SKIN-INSPIRED HYDROGEL-ELASTOMER COMPOSITE WITH APPLICATION IN A MOISTURE PERMEABLE PROSTHETIC LIMB LINER

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Recent advances in fields such as 3D printing, and biomaterials, have enabled the development of a moisture permeable prosthetic liner. This project demonstrates the feasibility of the invention by addressing the three primary areas of risk including the mechanical strength, the permeability, and the ability to manufacture. The key enabling technology which allows the liner to operate is the skin inspired hydrogel elastomer composite. The skin inspiration is reflected in the molecular arrangement of the double network of polymers which mimics collagen-elastin toughening in the natural epidermis. A custom formulation for a novel tough double network nanocomposite reinforced hydrogel was developed to improve manufacturability of the liner. The liner features this double network nanocomposite reinforced hydrogel as a permeable membrane which is reinforced on either side by perforated silicone layers manufactured by 3d printing assisted casting. Uniaxial compression tests were conducted on the individual hydrogels, as well as a representative sample of off the shelf prosthetic liners for comparison. Permeability testing was also done on the same set of materials and compared to literature values for traditional hydrogels. This work led to the manufacture of three generations of liner prototypes, with the second and third liner prototype being tested with human participants.

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PREFACE

This dissertation is the culmination of 11 years of study directed at the single aim of blurring the line between man and machine. What started as an overly broad, and ambitious goal to create the world's greatest prosthetic arm, has through the years been focused and refined into the product described here. My initial inspiration was from Dr. Todd Kuiken at the Rehabilitation Institute of Chicago. The targeted reinnervation work he was engaged in with Jesse Sullivan left an indelible mark on my mind. Many mentors along the way encouraged me to pursue this dream; first at Los Angeles Pierce College, then the University of California Berkeley, then at the University of California Los Angeles, and finally at the University of Pittsburgh. At every step of the way I have had research mentors that encouraged me and helped me to advance: Dr. Craig Meyer, Dr. Robert knight, Dr. Dwayne Simmons, Dr. Reggie Edgerton, Dr. Vijay Gupta, and Dr. David Brienza. Each one kept an open door policy with me, and only asked that I pay it forward by mentoring others, doing good work, and not giving up on my dream. I would like to thank the students that I have had the chance to mentor for all the help they have contributed to the success of this project including: Shawn O'Donnell, Mohamed Morsy, Helen Yang, Ryan McGlynn, Paul Michael, Doug Roberts, Erik McLane, and Celia Fanying Sun. I believe the results in this paper point to a novel unique way of melding man and machine into a beautiful, comfortable,

functional hybrid, and merit further research to improve, perfect, and make available to the millions of Americans living with limb loss today and in the future.

1.0 INTRODUCTION

This project addresses the long unmet need of moisture management in the prosthetic limb socket. This project was undertaken in an effort to address the engineering design topic in the field of prosthesis research with the greatest potential impact. The goal of this project is to create the world's greatest prosthetic limb. What defines greatness? That determination was the first question the project had to answer. We believe that ultimate greatness is comfort and utility to the amputee. To return the most utility and function to the amputee as possible is the greatest goal. An initial literature search was conducted to determine what the specific focus would be of this project. The search was conducted in such a way that recognized amputees as being the most authoritative individuals able to comment on what are the most important issues that need improvement in prosthetic limbs. Several papers have been reviewed which list the opinions of amputees as to which areas of prosthetic limbs are most unsatisfactory. Common among them is the almost universal dissatisfaction among amputees on some level with the current ability of their prosthetic limb to manage the moisture in their prosthesis. This point has been corroborated by surveys of prosthetists and prosthetic limb researchers as well.

1.1 MOTIVATION

Within the field of prosthetic limb research there are many popular areas of investigation. One of the most well-known areas of research is the development of advanced computerized joints that

seek to improve gait in lower limb amputees. These efforts, though noble, do little to improve the comfort of the residual limb where its attaches to the prosthesis. The prosthetic limb is a complex system. It can be thought of consisting of three major parts. One major part is the end effector, in lower limb amputees, it is a foot, and in upper limb amputees it is a hand. There is the tissue interface, which currently in lower limb amputees is most often a soft polymer sleeve placed over the residual limb for cushioning, and gripping. And lastly the third part is the supporting structures, this would be all the joints, and pylons and rigid sockets that support the weight of the body and direct it from the tissue interface to the end effector.

Historically the tissue interfaces were made of porous breathable materials such as wood, leather, and cloth, and were custom made for each individual by carving, stitching and sewing. These materials tend to be heavy, and require the use of bulky leather straps with metal buckles which add to the weight of the socket. Cloth wood and leather do have the advantage of providing better air flow and breathability to the residual limb and allow sweat to escape as vapor.

Modern prosthetic limbs no longer require the use of straps and buckles to keep it on the body. Lightweight aluminum componentry in prosthetic limbs, lightweight carbon fiber construction of end effectors, and lightweight polymer sockets have made alternative methods of attaching the prosthesis to the body possible. The most popular method of attaching these new lightweight prosthetic limbs to the body is through the use of a mild suction. An airtight seal is established around the skin of the residual limb where it is inserted into the socket. This is done by using a polymer sleeve known as a prosthetic limb liner. The materials most commonly used for prosthetic limb tissue interfaces are moisture impermeable oil based polymers such as silicone urethane, and thermoplastic elastomers. These materials repel water, and contain it

within the socket up against the skin. A prosthesis liner is the thin, pliable, polymer sleeve that is placed directly on the skin of the residual limb prior to inserting it into the prosthesis socket (Figure 1).

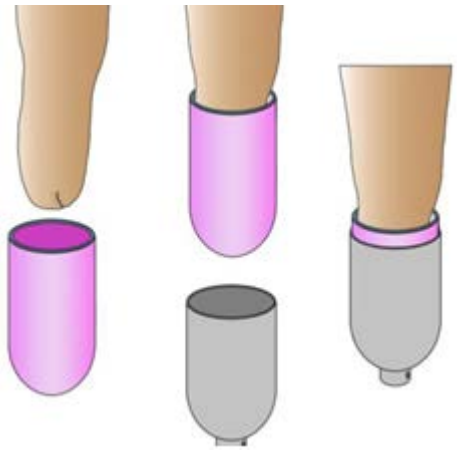


Figure 1 The liner fits over the residual limb like a sock, prior to insertion into the socket

The liner serves to provide a cushioning interface for the soft tissue to protect it from the rigid socket. The liner also provides linkage of the limb to the prosthesis. It prevents the residual limb from sliding against the inside of the socket, which can lead to tissue damage. A prosthesis socket is designed to work with many different prosthesis liners, thus the choice of liner is independent of a particular socket brand or model. In practice, several liners may be tried before a user finds one that meets their needs.

1.1.1 Excessive Moisture in the Prosthetic Limb

Excessive moisture accumulation within the prosthetic limb socket has consistently been shown to be one of the leading causes of discomfort and reduction of quality of life among people who use prosthetic limbs [1]. Although it is well and natural for the limb to sweat in response to

elevated core temperatures, during periods of exercise or increased environmental temperature, a fundamental flaw in the design of current prosthetic limbs leads to accumulation of sweat in the socket.

Current prosthesis comfort and function is reduced by the buildup of excessive moisture in the socket [1, 2]. A study in 2001 by Hagberg and Branemark surveyed 97 prostheses users and found the most common self-reported source of discomfort associated with prosthesis use that led to a reduction in quality of life was excess heat and sweating (72%), followed by skin irritation (62%) [1]. About the same time, Dillingham et. al. surveyed 78 amputees and found respondents were less satisfied with the comfort of their prosthesis (43% satisfied) than with appearance (58%), weight (58%), or ease of use (60%) [2]. The same study found 23% of the respondents also reported being “extremely” or “very” bothered by excess perspiration in the socket. Infections of the skin catalyzed by the presence of a warm, moist microclimate at the skin/liner interface is common on the residual limb [3]. Excess moisture at the interface reduces skin strength, increases friction and increases the risk for bacterial and fungal organisms to invade the tissues in contact with the socket and initiate infection [1-3].

Current liners are primarily made of homogeneous sealed sheets of solid silicone, polyurethane, or thermoplastic elastomers [4]. These materials are highly impermeable to moisture [5] and are generally thermal insulators [6]. When the residual limb sweats in response to warm weather or exercise, perspiration is unable to escape the impermeable liner. As a result, moisture accumulates leading to discomfort, impaired function and tissue damage.

Only one study was identified in the literature that examined the moisture permeability of prosthetic liners [5]. The study found that all common socket interface materials tested were essentially impermeable to moisture. Several studies reported moisture problems with liners,

with the latest being a 2010 review of the state-of-the-art in liner technology [2, 5, 7]. The bulk of the scientific literature researching prosthesis liners has focused on evaluation of commercially available products, either investigating their material properties, or examining their effects on walking performance and the ability to provide suspension [8].

Florida State University was recently awarded a 4.4 million dollar 2-year research grant from the U.S. Department of Veterans Affairs [9]. The goal of the project is to apply engineering materials not previously used in the field of prosthetics to the design of prosthetic sockets with improved comfort. The elements of the design are volume change management, temperature control, and socket environment monitoring. Dr. Chanchun Zeng, principal investigator on the project, is quoted as saying “Despite the advances made in prosthetics over the years, the socket continues to be a major source of discomfort for our amputees due to issues arising from poor fit, elevated temperatures and moisture accumulation”[9]. We are in complete agreement with this statement. However, we have taken an alternate approach to improving comfort. Dr. Zeng’s approach is to indirectly reduce moisture by active temperature control with the hope that it may reduce sweating from occurring [10]. Our approach to enhancing comfort is to directly address moisture via a socket liner system that allows moisture to pass through and dissipate away from the limb. We chose to address moisture directly. In addition, our solution for moisture control does not require powered cooling components.

1.1.2 Causes of Sweating

Sweating is caused by many factors within the body[11-13]. Most prominently, the body will sweat as a method of maintaining homeostasis of the core temperature of the body (37°C). The

evaporation of the sweat from the surface of the skin is an endothermic process which results in the loss of heat from the body. There are other factors which lead to sweating as well.

There are three broad primary undesirable effects of sweating in the socket [4, 14, 15]. The first undesirable effect is that the prosthetic limb will lose its grip on the user's residual limb (biomechanical). The second undesirable effect of excessive sweating in the socket is the mechanical weakening of the skin on the residual limb (physiological). The third undesirable effect of sweating in the socket is the proliferation of microbial organisms (biological).

The body perspires for a number of reasons [11, 12]. Sometimes we sweat when we are nervous, when we are sick, when we eat spicy food, but most of all we sweat when our body needs to cool off. Often times our bodies need to cool off due to external environmental temperatures, other times we need to cool off due to elevated metabolic activity such as immune response to illness, or energy expenditure during physical activity. The greatest predictor of perspiration is core temperature, with as little as 0.1°C difference in core temperature triggering onset of perspiration [16]. It is after all, the careful regulation of the core temperature, including the brain, and vital organs that is most important [13], also the core of the body has the smallest surface to volume ratio as compared to the extremities [17]. It is therefore understandable that the extremities, including the arms and legs are recruited to perspire as a mechanism for cooling the core through circulation of warm blood from hotter parts of the body to the cooler extremities, and there can be a considerable temperature gradient from the core the more distally you travel down the extremities with up to a 9 degree difference at the tips of the arm [18].

1.2 CURRENT SOLUTIONS

There are a few well defined methods of dealing with the problem of excessive moisture accumulation in the prosthetic limb. First of all there is the method of attempting to cool the residual limb with the goal of reducing the localized sweating reaction by the residual limb, thereby preventing any moisture accumulation from occurring within the prosthetic socket. Second of all there are approaches which attempt to remove sweat from the prosthetic limb socket after it has been excreted by the body. Third of all there are approaches which seek to prevent the limb from sweating through the application of antiperspirants or chemicals. And lastly there are approaches of simply providing an absorbent medium for the sweat to soak into which with the aim of diminishing the sensation of wetness, though the sweat has not been prevented or removed from the socket. For this discussion, we address the first two methods of dealing with sweat in the prosthetic limb: cooling and moisture removal. Prior innovation in prosthesis liner development has been driven largely by industry; and the state of the art is best represented in the patent literature. The Alpha SmartTemp (WillowWood, Columbus, Ohio) liner by WillowWood is a prosthesis liner which contains “Outlast™”. Outlast™ is crystalline powder that melts when exposed to temperatures near body temperature. The claim is that the thermal energy required to melt the crystal will result in reduced temperature on the skin, and that this in turn will lead to less perspiration. In their study of 16 participants, WillowWood found evidence to suggest that their liner resulted in less sweat [19]. In their study they examined sweat after only 30 minutes of sweating so the resulting quantities of sweat collected were very low in certain instances (<5% of one gram). Conducting the study over longer periods of time would be preferable. No strong evidence exists to suggest that the Alpha SmartTemp method of locally cooling the limb is effective at reducing sweat, or that the effect of the cooling will be relevant

over periods of time longer than 30 minutes–a fraction of the amount of time a person with limb loss can expect to wear their prosthesis in a day. The Alpha SmartTemp is a good comparison product for our invention as it addresses the problem in a novel way, is currently available in the market and has good reviews from customers.

A common misconception about sockets with cutouts in the sides is that the cutouts provide better ventilation, but this is not their purpose [20]. The purpose of the cutout areas is to direct areas of force transfer to desired areas of the residual limb while eliminating force transfer in other areas. Biodesigns, Inc. developed one example of a cutout socket in collaboration with DEKA Research and Development Corp, for the DARPA sponsored upper limb prosthesis project. The high fidelity (HI-FI) humeral or femoral interface with vector-enhanced compression and soft tissue release (VECTR) modification (Figure 2) incorporates predetermined areas of relief to direct forces to the bones for a more secure fit [21]. The purpose of the unique shape of the Hi-Fi Socket is to improve mechanical linkage of the prosthesis to the limb. Concerns are still under investigation as to whether or not this increased pressure over the bony areas of the residual limb will lead to ischemia sufficient to cause cell death or other adverse reactions [22].

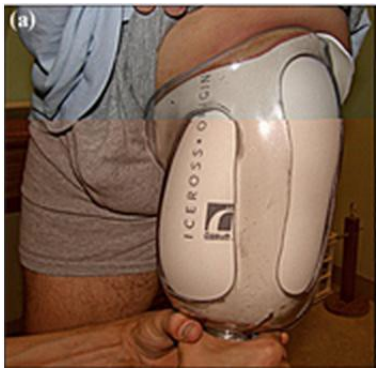


Figure 2 Biodesigns socket - No moisture can escape despite the cutouts because the liner that envelops the limb is made of impermeable silicone.

A socket liner that prevents accumulation of moisture will be more comfortable and reduce the incidence of skin irritations, infections and wounds. And, reducing moisture accumulation would reduce slippage between the prosthesis liner and the residual limb, thus increasing its functional characteristics. Users would be able to wear their prosthesis longer, more comfortably, more effectively, and without causing injury to the soft tissue of the residual limb.

One need only look at the claims made by the various manufacturers about their respective liners to understand the perpetual quandary the amputee community finds itself in with respect to selecting an appropriate prosthetic limb socket liner. Ossur (Reykjavik, Iceland), OttoBock (Duderstadt, Germany), WillowWood (Mt Sterling, Ohio), are top manufacturers which have designed prosthetic limb liners to “reduce perspiration”[23-25]. Some of the attempts have been attempts at improving fit, others have been attempts of cooling, and yet others have been to improve grip on the limb. The diversity of approaches for improving patient comfort suggest that there is no universal consensus as to the exact causes of moisture accumulation (and it is likely to be a multifactorial diverse set of causes [26]), and therefore how best to combat it. For certain folks the best answer so far is to apply cream astringents and antiperspirants [27] which can cause the skin’s pores to clog and become irritated. In the case of others the best case is to wear absorbent socks filled with silver molecules which kill bacteria and fungi which proliferate in the liner. Other techniques are to clamp onto the limb so hard that the bone inside is griped and grasped making a firmer fit in spite of slippery sweat accumulation [28]. There are approaches which have used perforated silicone liners to provide drainage points for sweat to drip out. This would theoretically solve the problem of sweat pooling excessively into the liner,

but also reduces the liners effectiveness as an airtight suction based linkage mechanism. How the liners with large holes drilled into them propose to make up for this loss of suction is still an unknown, and the consequences of it most likely are borne out by the lack of adoption we have seen with this option.

1.2.1 Previous Attempts at Cooling the Socket

Cooling the limb has been attempted in several ways. Some of the ways reported for cooling the limb involve complex systems such as battery powered thermoelectric coolers and fans[29]. Previous attempts at cooling the limb include:

Table 1 A representative sample of cooling devices

Name	Organization	Status
Aqualonix	Leto solutions	(prototype) [29]
Alpha SmartTemp	WillowWood	(commercially available) [30]
Prosthetic liner cooling system	Johns Hopkins	(research only) [31]
Evaporative Cooling and Perspiration Removal	Veteran's Administration	(research only) [32]

The most successful attempt at cooling the limb to prevent sweating has been the Alpha SmartTemp liner by Ohio WillowWood. The Alpha SmartTemp liner is designed using Outlast™ crystals in the material itself [33]. The Outlast™ company has not divulged the chemical formula of the phase change material they have included in their technology in order to facilitate the cooling effect as that is their proprietary intellectual property, but we can do a basic

thermodynamic analysis using a material which might fit based on known parameters. A quick search online reveals a few options with approximately appropriate thermodynamic properties listed, such as manganese(II) nitrate hexahydrate (MNH), or Trimethylolethane(TME) [34-36]. These materials were selected as being approximately appropriate by virtue of their melting point. The melting point of MNH is 25°C, and the melting point of TME is 29.8°C. The reason these melting points are useful for this application lays in the basic theory behind the melting of solids. As thermal energy is applied to a solid, its temperature will increase until it reaches its melting temperature. At this point the solid will continue to absorb thermal energy but will no longer increase in temperature. The thermal energy will instead be used to melt the solid and the temperature will be stabilized until the solid has completely turned into a liquid, at which point additional application of thermal energy will increase the temperature of the liquid.

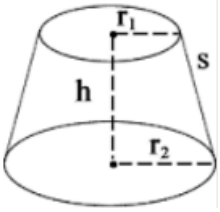
The following thermodynamic analysis reveals that the heat storage properties would quickly be exhausted at which point the material acts as a heat reservoir gradually releasing it back to the user long after the user cools. As such the ideal use case for this technology would be in short bursts of moderate activity, rather than in situations where sustained activity would be expected.

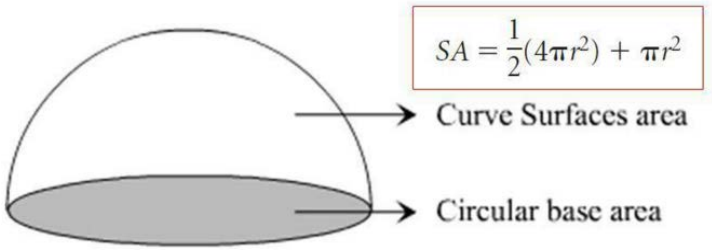
THERMODYNAMIC ANALYSIS:

A typical prosthetic liner is about half a kilo gram in weight, though that will vary on the thickness of the liner. If 10% of the liner is Outlast™ technology by weight then we can expect to find about .05kg of Outlast™ phase change material in the liner. We cannot know what phase change material is used in the liner for sure, but there are a few close candidates online which we can use as stand in place holders. Specifically I refer to Trimethylolethane (TME), which has a melting point of 29.8degres Celsius, and a heat of fusion of 218 kJ/kg, and a specific heat in

solid form of 2.75kJ/(kg*Kelvin), and in liquid form of 3.58 kJ/(kg*Kelvin) [35]. If the area of our theoretical residual limb that is in contact with the Alpha smart temp liner is 0.0762m^2[30], and we know the temp of the surface of the skin is roughly 30 degrees Celsius [19], then we get a net energy flux into the Outlast™ material of 7J/s, assuming it is uniformly dispersed within our silicone sleeve, of thickness, 1cm [37], made of silicone with a thermal conductivity of .2W/(m*K), (this is an middle of the road value for silicone)[38]. What we find is that it will take only a few minutes to warm out solid Outlast™ crystals to 29.8 degrees C, half an hour to melt them, and another few minutes for the melted liquid crystals to reach body temp if the initial temperature of the Outlast™ material was room temp (25°C).

Lateral surface **area** of a conical **frustum**: $S = \pi * (r_1 + r_2) * s = \pi * (r_1 + r_2) * \sqrt{((r_1 - r_2)^2 + h^2)}$





Where r1=3.31cm, r2=5.411cm, h=26cm, r=3.31cm

Total surface area $= 761.995\text{cm}^2$ [30]

$H = \frac{k*A*(Th-Tc)}{L}$

[39]

heat flux $= \frac{0.2W}{\text{m} * \text{K}} * [0.076\text{m}^2] * [\frac{5°\text{C}}{0.01\text{m}}]$

=7J/s = heat flux from skin through silicone into TME

Energy to warm .05kg solid TME from 25°C to 29.8°C:

$= \frac{2.75\text{kJ}}{kg*K} * 0.05\text{kgTME} * 4.8\text{K} \quad = .66\text{kJ}$

Energy to melt 0.05kg of solid TME into liquid:

$= \frac{218(\text{kJ})}{\text{kg}} * 0.05\text{kgTME} \quad = 10.9\text{kJ}$

Energy to warm 0.05kg liquid TME from 29.8°C to 31°C:

$= 7\frac{\text{J}}{\text{s}} * 3.58\frac{\text{kJ}}{\text{kg}*\text{kelvin}} * 0.05\text{kgTME} * 1.2\text{kelvin} = .228\text{kJ}$

Time needed to warm 0.05kg solid TME from 25°C to 29.8°C:

$= \frac{0.66\text{kJ}}{0.007(\text{kJ/s})} = 94.28$ seconds ~1.5mins

Time needed to melt 0.05kg of solid TME into liquid:

$= \frac{10.9\text{kJ}}{0.007(\text{kJ/s})} = 1557.14$ seconds ~ 25mins

Time needed to warm .05kg liquid TME from 29.8°C to 31°C:

$= \frac{0.228\text{kJ}}{0.007(\text{kJ/s})} = 32.57$seconds ~ ½ min

As you can see from our estimates the Alpha SmartTemp will exhaust its heat absorbing properties after about half an hour or so (Figure 3), depending upon how much Outlast™ they can mix into their silicone, and without ruining the silicones mechanical material properties. As the alpha smart temp is a proprietary product we do not know the exact materials or material specifications used. If we use values which are approximately equivalent to what we would expect to see then we can see that the heat absorbing properties of the material would quickly be exhausted in about half an hour because they attempt to achieve their gradient without an active system for removing heat.

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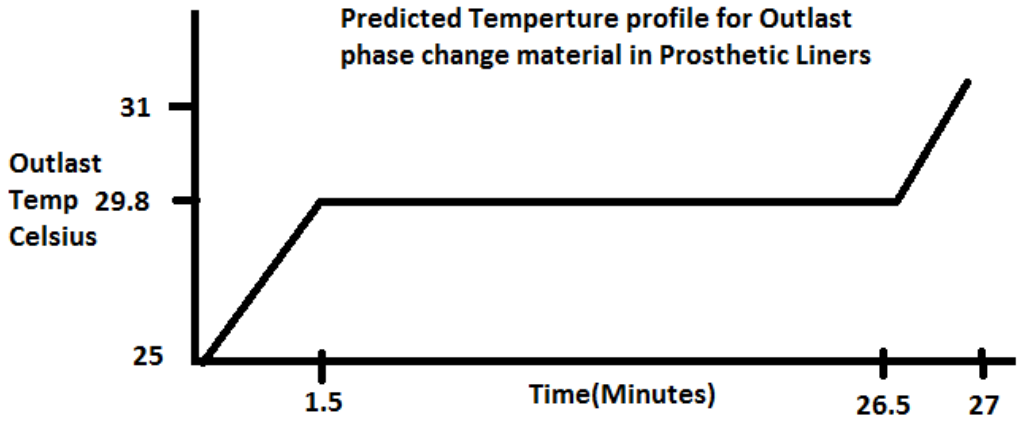


Figure 3: Predicted temperature curve for SmartTemp liner based on our model.

There are several limitations to this thermodynamic analysis, and if it were to be used to design a thermal management solution they would need to be addressed and the model improved upon. Its function here serves as an illustration of the principle with approximate results for demonstrations purposes. First of all the exact phase change material selected for the analysis is TME which is approximately appropriate, but there is no way to confirm that it is the material used in commercial prosthetic liners. Polyethylene Glycol Wax and Paraffin waxes are other materials which could have been used and which have long been studied for their phase change properties. We also do not know the exact quantity of phase change material included into the prosthetic liners. The present analysis uses a volume of 10%. This was selected as a reasonable quantity because it is low enough that it may not lead to catastrophic failure of the silicone curing process and mechanical strength properties, but s also high enough not to be negligible. Without further empirical experimentation to reverse engineer the formulation, we cannot be sure of the exact quantity of phase change material used. Another limitation of our analysis is the simplicity of the boundary conditions. In our example we assume the body is a steady source of

heat due to homeostasis which is fine, but we treat the liner as a perfectly insulated body, which does not lose heat to its surroundings. This approximation could lead to an underrepresentation of the amount of useful cooling time experienced by the end user.

The limitations of this analysis do not change the fact that the cooling effect is volume dependent. In order for the cooling through phase change materials to be more effective more mass must be used. Even if we were to assume optimal silicone mixing ratios, maximum heat absorption properties, and an ideal situation for the phase change enabled cooling liner, it would not change the fact that the basic principle of design is a mass based approach. In the extreme situation, in order to cool off the leg for a very long period of time the liners would grow to such large thicknesses and dimensions that they would end up looking like elephant legs. Although the phase change material approach may have its place, it needs a serious design review and would need to be reviewed once the actual phase change material content of the liners was established.

Part of the challenge when dealing with cooling is the fact that the cooling effect of the limb will constantly be attempting to battle the large heat source of the human body our circulatory system ensures that we will constantly be replacing any lost heat to our extremities. In light of this fact, a cooling system that is powered in some way would be recommended to overcome the limitations of the temporary cooling effect.

This once again is met with additional challenges because unlike a static mattress pad or a wheelchair cushion which is fitted to a power chair with a large battery at the ready; prosthetic limbs are designed to be light weight and can only practically manage a small battery. Another drawback to this is that there are limited options available for practical applications of cooling prosthetic limbs powered with batteries. As the body is constantly making heat, the cooling

element would constantly need to be turned on in order to cool the limb, and the battery would be quickly exhausted. Brief intermittent pulses of energy would not be sufficient to actually remove all the heat that would be generated throughout the day because our homeostasis ensures our core body temperature is maintained at 37°C through the metabolic break down of food.

1.2.2 Previous Attempts at Removing Moisture from the Socket

In contrast to attempting to prevent the moisture accumulation through the use of cooling of the residual limb, other approaches to moisture management have centered around removing moisture in the socket before it can cause negative side effects for the user. These approaches largely revolve around the use of perforated prosthetic limb liners which allow for the draining away of excess liquid moisture. The following products are representative of the moisture removal approach.

Table 2 A representative sample of moisture removing devices

Name	Organization	Status	Mechanism
Silcare Breathe	Endolite	(Commercially Available) [40]	Large perforations
SoftSkin Air	Uniprox	(Commercially Available)[41]	Small perforations
Silver Sock	Multiple	(Commercially Available) [42]	Absorbs Moisture

Moisture removal indirectly addresses all and any underlying causes of sweating, and if the rate of moisture removal can be matched to the rate of sweating no appreciable moisture accumulation is projected to take place. This would be an important factor in helping to diagnose and prevent negative aspects of hyperhidrosis. This approach assumes moisture cannot be prevented for some individuals.

1.2.3 Prior Art

There are many patents that address the need of moisture management in the prosthetic limb. The various patents take different approaches to moisture management. Some of the patents use active cooling, others use perforated prosthetic limbs, and others propose the use of membranes to draw out moisture.

Companies with the most significant liner patent portfolios include Ottobock, Ossur, WillowWood and Alps. Ottobock has a patent on a system of reducing moisture in the liner through vacuum and Teflon mesh; however a close analysis of the patent reveals the solution is infeasible. The patents that use this mechanism would fail for the following reason: moisture in the prosthetic limb is present as a liquid rather than as a vapor. The patents propose as a mechanism of moisture removal to use expanded PTFE sheet membranes, also known commercially by the brand name Gore-Tex. The problem with using Gore-Tex is that Gore-Tex allows only water vapor to pass through as a gas, but not as a liquid. Owing to the fact that sweat exists in the liner as a liquid, it would be unable to remove moisture effectively. Ossur has patented variations on the silicone liner by creating microsphere mixture composites. A working prototype is not required to file a patent, and thus far very little of the prior art found in the

patent literature related to moisture management has been introduced in the market for the benefit of individuals with limb loss.

Table 3 Examples of prior art attempting to solve the issue of moisture in the prosthetic limb

Title	Appl.No.:	Pub. No.:
Multi-Layered Polymeric Prosthetic Liner	12/407362	US 2009/0240344 A1
System and Method for Polymeric Prosthetic Liner Perspiration Removal	14/214788	US 2014/0277585 A1
Adjustable Prosthesis	12/769387	US 8480759 B2
Prosthetic Socket Apparatus and Systems	13/864675	US 2013/0274896 A1
Osmotic Membrane and Vacuum System for Artificial Limb	11/044133	US 6974484 B2
Lining Material for Use With Prosthetic ad Similar Devices and Method for Making and Using Same	123744	5480455
Orthopedic Cushion and Method for Production Thereof	13/140512	US 8999428 B2
Vacuum-Assisted Liner System		US 8308815 B2
Liner for Prosthetic and orthopedic systems	12/219953	US 8308817 B2
Fabric-Covered Polymeric Prosthetic Liner	13/078710	US 2012/0253475 A1
Hydrogel of (Semi) Interpenetrating Network Structure and Process for producing the same	10/513070	US 2005/0147685 A1

1.3 DESIGN APPROACH

The above sections outline the problem of moisture accumulation in the prosthetic socket, its extent, its causes, its negative effects on people, and previous attempts to solve the problem. This section outlines which design tools methods and approaches this project has made use of to solve this problem.

The design approach we have chosen to implement is a hybrid of theories from three different fields. Bioengineering design approach is characterized by treating the body as a system

and taking into account the needs of the body such that device developed should work to accommodate to the body through the use of specially designed biomaterials. Systems engineering is an organized method of ensuring the successful development of a system. Participatory action design stresses end user involvement in the design process.

1.3.1 Bioengineering

All rehabilitation science can be thought of occurring at the level of the cell, because our bodies are composed of cells [43]. The field of bioengineering has long faced the problem of interfacing manmade materials with the natural body, both internally and externally and consequently a rich library of biocompatible materials exists with a variety of biocompatible properties such as mechanical behavior and permeability to moisture. This project makes use of advanced biomaterials from the field of bioengineering known as super tough hydrogels. Where appropriate we have highlighted bioengineering influences and inspiration for the design we have chosen. This includes using biological systems for inspiration. This is known as biomimetic design principle. To apply this principle we first posed the question: how has nature solved this problem before? The closest thing we could find in nature to approximate the process which we would like to mimic is the sweating of skin. Where possible we have attempted to use skin as an inspiration for the design of the moisture management solution.

1.3.2 Systems Engineering

We have chosen to use the organizational structure and terminology defined in systems engineering for this design project as the prosthetic limb can be viewed as a complex technical

project with multiple parts which need to be separately designed and integrated to form the whole functional unit. Keeping track of the various design changes across the components which form the device to be developed requires a systematic method of documentation known as configuration management.

Further considerations were ease of use of the end user, and ease of maintenance by the practitioner. Using this organized approach we have concluded that the major design activities of this project should include addressing the major areas of functional risk associated with the success of the project [44]. For this project the main areas of functional risk includes the mechanical stability of the design. This is because the prosthetic limb must first be able to withstand the required forces of standing and walking. Another major area of risk identified is the ability of the design to manage moisture effectively. This is because after mechanical stability the second major area of effectiveness is how effectively the design can prevent moisture build up, because that is the goal of this project. And another area of risk is the feasibility of the design; this would include both being able to manufacture the device and its practicality in the real world. These areas of risk helped us to select the major objectives of this project. The development process we used is a cyclic approach (Figure 4) typical of a design process where the boundary conditions of the solution are not well understood at the outset of the effort.

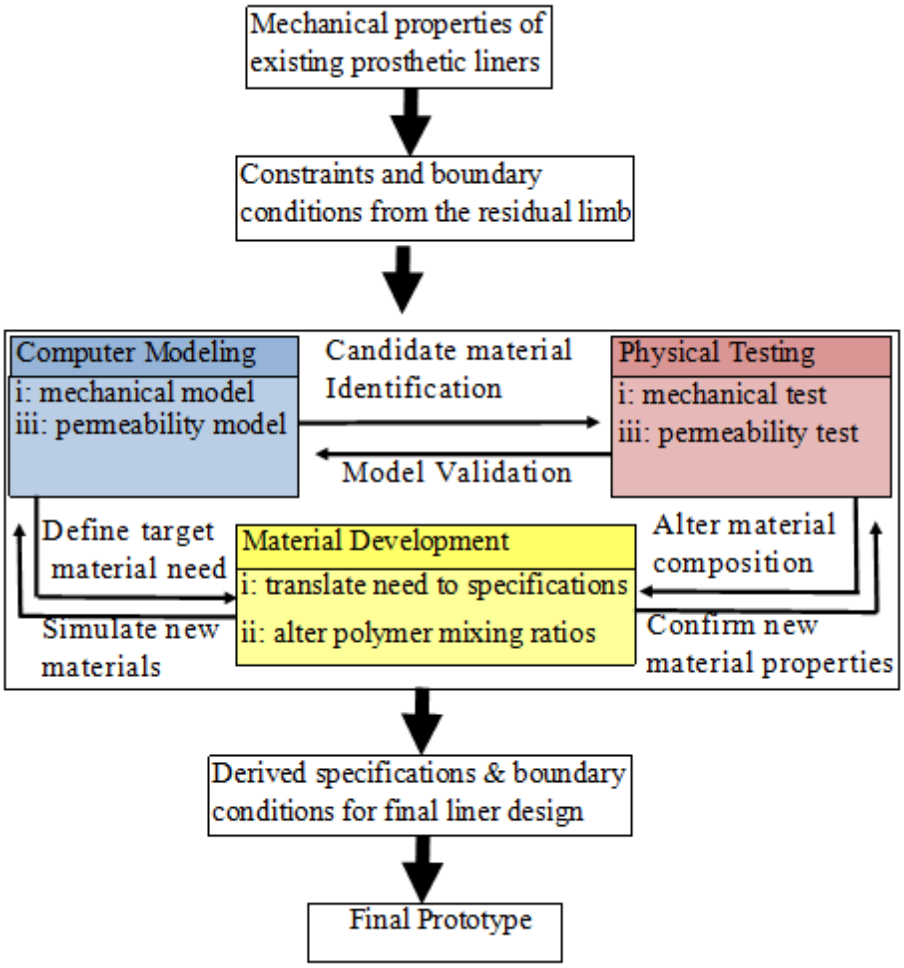


Figure 4 Development cycle

1.3.3 Participatory Action Design

In the field of rehabilitation science user adoption is of critical importance. More often than not, unlike the medical field in which patients vie to use the best therapeutic available, there are often multiple competing assistive technologies that the end user may select from, each with its own corresponding strengths and weaknesses. In order to maximize the success of the assistive

technology, participatory action design may be used to gauge user feedback and requirements. Participatory action design dictates that development projects should include stakeholder at every step of design including inception [45]. For this purpose we have conducted focus groups prior to the conceptual design and preliminary design stages, and included them in evaluation of the prototype as well.

1.4 OBJECTIVES

The development of a prosthetic limb that manages moisture perfectly is a problem that is most likely multifaceted and complex with limitless potential for ever increasing realism and comfort as it asymptotically approaches the feeling of a natural limb. We limited our current project to the following aims. Our first aim was to establish clear user needs and requirments. Our second aim was to characterize the mechanical strength of our design. The third aim was to establish the moisture permeability of our design. The fourth aim was to build and test prototypes of our design.

1.4.1 Aim 1: Establish Stakeholders' Requirements, and Conceptual Design

In keeping with the systems engineering design approach and the principles of participatory action design, our first task was to compile a comprehensive set of stakeholder requirements. All the requirements from all the stakeholders were compiled into the Stakeholder's Requirements Document (SRD). The SRD has design specifications, which list out as target design metrics translated from the needs and requirements of all stake holders in a way that engineers can use to

develop measures of effectiveness for the performance of the final products. The needs and requirements were collected through three mechanisms: literature search, user interviews, and analysis.

After considering all the available needs and requirments, as well as the available solution space using bioeigneering, we developed a conceptul design to address the problem

1.4.2 Aim 2: Characterize Mechanical Behavior of Design

The environment inside of the prosthetic limb is subject to large forces and pressures recorded during walking to be around 95kPa [46]. In addition to the strength of the final product, the device must be readily manufacturable from a physical point of view. The device must be capable of being produced and used without failing physically, as prosthetic limbs are principally devices of force redistribution. They are responsible for redirecting forces from the ground to the user's residual limb without failing. At a minimum the mechanical evaluation of the product should include compression testing which approximates the compressive forces seen in the prosthetic limb during normal operating conditions such as standing and walking. The prosthetic limb is by definition principally a device which is designed to transfer force from the ground to the body under compression.

1.4.3 Aim 3: Characterize Permeability Behavior of Design

After the strength and manufacturability of the device is established we address the other major performance measure which is the ability of the device to manage moisture to a clinically relevant degree. It is not enough that the device reduce moisture accumulation to statistically

significant degree but also to a clinically relevant degree. Clinical relevance was established in aim 1, through a combination of literature searches, user interviews and analysis.

1.4.4 Aim 4: Build and Test Prototype of Design Concept

The feasibility of the device design should be tested. As a systems engineering driven project, the development process is set up to optimize components of the complex system with well-defined boundary conditions then, during system integration, combine them to produce a functional prototype. We did establish the feasibility of the prototype with the help of end user participation. The first half of this aim will involve developing a method of manufacturing the prototype and the second half will include testing the prototype with human participants.

This document is organized so that each aim is contained in its own chapter. Chapter 2 discusses the collection of all the needs and requirments of the systems we have developed. Chapter 3 discusses the mechanical strength charachterization of the design. Chapter 4 Discusses the benchtop permeability testing of the design. Chapter 5 discusses the human subject assisted evaluation of the design. In chapters 2-5 a organization of introduction, methods, results and discussion is used. Chapter 6 discussess conlcusions and future work.

2.0 NEEDS AND REQUIREMENTS, AND CONCEPTUAL DESIGN

As shown in Figure 5 below, the first step to a development project is to clearly establish what the boundary conditions are and physical design constraints of your solution. These together with all the needs and requirements of the users are populated into the System Requirements Document. This need not be a literal physical document, but it refers to the compiled set of requirements in the systems engineering jargon.

1) Need	2) Conceptual Design	3) Preliminary Design	4) Detailed Design and Development	5) Construction or Production

Figure 5 Product development phases

Once all of the stakeholders are identified, a plan must be made to collect all their input. Many of these design criteria can be found online by doing literature searches. Others must be obtained from interviews with stakeholders. In instances when the data has not been directly reported, analysis must be done to approximate the requirement so that the design team can develop the device accordingly. Our plan for populating the SRD was three part. First we conducted a literature search to investigate the needs and requirements of the device from sources readily available online; these include well published databases from stakeholders such as insurance providers. Second, focus groups were conducted to ask the end users what their needs and requirements are for the device. This is critical because end users do not typically

report their needs and requirements online so they must be asked directly. After the needs and requirments were collected theconceptual design was done.

2.1 INTRODUCTION

2.1.1 Identifying Stakeholders

The stakeholders can be thought of as all the people connected to the project whose approval is required for a successful product adoption by the end user. The most immediately obvious stakeholder is the end user himself who must be satisfied with the final product enough to use it. Without that, the development project is a failure. The list of stakeholders grows as one begins to consider all people required to deliver, manufacture, sell, transport, dispose of, repair, service, pay for, and market the device. While some stakeholders are more influential than others, all should be considered to the extent that their involvement warrants. At this stage of development the most critical stakeholders are the end users themselves, the practitioners who provide the device and the payors who reimburse for the device.

Table 4 Stakeholders and information needed

Stakeholders:	Information Needed:
Manufacturers	manufacturability, commercially available materials, scalability
Clinicians	demand, complications, indications & contraindications, expected outcomes, existing alternatives
END USERS	comfort, use, triggers for sweating, consequences of sweating, current coping mechanisms, acceptable cost, quantity of sweat, durability
Insurers	cost coverage, product reimbursement amounts, product categorization

2.2 METHODS

2.2.1 Information Search for System Requirements

We conducted a search online to establish some of the needs and requirements from stakeholders such as insurance providers. We used publicly available databases from the Center for Medicare and Medicaid Services. Our goal was to plan for our device to be manufactured within the limitations of the reimbursement system for the United States. Other stakeholders with information online included prosthetic manufacturers. We also looked at bioengineering literature to idenftify materials and methods wich could enable a moisture management.

2.2.2 Focus Groups

Focus groups were conducted in Honolulu Hawaii and Pittsburgh Pennsylvania with lower limb amputees to identify qualitative design criteria that should be considered during the design process. The focus groups provided good design information which could not be obtained through other means.

The collection of end user need was accomplished in this study through a mixed interview/focus group qualitative data collection study. An application was submitted to the Institutional Review Board (IRB) at the University of Pittsburgh. As this study did not collect any personally identifiable information about the participants the IRB cleared the study as exempt.

Climate and temperature are considered to be important factors contributing to the amount of sweating experienced by prosthetic users. For this reason, data collection sites in cool climates as

well as in warm climates within the United States were considered. Pittsburgh PA, the location of our university, was the location of the cool climate data collection as it is located in a region of the United States which experiences large amounts of annual snow fall.

A total of four prosthetics clinics were contacted with requests for cooperation in temperate climates within the United States. The sites were selected using climate data from city-data.com using a combination of hottest summers, warmest average annual temperatures, or most humid climates. Of the four sites contacted, one site was in Florida, one site was in Louisiana, one site was in California, and one site was in Hawaii. Ultimately only Advanced P&O of the Pacific, Inc. located in Honolulu Hawaii agreed to collaborate with us and assist with patient recruitment as well as provide the space for the interview. Recruitment was done using posted flyers in prosthetics clinics. Eligibility for participation was at least 18 years of age and having experience using prosthesis gel liners. As a token of thanks, participants were given a gift card to Target worth 10 dollars.

Interviews and focus groups were done in a private setting and all conversations were audio recorded. Recorded conversations were then transcribed into Microsoft Word for analysis. No personally identifiable information except for sex and age group was collected. For the purpose of transcription, pseudonyms were created. The lone participant in Honolulu was codified as “P”. In Pittsburgh the participants were codified as “P1”, “P2”, and “P3”. In both sites the facilitator was codified as “F”. Using the codes listed below a directed content analysis approach was used to analyze the data [47]. The codes (Table 6) were derived before and during the data analysis. Directed analysis was chosen because the engineers had preformulated specific questions they wanted to get answered prior to the commencement of the data collection (see Table 4).

These involved parameters such as comfort, stability, texture, and cause of sweating, which are all critical design parameters they would need for the next phase of development, the preliminary design phase Table 5.

Table 5 Questions for focus goup participants

Question#1: “How has your experience been with using prosthetic liners?” Question #2: “It seems that when you have too much sweat it affects the linkage to the limb? Question #3: “Did you have fungus problems when beginning to use the liner?” Question #4 “Have you ever experienced pooling of sweat in your liner?” Question #5: “Have you ever placed a wicking material in the liner suck as a sock?” Question#6: “Is there specifically different times when you sweat more in your liner?” Question#7: “What would you say is your main complaint when using your liner in regard to moisture or any other topic?”

Four participants were interviewed across both sites. In Hawaii (site1) one female middle aged participant was interviewed. In Pennsylvania (site2) two middle aged men, and one senior man participated in a focus group.

Table 6 Code book for qualitative analysis

Code	**Meaning**
Comfort	Expected comfort of current or future interfaces
Trigger	Related to the triggers which cause excessive sweating
Consequence	Consequences of excessive moisture accumulation within the prosthetic socket
Coping	When excessive sweating occurs within the prosthetic socket what are the coping mechanisms or skills used?
Cost	Related to how much should a prosthesis with this interface cost
Quantity	Related to quantity of sweat
Durability	Related to expected durability of interfaces

2.3 RESULTS

2.3.1 Information Search Results

We determined the target price range for manufacture after considering the reimbursement rates from the website for Center for Medicare and Medicaid Services [48]. An understanding of stakeholder requirements and the supply chain, as well as available documents online helped us to determine our target manufacturing cost. The weight of any devices used as part of a prosthetic limb must be kept low. Some devices used for the cooling of the socket or the removal of sweat feature complex systems of tubes and pumps and batteries [29]. Our design requirement for weight is that the solution not exceed the weight of currently used prosthetic limbs. Space too is an important requirement for prosthetic limbs. Our design goal for the solution is to not exceed the space currently used by the prosthetic limb. Cost of the solution should not exceed the cost of current prosthetic limbs. Our target design metric for cost is that the solution should be covered by health insurance. This necessarily limits the physical conformation of the solution to match existing componentry so that it can be claimed under current insurance reimbursement codes. Our measure of effectiveness for cost is that the solution be covered. It would be considered a failing to have a solution that is prohibitively expensive, and not covered by insurance.

The desired solution therefore must not increase the weight of a prosthetic limb, must not increase the bulk of a current prosthetic limb, must be covered by insurance, and must be affordable. A promising form of providing a gradient to the liner system was discovered. Vacuum pressure pumps (Table 7) are devices which are used to improve linkage of the prosthesis to the body [24, 49]. The prosthetic liner concept is considered an FDA class 1 device. This reduces the number of regulatory constraints on the design of our device greatly.

Table 7 List of existing vacuum pumps for prosthesis use

Pump Brand Name	**Reported Vacuum Pressure Range : (-inches Hg)**	**Company**
Limb Logic	8-20	WillowWood
Edison™ Adaptive Vacuum Suspension	6-20	Ortho Care Innovations
Harmony P3	15-25	Ottobock
V-Hold	13-21.3	Innovative Neurotronics

In addition to providing information on the regulatory, and insurance aspects of the design constraints, and existing vacuum pumps, our information search in the field of bioengineering also hydrogels as an ideal material candidate. Basic hydrogel properties are described in this section for convenience as much of the technical information is used in later sections.

Hydrogels are fascinating materials which are currently the subject of much research and investigation in the fields of bioengineering, medicine, regenerative medicine, drug delivery, material science, chemistry and others [50]. At their core hydrogels are nothing more than polymers which have been swollen with water due to the hydrophilic nature of the polymer chains [51]. Hydrogels are both naturally occurring in nature as well as synthesized in the lab by scientists looking to investigate materials with properties closer to the chemistry of the body.

Hydrogels have been around for a very long time. Hydrogels are polymers of hydrophilic chains that swell with water. One example of a double network hydrogel found in nature is the dermis. The dermis of the skin in people is made of collagen and elastin network of polymer chains. In the case of the dermis the polymers are peptides that form the proteins that make the fibers. Collagen is very stiff, and inelastic, providing tensile strength. Elastin on the other hand is elastic and stretchy providing flexibility and extension.

We have endeavored to create an analogous material composite which mimics this resilient double network composition. Our tough double network hydrogel nicknamed "Aquagel" started out initially as being an adaptation directly from Jian Ping Gong's work on PAMPS/PAAMS double network hydrogel. In the PAMPS/PAAMS hydrogel there is a similar double network arrangement as in the dermis. In the case of PAMPS/ PAAMS, PAMPS, is a rigid brittle hydrogel, whereas PAAMS is a soft, highly extensible hydrogel. To understand a polymer first we must define the term monomer. A monomer is a reactive molecule, generally with two active sites for bonding. Common examples of monomers are bisphenol A, ethylene, and siloxane. When these monomers are bonded together in long chains end to end they become polymers. In the case of the monomers we just mentioned they become Polyacrylic (eyeglass lenses), Polyethylene (soda bottle plastic), and Lotrificon A (contact lenses) [52-54]. In addition to simply forming long chains the monomers may be cross-linked together, requiring the use of additional reagents known as crosslinkers. Crosslinkers provide a mechanism for bonding chains together so that rather than having a large collection of linear chains (like a bowl of spaghetti) you get a branching or cross-linked network (like a spider web). The monomers can also be modified by attaching functional groups to them which can modify their properties in a host of ways such as altering their hydrophobicity.

Hydrogels are a class of polymers which are distinguished by their capacity to absorb large amounts of water. Hydrogels are both naturally occurring (as is the case with hyaluronic acid found in cartilage), as well as synthetic (as with Lotrificon A) which can hold up to 24% water[55]. This stands in stark contrast to the materials currently being used as epidermis interfaces on the surface of the residual limb in prosthetic sockets. Current materials in this role are silicone, urethane, and thermoplastic elastomers. None of these materials are moisture

permeable and trap sweat from the residual limb against the skin which results in many problems for the user[56, 57].

Hydrogels are distinguished from other polymers in that their polymer chains are hydrophilic. The hydrophilic nature of the gels causes them to swell with water until they are fully saturated. The degree of saturation is related to the amount of crosslinking which has been used [58]. More crosslinking results in a lower water content and less crosslinking in higher water content. Hydrogels with more crosslinking become more brittle and firm, hydrogels with less crosslinking are softer and more gelatinous[58]. Classically hydrogels have been plagued by poor material mechanical strength. For this reason they have been used in applications requiring little resilience, such as in research settings serving as 3D tissue scaffolds for cultivating artificial tissues or injectable targeted drug delivery[59, 60]. In order to make the hydrogels firm enough to serve a tissue scaffold, a hydrogel will likely contain a greater degree of crosslinking than a hydrogel soft enough for injection which would contain fewer crosslinks. Softer hydrogels contain more water.

The moisture permeability of gels is what allows them to be swollen with water. However, without establishing a moisture gradient or pressure gradient the moisture will swell the gel only to equilibrium then it will no longer swell or absorb moisture, therefore the maximum water that enters the gel is predetermined by the physical volume of the initial gel, the chemical formula and degree of crosslinking.

The hydrogels investigated for use in the prosthetic liner are known as supertough hydrogels. Supertough hydrogels are a recent development in the field of materials science research, unlike normal hydrogels, super tough hydrogels feature improved mechanical strength characteristics coupled with high water content [61]. Previously hydrogels with large water

contents were weak and brittle. There are many ways researchers have used to impart the gels with these enhanced mechanical characteristics. There are sliplink hydrogels (which make use of clever molecule entanglement, but are difficult to manufacture), nanocomposite hydrogels (lower on the strength end compared to the others), homogeneous hydrogels (strengthened by their highly ordered molecular structure), and others [62]. We have focused on one class of super tough hydrogels known as double network hydrogels (DN gels). We selected DN gels from the list of new tough hydrogels for their ease of manufacture, low cost, and superior mechanical characteristics.

The exact hydrogel we are investigating for our application is the DN gel known as PAMP/PAAM gel. It is named this way because it is made from two separate types monomers, the first being 2-acrylamido-2-methylpropane sulfonic acid (PAMP), and the second being acrylamide (PAAM) [62]. This gel is much stronger, tougher and more resilient than traditional hydrogels. That is its key enabling feature. It would have been impossible to use traditional hydrogels for any weight bearing or load bearing application such as a prosthetic limb where the user is putting their full weight onto it with every step they take. The new hydrogels are able to withstand greater forces and are appropriate for this application; together with their moisture permeability they offer excellent potential for solving the long standing problem of excessive moisture in the socket.

DN gels are tougher than normal gels due to their independent network entanglement [62]. The two interpenetrating cross-linked polymer networks work together to result in a toughened hydrogel. To understand how the molecular structure is arranged, and how it imparts its strength it would be helpful to walk through the manufacture process.

The manufacture of these gels is a two stage process. First a monomer solution of PAMPS is prepared together with a crosslinking agent N,N'-Methylenebisacrylamide (MBAA), and photoinitiator 2-oxoglutaric acid. After 6 hours of UV curing by free radical polymerization we are left with a clear brittle gel with high water content. This fragile brittle gel is then soaked in a second monomer solution of acrylamide, more MBAA crosslinker and more photoinitiator for 24 hours under agitation. During this time the small acrylamide monomers are able to diffuse their way into the first brittle hydrogel, infiltrating it, and causing it to absorb more water. Once the gel is fully impregnated with the second monomer it is once again cured under UV light and the second network of polyacrylamide is formed in and around the original PAMPS structure[63].

Alone PAMPS is a brittle and weak hydrogel. Alone polyacrylamide is an elastic but weak hydrogel. When cured together in this independent interpenetrating network, they work synergistically to exhibit enhanced mechanical performance and strength as in Figure 6 below. This allows hydrogels with high water contents to be tougher than before. This can be thought of as being similar to epidermal skin tissue which is a combination of rigid collagen fibers and elastic elastin fibers that work together to make a tough tissue.

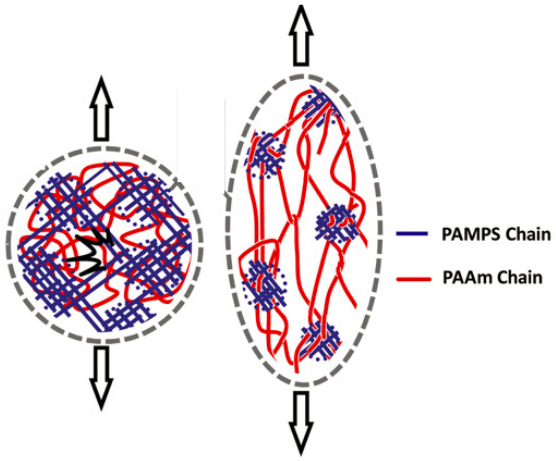


Figure 6 Illustration showing the toughening mechanism of double network hydrogels [62]

The mechanical strength of the DN PAMPS/PAAMS gel is its most important characteristic. The reagents used to make it are very cheap. The technology required in the lab to produce it is very minimal, only glass containers and ultraviolet lights are needed. The protocol is simple to follow and produces reliable results. Cleaning up the instruments is easy because the hydrogel makes use of water based chemistry so no toxic organic solvents are used. No flammable solvents are used. The final DN gel has strength characteristics similar to silicones thermoplastic elastomers and urethanes already in use as prosthetic liners. Due to the novelty of this material many of the final material properties of the material are as yet unknown. While hydrogels are permeable, and permeability results reported would be satisfactory when addressing single network hydrogels, it is still unpublished in any journal what the exact material permeability would be for the PAMP/PAAM DN gel. We are the first group investigating this property specifically for an application like this. As the PAMP/PAAM DN gel is distinguished primarily for its excellent strength characteristics, the research being done on it has focus on that aspect and little to no research has been done to report the permeability

coefficients as has been done for other older hydrogels. That said, given what we know about the swelling behavior of the gel, and the water content of the gel and comparing that to other previously measured hydrogels, we project that the permeability of this gel are acceptable for this application [64].

One important draw back is that is rather difficult to glue the water based gel to the silicone based liner. The two materials repel each other so it may be necessary to pursue covalent bonding surface treatments which could significantly delay the project [65]. Another con is that for the permeability we desire it would be difficult to manufacture gels that are thin enough for our application. Another con is that for the hydrogels have the propensity to dry out if not stored in a sealed container, similar to soft contact lenses. Another con is that the hydrogels have the tendency to absorb more than just pure water and my absorb bacteria and other pathogens. Another con is that the material may not have as long a service life as compared to average silicone liners. Another con is that the gel takes time to prepare and must go through a two stage process which can take up to 48 hours [63]. That is significantly longer than silicone curing time which is as little as 2 hours.

2.3.2 Focus Group Results

In Hawaii only one participant was available to participate in the focus group, so it would more acutrratly be called an interview or directed discussion. In Pittsburgh the remaining partipants were involved in a group discussion nor focus group. Over the course of the interviews, and focus groups we asked them if they think that simply cooling the skin on their leg would prevent sweating. They have said no and that sweating is a problem which is also caused by hot days and physical activity, and not simply by an insulated residual limb. Users indicated that they would

be open to trying new technologies provided the performance was improved over their current standard of care.

Table 8 Examples of transcript excerpts from focus group sessions

Example Transcript Excerpt from Honolulu (Site1): F "What would you say is your main complaint in using the liner in regard to moisture or any other topic." P "Just that it led to the feeling of losing full contact and I don't like that."
Example Transcript Excerpt from Pittsburgh (Site2): F "Have you ever felt that there was a pool of sweat, where if you inverted it you would get some drops out." P3 "Yes" P2 "Yes" P1 "Absolutely" P2 "I have taken my liner off a couple times and there's like a half a cup of sweat in there."

Comfort: Factors affecting liner comfort included mechanical compliance of the interface, fit of the socket following weight loss or limb atrophy, slippage of the prosthesis about the residual limb, and lubrication. Different types of materials and cloths may be used as long as they do not result in increased friction and irritation of the residual limb. All participants across both sites affirmatively stated that they would anticipate people in general would tolerate greater interface care requirements for more complex prosthetic liners if they provided improved comfort.

Trigger: All participants said both increase in physical activity as well as increase in climate temperature led to an increase in sweating into the prosthetic socket. Participant P at site1, and participants P1, and P2 at site 2 stated that warmer climates rather than physical activity contributed more greatly to their sweating into the liner.

Consequence: All participants at both sites stated that the greatest problem related to the excessive accumulation of sweat was the loss of a secure linkage to the prosthetic limb. This led

to feelings of fear, loss of balance, and unwanted movement of the prosthetic limb. Excessive pooling of sweat in the liner was also deemed to result in slippage of the limb inside to the socket leading to soft tissue irritation and blisters.

Coping: P2 at site2 stated that his limb rotated inside the prosthetic liner, but that the pin lock suspension mechanism allowed him to easily reposition his leg. Participant P1 stated he always tried to carry a towel with him in order to dry off his socket. Participants P1 and P3 at site 2 stated that they would need to physically remove the socket to allow it to dry and get relief from excessive moisture, with P3 further indicating public restrooms as a location to do this.

Cost: All participants at site 2 reached consensus that future interfaces should be covered by insurance and they should not cost in excess of what current liners are valued.

Quantity: All participants at both sites reported significant pooling of sweat in the prosthetic socket. Participant "P" at site1 (Honolulu HI) reported a few table spoons of sweat. Participant P2 at site2 reported half a cup of sweat.

Durability: At site2, all participants reached consensus that a conventional prosthetic should last at least a year to be deemed satisfactory. All participants at site2 agreed that a prosthetic interface which lasts half as long, but which costs half as much, would also be acceptable. P1, who used hand sanitizer as a lubricant, reported liners lasting short of six months. P2, who reported using Vaseline as a lubricant, reported no cracking in the interface but did experience delamination of the interface layers.

2.3.3 Population of the Stakeholder's Requirements Document

We compiled the user needs and requirements into the SRD. We chose to show this information in a number of ways. The user needs and requirements collected have been translated into a list of preliminary design metrics for use by rehabilitation engineers (Table 9).

Table 9: Preliminary engineering design metrics

1	The prosthetic interface should provide at least one year of normal use, although a cheaper, less durable liner would also be acceptable.
2	The primary measure of effectiveness (MOE) of a moisture permeable prosthetic interface should be its ability to improve linkage between the residual limb and the prosthetic socket.
3	The out of pocket cost for the end user should not exceed the cost of currently available products even in spite of the improved outcomes.
4	The product needs to meet the requirements necessary for it to be covered by insurance. The published ceiling and floor prices for Medicare/Medicaid reimbursement for similar products are $829 and $476.
5	A composite of several materials touching the skin would be acceptable as long as it does not result in increased skin irritation.
6	Over the course of a day the interface should remove anywhere from 30mL to 120mL of sweat.

2.4 CONCEPTUAL DESIGN

After considering all of the requirements we set to work investigating possible solutions to the problem. It was early on established through a consideration of preexisting solutions, and restriction of the design space, that the most optimal product to design would be a moisture permeable prosthetic liner. The requirement for this solution to work would be to identify a novel

material able to withstand the forces inside the socket as well as being permeable enough to remove moisture. Given the information serch results on hydrogels, we decided that the best solution would be a moisture permeable prosthetic limb liner which is enabled through the use of a thin moisture permeable tough hydrogel membrane (Figure 7). The major risk factors related to this approach are the strength of the hydrogel membrane, its permeability, and how to incorporate it into a prosthetic liner.

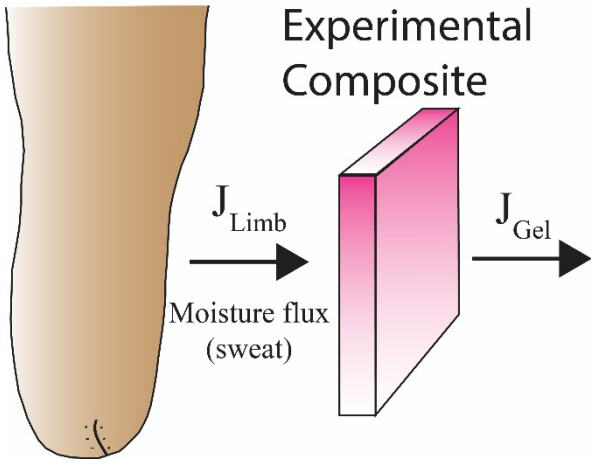


Figure 7 Basic concept, moisture permeable composite liner

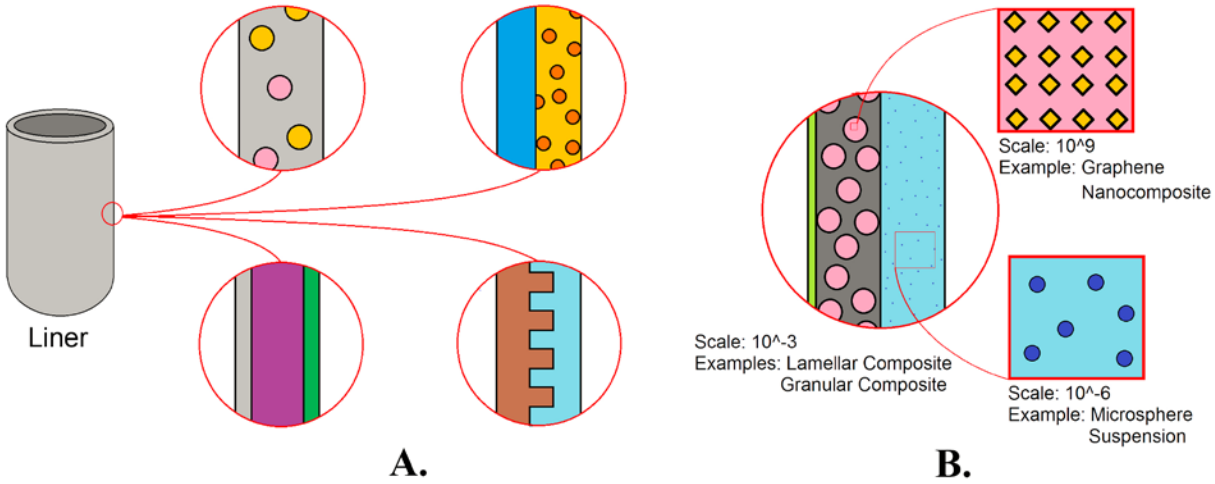


Figure 8 Variety of composite designs

The design space for the moisture permeable prosthetic limb liner is large. Within the traditionally 1cm thick uniform thickness of an average prosthetic liner, there are many opportunities to innovate. Figure 8 shows a variety of composites that are possible. Figure 8A starting from the lower left hand circle going clock wise shows: 1) laminar composite, 2) granular composite, 3) mixed laminar granular composite, 4) interlocking composite. All the composites in Figure 8A are macroscale composites, which means the various layers are on the scale of centimeters and millimeters. In Figure 8B we can see smaller scale composites which are also possible. Shown in Figure 8B are thin membrane laminar composites, nano composites and micro composites. Micro scale composites include the suspension of functional microspheres such as are used by Alpha SmartTemp which uses Outlast™ microsphere suspensions. Nano composites would be something along the lines of inclusion of graphene, clay or gold nanoparticles for improved strength. One popular clay option is Laponite XLG, which is a Nano-sized clay commonly used in cosmetics.

Understanding the well-known moisture permeability of hydrogels under pressure, and combining it with the common use of vacuum linkage systems for prosthetic limbs, led us to design the Aquapore Tissue Interface. The Aquapore T.I. is our name for the product platform of the tough hydrogel-elastomer composite enabled moisture permeable prosthetic liners.

A comprehensive overview of the product platform and the initial embodiment of such that we chose to investigate is depicted in Figure 9.

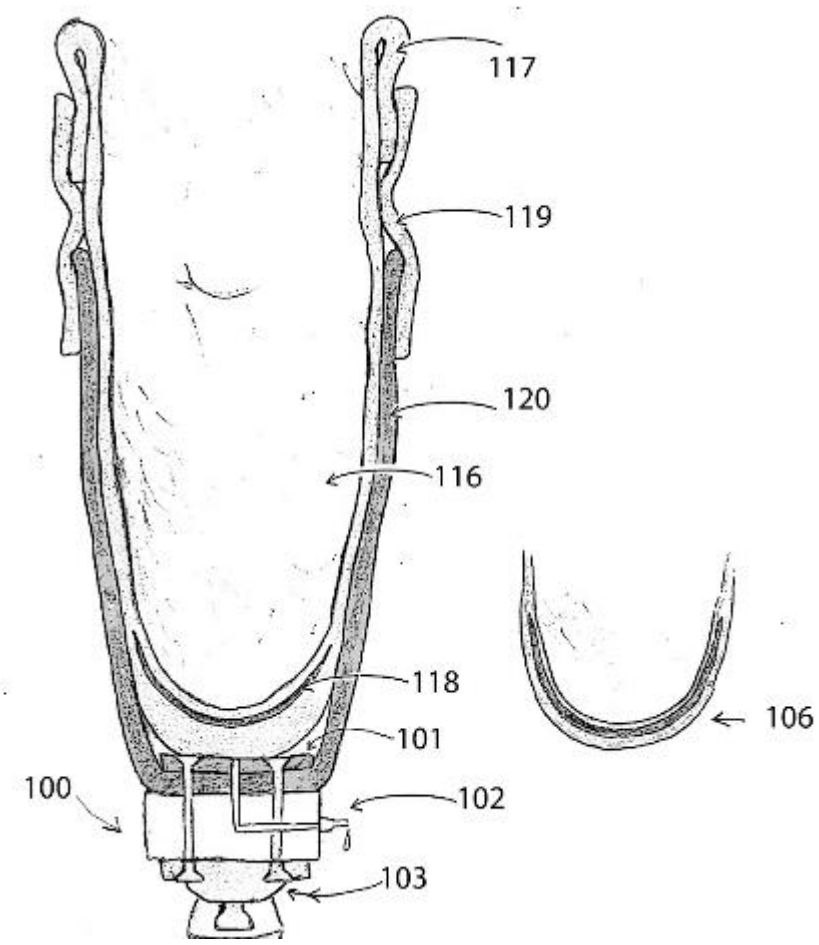


Figure 9 Rendition of moisture permeable prosthetic liner system

Figure 9 depicts one embodiment of the Aquapore T.I. concept. In Figure 9 we can see 117 which is the moisture permeable prosthetic liner. Included in 117 is 118, a thin moisture permeable hydrogel membrane, which is included in the distal end of the liner as a hydrogel-elastomer composite. 100 is the vacuum pump. Here a generic vacuum pump has been depicted of which there are a variety of commercially available options to choose from. 102 is the exit spigot for removed moisture. 116 is the limb of the user. 120 is the socket of the prosthetic limb. 119 is a sealing sleeve to help maintain vacuum if required. 101 is the inter-socket space between the liner and the socket where the vacuum pump maintains vacuum pressure in the neighborhood of -20 to -25inches HG. 103 is a standard pyramid adapter for adapting the socket to a standard

pylon. 106 is another embodiment of just the distal end position of the liner, with a thinner composite shown, rather than the thicker cushioning one in the main drawing 117.

The concept is that the device would function by drawing moisture out of the liner through the composite hydrogel membrane and passing through a porous support layer such as perforated silicone. Vaccum pressure would provide the gradient and the membrane would be bonded to the liner. There are many ways this can be achieved, we focused on the current embodiment after considering many options.

2.4.1 Feasibility Analysis

Hydrodynamic Analysis**:** This calculation shows the moisture flow through a thin membrane under vacuum, and demonstrates that physiological rates of sweat removal are possible.

Darcy Flow Equation:

$$K=\frac{(V*L*\eta)}{t*A*\Delta P}; \quad [66]$$

K=permeability coefficient of membrane (cm^2); V=volume of liquid (mL);

Ƞ=viscosity of fluid permeating through membrane (Poises) or (P);

t=time (seconds) or (s)

A=area (cm^2) ; L=membrane thickness (cm);

ΔP=pressure differential across membrane ($\frac{dynes}{cm^2}$);

Conversion Factors:

1 Poise = $\frac{0.1\ kg}{(m*s)}$ =$\frac{1g}{cm*s}$ = 0.1Pa*s=1P;

1mmHG≈1Torr=133.3224Pa

1dyne = $\frac{10^{-5}\text{kg}*\text{m}}{\text{s}^2}$ =1 $\frac{\text{g}*\text{cm}}{\text{s}^2}$ = 10^{-5} N

1P=1Poise= 0.1Pa*s;

1cP=1mPa*s= 0.001Pa*s=1 $\frac{\text{N}*\text{s}}{\text{m}^2}$;

Known Constants from Literature:

Temperature of residual limb in socket≈30°-33° Celsius [67]

Viscosity H20@30°C=797.3μPa*s=0.007973P [68]

Viscosity sweat@30°C=0.9cP [69]

Sweat rate in hot weather, or high exertion

=2.4 $\frac{2.4\text{kg}}{\text{m}^2*\text{day}}$= 0.1 $\frac{\text{L}}{\text{m}^2*\text{hour}}$ = 2.77*10^{-6} $\frac{\text{mL}}{\text{s}*\text{cm}^2}$ [70]

H20 % of super tough D.N.Hydrogels≈90% [63]

Permeability coefficient GMA@89.2% H20=19.96*$10^{-15\pm.61}$ [64]

Vacuum Pressure from prosthetic pump:8-20inchesHg=270,800-670,00dynes/cm2 [30]

Governing Equation Solved for Flux:

K=$\frac{(\text{V}*\text{L}*\eta)}{\text{t}*\text{A}*\Delta\text{ P}}$;

$$\frac{\text{V(mL)}}{(\text{t(s)}*\text{A(cm}^2\text{)}} = \frac{(\text{K(cm}^2\text{)}*\Delta\text{P(dynes/(cm}^2\text{))}}{(\text{L(cm)}*\eta\text{(Poise))}}$$

Flux Sweat through Skin:

2.4 $\frac{2.4\text{kg}}{\text{m}^2*\text{day}}$ =0.1$\frac{\text{kg}}{\text{m}^2*\text{hour}}$ = 0.1 $\frac{\text{L}}{\text{m}^2*\text{hour}}$

=2.77*10^{-6} $\frac{\text{mL}}{\text{s}*\text{cm}^2}$

Flux sweat through thin Hydrogel Membrane:

$$\frac{\text{V(mL)}}{(\text{t(s)}*\text{A(cm}^2\text{)}} = \frac{(\text{K(cm}^2\text{)}*\Delta\text{P(dynes/(cm}^2\text{))}}{(\text{L(cm)}*\eta\text{(Poise))}}$$

$$=\frac{(19.96*10^{-15\pm.61}(\text{cm}^2)*67000(\text{dynes/(cm}^2))}{(0.05(\text{cm})*.07973(\text{Poise}))}$$

$$=3.39*\frac{\text{mL}}{\text{s}*\text{cm}^2}$$

As you can see there is more flux through the membrane than through the skin when using vacuum supplied to a 0.5mm hydrogel membrane by an Ohio WillowWood brand prosthetic vacuum pump. This suggests that if the double network hydrogel is as permeable as the traditional hydrogels there should be no moisture accumulation in the prosthetic socket using the Aquapore T.I. This feasibility analysis was determined to be sufficient to merit further investigation into the mechanical properties of the material which is covered in the next chapter.

2.5 DISCUSSION

The participants in the focus group study were not randomly selected and the data was collected in a non-uniform way. The goal of the study was to generate ideas and learn things about the end user experience that could not be learned any other way. All end users are sure to have their individualized complications with prosthetic limbs and moisture. No detailed demographic data was collected on participants. The inclusion criterion for participation in the study was broad.

The mixed focus group interview format proved effective for quickly gathering qualitative data on a heretofore relatively ill-defined topic. The insights gathered herein provide a set of preliminary design metrics which engineers can use to begin the preliminary design phase of the product development effort. The directed content analysis approach allowed engineers to preformulate specific questions to be asked of the participants, and therefore predetermine codes for codification of the data. The analysis was also flexible enough to observe unexpected and interesting results.

Excessive pooling of sweat in the liner is a danger to users of prosthetic limbs as it reduces their stability and increases their chances of skin irritation. Inclusion of end users from the outset of product development has yielded useful information, verified the need reported in the literature and provided requirements for our product development efforts.

We performed initial calculations and simulations to demonstrate that the hydrogel membrane would be permeable enough to manage a clinically relevant quantity of moisture if it behaves as expected. The available literature suggest that there is enough space in the reported mechanical strength available in tough hydrogels to meet the pressures in the socket without failing, but only after selecting the final formulation can we confirm this.

Using a known value form the literature for rate of sweating [70], we determined an estimate for the amount of moisture the moisture permeable prosthetic liner would be required to manage to be clinically relevant. The reason is that it is easier to understand the analysis after the context of the conceptual design has been given. Although previous sections stated all user needs and requirements would be compiled and only afterward would analysis be done, the reality of the cyclic development process shown in Figure 4 necessitates that certain efforts are done in parallel not sequentially.

Our conceptual design is based on the idea that hydrogels are now strong enough at high enough water contents to serve as ideal moisture permeable membranes which are also water tight.

3.0 MECHANICAL CHARACTERIZATION OF TOUGH HYDROGELS

3.1 INTRODUCTION

From an engineering point of view a prosthetic limb is principally a device for redirecting mechanical forces. Its use with conventional prosthetic limb liners, however, necessitates the development of a moisture management system. Our chosen design to address this issue, the moisture permeable prosthetic liner, is enabled by a thin tough hydrogel membrane. These membranes need to be mechanically robust and permeable to liquid moisture found in a prosthesis. The core risk to the design is associated with this robustness. To test this robustness, we conducted uniaxial compression testing. Before we could conduct the compression testing, an optimal formulation needed to be selected. Challenges associated with the manufacture of thin hydrogel membranes required us to first investigate swelling properties of the hydrogels in order to select an optimally manufacturable formulation for our thin hydrogel membranes.

3.1.1 Manufacture of Thin Hydrogel Membranes

This section provides a description of the manufacturing process of the thin moisture permeable hydrogels developed for this project.

The major challenge with manufacturing the thin hydrogels comes when during the second soaking step the thin hydrogel buckles and fractures under its own expansion. Our design

specifications suggested that the target thickness for a moisture permeable tough hydrogel membrane would be around 0.5mm. During the manufacture process the repeated failure of the currently reported hydrogel formulations led us to develop a novel tougher hydrogel formulation.

One of the major areas of risk associated with this project is the concept of manufacturability. In order for the product to be a feasible device it must be easy to manufacture at least theoretically. The formulation for the hydrogel membranes had to be tuned and modified in order to overcome certain manufacturing challenges. The tough double network hydrogels has been previously reported in several places. Most often the structures built have a relatively high volume to surface area; this is to say they are thick. Our membranes are a different story. Our membrane is very thin and very wide. And has a very large surface to volume ratio. The formulations for the hydrogels and the steps to synthesize them are listed elsewhere in the paper in detail. For this section let it suffice to say that the synthesis of the hydrogels is a two-step process. In the first step the hydrogel starts as a viscous liquid, which is then poured between two glass plates and exposed to UV light to form a very thin wide flat membrane. In the second step, that thin membrane is then placed into a second liquid monomer solution. This soaking swells the membrane considerably up to 2 times the original size. This swelling is a major manufacturing challenge for the following reason: The first step gel, or first network gel is very brittle, and when upon swelling in size, it also becomes very prone to tears, and rips, and breaks and fractures. Our target dimension for maximal moisture flux through the membrane is below 1mm, ideally as thin as possible. The standard PAMPS/PAAMS double network hydrogel is not sufficient in this regard. When making thin membranes from the standard Gong gel we consistently failed the second step of membrane manufacture. When making testing disks, this was not a problem, as the compression test disks have a very large volume to surface area ratio.

A decision was made to address this problem through chemical engineering. Using the principles of bioengineering we decided to attempt two goals: the first, to increase the strength of the first network hydrogel, to make it less prone to fracturing, and the second goal was to reduce the amount of swelling that occurred when in the second step of manufacture.

3.2 METHODS

3.2.1 Swelling Experiments

We varied concentrations of salt, laponite, and monomer then measured the swelling behavior of the various formulations as a method of selecting a final formulation to manufacture the thin hydrogel membranes. Each formulation was tested 20 times and the average was taken. The formulation selected through this process was used later on for permeability benchtop testing as well as in the prototypes.

Initial efforts were towards reducing the swelling; we focused on biomimetic principle of hypertonic concentration of solution and cellular plasmolysis. Modeling a differential unit of hydrogel as a cell, we concluded that using a secondary soaking solution of an extreme hypertonic monomer concentration would be a good option for limiting membrane expansion during the second step soaking period. We created a 20 molarity solution rather than the Gong gel reported value of 3 molarity. We exploded our container and did not attempt this approach again. The high monomer concentration and high corresponding concentration of cross linker and photo initiator led to a rapid near instantaneous discharge of thermal energy boiling the

solution and solidifying and throwing the container across the room. Thanks to proper safety gear and lab technique no one was hurt.

Our next approach was to use a non-reactive solute to increase the hypertonicity of the solution without increasing the available oxidable materials that could subsequently lead to rapid thermal energy loss from the system.

3.2.2 Compression Testing

The compression testing closely followed the method described by Sanders[71]. Uniaxial compression of 11.1mm diameter disks was performed both on the experimental tough hydrogel formulation as well as four current industry standard liner materials. Each formulation was tested with n disks. For the various material types n differs as shown in Table 13. For each n disks, the individual disk was taken through 4 compressions up to a maximum of 300N at a rate of 10mm/min. The maximum strain cut off limit was 0.75, which means that the indiivual testing disks were compressed down to 0.25 their original thickness, or to a maximum of 300N, whichever came first. Our goal with the uniaxial compression testing was to determine how the tough hydrogel behaves when compared to industry standard liner materials. The hydrogels were only tested once per disk, as they were taken to failure, or had experienced some sort of visible cracking on the first test. The commercial liners tested were Alpha SmartTemp by WillowWood (Mt. Sterling, Ohio), Alpha Original by WilloWood (Mt. Sterling, Ohio), and Iceross by Ossur (Reykjavik, Iceland).

The manufacturability of the tough hydrogel membranes was a major deciding factor that determined which materials would be tested through mechanical uniaxial unconstrained compression testing. Compression testing was performed on the best formulation resulting from

the swelling experiments (L3S3), labeled 3b, and what we also refer to as “Aquagel”. We tested the 3b formulation in the first and second networks separately, after soaking in distilled water for 24 hours. In addition, we tested the Gong PAMPS/PAAMS gel 1st network. The purpose of testing these three gels specifically was to demonstrate the evolution of our material selection, rather than to serve as an exposition of material properties for the plethora of modified double network gels that can be made from a combination of the various components and ingredients. Following our membrane manufacturing process we started with the first network of the Gong gel, referred to as 1a. As the 1a gel proved to be inadequate for thin membrane purposes, we next tested our Laponite XLG modified 1st network PAMPS gel, labelled 3bFirstnetwork. As this modified formulation was a success and allowed us to proceed through manufacturing on to the next step in the process, we then tested the 3b second network.

3.3 RESULTS

3.3.1 Swelling Experiment Results

The various formulations created are presented Table 10. Using the swelling experiment as a basis of discrimination between formulations we selected the L3S3 or 3b formulation for continued development. 3b contains a laponite clay nanocomposite as well as a double network toughening mechanism this makes it a complex hydrogel composite with two toughening mechanisms. We conducted many tests modifying the formulation with the addition of salt, and quantified the resulting swelling. Each formulation was tested by making a 1st network gel disk, and swelling it in its corresponding 2nd solution, and recording the dimensions prior to and after

swelling had taken place. The dimensions of the disk were initially kept at a constant ratio of 2:1 diameter to height. Each formulation was tested 20 times and the average was taken and reported Table 11 and Figure 10.

Table 10 All combinations of hydrogel formulations tested

Material Data Base								
	1st Network Solution				2nd Network Solution			
Material	Salt	Pamps	Laponite	Code	Salt	Paams	Laponite	Code
A1, 1a	0	1m Pamp	0	J1	0	3m Paam	0	J2
A2	0	1m Pamp	0	J1	0	1.5m Paam	0	J12
A3	0	1m Pamp	0	J1	3m NaCl	0	0	J13
A4	3m NaCl	1m Pamp	0	J7	0	3m Paam	0	J2
A5	0	1m Pamp	0	J1	0	0	0	J0
A6	3m NaCl	1m Pamp	0	J7	0	1.5m Paam	0	J12
A7	3m NaCl	1m Pamp	0	J7	0	0	0	J0
A8	3m NaCl	1m Pamp	0	J7	0	3m Paam	0	J2
A9, S3	3m NaCl	1m Pamp	0	J7	3m NaCl	3m Paam	0	J14
S0.5	0.5m NaCl	1m Pamp	0	J8	.5m NaCl	3m Paam	0	J15
S1	1m NaCl	1m Pamp	0	J9	1m NaCl	3m Paam	0	J4
S2	2m NaCl	1m Pamp	0	J10	2m NaCl	3m Paam	0	J3
L1	0	1m Pamp	0	J1	0	3m Paam	3wt%	J16
L2	0	1m Pamp	0	J1	0	3m Paam	6wt%	J18
L3	0	1m Pamp	3wt%	J6	0	3m Paam	0	J2
S3L3	3m NaCl	1m Pamp	3wt%	J11	3m NaCl	3m Paam	0	J14
2a	0	1m Pamp	0	J1	1m NaCl	3m Paam	0	J4
2b	0	1m Pamp	0	J1	2m NaCl	3m Paam	0	J3
3a	0	1m Pamp	1.5wt%	J5	2m NaCl	3m Paam	0	J3
3b	0	1m Pamp	3wt%	J6	2m NaCl	3m Paam	0	J3

Table 11 Swelling ratio results from first series of swelling experiments

Specimen	Average Diameter Gain Ratio	Average Height Gain Ratio	Average Volume Expansion Ratio
A1	2.49	2.66	16.54
A2	2.6	2.73	17.83
A5	2.45	2.76	16.66
A3	1.45	1.44	3.05
A4	1.67	1.85	5.18
A6	1.78	1.90	6.05
A7	1.85	1.92	6.66
A8	1.37	1.37	2.59
A9	1.19	1.36	1.96

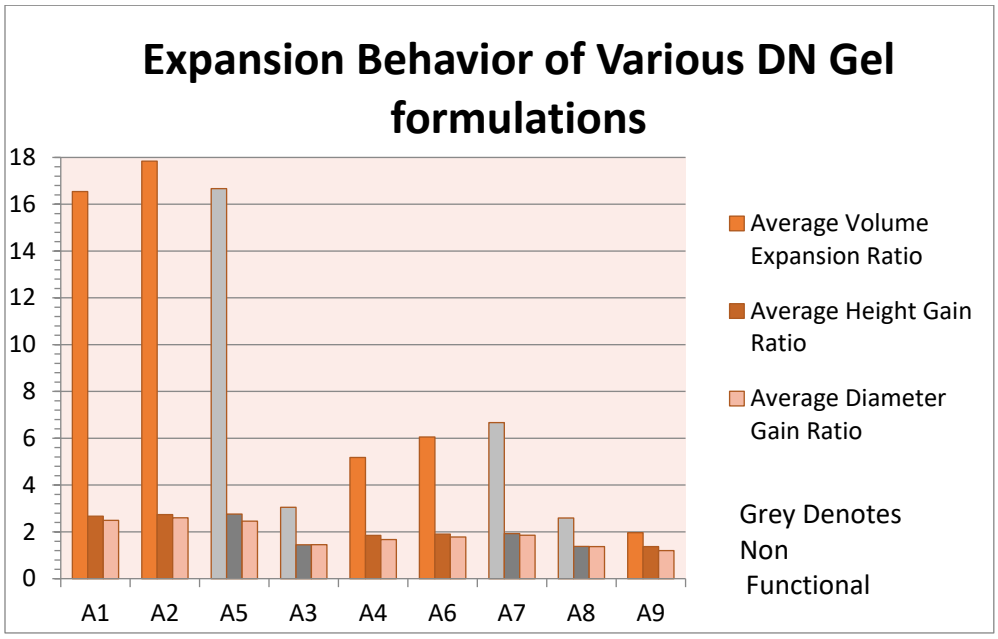


Figure 10 Swelling ratio results from the first series of swelling experiments

These tests demonstrated that the salt certainly played a big role in the reduction of swelling from one step of manufacture to the next. However, we continued to experience frustrating failures during the manufacture of thin membrane hydrogels, although the hydrogels were no longer expanding as much as they had been, they were still fracturing and were still very difficult to handle. For this reason we decided to reinforce the first netowrk hydrogel by the

inclusion of Laponite XLG, a synthetic clay which has been featured in various tough hydrogel formulations. We retested the salt content of the hydrogels to further examine the effect on swelling reduction, and also test the effect of including Laponite XLG into our formulations. These results are presented in Table 11 and Figure 11.

Table 12 Swelling ratio results from second series of swelling experiments

Specimen	Average Volume Expansion Ratio	Average Height Gain Ratio	Average Diameter Gain Ratio
A1	16.59	2.72	2.46
S0.5	3.20	1.60	1.41
S1	2.67	1.54	1.31
S2	2.29	1.42	1.26
S3	2.02	1.31	1.24
L3	10.49	2.36	2.10
L3S3	1.64	1.20	1.16

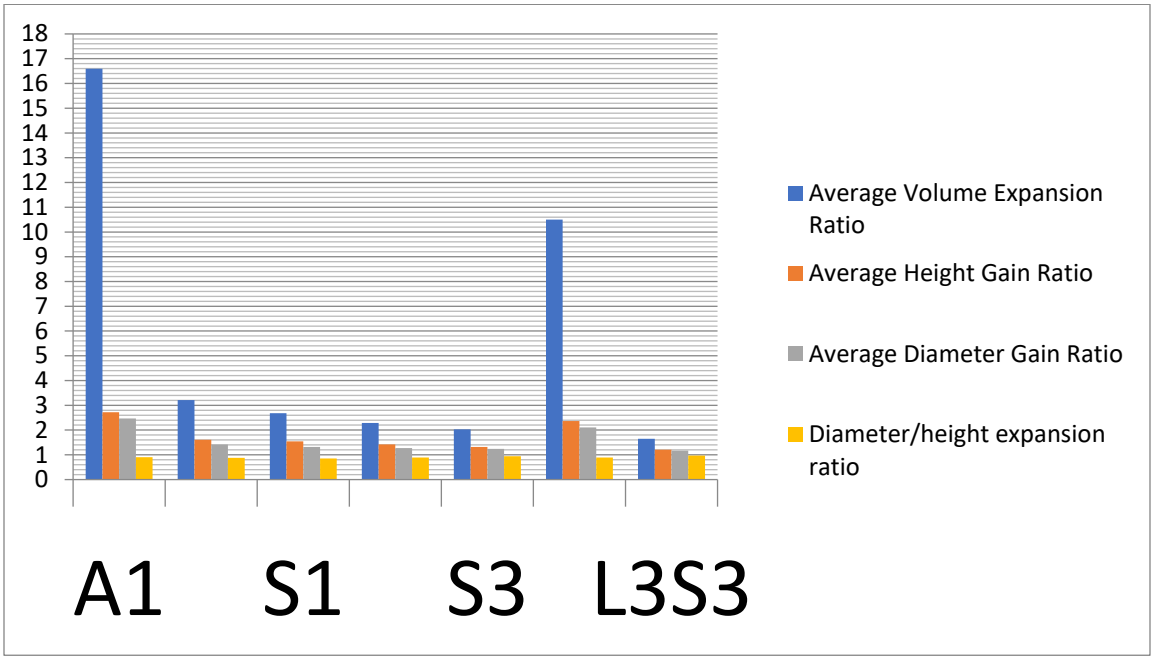


Figure 11 Swelling ratio results from second series of swelling experiments

3.3.2 Compression Testing Results

Figures 12-18 present the compression test results for the three hydrogel formulations and commercial liners tested. The individual compression tests are shown in blue and the average fitted curve is shown in red. The horizontal line at 95kPa represents the peak average stress observed in prosthetic limbs while walking [46]. We tested a total of 4 commercial liner materials for the purpose of comparison. We tested multiple hydrogel formulations to demonstrate the toughening effect of our novel formulation, although only one formulation was ultimately strong enough to use for permeability testing. The 3b, Aquagel, hydrogel formulation provided acceptable results.

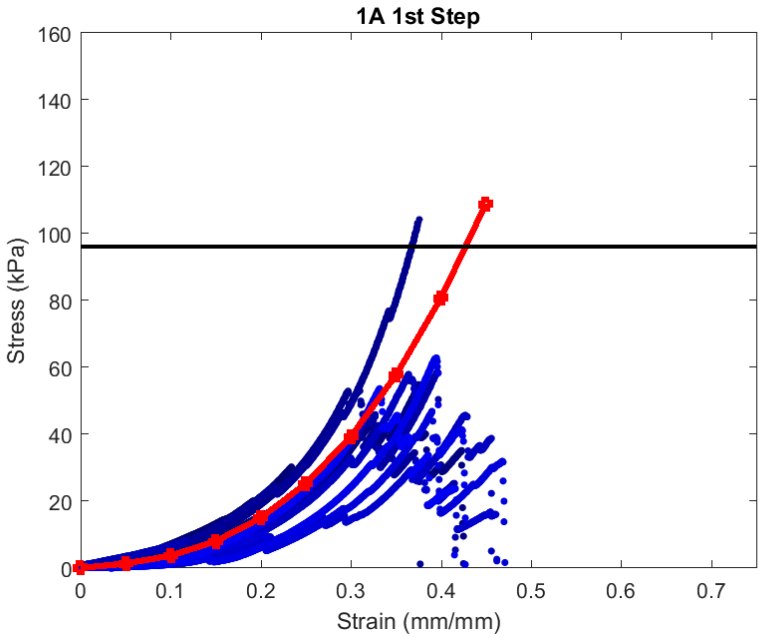


Figure 12 Hydrogel formulation 1A, first network only.

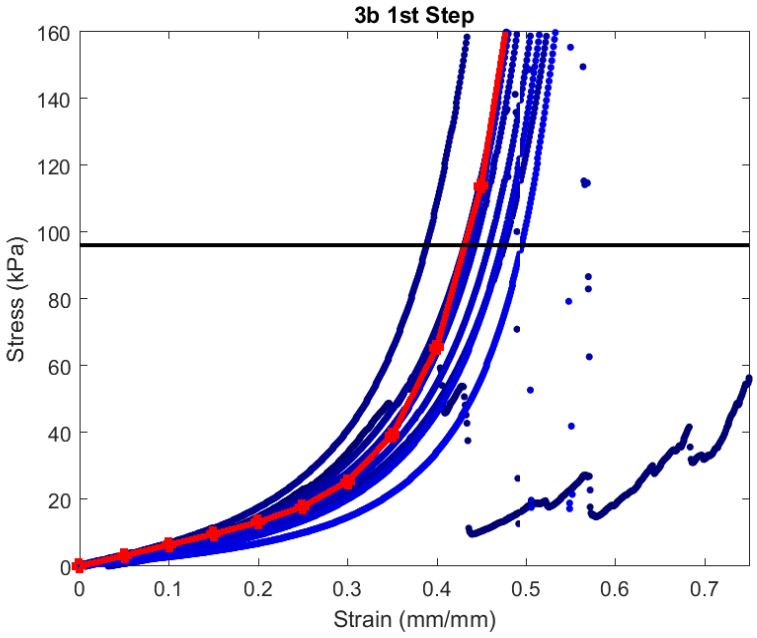


Figure 13 Formulation 3b first solution only

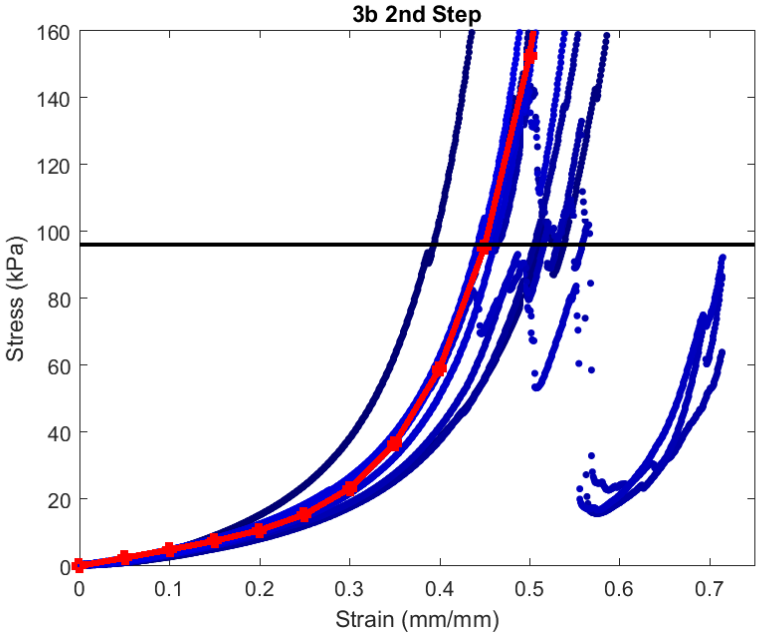


Figure 14 Hydrogel formulation 3b full strength second network.

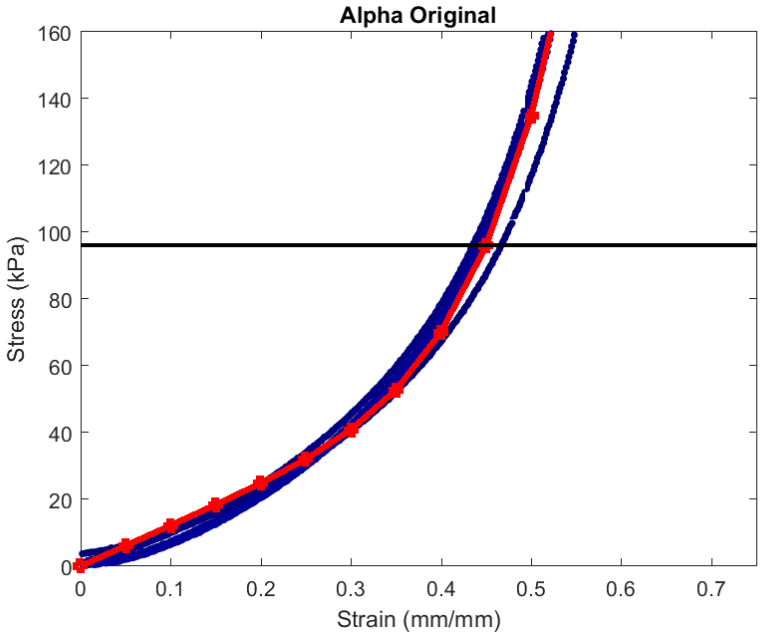


Figure 15 Commercially available Alpha Original Liner

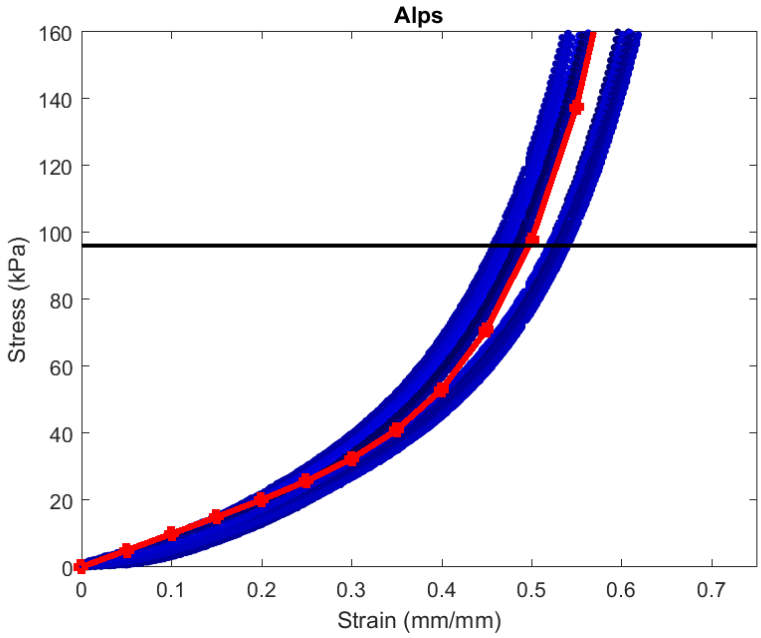


Figure 16 Commercially available Alps liner

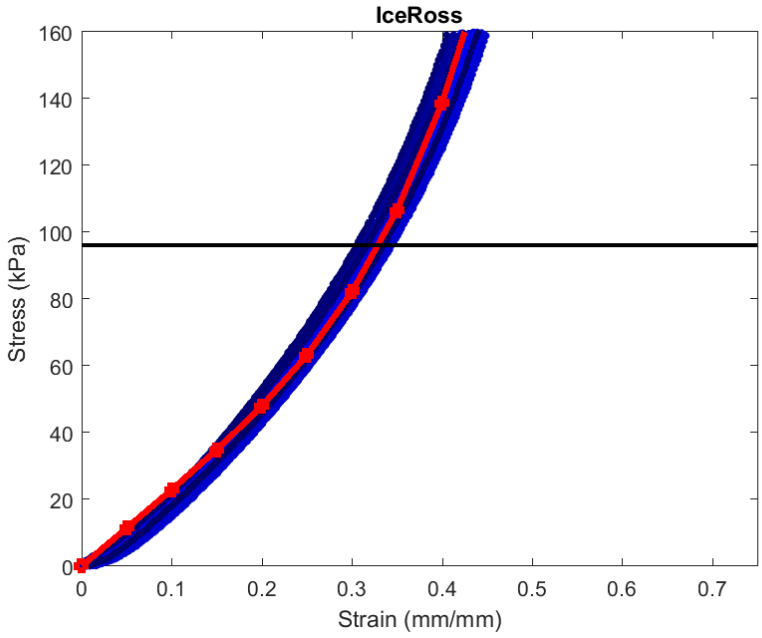


Figure 17 Commercially available Ossur Iceross silicone prosthetic limb liner

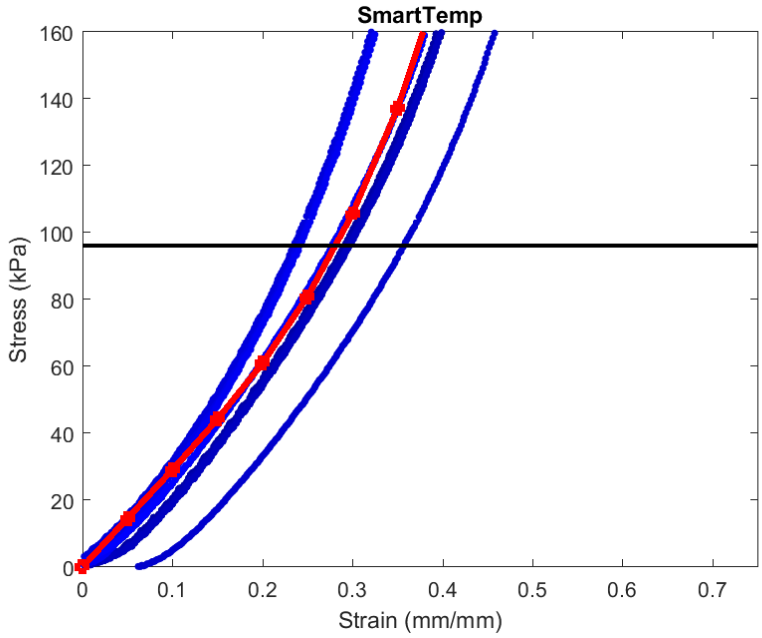


Figure 18 Commercially available Alpha SmartTemp

For all Figures 12-18 The blue lines represent the individual stress strain curve data collected during each trial. For each trial, the curves were fit to a power series equation shown in

Table 13. The red lines represent the average of all the coefficients across the trials. The black line represent the expected pressure on the prosthetic liner during walking.

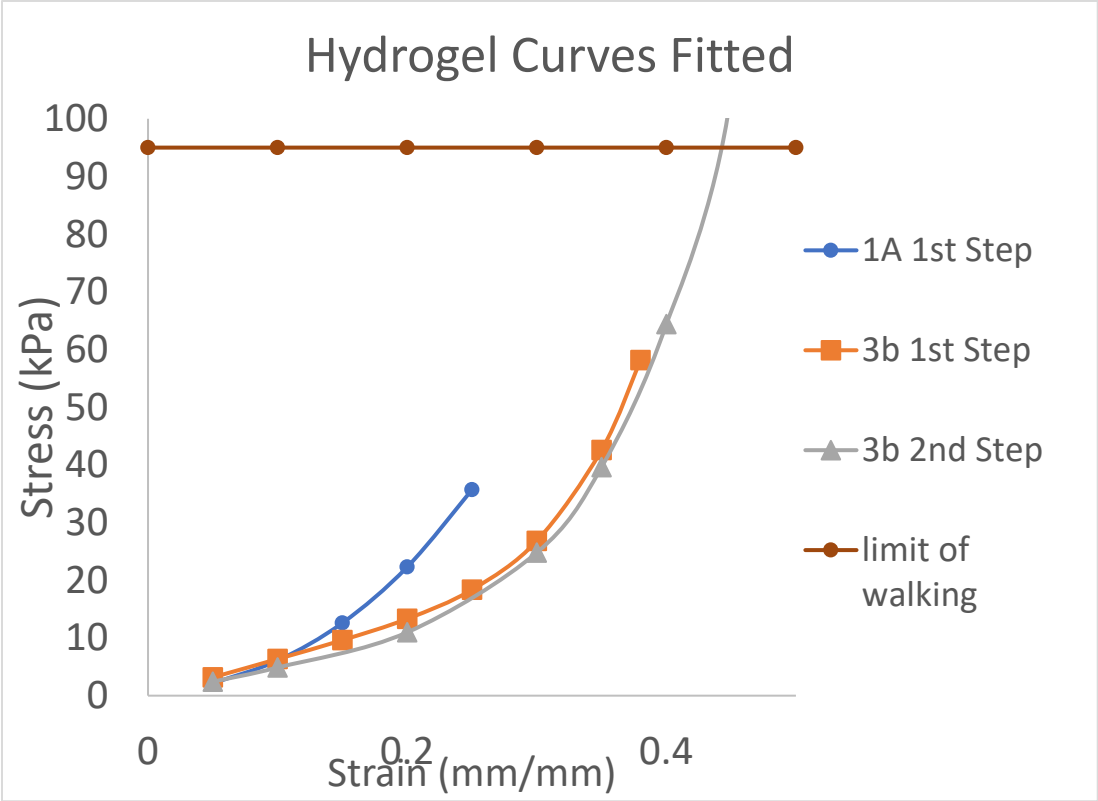


Figure 19 All fitted hydrogel formulations for collected data

Figure 20 and Table 12 present the fitted curves for the hydrogel formulations and commercial liners tested. Formulation 3B Aquagel features excellent material properties when compared to other materials commonly used for prosthetic limb liners. A selection of prosthetic limb liners was taken and tested. In Figure 20 the horizontal line at 95kPa represents the peak average stress observed in prosthetic limbs while walking [46].

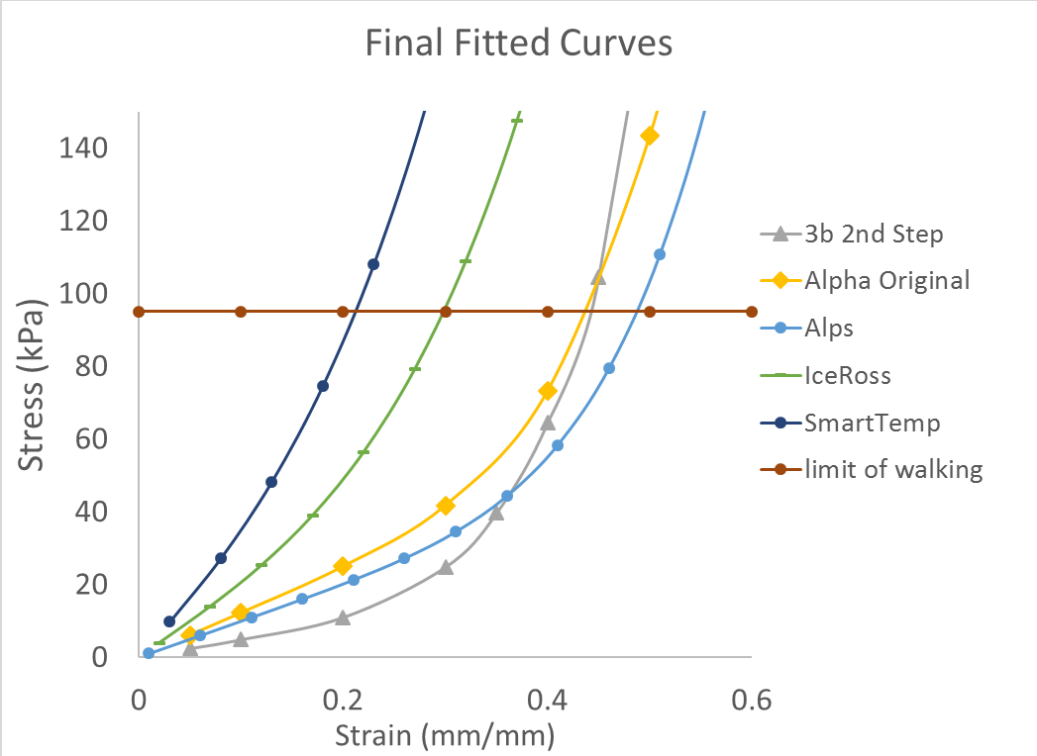


Figure 20 All fitted curves for collected liners

Table 13: List of power series fit curve coefficients

Material		A	B	C	D
1A 1st Solution	Mean	24.87	888.04	0.02	2.6
	N	11			
	Std. Deviation	20.54	558.37	0.02	0.59
3b 1st Solution	Mean	63.44	14422.78	0.005	6.33
	N	10			
	Std. Deviation	14.22	5777.38	0.00001	1.20
3b 2nd Solution	Mean	48.39	5001.3	0.005	5.21
	N	10			
	Std. Deviation	5.74	2572.34	0	0.61
Alpha Original	Mean	122.02	3545.80	0.005	5.50
	N	4			
	Std. Deviation	8.17	222.27	0	0.25
Alps	Mean	99.11	2576.6	0.005	5.66
	N	34			
	Std. Deviation	9.47	508.22	0	0.24
Iceross	Mean	227.43	2404.83	0.0159	4.09
	N	40			
	Std. Deviation	20.22	669.04	0.06	0.84
SmartTemp	Mean	289.10	2332.73	0.06	3.31
	N	12			
	Std. Deviation	99.94	1174.79	0.14	1.58
Total	N	121	121	121	121

3.4 DISCUSSION

3.4.1 Selection of Formulation

The result of our swelling experiments allowed us to select a novel hydrogel formulation not previously reported, which we arrived at through a systematic process of chemical engineering based on biomimetic swelling principles.

We selected formulation L3S3 which is 3wt% laponite, and 3 molality of sodium chloride. Although this L3S3 formulation proved to be very durable and reliably led to a reduction in breakage and fracture of the first network hydrogels, it also had the unintended side effect of stabilizing the laponite suspension. The laponite is a clay disk which forms a house of cards structure in salt concentrations above 2wt%. Our new L3S3 formulation now had the problem of spontaneous laponite gelation, in the first network, and due to higher tonicity, unstable exothermic gelation in the second network during soaking.

All of these problems were finally solved by eliminating salt from the first network, altogether, adding 3wt% laponite to the first network, and adding 2 molarity of salt to the second network for soaking purposes. This final gel formulaiton is novel, and we refer to it as 3b Aquagel. It is excellent in its properties for permability, durability and manufactuarability.

3.4.2 Comparison to Existing Liner Material

Our novel doubly toughened nanocomposite double network hydrogel formulation behaved similarly to existing prosthetic liner materials. The stress-strain curve of the hydrogel overlaps

heavily with the stress-strain curves of existing liner elastomers and falls somewhere in the middle with respect to their behavior at high extensions.

The bioengineering approach to altering the material formulations, systematically using concepts inspired by cells proved useful in improving the material properties. The previously reported material properties were insufficient for our application in that they fractured too easily while being manufactured. Our new formulation swells less during manufacturing, enabling it to survive the process until it is fully strengthened. The mechanical behavior of the new formulation is sufficient to make permeability testing prototypes, liner prototypes, and withstand compression to pressures observed in a prosthetic socket.

The fitted curves for the hydrogel results, shown in Figure 19, demonstrate how the Gong gel, while robust, has a lower fracture toughness than the laponite composite reinforced gel we ultimately selected for the first network of Aquagel. The results further show that with the addition of Laponite the gel becomes more elastic, and the modulus is lowered. Finally, the figure shows that after Aquagel is fully processed, its fracture toughness exceeds the pressure value reported for the maximal pressure observed while walking in a prosthetic socket of 95kPa [46].

In Figures 12-18 , the hydrogels show variability in the fracture strength as they were hand made and may include some stress risers such as minor cracks which are not visible but may play a role and explain the variability.

These findings have allowed us to now investigate the second major area of risk for this concept, its moisture management ability. Those investigations are covered in the next section.

4.0 PERMEABILITY OF TOUGH HYDROGELS

4.1 INTRODUCTION

There are three major risks associated with our design concept. The first major risk is the mechanical performance of the moisture permeable prosthetic liner. It may not hold up to the forces present in the socket. The previous section shows that it is reasonable to expect that it will. The second area of risk associated with the design is the permeability. The membranes we use in the liner design must be permeable enough to remove a clinically significant quantity of liquid moisture from the prosthetic socket. Moisture flow through the thin hydrogel membrane has been modeled using the Darcy flow equation as reported by White and others. [64, 66] To test permeability, a custom permeability testing device was developed.

4.1.1 Need for Low Cost Testing Method

Permeability is often an abused term. What exactly is signified by a material's permeability is dependent upon the material field. We use the term permeability to refer that property of our membranes which describes the permeability constant in the Darcy flow equation. The Darcy flow equation has been classically used to describe the permeability of liquid through porous media such as those found in geological settings, soil, sand rock etc. White is the earliest reference identified which uses the Darcy flow equation to report the flow of water through

hydrogels [66]. This convention later used by others [64] is what we report here for the purpose of direct comparison to other hydrogels previously reported.

Machines and methods do exist to test the permeability of materials. The limited budget of the current project necessitated the development of a low cost alternative testing method which is more ideally suited to our application.

A permeability testing apparatus was developed to mimic the conditions in the liner. Most permeability testing prior to this focused on vapor permeability. While there may be vapor in the prosthetic socket, it exists primarily as a fluid in the limb liner and there is no air gap present when worn properly. Therefore, we developed a permeability testing chamber that had a pool of liquid above the membrane at atmospheric pressure, with a vacuum chamber below separated by a moisture permeable membrane to be tested. The temperature and vacuum were recorded on the computer through the USB interface. This way we could use Darcy's law to estimate permeability constants. Using temperature we determined viscosity of the water from the known thickness, pressure gradient, total test run time, amount of fluid that passes through the membrane (collected in the lower chamber and measured by mass). We were able to calculate the permeability of the membranes using the data from this device.

Figure 21 Mobile permeability testing station

The moisture permeability testing station (Figure 21) included a Macintosh computer (Apple Computer, Cupertino, CA USA) for collecting data and three testing pods. Each pod featured a permeability testing chamber with temperature and pressure sensors, a power supply, and a vacuum pump.

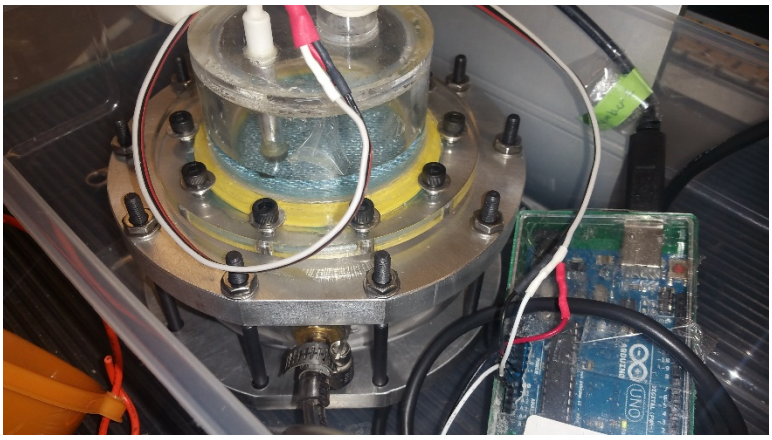


Figure 22 Permeability testing chamber

The permeability testing chamber Figure 22 makes use of sensors and an Arduino [72] to connect the sensors to the computer via an analog to digital converter. The chambers are held together with10 screws per junction to ensure uniform even pressure is applied to the membrane and gasket.

4.2 METHODS

Using the above described testing apparatus, we investigated the permeability of our custom thin hydrogel membrane. We conducted tests at various temperatures and pressures. Commercially available prosthetic limb liners were also tested for moisture permeability.

Testing was conducted by placing the sample gel liners in pressure chambers. Each liner was tested once. Water was added on top of the liner and allowed to permeate through the material, while a vacuum pump (ZENY) is connected to the bottom container and activated. Tests ran for 1 to 12 hours each. A 3-pin analog temperature sensor was fitted to the top of the chamber with 5V, A1, and GND pins inserted in a microcontroller board (Arduino Uno). A pressure transmitter (ASHCROFT) and a pressure gauge, used to manually confirm pressure

values, were installed with a tube that connects the bottom container of the chamber to the vacuum pump. Epoxy adhesive was used to seal the transmitter-manifold connection and ensure an airtight fixture. The 3-pin pressure transmitter was connected to a power supply (Tektronix PS280) set at 10 V, as well as the A0 and GND pins in the Arduino, which was connected by USB to a computer (iMac OS X v10.8.5). Variation in the power supply voltage output was found to have no effect on the collected pressure data.

Using the Arduino and Processing IDE software, two programs were initiated on the computer. Once uploaded onto the Arduino Uno board, the Arduino program collects temperature and pressure values, converts them from voltage to degrees Celsius and inches of mercury, respectively, rounds them to 2 decimal places, and prints them to the serial monitor at a 115,200-baud rate on a 30 second delay. The temperature and pressure conversions are as follows:

$$Temperature\ (℃) = \left(\frac{Sensor\ Value\ (V)}{1023} * 5\right) * 53.608 + .8846$$

$$Pressure\ (in\ Hg) = \left(\frac{Sensor\ Value\ (V)}{1023} * 5\right) * 21.607 - 51.419$$

Once the user edited the target number of readings in the code and ran it, the Processing program read data from the Arduino over the serial port and saved it to a data table every 30 seconds. Once the program was completed, the table was exported to a comma-separated values (CSV) file. Each reading in the table had columns for time, date, ID counter, pressure value, and temperature value. The saved file was imported to MATLAB, where a script analyzed the pressure and temperature values to find the permeability of the liner. Using multiple pressure chambers and Arduinos, three liner tests could be done at the same time following the described process.

The permeability of the material was determined using a similar method as White [66].

$K=\frac{(V*L*\eta)}{t*A*\Delta P}$;

K=permeability coefficient of membrane (cm^2); V=volume of liquid (mL);

Ŋ=viscosity of fluid permeating through membrane (Poises) or (P);

t=time (seconds) or (s)

A=area (cm^2); L=membrane thickness (cm);

ΔP=pressure differential across membrane $\frac{dynes}{cm^2}$;

To find the permeability K, known values were entered, and integrated over the temperature and pressure. The temperature is not present in the Darcy flow equation, but the viscosity of the liquid is. As we were unable to measure the viscosity of the liquid we used a known correlation between viscosity of water and temperature:

$$\text{Viscocity}\left(\frac{N*s}{m^2}\right)= 2.4.14*10^{-5} * 10^{\frac{247.8}{temp(Kelvin)-140}} \quad [68]$$

4.3 RESULTS

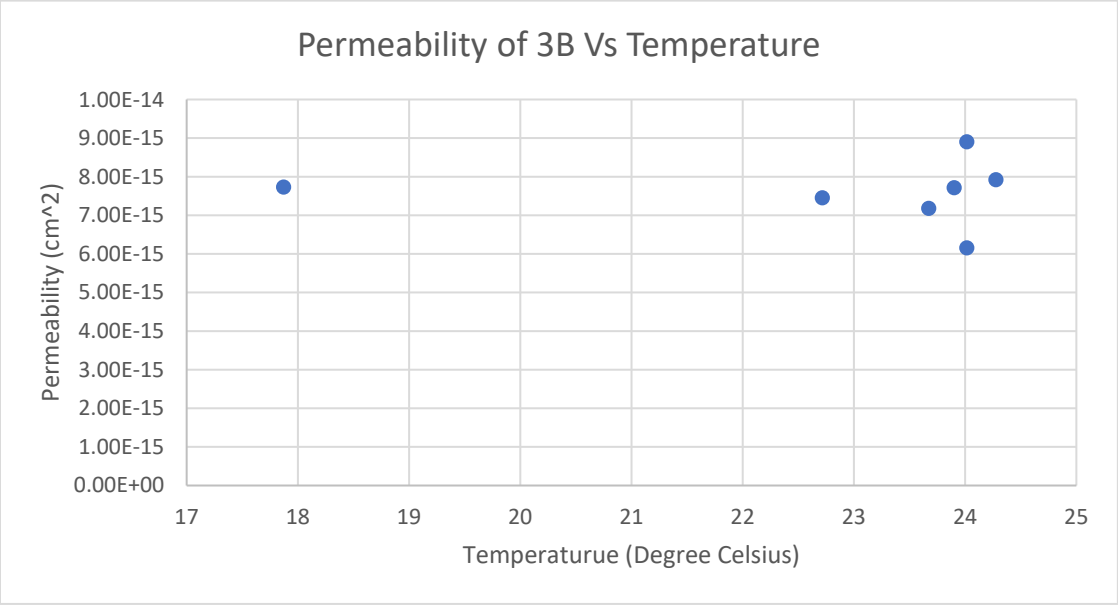


Figure 23 Permeability constant derived from experimental data for formulation

Moisture permeability is a property of the hydrogel material itself and is independent of dimensions, thickness, pressure applied or viscosity of liquid. Figure 23 demonstrates the range of permeability calculated for the hydrogel material over the range of temperatures we investigated. Our hydrogel membrane showed good permeability. The permeability was similar to the permeability of previously reported hydrogels [64, 66]. The permeability of the conventional off the shelf prosthetic liners was orders of magnitude less as expected, and was not significantly different than the control which is known to be impermeable.

Our testing chamber did not include any way of controlling the temperature, only recording the temperature. All the variations in temperature were due to the air conditioning in the room. In one instance the mobile testing station was placed directly beneath the air conditioning unit resulting in the low temperature observed. As can be seen the permeability has

a good agreement and does not vary much. Full results are shown in Table 15 Permeability results for Aquagel (formulation 3b).

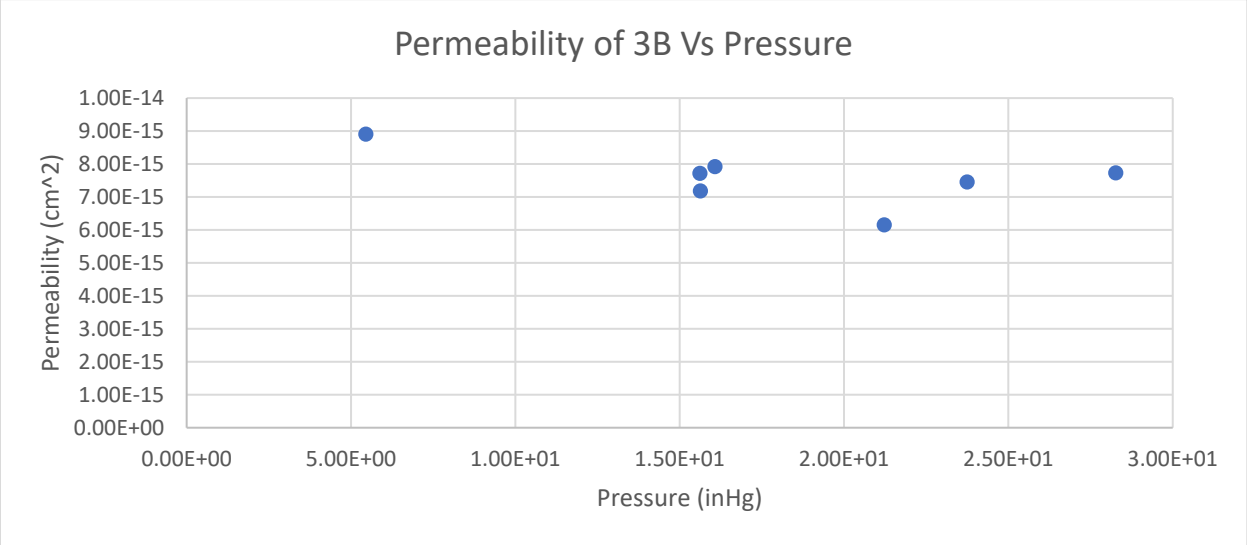


Figure 24 Permeability constant for formulation 3b tested at various pressures

Permeability also is by definition independent of the pressure applied to the membrane. Figure 24 shows the permeability results plotted against the various pressures we tested at. As we can see there was a relatively horizontal trend observed. This suggests that our permeability testing technique was adequate.

Although it is well known among material scientists that silicones are not permeable to liquid water, we went ahead and tested competitors liners. We expected the liners to show no permeability. Our results show that we were unable to detect any permeability of the existing liners at all above the noise we also observed in our control measurements. The control measurements results are shown in

Table 14. Polyether Polyethylene is reported by the manufacturer to be impermeable to liquid or air. This material is used to make inflatable waterproof rubber wheelchair cushions and mattress overlays. The average permeability for the control was on the order of 10^-17. This tells us that our error, (10^-17) is very small compared to the permeability we found for our hydrogel membrane (7*10^-15), or around one one-hundredth. This gives us good confidence in our permeability measurement for our hydrogel membrane.

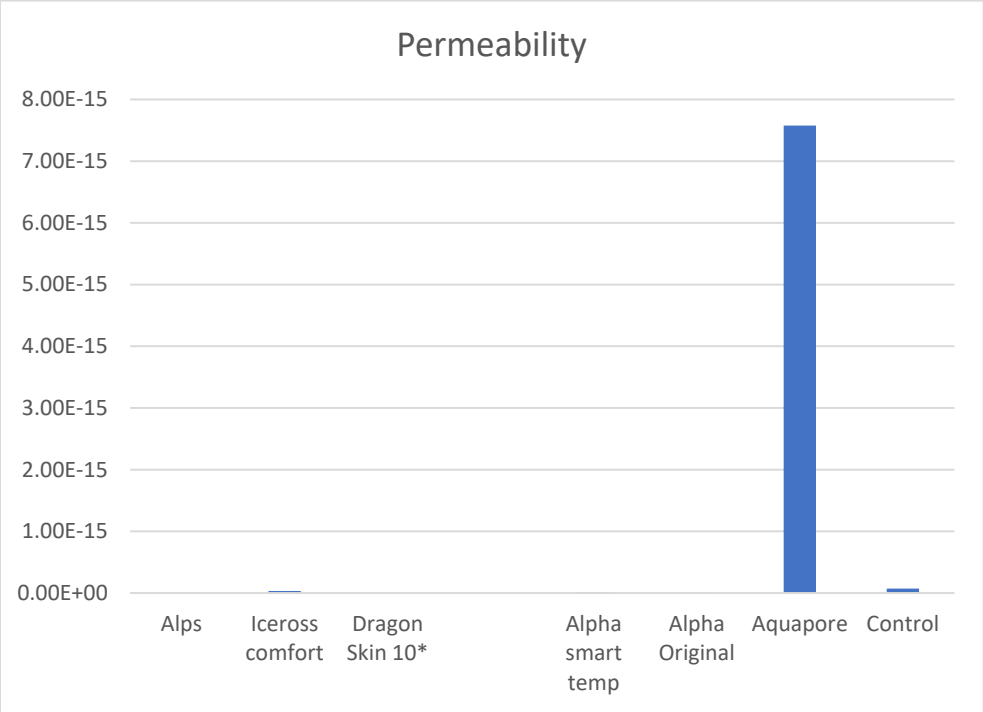


Figure 25 Permeability constant derived from experimental data

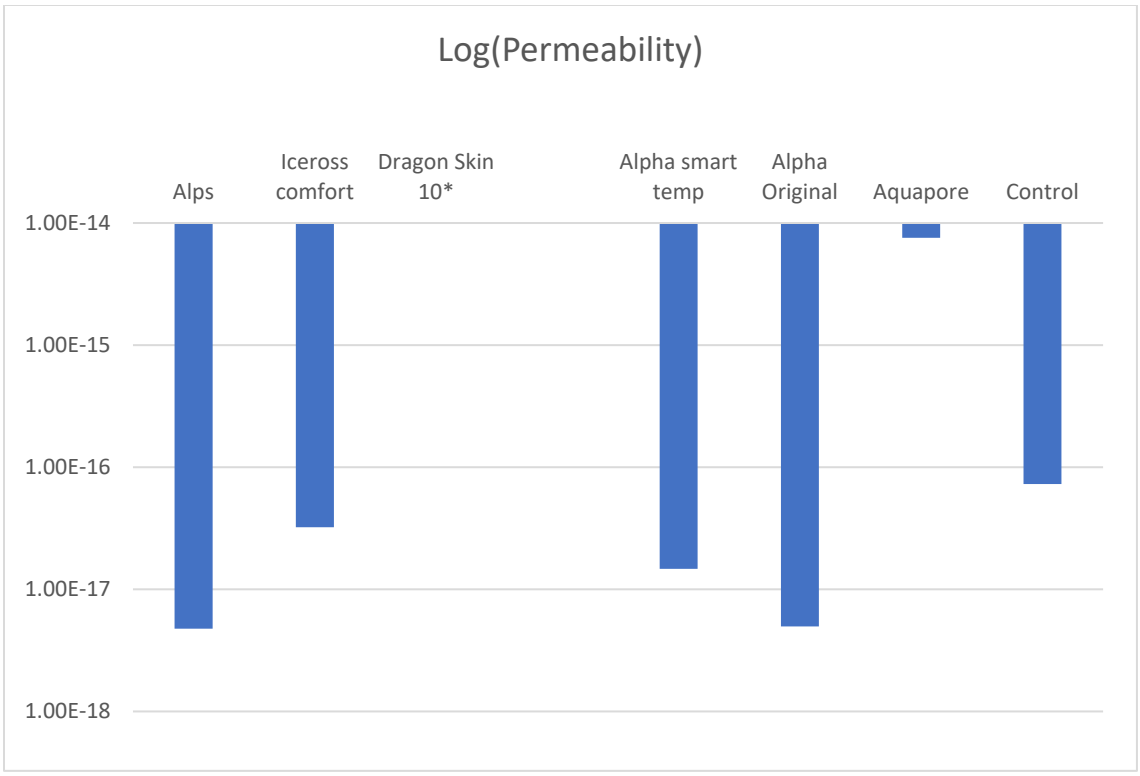


Figure 26 Permeability constant derived from experimental data shown on log scale

When we plot the permeability of our hydrogel liner membranes against the permeability of the off the shelf liners, it is difficult to even compare them on the same graph as in Figure 25. A better comparison is on a log scale axis for the y axis as in Figure 26. Notable on these graphs is DRAGON SKIN10, which is an off-the-shelf silicone material we used for initial prototypes. On that particular test we did not detect any moisture at all, even within the expected noise of our measurement as seen in the control. For this reason the permeability is zero.

Table 14 Permeability results for control

	Permeability (cm^2)
Control: Polyether Polyethylene	1.50E-16
	2.92E-17
	1.42E-16
	3.12E-17
	1.21E-17
Average	**8.81E-17**
STD	**6.72011E-17**

Table 15 Permeability results for Aquagel

	Permeability (cm^2)	Average Temperature (Degree Celsius)	Average Pressure (inHg)
3b Hydrogel: Aquagel (L3S3)	7.71E-15	23.90204861	1.56E+01
	7.92E-15	24.27734722	1.61E+01
	7.18E-15	23.67375	1.56E+01
	7.45E-15	2.27E+01	2.37E+01
	7.73E-15	1.79E+01	2.83E+01
	8.90E-15	2.40E+01	5.46E+00
	6.15E-15	2.40E+01	2.12E+01
Average	**7.58E-15**		
Standard Deviation	8.28E-16		

Table 16 contains perhaps the most telling information. We can see that for no material except for the hydrogel, was the permeability recorded greater than the control reading. We are therefore unable to conclude that any of the materials used for current prosthetic liners have a permeability that is greater than zero. Aside from the Hydrogel and the control, the individual liner materials were only tested once. Given their extreme moisture resistance, and our inability to detect anything other than the noise of our measurement, we decided further tests would be meaningless.

Table 16 Permeability results for all samples

Sample	Permeability (cm^2)
Control	7.29E-17
Alps	4.77E-18
Iceross comfort	3.22E-17
Dragon Skin 10*	0.00E+00
Alpha smart temp	1.47E-17
Alpha Original	4.96E-18
Aquagel	7.58E-15

4.4 DISCUSSION

The permeability of conventional single network hydrogels has previously been reported [64, 66]. The thin hydrogel membranes developed for this project show a similar permeability. The permeability of double network tough nanocomposite hydrogels has not previously been reported. These findings suggest that the double network nature of the hydrogel does not adversely affect the permeability of the material. The permeability of the conventional liner materials was, as expected, too small to record using our testing apparatus and was not detectable above the noise level expected. We used a control material, polyether polyethylene, to determine the sensitivity of our measurement.

There are a number of available methods of reporting permeability in hydrogels as shown in

Table 17. We selected to report the permeability “K” which is governed by the Darcy flow equation for a number of reasons. For any matter, or any type, to have an appreciable net mass transfer from one space to another, there needs to be some kind of gradient. Without some kind of gradient, there may be random motion governed by Brownian option, but it will tend to cancel itself out and no net mass movement will occur. In our application, due the convenience of the common use of vacuum pumps in use for prosthetics, we identified vacuum pressure gradient as being an ideal gradient to drive mass flow. The Darcy flow equation, originally developed as an empirical description for geological engineering, is an ideal model to report the mass flow of water through hydrogel membranes when the primary gradient is pressure. It has been used by previous studies to examine mass flow of water through hydrogels [64, 66]. An alternative approach would have been to report the water diffusivity through the membrane as shown in

Table 17. Although this was an option, it would not be the best descriptor of the behavior we are interested in. Unique among hydrogels, the dominating mechanism of mass transfer varies upon polymer content. Hydrogels with high polymer contents will tend to have smaller spaces between the polymer chains. Using a brush heap model to calculate net effective porosity, would result in narrow effective pore diameters. When the degree of crosslinking is lowand the hydrogels swell to greater water contents, the distance between polymer chains increases, thereby increasing the radius of the net effective pore size. When the net effective pore size is greater than twice the

diameter of a water molecule (1.5 Angstroms), viscous flow of water through the hydrogel predominates the mass transfer of water through the membrane. When the pore size is less than double, diffusive movement of water predominates. Porosity may be confused with permeability, but is not the same thing.

Table 17 Various measures of water movement through a membrane

Example	Measure	Units	Governing Equation	Description
White 1960[66]	Permeability "K"	cm^2	$Ks=\frac{VL\eta}{tA\Delta P}$	Steady state mass flux under pressure gradient appropriate for high water content. Viscous flow dominates when water content is high. When effective pore radius is more than twice radius of water.
White 1960 [66]	Pore size "r"	Cm	$r=\sqrt{\frac{8Ks}{S}}$	Brush heap model of effective porosity
White 1960 [66]	Diffusion coefficient "D"	(cm^2)/sec	$D=\frac{RTKs}{\epsilon V\eta}$	Diffusive flow of liquid for high polymer content (30%) plays a large role, diffusive flow dominates.
Forniasero 2008 [73]	EMS, Fickian diffusivity	(cm^2)/sec	Complex derivation	High polymer content,

Prior to the invention of super tough hydrogels, it was certainly possible to achieve high strength in hydrogels. It was quite a simple matter to add greater and greater quantities of crosslinking agents, and improve the strength of the gels. However, these gels were unequivocally not appropriate for mass transfer of water at high rates as their polymer contents were far too high to allow for the faster viscous flow to dominate, rather than the slower

diffusive flow. The proliferation of new and various tough hydrogels, is not novel for their strength per se, but rather for their combined properties of very high water contents, simultaneously with high strength, which was not possible before.

Our new material, Aquagel, has been demonstrated to be reasobaly strong enough, and reasonably permeable enough to merit further investigation. With the individual components having already been proven, as a next development step we decided to make prototype liners using the membranes and determine if it was feasible to manufacture such a device. The prototype investigation is covered in the following chapter.

5.0 MANUFACTURE AND TEST OF PROTOTYPE

5.1 INTRODUCTION

The third major area of risk is the assemblage of the various components of the liner together into a functional prototype unit. When this project was commenced in 2013, no commonly accepted method of robustly bonding hydrogels to silicones had been reported. In the summer of 2015, a method was reported by MIT [74] making use of benzophenone to covalently bond the two disparate materials together. This technique together with a newly developed method of 3d printing assisted injection molding of silicone liners was used and reported below. The liner prototypes were then tested with the helpof human participants to aid in development and evaluation of concept feasibility.

5.2 MANUFACTURING THE FIRST LINER PROTOTYPE

Putting the concept level design into practice involved a significant amount of additional detailed design. The basic concept for the device captures a number of possible embodiments. The embodiment chosen for the liner prototype features a distal end with a three layer composite comprising two outer perforated silicone layers, and an inner thin hydrogel membrane.

The initial prototype used a dog toy from the pet shop to provide the shape of the pores of the layers (Figure 27). A small spikey ball, had most of the spikes removed, then it was inverted inside out and plaster was used to make a negative half of a mold.

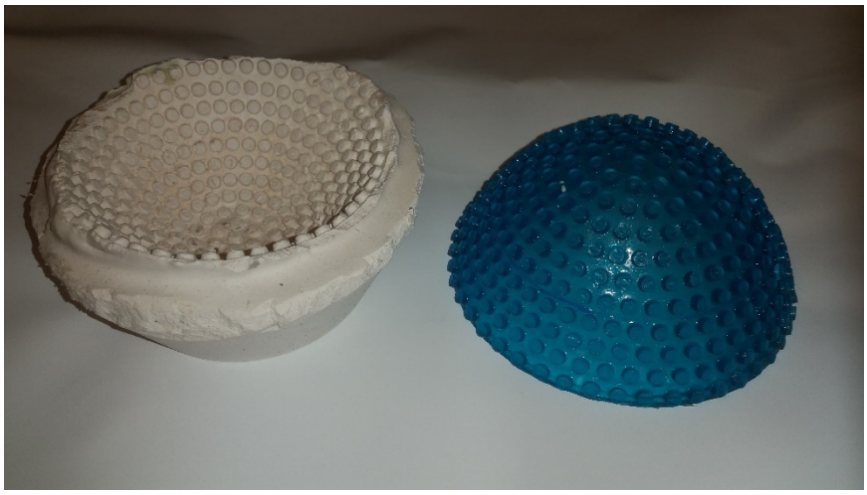


Figure 27 Plaster positive and original rubber positive mold

Figure 28 Three part plaster mold shown with distal end cap composite inserted into mold.

After the distal end pad was constructed it was placed in the distal portion of a three part mold of all plaster (Figure 28) and the mold was injected with silicone. This was a good proof of

concept as we were able to put the hydrogel layer where we wanted it between two perforated silicone layers. The resulting liner was good (Figure 29), except the holes were too large. Focus group participants had indicated that there should not be overly large physical textures on the interior surface of the liner. Th membrane used for the inner layer was a thick, 3mm layer of Gong PAMPS/PAAMS gel. Our computer modeling determined that this would most likely not be thin enough, and that target thickness should be less than 1mm. This was the first composite we developed, but there was a problem when the hydrogel would not stick to the silicone. The hydrogel was very wet with water, and the silicone would repel the water. At this point we could only seal the edges, but air was able to go around the edges and this moisture permeable composite was not air tight.

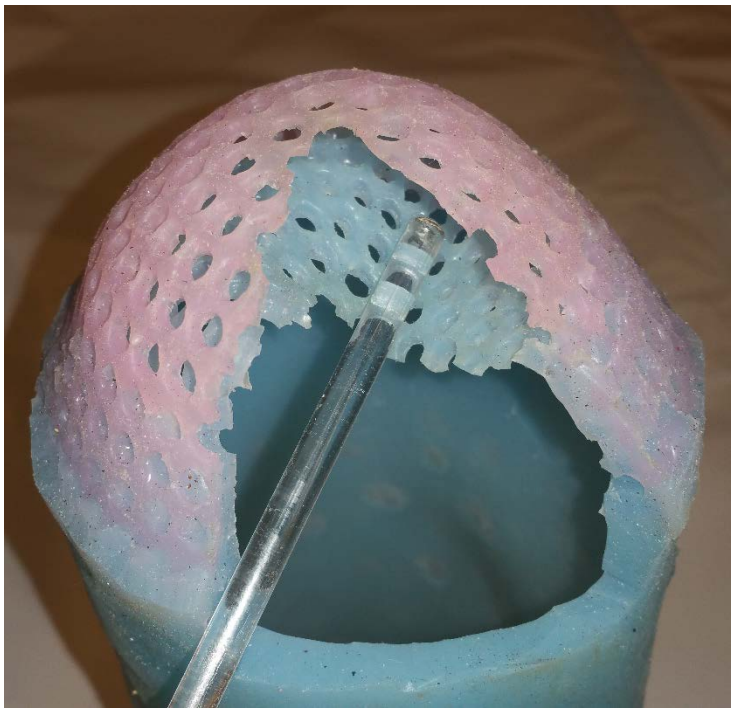


Figure 29 Completed three-layer composite dissected to show layers

5.3 MANUFACTURING THE SECOND AND THIRD PROTOTYPE

3D printing, or additive manufacturing, is an exciting emergent technology which promises to improve the field of rehabilitation science [75]. Prosthetic limbs stand to benefit greatly from additive manufacturing. This section discusses the benefits and challenges related to using 3D printing to assist in the manufacture of silicone prosthetic limb liners.

Silicone parts may be cast directly into plaster molds with no release agent. If the plaster surface is smooth it will peel off with little effort. The main advantage to plaster casting is its low cost. It can be done without expensive ovens or printers. One of the major drawbacks to plaster casting is the limited resolution for small detailed structures. When the silicone is cured and ready to be removed, it must be pulled from the mold with considerable force. Small plaster structures are easily broken during this process. In order to achieve detailed structures, such as conical perforations, a more rigid, and tough mold is required.

A prosthetic limb liner is a closed ended thin polymer sleeve that is placed on the end of a residual limb much like a sock prior to inserting it into a prosthetic socket. It serves to cushion the residual limb as well as link it to the socket. Current prosthetic limb liners are made from moisture impermeable elastomers such as silicone, urethane, or thermoplastic elastomers. These materials trap all the sweat and moisture released by the limb and can lead to negative health outcomes for the user [1]. A perforated double layer silicone prosthetic limb liner has been made to address this issue.

A perforated, double layer, silicone prosthetic limb liner has been made using a 3D printing assisted method of casting. The 3D printed parts provide a high level of detail, with minimal expense and effort. The manufacture of the prosthetic limb liner has made use of traditional liner fabrication techniques as well as newer 3D printing techniques. Platinum curing

silicone was injected into a custom made four part mold to make the inner layer. Silicone was also injected into a second two part mold to make the outer layer. This method can be adapted to other applications outside the field of prosthetics and is a useful way to expand upon familiar hand skills.

5.3.1 Fabrication of Outer PETG Clam Shell

The fabrication of the positive and negative molds for the gel liner involved many processes. The first was creating a positive plaster mold with a conical outer dimension the same diameter of the finished liner's inner dimension. This mold also has a cylindrical shape opposite to the end of the cone, and a diameter the same thickness as the finished liner's exterior. This was used as the stable platform for fabrication.

Figure 30 Traditional prosthetic hand skills are required to make a uniform plaster cone shape for the innermost portion of the four part liner mold.

A dummy was 3D printed to the same specifications as the conical end of the finished liner. Pelite (Fillauer, Chattanooga, Tennessee) was used to simulate the thickness of the gel, and wrapped to fill between the cylindrical end and the dummy. Indentations were grooved into the cylinder to create “keys” that allow the mold to be oriented correctly. This is the finished positive model to be used for fabrication of the two clam shell pieces that form the negative model. A sheet of quarter inch PETG (Polyethylene terephthalate) was heated in the oven and drape formed over the positive model. During drape forming the PETG was folded in half around the positive mold creating a seam that bisected the mold. Once cooled the plastic was trimmed and removed from the mold. The protective film was left on the side of the PETG sheet touching the mold to allow the seam of the plastic to be separated. Holes were drilled into the seams to allow for screws and wingnuts to hold the two sections of plastic together, and allow them to be

removed separately. With the positive outer and negative inner mold finished, the Pelite is then discarded and the fabrication of the gel liner can take place.

Figure 31 The fully assembled four-piece liner mold. The grey dummy can be seen at the top of the mold, on the distal end of the plaster cone

5.3.2 Injection of Silicone

The silicone is injected into the empty space left by the Pelite between the plastic and plaster mold. The silicone must also be injected into the space between the plaster mold and the 3d printed dummy. A separate simpler two part mold was also used to make the outer layer of the perforated limb liner. The two part mold made use of two 3d Printed parts.

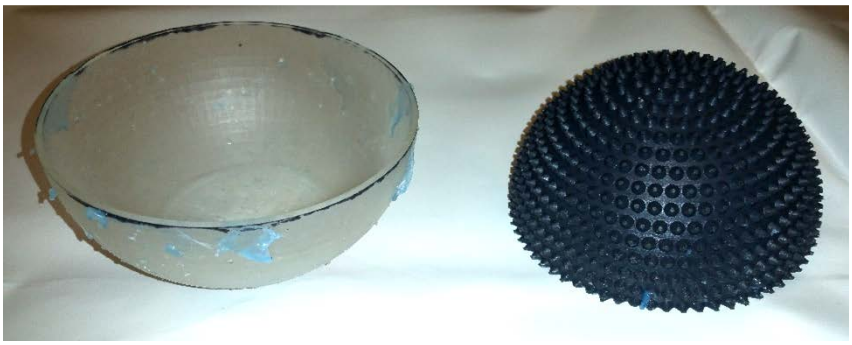


Figure 32 A simple two part mold to make the outer layer of prototype#2. Both parts are 3d printed.

Figure 33 Blue silicone is injected in the lower portion of the mold and allowed to flood the cavity left behind after discarding the Pelite layer.

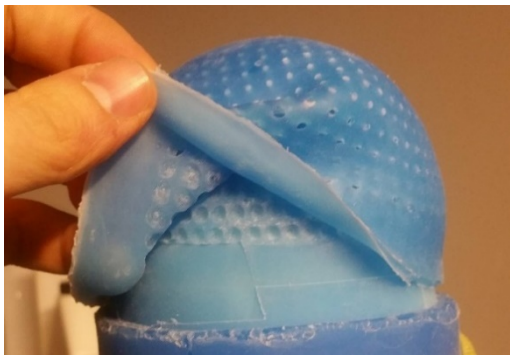


Figure 34 The two layers of the distal end of the perforated prosthetic limb liner can be seen here prior to bonding them permanently together in prototype#2.

5.3.3 Making the Hydrogel Layer for the Second Prototype

We attempted to make 3d hollow hemisphere shaped hydrogels using a curved glass surface. The small glass dome was covered with a latex positive mold, and then the latex covered glass dome was dipped into silicone, and was then encased in a two part plaster mold for additional support. After all had dried the latex positive layer was removed and was replaced with liquid hydrogel solution which was then cured through the glass dome by UV lights. This technique proved challenging as the Hydrogel would be thick at the bottom and very thin on the sides, and would not be strong enough to survive swelling in the second solution.

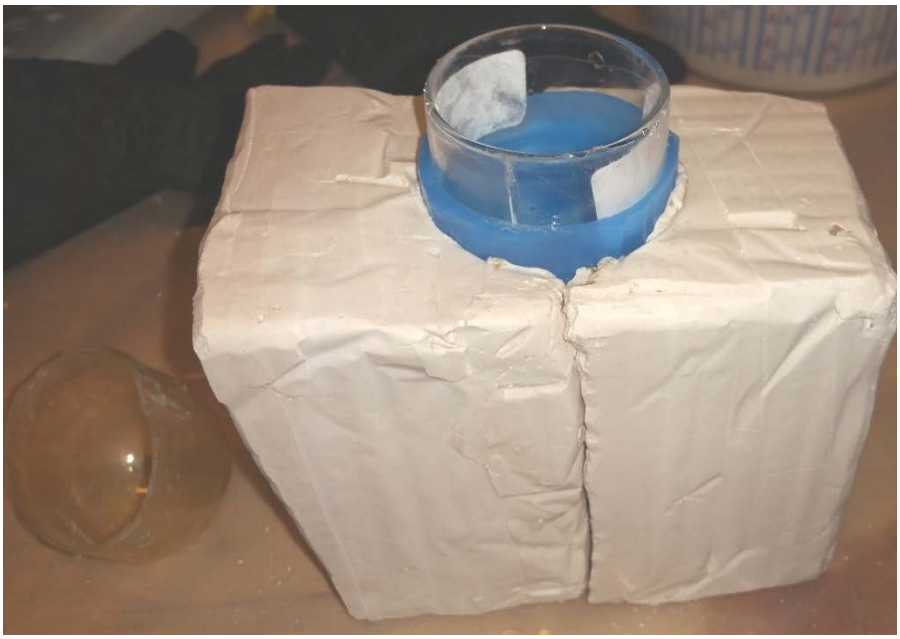


Figure 35 Curved gel mold

We ultimately decided to continue making flat gels and curving them to fit the curved liner surface.

5.3.4 Hydrogel Elastomer Composites

The distal end of the various liner prototypes are bonded together using benzophenone. This results in an air tight junction. In order to overcome the problem of hydrogel silicone adhesion we used benzophenone to covalently bond the two surfaces. This method is adapted from the method reported by Yuk [74].

1. Thoroughly clean elastomer surface with methanol and DI water
2. Completely dry elastomer surface with N_2 gas
3. Prepare benzophenone solution of 10 wt. % benzophenone in ethanol

4. Place elastomer in benzophenone so that its entire surface is covered for 2 mins at room temperature.
5. Wash elastomer with methanol three times and dry completely with N_2 gas.
6. Synthesize 1st network PAMPs gel
7. Soak 1st network PAMPs gel in 2nd network PAAM solution and place on treated elastomer surface and cook for 1 hr.
8. Large membranes were prepared, 100 inches squared in area, and .6 mm thick. These were then attached using the above method to the interior surface of the liner.
9. The liner was flattened by inverting it and placing it onto a round flat mold.
10. The gel was then trimmed to fit over the flattened liner and was cooked under UV for one hour until the gel stuck. The gel made a reasonably strong bond and would resist peeling under normal working conditions for prototype assembly.

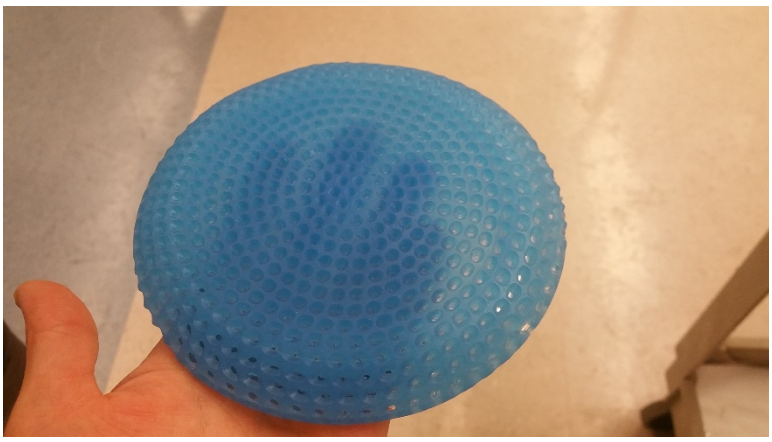


Figure 36 Outer layer of prototype#2 mounted on circular flat surface

Figure 37 Large hydrogel membrane 0.6 mm thickness

Figure 38 Outer two layers bonded together for prototype#2

Two final prototypes were made. Any perforations not covered by gel were filled with Silicone glue.

5.4 TESTING METHODS

The above sections describe the development of the manufacturing process of the liner prototypes. The following sections describe the evaluation of the various prototypes using participants with trans-tibial amputations.

5.4.1 Testing of Liner Prototype with End User Participants

The purpose of the human subject aided evaluation of the prosthetic liner prototype was to determine the feasibility of the embodiment selected for initial manufacture. The moisture permeable prosthetic liner is a class 1 medical device. Our moisture permeable prosthetic liner is similar to the standard liners being used except for the addition of small holes for drainage and the addition of a thin membrane embedded inside the liner. The moisture permeable prosthetic liner is used in the same fashion as the current liners. It is placed over the limb prior to inserting it into the socket. The thin membrane is made of hydrogel polymer. Hydrogels are currently used in many class 1 devices such as nipple pads for nursing mothers, and cushions for wheel chair seats. In addition, we did not ask any of our participants to walk with the limb, only to sit and remain seated for the duration of the test. This means that complications as a result of slipping and falling are eliminated. Also, one of the main risks when using prosthetic limbs is pressure on the bony prominence of the residual limb pressing against the hard socket. Because the users were seated, and their full weight was not be placed on their limb, they did not have the chance to develop bruises and pressure injuries. In addition, a certified prosthetist was present to monitor the tests and ensure that any issues that arise in patient comfort are addressed.

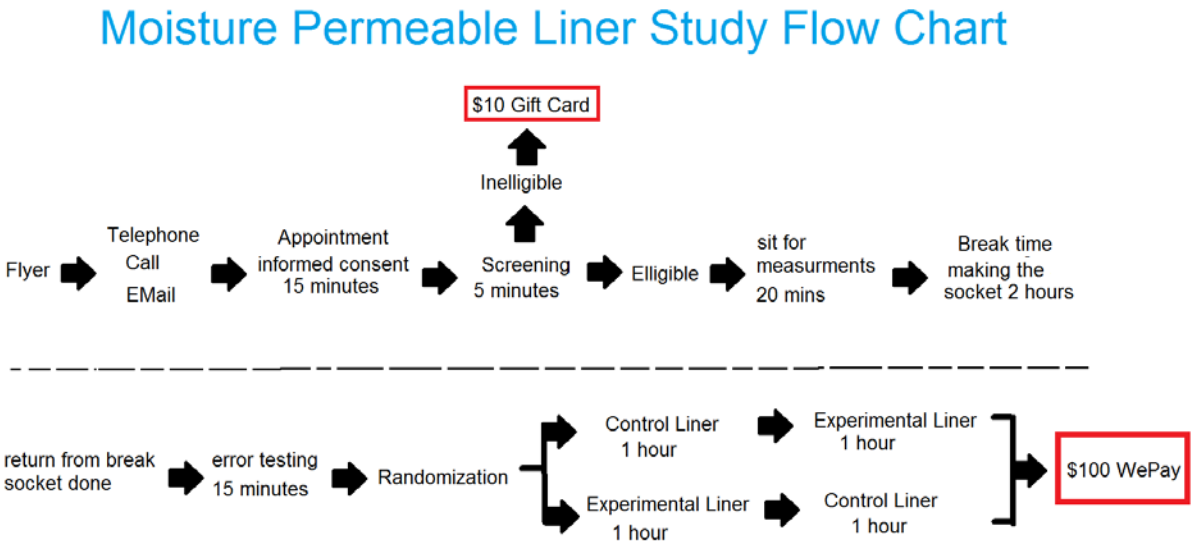


Figure 39 Flow chart for human subjects testing

This study is an experimental, randomized assignment repeated measures cross over design. The participants were randomized into the AB Group or the BA group where A represents the moisture permeable prosthetic liner prototype and B represents the control. The AB group first tried the prototype and after tried the control. The BA group first tried the control and then the prototype liner afterward. The control is distinguishable from the prototype, and the participant was not blind as to which they are trying. We used the commercially available WillowWood Alpha Original prosthetic liner for the control. The intervention liner was hand made in our lab. We did not expect there to be a bias on the part of the user as they do not have much control over how well the liner performs. Ability of the participant to know which treatment they are receiving; control or intervention is a common problem in rehabilitation science. If we are to compare our experimental liner to the standard of care commercial liner there is little else that can be done.

5.4.2 Detailed Description of All Clinical Research Activities:

To test the new liner, we recruited six participants. The participants were persons with lower limb, trans-tibial limb loss These participants were recruited by posting informational flyers. The flyers detailed the inclusion criteria, and exclusion criteria and relevant information. Participants contacted us through telephone after seeing the flyer and arrange to come in. During the telephone interview which was designed to assess a participant's interest, the participant was scheduled to come in and speak with us. Informed consent documents were signed once all the details of the study were explained, and understood by the participant.

After informed consent was given by the participant, we assessed the health of the residual limb of the participant. The limbs were confirmed to be healthy and the skin healthy with no injuries present.

The participants were given a new prosthetic limb for use only during the test, and were not be allowed to keep it. The participants were given a new prosthetic limb to ensure compatibility of the limb with the new experimental liner we are testing. We wanted to ensure that all experimental prosthetic limb liners fit properly together with the residual and prosthetic limb. This meant that the user's own prosthesis was not damaged during testing. The prosthetic limb they were provided took several hours to complete. While the limb was being made the participants were asked to leave and return the next day. After the participant had their new prosthetic limb, we provided them with 2 prosthetic limb liners. The first liner was a standard off the shelf prosthetic limb liner. And the second was an experimental moisture permeable prosthetic limb liner.

The measurement of how much moisture remained in the prosthetic limb had some error associated with it. To control for evaporation of moisture while the remaining liquid is poured

into a container, and the mass weighed, we used the off the shelf liner to first do 3 pre-trial tests. The pre-trial tests last 5 minutes each test. During the test, the prosthetic limb user were asked to wear the silicone off the shelf liner and a known quantity of saline solution (10 milliliters) was added. After 5 minutes the limb was removed and the quantity of remaining liquid measured by mass. This was repeated 3 times and the value of the moisture lost to evaporation during measurement was found by averaging the difference of the known quantity added, to the quantity measured after the trial. These pretrial tests were to be used to correct the later experimental liner permeability results. The amount of moisture lost to evaporation from the wet skin, and inside the liner is expected to be the same for the off the shelf and experimental liner. This measurement error is called the ME for measurement error.

After the error measurements were made, the order of the liner testing, control or experimental was randomized. The participant cannot be blinded to which liner is being tested as they are visually distinct. The off the shelf liner is clearly labeled with the manufacturers markings and the experimental liner is unlabeled and handmade, with perforations. The water was be applied to the interior surface of the prosthetic limb liner. This served as a mild artificial perspiration. The limb with liner was then inserted into the socket and was moistened by the saline solution. Next the liner was given the opportunity to perform its function of removing moisture. The moisture was removed for a period of 1 hour. After the liner had a chance to remove moisture for an hour, the prosthesis was be removed, and the amount of moisture remaining was be measured by pouring the remaining moisture into a container, using a paper towel to swab the limb and the inside of the liner, weighing the mass, and comparing it to the tare value. The moisture permeability measurement process was be identical for both the control and the experimental liner. The amount of moisture removed from the socket in one hour is the

variable known as the Hourly Moisture Removed (HMR).

If a participant fully completed the study, they were given 100 dollars on the WePay card. If a participant left early they were given 50 dollars on the we pay card to as a thanks for their effort. If they left early and withdrew from the study their data as be destroyed.

5.5 RESULTS

The first prototype which was manufactured to show proof of concept violated the design criteria set forth by the users in the focus groups. This was due to the fact that the interior of the first prototype had large holes which would constitute unnecessary interior textures. These textures had the potential to cause irritation so the prototype#1 was not tested with human participants. Five participants got through the study up until the randomization step. The second prototype was tested twice with participants but failed both times. The third prototype was tested one time with participants and was successful.

The testing took place over the course of three separate days. On the first day three participants came to the lab to test the equipment and aid in confirming the protocol. During this testing session the vacuum pump initially planned for use was found to be faulty and needed to be replaced. The participants were asked to leave and comeback when everything was working correctly.

During the next testing session two participants were asked to come in and test the liners. Two prototypes were prepared of the second generation prototype variety. Both prosthetic liners failed. The failure was apparent by the rapid loss of vacuum and all liquid. We would expect that for the surface area available to the liner for flux of liquid only a small amount of fluid would

pass through. In our testing both liners lost all 10mL in a matter of minutes. The tests with the experimental liners were cancelled for that reason. The vacuum was not stable in the liner signifying a leak. Approximately 2 inches of mercury vacuum pressure were lost every 6 seconds, or about 40 inches of mercury per minute.

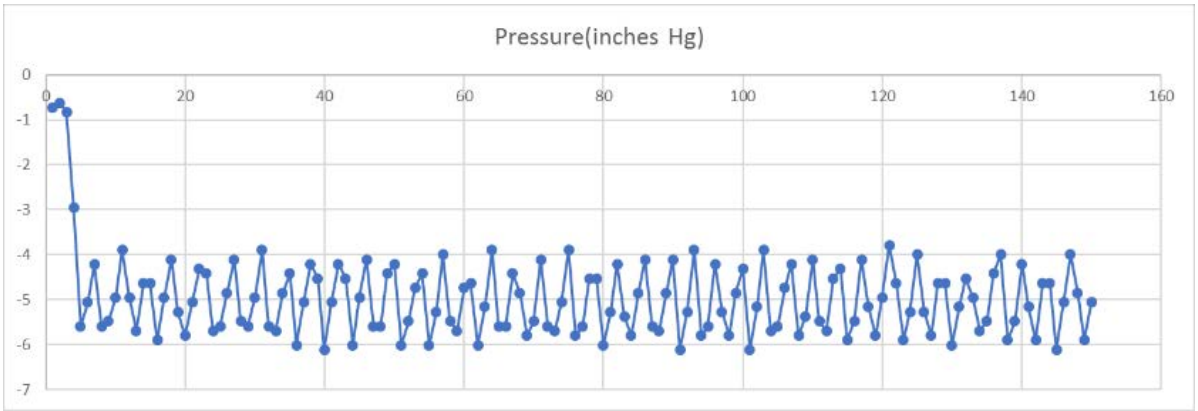


Figure 40 Pressure data for permeability testing of prototype#2

When it became apparent that the liner was going to fail as a result of failure of the distal end composite region to hold a vacuum, the testing time was shortened from one hour to 5 minutes. The reason for this reduction in testing time is to ensure that the skin of the residual limb of the participant is not subjected to prolonged periods of vacuum exposure. As the liner was unable to perform its moisture sweating function, and instead operated merely as a perforated liner, leaking out water, it was pointless to continue the test beyond the 5 minutes. After the five minute period was over the remaining quantity of moisture was assessed and determined to be near zero for both participants. A similar vacuum assisted test was done with the control liner and nearly all the moisture remained. This means that yes indeed it was a leak which led to loss of the moisture, rather than the controlled slow sweating of the moisture through the liner membrane. If it had operated correctly we would have expected to see a much slower rate of moisture removal of about 2ml/Hour through the experimental liner, against a 0.1-

0.2 measurement error, and a predicted outcome of 0.1-0.2mL/Hour for the control liner with a 0.1-0.2 error.

In both instances, the liner did not hold an airtight seal. The airtight seal was broken within the three layer hydrogel composite. The error was most likely due to a poor bonding strength of the hydrogel to the silicone elastomer. Although the hydrogel was adhered to the elastomer, it may have been a weak bond, or there may not have been enough bonded surface area. Upon donning the liner, the participants stretch the liner greatly; this places the liner into tension and opens it up to the possibility of damage. An important and common part of a typical prosthetic liner which our liner did not include is an external fabric sheath. The external fabric sheath is typically melted into the wall of the liner and is designed to prevent excessive stretching of the liner which operates primarily in compression when in use.

In order to overcome the failures of prototype #2 a new version of the Aquapore T.I. was designed to overcome the problem of leakage. One of the failed prototype#2 was dissected and an investigation was made as to the source of the leakage. The dissection revealed interesting information. The hydrogel membrane was intact inside the liner. It was therefore not likely that a failure of the hydrogel membrane led to the leak that was observed. The dissection of the failed prototype also showed another interesting result. The membrane while intact was not evenly adhered to the interior of the liner. Technically, from a purely design point of view prototype #2 should have been successful. The reality of the situation is that the margin of error for the design to be manufactured correctly is very thin. All the pieces must be adhered together with perfect accuracy, and with 100% success in order for the liner prototype #2 to work. It was therefore decided to sacrifice theoretical performance of the liner in order to improve the robustness of the design. The issue with the previous design is that the membrane was cut to cover the exact

surface area of the perforated silicone layer. For prototype#3 we decided to reduce the available area for moisture flux by reducing the number of perforations in the perforated silicone liner, which would have the consequence of increasing the area available for adhesion of the layers. This is a design trade off, and we felt at the time it was better to have a more robust design that was less able to remove moisture, than a design which could theoretically remove more moisture but which was not manufacturable. Notice in Figure 41 how many fewer perforations are present in protype#3 as compared to prototype#2. Note too how much larger the area is for smooth membrane adherence, highlighted in yellow. This made much more available space for excellent adhesion to take place uninterrupted by perforations (compare to Figure 38).

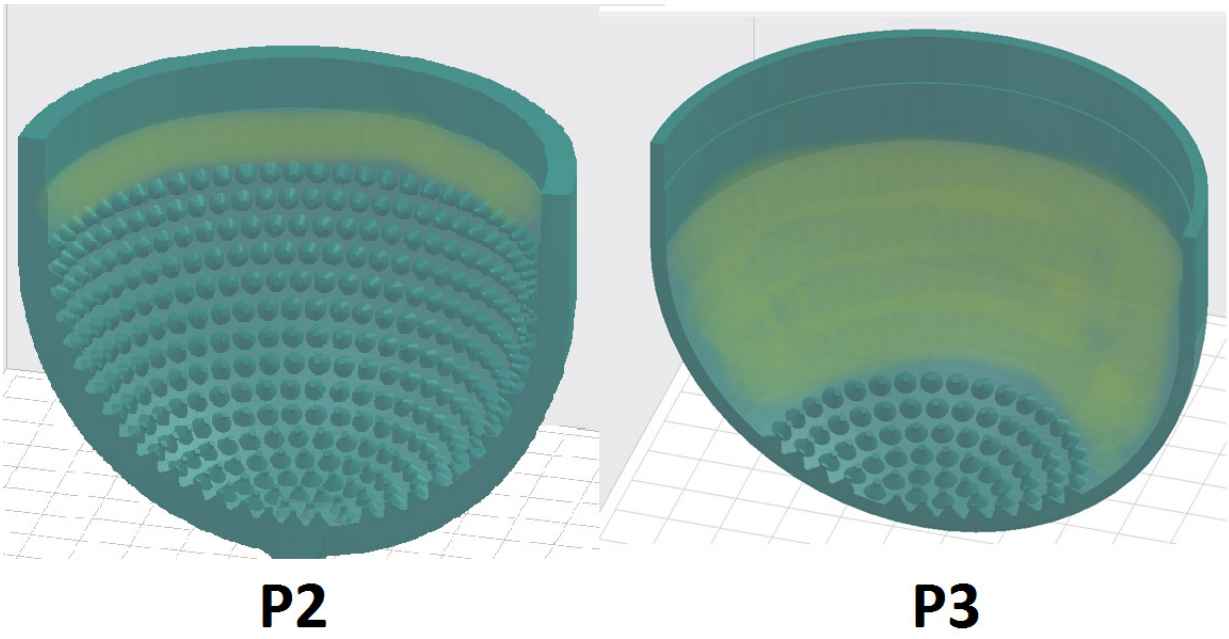


Figure 41 Comparison between the negative molds used for prototype #2 (P2) and prototype #3 (P3)

The third day of testing prototype#3 was tested with the help of a research participant. The prototype was able to hold a vacuum for much longer than the previous version. The previous version lost pressure at a rate of 40inchesHg/minute. Prototype#3 appeared to lose

vacuum at a rate of 0.25inchesHg/min, which is less than 1% of the vacuum loss of the previous prototype.

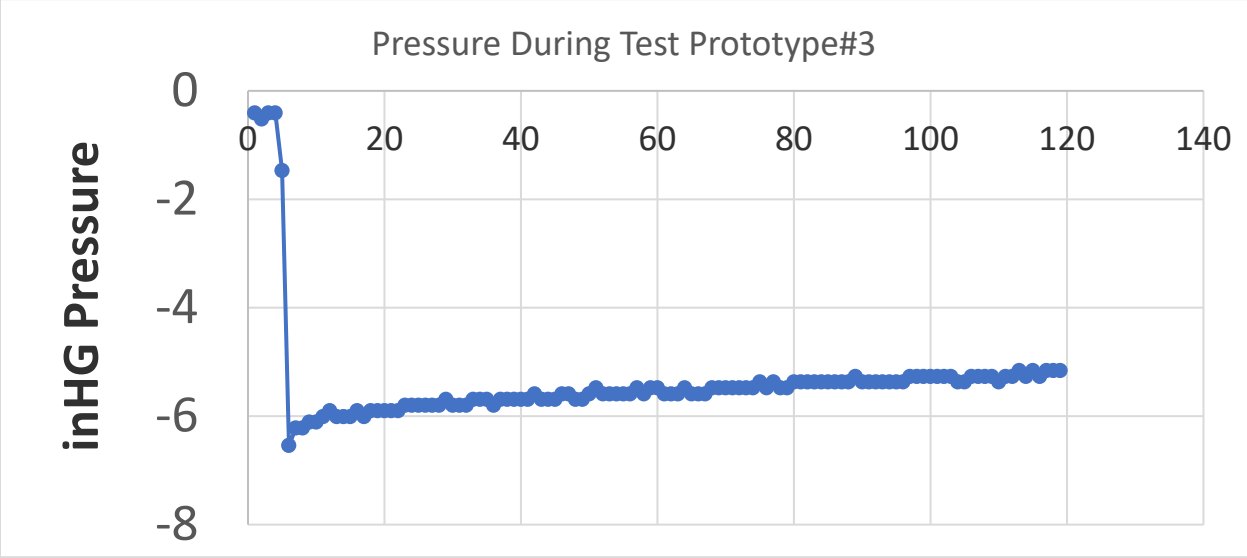


Figure 42 Pressure during test prototype#3

This alone represents an excellent improvement and constitutes a success. The liner, now able to hold a vacuum, was able to move about 2.5 ml from the interior of the socket liner out to the exterior where it was collected at the bottom of the socket. This represents a moisture removal rate of 2.5ml/hour which is clinically relevant.

5.6 DISCUSSION

The design improvements over the three prototypes are considerable. After the initial proof of concept prototype was manufactured, significant detailed design occurred to improve the pore dimensions to make it comply with the user requirements. The 3D printing approach was successful at manufacturing the prosthetic liner layers which were then bonded together using benzophenone. The first two prototypes were failures, but the third prototype demonstrated that a

hydrogel-elastomer composite enabled prosthetic liner can hold vacuum for a reasonable amount of time and draw moisture out from within the liner environment away from the skin. This approach to moisture management had not previously been reported. Further development is required to improve the design to reach an embodiment that is more easily manufacturable, and more robust, however the feasibility of the concept both in its theoretical derivation and its practical construction has been shown.

6.0 CONCLUSIONS AND FUTURE WORK

In the United States it is projected that the number of people living with limb loss will increase in the coming years due to an aging population and an increase in the number of people with vascular disease. While the most popular face of prosthetic limb research is the robotic limbs and closed loop neural feedback devices, such as those being developed at the Rehabilitation Institute of Chicago, there is another side of prosthetic limb research that is more intimate and less immediately obvious to those who do not use prosthetic limbs.

The comfort of a prosthetic limb is very important to the people who use them daily. Consistently through many surveys and studies, prosthetic limb comfort identified as being one of the top factors that determines the quality of life of the people that use prosthetic limbs. This study has endeavored to take a bottom up approach to improve the comfort of prosthetic limbs using the principles of bioengineering, systems engineering, and participatory action design. We have targeted excessive moisture accumulation because it is one of the most challenging, and persistent problems in modern prosthetic limbs that refuses to go away despite the variety of products on the market that attempt to solve this problem.

Through a systematic approach to first understanding the needs of stakeholders, considering all available options, and investigating the largest areas of risk first, this project has developed the Aquapore T.I., a novel approach to managing moisture in the prosthetic limb which uses a tough hydrogel-elastomer composite to remove moisture under vacuum pressure.

While the embodiment tested in the current study faces challenges in manufacturing and robustness, the feasibility of the overall conceptual product platform has been demonstrated. We believe that this project merits further investigation to improve the prototype and eventually reach a product which can impact consumers on a large scale.

The preliminary results described here will be useful in obtaining additional funding to continue the development and evaluation. The major challenge at this point is to streamline the manufacture of the liners as well as improve their airtight quality. The double network hydrogel is capable of achieving an airtight, robust composite liner. Further development of manufacturing techniques are needed to produce a viable product.

The next steps will include finite element analysis to aid in the design of the liner composites. The current liner composite design was selected for its simplicity, rather than its optimal configuration. It is impractical to build a prototype every time the design is changed. Instead, finite element analysis can be conducted to optimize the likelihood of success by comparing many competing embodiments first.

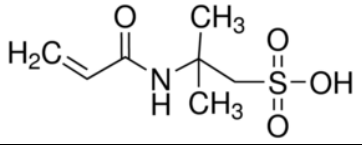
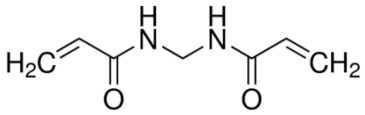
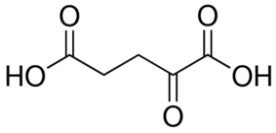
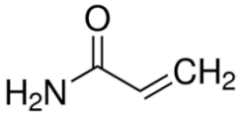
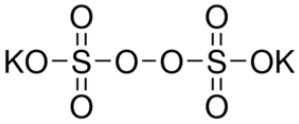
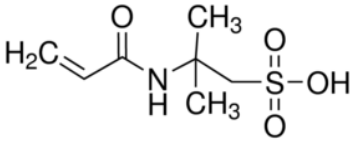
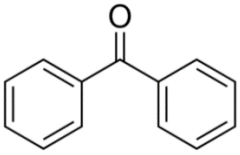
In addition to improving the configuration of the hydrogel-elastomer composite, further hydrogel formulation development is required. The advent of tough hydrogels is as yet still relatively new, and the future of material science will undoubtedly lead to better, stronger materials.

The most important step moving forward is the continued inclusion of end users in the design, analysis, and testing of the prosthetic liner. They are the ultimate beneficiaries of this project and the most important allies in ensuring its success moving forward. As more funding is secured in the future, larger and larger clinical trials will be planned to assess the practicality, efficiency, and success of the Aquapore T.I.

APPENDIX A

The above image shows a particularly large thing hydrogel membrane. Held together with only 5% by weight of polymer the hydrogel is .6mm thick and very strong.

APPENDIX B

Name	Description/ link	Chemical Structure
2-Acrylamido-2-methylpropanesulfonic acid (AMPS)	First network polymer large molecular weight http://www.sigmaaldrich.com/catalog/product/aldrich/282731?lang=en&region=US	
N,*N*′-Methylenebis(acrylamide)	Cross linker first network http://www.sigmaaldrich.com/catalog/product/sial/146072?lang=en&region=US	
2-Oxoglutaric acid	photo initiator first network http://www.sigmaaldrich.com/catalog/product/fluka/75890?lang=en&region=US	
Acrylamide	Polymer second network http://www.sigmaaldrich.com/catalog/product/fluka/01700?lang=en&region=US	
Potassium persulfate	Second photoinitiator http://www.sigmaaldrich.com/catalog/product/sial/216224?lang=en&region=US	
2-Acrylamido-2-methylpropanesulfonic acid (AMPS)	First network polymer large molecular weight http://www.sigmaaldrich.com/catalog/product/aldrich/282731?lang=en&region=US	
Benzophenone	Covalently bonding hydrogel to silicone https://www.sigmaaldrich.com/catalog/product/sigald/494437?lang=en&region=US	

This table includes a list and links to the chemicals used to make the hydrogels

APPENDIX C

This section contains all the worksheets for making the hydrogel membranes. These worksheets were printed out and used as a guide every time a hydrogel was made. All the worksheets together serve as a kind of recipe book.

Recipe for 3b – Verified by Esteban Ruiz 2-5-2017

	To Make 1 Liter of 3b First Network	Volume used	Molality (m)	Mole % w/ respect to monomer	Mass % w/ respect solvent	moles used	molar mass	**Mass used**	Half recipe	One quarter recipe	Source?
Solvent	Distilled water:	*1000.0 ml						**1000 grams**	500 grams	250 grams	Yasuda 2005, Haraguchi 2002
Monomer	2-Acrylamido-2-methyl-1-propane sulfonic acid		*1.0 molality			1.0 moles	207.25 g/mole	**207.25 grams**	103.625 grams	51.8125 grams	Yasuda 2005
Organic cross Linker	N,N'-Methylenebis(acrylamide)			*4.0%		0.04 moles	154.17 g/mole	**6.1668 grams**	3.0834 grams	1.5417 grams	Yasuda 2005
Photoinitiator	2-Oxoglutaric Acid			*0.1%		0.001 moles	146.10 g/mole	**.1461 grams**	.07305 grams	.036525 grams	Yasuda 2005
Inorganic Clay Crosslinker	Laponite XLG				*3.0%			**30.0 grams**	15.0 grams	7.5 grams	Huang 2005, Yang 2016
Salt	Sodium Chloride		2.0 molality			2.0 moles	58.44 g/mole	**116.88 grams**	58.44 grams	29.22 grams	Huang 2005, Hee Lee 2015
	To Make 1 Liter of 3b Second Network	Volume used	Molality (m)	Mole % w/ respect to monomer	Mass % w/ respect solvent	moles used	molar mass	**Mass used**	Half recipe	One quarter recipe	Source?
Solvent	*Distilled water:	*1000.0 ml						**1000 grams**	500 grams	250 grams	Yasuda 2005, Haraguchi 2002
Monomer	Acrylamide		*3.0 molality			3.0 moles	71.08 g/mol	**213.24 grams**	106.62 grams	53.31 grams	Yasuda 2005
Organic Cross Linker	N,N'-Methylenebis(acrylamide)			*0.1%		.003 moles	154.17 g/mole	**.46251 grams**	.231255 grams	0.115628 grams	Yasuda 2005
Photoinitiator	Potassium Persulfate			*0.1%		.003 moles	270.32 g/mol	**.81096 grams**	0.40548 grams	0.20274 grams	Yasuda 2005
Salt	Sodium Chloride		2.0 molality			2.0 moles	58.44 g/mole	**116.88 grams**	58.44 grams	29.22 grams	Huang 2005, Hee Lee 2015

Put laponite in water and mix thoroughly. Mix for 5 mins with vortex, and 2 hours no vortex. *(Huang 2005) Stir 10 mins, add monomer, crosslinker, vortex 1 hour, add imitator under ice bath and vortex 30 mins, also bubble at the same time.*yang 2016 Bubble the water Mix all together under ice water while stirring* Haraguchi 2002, (there is no concept of complete dissociation of platelets)

Stir laponite with vortex and bubble 1 hour with nitrogen

Add all the ingredients except for salt and initiator, mix 15 mins, add initiator and salt, cold, mix 15 mins* Esteban Ruiz shortcut original. MIX IN ALL REAGENTS VERY SLOWLY TO PREVENT CLUMPS!!!!

Put the 1st solution in UV for **6 hours, Soak it in 2nd network 24 hours, UV 2nd solution 6 hours**

A1: Protocol for Preparation of PAMP-PAAM Dual Network Hydrogel

"PAMPS gel, as the first network of DN gel, was obtained by radical polymerization using MBAA as a cross-linker and 2-oxoglutaric acid as an initiator. Monomer concentration was 1 mol/l, cross-linker was 4 mol% with respect to the monomer concentration, and initiator was 0.1 mol% with respect to the monomer concentration. Aqueous solution containing a monomer, cross-linker, and the initiator was bubbled with nitrogen for 30 min, and then injected into a cell consisting of a pair of glass plates separated by a silicon rubber. The cell was irradiated with a UV lamp (wave length 365 nm) for about 6 h."

"The DN hydrogel was synthesized by the sequential network formation technique (two-step method). The PAMPS gel (1st network) was immersed in an aqueous solution of 3 m DMAAm, containing 0.1 mol% MBAA, and 0.1 mol% potassium persulfate for 1 day until reaching the equilibrium. The 2nd network (PDMAAm) was subsequently polymerized in the presence of the PAMPS gel at 60 °C for 6 h between two plates of glasses. After polymerization, the PAMPS–PDMAAm DN gel was immersed in pure water for 1 week and the water was changed 2 times every day to remove any unreacted materials. PAMPS–PAAM DN gel was synthesized in the same procedure as that of PAMPS–PDMAAm DN gel."

Biomechanical properties of high-toughness double network hydrogels

Kazunori Yasudaa, Jian Ping Gongb, Yoshinori Katsuyamab, Atsushi Nakayamab, Yoshie Tanabea, Eiji Kondoa, Masaru Uenoc, Yoshihito Osadab
doi:10.1016/j.biomaterials.2004.11.021

To Prepare Double Network Hydrogel: 1 mol AMPS

Preparation of First Network, PAMPS

1) Weigh out 1mol AMPS (207.247grams)
2) Weigh out 0.04mol MBAA (6.167grams)
3) Weigh out 0.001mol 2-oxoglutaric acid (0.146grams)
4) Weigh out 1Liter H20 (1000.00grams)
5) Mix all together in a bowl very well
6) Inject between parallel glass plates desired thickness
7) Irradiate the PAMPS membrane with ultra violet light 6hours

Preparation of Second Network, PAAM

8) Weigh out 1mol AAm (71.078grams)
9) Weigh out .001mol MBAA (0.154grams)
10) Weigh out .001mol potassium persulfate (0.270grams)
9) Weigh out 1/3LH20 (333grams)
10) Mix together in a bowl
11) Soak PAMPS membrane in this secondary AAm Solution 24 hours
12) Return membrane to glass plates and irradiate with Ultra violet Light 6hours
13) Rinse gel continually using water pump for 2 days to remove unreacted material changing the water one daily

Specimen_A2: Standard Formulation 2

Specimen A2 is similar to A1, except the second solution is diluted by an equal volume of water to 1.5molal PAAM. The ratio of the PAAM to cross linker is the same in both A1 and A2

UV Times are 15 hours and soak times are 24 hours.

1st Solution: Monomer to Cross Linker Ratio: ____
2nd Solution: Monomer to Cross Linker Ratio: ____
UV 1 Cook time: ____
UV 2 Cook Time: ____
Soak Time: ___

To Prepare Double Network Hydrogel: 1 mols AMPS

Preparation of First Network, PAMPS

1) Weigh out 1 mol ((207.247grams))
2) Weigh out 0.04mol MBAA (6.167grams)
3) Weigh out 0.001mol 2-oxoglutaric acid (0.146grams)
4) Weigh out 1Liter H20 (1000.00grams)
5) Mix all together in a bowl very well
6) Inject between parallel glass plates desired thickness
7) Irradiate the PAMPS membrane with ultra violet light 6hours

Preparation of Second Network, PAAm

8) Weigh out .5mol AAm (35.539grams)
9) Weigh out .0005mol MBAA (0.077grams)
10) Weigh out .001mol potassium persulfate (0.270grams)
9) Weigh out 1/3LH20 (333grams)
10) Mix together in a bowl
11) Soak PAMPS membrane in this secondary AAm Solution 24 hours
12) Return membrane to glass plates and irradiate with Ultra violet Light 6hours
13) Rinse gel continually using water pump for 2 days to remove unreacted material changing the water one daily

Specimen_A3: Standard Formulation 3

Specimen A3 is similar to A1 for the first solution but is different for the second network solution.

The second network solution contains only 3M salt. So the second solution is nothing more than a 3M salt solution.

I think it would have been good to have done a pure water one. I wil do that next time, Currently all the trays are used up.

1st Solution: Monomer to Cross Linker Ratio: ____
2nd Solution: Monomer to Cross Linker Ratio:____
UV 1 Cook time: ____
UV 2 Cook Time: ____
Soak Time:___

To Prepare Double Network Hydrogel: 1 mols AMPS

Preparation of First Network, PAMPS

1) Weigh out 1mol (207.247grams)
2) Weigh out 0.04mol MBAA (6.167grams)
3) Weigh out 0.001mol 2-oxoglutaric acid (0.146grams)
4) Weigh out 1Liter H20 (1000.00grams)
5) Mix all together in a bowl very well
6) Inject between parallel glass plates desired thickness
7) Irradiate the PAMPS membrane with ultra violet light 6hours

Preparation of Second Network, PAAm

8) Weigh out 1mol AAm (71.078grams)
9) Weigh out .001mol MBAA (0.154grams)
10) Weigh out .001mol potassium persulfate (0.270grams)
9) Weigh out 1/3LH20 (333grams)
10) Mix together in a bowl
11) Soak PAMPS membrane in this secondary AAm Solution 24 hours
12) Return membrane to glass plates and irradiate with Ultra violet Light 6hours
13) Rinse gel continually using water pump for 2 days to remove unreacted material changing the water one daily

Specimen_A4: 3M NaCl +1M PAMPS 1st network

In this recipe we will investigate the addition of NACl to the 1st network solution. My hypothesis is that the addition of the NaCl will create an artificial swelling in the first network. As long as the NaCl plays no role in the 1st reaction, then we will have a gel which may swell less in the presence of the second network 3m Pamms solution.

Preparation of the 1st network solution:

1) Make the Standard 1m Pamps Solution from Specimen_A1.

2) Add enough NaCl (Molar weight=58.44grams/mol) to augment the solution to 3m Nacl

You should thus have a 1st network solution equivalent to the A_1Formulation but with the addition of salt.

Preparation of the second network:

The second network at this point is not yet established and will change, But perhaps it should be the standard 3M Pamms solution.

Therefore:

- Specimen_A4 will use the modified salty first solution listed but also use the standard 3M Paams as the second solution.
- Specimen_A5 Is the standard A1 1t solution and pure water as the second solution.
- Specimen_A6will be A4 for the first solution but 1.5M Pamms for the second solution as described in A2.
- Specimen A7 can be A4 for the first solution, but pure water for the second solution.
- Specimen A8 can be A4 for the first solution but 3M salt solution for the second solution.
- Specimen_A9 will be the A4 first solution, and a standard 3m Paams solution with an additional salt content so that the second solution is also 3m in NaCl.

Specimen_A5: Second solution is only pure water.

In this specimen I would like to test how much the gels swell in pure water.

In order to do this we will prepare the first network of of the standard A1 recipe, then soak it in only pure water, this is only done to investigate swelling propertires.

Sample_L1_2: Laponite Formulation_2

1st Solution: Monomer to Cross Linker Ratio: ____
2nd Solution: Monomer to Cross Linker Ratio:____
Laponite Content: 6 wt%
UV 1 Cook time: 6 hours
UV 2 Cook Time: 6 hours
Soak Time: 24 hours

Important Info – This recipe is very similar to the Specimen_L1 but it has double the wt%. In the literature the wt% for laponite in most polymers is 3%, for this experiment we wanted to see if doubling the laponite concentration would affect the formation of the second network. Does having too much laponite inhibit the first network from interacting with the second network? Will doubling the laponite concentration also double the gel toughness?

To Prepare Double Network Hydrogel: 1 mols AMPS

Preparation of First Network, PAMPS

1) Mass out 60g of Laponite

2 Weigh out 1 Liter H20 (1000.000grams) and add to the Laponite, mix on stir plate for 30 minutes

3) While the laponite is mixing Weigh out .5mol AMPS (207.246grams)

4) Weigh out 0.04mol MBAA (6.166grams)

5) Weigh out 0.001mol 2-oxoglutaric acid (0.156grams)

6) Add MBAA, AMPS, and 2-oxoglutaric acid to the same bowl and grind with mortar and pastel until it is a fine powder

7) Take Laponite solution off stir plate and filter it through a .45um filter syringe (get rid of chunks that didn't dissolve)

8) Put the solution on ice

9) Add the MBAA, AMPS, 2-oxoglutric acid mixture to the Laponite solution

10) Measure out 1.5g of Potassium Persulfate (Initiator) and add it to the solution

11) Pour solution into mold and irradiate for 6 hours

Preparation of Second Network, PAAm

1) Weigh out 1mol AAm (71.078grams)

2) Weigh out .001mol MBAA (0.154grams)

3) Weigh out .001mol potassium persulfate (0.270grams)

4) Weigh out 1/3LH20 (333grams)

5) Mix together in a bowl

6) Soak PAMPS membrane in this secondary AAm Solution 24 hours

7) Return membrane to glass plates and irradiate with Ultra violet Light 6hours

8) Rinse gel continually using water pump for 2 days to remove unreacted material changing the water one daily

Testing Notes:

Specimen_L2_1: Laponite Formulation_3

1st Solution: Monomer to Cross Linker Ratio: ____
2nd Solution: Monomer to Cross Linker Ratio:____
Laponite Content: 3 wt%
UV 1 Cook time: 6 hours
UV 2 Cook Time: 6 hours
Soak Time: 24 hours

Important Information: For this variation on the laponite hydrogel we wanted to see what would happen if the laponite was added to the second network. Are the laponite disks able to add at the same time as the second network? Will the laponite react with the second network before it has time to react with the first network? Is adding the laponite during the second network polymerization too late?

To Prepare Double Network Hydrogel: 1 mols AMPS

Preparation of First Network, PAMPS (1M)

1) Weigh out 1mol AMPS (207.247grams)
2) Weigh out 0.04mol MBAA (6.167grams)
3) Weigh out 0.001mol 2-oxoglutaric acid (0.146grams)
4) Weigh out 1 Liter H20 (1000.00grams)
5) Mix all together in a bowl very well
6) Inject between parallel glass plates desired thickness
7) Irradiate the PAMPS membrane with ultra violet light 6hours

Preparation of Second Network, PAAm (1M)

1) Weigh out 9.99g of laponite
2) Weigh out 1/3L of water (333g)
3) Add the laponite to the water and mix on a stir plate for 30 minutes
4) Weigh out 1mol AAm (71.078grams)
5) Weigh out .001mol MBAA (0.154grams)
6) Weigh out .001mol Potassium Persulfate (0.520grams)
7) Mix the AAm, MBAA, and Potassium Persulfate together.
8) Filter the laponite with a syringe filter and put on ice
9) Add the AAm mixture to the laponite solution and mix vigorously
10) Take solution off ice and soak the PAMPS membrane in this secondary solution for 24 hours
11) Return the membrane to the molds and irradiate it for 6 hours
12) Rinse gel continually using water pump for 2 days to remove unreacted material changing the water one daily

Testing Notes:

Sample_L2_2: Laponite Formulation_4

1st Solution: Monomer to Cross Linker Ratio: ____
2nd Solution: Monomer to Cross Linker Ratio:____
Laponite Content: 6 wt%
UV 1 Cook time: 6 hours
UV 2 Cook Time: 6 hours
Soak Time: 24 hours

Important Information: Specimen_L4 similar to Speciment_L2 by the fact that they both have double the laponite concentration for a polymer that was in the literature. The difference is in Specimen_L4 the laponite is in the second network and not the first. Will having this much laponite in the second network affect its ability to polymerize with the first network?

To Prepare Double Network Hydrogel: 1 mols AMPS

Preparation of First Network, PAMPS (1M)

1) Weigh out 1mol AMPS (207.247grams)
2) Weigh out 0.04mol MBAA (6.167grams)
3) Weigh out 0.001mol 2-oxoglutaric acid (0.146grams)
4) Weigh out 1 Liter H20 (1000.00grams)
5) Mix all together in a bowl very well
6) Inject between parallel glass plates desired thickness
7) Irradiate the PAMPS membrane with ultra violet light 6hours

Preparation of Second Network, PAAm (1M)

1) Weigh out 19.98g of laponite
2) Weigh out 1/3L of water (333g)
3) Add the laponite to the water and mix on a stir plate for 30 minutes
4) Weigh out 1mol AAm (71.078grams)
5) Weigh out .001mol MBAA (0.154grams)
6) Weigh out .001mol Potassium Persulfate (1.04grams)
7) Mix the AAm, MBAA, and Potassium Persulfate together.
8) Filter the laponite with a syringe filter and put on ice
9) Add the AAm mixture to the laponite solution and mix vigorously
10) Take solution off ice and soak the PAMPS membrane in this secondary solution for 24 hours
11) Return the membrane to the molds and irradiate it for 6 hours
12) Rinse gel continually using water pump for 2 days to remove unreacted material changing the water one daily

Testing Notes:

Sample_L1: Lanponite Formulation_1

1st Solution: Monomer to Cross Linker Ratio:
2nd Solution: Monomer to Cross Linker Ratio:
Laponite Content: 3 wt%
UV 1 Cook time: 6 hours
UV 2 Cook Time: 6 hours
Soak Time: 24 hours

Important Info – In this recipe for the Hydrogel the laponite was added into the first network. In theory the laponite should insert itself between the polymers that form in the first step and not affect how the first network interacts with the 2nd network.

To Prepare Double Network Hydrogel: 1 mols AMPS

Preparation of First Network, PAMPS W/Laponite

1) Mass out 30g of Laponite
2 Weigh out 1Liter H20 (1000.000grams)and add to the Laponite, mix on stir plate for 30 minutes
3) While the laponite is mixing Weigh out 1mol AMPS (207.247grams)
4) Weigh out 0.04mol MBAA (6.167grams)
5) Weigh out 0.011mol 2-oxoglutaric acid (0.146grams)
6) Add MBAA, AMPS, and 2-oxoglutaric acid to the same bowl and grind with mortar and pastel until it is a fine powder
7) Take Laponite solution off stir plate and filter it through a .45um filter syringe (get rid of chunks that didn't dissolve)
8) Put the solution on ice
9) Add the MBAA, AMPS, 2-oxoglutric acid mixture to the Laponite solution
10) Measure out .75g of Potassium Persulfate (Initiator) and add it to the solution
11) Pour solution into mold and irradiate for 6 hours

Preparation of Second Network, PAAm

1) Weigh out 1mol AAm (71.078grams)
2) Weigh out .001mol MBAA (0.154grams)
3) Weigh out .001mol potassium persulfate (0.270grams)
4) Weigh out 1/3LH20 (333grams)
5) Mix together in a bowl
6) Soak PAMPS membrane in this secondary AAm Solution 24 hours
7) Return membrane to glass plates and irradiate with Ultra violet Light 6hours
8) Rinse gel continually using water pump for 2 days to remove unreacted material changing the water one daily

Testing Notes:

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