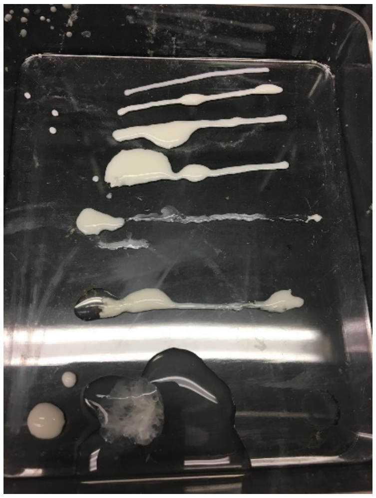


Figure 44: Test #1, Final Prints

### *Test #2: One Syringe Inside of Another*

For this test, a 5 mL syringe was filled with the rubber, and was put inside a 10 mL syringe filled with vinegar. The goal for this tool was to have the vinegar released completely surrounding the of rubber to ensure that it all reacted. The 18 gauge tip of the 5 mL syringe fit within the tip of the 10 mL syringe and prevented the vinegar from being dispensed until it was lifted up just out of the internal opening. Lifting the inner syringe and depressing the plunger of the inner syringe had to be timed just right to allow proper amounts of each liquid to flow onto the printing plate. When these actions were not sufficiently executed, the thickness of the 3D printed line became inconsistent (Figure 45).

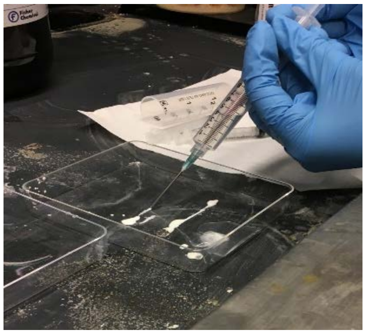


Figure 45: Test #2, One Syringe Inside of Another

### *Test #3: Reacting Remaining Aqueous Rubber with Vinegar Spray*

Due to the inconsistent dispersion of Test #2, there were sections of unreacted rubber where not enough vinegar had been deposited. To finish curing these sections a spray bottle of vinegar was used to mist the whole dish (Figure 46). The spray bottle was held two feet from the prints to ensure a fine, evenly dispersed mist. While this method worked on the surface of the unreacted rubber, the larger, deeper pools of rubber remained unreacted below the surface.

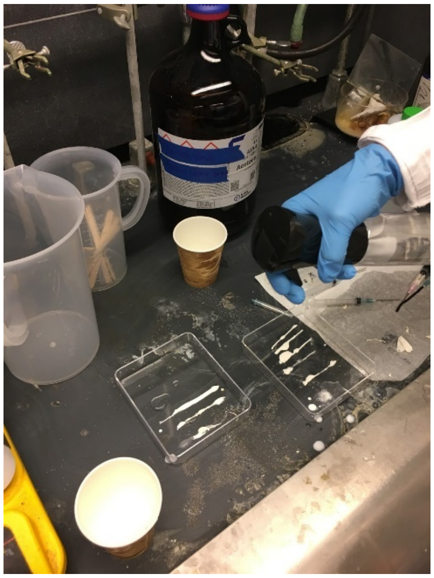


Figure 46: Test #2, Reacting Remaining Aqueous Rubber with Vinegar Spray

### *Test #4: Fully Curing Aqueous Rubber with Vinegar Spray*

To build on the positive aspects of the results from Test #3, eight thin lines of the aqueous rubber solution were drawn in the print bed, and the bottom four were sprayed with vinegar (Figure 47). These lines would better represent the layers that would be printed one at a time, so this test could give a better sense of whether or not this technique would work for our printing purposes. These lines did cure right away, however they retained little pockets of vinegar where the sprayed droplets had interacted with the rubber. Pressing down on any of the lines expelled excess liquid, which would get trapped between layers in a potential print. One of the lines that did not get sprayed with vinegar, was thin enough that it air dried, becoming transparent and essentially “set” without the need for a reaction with the vinegar (Figure 48).

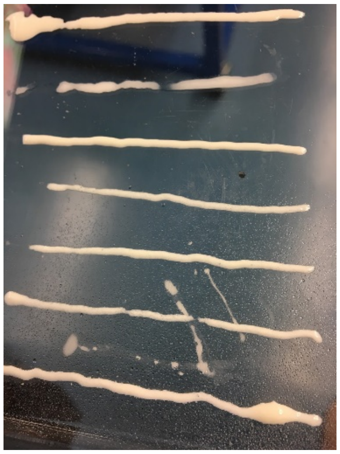


Figure 47: Test #4, Fully Curing Aqueous Rubber with Vinegar Spray

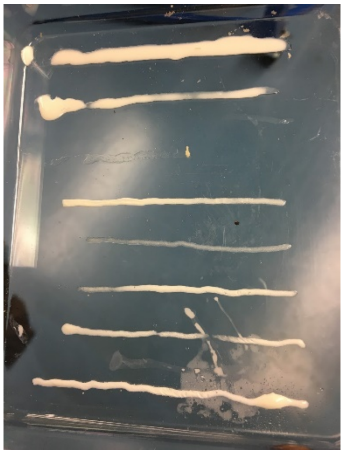


Figure 48: Test #4, Air Cured Lines

*General Notes:*

None of the double syringes worked well enough to evenly dispense the rubber and the vinegar at a consistent rate to make them worthy of printing with. While spraying vinegar on the unreacted rubber was successful in curing thin lines, the excess vinegar that remained trapped in the cured rubber would have created pockets and unwanted excess fluid in the final product. Knowing that vinegar was not essential for the scale of rubber we would be working with opened more printing options.  Future tests will move forward printing without the use of any vinegar (or water).

## Fourth Natural Rubber POC Experiment & Results

*February 2017*

*Materials:*

- Liquid Latex (fun world)
- Nitrile gloves
- Safety Glasses
- Lab Coats
- One 5 mL syringe
- One 18 gauge syringe tip
- Shallow containers (square, plastic)
- Masking tape
- Pen

### *Setup and General Procedure*

At this stage, we moved from drawing lines to starting to build structures. We also began to address specifics such as how long we could wait between adding new layers so that the first layer was set up enough that the new layer could build up off of it, but that the new layer would also adhere to the previous layer and not just peel off.

### *<u>Test #1: Building Structures</u>*

*Methods:* Rubber was printed by hand using a 5 mL syringe with a 18 G tip (Figure 49). Once each layer dried enough to become transparent (3-5 minutes), a new layer was printed on top. The final print was the result of 16 layers (Figure 50).

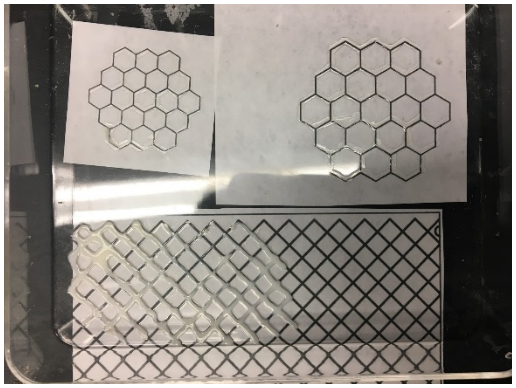


Figure 49: Test #1, Building Structures

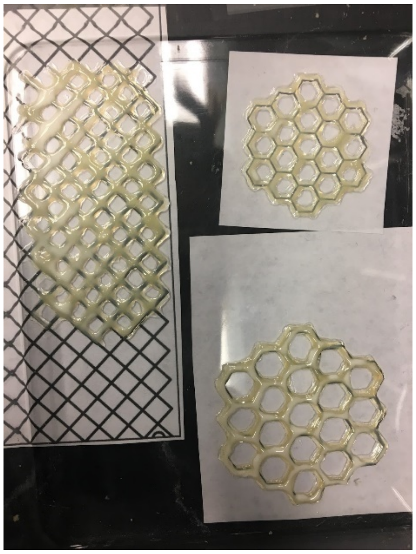


Figure 50: Test #1, Uncured Final Print

*Results:* The rubber set in place, and did not move or expand since it was finished (Figure 51). The final pieces were a transparent golden color with a mild shine. The pieces could be stretched about twice their initial size, while continuing to return to the same shape (Figure 52). One corner of the larger hexagon accidentally touched back and fused to itself. The piece could not be unfolded without ripping the material.

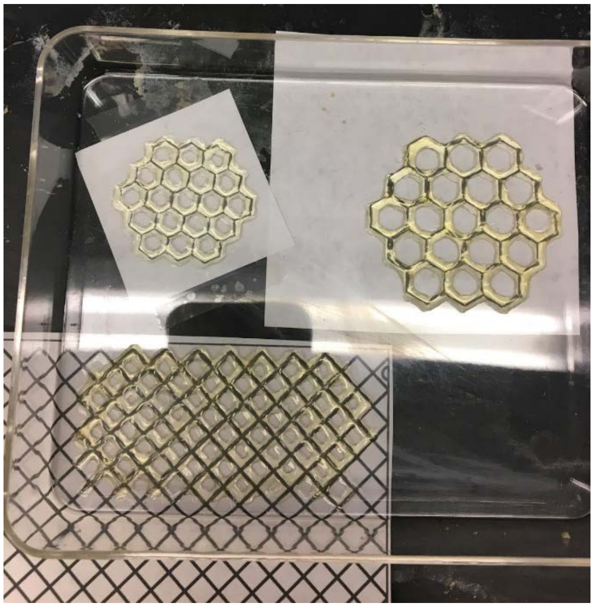


Figure 51: Test #1, Cured Final Print

Figure 52: Manually Testing Elasticity

### *Test #2: Adhesion to Previous Layers*

*Methods:* After seeing that the larger hexagonal piece fused to itself, this test was conducted to better understand what would happen when liquid rubber was added to previously set rubber. A small amount of liquid rubber was added to a cup with dried rubber and contained on one half (Figure 53).

Figure 53: Test #2, Adhesion to Previous Layers

*__Results:__* Besides the difference in thicknesses between the two sides of the cup, the new layer of rubber seamlessly adhered to the previous layer and could not be pried off (Figure 54).

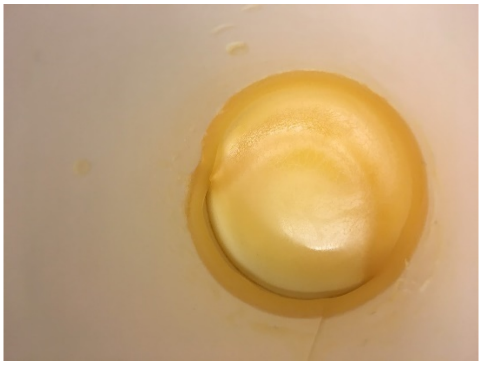


Figure 52: Test #2, Adhesion to Previous Layers Results

*General Notes:*

These tests helped to confirm that not only will the rubber adhere to the previous layer, despite the previous layer being completely dry, but the printed rubber is relatively strong and elastic at least from initial observation.

## Fifth Natural Rubber POC Experiment & Results

*February 6th, 2017*

*Materials:*

- Liquid Latex (fun world)
- Nitrile gloves
- Safety Glasses
- Lab Coats
- One 5 mL syringe
- One 25 gauge syringe tip
- One 30 gauge syringe tip
- Shallow containers (square, plastic)
- Masking tape
- Pen

*Setup and General Procedure*

One of the challenges of the last printed structure was maintaining precision when dispensing the rubber from the syringe. To try and improve the precision, smaller syringe tips were purchased and tested.

*Test #1: Building Structures (Continued)*

*Methods:* The same three stencils were used again and traced in one tray with 25 gauge syringe tips and traced in a second tray with 30 gauge tips (Figure 53). Both tips were so small that is was challenging to dispense any rubber at all. When rubber did pass through the tip, it came out in little bursts because of the pressure applied to get it out at all.

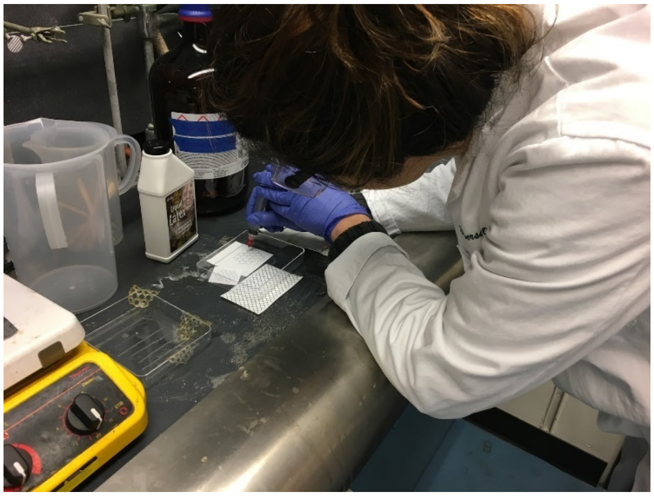


Figure 53: Test #1, Building Structures (Continued)

*Results:* The prints were thinner and less uniform than the previous set (Figure 54). Not as many layers were added due to difficulty printing with the new sized tips.

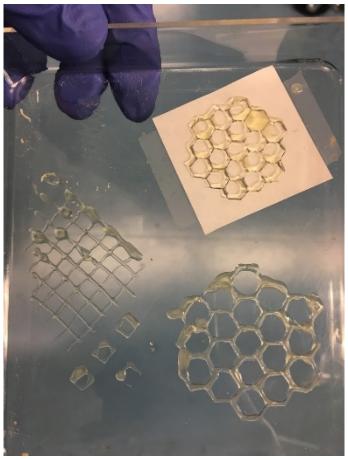


Figure 54: Test #1, Cured Structure

*General Notes:*

Struggling with clogging and unpredictable flow rates did not allow for the precision that had hoped to be achieved. Future printing will be done with larger syringe tips again.

### Sixth Natural Rubber POC Experiment & Results

*February 2017*

*Materials:*

- Liquid Latex (fun world)
- Nitrile gloves
- Safety Glasses
- Lab Coats
- One 5 mL syringe
- One 18 gauge syringe tip
- Shallow containers (square, glass)

- Masking tape
- Pen
- Ruler
- Sticky note
- Scissors

*Setup and General Procedure*

Created 16 layer 1x5cm latex strips for material testing purposes. These rubber pieces were made using a 10 mL syringe with an 18 gauge tip to trace over a 1 cm by 5 cm piece of paper underneath the dish. Layers were started by tracing the outside lines and working inward in a continuous spiral. Each piece was given about 5 minutes before the next layer was applied, for a total of 16 layers (Figure 55).

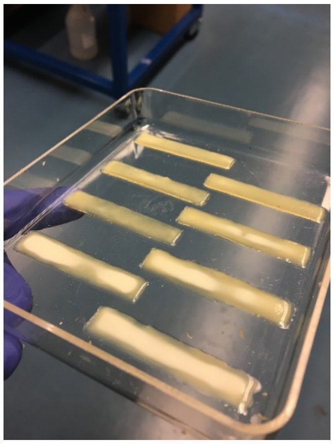


Figure 55: Sixth Natural Rubber POC

*Materials:*

- Liquid Latex (fun world)
- Nitrile gloves
- Safety Glasses

- Lab Coats
- One 5 mL syringe
- One 18 gauge syringe tip
- Shallow containers (square, glass)
- Masking tape
- Instron tensile tester

*How it Works*

The purpose of the Instron tensile tester is to slowly stretch a material until it breaks to provide data and create a graph of stress vs strain. This is a helpful tool for identifying materials weak points in terms of their limits of elasticity. Before the material is stretched, the machine is set to a gauge length (the distance from the top to the bottom of what's being pulled), whose elongation is recorded against the applied force.

The machine calculates engineering strain () by dividing the change in gauge length ( L)  by the initial gauge length ($L_0$) →  = $LL_0$

The machine calculates engineering stress () by dividing the applied force ($F_n$) by the nominal cross section of the sample ($A$) → = $F_nA$

*Setup and General Procedure*

- Set the first crosshead speed to 0.5 mm/min, and the second speed to 50.00 mm/min

  - Speed change at 0.2 mm
- Set the gauge length
- Place masking tape on the front and back of one end of the rubber covering about 15 mm (cut off excess tape around the edges)
- Use calipers to measure the gauge distance from the edge of the tape and mark the end of that distance with a second piece of tape on either side of the rubber (Figure 56 & 57)
  - The tape act as places for the machine to grip the material as the middle section is being stretched
- Take a rubber rectangle and measure the width, and thickness with calipers
- Enter this information into the computer program
- Carefully align the sample in the bottom clasps of the machine and hand tighten closed
- Use tweezers to align and adjust the top of the sample into the upper clasps and tighten in place (Figure 58)
- Use wrench to gently finish tightening the sample in place
- Start the machine and watch the rubber slowly being stretched (Figure 59, 60, & 61)
- When the rubber breaks, stop and reset the machine (Figure 62)
- Loosen the clasps to remove the rubber
- Prepare the next sample

Figure 56: Measuring the Gauge Distance

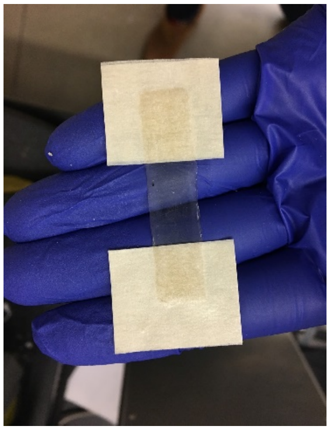


Figure 57: Preparing the Sample

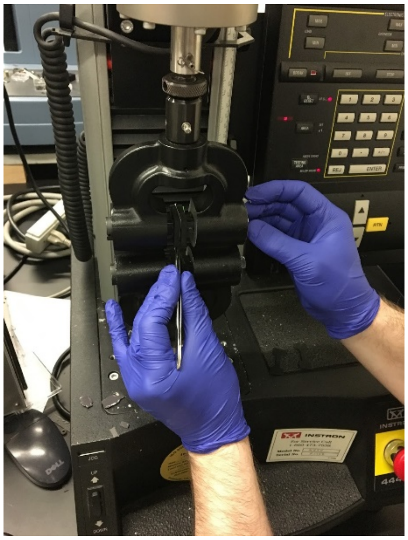


Figure 58: Adjusting the Alignment in the Instron Tensile Tester

Figure 59: Tensile Testing in Progress

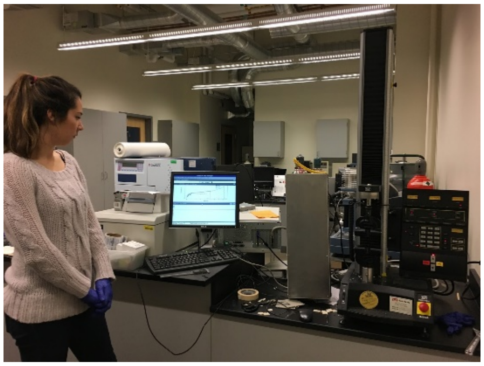


Figure 60: Monitoring the Test in Progress

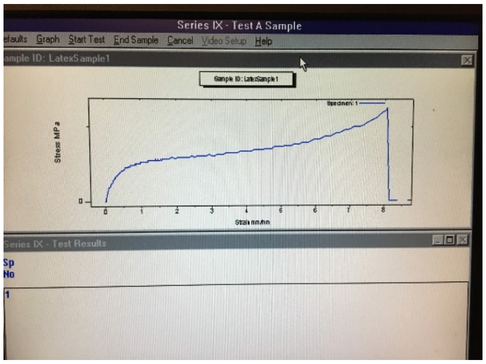


Figure 61: First Sample Stress vs Strain Graph

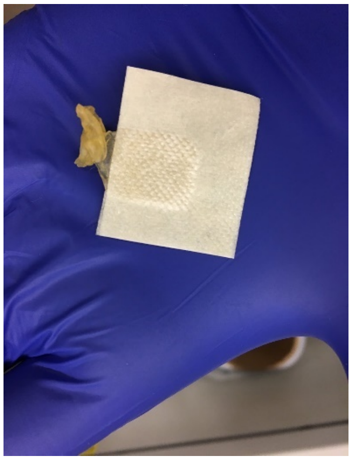


Figure 62: Sample Post Testing

*Results:*

We collected data from six tests, however the main objective of using the machine was to become familiar with the testing process so that we could test our final machine 3D printed structures later against traditional neoprene.

## Seventh Natural Rubber POC Experiment & Results

*March 2017*

Materials:

- Liquid Latex (fun world)
- Paraffin wax
- Polypropylene
- Petroleum jelly
- poly(tetrahydrofuran)
- Nitrile gloves
- Safety Glasses

- Lab Coats
- One 5 mL syringe
- One glass 10 mL syringe
- Seven 18 gauge syringe tip
- Two 100 mL glass beakers
- Two shallow plastic containers
- Four glass petri dishes
- Two paper cups
- One 10 mL glass vial
- Labeling tape
- Pen

### *Setup and General Procedure*

These tests all focused on printing the rubber with various support materials to discover which would work best moving forward. We were looking for a material with a low melting point that would be compatible when interacting with the rubber. Going into these tests, there were two options of methods of printing with the support material to try:

Option A: Working from the outside in (bottom to top)

- Use a plastic syringe to print latex in a hexagonal outline
- Use the glass syringe to print wax in a hexagon just inside the latex
- Use a syringe to print latex in a hexagon on top of the wax layer, making sure it still contacts the first layer of latex as well
- Continue to build up and in

Option B: Working from the inside out (top to bottom)

- Use a plastic syringe to print latex in a hexagon
- Use the glass syringe tool to print wax in a hexagon just outside the latex
- Use a syringe to print latex in a hexagon on top of the wax layer, making sure it still makes contact with the first layer of latex as well
- Continue to build up and out

*Test #1: Paraffin Wax*

For this test, a 100 mL glass beaker was filled with paraffin wax pellets and placed on a hot plate at 37ºC to melt. A heat gun was also used to speed up the melting process. A 10 mL glass syringe was then used to collect the melted paraffin and print a hexagon in a dish (Figure 63). One initial concern about using paraffin wax as a support material was that it would be too hydrophobic to use with liquid rubber. This proved to be true, for when the rubber was deposited next to or on top of the wax print, the rubber would bead up and roll off or away (Figure 64). Trying to follow the two options of printing the support material was given up. Instead, when the rubber refused to build on the paraffin, the rubber was then filled inside the wax (Figure 65). If this method had been repeated the wax could have been continued to be built up and out to contain additional layers of rubber.

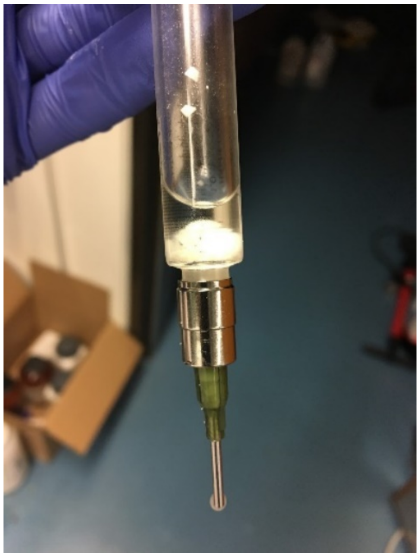


Figure 63: Test #1, Paraffin Wax

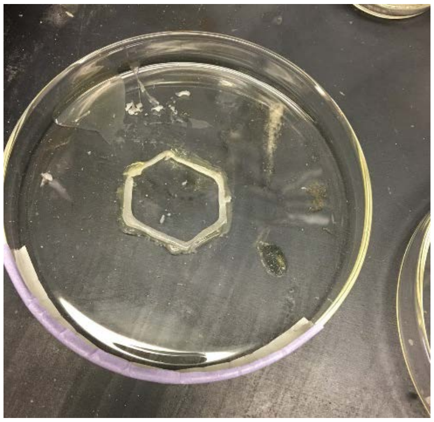


Figure 64: Test #1, Rubber On Top of Paraffin

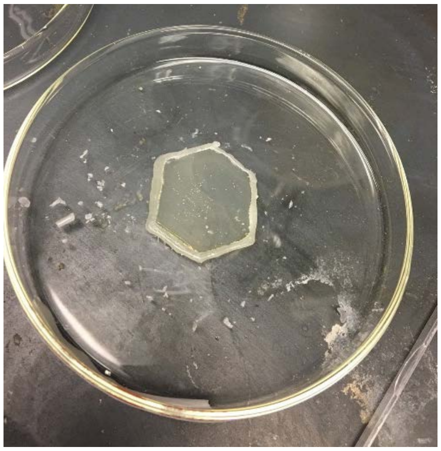


Figure 65: Test #1, Paraffin Boundary

### *Test #2: Polypropylene*

Polypropylene pellets were added to a small glass beaker and placed on a hot plate at 160ºC to melt. Once melted (with the assistance of a heat gun), the polypropylene was transferred into a glass syringe (through the back, rather than pulled up through the tip). The polypropylene cooled down too fast and solidified in the glass syringe before it could be extruded through the tip and printed with. This test was very experimental, and did not prove to be very successful as initially anticipated.

### *Test #3: Petroleum Jelly*

The benefit of printing with this material is that it does not need to be heated to be the right viscosity (Figure 66). If petroleum jelly was used as a support material though, it would be very difficult to clean off the final product. Despite not having to worry about temperature changes, the petroleum jelly still proved difficult to extrude at a consistent rate, which made it less desirable to print with.

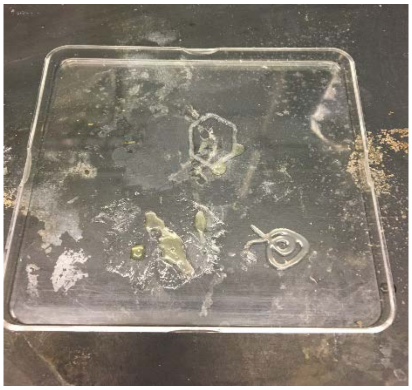


Figure 66: Test #3, Petroleum Jelly

*Test #5 Poly(tetrahydrofuran)*

The Poly(tetrahydrofuran) began as a solid inside a glass bottle, which was melted with a heat gun and poured into a 10 mL glass vial. A 10 mL glass syringe with an 18 gauge tip was then used to extract the liquid Poly(tetrahydrofuran) and print a hexagon and a line. The material was far enough past its melting point (23-28ºC) that it did not immediately cool down when printed.  Due to the low viscosity, it did not retain its form when printed and posed challenges of maintaining a consistent flow rate. The Poly(tetrahydrofuran) was left to sit for two hours (after all the other tests were completed) before it cooled down enough to fully solidify at which point rubber was added. This ended up producing the most promising results. The rubber sat on top of the poly(tetrahydrofuran) without beading up, even when printed in extremely thin lines (Figure 67).

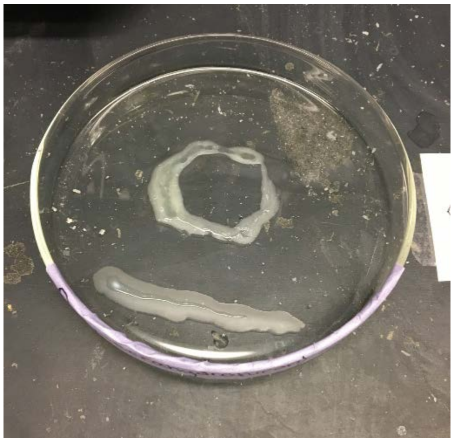


Figure 67: Test #5, Poly(tetrahydrofuran)

*Test #5: Paraffin with petroleum Jelly*

While the petroleum jelly physically interacted well with the rubber, the paraffin wax offered a much better consistency, so the two were combined. At first a teaspoon of petroleum jelly was added to a tablespoon of paraffin wax and combined into one cohesive mixture in a paper cup. This was then placed in a dime sized area in a dish and let cool. Rubber was then added with a plastic syringe to the surface (Figure 68). The rubber did not bead up as much as it had on the paraffin alone, so this mixture was repeated with an extra teaspoon of petroleum jelly. This mixture was even more compatible with the rubber, allowing medium weight lines of rubber to be printed on its surface (Figure 69).

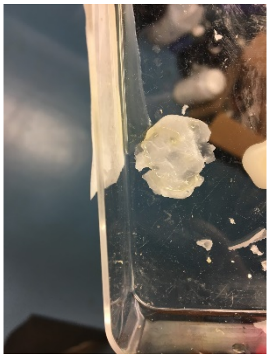


Figure 68: Test #5, Paraffin with a Small Amount of Petroleum Jelly

Figure 69: Test #5, Paraffin with a Large Amount of Petroleum Jelly

### *Test #6: Paraffin Covered in Baby Powder*

In an attempt to give the paraffin a rougher surface for the rubber to hold on to, baby powder was added to the surface (Figure 70). The rubber stayed in relatively straight lines, although it still beaded up a bit and trapped baby powder in the surface of the rubber.

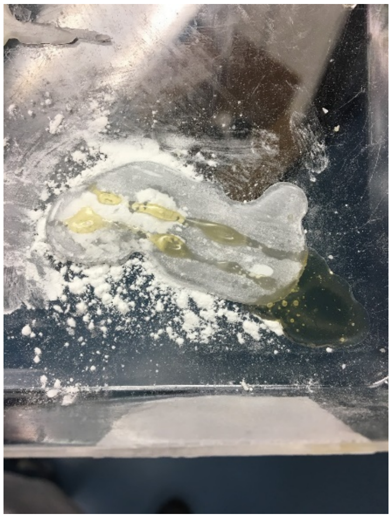


Figure 70: Test #6, Paraffin Covered in Baby Powder

### *Test #7: Paraffin with Baby Powder Mixed In*

To avoid the rubber picking up flecks of the baby powder, inspiration was taken from test #5 and the baby powder was combined with the paraffin in a paper cup. Approximately a tablespoon of baby powder was mixed into two tablespoons of melted paraffin. This test worked similarly well to test #5 in that the rubber could be drawn in medium thick lines on the surface of the paraffin, which was not possible before (Figure 71). When a circle was attempted to be drawn with the wax, however, the rubber still beaded up and merged toward the center.

Figure 71: Test #7, Paraffin with Baby Powder Mixed In

*General Notes:*

The poly(tetrahydrofuran) took so long to cool down to a high, but printable viscosity that it was not tested with rubber until the very end. At this point there was not enough time to run further tests such as following through with the initial two options of printing with support material. Future tests will continue to explore the possibilities and limitations of using poly(tetrahydrofuran) as the primary support material, as well as exploring new options.

## Eighth Natural Rubber POC Experiment & Results

*March 2017*

*Materials:*

- Liquid Latex (fun world)
- Soy wax
- Polycaprolactone diol (MW: 4000)

- poly(tetrahydrofuran)
- Nitrile gloves
- Safety Glasses
- Lab Coats
- One 5 mL syringe
- One glass 10 mL syringe
- Seven 18 gauge syringe tip
- Two 100 mL glass beakers
- Two shallow plastic containers
- Four glass petri dishes
- Two paper cups
- One 10 mL glass vial
- Labeling tape
- Pen

### *Setup and General Procedure*

In addition to conducting further testing with poly(tetrahydrofuran), these tests tried testing with additional materials that had not been used before.

### *Test #1: Soy Wax*

Soy wax pellets were added to a glass syringe, and melted with a heat gun (Figure 72). The initial assumption was that this wax would behave the same way as the paraffin was correct. It was tested just in case the assumption was wrong, but it too repelled the rubber, making it bead up and roll off (Figure 73).

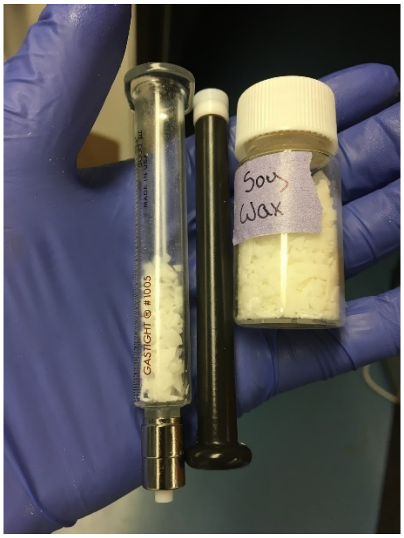


Figure 72: Test #1, Soy Wax

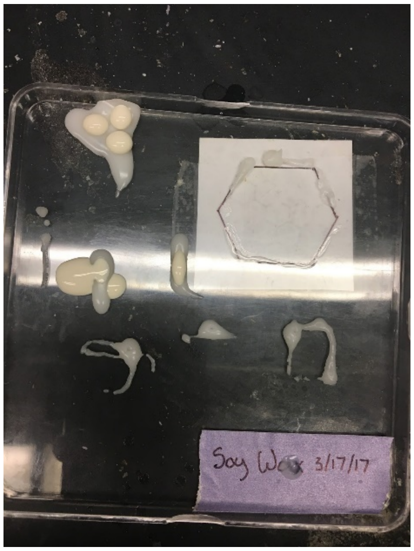


Figure 73: Test #1, Soy Wax Prints

### *Test #2: Poly(tetrahydrofuran)*

This test was used to better understand the ideal temperature that poly(tetrahydrofuran) needs to be to best print with it (Figure 74).

Figure 74: Test #2, Poly(tetrahydrofuran)

*Test #3: Polycaprolactone diol (MW: 4000)*

This seemed like a promising option because of its wax-like properties that gave it a low melting point and smooth consistent printability, however it also repelled the rubber, making it a poor choice for a support material (Figure 75).

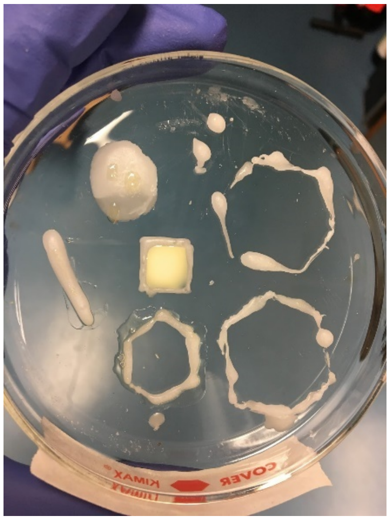


Figure 75: Test #3, Polycaprolactone diol (MW: 4000)

*General Notes:*

These tests confirmed that poly(tetrahydrofuran) will be the material that we move forward with as our support material when we receive the 3D printer from Hyrel. Until the printer arrives, there are not anymore tests that will be useful to do by hand because of the inconsistencies of human error.

## Thiokol Rubber Experiment & Results

*March 2017*

The purpose of this experiment was to synthesize Thiokol rubber. Thiokol is a synthetic rubber used for many industrial applications such as rubber hoses, gaskets, seals, and tires. The extreme conditions this material can withstand made it a good thermoset to pursue for 3D printing purposes. Before we could consider how to create a 3D printing method for Thiokol, we first needed to understand more behind the original synthesis.

*Materials:*

- 100 ml of distilled water
- 5g of sodium hydroxide
- 10g sulfur
- 20 ml of 1,2-dichloroethane
- Lab coat
- Nitrile gloves
- Safety glasses

*Procedure:*

1. In a beaker containing 100 ml of distilled water, dissolve 5 g of sodium hydroxide and heat to boiling (Figure 76 & 77).
2. Add 10 g of sulfur in small lots with constant stirring until a deep red solution is obtained due to the formation of sodium polysulphide (Figure 78).
3. Allow the solution to cool to below 83 degrees Celsius, the boiling point of 1,2-dichloroethane, and add 20 ml of 1,2-dichloroethane with stirring (Figure 79).
4. Continue to stir for 20 min while a rubber polymer separates out as a lump (Figure 80)
5. Decant the supernatant liquid and wash the product several times with water and leave in the fume hood for a few minutes to allow excess 1,2-dichloroethane to evaporate.

   (Synthesis of Thiokol Rubber)

*Results:*

The final ball of Thiokol rubber was a creamy yellow color and very dense. The ball also continued to smell of chemicals even after being washed.

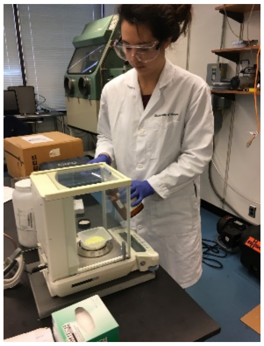


Figure 76: Weighing Sodium Hydroxide

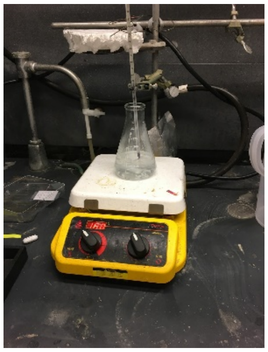


Figure 77: Boiling Sodium Hydroxide in Water

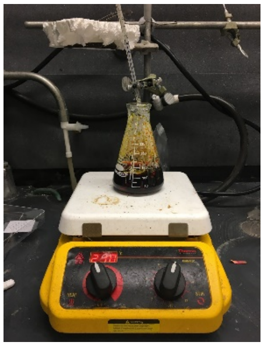


Figure 78: After the Addition of Sulphur

Figure 79: After the Addition of 1,2-dicholorethane

Figure 80: Thiokol Ball Begins to Separate Out

In deciding how to potentially print with Thiokol, Beth, my primary advisor, suggested a few options including:

- Dissolve in a solvent (then print and the solvent would evaporate in between printing each layer)
    - acetone, hexane, heptane, toluene, methylene chloride, chloroform, ammonia
- Mix the two parts that coagulate upon contact - time to contact at printer bed
- Layer one part on printer bed, and drop other part over in cross section
- “Melt” in some way
- Break into small chunks that can be re-adhered (similar to sintering of plastics or metals)

We moved forward with introducing a solvent to try and dissolve the Thiokol.

*Materials:*

- 10 ml acetone
- 10 ml chloroform

- 10 ml hexane
- 10 ml methylene chloride
- 10 ml toluene
- 628 mg Thiokol rubber
- 6 small glass vials
- Labeling tape
- Pen
- Lab coat
- Nitrile gloves
- Safety glasses

*Procedure:*

A piece of Thiokol was broken off the main ball that was previously synthesized, and weighed. This 628 mg piece was then divided into six similarly sized pieces, which were each individually weighed and added to their own glass vials. 10 ml of a solvent were then added to five of the vials, while the sixth was left empty as a control (Table #1). Each vial was vigorously shaken for a five seconds and left to sit in the fume hood. The vials were monitored closely for the first fifteen minutes, and then periodically for the next week.

| **Vial Number** | **Mg of Thiokol rubber** | **10 ml of Solvent** |
|---|---|---|
| #1 | 141.97 | Acetone |
| #2 | 93.30 | Chloroform |
| #3 | 109.20 | Hexane |
| #4 | 111.31 | Methylene Chloride |
| #5 | 69.13 | Toluene |
| #6 | 103.87 | Nothing (control) |

Table 1: Corresponding Vial Numbers, Rubber Weights, and Solvent Types

Results: Although fully dissolving all the Thiokol seemed unlikely, some swelling was expected, but did not take place. None of the pieces of Thiokol changed in any way even after a week of sitting in their respective solvents. This result put a hold on our mission to pursue printing Thiokol rubber, while we continued building on our successes printing with natural rubber.

## Round 2: Printing by Machine (Spring 2017)

In addition to having more freedom to experiment while we were printing by hand, we were also narrowing down the characteristics and capabilities that we wanted in a 3D printer before we ordered one. Most 3D printers on the market for at home consumers print using plastic filament, and are not built to handle any other form of material. We needed a machine that would allow us to print liquids and gels of our choosing, but still have the option to print with a filament when desired. In researching 3D printer companies, we came across Hyrel 3D, a business born from the frustration of limited offerings and poor quality of 3D printers on the market. Hyrel prides itself on the functionality and modular customizability of its machines to accommodate printing thousands of materials; as their website says “the only limitation is your imagination” (Hyrel 3D). We ordered the Engine SR with an Inspector Microscope, CSD-60 Extruder (plus compatible 60cc syringes),VOL-25 Extruder, and MK1-250 Extruder (http://www.hyrel3d.com/resources/forum/engine-sr/).

The Engine SR works with all Hyrel print heads, and includes an external tablet for controlling prints. The CSD-60 Extruder is a cold flow crosslinking head designed for printing low viscosity room temperature materials with 60cc syringes. The VOL-25 Extruder (the volcano) is a warm flow head designed for printing emulsifiable materials such as glues and waxes up to 100 ºC . The MK1-250 Extruder is a standard hot flow head made to print with the common 1.75mm filaments of other 3D printers, and offers service temperatures up to 250ºC. Each of these printheads can be changed out on the main body of the machine when we need them, or even used together for the same print.

As soon as we received our 3D printer, it blew a fuse upon plugging it in, and needed to be sent back immediately. When we received the printer again we proceeded with our planned tests as far as we could in the given time left. Tests not completed by the end of this thesis will still be carried out with the intention of publishing a paper in *The Additive Manufacturing Journal*.

## Initial Hyrel 3D Engine SR Setup

*May 2017*

In preparation for receiving the Hyrel 3D Engine SR, Beth and I had two hour-long Skype training meetings with one of Hyrel's founders Davo, to better understand how to use our new machine. Based on information gathered during the Skype calls and Hyrel video tutorials I learned how to set up and operate our new machine using the different extruder heads. With Beth's instruction, I also began to learn the basics of manipulating *gcode* to control the specifics of our print such as temperature, print head travel speed, extruder flow rate, etc.

To create a 3D print, I first began by using a computer-aided design program to digitally model the structures that I wanted to print. From here the STL file needs to go through a program that divides the object into printable cross sections and outputs gcode. One slicing program called Slic3r can be used either on a computer or the printer itself, although we found that editing the gcode before it gets uploaded is more straightforward. We also tried other slicing programs such as Cura Software to convert our file to gcode before uploading to the printer, however we primarily used Slic3r.

## First Engine SR Print Experiments

*May 2017*

### *Test #1: Hex1 Gcode*

(Figure 81 & 82)

- Print head: CSD-60
- Gauge: 18

For our first print in rubber with this machine, we were excited to see that it worked at all (Figure 83). The print head moved extremely fast (60 mm/sec) with a strong extrusion rate, which can be seen in the resulting thickness of the print. This print was stopped after a layer and a half when the tip started to clog because it was dragging though previous partially cured layers. These signs made it clear that we should adjust the gcode before moving forward.

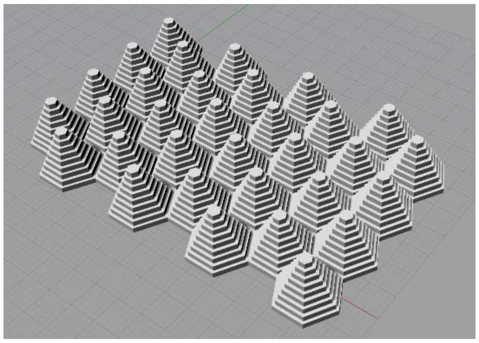


Figure 81: Hex 1 CAD Perspective

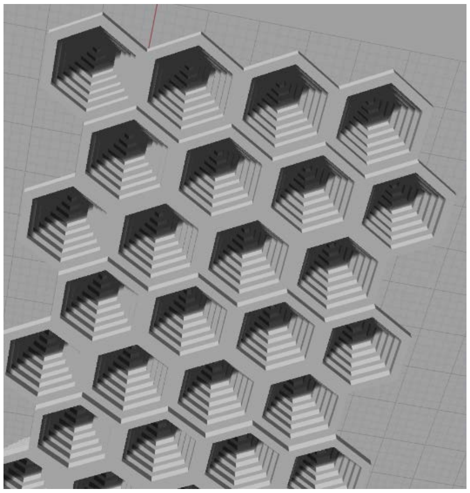


Figure 82: Hex 1 CAD Bottom View

Figure 83: Test #1, Hex 1 Gcode

*Test #2: Hex 3 (stl)*

- Print head: CSD-60
- Gauge: 18

(Figure 84 & 85)

The first line of this print went smoothly, although as it continued some areas were printed over again for second and third layers before the first layers were even laid down in other areas (Figure 86). The print should be built up one layer at a time across the whole print, so the instructions in the gcode must have been altered somewhere. Because the layers were being printed in a random order, the extruder tip dragged through the taller areas since the z axis did not move to accommodate the various heights. Again the tip became more prone to clogging after dragging though previous partially cured layers. The print head travel speed and extruder rate remained the same as the first print, and again proved to be too fast even for this new structure.

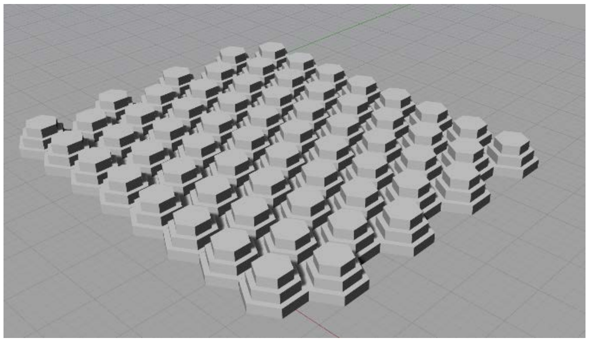


Figure 84: Hex 3 CAD Perspective

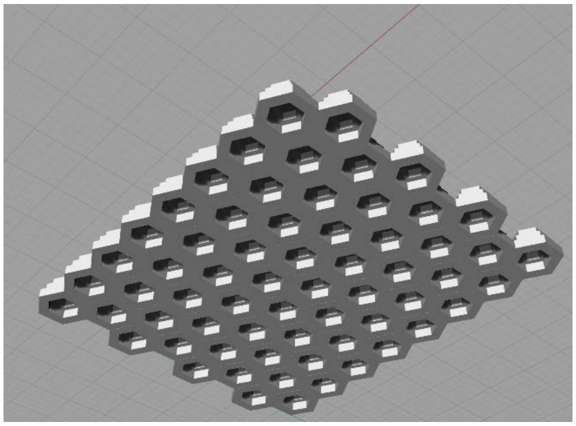


Figure 85: Hex 3 CAD Bottom View

Figure 86: Test #2, Hex 3

*Test #3: Hex 3 from Cura Software Gcode*

- Print head: CSD-60
- Gauge: 22

This print was stopped after two layers in order to see how the rubber dried before it ran together into one big mass. The speed and extrusion rate were also slowed down, in addition to using a finer tip, which helped produce a slightly higher resolution print.

Figure 87: Test #3, Hex 3 From Cura Software Gcode

*Test #4: Hex 3 from Slic3r Gcode*

- Print head: CSD-60
- Gauge: 22

This print was essentially the same as the previous one, but the gcode was prepared on a different software. There was only one issue with the tip clogging in this print, while the rest went fairly smoothly (Figure 88 & 89). One setback in this print was that the z axis did not appear to change levels again, which may be because the thickness of each layer is set to be thinner in the gcode than it was in reality so the print bed did move, but not enough (Figure 90).

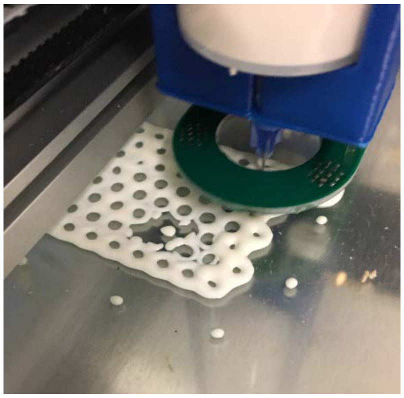


Figure 88: Test #4, Hex 3 from Slic3r Gcode

Figure 89: Test #4, Layer Two

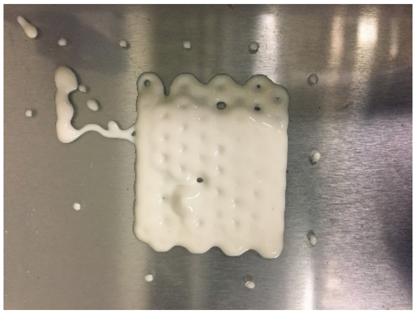


Figure 90: Test #4, Final Print

*Test #5: Hex 6 (stl)*

- Print head: CSD-60
- Gauge: 24

(Figure 91 & 92)

Instead of reducing the extrusion rate again, we tried using an even finer tip. We also tried printing with a new file in the hopes that the new shape with reduced angle walls would prevent the layers from being deposited so close to one another in each successive layer and merging into each other. The resolution of the print was not defined enough for this minor structural change to impact the print on this small scale (Figure 93, 94, & 95).

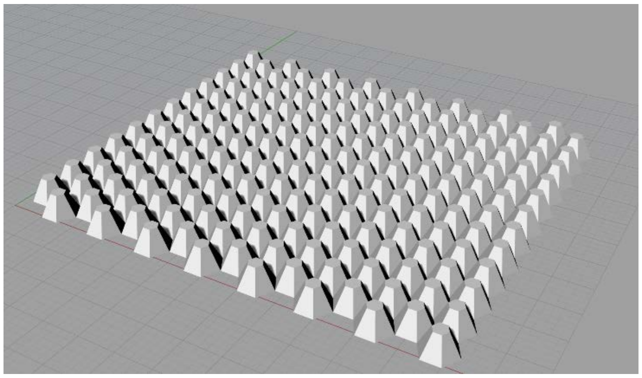


Figure 91: Hex 6 CAD in Perspective

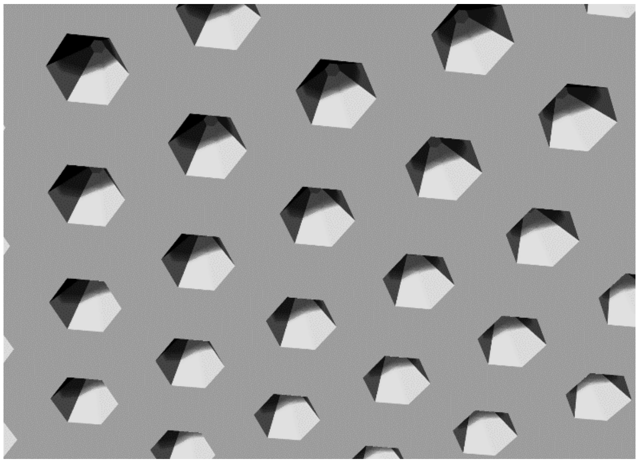


Figure 92: Hex 6 CAD Bottom View

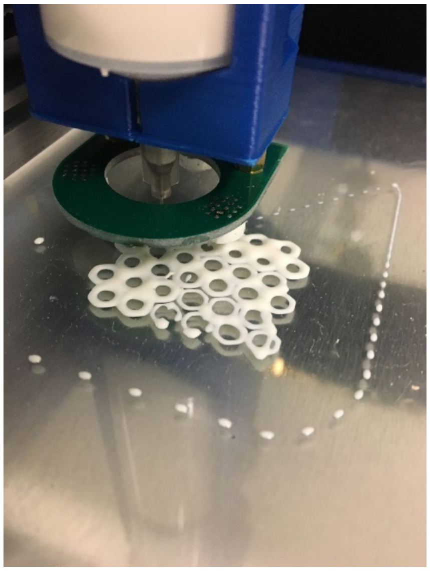


Figure 93: Test #5, Hex 6 (stl)

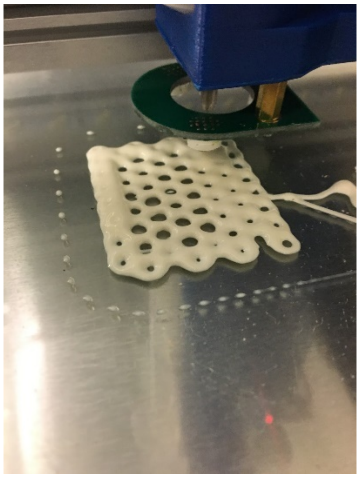


Figure 94: Test #5, Middle of Print

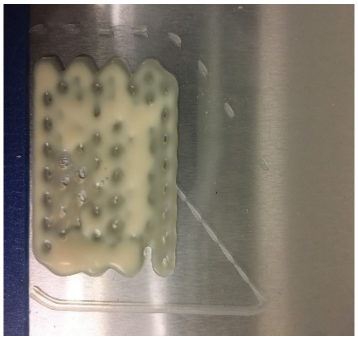


Figure 95: Test #5, Final Print

### *Test #6: Hex 6 Gcode01*

- Print head: CSD-60
- Gauge: 24

Figure 96: Test #6, Hex 6 Gcode01

Test #7: Hex 6 not default (gcode)

- Print head: CSD-60
- Gauge: 24

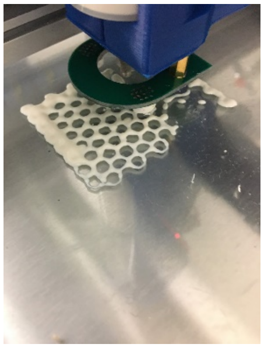


Figure 97: Test #7, Hex 6 not default (gcode)

*Test #8: Poly(tetrahydrofuran) – Hex 6*

- Print head: VOL-25
- Gauge: ~16 (extruder opening without additional tip)

This print also followed the hex 6 structure, but printed it in Poly(tetrahydrofuran). In the future we will use this material and print head for the support material, but we wanted to practice loading the material and setting the right temperature before printing alongside the rubber. The Poly(tetrahydrofuran) melts between 23-28$^{o}$C, so we needed it to be right on the cusp of cooling to a solid when we printed it. In this case the material was too warm when it was printed, and was not viscous enough to hold its shape, causing it to pool and spread (Figure 98 & 99). This will be a challenge to navigate as we move forward to make sure the temperature is just right before setting up the rest of the print.

Figure 98: Test #8, Uncured Poly(tetrahydrofuran)

Figure 99: Test #8, Cured Poly(tetrahydrofuran)

## Second Engine SR Print Experiments

*May 2017*

*Test #1: Hex 6 tool change (gcode)*

- Print head: CSD-60 and VOL-25
- Gauge: 25 and 20

Our goal for this test was to set up both the CSD-60 and VOL-25 print heads and print the rubber with the support material. When STL files are put into Slic3r, the program usually recognizes the need for support material and automatically generates the support structure. In the case of our file, Slic3r did not show any support material in the preview mode, nor did it add an additional head in the gcode. We manually changed settings in Slic3r to recognize a second print head with specific settings, but this information was still never translated into the gcode. When the two print heads were plugged into the printer, both were recognized by the printer software, however only the CSD-60 would print since that was the only print head written into the gcode. By at least setting up the print heads we were able to troubleshoot a new problem so we were prepared to handle it down the road. The tips of the CSD-60 and VOL-25 were drastically different distances away from the print bed, and although the height of the extruders can be slightly adjusted to align two heads, these were too far off to level mechanically. To compensate for the height difference, we used an extra-long syringe tip on the CSD-60 and trimmed it with wire cutters to match the VOL-25 tip.

*Test #2: Hex 6 300 percent (gcode)*

- Print head: CSD-60
- Gauge: 24

Since Slic3r did not recognize that previous print needed support material, we decided to enlarge the print so that there would be larger gaps creating increased need for support (Figure 100). Again, Slic3r did not automatically add support material, but we decided to go ahead with the print to see if the structure did not in fact need support material after all. We ultimately stopped monitoring the machine, and came back in the morning to find that the extruder tip had clogged and the print slowly faded out, never making it to the second layer (Figure 101). Each hexagon also printed individually instead of being connected to the surrounding ones, which is most likely because the shapes were only connected at an edge in the CAD file, which is not received well when converting the surface to an STL file.

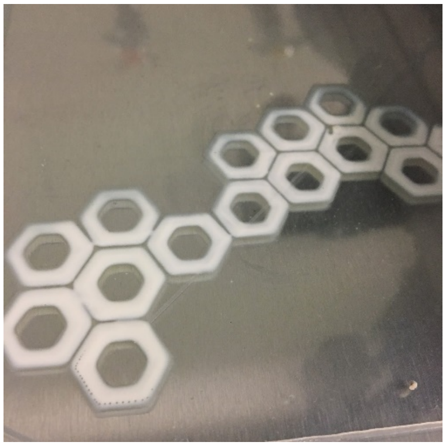


Figure 100: Test #2, hex 6 300 percent (gcode)

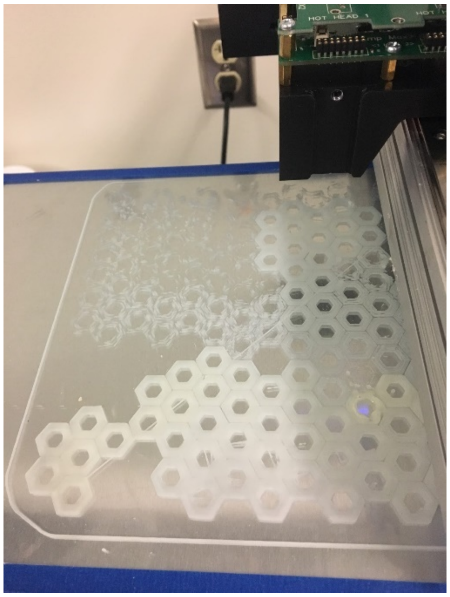


Figure 101: Test #2, Final Print

## Third Engine SR Print Experiments

*May 2017*

*Test #1: Hex 6 300 percent (gcode)*

- Print head: CSD-60
- Gauge: 21 and 23

There was some trouble with the extruder head clogging again with this print, however the main issue was that the extruder mechanism on printer stopped depressing the syringe of rubber, so we had to apply pressure to the syringe plunger manually as the extruder head traveled across the print bed. Manually operating the syringe pressure caused the syringe to sometimes point an angle opposed to remaining perfectly vertical, which was responsible for the misalignment between layers (Figure 102).

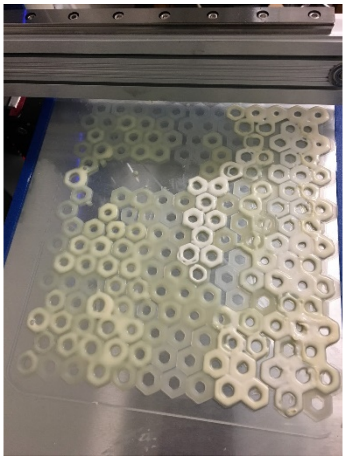


Figure 102: Test #1, Hex 6 300 percent (gcode)

*Test #2: Hex 6 original size 30mm speed*

- Print head: CSD-60
- Gauge: 21 & 23

This print returned the hex 6 file to its original size, but reduced the printer speed. When the first few hexagons printed well, the machine began to extrude material at a faster rate a minute into the print. This can be seen as the rubber runs together, and becomes indistinguishable as different shapes (Figure 103).

Figure 103: Test #2, Hex 6 original size 30mm speed

*Test #3: Hex 6 original at 20mm speed*

- Print head: CSD-60
- Gauge: 24 & 25

After discovering that the last print still ran a little fast, we reduced the speed again so that the printer traveled only 20 mm per second. We let this print run longer than the previous one, and found that despite changes made since the earlier hex 6 prints, the printer still tried to print the second and third layers in some areas before printing the first layer in other places (Figure 104).

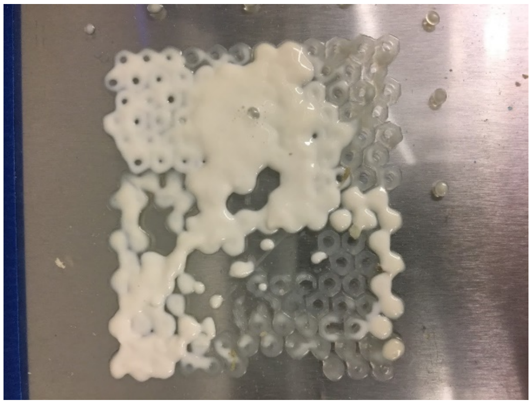


Figure 104: Test #3, Hex 6 original at 20mm speed

## Fourth Engine SR Print Experiments

*May 2017*

### *Test #1: Hex 6 with Support Material*

- Print head: CSD-60 & VOL-25
- Gauge: 25 & 21

Instead of relying on Slic3r to generate support material for my structure, I created a new file of the support material so that we had two files to feed the printer, one for each print head. After realigning the print heads, calibrating the offset between the two heads on the printer, and preparing the two files in the printer's software, we tried to run the first print. As seen in the photo, the printer only printed the rubber, and in two different places (Figure 105). Based on Hyrel's tutorial videos, we knew that we were missing a few lines of gcode that we were supposed to insert to tell the printer to switch print heads, however this code is specifically programmed by Hyrel and was unavailable on their website. In absence of the code, we followed all the other procedures in setting up the printer's settings to account for using two print heads, so we initially had hope that they might print without the extra gcode, but we were wrong. The software on the tablet that controls the printer also kept freezing and crashing, so we often had to stop and restart our work when we were in the middle programming instructions.

Figure 105: Test #1, Hex 6 with Support Material

**Future Engine SR Print Experiments**

*May-June 2017*

Moving forward, I will revise my CAD structures based on the printer accuracy and level of success printing with support material. At this time I know I want to at least change the file so that more than a single edge of the hexagonal structures are connected to try and fix the way that intersection is translated into the STL file and ultimately the gcode. Once we have produced successful prints that we anticipate using for material testing, we will experiment with cross-linking the rubber after it is printed. This vulcanization process can take place by either baking the rubber, submerging it in boiling water, or leaving it exposed to air for five days.

## Future Material Testing

*May-June 2017*

*Test #1: Conductivity*

This test will mimic the conditions a wetsuit would be in so that we can measure how much energy it takes to keep the body warm. While we could have designed a test to see how much energy passed through the neoprene compared to our rubber samples by taking the temperature on the ice bath side, this system would lead to complex logarithmic data whose results would be challenging to determine. By measuring the amount of energy it takes to maintain a stable body temperature on the inside of the suit, we will be able to produce a linear graph with our data that has a meaningful slope.

*Materials:*

- 2.5mm Hook Compatible Neoprene (Velour Royal/Black)
- 3mm Neoprene (Royal/Black)
- 6.6mm Neoprene (Black/Black)
- Our printed rubber pieces
- Ice bath
- 10 Watt resistor
- Power source

*Procedure*

First attach the inside of the material sample to a 10 watt resistor. As this resistor slows down the path of the current, it will heat up, simulating the human body inside a wetsuit. The outside of the material sample will be exposed to the surface of the ice bath to simulate freezing ocean temperatures experienced by cold weather surfers. Once the system is in place, we will introduce an electrical current to the inside (resistor side) of the material sample while measuring the temperature on the same side. By tracking how much energy it takes to maintain a certain temperature (body temperature) on the inside of that material, we can determine the insulative properties of the sample.

### *Test #2: Tensile Strength*

These tensile tests will follow the same procedure that we used before when testing the strips of 3D printed natural rubber, the only difference will be the materials that we are testing.

### *Materials:*

- 2.5mm Hook Compatible Neoprene (Velour Royal/Black)
- 3mm Neoprene (Royal/Black)
- 6.6mm Neoprene (Black/Black)
- Our printed rubber pieces

### *Procedure*

We will use the tensile strength machine (same procedure as before) to test three types of neoprene and our 3D printed rubber samples. We will run about six trials per type of material to find an average strength for each material. The data will be plotted into graphs and used to compare the tensile strengths between the materials.

# Theory

Going into this research, I predicted that 3D printed structures would have the ability to trap more air in more regular patterns opposed to traditional neoprene, and as a result could offer better thermal insulation properties with thinner material. While this theory made sense logically, I found that researchers had taken on this concept in the study *3D printed cellular solid outperforms traditional stochastic foam in long-term mechanical response,* published in Scientific Reports in April 2016 (Maiti). The article states:

> Traditional foams are associated with non-uniform microstructures involving quasi-stochastic organization of materials and voids that involve significant dispersion in size, shape, thickness, connectedness, and topology (see Fig. 1(a)). Although, depending on the application, the overall porosity (and therefore density) and the average pore size can be controlled to some degree, the lack of control at the microstructural level makes it difficult to predict the long-term stability in structure and performance of such materials. (Maiti)

This study conducted “multi-year-long accelerated aging studies under compressive strain followed by a time-temperature-superposition analysis using a minimum-arc-length-based algorithm,” to look specifically at compression and load retention properties of a an open-cell stochastic foam and an additively manufactured (AM) foam with the face-centered-tetragonal (FCT) lattice structure (Maiti). The diameter of each cylindrical strut in their 3D printed structure was a mere 250 μm, whose resolution was achieved by *direct ink writing*. At the end of the study, the researchers found that the “resulting master curves predict clearly superior long-term performance of the AM foam, both in terms of compression set and load retention,” (Maiti). They also naoted that this result “was remarkable given that the AM foam is created out of rubber with three times the stronger propensity for permanent deformation as compared to the rubber constituting the stochastic foam,” probably because the regular patterns of the 3D printed foam distribute outside forces better, sparing the point of impact from the brunt of the stress inflicted on the material (Maiti). While this study celebrated their initial promising results, they also recognize that there is even further room for exploration into even better performing 3D structures.

In addition to 3D printed material performance, the performance of the rubber itself is a key factor in the success of a new wetsuit material. Initially our goal was to find a way to print with synthetic rubber because of the advantages of thermosets, however due to the success we were having with natural rubber we chose to stay on that track. This decision was made based on feasibility rather than material performance, although according to the study *Comparative Studies of Natural and Synthetic Rubber*, we may have chosen the better material after all.

For this study, researchers prepared a rubber ball from natural latex and synthesized Thiokol, both of which they used for a rockwell hardness test, abrasion test, compression test, and accelerated ageing test. While the Thiokol did exhibit better mechanical properties overall, it lacked any room for customization or improvement upon its chemical attributes. Natural rubber, on the other hand, has “certain typical properties which can be further improved by vulcanization,” so overall, “we are concluding that the synthetic rubber even though holding many advantages in applications compared to natural rubber it is beneficial to use natural rubber (vulcanized) where we can get more special and improved properties than Thiokol rubber," (Vijetha). We do plan to vulcanize our natural rubber prints, however we have not yet discussed how to manipulate the natural rubber's properties through vulcanization, although this could be an opportunity to explore in future research.

# Results & Discussion

I chose to present the results of each experiment within the previous sections as to walk through them chronologically and show how each set of results guided the next decisions. For discussion context, here is a summary of our results in the form of accomplishments and information that we collected from each stage of this project:

*Round 1: Printing by Hand (Spring 2016-Winter 2017)*

- We made progress with silicone, but other companies already had a good handle on it
- We used natural latex with water and vinegar and found the main challenges to be deposition
- We used just latex and had success with layers curing on time and adhering to the next layer
- We found poly(tetrahydrofuran) to be a compatible support material for the rubber that still exhibited ideal properties

*Round 2: Printing by Machine (Spring 2017)*

- We were able to have the SR Engine print just rubber
- We had success manipulating the gcode to control printing variables
- We got the poly(tetrahydrofuran) to print by itself, although it kept getting too hot

- We found a way to level the CSD-60 and VOL-40 extruder heads (they are not designed to print together)

*Future*

- Expecting success printing with two heads once we receive the right gcode from Hyrel that dictates when the printer should switch between each extruder head
- Even if poly(tetrahydrofuran) is a bit runny it will still help hold the space in the center of the rubber
- Will probably need to refine structure once we see how printing with the support material works out
- Hopefully our structure proves to be a better insulator than traditional neoprene

The main challenges we faced throughout this research came down to flow rate, cure time, material compatibility, and structure. Our natural rubber results in Round 1 were very experimental, and were driven by our lack of knowledge about the specifics of the chemical reactions in the preparation of natural rubber from liquid latex. We knew that the addition of vinegar to the aqueous rubber solution reacted with the ammonia, thereby removing the ammonia from the liquid latex and allowing the rubber to coagulate. What was initially unclear was why we needed to add water to the latex to begin with, and if there was an alternative way to remove the ammonia besides adding vinegar. As we discovered, the rubber could simply be left out and the ammonia would evaporate, changing the rubber from a liquid to a solid. In finding a suitable support material we knew that we wanted something with a low melting point that could easily be removed from the final structure and reused. The idea of wax came up as meeting the initial criteria, however its hydrophobic properties caused the liquid rubber to bead up and roll away. We tried using poly(tetrahydrofuran) because it has similar properties to wax and was readily available. Looking at the chemical structure and solubility of poly(tetrahydrofuran),  helped give us some insight into why it is compatible with the rubber when wax is not.  Ethylene oxide, which is completely soluble in water, has a chemical structure of $–[CH_2CH_2O]–$, while wax, which is not water soluble, is made of basic hydrocarbons: $–[CH_2]–$. Poly(hydrotetrafuran) falls somewhere in between both structurally, $–[CH_2CH_2CH_2CH_2O]–$, and in terms of its properties being partially water soluble.  This means that poly(tetrahydrofuran) has a higher surface tension than ethylene oxide, but lower than wax, so it will not immediately mix with our liquid latex nor cause the rubber to bead up and roll away.

In Round 2 our success came from our familiarity with the materials and standard 3D printing methods, while our challenges stemmed from technical issues with the printing program and machine itself. Troubleshooting problems as they arise has helped us to become more familiar with how the printer operates and how to approach solving the next problem. That being said, a fair amount of the technical issues are out of our control such as the freezing and crashing of the program, which has led to more frustration than learning opportunities.

In the end we found that the best way to 3D print with a thermoset is by using a Hyrel SR Engine to print natural liquid latex with the CSD-60 extruder, and poly(tetrahydrofuran) as the support material with the VOL-25 extruder, and vulcanizing the print post production.

Regardless of the levels of success we achieved, there is always room for improvement looking back and moving forward. Criticism may arise over the fact that the proof of concept tests were not scientifically conducted, but we did not need them to be, and the freedom let us be more creative with our methods and research process, leaving more room for unexpected discoveries. I could have taken more detailed notes on each procedure, and in retrospect I should have used one lab book solely dedicated to this research to compile my work. The resolution of the printer is not ideal (smaller printer tips are more prone to clogging) and may impede accurate data collection in terms of material performance. To be able to accurately test the performance of my 3D printed material, the form would need to be crisper, so that the right patterns and dimensions could be achieved. The software was very difficult to work with and constantly provided additional setbacks that sometimes impacted the quality of the prints. When the printer tips clogged, we had to remove the syringe to clean the tips, and upon returning them to the machine, the calibration was sometimes disturbed or rubber started dripping on its own accord and would pool on the print.

# Application of Rubber Additive Manufacturing + Material Research

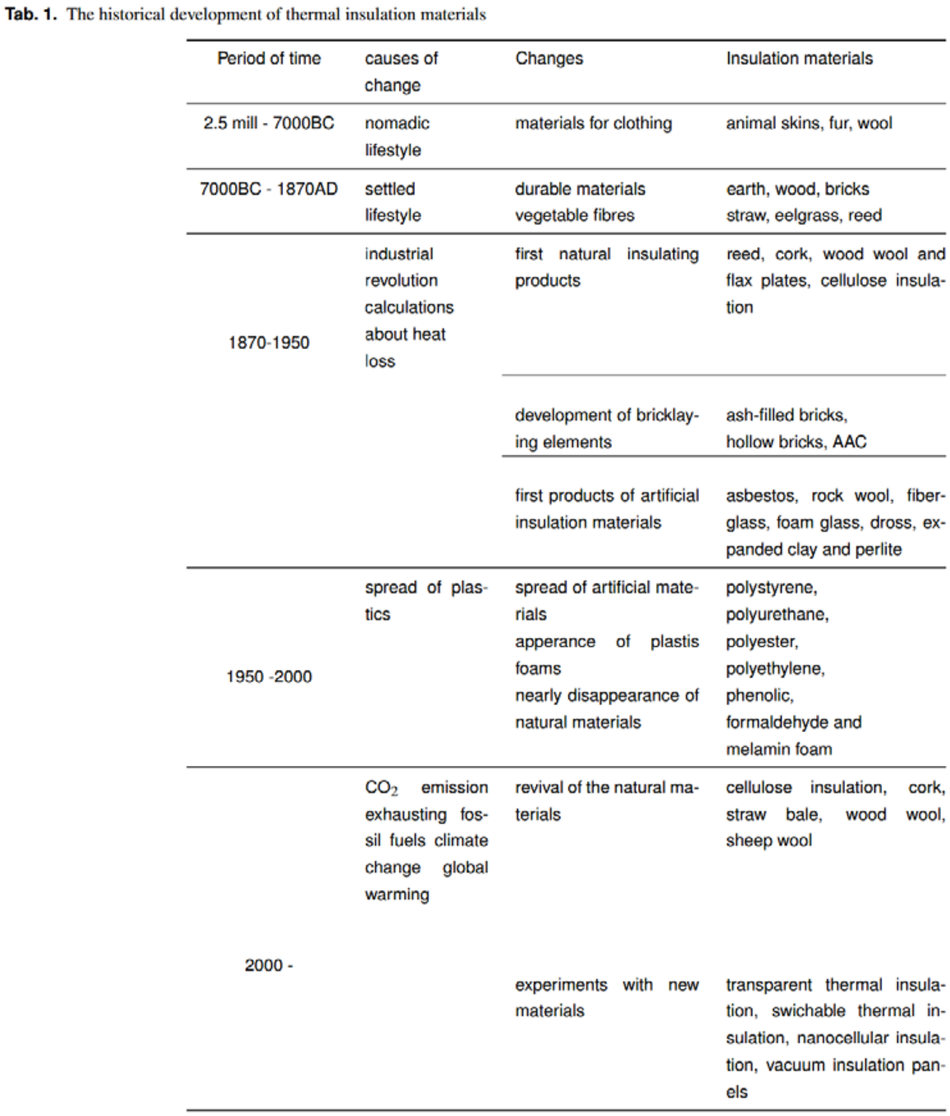
In addition to developing a new rubber manufacturing method, this thesis aims to show why this new method is so important, and how it will open up the possibilities for designs that have never been possible before. To achieve this, I began brainstorming industries and activities that would benefit from a product that took advantage of the combination of 3D printing and thermoset materials. Some of these needs included having complex geometries, withstanding high temperatures, being extremely durable, being chemically inert, and being flexible. Initially I focused a lot on sports industries and healthcare applications, looking into products from shoe soles to pediatric heart valve implants, however I ultimately decided to pursue insulation. I drew inspiration from Patagonia’s natural rubber wetsuit, and decided to build on their foundation to design a 3D printed rubber material to further increase the insulative abilities of wetsuits.

## *Biomimicry*

My research began by exploring different types of insulation, both in nature and in products to better understand how it worked and how it has been developed by humans. In nature, I examined the blubber patterns of arctic mammals to see if I could replicate the lipid structure of their adipose tissue. Despite the lipid structures being highly organized on a microscopic level, printing them on a larger scale probably would not yield the same results. In addition, printing these amorphous forms on a larger scale could be done by hand and would defeat the purpose of the 3D printer’s precise technical abilities. Through this research on natural insulation structures and relevant applications, I found a study conducted at MIT where engineers produced a beaver-inspired wetsuit, utilizing the air pockets that get trapped in the animal's fur (Chu). Essentially "three-millimeter polydimethylsiloxane (PDMS) rubber hairs are attached to the outside of a thin rubber base layer. As the fibers meet the water, the weight of the liquid pushes air into the space between the hairs, which are about one millimeter apart. That pressure creates tiny air pockets," (Averill). Graham Averill also notes in the article in *Outside Magazine* that "the thermal conductivity of air is two to five times smaller than that of rubber," so the resulting wetsuit should ideally be two to five times thinner while retaining the same level of warmth (Averill). This study provides a good example of the use of air as the primary insulator, and the mission to improve performance through material innovation within the wetsuit industry. Even Hub Hubbard, a wetsuit developer at Patagonia, finds the project to be exciting and wishes it the best of luck.

### *A Brief History of Insulation*

Building off of my research in the pursuits of biomimicry, I moved on to researching the history of manmade insulation, which primarily resulted in building materials rather than apparel. In Dávid Bozsaky's article *The Historical Development of Thermal Insulation Materials*, he recounts the five main periods of building insulation trends, and the events that led to each shift in material usage (Figure 106).



**Tab. 1.** The historical development of thermal insulation materials

| Period of time | causes of change | Changes | Insulation materials |
|---|---|---|---|
| 2.5 mill - 7000BC | nomadic lifestyle | materials for clothing | animal skins, fur, wool |
| 7000BC - 1870AD | settled lifestyle | durable materials<br>vegetable fibres | earth, wood, bricks<br>straw, eelgrass, reed |
| 1870-1950 | industrial revolution calculations about heat loss | first natural insulating products | reed, cork, wood wool and flax plates, cellulose insulation |
| | | development of bricklaying elements | ash-filled bricks,<br>hollow bricks, AAC |
| | | first products of artificial insulation materials | asbestos, rock wool, fiberglass, foam glass, dross, expanded clay and perlite |
| 1950 -2000 | spread of plastics | spread of artificial materials<br>apperance of plastis foams<br>nearly disappearance of natural materials | polystyrene,<br>polyurethane,<br>polyester,<br>polyethylene,<br>phenolic,<br>formaldehyde and melamin foam |
| 2000 - | $CO_2$ emission exhausting fossil fuels climate change global warming | revival of the natural materials | cellulose insulation, cork, straw bale, wood wool, sheep wool |
| | | experiments with new materials | transparent thermal insulation, swichable thermal insulation, nanocellular insulation, vacuum insulation panels |

Figure 106: The Historical Development of Thermal Insulation Materials (Bozsaky 55)

In looking at the history of insulation, I recognized patterns of what made some insulation perform better than others, and what drove the change of materials throughout various periods of time. The ultimate goal is to trap and hold as much air as possible as the primary insulator no matter the structural material. New waves of insulation trends are primarily driven by advancements in manufacturing and science, although the importance of sustainability has now taken priority. Most recently he writes: “the production of artificial thermal insulation materials needs significant amounts of energy and further use of fossil fuels, therefore the demand for natural thermal insulation materials is on the rise,” (Bozsaky 54). While the current trend is to move away from artificial insulation materials again, people are still wary of natural alternative because of perceived inferior performance. Despite designing my insulation specifically for wetsuits, the idea of 3D printed insulation has the potential to be translated to building materials in the future. Either way, my project needs to capitalize on the sustainable movement, while gaining trust through material testing data.

### *Neoprene*

I also studied the history of neoprene to understand how it became the most common insulation material used for wetsuits today. The 1920’s proved to be a popular time for natural rubber, and as the demand increased, so did the prices. In response, chemists began to search for a synthetic rubber option. In 1930 Wallace Carothers, a chemist for Dupont, produced a rubber-like substance when he performed a polymerization experiment using chloroprene (Seventhwave, neoprene: a brief history). DuPont used the trade name Duprene for its new material from 1931 until 1937 when it changed to neoprene, signifying that the synthetic rubber was a starting material opposed to a finished product. During World War II the military claimed all the neoprene on the commercial market, which led Dupont to purchase a government owned neoprene plant after the war to meet the demands of the public (Seventhwave, neoprene: a brief history). The first use of neoprene in a wetsuit took place in the 1950s. “Hugh Bradner, a University of California, Berkeley physicist is often considered the original inventor and ‘father of the modern wetsuit’," concluding that the water that seeped into the suit would be warmed by the body and remain that temperature, eliminating the requirement of a dry suit.  Bradner understood that the most important part was that the air trapped in the neoprene itself served as a good insulator. Jack O’Neill is also sometimes credited with inventing the first wetsuit after being introduced to neoprene by his friend Harry Hind and making his own neoprene vests. In 1952 Jack would go on to start his own wetsuit manufacturing company “O’Neill”. While Americans were falling in love with neoprene, in Europe, neoprene was not the material of choice for early wetsuits. “The French-made Pêche-Sport Suit and the UK-made Siebe Gorman Swimsuit were both made out of sponge rubber,” while “the Heinke Dolphin Suit of the same period, also made in England… [was] manufactured from natural rubber lined with stockinet,” (Seventhwave, neoprene: a brief history). Back in the U.S. the 60’s gave rise to new innovations such as laminating nylon elastic jersey to the surface of the neoprene, and using a zig-zag stitch to strengthen the wetsuit pieces and make the raw foam-rubber easier to put on over bare skin. At the same time, the Yamamoto Corporation from Osaka, Japan, also developed a new process of manufacturing neoprene that relied on different raw materials.

Traditional neoprene manufacturing involves using oil and other petroleum based chemicals to create chloroprene rubber chips through the polymerization of chloroprene. This is a chemical reaction where many individual chloroprene molecules bind to the other molecules, such as butadiene to create chains of repeating structural units. These chloroprene chips are then “melted and mixed together with foaming agents and carbon pigments, and then baked in an oven to make it expand,” (Seventhwave). After the oven, the neoprene is cut into sheets, ready for nylon fabric lamination. While the second half of the process remains the same, the Yamamoto Corporation discovered a new way to create the chloroprene rubber chips from acetylene derived from the calcium carbonate found in limestone, instead of oil-based methods. According to Seventhwave, a New Zealand based wetsuit company, besides eliminating the need for oil exploration, mining, and transportation, limestone neoprene offer many other benefits over oil-based neoprene. Seventhwave claims that limestone neoprene has 30% more air bubbles inside than oil-based, which make the material impermeable, lighter in weight, warmer, more durable, and stretchier. On the other hand Todd Copeland from Patagonia says "limestone-based polychloroprene is not inherently stronger or more flexible than petroleum-based polychloroprene nor does it insulate better. Any advantage of one fabric or another relies on differences in manufacturing methods," (Copeland). The following photos give visual context of the amount of air bubbles in traditional neoprene versus Yamamoto’s limestone-based neoprene. Figure 107 shows neoprene latex at 2,500 magnification, while Figure 108 shows neoprene latex at 25,000 magnification, and FIG. # shows Yamamoto’s comparison.

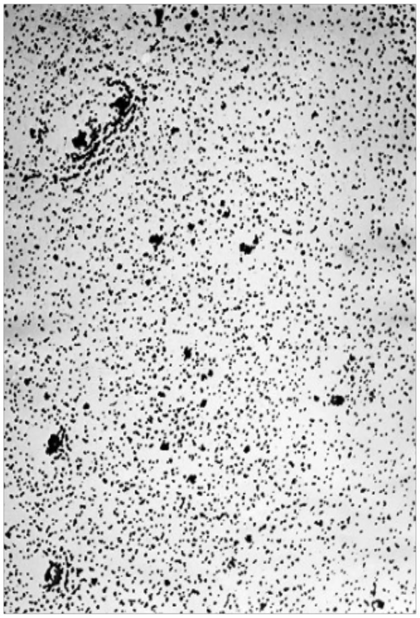


Figure 107: Neoprene at 2,500 Magnification (Neoprene Latex at 2500 Magnification)

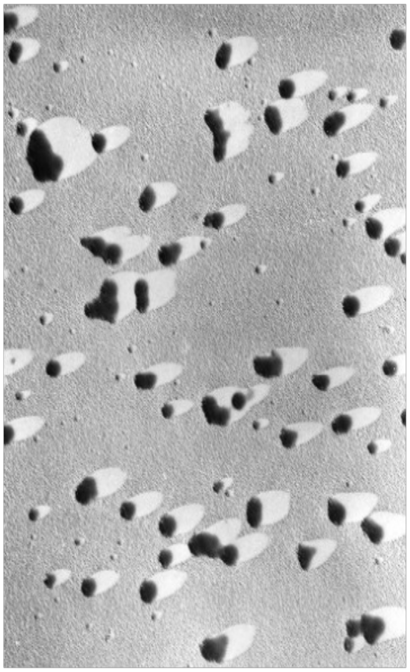


Figure 108: Neoprene at 25,000 Magnification (Microscopic View of Neoprene Latex)

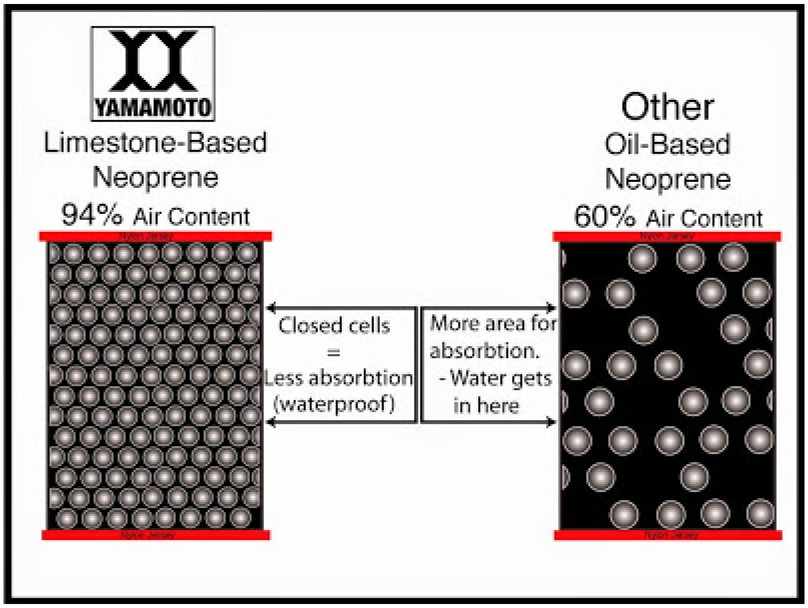


Figure 109: Air Content of Limestone-Based Neoprene vs. Oil-Based (Seventhwave Blog)

*Wetsuit manufacturing*

When it comes to wetsuit manufacturing, they can either be mass produced in a factory or individually custom made. Custom wetsuits are common among pros and avid surfers, however their high price is a prohibitive factor for many wetsuit buyers. Having a perfectly fitted wetsuit is key for maximum mobility and warmth, so ideally everyone would have their wetsuits custom made.

For the first step of creating a custom wetsuit, a tailor takes many measurements of the customer from the neck to the ankles. These measurements are then translated into 15-30 pieces that will make up the wetsuit. A team cuts out cardboard patterns of each piece and traces these onto the neoprene. Once the pieces are cut from the neoprene, a single piece is placed in a heated press, the company logo is applied, and then re-pressed to melt it in place. Waterproof rubberized glue is then added to the edges of the panels. It’s important that the right amount of glue is added; too little and there will be poor adhesion and waterproofing between the panels, too much and the glue will seep into the colored panels. The glued panels are then pushed together at the seam, first by hand, and then with compressed air driven crimpers to ensure that the glue gets into the open-air cells on each side of the seam. Once the top and bottom halves are each fully assembled, paper is inserted into the wetsuit to protect the inner neoprene while the middle seam is sealed to join the two halves. After about 45 minutes this assembly stage is finished and it’s time to sew it all together. A seamstress turns the wetsuit inside out and using a curved needle, blind stitches the seams so that they lie flat and only one side of the neoprene is punctured. Using a hot roller, the seamstress attaches a nylon tape to the back of the seams for extra waterproofing. An additional hose of hot air helps melt the adhesive to the fabric. A plastic zipper is then sewn in, along with a hook and loop stopper to prevent unzipping. A different team member paints rubberized glue around the zipper, and presses a neoprene panel over this area to waterproof the zipper. In total, this fabrication process takes 5-6 hours. After quality testing and a final fitting, the customer is ready to take home their new wetsuit (Wet Suits | How It's made).

The basic steps of mass producing wetsuits is very similar to creating just one, with a few adjustments to allow for more volume and general customer sizes. One of the early differences in the process is that computers are used to minimize the effort necessary to alter wetsuit designs to fit different people. Based on existing data and computer programs, wetsuit pieces are created digitally, and arranged by workers on a computer pattern simulating the roll neoprene. Pre-arranging the pieces in whatever orientation allows them to be closest together will help reduce wasted material between pieces when it comes time to cut them out. Once the pattern has been arranged, a plotter draws the pattern on a sheet of paper the same size as the roll of neoprene fabric. Workers can cut up to 50 sheets of neoprene at a time with a jigsaw-like took, using the paper pattern as a guide. Logos are silkscreen printed and cured with heat just prior to gluing. Workers then apply glue three times to the edges of each piece, which is reactivated with a solvent when the pieces are ready for assembly. Just as before, pieces are brought together by hand and the connection is reinforced using compressed air driven crimpers squeeze the glue into the open air cells on each side of the seam. Stitching or tape is used to finish the seams, however not necessarily both. Once again the wetsuits undergo quality control checks and fitting tests (this time on special fit models) before they are officially finished. Wetsuits are organized and stored in the factories until orders come in from companies, at which point they are packaged and shipped out ("How is made - Scuba Dive Wet Suits").

While both these manufacturing methods follow similar steps, the material choices and construction details make all the difference in terms of quality and performance during a given activity. The first things to consider are what activity the wetsuit is for and what environment it will be used in. The answers to these questions will determine three main aspects of the wetsuit: style, neoprene thickness, and seam construction. While wetsuits are worn for any cold water sport, I am focusing on wetsuits for surfing due to their need to be warm but as thin as possible to increase mobility for paddling. Depending on the climate of the surfing location, common styles include wetsuit vests, jackets, short johns, long johns, spring suits, short arm steamers, and full suits. Neoprene thicknesses come in a range from 2mm to 8mm, although typically top out at 6mm for surfing. Scuba suits require thicker neoprene for warmth because they cannot have very many air bubbles trapped in the neoprene or else the suit will be too buoyant for deep diving. For full surfing suits, neoprene thicknesses vary between the torso, legs, and arms. Quicksilver's Wetsuit guide provides four temperature ranges and corresponding neoprene thickness combinations:

39-46 degrees F → 6/5/4 (6mm torso - 5mm legs - 4mm arms)
44-55 degrees F → 5/4/3
53-60 degrees F → 4/3 (4mm torso - 3mm arms and legs)
59-66 degrees F → 3/2
(Quicksilver)

Seams offer both benefits and potential points of weakness. Having more seams allows for a better fitting wetsuit, however more seams reduces the flexibility and increases the chances of chafing caused by a seam. On the other hand, fewer seams provide fewer chances of water entering the suit (especially as the seals on the seams wear down), but offer a slightly poorer fitted suit.

The type of stitching also plays a role in the warmth of the wetsuit, and varies by product quality.  Overlocked seams use the simplest stitch, and are only found in either summer suits or cheap suits (Figure 110). This stitch allows the most amount of water in, reduces flexibility, and creates a bulging seam inside the wetsuit, which can cause chaffing.

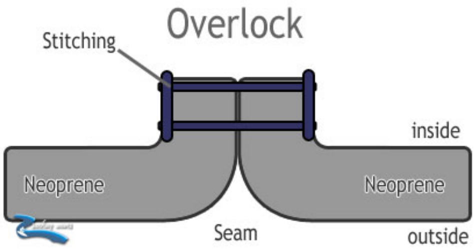


Figure 110: Overlocked Stitch

Flatlock stitching provides a stronger, more flexible option than overlock stitching, but due to the number of stitches required, the resulting holes usually allow a fair amount of water in (Figure 111). This stitch is a good choice for summer or warmer climate surfing wetsuits.

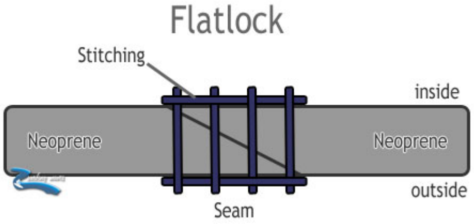


Figure 111: Flatlock Stitch

Blindstitching is the ideal method for constructing wetsuits for cold water, and are used in all high-quality suits. For this stitch, the edges of the neoprene are glued together and a curved needle is used to penetrate only one side of the seam, lashing them together (Figure 112). Double blindstitching involves applying the blindstitch to both sides of the seam. These seams are watertight, flexible, strong, and flat.

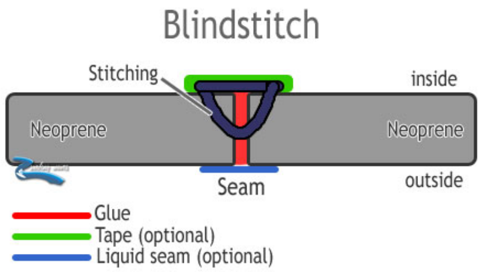


Figure112: Blindstitch

In order to increase the strength and waterproof quality of seams, various sealants are often used. While glued seams are standard for blindstitching, the addition of glue can also increase water impermeability in other kinds of stitching as well. Spot taped seams and fully taped seams refer to gluing tape over either critical areas or all the seams. Ideally all seams would be liquid taped, which uses a special liquid rubber to make the seams completely waterproof (Surfing Waves).

*Interview with Jake*

To better understand a surfer's relationship with his wetsuit, I interviewed Jake Sandblom, a University of Oregon student and active surfer. While the traditional design research process would require much more user contact than a single interview, it was sufficient for the purpose of this project. My goal is not to not to bring this particular product to market; instead I intend to provide background and reasoning to best show off the design opportunities of 3D printing, especially when using materials beyond standard thermoplastics. Interviewing Jake allowed me to connect my secondary research to a potential user's personal experience and opinions.

- How often do you go surfing/wear a wetsuit?

*It really depends at the moment just due to being a full time UO Student… During the term: anywhere from 0-5 times depending on my schedule, the waves and weather conditions, and especially winter and spring snowboarding is my alternative. During breaks: every day, sometimes twice in a day. Back home(Southern CA): every day mostly, 5-7 times each week if I'm working a lot or the conditions are bad. In all of these occasions I'm likely wearing a wetsuit. At the minimum I'll wear a wetsuit top or "jacket" and also wear springsuits and fullsuits for winter and surfing in Oregon.*

- Where do you usually go surfing?

*In Oregon I typically surf Florence South Jetty since it is the closest to UO. I also really like Shorts Sands in Cannon Beach, or surfing in Newport. Back at home I surf all over, but my favorite spots are in Dana Point and San Clemente, CA.*

- What season do you usually go surfing?

*All seasons! That's a beautiful part about surfing :)*

- What do you look for in buying a wetsuit?
    - Material? Thickness? Temperature rating? Flexibility? How do you prioritize warmth vs flexibility?

*The first thing I think about when buying a wetsuit is what season or location I'll be using it for. Typically I'll look for the thickness and temperature first which pretty much go hand in hand. Then I'll look at my options based on my previous* *wetsuits and wetsuit-making brands that I liked. I have some bias towards Rip Curl wetsuits after interning there and using their wetsuits, but I also like Quiksilver and would love to buy one from Patagonia. I think what I'm getting at is quality of the wetsuit, and how long it'll last.*

*I'd generally prioritize warmth first and then look at flexibility. It's tricky because the thickness of the suit correlates so much to both warmth and flexibility or lack thereof. The good news is wetsuits are becoming warmer and more flexible every year so I don't really have to choose one factor over another. The material is less of a factor for me because I don't have much money...I generally buy neoprene wetsuits.*

- What style of wetsuit do you have? (vest, jacket, short john, long john, springsuit, short arm steamer, full suit)

*At the moment I have a lot. I have a 5/4 hooded wetsuit, a 4/3 fullsuit, a 2mm springsuit and then a jacket.*

- What kind of stitching and sealing do you prefer, and why? (overlocked, blindstitch, flatlock, liquid taped, spot taped, etc.)

*I generally prefer suits that are fully sealed with taped seams since they're much warmer. Some of my suits are blindstitched, and I care less about the stitching in the springsuits and jacket since I'm surfing in them in warmer water anyway.*

- What zipper placement does your wetsuit have, and are you happy with this location?

*Most of my wetsuits are chest zip suits, but I now have my first zipper free wetsuit which is awesome! It works just as well as the chest zip suits-super cool. I have also owned back zip suits, but I like chest zip or zip free best since it increases flexibility and warmth on my back.*

- Do you own a custom wetsuit?
    - If not, have you ever been interested in getting a custom made wetsuit?

*I do not, but it would be sick to have one...the ones I know of are super expensive.*

- Have you owned more than one wetsuit?
    - If so, how many/how frequently have you bought them? How do you decide when you need a new one?

*Oh yeah! I usually buy a new wetsuit every 2-4 years depending on how much I use and abuse it. I really try to make them last and generally take good care of them! I decide to get a new one once the current suit gets tears in it, loses warmth, or it isn't fitting as snug as it once did. For example, one of my suits ripped at the shoulder after a couple years, and another started to get ragged at the wrists and ankles.*

- How would you rank the top three most important features in a wetsuit?

1. *Warmth*
2. *Quality*
3. *flexibility*

- What are your favorite and least favorite features of your wetsuit?

*I like the chest zip and zip free suits I own, they have a small pocket or loop for my car key when I'm in the water, and my newest suit dries incredibly fast! It is awesome. (It's a Rip curl Flashbomb)*

- Are you familiar with Patagonia's natural rubber wetsuit?
  - If so, what are your thoughts on using natural rubber instead of traditional neoprene or limestone based material?

*I am! I think it is a super cool idea, and I plan to buy one once I am out of college making a real salary. I think what they are doing is awesome and I hope that we begin to see other wetsuit makers follow suit...traditional neoprene and traditional surfboards too are really not great for the environment. I can't speak to the performance of natural rubber, but if it works as well as regular neoprene then we should all start using natural rubber I think.*

- What do you think about the idea of wetsuits made out of 3D printed pieces of insulative material?

*I think it is a really interesting idea. It would be so cool to test one out or have the ability to print yourself a new wetsuit when you needed one. Again, I'd say that if it can compete with the wetsuits on the market, then people will start using them!*

- How important is sustainability to you when choosing a wetsuit? How much do you think sustainability is a factor for other surfers?

*I think sustainability is super important to me when purchasing any product, but the unfortunate truth is that as a college student (low income) I can't afford a more sustainably sourced wetsuit yet. To counter this, I try to make the wetsuits that I do have last as long as I can, or even use neoprene glue to patch them to last longer. I think sustainability is becoming an increasing concern for other surfers, but I don't think a majority of them have it as a top three factor. I think surfers will always prioritize the warmth and flexibility of the wetsuit first, but if a sustainably sourced wetsuit matched non-sustainable ones then they would choose the more sustainable suit.*

- If you could change anything about standard wetsuit designs/options on the market, what would you change?

*I'd like the prices to be lower, but I know that's a dream...I think that the existing wetsuits on the market are excellent and get better every year, but as far as I can tell nobody is really pushing the boundary on materials or natural rubber the way Patagonia is. I wish that more wetsuits were made using less harmful chemicals and processes. Quite frankly, I think it would even cooler if there was a way to take waste and existing recycled material and incorporate that into wetsuits instead of creating more and more new material. Or, just a better way to recycle and repurpose existing wetsuits. I got kind of off topic...aside from the materials, I think the existing suits are great and I love that they're now being made without any zippers. I also love how fast* *my new wetsuit dries out because it means I can surf again in it within a short period and it is completely dry when I put it back on!*

- Any additional thoughts?

  *I think that the surf industry turns a bit of a blind eye to some aspects of environmental issues, but I hope that companies will start to make change and Patagonia can be a disruptor to the market. As surfers I think we are generally ocean lovers, and by association ambassadors for the environment but we don't always show it with our purchasing decisions. I hope more brands follow Patagonia's lead.*

Overall Jake's responses helped add to and confirm the qualitative information that I had gathered from reading surfing blogs, community forums, and company websites. He provided insight into how to prioritize the importance of the information I had learned, and voiced promising curiosity and excitement around the prospects of a 3D printed wetsuit.

Some of my biggest takeaways from Jake's answers:

- Custom suits are ideal but too expensive
- It's best to have no zipper - this makes suits warmer and more flexible
- Quick dry material is important - especially for being able to surf multiple times a day
- Thoughtful details like a clip for keys are much appreciated
- Function and price are high priorities

- Warmth is the most important feature
- Jake, and surfers in general would readily embrace a greener solution as long as performance is not sacrificed

Jake’s responses also reinforced appreciation for four of the top five new wetsuit technologies of 2016: zipper-free, quick-dry, limited seams, and Patagonia’s rubber suits (Ciaramella). Fortunately, 3D printing a rubber insulation material addresses many of these needs.

*Patagonia Case Study*

So what is all the hype about Patagonia’s wetsuits? For starters, they are the only company currently manufacturing wetsuits using natural rubber. In addition, Patagonia goes above and beyond to ensure their wetsuits are leading the industry in sustainable material sourcing and manufacturing practices. The video *Patagonia’s New Natural Rubber Wetsuits*, notes that “the beautiful thing about this project that Patagonia is doing, is that they are improving the quality of wetsuits. A wetsuit that previously would be manufactured from petroleum and harmful chemicals, is now made of natural rubber without sacrificing advances in the technology,” (Patagonia's New Natural Rubber Wetsuits). Many people are skeptical of the performance of a neoprene alternative, however Patagonia assures that not only is performance not compromised, it is actually improved. As their website states: “still the material of choice for a wide range of products with demanding performance requirements, such as airplane tires and medical gloves, natural rubber is both stronger and more flexible than its synthetic substitutes. Its strength, elasticity and consistent stretch transfer superbly into wetsuits—meaning that not only are we not contributing to deforestation, Yulex natural rubber is a step forward for performance, too," (Patagonia). The innovation and commitment to sustainability and utility demonstrated through this product are what inspired the design focus of my project. Patagonia looks at the bigger picture and examines implications of material sourcing on the surrounding environment and community to make sure they do no harm. They also conducted manufacturing environmental assessments and found that "because the polyisoprene polymer was produced in trees instead of factories, using solar energy instead of generated electricity, up to ~80% less climate-altering CO2 was emitted in the manufacturing process when compared to traditional neoprene" (Patagonia's New Natural Rubber Wetsuits). If all wetsuits could be produced out of sustainably sourced rubber, CO2 emissions could be cut down dramatically, and 3D printing could continue to bring down those numbers.

### *End of life*

As a thermoset, neoprene does not recycle well like thermoplastics do. The same properties that give thermosets superior heat resistance and durability are exactly what prevent them from easily being melted back down and turned into a new product. While thermosets can be melted down, they will never achieve the same level of performance as when they were a virgin material.  Since melting down neoprene is energy intensive, and produces an inferior material, several companies have focused on reusing old neoprene from wetsuits to create other products. Suga shreds up old wetsuits and processes them into yoga mats, while other companies such as Green Guru makes laptop cases, and Neocombine make bracelets and luggage tags (Morton). Despite natural rubber having the potential to be vulcanized to become a thermoset, it still offers better end of life degradation properties (Rose & Carsten).

### *Design Development*

To create the 3D structures I began sketching potential options by hand and quickly moved on to using CAD (Figure 113). While I first set out to try four different shaped patterns, I quickly discovered with CAD that there were far more variables to each shape than I had initially considered (Figure 114, 115, & 116). As I began to create hexagonal patterns, I slowly began to change one variable at a time thinking about the:

- height of each hexagon
- width of each hexagon
- pointed vs truncated top
- smooth vs terraced sides
- wall thickness of hollow shapes

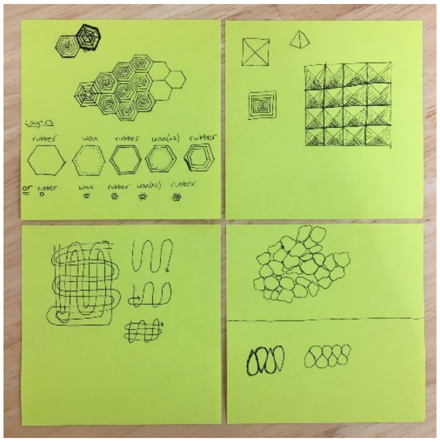


Figure 113: Hand Drawn Potential Structures

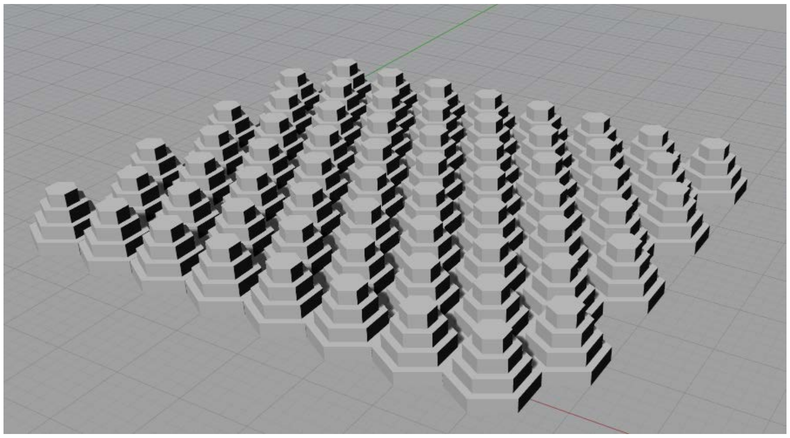


Figure 114: Hex 2 CAD Structure

5mm wide hexagons, 1mm layers, 4mm tall.

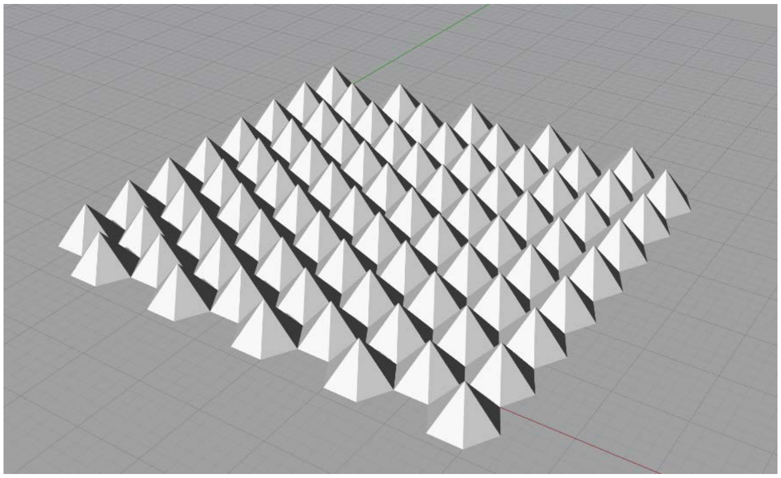


Figure 115: Hex 4 CAD Structure

5mm wide hexagons, built with smooth wall (opposed to terraced), 3mm tall

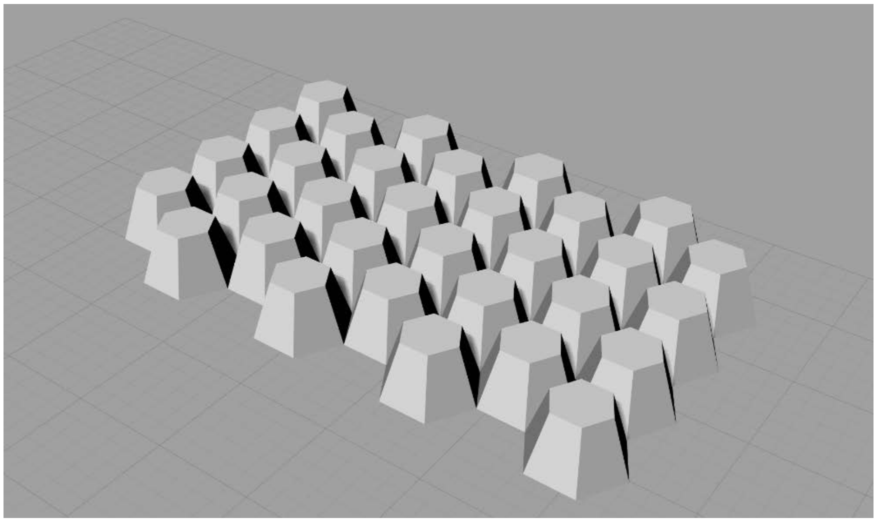


Figure 116: Hex 5 CAD Structure

5mm wide bases, 3mm tops, 3mm tall

My thought was that since hexagons are the most efficient way to pack spaces together (something we have learned from honey bees and proved with math), and the goal is to fit the most air pockets together, then it did not make as much sense to use the square based shapes. Mathematician Thomas C. Hales, proves in *The Honeycomb Conjecture* that “any partition of the plane into regions of equal area has perimeter at least that of the regular hexagonal honeycomb tiling,” (Hales 1).

While the technology is still a ways out, ideally it would reach a point where the average consumer could reliably print rubber at home. In the future, 3D scanning technology could be used to take exact body measurements, which could be translated to a digital patterning program, and run straight to the 3D printer. Making more of the process digital could also reduce some of the financial burden of individual production. Even regardless of body scanning technology, the customizability of 3D printing would allow people to take their own measurements and print their own custom wetsuits to fit their body. Most wetsuits are made for “average” body shapes/sizes, so making customizability accessible would allow people who do not fit in typical factory standard sizes to have an alternative to current expensive custom suits. This aspect of fit is vital to retaining heat, and can be an excellent opportunity to take advantage of the features of 3D printing. By 3D printing rubber wetsuits, the need for zippers could also be designed around and eliminated. The closed cell construction of the rubber insulative material already prevents the suit from absorbing water, so the quick dry feature is essentially already built in. Another advantage is that since each piece of the wetsuit would be individually printed, the process eliminates the wasted rolls of neoprene left over from cutting out pieces.  Patagonia has already shown that using rubber improves wetsuit performance, so as long as the insulation structure is carefully designed, cold water surfers will be able to stay even warmer while embracing the sport they love and knowing that they are riding a sustainable wave of change in the industry.

# Conclusion

We achieved what we set out to discover: how to 3D print with rubber. Given this exciting start, we still have a long way to go in refining our method and integrating support material before this manufacturing process can be a viable option for producing final products. With this research we have laid the foundation for others to build on. We have done the leg work in testing different kinds of rubbers, selecting a compatible support material, and finding a 3D printer whose hardware and software can accommodate simultaneously printing with the appropriate style and temperature extruder heads. Moving forward, there will need to be a better system to prevent the rubber from clogging the printer tip. This may mean filtering the rubber before putting loading it into the syringe to remove any coagulated bits form the liquid, or installing a self cleaning feature for the tip perhaps in the form of an interior needle that can be internally deployed to clear the tip channel. The printer program crashing issues may be resolved if the printer is hooked up to a monitor instead of the tablet that it came with. The crashes could be a result of the printer software overloading the tablet’s processing capacity.

My next step is to finish creating successful prints of my wetsuit insulation using support material, and testing their tensile strength and insulative properties against three different samples of neoprene. At the end of this research I intend to publish a paper in the Journal of Additive Manufacturing. So how will 3D printing in new choices of materials change the world of design? That is what designers are working to figure out. The simple and most thrilling answer is: everything.

# Glossary

Additive Manufacturing: a process where material is added to create something rather than being taken away such as in most manufacturing method; for example, wood working where material is cut, carved, shaved, and sanded away to make the final piece. Also used as a synonym for 3-D printing.

Chemical Stability: is when a material has the ability to resist change or decomposition, which occurs when a system is in its lowest energy state or at chemical equilibrium with its environment.

Computer-Aided Design (CAD): computer programs that allow designers to digitally create representations of physical objects.

Computerized Numerical Control (CNC): is a computer controlled machine similar to a hand held router that cuts wood, metal, composites, foam, etc.

Creep: the deformation of a material under stress overtime (while sometimes temperature dependant, plastics can creep at room temperature).

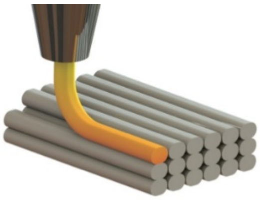
Dielectric Strength: the maximum electric field that a pure material can withstand under ideal conditions without breaking down.

Dimensional Stability: ability for a material to maintain its original dimensions while being used for its intended purpose and subjected to changes in temperature and humidity.

Direct Ink Writing: also referred to as robocasting, is similar to FDM but once the material has been printed it does not need to dry/cure to maintain its shape.

Emittance: the energy radiated by the surface of a body per second per unit area.

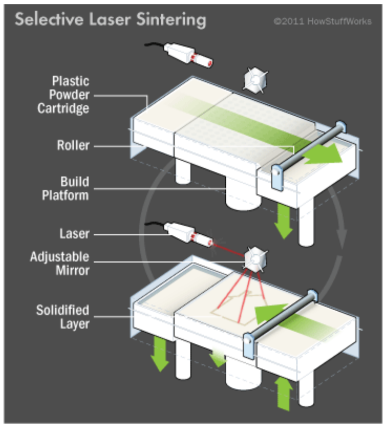
Fused Deposition Modeling (FDM): melts polymer filaments and pushes them through a small extruder head as they are laid down in layers onto a printer bed.



Gcode: The code language used to give CNC machines instructions such as how are where to travel across X, Y, and Z coordinates.

Proof of Concept (POC): showing that a certain method or idea is in fact feasible and to verify that it has the potential to be used in further applications.

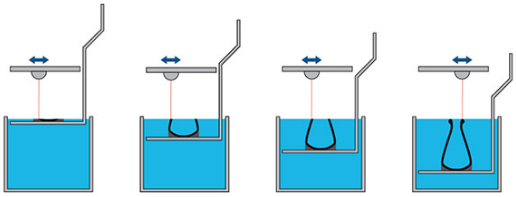
Selective Laser Sintering (SLS): has a powder layer in the printer bed that it sinters (melts) with a laser, layer by layer.



Shrink: when a material is drying the loss of water results in a reduction in volume causing the material to shrink in on itself (often around the edges for plastic).

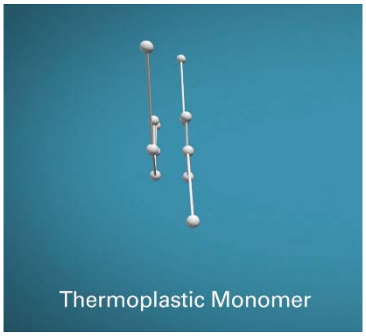
Strength-to-Weight Ratio: also known as specific strength, measures how strong a material is compared to the material's weight.

Stereolithography (SLA): selectively cures a base resin liquid in the printing bed one layer at a time to build a solid form.

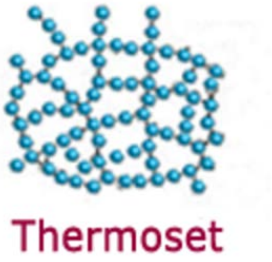


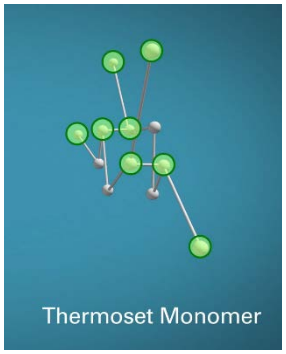
Thermal Properties: include thermal conductivity, thermal insulation, thermal expansion, etc.

Thermoplastic: substances (especially synthetic resins) that become plastic on heating, harden on cooling, and are able to repeat these processes. These materials are made of polymers linked by intermolecular interactions or van der Waals forces, forming linear or branched structures.



Thermoset Plastic: synthetic materials that strengthen when they are heated, but cannot be successfully re-melted or re-molded after their initial heat-forming. These materials are made by polymers joined together by chemical bonds, acquiring a highly crosslinked polymer structure.





Viscous: having a thick, sticky consistency.

Vulcanization: the curing process that occurs using heat and sulphur.

# Bibliography

3D Printing Industry. (2013). History of 3D Printing. Retrieved April 14, 2016, from http://3dprintingindustry.com/3d-printing-basics-free-beginners-guide/history/

Averill, Graham. "Your Next Wetsuit Will Mimic Otter Fur." Outside. N.p., 24 Oct. 2016. Web. 4 May 2017. <https://www.outsideonline.com/2127826/your-next-wetsuit-will-mimic-otter-fur>.

Bensoussan, Hannah. "The History of 3D Printing: 3D Printing Technologies from the 80s to Today." Blog post. Sculpteo. N.p., 14 Dec. 2016. Web. 4 May 2017. <https://www.sculpteo.com/blog/2016/12/14/the-history-of-3d-printing-3d-printing-technologies-from-the-80s-to-today/>.

Bozsaky, Dávid. "The historical development of thermal insulation materials." Periodica polytechnica (2010): 49-56. Web. 25 Apr. 2017. <https://pp.bme.hu/ar/article/viewFile/12/12>.

Chu, Jennifer . "Beaver-Inspired Wetsuits in the Works." MIT News. Massachusetts Institute of Technology, 5 Oct. 2016. Web. 4 May 2017. <http://news.mit.edu/2016/beaver-inspired-wetsuits-surfers-1005>.

Ciaramella, Michael. "The Top 5 New Wetsuit Technologies of 2016." Surfer. The Enthusiast Network, 5 Nov. 2016. Web. 30 Apr. 2017. <http://www.surfer.com/surfing-magazine-archive/surfing-news/top-5-new-wetsuit-technologies-2016/#kq5i4LMpugBX4I43.97>.

Copeland, Todd. "Green Neoprene? [Updated]." Web log post. The Cleanest Line. Patagonia, 21 Aug. 2013. Web. 4 May 2017. <http://www.patagonia.com/blog/2008/05/green-neoprene/>.

Fripp, Tom, Neil Frewer, and Lewis Green. Method and Apparatus for Additive Manufacturing. Fripp Design Limited, assignee. Patent WO 2015059502 A1. 30 Apr. 2015. Print.

Grunewald, Scott. "Fripp Design Finally Gains Patent for 3D Printed Silicone Picsima Process and Is Now Seeking Partners." 3D Print. 3DR Holdings, 16 Mar. 2016. Web. 30 Aug. 2016.

Hales, T. C. "The Honeycomb Conjecture." Discrete Comput. Geom. 25.math. MG/9906042 (1999): 1-22.

How is made - Scuba Dive Wet Suits. Dir. Www.ScubaTraveller.com. YouTube. Scuba Traveller, 31 Jan. 2010. Web. 26 Apr. 2017. <https://youtu.be/laZaa7GPG68>.

Hyrel 3D. "Home Page." Hyrel 3D. N.p., 2017. Web. 21 Apr. 2017.

Katz, David A. "Preparation of Synthetic Rubber." Chymist. N.p., 2010. Web. 4 May 2017. <www.chymist.com/Synthetic%20Rubber.pdf>.

LUKIC, M. ... et al, 2016. Printability of elastomer latex for additive manufacturing or 3D printing. Journal of Applied Polymer Science, 133 (4), 42931.

Maiti, A., W. Small, J. P. Lewicki, T. H. Weisgraber, E. B. Duoss, S. C. Chinn, M. A. Pearson, C. M. Spadaccini, R. S. Maxwell, and T. S. Wilson. "3D Printed Cellular Solid Outperforms Traditional Stochastic Foam in Long-term Mechanical Response." Natureresearch (2016): n. pag. Springer Nature. Web. 22 Apr. 2017. <https://www.nature.com/articles/srep24871>.

Microscopic View of Neoprene Latex. 1959. DuPont Company Product Information Photographs (Accession 1972.341), Audiovisual Collections and Digital Initiatives Department, Hagley Museum and Library. Hagley Digital Archives. Web. 26 Apr. 2017. <http://digital.hagley.org/islandora/object/islandora%3A2224378>.

Morton, Brooke. "Neoprene Reborn: Five Ways to Recycle Your Wetsuit." Sport Diver. N.p., 15 Jan. 2014. Web. 29 Apr. 2017. <http://www.sportdiver.com/article/news/neoprene-reborn-five-ways-to-recycle-your-wetsuit>.

Neoprene Latex at 2500 Magnification. 1959. DuPont Company Product Information Photographs (Accession 1972.341), Audiovisual Collections and Digital Initiatives Department, Hagley Museum and Library. Hagley Digital Archives. Web. 26 Apr. 2017. <http://digital.hagley.org/islandora/object/islandora%3A2224378>.

Obama: "America Must Invest in Manufacturing" -SOTU 2013. Prod. Wall Street Journal. Perf. President Barack Obama. YouTube. N.p., 12 Feb. 2013. Web. 29 Apr. 2017. <https://www.youtube.com/watch?v=TPSkwndBUpQ>.

Patagonia. "Yulex." Patagonia. N.p., 2016. Web. 22 Apr. 2017. <http://www.patagonia.com/yulex.html>.

Patagonia's New Natural Rubber Wetsuits. Prod. Patagonia. Perf. Elissa Loughman, Keri Hess, Jeff Martin, Tetsuya O'hara, Jason McCaffrey, Hub Hubbard. YouTube. Patagonia, 12 July 2016. Web. 29 Apr. 2017. <http://www.patagonia.com/yulex.html>.

The PICSIMA Method. Prod. PICSIMA. PICSIMA. Fripp Design Limited, 2016. Web. 30 Aug. 2016.

Quicksilver. "Wetsuit Guide: Thickness." Quicksilver. N.p., 2017. Web. 29 Apr. 2017. <http://www.quiksilver.com/wetsuit-thickness/>.

Rose, Karsten , and Alexander Steinbüchel. "Biodegradation of Natural Rubber and Related Compounds: Recent Insights into a Hardly Understood Catabolic Capability of Microorganisms." *Applied and Environmental Microbiology* 71.6 (2005): 2803-812. *American Society for Microbiology*. Web. 18 Apr. 2017.

Seventhwave. "Can neoprene be green or eco-friendly?" Seventhwave: New Zealand. Seventhwave Wetsuits Ltd, 2016. Web. 26 Apr. 2017. <http://www.seventhwave.co.nz/wetsuits101/Neoprene Info/Can neoprene be green or eco-friendly.html>.

Seventhwave. "Neoprene: a brief history." Seventhwave: New Zealand. Seventhwave Wetsuits Ltd, 2016. Web. 26 Apr. 2017. <http://www.seventhwave.co.nz/wetsuits101/Neoprene Info/Neoprene a brief history.html>.

Seventhwave Blog. "Did You Know? 1. Limestone neoprene vs Oil-based Neoprene." Blog post. Seventhwave - The Wetsuit Specialists. N.p., 28 May 2015. Web. 5 May 2017. <http://seventhwavenz.blogspot.com/>.

Surfing Waves. "Wetsuit Stitching." Surfing Waves. N.p., 2011. Web. 29 Apr. 2017. <http://www.surfing-waves.com/equipment/wetsuit-stitching.htm>.

"Synthesis of Thiokol Rubber." Scribd. N.p., n.d. Web. 4 May 2017. <https://www.scribd.com/doc/139110565/Synthesis-of-Thiokol-Rubber-412C>.

Thompson, Rob. Manufacturing Processes for Design Professionals. New York: Thames & Hudson, 2007. Print.

Vijetha, P., Y. Prasanna Kumar, K. Kumaraswamy, Alka Kumari, Pragati Singham, and N. Satyasree. "Comparative Studies of Natural and Synthetic Rubber." Research Journal of Pharmaceutical, Biological and Chemical Sciences (2014): 851-57. Web. 16 Mar. 2017.

Wet Suits | How It's made. Prod. How it's Made. YouTube. Science Channel, 10 Jan. 2016. Web. 26 Apr. 2017. <https://www.youtube.com/watch?v=JkqBWJslHLw>.

"Wetsuit Stitching." Surfing Waves. N.p., 2011. Web. 26 Apr. 2017. <http://www.surfing-waves.com/equipment/wetsuit-stitching.htm>.

Woodland Plastics Corporation. (2015). Understanding Thermoset Plastics. Retrieved April 14, 2016, from http://www.woodlandplastics.com/understanding-thermoset-plastics.html