Winter 2014

Encapsulation of Anti-Traction Material

Brian Zukas
University of New Hampshire, Durham

ENCAPSULATION OF ANTI-TRACTION MATERIAL

By

Brian Zukas

B.S. Chemical Engineering, University of New Hampshire, 2012

THESIS

Submitted to the University of New Hampshire

in Partial Fulfillment of

the Requirements for the Degree of

Master of Science

In

Chemical Engineering

December, 2014

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Brian Zukas

This thesis has been examined and approved.

Thesis Director, Nivedita Gupta, Associate Professor of Chemical Engineering

Glenn Shwaery, Assistant Dean of Research of the College of Engineering and Physical Sciences

Kyung Jae Jeong, Assistant Professor of Chemical Engineering

On November 12, 2014

Original approval signatures are on file with the University of New Hampshire Graduate School.

Acknowledgements

I sincerely thank Dr. Gupta for bringing me on as her graduate student to work on this project and for all of her help over the course of this project. I am truly looking forward to my continued work with her as a PhD student.

I would like to thank Dr. Shwaery for the help that he provided during the course of this project and for taking time to serve on my thesis committee. I would like to thank Dr. Jeong as well for giving his time to serve on my thesis committee. I also would like to thank Tristan Carrier for his work through the whole patenting process that resulted from some of this work.

I greatly appreciate all of the help that Amy Kasabian, Brett Kolmeister, and Sachi Nagada provided during the course of this project.

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Abstract

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Anti-Traction Material (ATM) is a highly viscous and viscoelastic aqueous polymer solution that has been demonstrated as an effective area denial, non-lethal technology. However, current means of dispersing ATM require on site pumping of the reagents and large tanks for reagent storage. The moment that ATM is dispensed onto a surface it also begins to dry out, starting the clock on the time it is effective. To counter these problems, ATM has been successfully encapsulated using the inverse alginate gelation technique. To produce capsules of ATM, a novel method of producing drops of the highly viscous and viscoelastic ATM solution was developed. The difference in effective duration between unencapsulated and encapsulated ATM was evaluated through coefficient of friction measurements. An emulsion of 40 wt% alginate solution and 60 wt% silicon oil produces a capsule that offers at minimum an 118% increase in the effective duration of ATM. The capsule's ATM contents can then be dispensed by a rupturing pressure on the order of $3x10^4$ Pa, coating the rupturing object and the surface under it with ATM. Optimization of the capsule size and the concentration of ATM core was investigated. Increasing capsule size was shown to decrease the drying rate by 21% at 48 hours. Decreasing the initial concentration of ATM in the capsule core may also have a similar positive effect on the drying rate.

Chapter 1: Introduction

1.1 <u>Motivation</u>

Static methods of area denial are often an important component in preventing or greatly slowing access of critical government buildings, strategic locations, or sensitive commercial buildings. Area denial is often accomplished by the use of concrete barricades, walls, and/or fences. While these barriers are commonly used, they have inherent weaknesses that can easily be overcome by determined individuals or groups. Barriers often require heavy equipment for installation and removal, requiring extensive preplanning prior to use. More mobile barricades are often effective only against specific threats, fences may not be effective against vehicles, and barricades for vehicles are not necessarily effective against individuals on foot.

Anti-Traction Material (ATM) was designed to address these weaknesses. It is an aqueous polymer solution that when coating a surface produces a very low friction surface. The low friction of the surface makes controlled travel across the coated surface extremely difficult. It is effective against both foot and vehicle traffic and is very difficult to defeat through counter measures. It also requires much less equipment to disperse a coating of ATM than to set up most barricades. Current ATM dispersion methods are also mobile, allowing the rapid dispensing of ATM if needed.

Spray coating a surface with ATM has been demonstrated as a highly effective non-lethal technique in many different area denial scenarios. Currently, the method for dispensing large quantities of ATM requires that large volumes of water and dry ATM powder be transported to the intended area of use. Once at the area of use, the water and dry ATM entrained in a compressed

air stream must be mixed at the tip of a mixing nozzle. This method may be cumbersome for certain situations, requiring a water tank, a hopper for the ATM powder, a pump, an air compressor, and a power supply to drive the pump and compressor [1]. On top of the large equipment requirements, ATM is an aqueous solution and immediately begins to dry as soon as the coating is dispensed. As ATM dries, the coefficient of friction of the coated surface begins to increase; once the coefficient of friction is high enough, the surface it is coating may be successfully traversed.

1.2 Encapsulation

Encapsulation of ATM addresses both the equipment burden necessary to cover an area with ATM, but also the duration of its effectiveness. ATM capsules can be made prior to their dispersal on a surface, requiring only a container to transport them and a simple dispensing mechanism. Once dispensed the capsule shell acts as a water vapor barrier, slowing down the rate of water evaporation from the ATM solution. The shell protects the ATM core from water loss until a foot step or a vehicle ruptures the shell. Once the capsule is ruptured, dispensing its ATM contents, the surface is coated with ATM just as it would be using the nozzle method. The shell fragments would ideally not interfere with the low friction properties of the ATM.

In order to encapsulate ATM, drops of ATM must be produced first. This required the development of a novel method for producing filament free, discrete drops of a highly viscous and viscoelastic fluid. Newtonian drop formation is relatively easily accomplished and is a well-studied phenomenon. Newtonian drops can be made from a slowly dripping faucet, a liquid stream introduced into another flowing, immiscible fluid, atomization, etc. Since ATM is a concentrated polymer solution it displays non-Newtonian behavior that is common to polymer solutions, e.g. shear thinning, filament formation and beads-on-a-string effect. Shear thinning is the rheological

behavior of a fluid that experiences a decrease in viscosity as the shear acting on the fluid increases. Filament formation can occur in both Newtonian and non-Newtonian fluids. In drop formation of Newtonian fluids with high viscosity, filament formation is the result of the fluid's viscosity resisting the surface tension forces trying to pull the fluid into a sphere, causing a filament to form. In a non-Newtonian fluid such as a polymer solution, it is the entangled polymer chains in solution that cause filament formation. Unlike a Newtonian fluid where the filament even for very viscous fluids will eventually break, filaments caused by entangled polymer chains will not necessarily break. These non-Newtonian filaments can persist to the point where multiple drops of fluid are connected together by a filament. This behavior is known as the beads-on-a-string effect, since the connected drops of fluid look like a beaded necklace. Handling of and drop formation of ATM is very difficult to accomplish due to ATM's high zero shear viscosity and the previously mentioned non-Newtonian behavior.

Once a drop of ATM has been formed another process can be used to produce the desired capsule shell around it. There are several standard methods used for encapsulating a wide range of materials. There are mechanical methods of encapsulation such as spray coating, extrusion, and spray drying. The other category of methods includes chemically controlled processes, such as: interfacial reactions, layer by layer processes, and emulsion polymerization. In the work presented here, three different methods were used to produce a capsule shell. The first method was interfacial crosslinking to produce a hydrogel membrane. The second method was dip coating a capsule with poor water vapor barrier properties with a molten wax coating. The third method involved producing a hydrophobic liquid monomer layer around either a drop of ATM or a capsule of ATM and then cross linking the monomer to form a solid plastic shell.

1.3   Desired Capsule Properties

In order for ATM capsules to be an effective replacement for spray coating surfaces with ATM there are a number of concerns that must be considered and essential criteria that must be met. One of the most important criteria is to improve the effective operating life span of ATM. The capsules must prevent moisture loss from the ATM contents, enabling capsules that are dispensed in the field to contain encapsulated ATM that retains its low friction properties longer than a spray coating of ATM would. The capsules should be able to create a low friction surface on as wide of a range of surfaces as unencapsulated ATM is. The capsules themselves should be robust enough to withstand post-fabrication handling, storage, and dispensing mechanisms. The capsules must also be weak enough that they can be ruptured by the foot pressure of a person traversing a surface covered with the ATM capsules. To provide a wide range of scenarios that that capsules would be effective for, the ATM contents should be viable over as wide of a temperature range as possible.

The process used for forming the capsules would ideally be quick and relatively simple. Long reaction times lead to smaller production yields or require more equipment to meet production needs. Complicated reactions requiring multiple steps, high temperatures and hazardous chemical handling are not desired since it would serve to increase the complication of producing large quantities of capsules and lead to higher production costs. Any material remaining on or in the capsule after whatever fabrication process is used for capsule production should be safe for human contact and environmentally safe as well. When the capsules are used in the field there is a chance that the capsule materials, both shell and core, will come into contact with parts of the body such as the skin or eyes. Since large quantities of the capsules will be used in field, the capsule materials should not be an environmental contaminant in order to prevent complications arising from both their use and the clean up after use.

1.4   Objectives

Encapsulating ATM produces an easier to handle form of this effective area-denial non-lethal technique and improves its operational duration. The goals of the work presented in this thesis are:

- Develop method of continuous production of capsules containing ATM cores.

- Explore various encapsulant materials and encapsulation techniques for preventing water loss, ease of handling, and reaction times.

- Identify the best encapsulant and optimize formulation for maximizing effective life span.

- Determine the effectiveness for the best encapsulant formulation by measuring coefficient of friction and rupture strength of the ATM capsules.

In Chapter 2, I will discuss the current methods of producing drops of fluids and the materials used for creating capsules and water vapor barriers. In Chapter 3, I will describe the materials used in the experiments, experimental setup and equipment used for analysis, and analysis conducted. In Chapter 4, I will discuss the results of the experiments to determine the best encapsulant materials and fabrication of ATM capsules. Chapter 5 contains a summary of the work completed and future recommendations.

Chapter 2: Background

2.1 Commercial Encapsulation Methods

Encapsulation is used in a very large range of industries for an even wider range of uses. From cosmetics to food products, and vitamins to self-healing materials, encapsulation is key to making many modern products. Generally commercial methods of encapsulation break down into two groups, encapsulation through mechanical methods and encapsulation through chemical methods. Each group has its benefits and detractions which will be discussed briefly here, as well as the applicability of each process with the problem of encapsulating ATM.

2.1.1 Mechanical Encapsulation

Mechanical encapsulation essentially uses machinery to produce capsules of a desired material. While there are certainly chemical and physical processes occurring in these methods, it is the machinery used in these processes that define the method. Often mechanical methods have higher throughput and can produce a less expensive overall product [2]. One common and relatively inexpensive method of producing encapsulated materials is through rotating disk spray drying. In this method the core material is dispersed throughout an encapsulant phase. The homogenized solution is then dispensed onto a rotating disk and as the solution reaches the edge of the disk it is flung off where it breaks into droplets due to surface instabilities. The drops are then usually freeze dried to produce a solid capsule [2]. This is a continuous, high throughput process that is highly scalable. This method however is not applicable to encapsulation of ATM due to the requirement that all fluids easily form drops and have a low viscosity.

Another method of producing encapsulated materials is co-extrusion of fluids. This typically involves two immiscible fluid streams flowing concentrically through a nozzle. When the fluids leave the nozzle tip they spontaneously form drops or if the fluids cannot readily form drops then a valve or blade may be necessary to form discrete volumes of the fluids. The outer fluid can be a wide range of materials such as a molten solid that solidifies through cooling, a polymer solution that hardens through solvent evaporation, or a monomer that is polymerized to form a solid shell [2] - [3]. Co-extrusion is capable of producing capsules in a wide range of sizes, with a monodisperse size range. This method is not directly applicable to the encapsulation of ATM due to the difficulty in producing discrete drops of ATM. ATM is a highly non-Newtonian fluid and would not form discrete drops in a co-extrusion system.

Fluidized bed coating of particles is another high throughput, mechanical method of producing encapsulated material. This method introduces solid particles into a chamber where they are entrained in a moving gas stream. As the particles move through the chamber they are sprayed with a fluid containing the desired coating material. This material can either be a molten material such as a lipid or wax, or a polymer dissolved in a solvent [4]. Often, the chamber used for the coating process has an increasing radius towards the top; since the gas flow rate entraining the particles is constant, as the radius of the chamber increases the average gas velocity decreases. The average velocity will eventually decrease to the point where it cannot entrain the particles anymore and the particles will fall back down through the spray. Eventually the particles will be sprayed with enough material that they cannot be entrained anymore and they fall out of the chamber [5].

A variation of this process is done with a horizontal, rotating chamber where particle tumble through the chamber and are coated by a spray. These spray coating techniques may be useful for the large scale production of pure alginate capsules coated with a wax shell. Due to the expense of

the equipment necessary for this method, it was not possible to investigate it for the work presented here.

2.1.2   Chemical Methods of Encapsulation

Chemical methods of encapsulation are methods that do not rely on specific equipment to accomplish encapsulation but instead rely on chemical reactions or thermodynamics to drive the creation of an encapsulated product. These are typically slower processes due to the requirements of the encapsulation reactions, and may be conducted in batch [2]. These two factors may reduce the overall throughput of chemical encapsulation method when compared to a mechanical, continuous process. Interfacial encapsulation reactions can be accomplished by a number of different reactions, all achieving the result of forming a membrane radially outward from the core of the capsule. There are also layer-by-layer or self-assembly techniques that take advantage of the spontaneous arrangement of species to form a thermodynamically favored product, such as a liposome [6]. Solvent evaporation can be coupled with emulsion formation to form a solid capsule shell around a liquid drop.

2.2   Drop Production

As discussed previously, it is necessary to produce drops of the ATM solution in order to then perform an encapsulation method/reaction to form a capsule of ATM. There are numerous methods used to produce drops, both Newtonian and non-Newtonian. One of the easiest ways to make drops is to simply drip a fluid from a nozzle, like the extrusion method discussed earlier. A volume of fluid will form at the tip of the nozzle, held in place by capillary forces. As the weight of the drop increases, eventually the weight of the drop will overcome the capillary forces, causing it to fall. As the drop falls from the nozzle tip, surface tension will cause the drop interface to pull into a

closed drop. If the viscosity of the fluid is high enough, the effects of the surface tension can be resisted by the fluid, causing long filament formation to occur before a separated drop is formed. This process can behave somewhat differently depending on the viscosity of the fluid, a more viscous drop is going to form a long filament that must be thinned before surface tension can pinch off a drop [7].

Faster drop production and tighter control over droplet size can be achieved by introducing one fluid stream into another bulk flow. The bulk flow can be a liquid or a gas and different flow designs can be used. Two of the most common designs are a T-junction and co-flowing streams. In the T-junction one stream is introduced perpendicular to another. The T-junction can be used to create monodisperse droplets continuously. The other common design is a co-flowing or flow focusing system. For both of these systems two streams of fluid are used where one is centered in the other. For co-flowing drop breakup, drop formation occurs similar to a dripping nozzle at low flow rates, except it is the drag forces of the bulk flow that overcome the surface tension holding the drop in place. At higher flow rates interfacial tension between the two streams cause drops to break off of the jet of the inner fluid [8]. For a flow focusing device the drop breakup is done by flowing both fluids through a constriction. There are many different breakup regimes for a flow focusing system but in general the constriction creates a region of higher shear allowing for the formation of drops an with a diameter an order of magnitude smaller than the channel diameter [9].

These systems quickly face difficulty when it is desired that a viscoelastic fluid be broken into droplets. For a viscoelastic polymer solution for example, during the pinch off phase of the drop formation, the polymer molecules will align in the filament formed during pinch off. The filament will not be broken by surface tension and can cause the bead-on-a-string effect. For polymer

solutions of a high enough concentration, the filament will not break because it is actually a highly entangled string of polymer molecules [10]. For some systems the filament will spontaneously break, creating a row of small satellite drops which can be undesirable. Some success has been made in producing controllable droplet sizes from viscoelastic fluids. This was demonstrated by flowing a viscoelastic fluid centered in a Newtonian fluid that is in turn centered in a bulk flow. The middle Newtonian fluid chaperones the inner viscoelastic fluid through breakup since the Newtonian fluid will strongly form drops as discussed previously [11]. This method however does not overcome satellite drop formation and is only applicable for a narrow range of viscoelastic fluids. ATM is a highly viscous, viscoelastic fluid and cannot be formed into drops by any of the methods discussed here.

2.3   Encapsulation

The difficulty of producing discrete drops of ATM led to the choice of a simple encapsulation process, which would be independent of the method used to produce drops of ATM. Based on this consideration, alginate was chosen as the material used to form capsules. While alginate is not an ideal water barrier, it is easily crosslinked and, as will be discussed below, much work has been done to modify alginate or related hydrogels.

2.3.1   Pure Alginate Capsules

Alginate films have been investigated as coatings for the preservation of food products. Since alginate films are non-toxic and are easy to form and have good resistance to oxygen diffusion, they are almost an ideal biologically based coating material. It is not a good water vapor barrier material since crosslinked alginate is a hydrogel [12]. However, much work has been done to

improve the water barrier properties of alginate. Due to the easy cross linking of alginate solutions by a variety of cations, much work has been done on the production of alginate capsules and beads.

The inverse gelation method was used to produce capsules with a liquid core surrounded by an alginate membrane. This capsule forming method uses a liquid drop, which contains solvated Ca^{2+} ions, immersed in a solution of sodium alginate. As soon as the drop makes contact with the alginate solution, the crosslinking reaction begins at the interface of the drop and alginate solution forming a membrane around the drop. The crosslinking continues radially outwards until either the Ca^{2+} ions are consumed or the capsule is removed from the bath [13]. This method can be performed at room temperature, with benign chemicals, and with reaction times on the order of 10 minutes. It has been demonstrated with both aqueous drops and oil drops, forming capsules that contain these fluids as a core [14].

2.3.2   Corn Starch

Hydrogel films and beads can be made from a slurry of starch and hydrogel solution. The incorporation of starch plays a couple of different roles in reducing the water vapor permeability of the hydrogel. Starch is a much more hydrophobic material than a hydrogel and has lower water vapor permeability than the hydrogel. In a study looking at the water sorption of lyophilized alginate beads, incorporating starch into the alginate reduced water sorption by 6 fold over pure alginate beads [15]. By incorporating starch into the hydrogel matrix it acts as a filler, occupying volume that would otherwise contain the more permeable hydrogel [16]. The presence of the starch in the hydrogel matrix also creates a much more tortuous path for a water molecule to travel during diffusion through the capsule membrane. It can also serve to improve the mechanical strength of the hydrogel.

2.3.3   Starch Nano-Crystals

Starch nano-crystals have also been used to decrease the water vapor permeability of hydrogel membranes. These nanoparticles are formed from the acid hydrolysis of commercially available starch [17]. When a solid is in a gel matrix, there are three possible dispersions that the solid can take on. Flocculated particles are just agglomerations of particles that sit in the hydrogel, forcing the gel to form around the large particle clusters. Intercalated particles are particles that still sit in clusters but the gel is able to penetrate the clusters to an extent. Exfoliated particles do not form particle clusters. Instead each particle is completely impregnated in the hydrogel matrix, and is separated from its neighboring particles by gel. Since each particle is tightly incorporated into the gel, it should increase the strength of the membrane, and also improve the water barrier properties of the membrane since the particles are more uniformly dispersed in the gel [18]. Due to their small dimensions, starch nano-crystals can incorporate into the hydrogel matrix much more fully. This creates an exfoliated particle dispersion in the hydrogel where the crystals do not form agglomerations with themselves but are instead individually, fully surrounded by the crosslinked hydrogel polymer. The incorporation of these starch particles into the hydrogel is believed to create a more tortuous path for a diffusing water molecule to take, reducing the overall rate of water diffusion. Corn starch nano-particles have been found to decrease the water vapor permeability of starch films by up to 40%. [18]

2.3.4   Bentonite Clay

Using the same concepts as the incorporation of starch into a hydrogel, bentonite clay has been investigated as a means of increasing the barrier properties of coatings. Bentonite clay is a cheaply available material with particles that are in the shape of wide platelets. The presence of the clay

particles in the film is intended to again increase the tortuosity of a molecule diffusing through the film. Bentonite swells in the presence of water, producing a larger surface area than a dry particle, which could lead to a more uniform layer of clay in the gel [19]. In dried alginate films, the presence of 3 wt% bentonite clay particles was found to reduce the diffusion coefficient of bezaldehdye by almost 1/3 [20].

2.3.5   Polystyrene Particle Sintering

Colloidosomes are liquid drops that are stabilized in a bulk fluid by the preferential alignment of solid particles along the interface between the drop and the bulk fluid. Much work has been done with various applications of this material but the one of interest for this work involves the sintering of the particles that are aligned on the interface. Normally when the particles self-assemble to surround a drop, forming a colloidosome, the particles are only held in place by weak forces and can be displaced through agitation. However by using polystyrene particles it has been demonstrated that a uniform, solid shell can be made from the collection of particles by sintering them together [21]. Sintering joins the polystyrene particles together by heating them below the melting point of polystyrene, but enough so that particles in close vicinity to each other are joined together. These fused particles then behave as a capsule with a liquid core instead of a self-assembled monolayer of particles.

2.3.6   Esterification of Alginate

Being a hydrogel, crosslinked alginate falls squarely in the category of being a hydrophilic material. However, this property does not lend itself to producing a good water vapor barrier to prevent the drying an ATM core. The hydrophilicity of alginate can also create problems for drug encapsulation of hydrophobic materials. Work was done to place ester groups on the alginate

molecule in order to increase the hydrophobic nature of crosslinked alginate. This was accomplished by using Fisher esterification with butanol and a concentrated sulfuric acid catalyst [22]. The most important aspect of this modification was that it retains the alginate molecule's ability to crosslink in the presence of Ca^{2+}. Beads of the esterified alginate were successfully produced by dripping a solution of the esterified alginate into a $CaCl_2$ bath.

2.3.7   *Lipid Addition to Alginate Films*

Lipids have been used in hydrogel films to improve the water barrier properties of the films through the addition of a hydrophobic material to the gel matrix. For gellan films, the addition of lipids has been found to reduce the water vapor permeability up to 20% over pure films [23]. Studies using alginate however have not shown large decreases in water vapor permeability because of the low fraction of oil used to produce the films. Low oil content was used because the studies dealt with a film that would be used for food coating and higher oil content would lead to oil exudation, making an undesirable food product. At low sunflower oil concentrations, 0.25 w/v% sunflower oil in alginate solution, there was no significant change in the decrease of the water vapor permeability of the alginate films studied. There was though a decrease of the water vapor permeability of the gellan films in the same study [12]. For the work presented here there was no concern about whether or not the oil would exude from the capsule surface, leading to the investigation of capsules made from emulsions with high fractions of oil.

2.4   Encapsulants Studied

Using the encapsulation methods discussed above, 13 different encapsulants and capsule modifications were investigated to find those that produced the lowest mass loss due to water vapor diffusion. Other capsule properties taken into account were the reaction time necessary to form the

capsule, and the strength of the resulting capsule. Encapsulants are unique formulations used to form a capsule shell around a drop of ATM and capsule modifications are additional processes used to modify one of the formulations studied.

Encapsulants Studied:

- Pure alginate capsules
- Corn Starch/alginate slurry
- Heat moisture treated starch slurry
- Starch nanocrystal/alginate slurry
- Bentonite clay/alginate slurry
- Polystyrene particle/alginate slurry
- Esterified alginate
- Wax coating of pure alginate capsules
- Poly (methyl methacrylate) (PMMA) coating
- Safflower oil/alginate solution emulsion
- Silicon oil/alginate emulsion

Capsule Modifications:
- Heat treated alginate
- Sintered polystyrene particles

The majority of the encapsulant formulations listed here are modifications of the methods discussed in Section 2.3. Wax coating was done as a means of easily producing a hydrophobic shell around and alginate capsule and was not based on any previous procedure. Heat treated alginate was investigated after observations of the capsules during the polystyrene particle sintering experiments. Silicon was investigated as a substitute for safflower oil since it would not be susceptible to oxidation, which could be a concern for long term capsule storage. PMMA

coating was investigated as a hydrophobic coating that would be stronger than the wax coating, while still offering the good water vapor barrier properties observed with the wax coated capsules [24].

Chapter 3: Experimental Methods

In this work, I conducted experiments on a wide range of potential formulations suitable for encapsulating ATM. Almost all of the formulations however, were based on an alginate membrane. In this chapter, the method of fabrication and testing of the various encapsulants is described. For preliminary experiments on assessing the range of encapsulants, polyacrylamide was used in place of ATM, since polyacrylamide is the primary polymer in ATM [25].

3.1   Materials and Chemicals

Table 3.1: Materials and chemicals used in ATM capsule membrane experiments.

Chemical	Manufacturer
Anti-Traction Material	Southwest Research Institute
Acetone (NF Grade)	Pharmco-Aaper
Alginic Acid, Sodium Salt	Sigma Aldrich
Bentonite, sodium form	Alfa Aesar
Benzoyl Peroxide	Sigma Aldrich
Butanol	Pharmco-Aaper
Calcium Chloride Dihydrate (lab grade)	Fisher
Corn Starch	Red Mill
Methyl Methacrylate	Acros Organics
Paraffin Wax	Gulf Wax
Poly(acrylamide)	SNF Inc.
Poly(methyl methacrylate)	Sigma Aldrich
Poly(vinyl alcohol)	MP Biomedicals
Polystyrene	Sigma Aldrich
Safflower Oil	Hollywood Oils
Silicon Oil, 10 cst	Clearco Products
Sulfuric Acid (ACS Grade)	JT Baker

3.2   Rheological Experiments on PAM and ATM

The method used for fabrication of ATM capsules depends on the rheology of the desired concentration of aqueous solution of ATM. To establish the rheology of the ATM solution, I conducted experiments on a 9.09 wt% aqueous ATM solution using a TA Instruments AR 550n rheometer with a 40 mm, 2˚, cone geometry. The AR 550n rheometer is capable of both steady state measurements and oscillation measurements which are necessary for the investigation of non-Newtonian fluids. The rheometer is controlled by the Rheology Advantage Instrument Control program where rheometer settings and experiment routines are entered. The rheometer's bottom plate's temperature is controlled by a Peltier plate, held constant at 25˚C for the experiments conducted in this work. I also conducted experiments on a 9.09 wt% aqueous solution of PAM to confirm that PAM could be used as an alternative core material to conduct some of the preliminary capsule experiments.

Three rheological tests were conducted on the fluids. A steady state flow experiment was conducted to determine the polymer solution's viscosity dependence on shear rate. To collect this data, the desired range of shear rates to investigate is set on the rheometer's software. By measuring the torque necessary to produce the specific shear rate at each step of the experiment, the viscosity of the solution as a function of shear rate is determined. Two oscillatory tests were performed on the polymer solutions, an oscillatory stress sweep and an oscillatory frequency sweep. An oscillatory stress sweep applies small oscillations, at a constant angular velocity, through the cone and measures the resulting response in the liquid. The responding oscillation can be broken into two components, an in phase and out of phase component. The in phase component of the response is the storage modulus, G' and the out of phase component is the loss modulus, G". These two

moduli have a physical meaning as well. G' represents the elastic nature of the solution, much like a rubber band or spring that when stretched stores energy. G" represents the viscous nature of the solution or the energy dissipation [26]. The results from this experiment are typically plotted as G' and G" versus oscillatory stress. Plotting this data as a log-log plot, there will usually be a range of stress the produces a constant G' and G" curve. This region is known as the linear viscoelastic region (LVR) and this represents the values of stress that do not damage the polymer structures in the solution being studied. For stress values that are higher than this region, large changes in G' and G" usually are seen. This represents a breakdown of the polymer structures in the fluid being tested and if future experiments are conducted in this region the results would not be considered valid.

Using a value of oscillatory stress within the LVR of the polymer solution, an oscillatory frequency sweep was conducted with both polymer solutions. The frequency sweep performs a very similar test to that of the oscillatory stress sweep, except in this case the stress is held constant and the rheometer runs the test through a range of angular velocities. The data from this experiment shows the dependence of G' and G" on angular velocity.

3.3   Capsule Fabrication Procedures

Aqueous solutions of ATM and PAM were prepared by mixing ultrapure water (Millipore Direct-Q 3 UV, resistivity of 18.2 MΩ cm) to produce a 9.09 wt% polymer solution. The solution sat in a wide container or petri dishes to maximize the contact area between the dried polymer and the water. The polymer was allowed to dissolve for at least 2 days before being used. The solution was stirred after 1 day to facilitate the solvation of the polymer. If a dish was being used for holding the solution, an air tight lid was used to cover the dish. If petri dishes were used, the dishes were

placed in a closed Tupperware container with a shallow layer of water at the bottom to inhibit drying.

For capsule formation with polymer solution cores, a $CaCl_2$ solution was used to produce the ATM or PAM solution in place of pure water. The solution preparation method was the same as the polymer solution preparation that used pure water. Three $CaCl_2$ solutions were used in this work, 3 wt%, 5 wt%, and 7 wt%. The results of each experiment will note what concentration of $CaCl_2$ solution was used to make the polymer solution in the capsule's core. For the experiments conducted with PAM, the desired mass of PAM solution was manually cut from a larger volume of PAM. The weight of the PAM core for these experiments was 0.40 g. For the experiments conducted with capsules containing ATM solution a syringe pump was used to dispense a set volume of ATM/$CaCl_2$ solution, the desired volume having been previously calibrated to the desired weight of ATM. The mass of ATM was then removed from the end of the syringe with an exacto knife. The weight of the cores used in these experiments was 0.14 g unless otherwise noted.

3.3.1 Pure Alginate Capsule Fabrication

The pre-dispensed volumes of PAM solution were dropped into a beaker of 0.5 wt% alginate solution, beginning the membrane formation reaction. The membrane forms radially from the surface of the ATM piece as the alginate is cross-linked by the calcium ions diffusing outwards. The membrane formation reaction proceeded for either 10, 20, or 25 minutes. Once the desired time had passed, the capsules were removed from the alginate solution and placed in a beaker of $CaCl_2$ solution for 10 minutes. The concentration of the $CaCl_2$ solution in this step was matched to the concentration of the $CaCl_2$ used to make the PAM solution in the capsule core. This ended the membrane growth and finished crosslinking any un-crosslinked alginate in the membrane. The capsules were removed from the $CaCl_2$ solution after 10 minutes and placed briefly in a Milli-Q

water rinse. At this point a fully formed capsule has been fabricated. Prior to any drying experiment, the capsules were briefly wrapped in a lab napkin to remove excess water from the surface of the capsule to help ensure uniform initial capsule conditions.

3.3.2 Alginate/Corn Starch Capsule Fabrication

The corn starch alginate solution was prepared by mixing the desired amount of cornstarch with the 0.5 wt% alginate solution. Cornstarch weight fractions of 10, 20, 30, 40, 50, and 60 wt% were investigated. The capsules for these experiments were made from PAM cores that had been prepared using 5 and 7 wt% $CaCl_2$ solutions. Membrane reaction times of 10 and 20 minutes were used. The capsule fabrication procedure followed the steps outlined in Section 3.3.1.

3.3.3 Heat Moisture Treatment of Starch

Before using the starch the same as was done in the preparation of the corn starch capsules discussed in Section 3.3.2, the corn starch in this formulation was subjected to a heat treatment step. A 70 wt% starch, 30 wt% water mixture was made and placed in an air tight canister. The canister was then placed in an oven for two hours at 120˚C. The canister was then taken out of the oven, opened, and allowed to cool and dry out overnight. This starch was then used the same as described in Section 3.3.2. For the trials conducted using this formulation, capsules with PAM cores were used. The PAM solution was made from $CaCl_2$ solutions of both 5 and 7 wt% $CaCl_2$. Membrane reaction times of both 10 and 20 minutes were used for this formulation.

3.3.4 Starch Nanocrystal Impregnated Capsule Fabrication

The starch nanocrystals were made by stirring in 10 g of corn starch in with 80 mL of a 3.28 M sulfuric acid solution at 40˚C for five days. After the five days water was added to the mixture in order to dilute the sulfuric acid. In order to separate the solids from the liquids they were

centrifuged and the liquid was decanted. The solids were then rinsed and centrifuged three more times in order to thoroughly rinse off the sulfuric acid. The solids were then placed in a petri dish and allowed to dry. Once dry, the particles were mixed into 20 mL of 0.5 wt% alginate solution and capsules were fabricated as described in Section 3.3.1. Membrane reaction times of 10 and 20 minutes were used in these trials. The capsules were fabricated with 9.09 wt% PAM cores made from both 5 and 7 wt% $CaCl_2$ solutions.

3.3.5 Alginate/Bentonite Capsule Fabrication

Similar to Section 3.3.2, solid bentonite was mixed with 0.5 wt% alginate solution to form a slurry. Slurries of 1, 2, 3, 4, 5 and 6 wt% bentonite were used to form capsules that contained PAM cores made from both 5 and 7 wt% $CaCl_2$ solution. Two different membrane reaction sequences were used for this material. The first method used was the same as for pure alginate capsules as described in Section 3.3.1. Membrane reaction times of 10 and 20 minutes were used to form the capsules in these drying trials.

To improve the membrane strength and retain the desired properties of bentonite a two step process was employed. Using either a 1 or 2 wt% bentonite slurry, an initial membrane layer was formed after a 7 minute membrane reaction time. After the 7 minutes was complete, the capsules were then transferred into a 0.5 wt% alginate solution and second membrane was formed for another 7 minutes. After this step was complete the capsules were but in $CaCl_2$ solution for 10 minutes. PAM cores of both 5 and 7 wt% were used to form capsules from this method.

3.3.6 Alginate/Corn Starch/Bentonite Capsule Fabrication

Cornstarch was mixed in with the bentonite-alginate slurry in an attempt to improve the mechanical strength of the membrane. PAM cores made from both 5 and 7 wt% $CaCl_2$ solutions

were used for these trials. The following 0.5 wt% alginate based slurries were made for capsule fabrication: 2 wt% bentonite and 2 wt% cornstarch, 3 wt% bentonite and 3, 5, and 7 wt% cornstarch. All underwent a membrane reaction time of 20 minutes followed by a 10 minute $CaCl_2$ rinse.

3.3.7   Polystyrene Particle Impregnated Capsule Fabrication

Polystyrene was dissolved in acetone to form a concentrated solution, the solid polystyrene particles were stirred for over a week. 20 mL of the polystyrene solution was then mixed with 30 mL of the 0.5% alginate solution in a round bottom flask. The round bottom flask was attached to a distillation apparatus and heated while being stirred. The heat stripped off the acetone from the alginate solution, causing the polystyrene to precipitate. The acetone vapors were condensed and the resulting distillate was collected. When the solution temperature in the round bottom flask began to rise, the flask was removed from the heat and allowed to cool. The capsules were then formed using either one of two methods. The first method is the method outlined in Section 3.3.1, using a membrane formation time of 20 minutes and a $CaCl_2$ bath of 10 minutes. The capsules were formed using a PAM core made from either a 5 or 7 wt% $CaCl_2$ solution. The second method adds a 30 or 60 minute heating step in a 40˚C water bath in an attempt to sinter the polystyrene particles present in the membrane together.

3.3.8   Heat Treating Alginate

Capsules are made using the pure alginate capsule fabrication method described in Section 3.3.1, except for the $CaCl_2$ rinse step. The membrane reaction proceeded for 20 minutes during each trial of this procedure. For the hot $CaCl_2$ bath step, a $CaCl_2$ solution was maintained at approximately 80˚C and the capsules were placed in this bath for 10 and 20 minutes.

3.3.9 Alginate Esterification

1 g of dry alginic acid was mixed with 30 mL of butanol and 2 mL of sulfuric acid for 24 hours. After 24 hours vacuum filtration was used to separate the solids from the liquids. The solids were also rinsed thoroughly with ethanol and then allowed to dry overnight. The alginate was then mixed into Milli-Q water to form the 0.5 wt% alginate solution necessary for membrane formation. 2 wt% cornstarch and 2 wt% bentonite were mixed into the alginate solution in order to increase the mechanical strength of the capsules. The capsules made from this formulation contain PAM cores made only from 7 wt% $CaCl_2$ solution. A membrane reaction time of 20 minutes was used for this formulation.

3.3.10 Wax Coated Capsule Fabrication

Pure alginate capsules with PAM cores were fabricated as described in Section 3.3.1. The PAM solution was made from either a 5 or 7 wt% $CaCl_2$ solution. The membrane reaction proceeded for 20 minutes in all cases. Paraffin wax was melted in an aluminum foil tray that was heated by a beaker of hot water. Once these capsules were fully formed they were dip coated into the wax. The capsules were removed from the tin, allowing the wax to cool and harden around the capsule. For one trial, prior to the capsules being dip coated they were sprayed with Rain-X to increase the exterior hydrophobicity of the capsule and promote any bonding interaction between the alginate and the wax.

3.3.11 Poly methyl methacrylate (PMMA) Coated Capsules

In order to form alginate capsules or unencapsulated PAM with a coating of poly(methyl methacrylate) (PMMA) the solid capsules or masses of PAM were dispersed into a stream of methyl methacrylate (MMA). In order to increase both the viscosity and density of the MMA,

PMMA was dissolved into the monomer. A solution of 29% PMMA in MMA was used. The thermal initiator benzoyl peroxide was used to initiate the polymerization and was dissolved in the MMA as well, at a 2 wt% concentration. The stream of MMA was introduced into either a quiescent volume of water or a co-flowing stream of water. The polymerization of MMA to The polymerization was run at 70˚C in a jacketed reactor.

3.3.12 Safflower Oil/Silicon Oil Emulsion Fabrication

0.5% alginate solution was mixed with either safflower oil or silicon oil to form an emulsion. The total volume made was 60 g for each batch and the relative masses of the aqueous and oil phases were adjusted to the desired ratio for the trial at hand. For safflower oil, emulsions containing 20, 40, and 50 wt% oil were used. For silicone oil, emulsions containing 40, 50, and 60 wt% oil were used. For each emulsion, 0.033 g of Triton X-100 surfactant was added to the emulsion to decrease the size of the oil droplets and to improve the emulsion stability. Each emulsion batch was allowed to stir for two days prior to use to form capsules in order to improve batch to batch consistency. A 9.09 wt% ATM solution made from a 5 wt% $CaCl_2$ solution was used to fabricate these capsules. The capsule fabrication process follows the same steps as the one outlined for the fabrication of pure alginate capsules. However different times were used for the reaction steps in this process. The membranes reaction step proceeded for only 8 minutes and the $CaCl_2$ bath step was 8 minutes long.

3.4   Assessment of Encapsulant Materials

Initial, 5-6 hour long, drying experiments were conducted to evaluate as many different encapsulant formulations as possible. These drying experiments were conducted with capsules made with PAM cores, lasted no longer than 24 hours and were conducted in a controlled humidity

environment and ambient temperature. These drying trials identified what encapsulants should be used for longer duration, and more detailed drying and property characterization experiments.

All the encapsulants investigated in the first round were compared on drying rate, capsule fabrication reaction time, and other observations such as fragility or difficulty of reaction seen in Section 4.2.13. The second round of trials were conducted for 48 hours and were conducted in order to optimize the formulation of the initial best two encapsulants. The capsules used in these experiments were made with ATM cores. Similar to the initial drying experiments, these were conducted in a controlled humidity environment, and left at ambient temperature.

The optimized formulation from the second round of drying experiments that produced the lowest % mass loss after 48 hours was then used to produce capsules that were used for property characterization and preliminary initial reaction condition optimization. Due to time constraints these last steps were done concurrently, forcing the use of the best capsule found from the second round of drying experiments and not the best capsule found from the initial reaction condition optimization. The two property characterization experiments investigated the coefficient of friction produced by the ruptured capsules at four drying time points, and the force necessary to rupture the capsules at three drying time points. Experiments done to investigate the optimization of the initial reaction conditions were the effect of the initial mass of the ATM drop used to form the capsules on drying rate and the effect of the initial ATM concentration of the drop used to form the capsules on drying rate.

3.4.1   Capsule Drying

Initial capsule drying measurements for trials lasting six hours or less were conducted in an enclosed environment maintained at 40% humidity and ambient temperature. The humidity in the

enclosure was maintained by bubbling compressed air through an air stone immersed in a glycerol/water solution [27]. The ratio of water to glycerol was used to control the humidity in the outgoing air stream to the enclosure. Individual capsules were place on trays in the enclosure and the masses were measured every hour to track mass loss. For each different capsule formulation, one capsule was measured at a time in order to increase the initial number of formulations that could be investigated. Humidity and temperature were measured using a VWR Digital Humidity/Temperature Sensor. For the capsules used in these experiments the drying of the capsules at any time, t, was calculated as the % mass loss for an individual capsule.

$$\% \ mass \ loss = \frac{mass_{initial} - mass_t}{mass_{initial}} * 100 \qquad (3.1)$$

Where $mass_{initial}$ (g) is the initial mass of one capsule and $mass_t$ (g) is the mass of one capsule at any time, t.

For drying trials lasting up to 48 hours a custom designed automated system was used to control the humidity in an enclosure and track the mass loss of the capsules as they dried. Humidity was added to the enclosure by a Sunbeam Cool Mist Humidifier, which was controlled by a Willhi WH8040 Humidity Controller. Dry air was supplied continuously to the enclosure through a line connected to the building's compressed air supply in order to prevent the humidity in the chamber from rising above 40%, especially on days with humid weather. The humidity and temperature in the enclosure were measured using a VWR Digital Humidity/Temperature Sensor while the total mass of eight capsules, all the same formulation, was measured using a Mettler Toledo PB303 digital scale inside the enclosure. The LCD screens of the scale and hygrometer were recorded every half hour for 48 hours using a Pixelink USB camera to track the total mass, humidity, and

temperature. The drying of the total collection of the eight capsules in this configuration at any time, t, was calculated as the % average mass loss.

$$\% \ average \ mass \ loss = \frac{total \ mass_{initial} - total \ mass_t}{total \ mass_{initial}} * 100 \qquad (3.2)$$

Where total mass$_{initial}$ (g) is the initial mass of the eight capsules and total mass$_t$ (g) is the mass of the eight capsules at any time.

3.4.2   Coefficient of Friction Measurements

The coefficient of friction experiments were conducted on a rubber surface with a sled whose bottom was covered in the same rubber material. The rubber surfaces were chosen for the relatively high static coefficient of friction the two surfaces produced. The experimental procedure was based on the ASTM standard for testing static and kinetic coefficients of friction [28]. The experimental set up is shown in Figure 3.1 A Velmex XSlide was used as the moving plane for the apparatus which was driven by a NEMA-17 stepper motor. The stepper motor was driven by an Automation Direct STP-DRV-6575 stepper drive and the pulses to the drive were supplied by an Arduino UNO microcontroller executing a custom code. The stage moved at a speed of 0.509 m/min. A Neulog NUL-211 Force Logging Sensor was used to record the force required to hold the sled during the experiment and the data was analyzed in Excel.
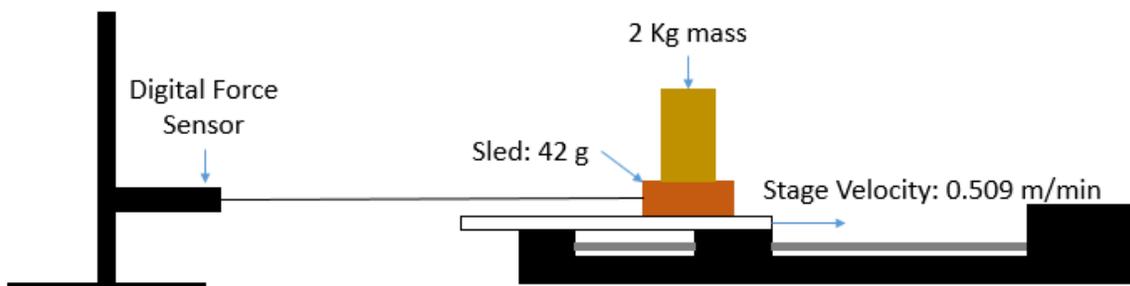
Figure 3.1: Coefficient of friction apparatus.

To run a coefficient of friction trial the sled was placed on the back edge of the stage. The distance from the force sensor to the sled was adjusted so that the nylon line connecting the sled to the force sensor had as little slack as possible. When testing the coefficient of friction for the dry rubber no special steps were taken before starting the apparatus. For testing the coefficient of friction for oil on the rubber substrate, care was taken to ensure that the sled bottom was entirely coated with oil. For testing films of ATM a film was first formed in a petri dish by mixing the ATM powder and water. If a film being tested required an ATM concentration higher than the initial 9.09 wt% ATM, the film was dried in the humidity enclosure until the desired concentration was reached. The films were then placed onto the stage and the sled placed on top of the film. The sled was pressed down briefly onto the film to cover the entire bottom surface area of the sled. Once the film was spread, the sled was picked up to remove any additional adhesion that may have occurred during the pressing. For trials done with capsules of ATM, the capsules were first placed in a plastic ring on the stage and pricked open with an exacto knife. Pricking the capsules was necessary to ensure that for every trial all the capsules were dispensing their ATM contents. This was seen as the best way to ensure repeatability for each trial. Once the capsules were pricked, the ring was removed

and the sled and weight placed on top of the capsules. For the trials done the coefficient of static

friction, μ_s, was measured.

$$\mu_s = \frac{F_{x,max}}{F_N} \tag{3.3}$$

where $F_{x,max}$ (N) is the maximum force measured in the x direction, this is the force required to

move the stationary sled, and F_N (N) is the normal force.

3.4.3   Rupture Strength
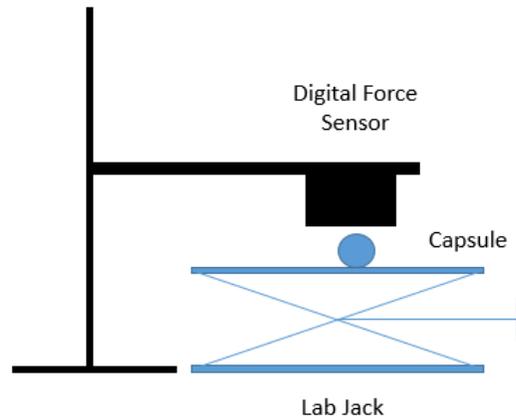
Figure 3.2: Rupture strength apparatus.

The rupture strength of the capsules was determined by pressing a single capsule vertically against

the Neulog Force Sensor by using a lab jack. The point of rupture was detected as the point when

the force readings suddenly dropped, as analyzed in Excel. The lab jack was raised by hand using

a wrench attached to the handle in order to improve how smooth the jack could be raised.

3.5   Continuous ATM Drop Production

In order to make an encapsulated form of ATM, there must first be a method of producing discrete drops of ATM that a capsule shell can be formed around. As discussed in Section 2.2, all of the common methods available for producing drops in a controllable manner are not suitable for the very viscous and viscoelastic ATM. The presence of the difficult properties in a solution of ATM or PAM necessitated the development of a novel method of drop production. This method was developed and investigated using a 9.09 wt% PAM solution as an analog for ATM. Producing drops of PAM controllably and repeatedly on the macro scale was done in a PDMS channel fabricated by casting hypodermic tubing, positioned in the desired channel design, in a tray that was then filled with PDMS. The PDMS was a ratio of 1:10 by weight of curing agent to pre-polymer. After the PDMS was cured at 65°C for 2 hours, the tubing was pulled out, leaving behind cylindrical channels of approximately 2 mm in diameter. Inlet and outlet tubing was then connected to the respective ports of the channel.

The bulk fluid flow of silicon oil was injected into the channel using compressed air driven syringes (Fisnar). The pressure to the cylinders was controlled upstream by a relieving style regulator. Each syringe was attached directly to a NITRA AVS-3 solenoid valve in order to control the length of time that air flow to the syringe was open. Each solenoid valve was controlled by an Arduino UNO Rev 3 microcontroller through custom written code. This microcontroller also controlled the Tower Pro servo motor driven outlet valve of the channel.

The PAM was injected into the channel with a custom syringe pump built from a Velmex XSlide linear stage. The linear stage was powered by a NEMA 17 stepper motor which was driven by an Automation Direct STP-DRV-6575 stepper drive. Pulses to the stepper drive were supplied by an

Arduino UNO Rev 3 microcontroller executing a custom written code. The microcontroller would receive commands to inject PAM from the microcontroller that controlled the solenoid valves using the Inter-Integrated Circuit (I^2C) communication protocol. The linear stage carriage was equipped with a button on the face of the carriage in the contact with the syringe in order for microcontroller to detect the syringe's position during different steps of the injection cycle.
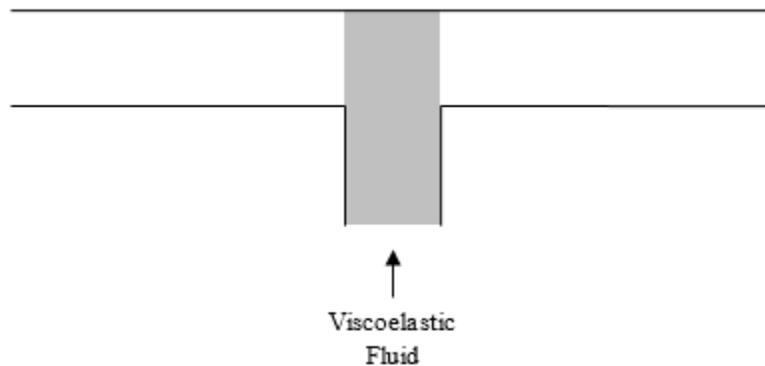
Figure 3.3: Injection of fluid in T-Junction

The injection process begins with the valve microcontroller sending a command to the syringe pump microcontroller to inject ATM into the channel. With the outlet valve open, the linear stage carriage would advance forward until contact was made with the button on the stage and the syringe. The carriage would then advance the desired distance in order to inject the required volume of PAM. Once the PAM was injected, the carriage would be reversed until the button was no longer in contact with the syringe. This relieved the pressure on the syringe, stopping additional flow of PAM into the channel.

Figure 3.4: Shifting of fluid plug backwards to interrupt polymer alignment.

The servo motor on the outlet valve would then close the valve and a solenoid valve would open to dispense silicon oil into the channel, shifting the PAM plug backwards. Prior to shifting the plug backwards all the fluids in the system are at rest. Since the PAM is a shear thinning solution, when it is at rest it has a very high viscosity, which will be discussed further in Section 4.1.1. When the viscosity of PAM increases, its resistance to deformation and flow is increased, allowing the two perpendicular volumes of PAM to move independently of each other. It has been empirically found necessary to use a step of shifting the plug away from the outlet after it has been injected, as demonstrated in Figure 3.4. Without this step long filaments will form as the plug moves towards the outlet. This may be due to the current design of the system where the solution will fill the horizontal channel in the direction towards the outlet, causing the polymer molecules to arrange in that direction. By reversing the plug backwards it appears to disrupt this alignment and disrupt the polymer memory, allowing for a clean break in the next step.
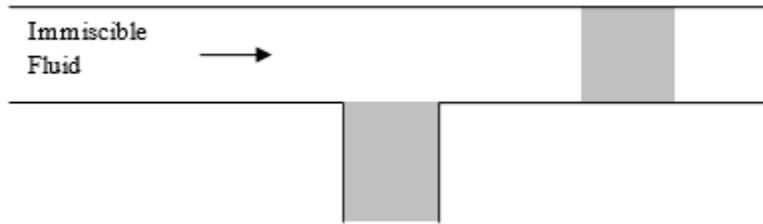
Figure 3.5: Clearing the plug from the channel, making the channel ready for use.

The servo motor would then open the outlet valve and the second solenoid valve would be opened to inject silicon oil that cleared the PAM plug from the channel. Once the plug was cleared the solenoid valve would be closed and the process would start again. Once the PAM plug is cleared from the T-junction, the process can be cycled through again. If this process were done where both fluids were in motion at the same time the PAM plug would form long strands in the direction of the immiscible fluid flow. These strands would continue for the length of the channel without necessarily breaking up. This discrete volume of PAM can then go through additional processes to coat the material, form a membrane around it, or use it as an unmodified volume of fluid that has been cleanly separated.

(a)   (b)
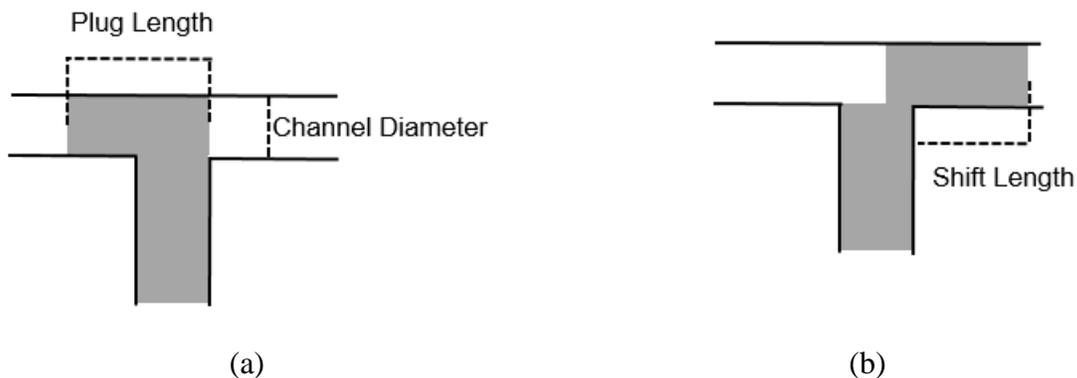
Figure 3.6: Measurement positions for the calculation of K (a) and λ (b) to determine parameters involved in clean drop breakup.

$$K = \frac{plug\ length}{channel\ diamter} \qquad (3.4)$$

$$\lambda = \frac{shift\ length}{plug\ length} \qquad (3.5)$$

In order to investigate the conditions that produce the clean formation of a plug of ATM in the breakup cycle, two non-dimensional parameters were used to characterize the system's behavior. Figure 3.6 (a) and (b) indicates the positions used to measure the parameters K and λ and Equations 3.4 and 3.5 show the calculation of the two parameters. These two parameters were found to relevant to controlling clean plug breakup during the initial investigations of the system described here. At least for the method and system outlined here, there will be a minimum K and λ value where all plug sizes and shift lengths below that will lead to poor breakup. The interaction of these two parameters was used to construct a breakup phase diagram shown in Section 4.4.

Chapter 4: Results and Discussion

4.1 <u>Polyacrylamide (PAM) as ATM substitute</u>

During the encapsulant investigation phase of the project, it was necessary to produce a large number of capsules to investigate encapsulant formulations of interest. In order to reduce the amount of ATM used over the course of the work, polyacrylamide (PAM) was investigated as a substitute for ATM. ATM is primarily compose of polyacrylamide, however to confirm that the PAM solution would behave similarly to ATM, rheological tests were necessary. The results of the tests also provided insight into the difficulties that arose in handling either polymer solution.

A steady state flow experiment was conducted in order to determine the behavior of each fluid's viscosity as a function of shear rate. Since both are polymer solutions the viscoelastic nature of the two fluids is an important parameter to characterize. An oscillatory stress sweep was conducted to find each fluid's linear viscoelastic region (LVR). A frequency sweep test was then conducted within the LVR to find each polymer solution's storage and loss moduli's response to a range of angular velocities.

4.1.1 ATM Rheology

Since ATM is a highly viscous, non-Newtonian polymer solution, it was necessary to perform rheology experiments in order to understand the fluid's behavior and gain insight into how to handle it. Using the steady state flow procedure, the dependence of the ATM and PAM viscosity on shear rate was determined. In Figure 4.1 it is clear that at 25°C both the ATM and PAM solutions are highly shear thinning; the viscosity of both solutions decreased almost five orders of magnitude

over the range of shear rates tested. The straight section of the viscosity curves of each fluid were fitted to the power law expression in Equation 3.1 in order to find the values of m and n.

From the equations displayed in Figure 4.1 the behavior of ATM produces a consistency index, m, of 226 and an n of 0.13. The behavior of the PAM solution produces a consistency index of 403 and a flow behavior index, n, of 0.14. The 78% increase in the value of m seen in the PAM solution can most likely be attributed to any proprietary additives present in the ATM powder and any molecular weight differences between the polymer chains that make up either solution. What is more important though is the value of n for both fluids since this parameter describes the shear thinning behavior of both solutions. The value of n for both is less than 1, confirming the shear thinning nature of both solutions, and there is only an increase of 7.5% in n from ATM to PAM. This confirms that both solutions have very similar shear thinning behavior.
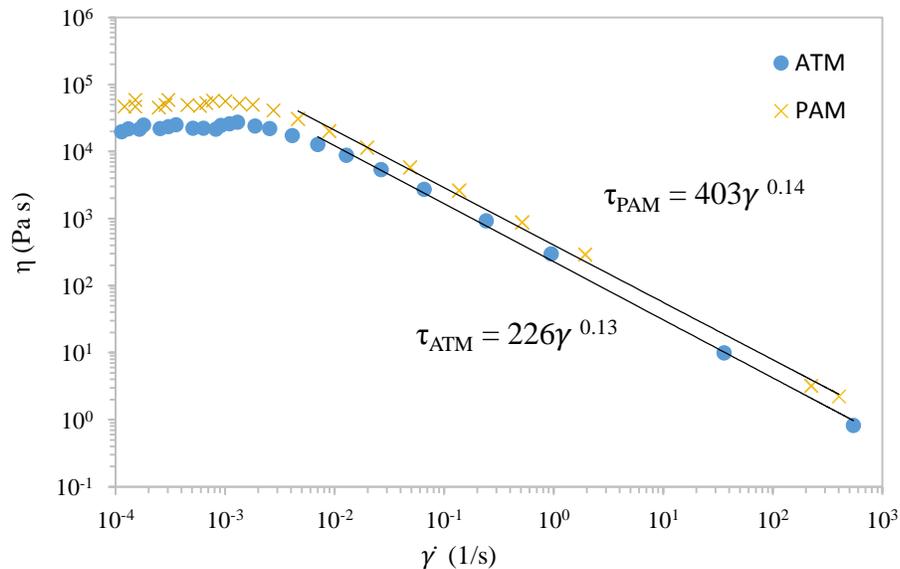
Figure 4.1: Viscosity, η, dependence on shear rate, $\dot{\gamma}$ for 9.09 wt% ATM and PAM. Experiment run at 25°C.

The shear thinning behavior helps to explain the effectiveness of ATM as a lubricant. At zero shear or very low shear it is essentially a gel, with a viscosity over $2\text{x}10^4$ Pa s, which prevents the ATM coating a surface from being easily displaced or from seeping into crevices like an oil coating would. When shear is applied to ATM, such as when a foot steps on a surface that is coated with ATM, the viscosity decreases, allowing the ATM to spread creating an unstable surface. The viscosity of a 9.09 wt% PAM solution has very similar behavior to that of the 9.09 wt% ATM solution, seen in Figure 4.1. There is an approximately 111% difference in the low shear rate viscosity from the ATM solution to the PAM solution, but both are still in the same order of magnitude. Both also display the rapid shear thinning, while the PAM solution does not reach as low of a viscosity as ATM at high shear rates. At a shear rate of 542 s^{-1} the ATM solution has a viscosity of 0.83 Pa s, while at a shear rate of 696 s^{-1} the PAM solution has a viscosity of 2.7 Pa s. Even though there are differences in the viscosity of the two solutions, the general behavior is close enough for PAM to be used as a substitute for the early experiments. The viscosity of the PAM solution at rest needed to be high so that the drops of the polymer solution would maintain their shape during the fabrication steps.
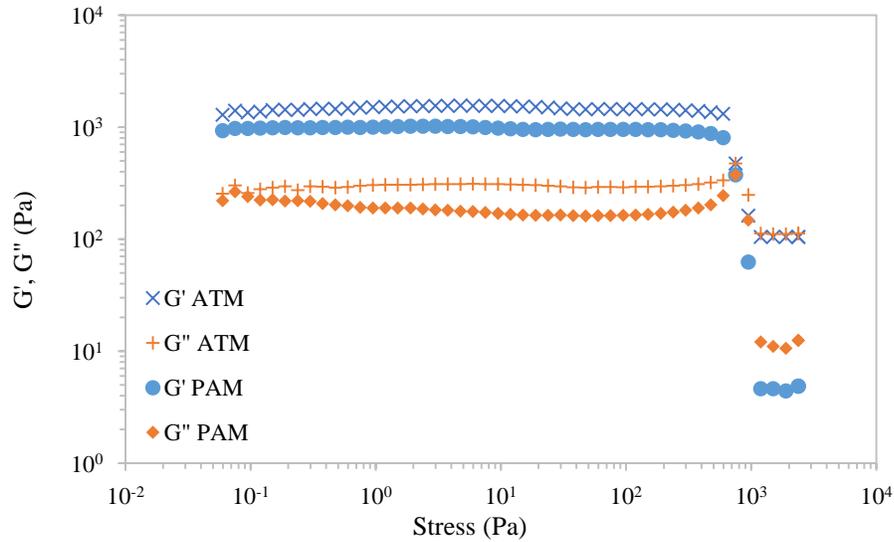
Figure 4.2: G' and G" of 9.09 wt% ATM and PAM solutions as a function of stress. Experiment conducted at a constant angular velocity of 6.283 rad/s and at 25˚C.

Figure 4.2 provides information on the linear viscoelastic region and an indication of the values of the storage modulus, G', and the loss modulus, G". For ATM, G' is above 1000 Pa for the entire range of stress while G" stays near 300 Pa. The high value of G' relative to G" indicates that ATM is a highly elastic fluid. The linear viscoelastic region of a 1:10 ATM solution spanned the entire range of stress investigated in Figure 4.2. The polymer network is strongly entangled and strongly resists breaking down. The elastic nature of the 9.09 wt% PAM solution was also very similar to the ATM solution. Figure 4.2 shows the same very wide linear viscoelastic region for the PAM solution and the values of G' and G" are in the same order of magnitude as the ATM solution. The linear viscoelastic region for both solutions was also used to find a value of stress that is valid to use in the oscillating frequency sweep test.
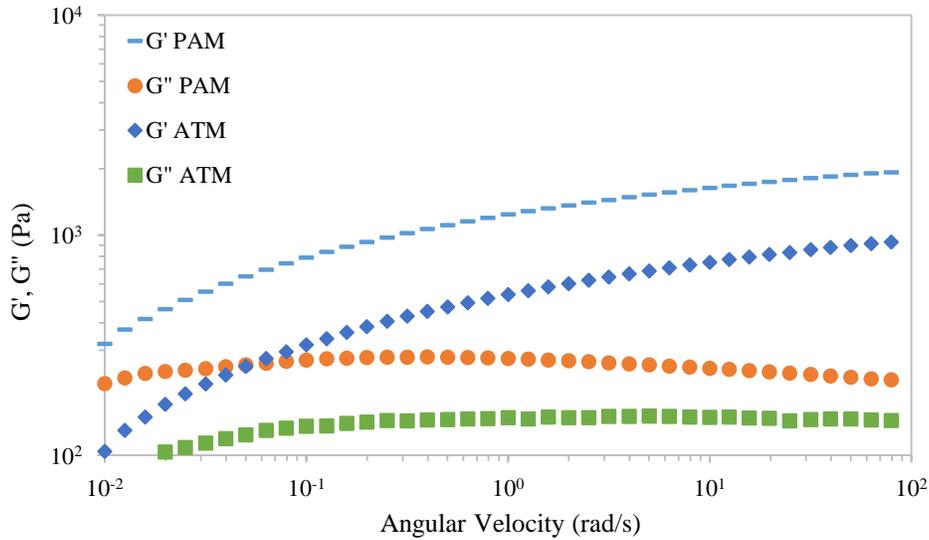
Figure 4.3: G' and G" of 9.09 wt% ATM and PAM solutions as a function of angular velocity (rad/s). Experiment conducted at a constant oscillatory stress of 10 Pa and at 25°C

Since the results in Figure 4.2 are conducted at a constant angular velocity, Figure 4.3 shows how the storage and loss moduli of ATM behave as a function of angular velocity. For the range of velocities investigated there is no point where G' is less than G": the elastic nature is always dominant over the viscous. With this information it is clear that the common methods of producing liquid drops would not be applicable to ATM. Most methods of drop production rely on viscous forces to pinch off droplet from a stream of liquid. With ATM, the elastic nature strongly resists pinching off. This behavior coupled with the strong shear thinning nature of ATM made it a very difficult fluid to dispense. For the PAM and ATM solutions the storage and loss moduli response to changing angular velocity shows a similar overall trend, close values for G' and G" at low velocity and large separation at higher velocities. Exact matching of the values for both solutions was not the goal for these tests. The rheological tests conducted with PAM were a validation that PAM would behave similarly enough to ATM that early capsule testing could be done with PAM instead of ATM.

4.2   Initial Evaluation of Encapsulant Materials

Using PAM as the encapsulated material, the various encapsulant materials described in Section 3.3 were evaluated for prevention of water loss at 6 and 24 hours, and also the overall reaction time. The encapsulant materials fall into 5 categories, pure alginate capsules, capsule membranes made from alginate slurries, capsule membranes made from modified alginate, capsules with a secondary coating and capsule membranes made from alginate/oil emulsions. For the work done prevention of water loss was the primary concern when choosing an encapsulant. The overall reaction time was evaluated in order to direct later commercialization efforts since a longer reaction time could decrease throughput or require multiple reactors operating in parallel. Other parameters such as fragility of the membrane, fabrication difficulty, hazardous chemical requirements were noted for consideration during final evaluation of all twelve encapsulants. The top two encapsulants out of the twelve had their drying rates investigated for 48 hours. Further optimization and property evaluations were then conducted on the best encapsulant of the final two encapsulants as discussed in Section 4.3.

4.2.1   Alginate Capsules

As a baseline investigation, pure alginate capsules containing PAM were fabricated to determine what role membrane reaction time, and concentration of $CaCl_2$ in the PAM solution had on capsule drying. $CaCl_2$ concentrations of 3 wt%, 5 wt%, and 7 wt% were investigated since concentrations lower than 3 wt% did not produce an adequate membrane at shorter reaction times. Reaction times of 10, 20, and 25 minutes were studied since times shorter than 10 minutes also produced very

weak membranes that did not properly encapsulate the PAM core. These effects have been

demonstrated for alginate capsules made from liquid cores but were verified here with PAM cores

[14].
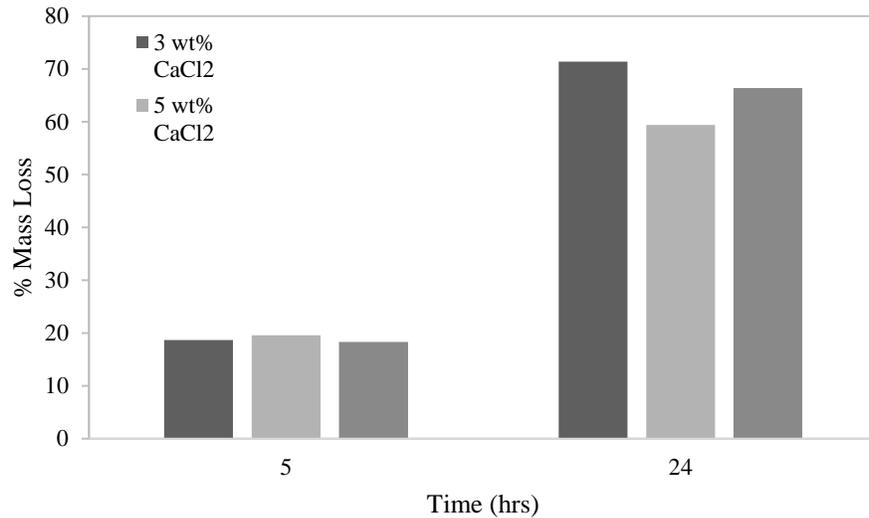
Figure 4.4: % Mass Loss at 5 and 24 hours for capsules with a 25 min membrane reaction time. PAM solution contained either 3, 5, or 7 wt% $CaCl_2$. Each trial is the % mass loss of 6 capsules, n=1.
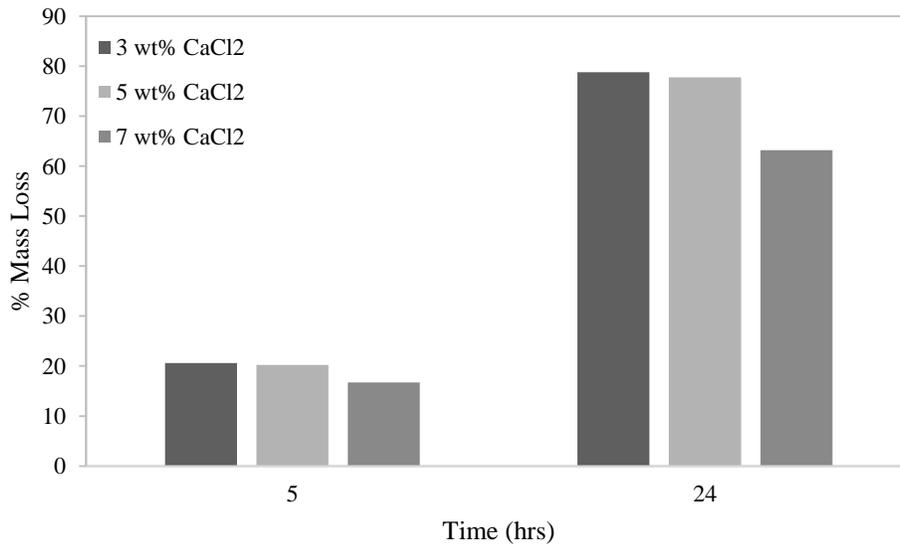
Figure 4.5: % Mass Loss at 5 and 24 hours for capsules with a 20 minute membrane reaction time. PAM solution contained either 3, 5, or 7 wt% $CaCl_2$. Each trial is the % mass loss of 6 capsules, n=1.

As seen in Figure 4.4 and Figure 4.5, all trials experienced over a 60% mass loss at 24 hours and showed no large variation with respect to reaction conditions. While the capsules may not have completely dried out, there was not enough PAM remaining in the dried capsules to be effective. For both membrane reaction times of 20 and 25 minutes there is no clear trend associated with the concentration of $CaCl_2$. At the 24 hour mark, capsules made with a PAM solution containing 5 wt% $CaCl_2$ and capsules made with a PAM solution containing 7 wt% $CaCl_2$ show the least % mass loss for reaction times of 25 minutes and 20 minutes respectively. More trials would need to be conducted to determine if these were truly significant. Since at 24 hours all the capsules in the trials were essentially dry, they were deemed ineffective as a means of dispensing PAM.
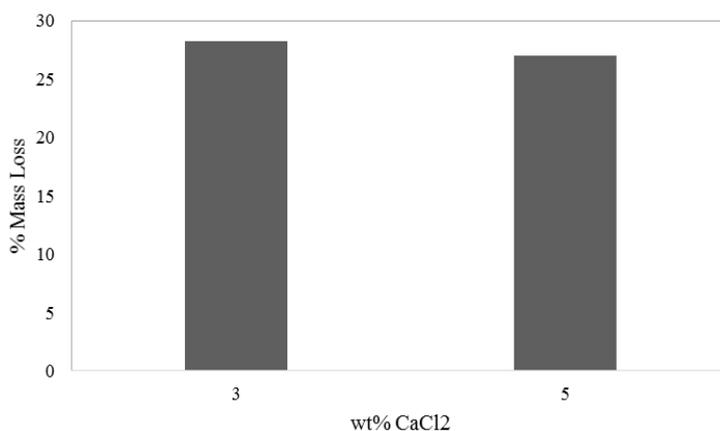
Figure 4.6: % Mass Loss after 6 hours of drying for capsules with a 10 minute membrane reaction time. PAM solution contained either 3 or 5 wt% $CaCl_2$. Each point is the measurement of one capsule, n=1.

Drying experiments were conducted for alginate capsules with 3 and 5 wt% $CaCl_2$ added for a membrane reaction time of 10 minutes. As seen in Figure 4.6 the mass loss for both capsules are similar, 27% and 28%. These measurements were taken at the 6 hour mark so it is difficult to draw

comparisons between these results and the 5 hour results for membrane reactions of 20 minutes. However, the values in Figure 4.6 do not appear to be qualitatively different from the results seen of the other drying trials.

4.2.2   Cornstarch/Alginate Capsules

A slurry of cornstarch and alginate solution was used to produce capsules with corn starch incorporated into the hydrogel membrane in an effort to reduce water loss through evaporation. Cornstarch in the membrane acts as a filler, occupying space that would otherwise be filled with alginate. Cornstarch is only slightly soluble in water and its presence in the membrane creates layers of higher hydrophobicity, creating a tortuous path for a water molecule to travel during diffusion.
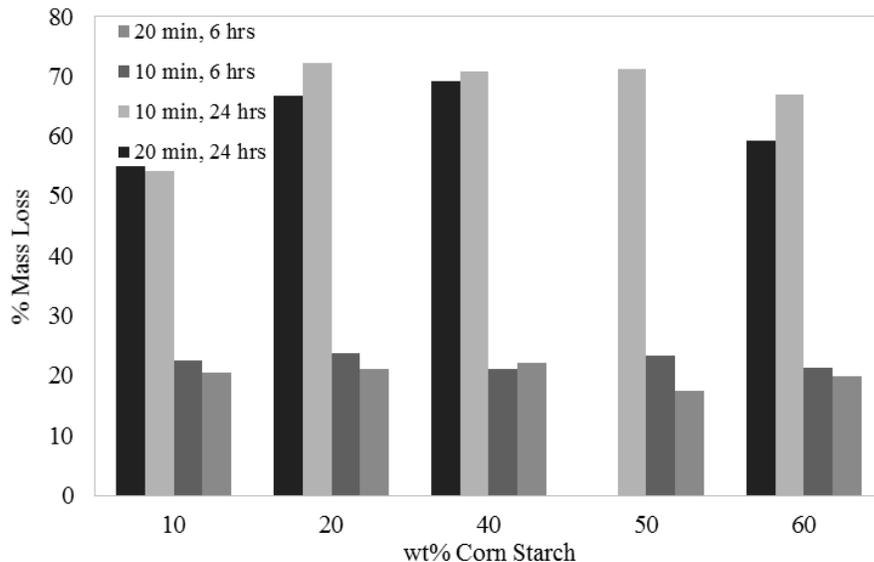
Figure 4.7: Effect of content of corn starch on % mass loss for capsules made from a 5 wt% $CaCl_2$ PAM solution and with a membrane reaction time of 10 minutes and 20 minutes, as noted in the graph legend. Each point is the measurement of one capsule, n=1.

For all the trials completed with corn starch and alginate membrane capsules, no clear trend developed for the % mass loss measured at 6 hours. The % mass loss at 6 hours experienced by these capsules containing various amounts of cornstarch actually have similar moisture loss as pure alginate capsules at 6 hours, indicating that the cornstarch does not have a significant improvement in preventing moisture loss during the initial 6 hours of drying. The presence of cornstarch in the alginate membrane was confirmed by through the observation that capsules made from the cornstarch slurry had a membrane that was white and opaque. The actual weight fraction of cornstarch contained in the membrane was not determined.

Measurements taken at 24 hours do demonstrate that at certain contents the presence of cornstarch does reduce the rate of water loss through evaporation. For capsules made from PAM solutions containing 5 wt% $CaCl_2$, as seen in Figure 4.7, the presence of 10 wt% cornstarch in the cornstarch/alginate slurry appears to decreases the % mass loss at 24 hours. More trials will need to be conducted to determine if the decrease seen is statistically significant. For both membrane reaction times of 10 and 20 minutes capsules made from slurries with 10 wt% corn starch the capsules experienced a mass loss of 54% and 55% respectively. Compared to the % mass loss of the other amounts of corn starch used for subsequent trials of capsules made from PAM solutions with 5 wt% $CaCl_2$, all capsules experienced a % mass loss of 60% or higher. Even though these trials were not replicated individually, the results are consistent in both the trials using either 10 or 20 minute membrane reaction times.
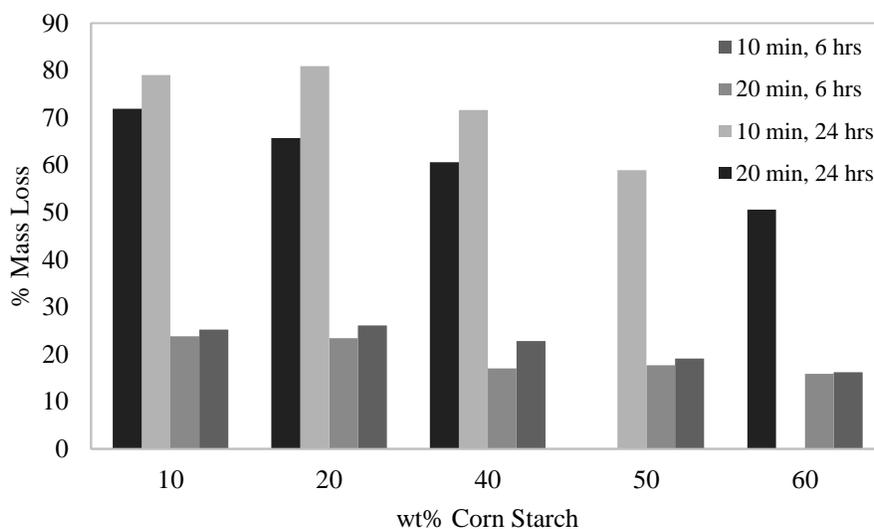
Figure 4.8: Effect of content of corn starch on % mass loss for capsules made from a 7 wt% CaCl$_2$ PAM solution and with a membrane reaction time of 10 and 20 minutes. Points without error bars are the % mass loss for one capsule. Each point is the measurement of one capsule.

Capsules made from PAM solutions containing 7 wt% CaCl$_2$ show a trend opposite of that seen in the 5 wt% CaCl$_2$ capsules. In Figure 4.8, the % mass loss decreases with increasing cornstarch content, which is more in line with what would be expected for this membrane formulation. As the cornstarch content increases there should be less and less membrane volume occupied by alginate and more occupied by cornstarch, creating less pathways for water loss during diffusion. For capsules that underwent a membrane reaction time of 10 minutes, capsules made from a slurry of 50 wt% corn starch had a % mass loss of 58.9% at 24 hours. Capsules that underwent a membrane reaction time of 20 minutes had a % mass loss of 50% at 24 hours. Capsules made from a 5 wt% CaCl$_2$ PAM solution have a 21% and 32% percent increase in % mass loss at those respective time points and reaction conditions.

Since alginate gelation is dependent on the concentration of CaCl$_2$, it is possible that the membranes formed from PAM cores containing 7 wt% CaCl$_2$ produced membranes that were

crosslinked more tightly than those produced from 5 wt% $CaCl_2$ [14]. Increasing the concentration of cornstarch in the slurry produced a weaker membrane, as there is less alginate to form a crosslinked hydrogel network in order to form a closed capsule. More work would need to be performed to determine if the possible structural changes could lead to different drying rates.

Regardless of the mechanism that produces the differences between the capsules made from 5 wt% and 7 wt% $CaCl_2$, no capsule formulation produced a capsule that was useable after 24 hours of drying. At 24 hours all capsules were very brittle and essentially dry. During the course of drying the capsules became increasingly fragile, especially as the cornstarch began to dry. While incorporating corn starch into the membrane of alginate capsules offered a decrease in mass loss, it did not come close to matching the capabilities of the oil emulsion membranes. Also the cornstarch membranes were found to be very susceptible to mold formation, particularly in environments where there was approximately 50% humidity.

4.2.3   *Heat-Moisture Treatment of Corn Starch*

In an attempt to improve the water barrier properties of capsules made from corn starch, the starch was subjected to a heat moisture treatment step prior to being mixed with alginate to form a slurry. Heat moisture treating starch is a process that is supposed to increase a starch's resistance to gelatinization and increase the hardness of the crystalline structure. If a starch is more resistant to gelatinization then the hypothesis was that it would interact with water in the capsule even less, decreasing the rate of water loss from the capsule.
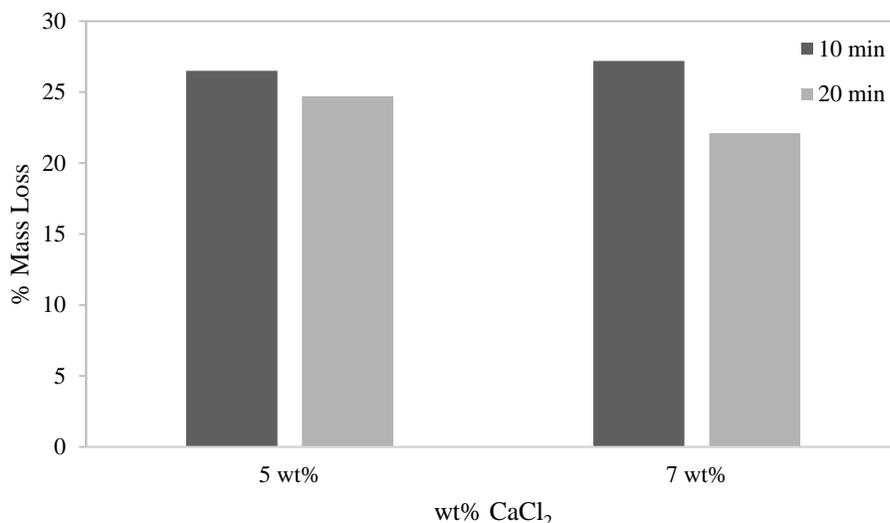
Figure 4.9: % Mass loss at 6 hours for capsules containing heat moisture treated starch. Capsules underwent two membrane reactions times, 10 and 20 minutes. Each point is the measurement of one capsule, n=1.

The capsules for the trials presented in Figure 4.9 were made from a starch alginate slurry containing 10 wt% starch. These capsules did not offer an improvement in the % mass loss at 6 hours when compared to non-heat treated starch capsules, nor when compared to the other formulations presented.

4.2.4   Starch Nano-Crystals

Creating starch nano-crystals was a way to improve the level that the starch was exfoliated in the alginate membrane. Due to the small size of the starch crystals, it would be easier for them to impregnated the gel as exfoliated particles, instead of clusters as was most likely the case with the unmodified starch. A very small quantity of nano-crystals were produced for the trials shown in Figure 4.10. The alginate solution used to form the capsules only contained 0.44 wt% of nano-crystals. This was most likely far too small of a weight fraction to make a difference in the water

barrier properties of the capsule. Due to the length of time required to produce the crystals, and the multistep fabrication process, more crystals were not made in order to repeat the trials.
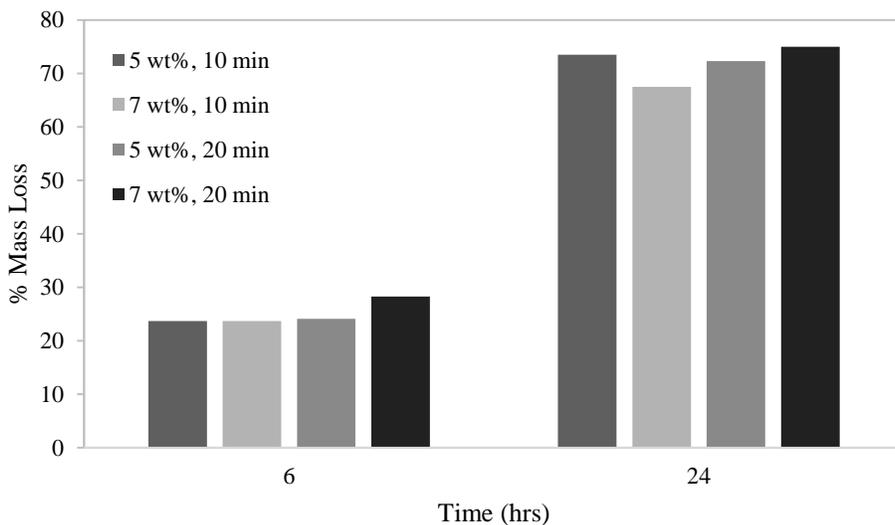
Figure 4.10: % Mass loss at 6 and 24 hours for capsules containing starch nano-crystals. Capsules were fabricated using either 10 or 20 min membrane reaction times, and 5 or 7 wt% CaCl$_2$. Each point is the measurement of one capsule, n=1.

4.2.5 Bentonite Clay/Alginate Capsules

Using a similar idea to incorporating cornstarch into the alginate hydrogel membrane as a filler, bentonite clay was used to produce a slurry with the 0.5 wt% alginate solution. Bentonite clay particles are typically thin platelets, which would allow them to intersperse easier into the gel matrix and create distinct layers of bentonite. An important difference from bentonite and corn starch is bentonite is not a hydrophobic solid. It does absorb water and swell as the water is absorbed.
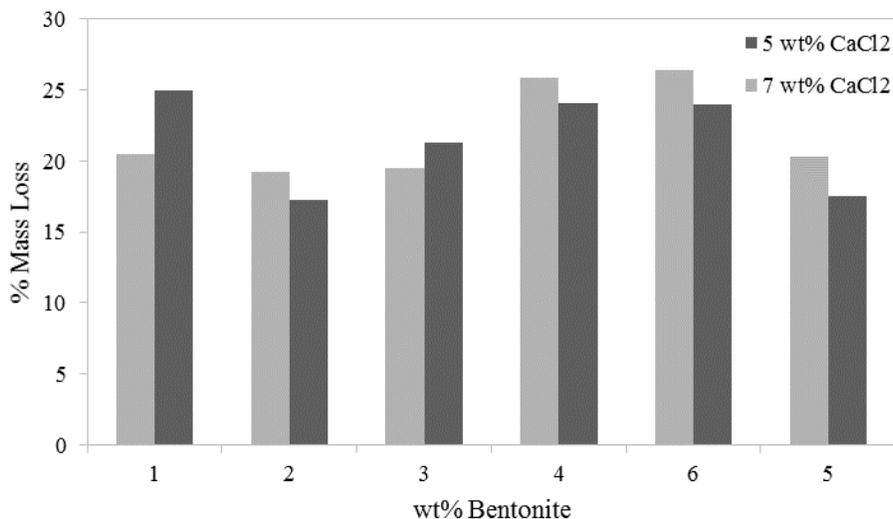
Figure 4.11: Effect of bentonite concentration on % mass loss at 6 hours of drying. Capsules made from PAM solution with 5 wt% or 7 wt% $CaCl_2$ and with a membrane reaction time of 20 minutes. Each point is the measurement of one capsule, n=1.

As seen in Figure 4.11, the % mass loss for capsules made from either 5 wt% or 7 wt% $CaCl_2$ with various bentonite concentrations follow very similar trends. In general it appears that increasing the concentration of bentonite in the slurry serves to increase the % mass loss measured at 6 hours. There is one anomaly in this trend: capsules made from both 5 wt% and 7 wt% $CaCl_2$ and a 5 wt% bentonite slurry show a lower % mass loss than capsules made from either a 4 or 5 wt% bentonite slurry. It is difficult to exactly explain the cause of the decrease in % mass loss at that point without further investigation and more trials to determine if it is a statistically true decrease. A major problem that was observed with capsules made from a bentonite alginate slurry was their tendency to split open during the course of drying. If the bentonite clay particles cannot exfoliate into the capsules membrane then agglomerations of the particles may cause weak spots in the membrane, causing the membrane to split. A capsule that spontaneously splits open is certainly not a desired behavior.

In an attempt to correct the issue of the bentonite capsules rupturing during the course of their drying, low weight fractions of corn starch were added to the alginate slurry. While it was observed during experiments with high weight fractions of corn starch that the capsules became increasingly fragile, low concentrations of corn starch did actually help to improve the mechanical integrity of the capsules. Before, with only bentonite in the slurry, the capsules would rupture during the course of the drying time but with the addition of corn starch no rupturing was observed.
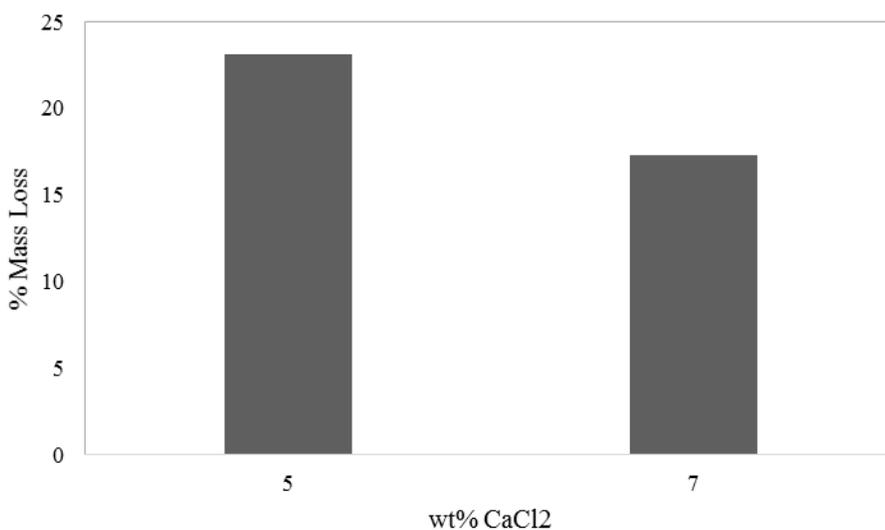
Figure 4.12: Capsules made from alginate solution containing 2 wt% bentonite, and 2 wt% Cornstarch. Capsules made from PAM solution containing 5 and 7wt% $CaCl_2$. Each point is the measurement of one capsule, n=1.
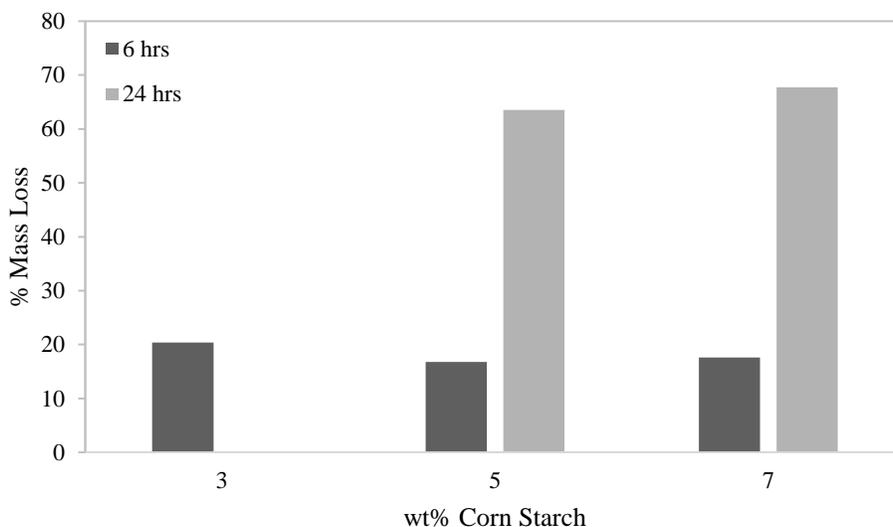
Figure 4.13: Capsules made from alginate solution containing 3 wt% bentonite and varying concentration of corn starch. Capsules made from PAM solution containing 5 wt% $CaCl_2$. Each point is the measurement of one capsule, n=1.
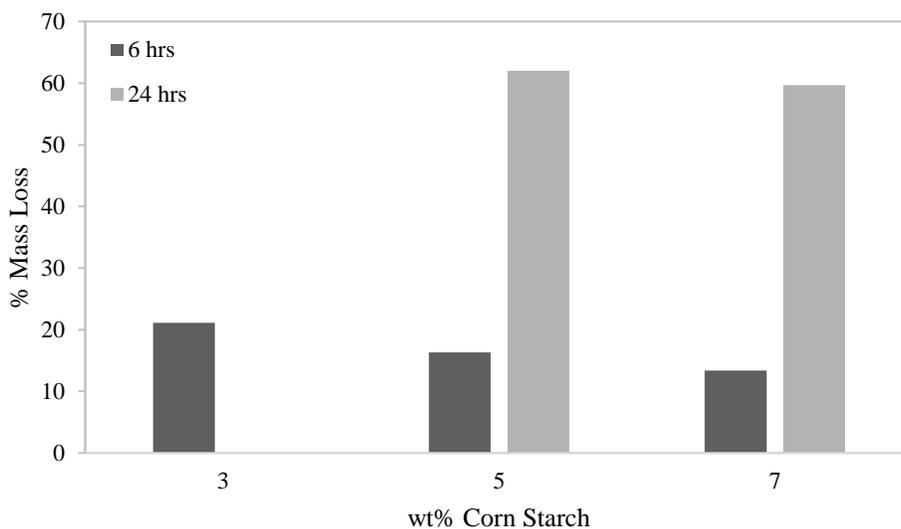
Figure 4.14: Capsules made from alginate solution containing 3 wt% bentonite and varying concentration of corn starch. Capsules made from PAM solution containing 7 wt% CaCl2. Each point is the measurement of one capsule, n=1.

The combination of the two solids does appear to have a positive effect on reducing the mass

loss at the 6 hour point. Of the eight formulations investigated in Figures 4.12-4.14, five had a

percent mass loss under 20% at six hours, and the three that were above 20% were at 23.1, 20.4 and 21.1%. Unfortunately at the 24 hour mark all the formulations were essentially dry.
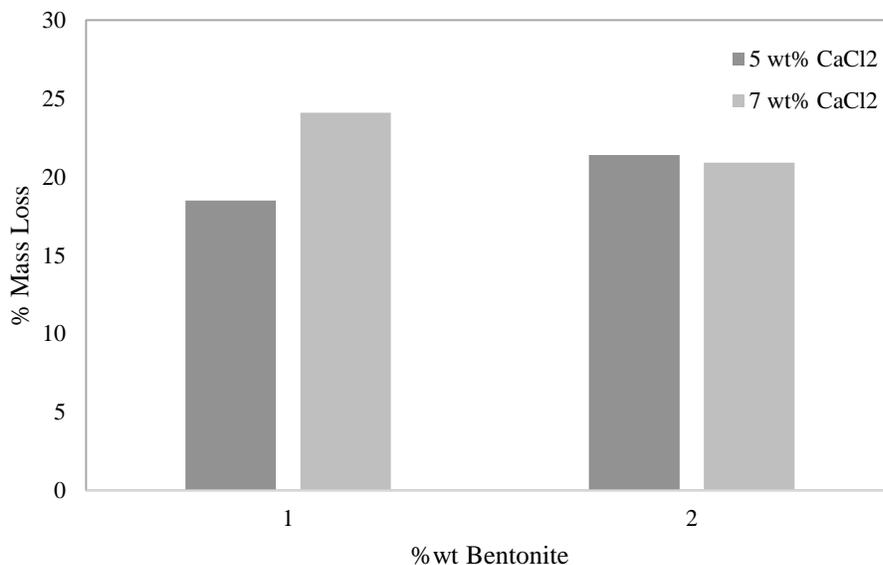
Figure 4.15: % mass loss at 6 hours for bentonite capsules made using two layer process with pure alginate as the inner layer and the outer layer made from either 1 or 2 wt% bentonite slurry. Each point is the measurement of one capsule, n=1.

Another method of preventing the spontaneous rupturing of capsules made from a bentonite slurry was a double layered capsule. As described in Section 3.3.3, a pure alginate membrane was first created around the PAM core, then this capsule was placed into a bentonite/alginate slurry to finish the membrane formation. This method did successfully create two membrane layers, neither of which ruptured during the drying experiments conducted with these capsules. However, these capsules appear to prevent water loss no better than the capsules containing cornstarch and bentonite; while at the same time requiring the additional step of a second membrane reaction.

4.2.6   Polystyrene Particles

Incorporating corn starch into the alginate membrane was an attempt to introduce semi-hydrophobic material into the hydrogel matrix. Since that was not deemed a successful in reducing the rate of moisture loss through the membrane, a procedure for incorporating highly hydrophobic material into the membrane was developed. Polystyrene particles would take on the same role that had been attempted with corn starch and bentonite, as a filler and hopefully a material that would create a difficult path for water loss through the membrane.   The fabrication procedure of producing polystyrene particles through the stripping of acetone saturated with polystyrene appeared to be successful. After the acetone had been stripped off, the remaining alginate and polystyrene slurry was an opaque white color. Capsules were successfully produced from this slurry using the normal fabrication steps.
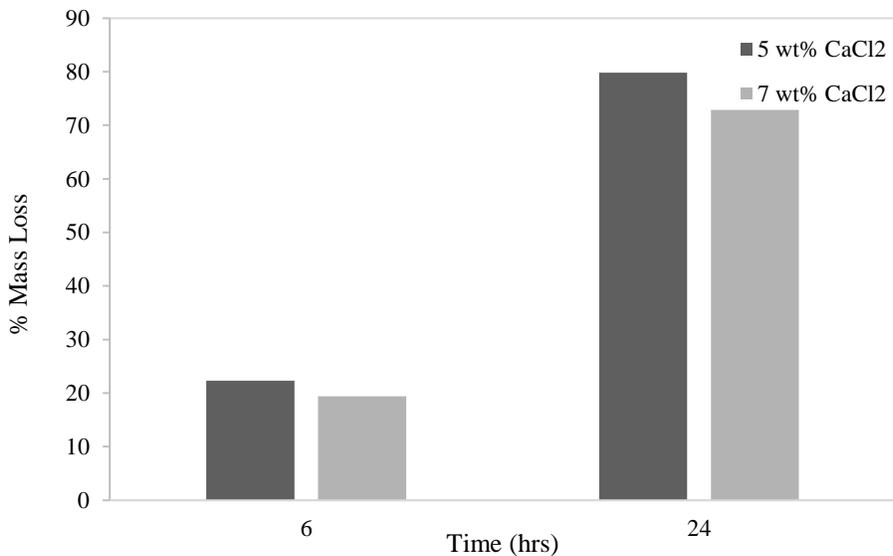
Figure 4.16: % Mass loss at 6 and 24 hours for capsules containing polystyrene particles. Each point is the measurement of one capsule, n=1.

While it was possible to produce capsules that appeared to have polystyrene particles present in the membrane, it is possible they were not present in a high enough weight fraction to make a difference in the rate of water loss. The exact weight fraction of polystyrene particles was not known, but attempts were also not made to make higher weight fraction solutions due to the length of time required to produce the polystyrene slurry used for the trials shown here. As seen in Figure 4.16: % Mass loss at 6 and 24 hours for capsules containing polystyrene particles., there is essentially no difference in the behavior of the capsules containing polystyrene particles than the ones already presented that contain other solids in the membrane.
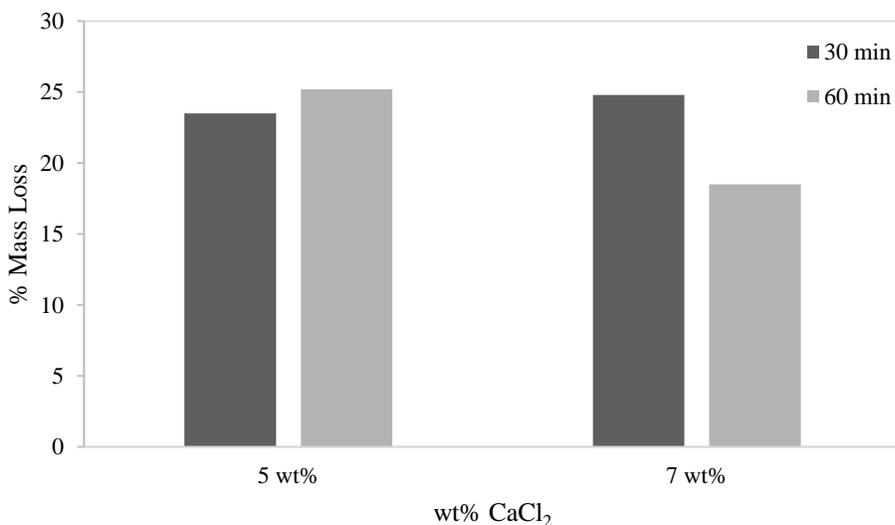
Figure 4.17: % Mass loss for capsules containing polystyrene particles at 6 hours. Capsules were formed with a 20 minute membrane reaction. Prior to drying capsules were subjected to a heating bath of $CaCl_2$ solution for either 30 or 60 minutes. Each point is the measurement of one capsule, n=1.

Drawing from work done with polystyrene colloidosomes, where the polystyrene particles that had orientated themselves on the surface of a droplet were sintered in place using moderate heating,

the same was attempted with capsules containing polystyrene particles. If the particles were not offering a resistance to water loss in the work shown in Figure 4.16, then perhaps sintering particles together may improve the capsules' resistance to water loss. After the 10 minute $CaCl_2$ rinse in the fabrication step, the capsules were placed in a 50˚C $CaCl_2$ solution for 30 and 60 minutes. While this was not near the melting point of polystyrene, it has been demonstrated that polystyrene particles will sinter together at temperatures below the melting point of polystyrene [21]. However, in Figure 4.17, none of the heating trials attempted demonstrated a large decrease in the % mass loss at 6 hours as compared to other, simpler fabrication processes presented here.

4.2.7   Hot $CaCl_2$ Bath

As shown in Section 4.2.6, subjecting the capsules that contained polystyrene particles to a hot bath in an attempt to sinter the polystyrene particles together did not appear to have a drastic effect on capsule drying. During the experiments conducted with polystyrene particles it was observed that the alginate membrane appeared to change texture. To see if these change in texture represented a beneficial change in the moisture barrier properties of the alginate, experiments similar to those in Section 4.2.6 were done without the presence of polystyrene particles. To complete the investigation of subjecting the capsules to a hot bath step prior to drying, pure alginate capsules were placed in an 80˚C, $CaCl_2$ solution.
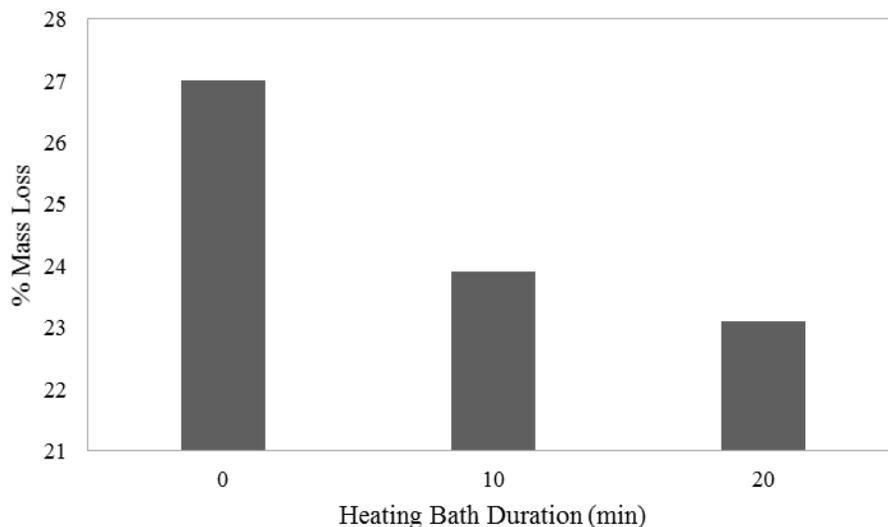
Figure 4.18: % Mass loss at 6 hours for alginate capsules placed in an 80˚C CaCl2 solution for 0, 10 and 20 mins. Capsules were fabricated with a 20 min membrane formation step. Each point is the measurement of one capsule, n=1.

The temperatures for this trial were higher than those in the polystyrene sintering trials in Figure 4.17, but the results in Figure 4.18 shows that these capsules dry faster than the polystyrene capsules, and slower than some forms of the pure alginate capsules. This potentially indicates that the higher rates of % mass loss seen in some of the polystyrene containing capsules may not be due to the polystyrene particles worsening the situation, but may be the result of the alginate being subjected to a heating step. The lower % mass loss for these capsules as compared to the pure alginate capsules not subjected to the heating step may be the result of the capsules from the heating step absorbing water from the bath.

4.2.8   Alginate Esterification

Crosslinked alginate is a very hydrophilic gel which, as has been demonstrated, does not act as a strong water vapor barrier. Performing esterification of alginate powder was a possible route to

reducing the hydrophilic nature of alginate, while at the same time retaining the simple crosslinking reaction that allows the rapid formation of capsules around a polymer core. The alginate esterification reaction places butyl groups on the alginate molecule which decreases the hydrophillicity of the alginate but maintains the ability of the alginate to covalently crosslink into a gel. The important aspect of this reaction is that the crosslinking property of alginate is retained, despite the modification to the alginate molecule [22].
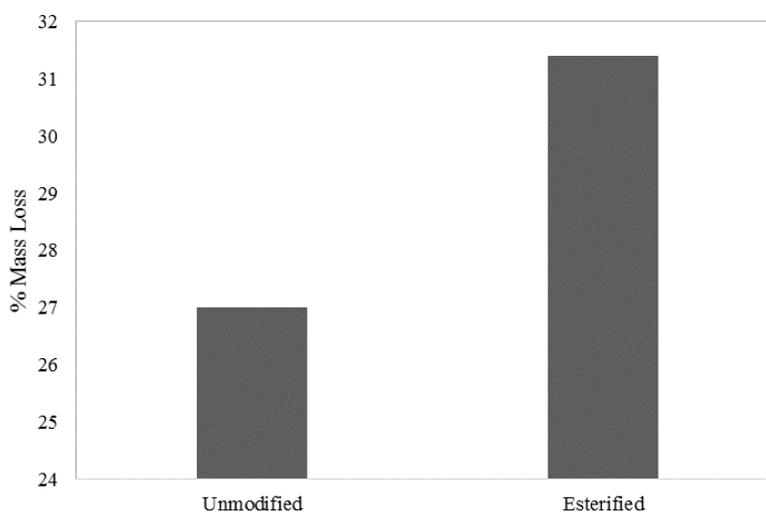
Figure 4.19: % Mass loss for unmodified and esterified alginate capsules at 6 hours. Each point is the measurement of one capsule, n=1.

Qualitative visual assessment of capsules made from the modified alginate indicated that the esterification reaction did appear to successfully modify the alginate, and a capsule was formed just as easily as any of the other fabrication processes used. The crosslinked esterified alginate appeared more gray and translucent than unmodified crosslinked alginate. In Figure 4.19, the % mass loss at 6 hours is above that of unmodified alginate capsules fabricated under similar conditions, 27.0%. This could be due to the modified alginate not being able to form as tight of a crosslinked gel matrix with the butyl groups present. In the experiments conducted with pure

alginate capsules, higher wt% of $CaCl_2$ may have produced capsules that lost a lower amount of water over time. This was believed to be due to the higher concentration of $CaCl_2$ forming a more crosslinked gel matrix. If the butyl groups cause a change in the structure of the crosslinked gel then that may be a possible explanation for the almost doubling in % mass loss seen inFigure 4.19.

4.2.9   Paraffin Wax Coating

Dip coating alginate capsules into liquid paraffin wax was an easy and effective way to form a firm, hydrophobic coating around the hydrogel alginate membrane of the capsules. Pure alginate capsules were prepared using the same procedure as the capsules discussed in Section 4.2.1. Two different PAM solutions were used for forming the alginate capsules, one containing 5 wt% $CaCl_2$ and the other containing 7 wt% $CaCl_2$.
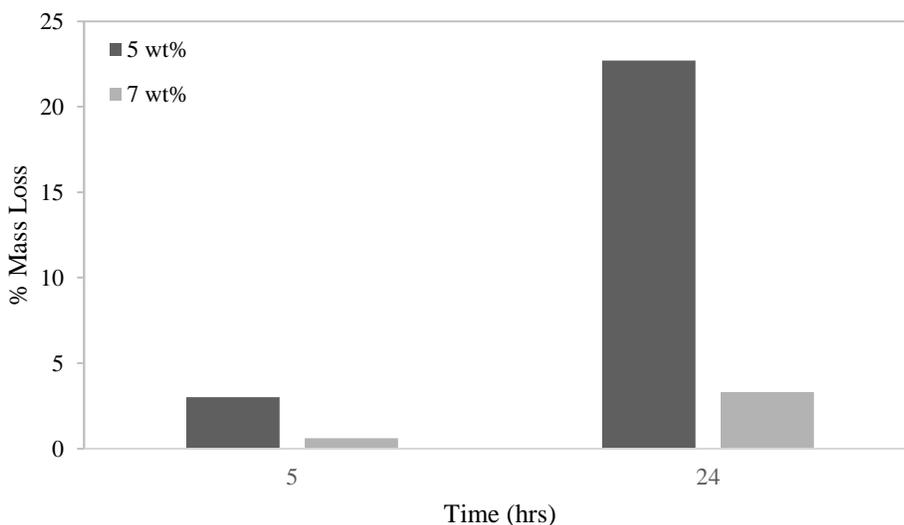
Figure 4.20: % Mass loss at 5 and 24 hours for paraffin wax coated alginate capsules. Capsules all made with a 20 min. membrane formation time and 10 min $CaCl_2$ bath. Each trial contains one capsule. The % mass loss at 5 hours for each formulation was measured in two trials.

Figure 4.11 shows the % mass loss for capsules made from PAM solutions with either 5 or 7 wt% $CaCl_2$. The % mass loss at 24 hours for both capsule formulations in Figure 4.20 are well under

the 60-70% mass loss seen in just pure alginate capsules. The large difference in % mass loss at both 5 and 24 hours seen between the two $CaCl_2$ concentrations used is most likely not the result of the difference in the PAM solutions used. While paraffin wax coating was very effective at reducing moisture loss over time, the coating process itself was highly variable. It was very difficult to get a uniform coating of wax on a capsule, often resulting in very thin areas of wax or areas with no wax at all. If a thick enough coating was not initially applied to the capsule, there was a risk of the coating flaking off the capsule.
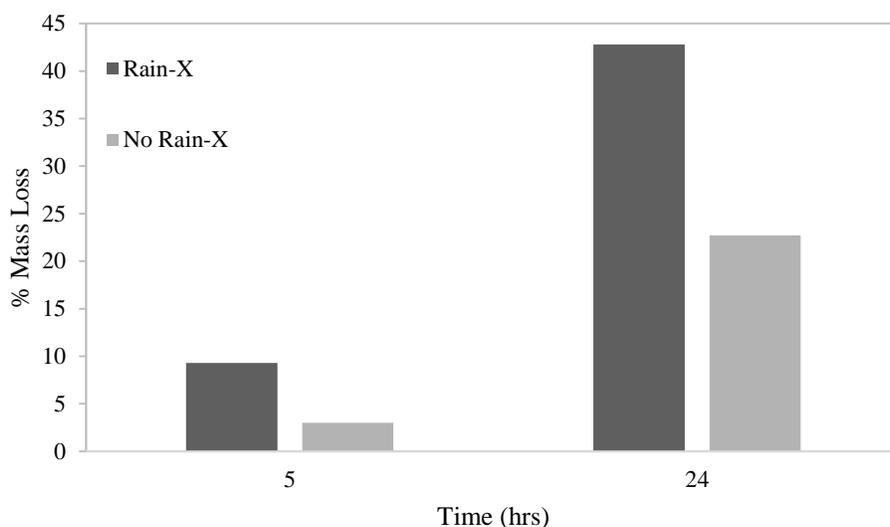
Figure 4.21: % Mass loss at 5 and 24 hours for alginate capsules coated with paraffin wax. Capsules were either coated with Rain-X prior to wax coating or were not. Each trial contains one capsule. The % mass loss at 5 hours for each formulation was measured in two trials.

As the alginate membrane is highly hydrophilic and the wax is highly hydrophobic it is not surprising that there were issues producing an even coating of wax. Alginate capsules were coated with Rain-X in an attempt to resolve the wetting issue of wax on the alginate membrane. Rain-X is a commonly available silane primarily used for making car windshields hydrophobic. If the alginate could be made slightly more hydrophobic then it may improve the liquid wax wetting. A

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comparison of the % mass loss for capsules with and without Rain-X treatment is seen in Figure 4.21. As seen in Figure 4.21 capsules that received the Rain-X treatment had a larger % mass loss compared to the untreated capsules. The pre-treatment with Rain-X also did not help in the fabrication of paraffin wax-coated capsules. When attempting to dip coat capsules that had been treated with Rain-X, it was observed that it was more difficult to achieve complete coating of the treated capsules. The presence of Rain-X on the capsule exterior affected the wetting of the liquid paraffin wax, causing it to retreat from the capsule surface before the wax could be hardened around the capsule.

4.2.10 Poly (methyl methacrylate) (PMMA) Coating Using Co-Flow Apparatus

The promising results seen in coating the alginate capsules with paraffin wax spurred much work into producing alginate capsules with a PMMA coating. PMMA can produce a strong coating that can tolerate handling without breaking, unlike the hydrophobic paraffin wax coating. The relatively simple polymerization reaction of methyl methacrylate using the initiator benzoyl peroxide is well established [24]. Co-flowing systems are commonly used to produce drops of a liquid in the bulk flow of an immiscible liquid. To encapsulate an alginate capsule in a drop of PMMA, alginate capsules were dispersed in a stream of PMMA solution. A concentric pipe containing the PMMA solution was then injected into a bulk flow of poly (vinyl alcohol) (PVA) solution. Ideally the PMMA flow would break into drops as it entered the flow of the main pipe, and if the drop formation was timed correctly, each drop would contain a single alginate capsule. This setup would allow the production of PMMA shells around the alginate capsule with a controllable thickness. Controlling the thickness of the PMMA shell was necessary since too thick of a shell would make it impossible for the shell to rupture under foot pressure.

There were many challenges faced with this setup. The first problem and possibly the most difficult to solve without developing a complex dispensing system is the axial spacing of the capsules in the PMMA stream. Droplet formation in continuous flowing systems occur at specific time intervals. If the capsule is not spaced correctly in the PMMA stream it will exit the nozzle into the PVA stream either too early or too late and not be coated by the droplet of PMMA. Since PMMA does not wet alginate very well to begin with, any exposed alginate causes the surface tension of the PMMA solution to retract away from the region of exposed alginate and peel off the capsule. When a capsule was successfully coated, it was difficult for it to stay that way. Any disturbance in the flow was enough to disrupt the coating and cause it to dewet from the capsule. Often flow disturbances were caused by filaments of PMMA that had developed during the droplet formation and then stuck to the sides of the pipe. Filament formation and daughter drop formation could not be avoided due to the need to dissolve PMMA in MMA to have a dense enough stream that it would be neutrally buoyant in the PVA flow.

4.2.11 PMMA Coating Using a T-Junction

In the T-junction method of attempting to coat alginate capsules with PMMA, instead of using a concentric tube to introduce the PMMA stream, the PMMA stream was injected by a perpendicular pipe into the PVA stream. This method presented all the same issues as the co-flow system did as well as a new problem. Since the PMMA was entering in the side of the PVA stream, the PMMA had a strong tendency to wet the side of the pipe containing the PVA stream. This would cause the alginate capsule to fall directly in the PVA stream without a PMMA coating. Once the PMMA coated the side of the bulk flow pipe it was very difficult to clean out, often requiring the device to be disassembled.

Using a similar scheme as the one used to produce drops of ATM, a stop flow method was attempted to produce a PMMA coating around the alginate capsules in the T-junction. A volume of PMMA solution containing an alginate capsule was injected to the pipe containing a stationary volume of PVA solution. Once the capsule was injected and the desired volume of PMMA was surrounding it, the PMMA flow was stopped. The PVA flow was then started to clear to the T-junction. This method worked perfectly in the immediate vicinity of the junction. However as the plug of PMMA with the capsule traveled down the pipe, the capsule had the tendency to fall out of the PMMA volume. Another drawback of this system was that it produced a PMMA coating in the gap between the capsule and the pipe the capsule was in. To achieve a thinner coating the gap thickness would need to be decreased. The system would also require substantial automation in order to produce high quantities of capsules.

4.2.12 PMMA Encapsulation in a Stagnant Volume of Water

Due to the level of difficulty experienced with attempting to perform PMMA breakup in two flowing streams, breakup was done in a reactor with a stagnant volume of water. While this did remove the variable of the flow rate of the PVA solution affecting the breakup of the PMMA coating around an alginate capsule, it did not solve the encapsulation problem. The same capsule space issue presented itself in this setup. As seen in Figure 4.22, a capsule is in the bottom of the pendent of PMMA right as the drop is about to break off. If the capsule had not been spaced correctly in the PMMA stream it would be too early or late for the pendent formation and would fall into the water. When the capsule did enter the pendent at the right time, success was still not guaranteed. Due to the large density differences between the capsule and PMMA coating, the capsule would settle to the bottom of the pendent. Once the capsule reached the bottom of the reactor the capsule rarely stayed within the pendent. Either the PMMA would quickly dewet, or as

the polymerization process proceeded the capsule would be squeezed out of the PMMA. All of these difficulties in encapsulating an alginate capsule in a coating of PMMA, combined with the hazardous nature of the chemicals involved in the polymerization of MMA led to the abandonment of this path.

(a) (b) (c)
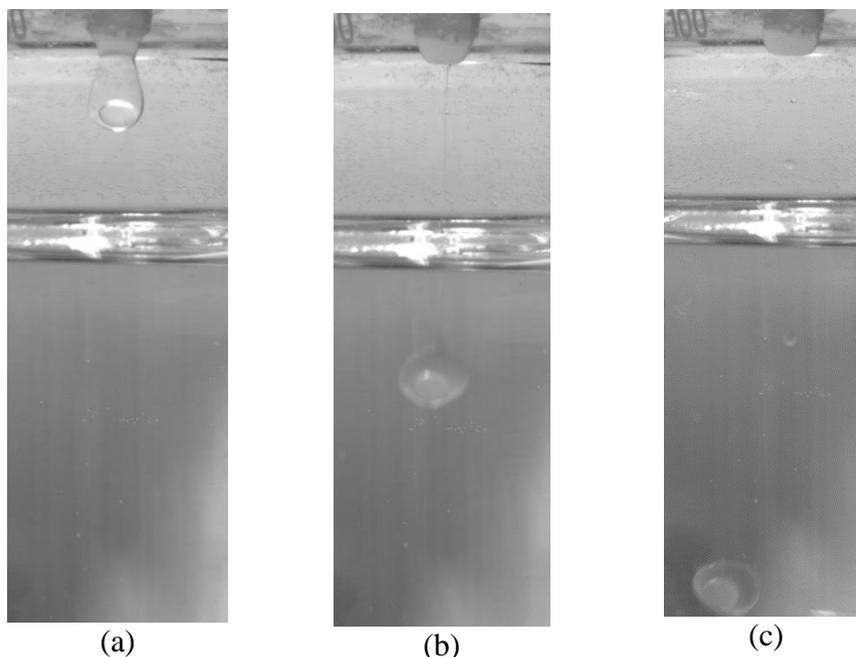
Figure 4.22: Alginate capsule in a drop of PMMA solution undergoing breakup in a stagnant volume of water. (a) Alginate capsule rests at bottom of pendant of PMMA solution. (b) Primary drop forms during separation from remnant volume, filaments are visible. (c) Primary drop with alginate capsule fully separates from remnant volume, satellite drops are visible.

4.2.13 Silicon Oil Emulsion

Capsules with an ATM core were formed from 10 cSt silicon oil/alginate emulsions with oil content as high as 60 wt%. Silicon oil is a very stable oil, and is non-reactive, making it an ideal coating to use as a water barrier. Once the oil/alginate emulsion is formed the emulsion is opaque white due to the size of oil particles that are produced through stirring. Measurements of the emulsion droplet size was attempted but due to the high oil concentration it was too difficult to

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dilute a sample of the emulsion enough to characterize the droplet sizes while still preserving the

original size distribution in the emulsion.
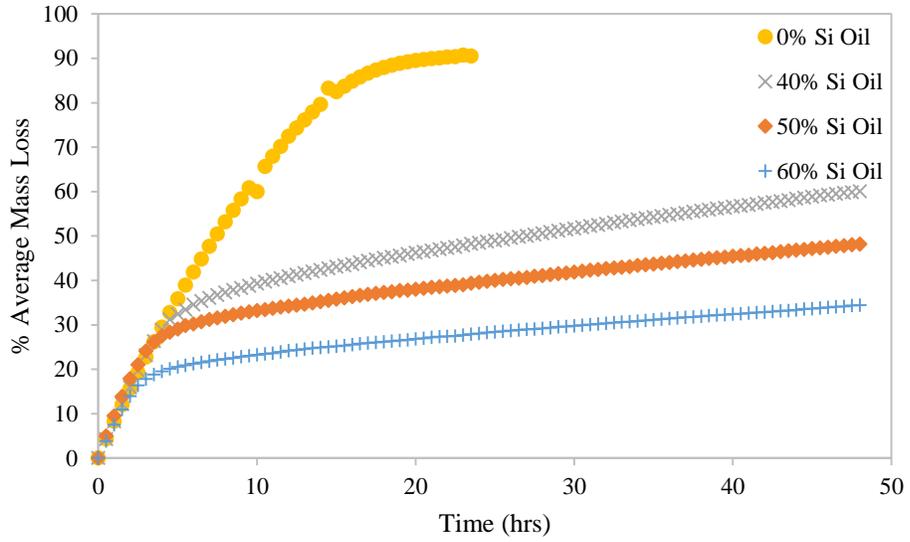
Figure 4.23: % Average mass loss over time for 3 silicon emulsion formulations and a pure alginate capsule. These plots are from one trial of each formulation. Each trial contained 8 capsules being dried.
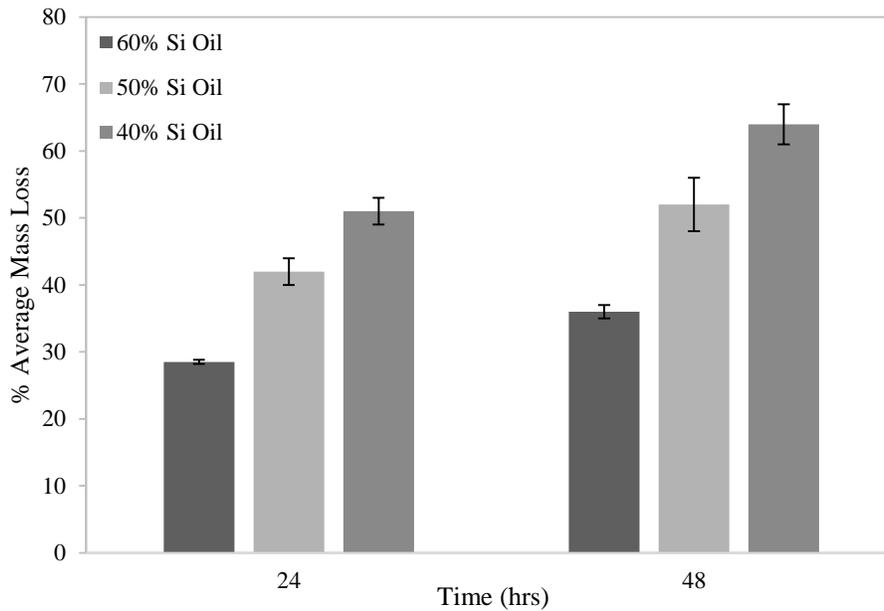
Figure 4.24: % Average mass loss for 3 silicon oil emulsion capsules at 24 and 48 hours. Each trial contained 8 capsules being dried, n=3.

Drying experiments were conducted on three formulations of silicon oil/alginate emulsions – 40% Si oil / 60% alginate, 50% Si oil / 50% alginate, and 60% Si oil / 40% alginate. The results of the % average mass loss for a collection of 8 capsules as a function of time for the three formulations is shown in Figure 4.4. These results are compared with pure alginate capsules shown as 0% Si oil capsules. The % average mass loss for each capsule with the three formulations of silicon oil / alginate at the end of 24 hours and 48 hours of being subject to a controlled 40% humidity atmosphere and an uncontrolled temperature of approximately 21˚C is shown in Figure 4.5. As seen in Figures 4.4 and 4.5, any level of oil addition to the alginate solution produces a capsule that has improved water barrier properties than a pure alginate capsule. The % average mass loss decreases as the oil content in the emulsion increases, with the 60% silicon oil emulsion producing the lowest % average mass loss of 36% at 48 hours. Most importantly there is still a viable volume of ATM in the capsule after drying for 48 hours as will be discussed in Section 4.3.1. In the interest of time, trials where not conducted beyond 48 hours but the data shown here and in Section 4.3.1 indicate that the capsule should still be viable beyond 48 hours.
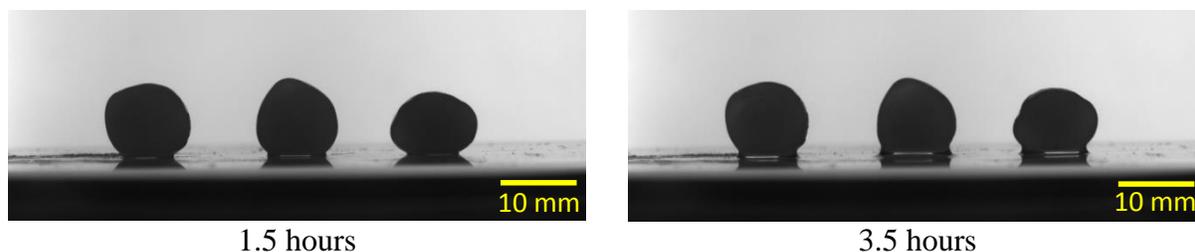
| 1.5 hours | 3.5 hours |

Figure 4.25: Capsules made from 60% silicon oil emulsion at 1.5 hours (left) and 3.5 hours into drying at 40% humidity.

The drying behavior of the capsules containing oil in the alginate membrane is indicative of the mechanism that enables the slow drying rate of these capsules. As seen in Figure 4.23, all the drying curves for capsules with oil pass through an inflection point, whereas the pure alginate

capsules do not. This inflection point is caused by the oil that exudes to the surface of the capsule and coats it. Since water traveling through silicon oil has a much lower diffusivity than that of alginate, the slope of the drying curve undergoes a sharp inflection. As the alginate membrane dries, the volume of the gel is reduced and the droplets of oil are constricted. Since the volume of oil must go somewhere, the path of least resistance is towards the surface of the capsule. The inflection point does not occur at the first appearance of oil exudation though. As seen in Figure 4.25, at 1.5 hours of drying there is a small amount of oil that is pooled at the bottom of the three capsules. By the time 3.5 hours has passed, the time where the inflection point appears in Figure 4.23, there is more oil pooled at the bottom of the capsules. This may indicate that at 1.5 hours the oil coverage on the surface of the capsules may not be a complete film, therefore not offering a larger resistance to diffusing water molecules.
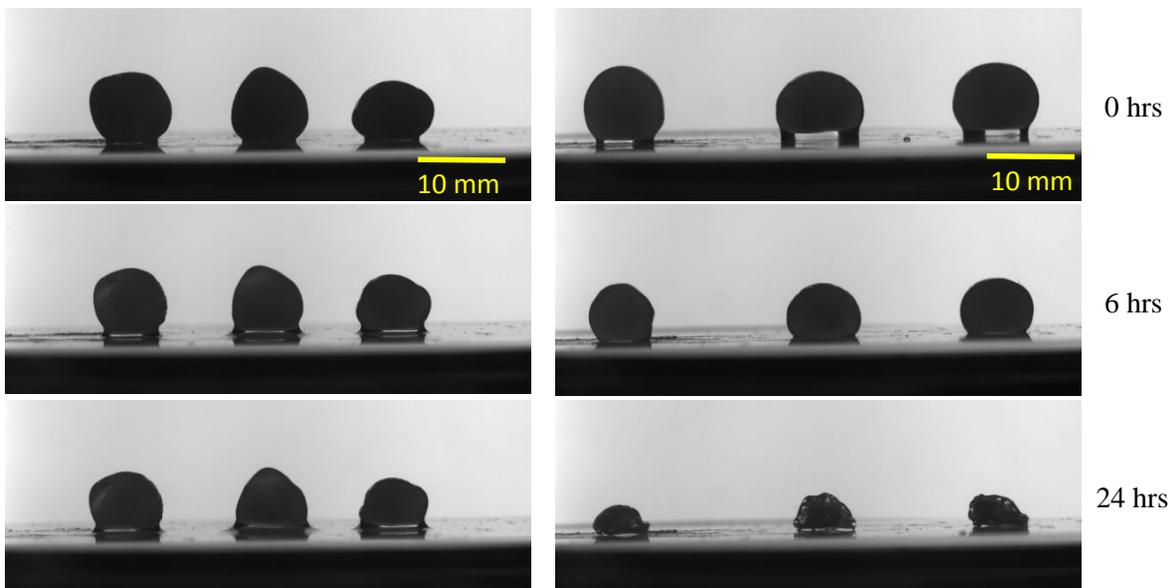
Figure 4.26: Drying progression of a 60% silicon oil/40% alginate capsule (left column) and a pure alginate capsule. All capsules contain an ATM mass of approximately 0.14 g.

In Figure 4.26, the effect of drying time on one set of three capsules made from the 60% silicone oil/40% alginate emulsion and another set of three pure alginate capsules is compared. Initially both capsules appear the same, there is no oil exuding from the emulsion capsules and the clear membrane of the pure alginate capsules is visible towards the bottom of the three capsules. At six hours, the differences appear: the emulsion capsules have already started to exuded oil with noticeable puddles of oil around the capsules, while the alginate membrane is no longer visible in the pure alginate capsules. At 24 hours the alginate capsules are dried and shriveled. During the drying of the 60% silicon oil capsule the majority of the mass loss appears to be from the membrane. If the core was experiencing water loss dimples in the capsules should begin to appear as the core loses volume.

4.2.14 Safflower Oil Emulsion

Using the same principles as the silicon oil emulsion capsules, ATM containing capsules were made from emulsions of safflower oil and alginate. Plant based oils have been used in the food industry to reduce the permeability of alginate films in order to create natural coatings for perishable food items [12]. However in the case of coating food items, exuding oil on the surface of the film is not a desirable product in the eyes of a consumer, so the oil content is kept low. Since safflower oil is a lipid based oil, the oil contains hydrophobic and hydrophilic sections, which improves the oil's interaction with the aqueous alginate solution, while still offering the high water barrier property of a hydrophilic oil.
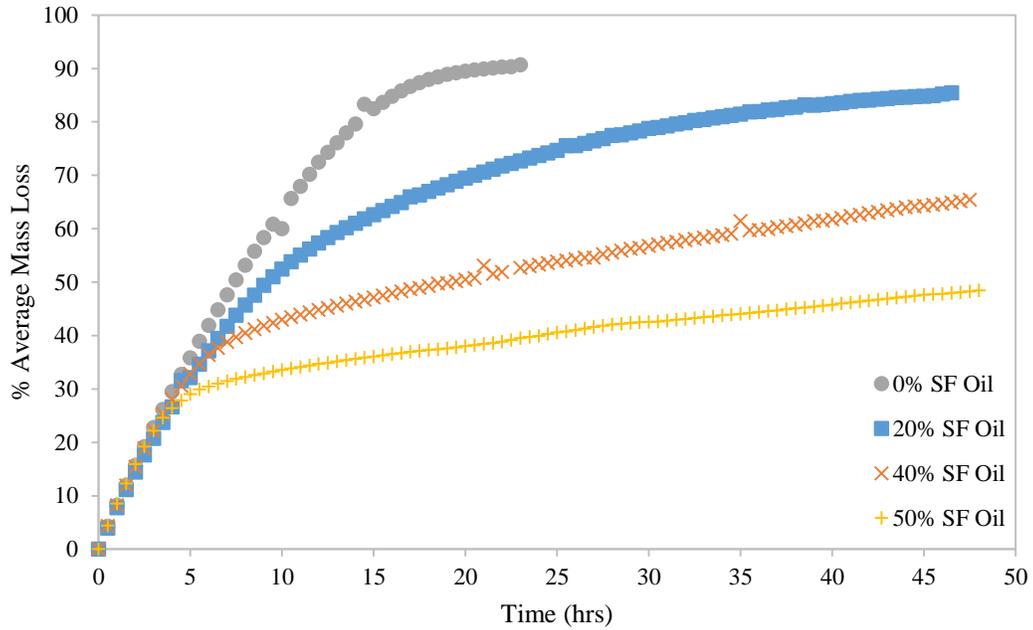
Figure 4.27: % Average mass loss over time for 3 safflower oil emulsion formulations and a pure alginate capsule. These plots are from one trial of each formulation. Each trial contained 8 capsules being dried, n=3.
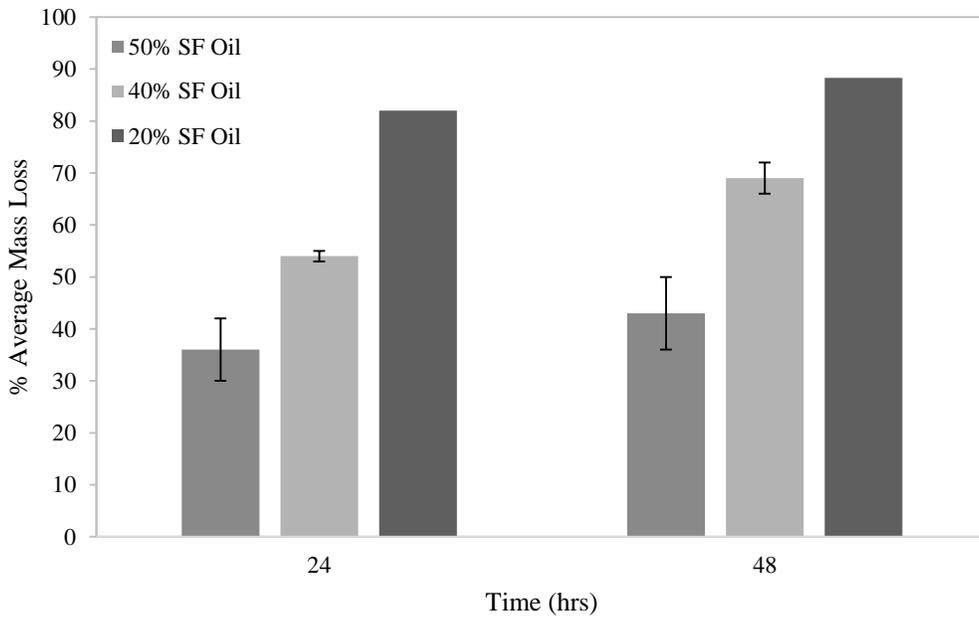
Figure 4.28: % Average mass loss for 3 safflower oil emulsion capsules at 24 and 48 hours. Each trial contained 8 capsules being dried. The results for 20% safflower oil are for one trial, all other trials were done in triplicate.

For capsules made from a safflower oil emulsion, the drying behavior is very similar to that of the capsules produced from silicon oil emulsions. In Figure 4.27, all drying curves for capsules with some level of oil content display the inflection point in the slope of the curve as the safflower oil begins to coat the exterior of the capsule. An emulsion containing 50 wt% of safflower oil was the highest oil content that could still support membrane formation. Interestingly in Figure 4.28, the % average mass loss experienced by capsules containing 50 wt% safflower oil is 43% at 48 hours, compared to the 52% for a 50 wt% silicon oil capsule. There may be a benefit to the lipid interaction with the alginate solution, but this benefit is defeated by the inability to form capsules with higher safflower oil content.

4.2.15 Encapsulant Comparison

The results for 14 different capsule formulations has been presented here, however out of all the data shown, a method of determining what formulation is the best must be developed. For the work done on this project the most important category was mass loss after 24 hours. Since the capsules were tested at ~40% relative humidity, and below 80˚F, the mass loss at 24 hours was a good measure of the capsule locking in the water content of the ATM. If the capsules are deployed in a hot and arid environment then a capsule with good 24 hour behavior should still be effective through the majority of a day. Reaction time will be a concern for future scale up efforts of this project. The shorter the reaction time to produce a batch of capsules should indicate an easier path to scaling up production.

Table 4.1: Encapsulant comparison table for determining the best formulation to pursue further.

Formulation	Mass Loss After 5 hrs	Mass Loss After 6 hrs	Mass Loss After 24hrs	Reaction Time	Comments
Safflower Oil Emulsion	29%	31%	36%	20min	Good water barrier
Silicon Oil Emulsion	21%	21%	29%	20min	Good water barrier
Wax Coating	0.6%	-----	3.1%	20 min	Fragile
Corn Starch	-----	22%	54% (Dry)	30 min	Mold growth, fragile, high solids content
Pure Alginate	16.7%	-----	59% (Dry)	30 min	Poor water barrier
Polystyrene particles	-----	19%	73% (Dry)	30 min	Difficult reagent prep, poor water barrier
Starch Nanocrystals	-----	24%	67% (Dry)	30 min	Difficult reagent prep
Heat-Moisture Treating Starch	-----	22%	Dry	30 min	Poor water barrier
Bentonite	-----	17%	Dry	30 min	Poor water barrier
Esterification	-----	31%	Dry	30 min	Poor water barrier
Polystyrene particle sintering	-----	18%	Dry	60 min	Difficult reagent prep, poor water barrier
Heat Treating Alginate	-----	23%	Dry	60 min	Poor water barrier
PMMA	N/A	N/A	N/A	3 hrs	Hazardous reagents, difficult fabrication

The three top scoring formulations, safflower oil emulsion, silicon oil emulsion, and paraffin wax performed better the other formulations in terms of preventing the drying of ATM. The final assessment of the encapsulant material was done on the top two formulations, safflower oil and silicone oil emulsions, due to their success as a water vapor barrier and ease of fabrication. While many of the formulations appear to have only small differences in the % mass loss measured at 5 or 6 hours, and some were not measured at 24 hours, the conclusions about the safflower oil and silicone oil were still true. All capsule formulations were observed at 24 hours, regardless of whether or not a measurement was taken then. All capsules except for the oil/alginate capsules and

the paraffin wax capsules were not viable at 24 hours. They had loss moisture content to the point where the capsule could not dispense the core contents upon breaking the membrane, similar to what is seen in the 24 hour pure alginate capsule image in Figure 4.26.

Paraffin wax coating was a highly effective coating material for inhibiting water loss and had a slower drying rate for the first 6 hours of drying compared to the oil emulsion encapsulants. It was not pursued further, however, due to the fragility of the wax coating. A wax coating would also be susceptible to weakening or even failure if exposed to high temperatures. These may be problems that can be worked around if this coating is considered desirable in the future. However due to the immediate difficulties that the fragility issue presented, paraffin wax coating was not pursued further.

As both silicone oil and safflower oil capsules showed great promise as effective water barriers, more effort was placed on investigating what reagent conditions produced the best drying results. In the end, capsules made from a 60% silicon oil emulsion have an edge over the 50% safflower oil emulsion capsules. At 48 hours the capsules made from a 60% silicon oil emulsion had a % mass loss of 36% while the 50% safflower capsules had a % mass loss of 43%. It is for this reason that the 60% silicon oil emulsion capsules were chosen for further investigation in the succeeding section.

4.3   Final Encapsulant Choice Assessment

4.3.1   *Coefficient of Friction*

Collecting drying data to evaluate capsule performance is an easy metric to use in order to compare capsule formulations against each other. Drying data does not, though, completely demonstrate what is happening to the ATM inside the capsule. Since there is water in both the capsule

membrane and the ATM solution, it is not possible to state specifically if the mass loss is from the core, the membrane, or some ratio between the two. Since these capsules would be used to create a low friction surface once their cores are dispensed, the best way to evaluate if a certain mass loss is acceptable for a given capsule formulation is to preform coefficient of friction measurements.

In order to simulate the effects of drying on the films or the capsules as it would happen if they were being used in the field, the 11 grams of the materials was dried without the addition of more material to maintain original mass. Since the 60 wt% silicon oil, 40 wt% alginate capsule was the one that produced the lowest mass loss after 48 hours it was the formulation used for the coefficient of friction measurements. For control experiments, the coefficient of friction for the dry rubber on rubber was measured, $\mu_s= 0.89 \pm 0.04$, as was the coefficient of friction for the same rubber on rubber coated with 10 cSt silicon oil, $\mu_s=0.7 \pm 0.2$.
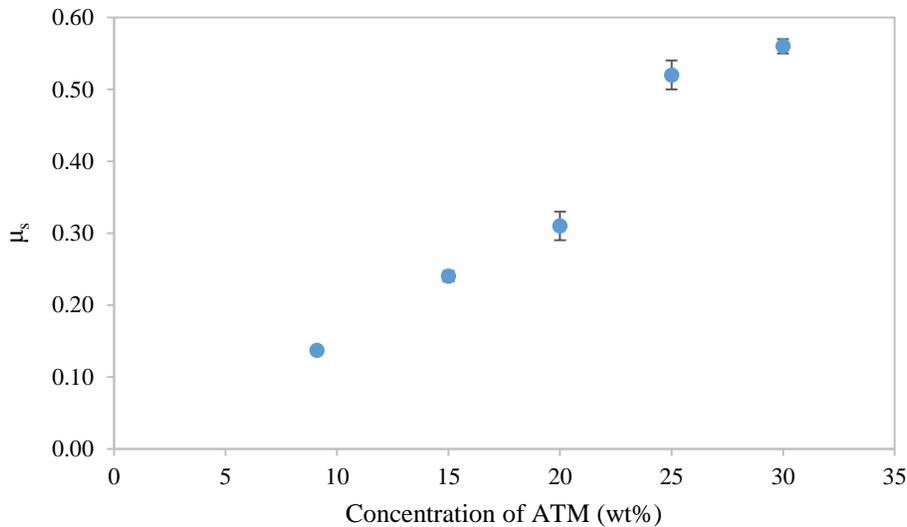
Figure 4.29: Static coefficient of friction for ATM films at increasing concentrations of ATM. Films start at 11 g of 9.09 wt% ATM solution and are dried until the concentration of interest is reached. Each point is the average of three trials. Error bars represent standard deviation.

In Figure 4.29, the presence of the ATM films at all the concentrations tested offered a reduction in the coefficient of friction for a rubber on rubber surface. The United States Access Board deems a flat surface with a coefficient of friction of 0.5 or higher to be safe to walk on [29]. As seen in Figure 4.29, films of ATM with an ATM concentration of 25 wt% or higher produced coefficients of friction greater than 0.5. The 30 wt% films are stiff and are close to the point of not spreading when compressed by the weight of the sled. The increase of μ_s with increasing concentration of ATM seen in Figure 4.29 is due to the increasing viscosity of the films. Viscosity is the measure of a fluid's resistance to motion, the higher the viscosity, the harder it is to deform a film at rest during the coefficient of friction test. Tests that have been attempted on films dried to 40% show that it is not possible to get usable data for concentrations that high with the current apparatus. This is because the films have become too viscous or may be behaving more as a solid, preventing the films from spreading during the test and leading to poor measurements of μ_s.
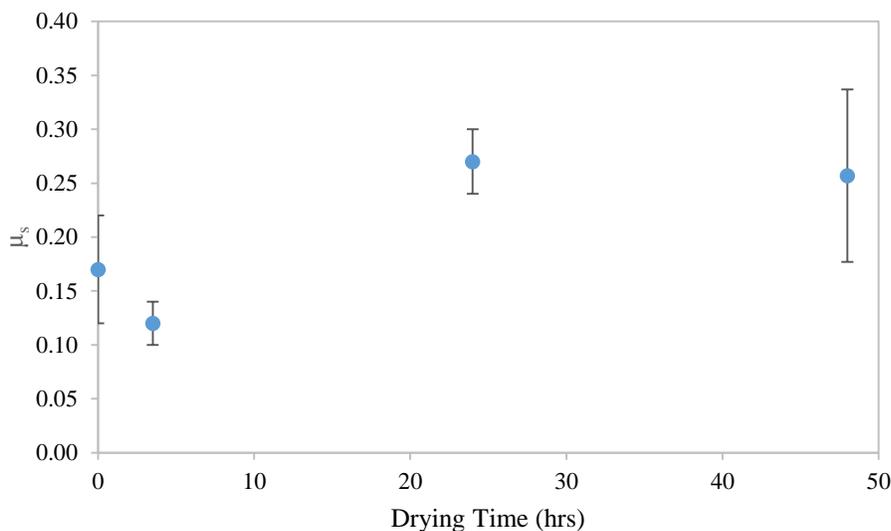
Figure 4.30: Static coefficient of friction for 60% silicon oil capsules at increasing drying time. 11 g of capsules were used for the initial time point. All subsequent points are capsules that initially weighed 11 g and underwent drying. Each point is the average of three trials. Error bars represent standard deviation.

Figure 4.30 shows that after 48 hours of drying the ATM that had been encapsulated still behaves as an effective lubricant. At 48 hours the capsule dispensed ATM has the same coefficient of friction of as a film of ATM with approximately 15 wt% ATM. According to the values in US Patent 7,186,443, a film containing approximately 15 wt% is still an effective lubricant [1]. Also capsules aged 48 hours dispensed ATM that still clung to both the underside of the sled and test surface when the sled was picked up, showing better spreading and adhesion behavior than the films at 20 and 25 wt% ATM. Interestingly as well in Figure 4.30 is the decrease in the static coefficient of friction at 3.5 hours. This may be due to the presence of oil on the surface of the capsules at this point in the drying. A drying time of 3.5 hours corresponds to the inflection point in the drying curve for 60 wt% silicon oil capsules. The oil on the surface of the capsule may be enough to coat the substrate or ATM when the capsules are ruptured, reducing the coefficient of friction to below what fresh encapsulated ATM can produce.

Drying tests with films of ATM showed the films reaching 30 wt% ATM in approximately 22 hours, in a 40% humidity environment. As the friction tests have shown it may be possible to traverse a surface that is coated with a film of 30 wt% ATM. With the capsules providing a coefficient of friction of 0.257 at 48 hours, they are at a minimum offering a 118% improvement in the time that the ATM will be effective.

4.3.2   Rupture Strength

The rupture strength of the capsules were measured to ensure that the membranes formed were weak enough that they could be ruptured by foot pressure. The strength of the membranes may also inform choices in the future on how to best store and dispense the capsules. The tests measured the strength of the membrane of the 60 wt% silicon oil, 40 wt% alginate capsules at their initial point of fabrication, 24 hours after, and 48 hours after fabrication.
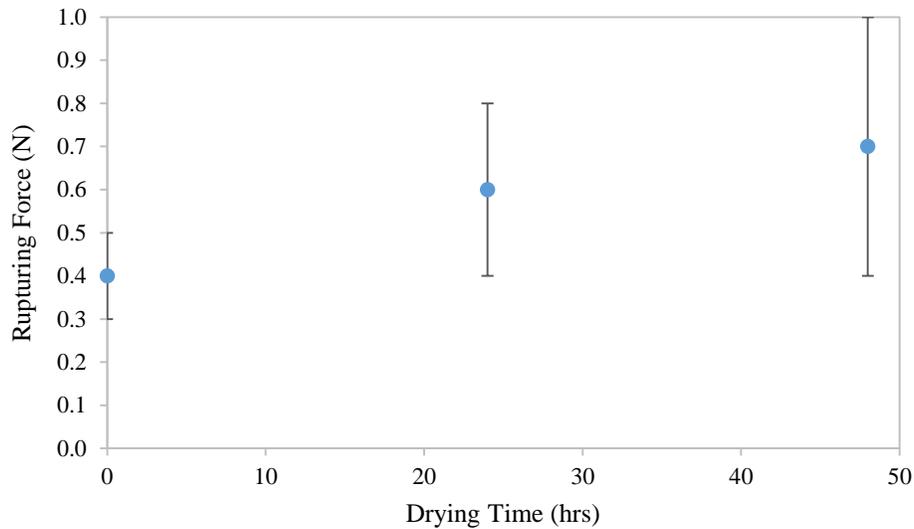
Figure 4.31: Force required to rupture 60% silicon oil capsules at various drying points. Each point is the average of 5 measurements.

In order for the capsules to effectively dispense their contents they must at a minimum be able to rupture from the pressure of a foot step. In Figure 4.31, a maximum rupture strength of 0.7 N is seen at the 48 hour drying point. For a 10 mm diameter capsule the rupturing pressure would be $3.5x10^4$ Pa, using the cross sectional area at the capsule's equator. A human with a weight of 140 lbs. can produce a foot pressure of approximately $2x10^5$ Pa when walking on concrete, grass or carpet [30]. Surface specific testing should be conducted in the future to ensure that capsule rupture is possible on deformable surfaces.

4.3.3   Capsule Fabrication Parameter Investigation

Since the 60% silicon oil 40% alginate emulsion produced the best results in terms of mass loss over time, this formulation was then used to perform two more experiments exploring possible optimization routes for future work. The experiments investigated the effect of the initial mass of the ATM core on drying and the effect of the initial concentration of ATM on drying. With a higher

encapsulated mass of ATM, the drying rate over 48 hours is decreased as seen in Figure 4.32. The trend extends for all three masses investigate, and while the error is large at 48 hours for the capsules containing 0.42 g of ATM, the 24 hour % mass loss still shows the trend. The decrease in % mass loss with increasing mass may be explained through the volume to surface area ratio of the capsules. When the volume of a sphere is increased, the ratio of the surface area to the volume decreases. With less surface area to volume, the evaporation rate should be reduced since the rate of evaporation is highly dependent on the available surface area for water vapor loss. The greater volume of ATM may also provide increased mass transfer resistance for water closer to the core of the capsule.
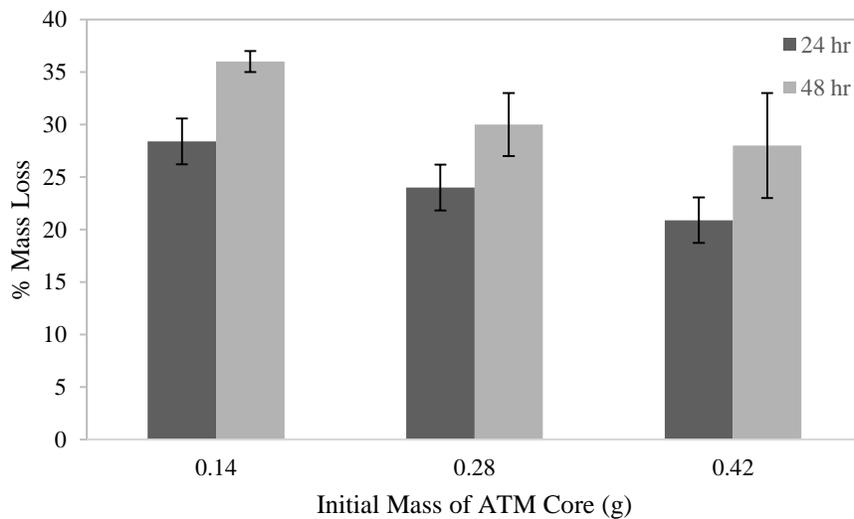
Figure 4.32: Dependence of the % average mass loss at 24 and 48 hours for capsules containing increasing masses of ATM. Each point is the average of three trials. Error bars represent standard deviation.
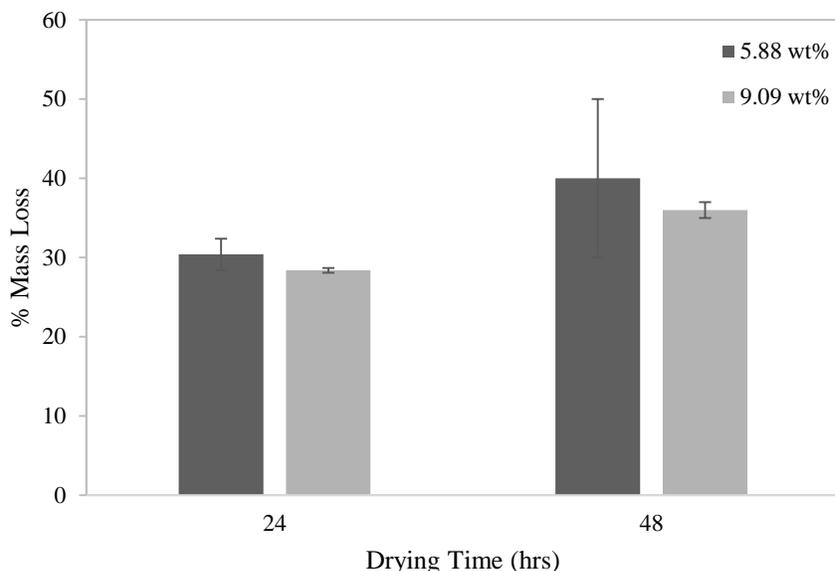
Figure 4.33: % Average mass loss dependence on the initial concentration of ATM. Each point is the average of three trials. Error bars represent standard deviation.

When investigating the role of the initial concentration on % mass loss over time, two concentrations were use. The 9.09% ATM concentration used in all previous experiments was based on the stated optimal concentration in US Patent 7,186,443. The lowest ATM concentration stated as desirable was 5.88% or a ratio of 1:17 [1]. The total mass of the initial ATM volume was kept constant at approximately 0.14 g for these experiments.

In Figure 4.33 the capsules containing the less concentrated ATM solution do lose a greater percentage of their mass than the standard 9.09% ATM capsules, 30.4% compared to 28.4%. The % mass loss of the capsules in this case though is not the whole picture. If the worst case was considered where all the mass loss was occurring from the ATM, at 48 hours the ATM concentration for the initially lower concentration capsules would be approximately 14%. The standard 9.09% ATM capsules would, in the same situation, have an ATM concentration of 26% at 48 hours. Friction testing will of course be the true measure of a specific formulations

effectiveness over time but diluting the ATM concentration may be a possible path forward for improving the life span of the capsules.

4.4 Automated PAM Drop Breakup

While all the of the drops of ATM or PAM used to form the capsules discussed in Section 3.3 and 3.4 were broken off manually from a larger mass of the ATM or PAM solution, this method could not be used for commercial production of capsules. The results for an automated method of producing precise drops of a 9.09 wt% PAM solution is presented here. While this process has not been connected directly to the capsule fabrication process, it would not be difficult to link the two together.
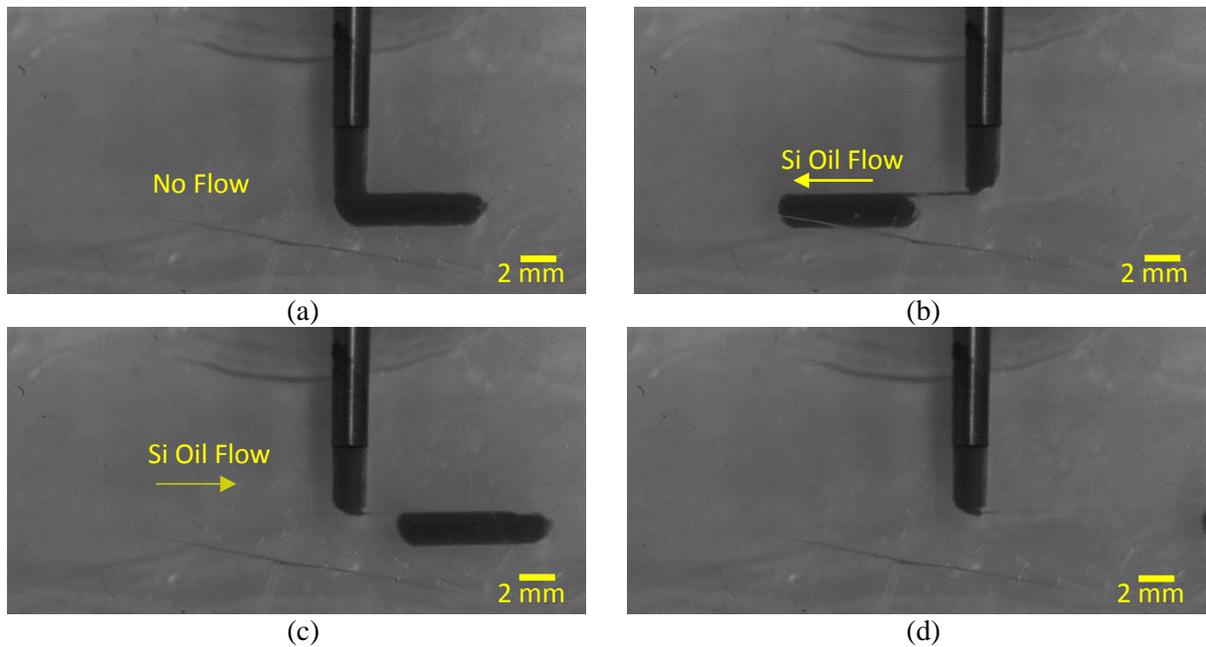
Figure 4.34: Breakup cycle for a 9.09% PAM solution drop, bulk fluid is 500 cst silicon oil. (a) Solution is injected into T-junction, forming plug. (b) Plug is shifted backwards to disrupt polymer alignment. (c) Flow is reversed to clear plug. (d) Channel is cleared, ready for next injection.

In Figure 4.34, the formation and breakup of the 9.09% PAM solution drop is shown. A clean drop of the highly viscoelastic fluid is formed in a bulk flow of 500 cst silicon oil. The channel shown in these Figures is made of PDMS and has a diameter of 2.1 mm. The tendency of the fluid to still form thin filaments is seen in Figure 4.34(b). The short filament that is connected to the two perpendicular volumes of PAM solution merges with the horizontal plug when the fluid flow is reversed in Figure 4.34(c). The filament formation on the back cycle can be suppressed with the appropriate flow rate of the bulk fluid. The filament forms as a result of higher local shear at the T-junction. In both cases shown, the flow rate on the backward cycle was slightly higher than optimal. However, if the filament can be tolerated on the back cycle, it does not necessarily affect the final formation of a clean drop of viscoelastic fluid.

(a)   (b)
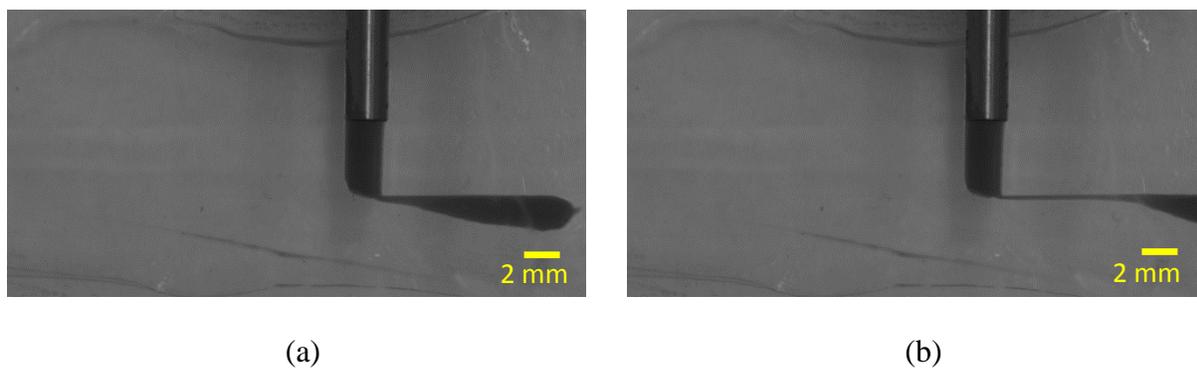
Figure 4.35: Poor breakup for 9.09 wt% PAM solution with no shifting step in breakup cycle. (a) and (b) show the plug's translation through the channel towards the outlet.

Figure 4.35 shows the importance of the shifting step in the breakup cycle for a 9.09 wt% PAM solution. At least for the system used in these experiments, if the shifting step is not used, long filament formation occurs during the channel clearing step. This is most likely due to the way the PAM plug fills the channel during injection, since it fills the channel mainly in the direction of the outlet. This creates an alignment of the polymer chains in the direction of the outlet which makes breakup very difficult if the drop is only moved in the direction of the outlet. The reverse shifting

disrupts this alignment as well the memory that the polymer chains have of their previous state. For the current system, the shifting step is necessary for clean breakup.

For the 9.09 wt% PAM solution it was shown that to achieve a clean break, the length that the drop must be shifted for a desired drop size depends on the flow rate used for drop translation. In Figures 4.36-4.38, a phase diagram for three different bulk oil flow rates is shown. The non-dimensional drop length, K, is the ratio of the drop length over the drop diameter. The non-dimensional shift length, λ, is the ratio of the length the drop is shifted backwards over the drop diameter. To qualitatively assess the breakup of the drop from the remnant volume of PAM, the level of filament formation during the breakup process was observed through video recordings of the breakup cycle. The level of breakup that was observed in the video for a given operating condition was given one of three grades, poor, acceptable and good. Poor breakup entailed either no breakup, where the drop is not separated from the injection volume, or long filament are formation. Acceptable drop breakup had slight filament formation during breakup. Good breakup had no optically observable filament formation during breakup.
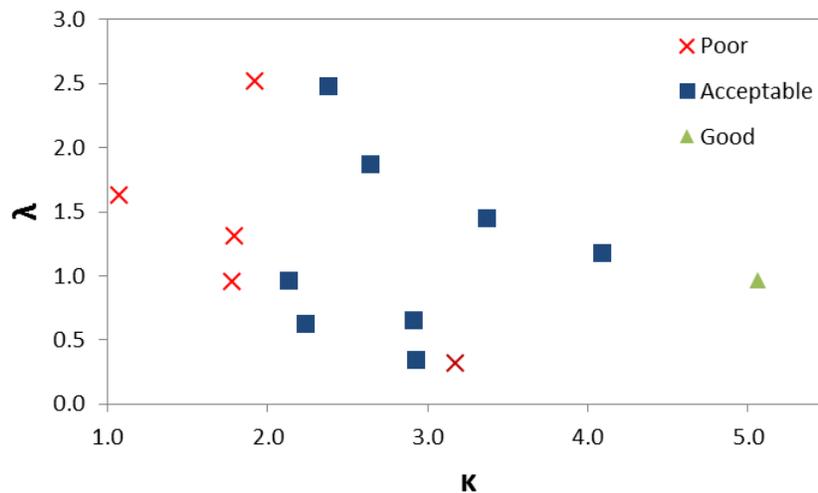
Figure 4.36: Breakup phase diagram for 9.09 wt% PAM solution. Showing relation between non dimensional shift length, λ, and non-dimensional plug length, K, for a bulk 500 cst silicon oil flow rate of 0.0538 mL/s.

For a flow rate of 0.0538 mL/s, Figure 4.36, only breakup for a very long drop with a shift length equivalent to its length achieves a good breakup. In the phase diagram it appears that a K of 2 is a transition from poor to acceptable. This is the length that fully blocked the channel cross section, preventing the bulk oil from seeping around the plug at this high of a flow rate. If oil can seep around the drop it may cause the plug to deform in the radial direction, decreasing its viscosity and negatively affecting breakup.
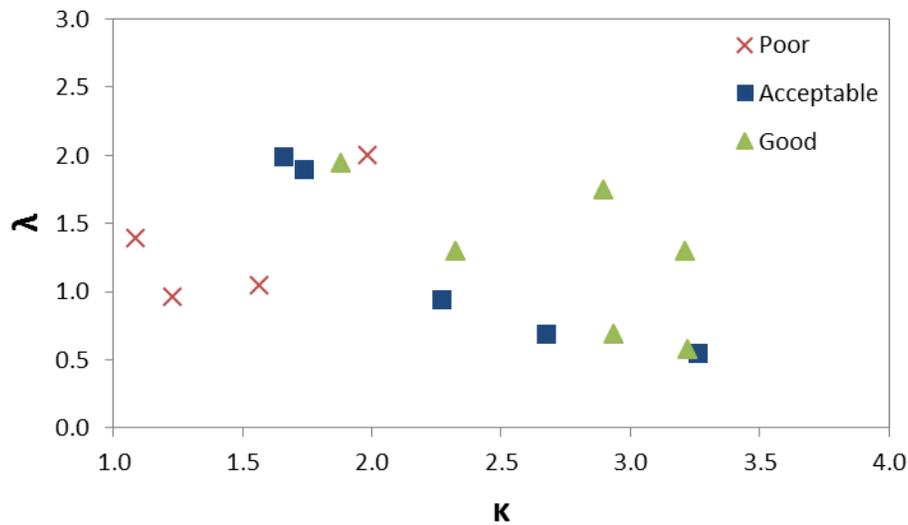
Figure 4.37: Breakup phase diagram for 9.09 wt% PAM solution. Showing relation between non-dimensional shift length, λ, and non-dimensional plug length, K, for a 500 cst silicon oil bulk flow rate of 0.0354 mL/s.

Reducing the flow rate to 0.0354 mL/s, Figure 4.37, improved the breakup results for a similar range of drop sizes and shifting lengths. A similar size cut off is still present for a K of 1.5 to 2. The presence of acceptable breakup occurring around a K of 1.5 indicates that a lower flow rate is less likely to seep around the plug. A lower flow rate also reduced the overall shear in the system which suppressed the formation of filaments. Similar results are shown in Figure 4.38 for a flow

rate of 0.0144 mL/s. Good breakup can be expected in this system for a K range of 1.5 to 3.0 and

λ from 0.5 to 2.0. The phase diagrams are not complete but show that for given operating

conditions, there will be optimization necessary to achieve the best results. The phase diagrams

also indicate that there is a region of optimal operating conditions that are bounded by critical K

and λ values. From the work done so far, it appears that lower flow rates maximize the area of this

optimal region.
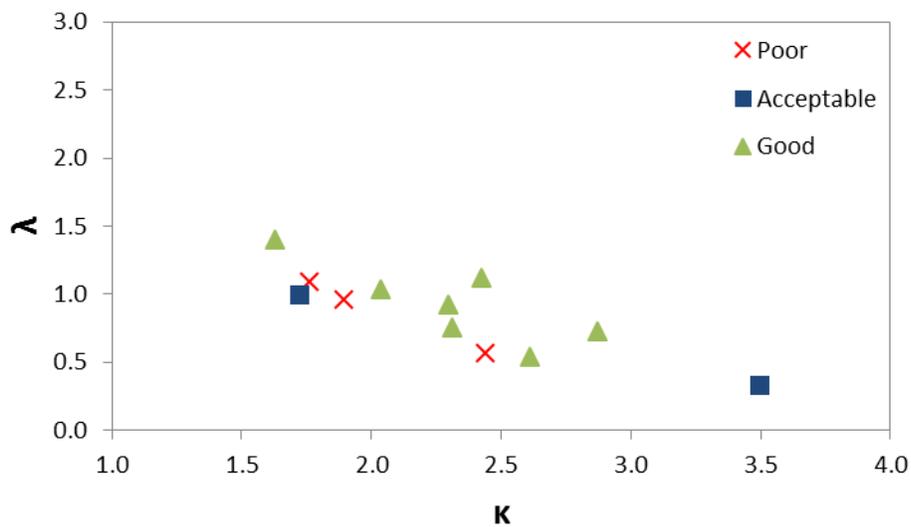
Figure 4.38: Breakup phase diagram for 9.09 wt% PAM solution. Showing relation between non-dimensional shift length, λ, and non-dimensional plug length, K, for a 500 cst silicon bulk flow rate of 0.0148 mL/s.

Chapter 5: Summary and Future Work

5.1 Conclusion

The goals of the work presented in this thesis were to encapsulate ATM in a commercially feasible manner that reduced moisture loss, and allowed for a pressure triggered release of the ATM contents. The resulting capsules should be safe for human contact and environmentally benign. In order to encapsulate ATM, a method for producing drops of ATM needed to be developed as well. In the work presented in this thesis, capsules of ATM were fabricated and dried in a humidity controlled environment. The different capsule formulations investigated were evaluated and those with the lowest % mass loss and best qualitative properties, discussed in

Table 4.1, were investigated using 48 hour drying studies. The best capsule formulation from the 48 hour studies was then used to investigate the coefficient of friction of the encapsulated ATM and the rupture force necessary to dispense the ATM from the capsule. The effect of capsule parameters such as initial mass of the encapsulated ATM, and the concentration of the ATM, on the drying rate of the best capsule formulation was also investigated. Finally, an automated method of producing discrete drops of a 9.09 wt% PAM solution was also presented.

In the work presented here, 13 different encapsulants were investigated for their suitability to form capsules of ATM. The capsules made from the different formulations were evaluated for mass loss over time, and overall reaction time. Other factors considered were the reaction requirements of the capsule fabrication process, e.g. high temperature requirement, hazardous chemical use, or multi-step processes. Also noted was if the capsules fractured or ruptured spontaneously during

the course of any of the experiments. These observations were considered as part of the evaluation since they highlighted potential weaknesses that would hinder potential commercialization of encapsulated ATM.

Of the 13 encapsulants investigated, a safflower oil/alginate emulsion and a silicon oil/alginate emulsion were found to produce the lowest % mass loss over time. Further drying experiments revealed that a 60 wt% silicon oil, 40 wt% alginate emulsion produced the lowest % mass loss of water after 48 hours, a % mass loss of 35%. The 60 wt% silicon oil emulsion was used to produce capsules to determine the coefficient of friction of the ATM contents of these capsules, the rupture strength of the capsule membrane, and fabrication parameter optimization experiments.

Coefficient of friction tests with ATM capsules made from a 60 wt% silicon oil emulsion were conducted to determine if during the course of drying the ATM in the capsule remained a viable lubricant. For each time point investigated the capsules were ruptured in order to measure the coefficient of friction of the ATM contents. At each time point measured, 0 hours, 3.5 hours, 24 hours, and 48 hours, the coefficient of friction was below that of what is considered a safe surface, $\mu_s < 0.5$. Specifically, at 48 hours the measured coefficient of friction was 0.26. At a minimum this is an 118 % improvement in the effective lifespan of ATM when compared to unencapsulated ATM films. The rupturing force needed to dispense the ATM contents of the capsules made from 60 wt% silicone oil that had dried for 48 hours was 0.7 N.

Using the 60 wt% silicon oil emulsion, the effect of the initial mass of ATM and the concentration of ATM on the drying rate of the capsules was investigated. Using a mass of 0.42 g of a 9.09 wt% ATM solution decreased the 48 hours % mass of the capsules to an average of 28%. Diluting the ATM concentration to 5.05 wt% was found to produce an increase the % mass loss at 48 hours

from 28.4% to 30.4%. However this increase may only produce an internal ATM concentration of 14 wt% at 48 hours.

An automated method of dispensing a 9.09 wt% PAM solution was developed in order to produce capsules of ATM on a large scale in the future. Due to the high viscosity and viscoelastic nature of PAM and ATM, current methods of fluid dispensing or droplet production cannot work for these fluids. A stopped flow method of producing drops of the polymer solution was developed. When operated under the correct conditions, this method of shifting stationary volumes of the polymer solution does not suffer from filament formation or the beads-on-a-string effect. Preliminary investigation into the drop break up process indicates that there is an optimal operating region bordered by critical drop sizes, K, and shifting lengths, λ. Slower bulk fluid flow rates appear to allow for the maximum range of operating conditions within the optimal region.

5.2 Future Work

Long term stability of the encapsulant formulation requires assessment in future work. Also, work should be done to look into how to best store fabricated capsules, and how the capsule membrane behaves in long term storage. Since these capsules will be made long prior to their use and away from the areas of their use, this information is necessary to test feasibility of the current design.

Scaling up the production of these capsules from the lab bench to the pilot plant scale is also a task of great importance. Currently the capsules are produced in a batch fashion which likely will not be the most efficient method for large scale production. A continuous production method based on a tubular flow reactor may offer benefits in terms of throughput, scalability, reaction rates, and improved process control. If the alginate emulsion membrane is chosen for future work then a

scaling up of the reactor will also need to include work on producing an appropriate emulsion in large volumes.

Whichever reactor style is chosen for pilot scale production, it must be able to be tied to the method of drop breakup described previously. This method of producing drops of ATM is currently the only method known and drops of ATM are necessary to produce individual capsules. Current work has demonstrated the method necessary to produce clean drops of ATM. Further work should be done to investigate multiplexing schemes for increased throughput. This may be as simple as running multiple apparatus in parallel or move towards using one apparatus to produce multiple ATM drops per cycle.

Field testing the capsules will also obviously be an important step. The process of deploying capsules must be developed, the capsules effectiveness in dispensing a coating of ATM to the surface of interest, and the capsules long term effectiveness in an uncontrolled environment. Capsule strength will have to be evaluated as well, if the capsules are deemed too weak there may be options for improving the strength. These options may include longer reaction times, incorporating a low weight fraction of fibers into the membrane, or partially crosslinking the silicon oil as it exudes.

The progress made so far seems to have resulted in capsules that are effective for 48 hours, if not longer. There is however a large difference between lab bench production and pilot scale production. The future outlined above are key to determining the future feasibility of using an alginate based membrane to form a capsule of ATM.

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