ABSTRACT

HIGHAM, ALINA KIM-THAO. Functional Nanofibers and Gels: A Study of Novel Needleless Electrospinning Technologies and Gelation Kinetics of Thiol-Acrylates and Hydrogels. (Under the direction of Dr. Saad A. Khan).

Advanced functional materials are generating a considerable amount of interest as consumer needs and demands in our society continue to grow and require materials to behave smarter and more efficiently. The opportunities and applications for these materials seem limitless as specific functionalities can be added or removed via additional processing steps. Some applications of interest include use as tissue scaffolds, particle delivery vehicles, sensors, catalysts, and many more. The fabrication of functional materials consists of three main steps: the raw materials, the manufacturing process, and the final product. This dissertation focuses on the relationships between processing parameters, material microstructures, and final product properties. We specifically focus on three distinct materials.

The first materials under investigation are electrospun nanofibers, which are fibers with diameters less than 500 nm. We focus on developing a novel manufacturing process capable of simultaneously fabricating multiple fibers without a needle, called foam electrospinning. In this method, nanofibers are electrospun from the surface of a foamed column by injecting compressed gas through a porous plate into a polymer solution. Using two model aqueous electrospinning systems, poly vinyl alcohol (PVA) and poly-ethylene oxide (PEO), we identify the effects on fiber properties (e.g. morphology, diameter,) from modulations in key design, process, and solution parameters, such as electrode geometry, collection distance, electric field strength, and polymer concentration.
The second part of this work focuses on rheological analysis of thiol-acrylate systems during the crosslinking reaction and understanding the evolution of time dependent material properties such as the storage ($G'$) and viscous ($G''$) moduli during the fabrication process. The polymerization scheme used herein contains an *in situ* catalyst that is integrated into the crosslinked network during the crosslinking reaction, negating the need for external ultraviolet (UV) sources and post processing steps for free radical removal. This unique thiol-acrylate polymerization scheme has been used for the fabrication of microfluidic devices and for osteogenic applications such as bone replacement. Using small amplitude oscillatory techniques, we investigate the effects of changes to catalyst concentration on the time required for gelation and properties of the developing microstructure.

The last portion of this work uses rheological techniques to monitor the photoinitiated crosslinking reaction of alginate chains with calcium cations, systems that can be used for biomedical applications and photo-templating. The UV initiated reaction is monitored *in situ* using a UV light accessory, allowing for real-time collection of the changes in $G'$ and $G''$. We evaluate the effects of solution properties (i.e., alginate and calcium concentration) and processing parameters (i.e., UV light intensity, exposure time) on the gelation dynamics, gel point, and final hydrogel properties. We also investigate a possible mechanism for dark curing, which is defined as continuing gelation in the absence of UV light.
Functional Nanofibers and Gels: A Study of Novel Needle-less Electrospinning Technologies and Gelation Kinetics of Thiol-Acrylates and Hydrogels

by
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DEDICATION

This dissertation is dedicated to my nana, Van Duong, for without your strength and courage to immigrate our family to the United States, I would not have been given the opportunities that I will be forever grateful for. And to my family and future husband, David Latshaw II, without your love, support, and encouragement, I would have never made it this far.
BIOGRAPHY

Alina Higham was born and raised in California, by her parents John and Tran Higham. After graduating from Valley Christian High School in 2004, she moved across the country to major in Chemical Engineering at Florida Institute of Technology. After earning her Bachelor of Science degree in the spring of 2008, she began her graduate studies in the Department of Chemical and Biomolecular Engineering at North Carolina State University in the fall, advised by Dr. Saad Khan. Following completion of her graduate studies in October 2013, Alina will join TA Instruments in New Castle, DE.
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CHAPTER 1

Motivation, Goals, and Background
1.1 Motivation and Goals

Advanced functional materials are an integral part in the development and advancement of technology and our scientific world, typically comprised of polymer systems. The fabrication or manufacturing of functional materials is divided into three main stages: the raw materials, the manufacturing process, and the final product, Figure 1.1. This dissertation investigates two functional materials: electrospun nanofibers and gels. We further investigate the structure-product-property relationships and their effects on product and process development.

It is important to understand the consequences and influences that changes in the manufacturing process have on the system microstructure and final product properties, as knowledge in this area helps in the development of novel products and processes. In this dissertation, we focus on changes in microstructure and characteristics of dynamic systems during the manufacturing process and the relationship these changes have on product properties and how they affect product development, specifically for the polymerization of thiol-acrylates and gelation of hydrogels. Further, we focus on process development for electrospun nanofibers and relating modulations in the manufacturing process to the final product properties.

The overarching goal for each chapter in this dissertation focuses on identifying the effects of modulations in solution properties and/or process conditions on final product properties of the functional material under investigation and the fundamental mechanisms behind the changes. More detailed goals are provided in subsequent sections as they pertain to each individual chapter.
1.2 Background

This section provides a brief discussion pertaining to the general background aspects and includes more detailed goals specific to each topic covered in this dissertation. Each subsequent chapter may be read independently as they are self-contained.

1.2.1 Electrospinning of Nanofibers

Electrospinning is a simple and facile technique to fabricate nanofibers which has drawn interest in recent years. Nanofibers possess diameters less than 500 nanometers (nm), much smaller than a human hair, Figure 1.2. The high surface area to volume ratio and high degree of porosity (comprised of small pore sizes), characteristic to nanofiber mats, render them extremely beneficial in a host of applications such as catalysis, tissue scaffolding, protective clothing, drug delivery, and gas sensors, among many others.\textsuperscript{1-11} Additional processing steps, such as the addition of nanoparticles\textsuperscript{12,13} and biological moieties\textsuperscript{14-16} to the fiber surface, provides extra functionality to the fibrous mat, expanding the field of potential applications to areas such as selective filtration, energy storage, fluorescence, and many others.\textsuperscript{17-19}

The electrospinning process\textsuperscript{20-23} typically involves the application of an electric field to a polymer droplet protruding from a spinneret tip (most often a needle tip), Figure 1.3. The polymer droplet is distorted into a conical shape, known as the Taylor cone,\textsuperscript{24} as induced charges collect on the surface. Upon increase in applied voltage, a polymer jet ejects from the apex of the cone, flying towards the grounded collector plate where whipping from a bending instability and solvent evaporation reduce the jet diameter into the nanometer scale.\textsuperscript{25,26} The
polymer fiber is then randomly deposited onto the collection plate, producing a nonwoven nanofiber mat. Although this technique is simple to use, low polymer concentration and low flow rates, typically below 1 mL/hr, limit fiber production rates. Additionally, needle clogging, which occurs when dried polymer remains on the spinneret tip when solvent evaporates before the solution can be electrospun, prevents fiber fabrication during the electrospinning process. Many studies developing novel electrospinning methods to improve fiber production rates have been published, such as the use of multiple spinnerets to form multiple jets,\textsuperscript{27} electrospinning from an extruder to increase flow capacities,\textsuperscript{28} and some needleless techniques.\textsuperscript{27,29,30} However, many of these techniques result in broad fiber distributions or require the use of multiple needle tips, which require extensive calculations for adequate spatial distribution of the spinneret tips to prevent adjacent fibers from interacting and impeding production.\textsuperscript{31} We focus on an alternative approach to the fabrication of nanofibers by electrospinning from a foamed column, which is discussed in-depth in Chapter 2.

Another factor preventing electrospun nanofibers from becoming widely commercialized is that the processing parameters for fabricating uniform electrospun nanofibers varies greatly depending on the electrospinning system (e.g. polymer/solvent system). Each electrospinning system possesses a unique “electrospinning window” which is heavily dependent on solution properties\textsuperscript{32-35} such as polymer concentration, which affects polymer entanglement, solution conductivity, viscosity, and surface tension, as well as processing parameters such as collection distance, applied voltage, and flow rate.\textsuperscript{36-38} Although the parameters necessary for producing uniform fibers from a wide array of
polymer systems are available, many of these parameters only apply to the syringe electrospinning setup and must be reevaluated when electrospinning with novel and scaled-up devices. Although reinvestigating the parameters necessary to access the “electrospinning window” for electrospinning solutions in novel systems is laborious, it is still necessary when attempting to understand the relationships between the processing parameters and properties of the final product. Specifically, we focus on the following issues:

- Can a needle-less electrospinning process be developed that is an improvement from traditional electrospinning throughputs?

If so,

- What are the parameters with the greatest effect on nanofiber quality and how do specific modulations in said parameters affect final product properties?
- Are the mechanisms for change and resultant effects similar to those seen for traditional electrospinning?

1.2.2 Gels

Gels are another polymer based functional material that is relatively easy to synthesize. These insoluble materials are comprised of polymer chains either chemically (chemical gel) or ionically bonded (physical gel) to adjacent polymer chains in the system, forming a three dimensional microstructure. The biggest difference between a chemical and physical gel is the ability to reverse the crosslinking reaction and dissociate the network, converting the gel back into a solution. These deviations in fabrication method and crosslinking mechanism translate into a variation in final gel properties (gel strength,
stiffness, porosity, degradation rate, etc.) allowing gels to be used in a plethora of applications ranging from tissue scaffolding\textsuperscript{40,41} to microfluidic devices\textsuperscript{42-44} to drug delivery,\textsuperscript{45,46} and so forth. In addition, the gel properties can be tailored by manipulating concentrations and crosslinking conditions, as the final gel properties are directly related to the internal microstructure of the gel.\textsuperscript{47-49} As such, knowledge regarding the gelation kinetics, mechanism, and state of the microstructure during all stages of gel formation (before, during, and after gelation) is quite beneficial.

1.2.3 Rheological Methods for Studying Gelation

One technique commonly used to characterize a crosslinking reaction is dynamic rheology, since changes in a sample’s microstructure directly affect the rheological properties. Specifically, small amplitude oscillatory shear (SAOS) measurements are performed as these experiments are able to determine rheological properties during the reaction without disturbing or destroying the formation of the fragile microstructure.\textsuperscript{50} Using this technique coupled with a strain or stress controlled rheometer, the changing rheological properties can be monitored in situ after the reaction is initiated via self-initiation from the addition of reagents or external stimuli, such as heat or ultra-violet (UV) light.

Complex viscoelastic crosslinking systems possess both solid-like and liquid-like characteristics which are represented by the storage (G’) and loss (G”) moduli, respectively. Small amplitude dynamic oscillatory experiments deform the sample sinusoidally, creating a sinusoidal response which is measured by the rheometer. The sample response is often in the same frequency, but shifted by a phase angle, $\delta$, which can be decomposed into two waves of
the same frequency, one that is in phase and one that is out of phase. The solid-like portion of the sample stores the energy and responds in phase, while the liquid-like portion will dissipate the energy and respond out of phase. This relationship is shown mathematically as:

$$\tau(t) = \gamma_0 \left[ G'(\omega) \sin \omega t + G''(\omega) \cos \omega t \right]$$

where $\omega$ represents the frequency of oscillation, $\gamma_0$ is the strain amplitude, $t$ is time, and $\tau$ is the sample stress response. The magnitudes and behavior as a function of frequency of $G'$ and $G''$ are used to analyze the microstructure of the sample. In addition, the ratio of the two, known as $\tan \delta$ is also of interest for pinpointing the gel point using the Winter-Chambon method, as the two are related mathematically, as shown below.

$$\tan \delta = \frac{G''}{G'}$$

Prior to gelation or in the early stages, $G'' > G'$ as the polymer chains are short in length and able to dissipate the energy from the applied stress during the length of the measurement. The fluid will also contain limited connectivity amongst adjacent chains, if any at all. As the crosslinking reaction propagates, $G'$ will increase in magnitude as the microstructure continues to grow, causing the value of $\tan \delta$ to decrease. Eventually, $G'' \approx G'$, typically around the gel point, which is defined as the time at which the molecular weight increases to infinity or the microstructure (critical gel) first reaches from plate to plate in the rheometer. This point in time is important for manufacturing purposes as samples are rarely pliable at times after the gel point, posing a problem for any remaining processing steps since the viscosity dramatically increases as well. The gel point is normally pinpointed using the
Winter-Chambon which states that $G’$ and $G”$ depend on frequency in the same manner, which is graphically portrayed as the intersection of tan $\delta$ over time shown for varying frequencies.$^{54}$ Beyond the gel point, the microstructure will continue to develop, forming adjacent crosslinks, causing the magnitude of $G’$ to surpass that of $G”$, eventually becoming frequency independent and plateau at a value corresponding to the gel’s maximum modulus. Information gathered from rheological experiments in this dissertation include but may not be limited to, detection of the gel point, the magnitude of the plateau modulus, and the time required for the transition from a solution to gel.

1.2.4 Thiol-Acrylate Polymerization

Fabrication of functional materials comprised of thiol-acrylate systems, typically synthesized via thiol-ene chemistry (the addition of a thiol group over a carbon-carbon double bond), has experienced a renewed interest. The polymerization reaction is a solvent-free, rapid process that can occur at room temperature and ambient pressure, producing materials with high conversion percentages$^{55}$ and uniform crosslink densities.$^{56,57}$ These traits are beneficial in various applications such as functionalization of nanoparticles,$^{58,59}$ surface modification,$^{60}$ and fabrication of biomaterials and microfluidic devices.$^{42}$

Unfortunately, most thiol-acrylate polymerization schemes currently in use are photoinitiated.$^{61-63}$ Energy from ultra-violet (UV) light, which is emitted from an external light source, creates radicals from a photoinitiator mixed with chemical compounds containing thiol and acrylate functional groups. The radical from the energized photoinitiator attacks the reactive thiol group by abstracting a hydrogen atom, creating another radical
which reacts across the carbon-carbon double bond located on the acrylate functional group. The polymerization continues to propagate to very high conversions, creating a three-dimensional crosslinked network. Unfortunately, the free radicals formed from the dissociation of the photoinitiator may remain in the final product and harmfully leach into the body if the system is used in any biomedical applications. Alternatively, thiol-acrylate polymerizations have been shown to initiate in the presence of a primary, secondary, or tertiary amine catalyst for hydrogen abstraction, in lieu of a photoinitiator.\textsuperscript{60,64,65}

The system explored in this dissertation, first reported by Bounds et al., exploits this benefit by creating a tertiary amine from reacting a secondary amine with the carbon-carbon double bond on a tri-functional acrylate, which is referred to as an in situ catalyst/comonomer.\textsuperscript{42} The tertiary amine is then able to deprotonate the thiol group, initiating the reaction which propagates via Michael addition and subsequent chain transfer, similar to anionic step growth. The reaction scheme is shown in Figure 1.4. Additionally, the catalyst/comonomer contains available acrylate functional groups, allowing the molecule to be integrated into the crosslinking network. Polymerization via a step growth mechanism and the integration of the catalyst/comonomer alleviates concerns of free radicals leaching from the final material, making this system specifically beneficial in biomedical applications, such as microfluidic devices,\textsuperscript{42,66} osteogenic foams for bone replacement,\textsuperscript{67} and next generation tissue scaffolds.\textsuperscript{68} This system maintains all of the benefits of photopolymerized thiol-acrylate systems without the need of a photoinitiator or ultra-violet (UV) light source for initiation or post processing steps for the removal of free radicals.
As this polymerization scheme is beneficial in a myriad of applications, it is important to identify the processing window, specifically the gel point, as the sample quickly transitions from a viscous liquid to a crosslinked thermoset polymer. It has also been shown that the gel point may be tuned by modulating the concentrations of the respective components (e.g. thiol concentration, acrylate concentration). Additionally, developing a fundamental understanding of the gelation kinetics and any correlation between composition and gel time would be advantageous. In this study, we specifically focus on:

- Do modulations in the in situ catalyst concentration affect the gelation kinetics of the polymerization, and if so, what are the underlying mechanisms responsible for these changes?
- Are we able to glean any information concerning the three-dimensional microstructure of the critical gel (sample at the gel point)?
- How do the final gel properties change as a function of in situ catalyst concentration and do they relate to the microstructure of the critical gel?

1.2.5 Alginate Hydrogels

Alginate is a polysaccharide derived from species of brown algae, capable of crosslinking chemically or ionically to form hydrogels, for use in applications such as tissue engineering\textsuperscript{40,41} and drug delivery,\textsuperscript{45,46,49} among many others. Based on its chemical structure, Figure 1.5, alginate chains are able to crosslink via many different routes. Chemical crosslinking can occur from chemical reactions between hydroxyl groups or carboxylic acid groups using glutaraldehyde and adipic acid, respectively.\textsuperscript{69,70} Photoinitiated chemical
crosslinking can also occur for chemically modified methacrylated alginate chains, in the presence of a photoinitiator.\textsuperscript{71} Although chemical crosslinking has the ability to produce strong hydrogels, the crosslinking methods often require toxic solvents.

In lieu of chemically modified alginate, some research has focused on exploiting alginate's ability to physically crosslink with divalent cations (e.g. Ca\textsuperscript{2+}, Mg\textsuperscript{2+}). Alginate is comprised of β-D-mannuronate (M) and α-L-guluronate (G) residues which may be arranged in alternate (MG), repeat M residues (M-blocks), or repeat G residues (G-blocks), the sequence of which is dependent on the alginate source. Repeat G residues form an “egg-box” shape able to accommodate divalent cations via a chelating effect, creating what is known as an “egg box junction,” Figure 1.\textsuperscript{5,72,73} Linkages can form in the presence of divalent cations when G-blocks from adjacent alginate chains bond with the same cation. This provides a means of fabricating alginate hydrogels in the absence of excess chemicals. Specifically, much research is focusing on photoinitiated crosslinking as it provides a means for in situ gelation or photo patterning, as only areas exposed to UV light will crosslink, allowing for selective hydrogel fabrication.

Only a few studies have focused on photoinitiated alginate crosslinking: the chemical crosslinking of methacrylated alginate\textsuperscript{71} and release of calcium cations from expensive moieties such as modified lyposomes\textsuperscript{74} and caged calcium.\textsuperscript{75,76} However, to this day, there lacks a rheological study devoted to understanding the mechanisms and kinetics of photoinitiated alginate hydrogels undergoing physical gelation with calcium cations. A study investigating the above relationships would be useful in the determination of specific processing parameters capable of producing alginate hydrogels with the desired properties.
required for a specific application. Using TA Instrument’s UV curing light guide accessory, Figure 1.6, we can characterize the gelation mechanism in situ. We focus specifically on:

- What is the relationship between UV light parameters (UV intensity, exposure duration) on the gelation kinetics and final gel parameters?
- How do modulations in chemical composition affect the crosslinking mechanisms and overall gel properties?
- What role does the light exposure play the crosslinking mechanism and is there a way to tailor the final gel characteristics by modulating processing parameters?

1.3 Organization of Dissertation

Chapter 2 focuses on the development of foam electrospinning and identifying the roles of key design, process, and solution parameters in the fabrication of uniform nanofibers and their properties. In chapter 3, we focus on the rheological study of a polymerizing thiol-acrylate system and the role of an in situ catalyst. A rheological study focusing on gelation kinetics and the role of processing parameters relating to UV light exposure for a photocrosslinkable alginate hydrogel undergoing physical gelation can be found in Chapter 4. Chapter 5 summarizes the key findings of this study and proposes areas for future work.
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**Figure 1.1.** Schematic depicting the general steps required for the fabrication of functional materials.
Figure 1.2. SEM micrograph of nanofibers from an electrospun solution of polyvinyl alcohol (PVA) in water compared to a human hair.
Figure 1.3. Schematic of the traditional syringe electrospinning technique for the fabrication of electrospun nanofibers.
Figure 1.4. Polymerization scheme for the reaction of tri-acrylate and tri-thiol monomers containing an *in situ* amine catalyst, adapted from Bounds et al.\textsuperscript{42}
Figure 1.5. Conformations of β-D-mannuronate (M) and α-L-guluronate (G) residues found in alginate and conformation of possible block sequences and schematic representation of the two-step UV initiated alginate crosslinking reaction with PAG and CaCO₃. Adapted from Javvaji et al.⁷⁷
Figure 1.6. Schematic of TA Instrument’s UV curing light guide accessory for the real-time determination of rheological properties for UV curing samples, compliments of TA Instruments.
CHAPTER 2

Foam Electrospinning: A Multiple Jet, Needle-less Process for Nanofiber Production

Foam Electrospinning: A Multiple Jet, Needle-less Process for Nanofiber Production


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Abstract

We present a multiple jet, needle-less process to fabricate electrospun nanofibers from foamed columns, produced by injecting compressed gas through a porous surface into polymer solutions, capable of circumventing syringe electrospinning shortcomings such as needle clogging and restrictions in production rate. Using polyvinyl alcohol and polyethylene oxide as model electrospinning systems, we identify key design, processing, and solution parameters for producing uniform fibers. Increasing the electrode surface area produces thicker mats, suggesting that distributing charges through the bulk foam facilitates electrospinning. Similar trends between foam and syringe electrospinning were seen for collection distance, electric field strength, and polymer concentration. Specifically, the empirical correlation between polymer entanglement and fiber formation appears to hold for foam electrospinning, thus providing a guideline for determining electrospinnability of polymer systems with this process. Foam electrospinning with solutions of 5 wt.% PEO and 0.1 wt.% Triton X-100®, a non-ionic surfactant, yield production rates as high as 1.5 mL/min, a 300 fold increase compared to typical syringe electrospinning throughputs. The
use of a non-ionic surfactant can improve throughput without affecting resulting fiber properties, such as fiber diameter and crystallinity.
2.1 Introduction

Nanofibers, fibers with average diameters ranging from less than 500 nm to several microns, are currently used in several applications such as catalysis, tissue scaffolding, protective clothing, drug delivery, and gas sensors, etc., due to their high aspect ratios.\textsuperscript{1-7} These nanofibers are traditionally fabricated via a simple technique called electrospinning,\textsuperscript{8-11} where an electric field is applied to a droplet, deforming it into a conical shape, known as a Taylor cone.\textsuperscript{12} Once the induced charges overcome the solution surface tension, a jet ejects from the apex of the cone towards a grounded collection plate where whipping and solvent evaporation reduce the jet diameter and the resulting fiber is deposited as a nonwoven mat.\textsuperscript{13,14}

Although simple, syringe-based approaches involve inherent challenges, such as toxic or corrosive solvents, and needle clogging, which occurs when dried polymer remains on the spinneret tip when solvent evaporates before the solution can be electrospun, preventing fiber production. Additionally, low polymer concentration solutions and low flow rates, typically below 1 mL/hr are used, limiting fiber production rates. Multiple needles cannot be placed at high spatial density to improve the rate of nanofiber production due to strong charge repulsion between the jets.\textsuperscript{15-20} Developing techniques capable of improving process throughput and preventing needle clogging has been an area of recent interest.

Recently, electrospinning polymer nanofibers from bubbles has been demonstrated using a single-nozzle apparatus,\textsuperscript{21-24} and empirical relationships were reported correlating fibers to select process parameters, such as electric field strength\textsuperscript{25} and solution concentration.\textsuperscript{26-28} However, these studies were limited to single bubble or submerged nozzle
setups operating at gas pressures less than 0.5 psi.\textsuperscript{25} Additionally, electrospinning from a single bubble in a polymer bath leads to the possibility of fibers initiating from locations other than the bubble surface, such as the container edge and solution surface. A comparison of electrospun fibers from novel approaches to syringe electrospun fibers has yet to be established.

In order to improve nanofiber throughput, we present a needle-less strategy using elevated pressure to simultaneously produce multiple jets from charged foams. We explore the effect of process parameters and foam properties on resulting fiber properties. We compare this foam based technique to traditional syringe electrospinning, specifically examining the relationship between fiber formation and polymer chain entanglement in order to help guide choice of polymer/solvent systems.

\section*{2.2 Materials and Methods}

\subsection*{2.2.1 Materials}

Polyvinyl alcohol (PVA) (average molecular weight 205,000 g/mol, 88\% hydrolyzed), non-ionic Triton X-100\textsuperscript{®} surfactant, and Rhodamine B dye were used as received from Sigma Aldrich. Polyethylene oxide (PEO) was used as received from Polysciences (average molecular weight 600,000 g/mol).

\subsection*{2.2.2 Solution Preparation and Characterization}

PVA was dissolved in de-ionized water between 1 and 9 wt.\% and stirred at 60°C until homogenous, while PEO was dissolved in de-ionized water between 1 and 7 wt.\% and
stirred at room temperature overnight until homogenous. In some cases, Triton X-100® was dissolved along with PEO in de-ionized water. Zero-shear viscosity was measured at 25°C using a 40 mm diameter, 2° cone and plate geometry (TA Instruments AR-G2 rheometer).

2.2.3 Electrospinning

Electrospun fibers were created by injecting compressed carbon dioxide (Airgas National Welders) at a constant flow rate of 310 cubic centimeters per minute (ccm) and pressure of 20 pounds per square inch (psi) into polymer solutions through a fritted funnel (Fisher Scientific, pore size 4 – 5.5 μm for fine and 40 – 60 μm for coarse) coupled with a power supply (Matsusada High Precision, model AU-60P*0.5). Foam electrospinning parameters varied between 15 and 50 kV for voltage and 6 to 30 cm for collection distance (measured as the distance between the top of the funnel and grounded plate). For comparison, a syringe electrospinning method using a syringe fitted with a stainless steel needle (0.508 mm inner diameter). A flow rate of 0.5 mL/hr, collection distance of 20 cm, and applied voltage of 10 – 22 kV were used. The Nanospider™ manufactured by Elmarco was used containing a customized 10 cm droplet electrode as additional comparison (for photographs, see supplemental information, Figure S2.1).

The production rate from the foam electrospinning process was measured by subtracting the weight of remaining solution after electrospinning for a set amount of time from a known volume of solution. Calculation assumes all consumed solution forms fibers.
2.2.4 Fiber Characterization

Resulting fiber mats were coated with a ~10 nm layer of gold and imaged using a scanning electron microscope (SEM) (FEI XL30 field emission SEM). Fiber size distributions and average diameters were obtained from the measurements of 100 fibers using ImageJ analysis software. Electrospun fiber crystallinity was measured by heating samples from 25°C to 95°C at a rate of 10°C/min in a nitrogen environment using differential scanning calorimetry (DSC) (TA Instruments Q2000 calorimeter) and x-ray diffraction (XRD) patterns (Philips X’Pert PRO MRD HR XRD System), acquired at room temperature with Cu Kα radiation.

2.3 Results and Discussion

2.3.1 Foam Electrospinning

We produce polymeric foams by injecting compressed carbon dioxide through a porous plate into a polymer solution. High voltage charge is applied to the system by immersing a copper electrode coupled to a high voltage power supply into the polymer solution, Figure 1A. Bubbles form and rise to the surface, producing a column of foam. When an electric field is applied, several perturbations form on the foam surface, resulting in multiple polymer jets ejecting towards the collection plate directly above the foam, Figure 1B.

During the process, some bubbles deform into upwards-directed, hollow conical shapes, Figure 1C, analogous to the Taylor cone in syringe electrospinning. This phenomenon has been previously reported by Varabhas, who found the angle of the Taylor
cone-like perturbation on the bubble surface to be equal to that reported for syringe electrospinning. Additionally, we have observed the formation of multiple perturbations on a single bubble, which has not been previously reported in single bubble studies. Further, we occasionally observe undulating movements along the surface of some bubbles as the electrospinning jets move across the bubble surface. This movement may suggest the jet self-stabilizes itself during the dynamic foam electrospinning process. The continual growth of foam from the constant influx of compressed gas alters the induced charges of the system. Movement of the electrospinning jet along the bubble surface helps to perpetuate the electrospinning process. Additionally, the influx of gas may cause some bubbles to grow beyond their maximum size and burst, presenting a discontinuity which may lead to fibers of finite length.

As the electrospun jets initiate from the surface of a foam compared to a point source in syringe electrospinning, the geometry of the electrode and manner for charging the system must be considered for design of the process. The study includes a solution of 7 wt.% PVA in water, as it is a model electrospinning system, and three electrode geometries: a ringed wire (one-dimensional, 0.25 in² surface area), a wire mesh (two-dimensional, 1.9 in² surface area), and a wire “bird’s nest” (three-dimensional, 5.8 in² surface area), shown in Figure 2. Using the one-dimensional electrode, few jets eject from the foam surface, producing a sparse mat. Two- and three-dimensional electrodes produce thicker mats. We attribute the improved fiber yield to the increase in electrode surface area, which improves the distribution of electrical charges throughout the polymer solution and foam. Since the two- and three-dimensional
electrodes produce similar fibers under comparable process parameters, the two-dimensional electrode was used in subsequent experiments due to simplicity.

2.3.2 Process Parameters

Using 7 wt.% PVA as a model system based on our previous work,\textsuperscript{31} we explored the effect of various apparatus parameters including electric field strength and collection distance. The effects of electric field strength and collection distance on the yield and morphology of nanofibers produced in foam electrospinning were investigated using electric field strengths between 250 kV/m - 420 kV/m and collection distances of 6 - 10 cm. No fibers are produced below 250 kV/m, indicating a threshold electric field strength. Electric field strengths between 250 and 330 kV/m with collection distances of 6 cm and 8 cm yield sparse, non-uniform mats with signs of fiber fusion and other artifacts related to incomplete drying (films with fiber shaped outlines). Further, extensive fiber fusion can be seen directly above the funnel, likely caused by bubbles bursting and spreading solvent onto the surface of the collection plate, Figure 3B. Yet, a fibrous mat, Figure 3A, collects along the outer perimeter of the collection plate, which is located farther from the axis of the foamed column. However, increasing the collection distance to 10 cm provides ample time for solvent evaporation which minimizes solvent splatter and leads to smooth fiber morphology and mat uniformity (for additional micrographs, see supplemental information, Figure S2.2).

Electric field strengths of 420 kV/m (the highest strength tested), yielded electrospun mats with excessive fiber fusion, despite changes in collection distance. At these electric fields we observed entire bubbles being drawn out of the foam towards the collection plate,
resulting in excessive solvent on the nonwoven mat (for additional micrographs, see supplemental information, Figure S2.2). These results are comparable with electric field strengths previously reported for bubble spinning polyvinylpyrrolidone (PVP). However, fiber fusion was not reported when using PVP in a mixture of alcohol and water, likely due to the difference in solvent volatility.\textsuperscript{25} Based on these results, there is an electric field strength window for the fabrication of uniform fibers via foam electrospinning, which is not generally observed in other methods of electrospinning, such as syringe electrospinning.

### 2.3.3 Concentration Effects

In syringe electrospinning, it is generally accepted that polymer entanglement, predicted using solution dynamics, is required for the formation of fibers.\textsuperscript{32-35} Empirically, the onset of beaded fibers occurs at the critical entanglement concentration ($C_e$), 2.5 wt.% for aqueous poly-vinyl alcohol (PVA), indicated rheologically by a change in slope when plotting specific viscosity as a function of polymer concentration. The onset of uniform fibers, the critical concentration ($C_c$), generally occurs at 2-2.5 times $C_e$, i.e. 6 wt.% PVA.\textsuperscript{31} Figure 4. Foam electrospinning concentrations below 2.5 wt.% PVA result in dried polymer droplets due to deposition of debris from bursting bubbles and inadequate polymer entanglement, Figure 4, while 5 wt.% PVA yields beaded fibers. Concentrations above 6 wt.% PVA produce uniform fibers for both electrospinning methods, with fiber size increasing with concentration as expected (for additional micrographs and histograms of other concentrations, see supplemental information, Figure S2.3).\textsuperscript{36,37} Fiber distributions and average fiber diameters of 313 nm and 267 nm for 7 wt.% PVA are comparable for foam
electrospinning when compared to syringe electrospinning, respectively. Data shows the empirical guideline relating polymer entanglement and electrospun fiber morphology applies to foam electrospinning aqueous PVA solutions.

In order to demonstrate versatility, fibers from aqueous polyethylene oxide (PEO) were fabricated via foam electrospinning. Due to an increase in viscosity compared to PVA solutions, the coarse fritted funnel was used for electrospinning PEO solutions as the increased pore size facilitated foaming. Utilizing the previous empirical correlation, the critical entanglement concentration ($C_e$) of aqueous PEO occurs at 1.4 wt.%, while the onset of uniform fibers, $C_c$, occurs at approximately 3.5 wt.% PEO, Figure 5. Concentrations below 2 wt.% result in polymer droplets, while 2 wt.% produces beaded fibers for both electrospinning methods. Increasing the polymer concentration above 5 wt.% PEO results in the fabrication of uniform nanofibers from both electrospinning methods, (for additional micrographs and histograms of higher concentrations, see supplemental information, Figure S2.4). Further analysis for 5 wt.% PEO shows that average fiber diameter and fiber distribution are comparable for both methods, Figure 6. We have shown the polymer concentrations required for fabrication of uniform electrospun fibers for PVA and PEO are comparable in foam and syringe electrospinning, further demonstrating that the relationship between polymer chain entanglement and uniform fiber fabrication also applies to the foam electrospinning process. Therefore, this relationship can serve as a guide to predict the electrospinnability of polymer solutions via foam electrospinning, implying that polymer systems found to electrospin uniform fibers via syringe electrospinning should produce uniform fibers via foam electrospinning.
In order to enhance the stability of the polymer foams to further facilitate electrospinning, Triton X-100® was added in 0.01 wt.% and 0.1 wt.% to 5 wt.% PEO solutions. Addition of the surfactant resulted in polymer foams with increased cell quantity and size, measured qualitatively, while also extending the lifetime of the foams. Fibers fabricated from Triton X-100® infused foams show uniform morphology. A comparison of as spun fibers fabricated from syringe and foam electrospinning, Figure 6, shows the average diameters and fiber distributions remain comparable for both solutions containing up to 0.1 wt.% Triton X-100®. Additionally, the average diameter and distribution of foam electrospun fibers seems unaffected by the addition of surfactant for 5 wt.% PEO. This suggests that the addition of non-ionic surfactant in small amounts to electrospinnable solutions can improve foam creation and duration, without sacrificing desired fiber morphology.

Since multiple jets form simultaneously, foam electrospinning can improve production rates when compared to syringe electrospinning. Typical throughputs for syringe electrospinning from a single needle range on the order of 5 μL/min to 20 μL/min. Experiments with 5 wt.% PEO and 0.1 wt.% Triton X-100® (added for foam stabilization) yield production rates as high as 1.5 mL/min. When foam electrospinning from a 30 mm diameter funnel, experimental results show a 300 fold increase in production rate when compared to typical throughputs via syringe electrospinning. We believe increasing the size of the funnel and available surface area for foam electrospinning could further improve the production rate.

The Nanospider™ by Elmarco is widely used for high throughput production of electrospun nanofibers. For comparison, solutions of 7 and 9 wt.% PVA were electrospun on
the Nanospider™ using a customized droplet electrode which is 10 cm in diameter, at varying voltages. SEM micrographs, Figure 7, show as spun fibers from the Nanospider™ but the defects in the nonwoven mat due to excessive solvent are evident. Figure 7 also shows SEM micrographs of uniform electrospun fibers fabricated from 7 and 9 wt.% PVA solutions via syringe and foam electrospinning from a 30 mm diameter funnel. Although still in development, foam electrospinning provides an alternate approach for high throughput production of uniform electrospun nanofibers.

2.3.4 Electrospun Fiber Crystallinity

An interesting issue is the effect of electrospinning method on the crystallinity within resultant fibers. Liu et al. has reported percent crystallinity of PVP fibers fabricated via bubble electrospinning. However there is no report of the crystallinity of electrospun fibers from a curved surface as in foam electrospinning compared to the crystallinity of electrospun fibers from a droplet as in syringe electrospinning. XRD measurements showing intensity as a function of 2θ for electrospun PEO fibers and as received PEO powder, Figure 8, show peaks at 2θ = 19° and 23°, which correspond to the 120 and 112 crystal planes, respectively. The peak intensity decreases dramatically within electrospun fibers compared to the as received powder, independent of electrospinning method. This trend has been previously shown for various electrospinning systems. In addition, higher order reflections are seen for the as received powder at 2θ = 26° – 28°, which are indicative of well developed crystalline microstructures. XRD measurements for foam electrospun
samples of PEO and varying amounts of Triton X-100® show no significant change, further indicating the addition of surfactant does not change the fiber morphology or structure.

The percent crystallinity was quantified using DSC, endotherms shown in Figure 9, and calculated by normalizing the area under the curve with the heat of fusion for 100% crystalline PEO, reported as 197 J/g. The percent crystallinity of 5 wt.% PEO with and without surfactant for both foam and syringe electrospinning can be found in Table 1. As crystallinity within the electrospun fibers is due solely to the PEO content, percent crystallinity calculations for samples of PEO and surfactant were normalized by the weight proportion of PEO within the fibers. Crystallinity and the melting peak temperature of fibers produced via foam and syringe electrospinning methods is consistently lower than that of the PEO powder, corroborating data shown via XRD. It is believed that rapid solvent evaporation during processing hinders polymer chain interaction and thus crystallization within the polymer fiber.

Interestingly, the percent crystallinity is consistently higher in fibers fabricated from foam electrospinning compared to syringe electrospun fibers, increasing from 70.3% to 78.5% for 5 wt.% PEO, and 67.5% to 75.1% when introducing 0.1 wt.% Triton X-100®, shown in Table 1. Enhanced polymer crystallinity within electrospun fibers has been linked to improvements in mechanical and structural properties, specifically degradation rates and hydrophobicity for tissue engineering applications. An improvement in crystallinity may be due to a combination of solvent evaporation and restricted chain orientation. As the foam electrospinning process is an open system, slow solvent evaporation and solvent drainage within the foam may occur over the duration of the experiment, increasing the
effective concentration on the surface of the foam compared to the bulk concentration. It has
been previously shown that concentration gradients within foams exist as the solvent
gravitates towards points where three or more cells meet for entropic reasons. Another
contributing factor may be due to the restriction of chain orientation within the thin bubble
surface, possibly promoting biaxial orientation of the polymer chains. As the chance for
polymer chain interactions increases, polymer crystal formation and growth is promoted.
These factors will need to be investigated in future papers.

2.4 Conclusions

We demonstrate a multiple jet electrospinning technique wherein nanofibers are
produced from foamed polymer solutions. Distribution of electrical charge throughout the
bulk of the foam is necessary for the formation of uniform fibers. An electric field strength
window exists for the formation of uniform fibers via foam electrospinning. When the
electric field strength is too weak, little to no fibers form, while stronger fields result in a
fiber-infused film. At a given electric field strength within the electrospinning window,
increased collection distances aid in sufficient solvent evaporation, improving mat
uniformity. Concentrations at which beaded and uniform fibers form using foam
electrospinning and the resulting fiber sizes are comparable to those reported in syringe
electrospinning for PVA and PEO for all concentrations presented. This work shows that the
relationship between polymer entanglement and fiber formation in electrospinning holds for
this process. The addition of surfactant in the case of PEO improves production rate while
fiber diameter and distribution remain unaffected. Production rates for foam electrospinning
were improved as much as 300 times compared to syringe electrospinning. Fiber crystallinity was also enhanced via foam electrospinning, most likely due to the combination of gradual solvent evaporation, biaxial polymer chain orientation within the thin film bubble boundary, and increased effective concentration on the foam surface, promoting chain interactions and polymer crystal formation and growth. Foam electrospinning serves as an alternate approach to nanofiber fabrication with improved production rate and fiber crystallinity, without the need for alterations or additional experiments to discover appropriate conditions, as the parameters and trends for uniform fiber fabrication are comparable to syringe electrospinning.

2.5 Acknowledgements

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2.6 References


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Figure 2.1. (A) Schematic of foam electrospinning apparatus. Digital photographs of the foamed column during experiments showing (B) multiple polymer fibers (some shown by arrows) forming when foam electrospinning 5 wt.% PEO and 0.1 wt.% Triton X-100® and (C) bubble deformation occurring during electrospinning at using 7 wt.% PVA and 0.1 wt.% Rhodamine B dye for visualization.
Figure 2.2. Schematics and resulting electrospun fibers for 7 wt.% PVA in water utilizing A) one-dimensional, B) two-dimensional, and C) three-dimensional electrodes.
**Figure 2.3.** Foam electrospinning schematic and SEM micrographs showing the contrast in fiber morphology collected at a location (A) outside of the funnel and (B) directly above the fritted funnel at shortened collection distances.
Figure 2.4. SEM micrographs comparing fibers fabricated from syringe and foam electrospinning using 1, 5, and 7 wt.% PVA in water, with average fiber diameter and distribution for 7 wt.% PVA, and specific viscosity as a function of PVA concentration, adapted. The average fiber diameters and fiber distribution remain comparable for both electrospinning methods.
Figure 2.5. SEM micrographs comparing fibers fabricated from syringe and foam electrospinning using 1, 2, and 5 wt.% PEO in water. Utilizing foam electrospinning, the concentration at which beaded and uniform fibers ($C_{c,f}$) form is comparable to that required for syringe electrospinning, denoted as $C_e$ and $C_{c,s}$, respectively.
Figure 2.6. SEM micrographs and histograms comparing fibers fabricated from syringe and foam electrospinning using 5 wt.% PEO with and without Triton X-100® in water. The fiber morphology, average diameter, and diameter distribution of electrospun fibers from foam electrospinning are comparable to syringe electrospinning.
Figure 2.7. SEM micrographs of 7 wt.% and 9 wt.% PVA fabricated via syringe electrospinning, foam electrospinning and the Nanospider™ by Elmarco. Uniform fibers are fabricated via syringe and foam electrospinning with higher mat quality compared to the Nanospider™ using a droplet electrode.
Figure 2.8. XRD measurements comparing fibers from syringe and foam electrospinning with as received PEO powder. Additional XRD measurements of fibers created via foam electrospinning with varying amounts of Triton X-100®.
Figure 2.9. DSC melting endotherms of electrospun fibers utilizing foam electrospinning and syringe electrospinning from various PEO solutions along with as received PEO powder.
Table 2.1. Percent crystallinity and melt peak temperatures as measured by DSC of various PEO solutions using foam electrospinning and syringe electrospinning.

<table>
<thead>
<tr>
<th>System</th>
<th>Electrospinning Method</th>
<th>Melt peak temperature (°C)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO as received</td>
<td>---</td>
<td>71.1</td>
<td>92.5</td>
</tr>
<tr>
<td>5% PEO</td>
<td>Foam</td>
<td>67.5</td>
<td>78.5</td>
</tr>
<tr>
<td></td>
<td>Syringe</td>
<td>70.1</td>
<td>70.3</td>
</tr>
<tr>
<td>5% PEO + 0.1% Triton X-100®</td>
<td>Foam</td>
<td>67.7</td>
<td>75.1</td>
</tr>
<tr>
<td></td>
<td>Syringe</td>
<td>68.5</td>
<td>72.5</td>
</tr>
</tbody>
</table>
2.7 Supplemental Information

**Figure S2.1.** Photograph of the 10 cm wide customized droplet electrode from the (A) side and (B) top down, showing the concaved indent which houses the solution.
Figure S2.2. SEM micrographs of foam electrospun samples from 7 wt.% PVA at varying collection distances and electric field strengths.
**Figure S2.3.** SEM micrographs of foam electrospun samples from 7, 8, and 9 wt.% PVA, with average fiber diameters and distributions. Average fiber diameters gradually increase as PVA concentration increases, while fiber morphology remains unaffected by electrospinning technique.
Figure S2.4. SEM micrographs of foam electrospun samples from 3, 4, 6, and 7 wt.% PEO, with average fiber diameters and distributions when applicable.
CHAPTER 3

Gelation and Crosslinking in Multi-Functional Thiol and Multi-Functional Acrylate Systems Involving an *In Situ* Comonomer Catalyst

Chapter 3 is essentially a manuscript by Alina K. Higham, Leah A. Garber, David C. Latshaw II, Carol K. Hall, John A. Pojman, and Saad A. Khan submitted to *Macromolecules*.
Gelation and Crosslinking in Multi-Functional Thiol and Multi-Functional Acrylate Systems Involving an In Situ Comonomer Catalyst

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Abstract

Dynamic rheology in combination with Fourier Transform Infrared Spectroscopy (FTIR) is used to examine the gelation kinetics, mechanism and gel point of novel thiol-acrylate systems containing varying concentrations of an in situ catalyst. Gelation, as evidenced from the gel time determined using the Winter-Chambon criterion, is found to occur more quickly with increasing catalyst concentration up until a critical catalyst concentration of 22 mol%, whereupon the gel time lengthens. Such a minimum in gel time may be attributed to changes in the number of available reaction sites and percent conversion required for gelation. Chemical conversions at the gel point measured for representative samples are consistent with theoretical values calculated using Flory-Stockmayer’s statistical approach, confirming our hypothesis. Relaxation exponents of 0.97 and fractal dimensions of 1.3 are calculated for all samples, consistent with coarse-grained discontinuous molecular dynamics (DMD) simulations. The elevated value of $n$ may be due to the low molecular
weight prepolymer. The relaxation exponent and fractal dimensions are invariable over all systems studied, suggesting the crosslinking mechanism remains unaffected by changes in catalyst concentration, allowing the gel time to be tailored by simply modulating the catalyst concentration.
3.1 Introduction

Polymerization via thiol-ene chemistry, the addition of a thiol group over a carbon-carbon double bond, has experienced a renewed interest in recent years. Materials synthesized using this approach are easily processed due to a solvent-free, rapid synthesis that can occur at room temperature and ambient pressure, yielding materials with high conversion\(^1\) and uniform crosslink densities.\(^2,3\) As a result of these benefits, thiol-ene polymerization schemes are being used in various applications such as functionalization of nanoparticles,\(^4-7\) surface modification,\(^8,9\) and fabrication of biomaterials.\(^10\)

Despite the strong interest, most thiol-ene systems currently investigated are produced via photoinitiation\(^11-13\) which requires an external light source and photoinitiator. Additionally, these reactions produce radicals that may remain in the final product and leach into the body when used in biomedical applications. It has been shown that thiol-acrylate systems, created using thiol-ene chemistry by reacting a thiol functional group with an acrylate functional group\(^1,3,14\) can be polymerized using primary, secondary, and tertiary amine catalysts in lieu of a photoinitiator.\(^8,14,15\) The amine catalyst acts as a base, thereby deprotonating the nucleophilic thiol group. Exploiting this benefit, Bounds et al. established a thiol-ene chemistry reaction to polymerize a thiol-acrylate network by introducing a tertiary amine as the effective \textit{in situ} base catalyst/comonomer.\(^16\) This novel system preserves all of the benefits of photopolymerized thiol-acrylate systems without the need of a photoinitiator and ultra-violet (UV) light source.

The \textit{in situ} catalyst/comonomer is fabricated by reacting a secondary amine (diethylamine, DEA) to a tri-functional acrylate (pentaerythritol triacrylate, PETA),
producing a tertiary amine, labeled as the catalyst/comonomer, as shown in Figure 3.1. The catalyst/comonomer reacts with a tri-functional thiol (trimethylolpropane tris(3-mercaptopropionate), TMPTMP) via Michael addition to create a thyl radical which is used to initiate polymerization, shown as initiation in Figure 3.1. The thiolate anion initiator then reacts across the electron deficient double bond of the acrylate functional group, present as a tri-acrylate in this synthesis via another Michael addition, shown as propagation step 1 in Figure 3.1. An electron deficient carbon is created on the backbone, which can react with a tri-functional thiol to create another radical which can continue the reaction, as shown in propagation step 2 in Figure 3.1. The polymerization propagates via sequential chain transfer step growth after each addition, thereby having the attributes of an anionic step growth mechanism. Polymerization via step growth mechanism alleviates concerns of unreacted radicals leaching from the final material, typical of photoinitiated thiol-acrylate systems, which propagate via free radical polymerization. Additionally, post-processing steps are not needed to remove the catalyst since it is incorporated into the thermoset network. This reaction scheme is ideal for use in biomedical applications, such as microfluidic devices, osteogenic foams for bone replacement, and next generation tissue scaffolds. For many of these applications, minimally invasive procedures, such as in situ polymerization, are desirable. However, a fundamental understanding of the crosslinking mechanism and effects of material composition on gelation time are required before new polymerization schemes may be employed, especially since these systems transition from low viscosity liquids to high molecular weight networks over the course of time. In this study, we examine the gelation kinetics, mechanism, and microstructure of a thiol-ene system containing an in situ
catalyst/comonomer as a function of material composition. The ability to alter or tune the gel point for these materials together with the incorporation of the catalyst/comonomer into the polymer network makes this system ideal for in situ polymerization applications. However, these systems are easily processed only at times before the gel point. It is therefore important to quantify and understand the role of material composition on the gel point so that a known processing window is readily available.

Small amplitude dynamic oscillatory rheological techniques provide a powerful approach for monitoring the gelation of polymerizing systems. Information such as the evolution of material properties such as the elastic ($G'$) and dynamic ($G''$) moduli, as well as pinpointing the gel point can be gathered without disturbing the fragile microstructure. The gel point (GP) is defined as the moment at which the weight-average molecular weight diverges to infinity or an initial microstructure cluster first reaches from plate to plate. At this moment in time, the system has reached a critical extent of reaction ($p = p_c$), where $p$ represents the fraction of functional groups lost. As the reaction continues to progress ($p > p_c$) the overall sample stiffness will increase as remaining molecules are integrated into the polymerizing network, resulting in a sample not soluble in even good solvents. Winter and Chambon have identified two rheological criteria for determining the gel point. Based on scaling theory, it has been shown that at the GP, $G'$ and $G''$ depend on frequency in the same manner. As a result, the ratio of $G''$ to $G'$, defined as $\tan \delta$, is independent of frequency at the gel point. This independence is graphically depicted as the point of intersection when monitoring $\tan \delta$ over time for varying frequencies. This relationship is mathematically shown in the following equation:
\[
\tan \delta = \tan \frac{G'}{G''} = \tan \left( \frac{n\pi}{2} \right)
\] 

where \( n \) is defined as the relaxation exponent, with a value in the range of \( 0 < n < 1 \), and also represents the slope of the dynamic moduli at the gel point in a frequency spectrum. Although the Winter-Chambon method for gel point determination is well documented, it may require multiple experiments. Combining small amplitude oscillatory dynamic rheology with Fourier transform mechanical spectroscopy (FTMS), a multiwave approach, provides a means to monitor the evolution of \( G' \) and \( G'' \) over time for several frequencies within one experiment.\textsuperscript{24,25}

In this study, we use dynamic rheology coupled with FTMS and the Winter-Chambon gel point criteria to characterize the microstructure growth of novel tri-thiol tri-acrylate systems utilizing an \textit{in situ} catalyst/comonomer. We evaluate the gel point and evolution of the dynamic moduli as functions of time and diethylamine concentration relative to acrylate functional groups. In addition, we combine rheological techniques with Fourier transform infrared spectroscopy (FTIR) to understand the relationship between percent conversion and gel strength. The properties of the microstructure (i.e., fractal dimension) at the gel point are analyzed using rheological techniques and correlated with computer modeling calculations.
3.2 Materials and Methods

3.2.1 Materials

All materials were used as received. Pentaerythritol triacrylate (PETA) was obtained from Alfa Aesar. Trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) and diethylamine (DEA) were purchased from Sigma Aldrich.

3.2.2 Sample Preparation

The catalyst/comonomer solution was prepared by adding appropriate amounts of DEA to PETA in a glass vial containing a magnetic stir bar. DEA concentrations were calculated based on the molar ratio of amines with respect to acrylate functional groups. Once added, the vial was then capped, inverted several times, and stirred for a minimum of three hours. When needed for rheology experiments, appropriate amounts of catalyst/comonomer were added into a glass vial with a magnetic stir bar. TMPTMP was then added to the solution in a stoichiometric 1:1 molar ratio of thiol to acrylate groups, based on the remaining amount of functional acrylate groups after the catalyst/comonomer reaction. The total volume of sample was maintained at 2 mL. The samples were then mixed gently for 2 minutes before loading the sample onto the rheometer.

3.2.3 Rheological Measurements

All rheology experiments were conducted using a TA Instruments (New Castle, DE) G2 stress-controlled rheometer and a 40 mm, 2° cone and plate geometry. The absence of slip was verified by running experiments with various geometries and gap heights.26
Measurements were obtained at 25°C which was controlled via water bath and temperature controlled Peltier plate. Solution gelling behavior was monitored using small amplitude dynamic oscillatory time sweeps, where time zero represents the addition of TMPTMP. Multiwave experiments were performed with a fundamental frequency of 1 rad s⁻¹ with harmonics of 5, 10, and 20. The stress applied to the sample was kept constant at 1 Pa, which was within the linear viscoelastic regime (LVR).

### 3.2.4 FTIR Spectroscopy

Thiol and acrylate conversions over time were calculated from changes in Fourier transform infrared spectroscopy (FTIR) (Bruker Tensor 27 FTIR Spectrometer) spectra. FTIR samples containing varying amine concentrations were prepared via the addition of TMPTMP initiator into the catalyst/comonomer solutions. The samples were mixed and aliquots were deposited between two potassium bromide salt crystals. FTIR scans were run every two minutes for a 24 hour period.

### 3.3 Results and Discussion

#### 3.3.1 Evolution of Thiol-Acrylate Polymerization

We first examine the role of the tri-functional thiol, trimethylolpropane tris(3-mercaptoproprionate), henceforth referred to as TMPTMP, in the crosslinking process. Figure 3.2a shows the frequency spectra of the elastic (G’) and viscous (G”) moduli at varying times before and after the addition of TMPTMP. Before the addition, samples contain only pentaerythritol triacrylate (PETA) and the in situ catalyst, which is formed from
the addition of diethyleamine (DEA) to PETA. Rheological experiments of these samples show typical solution behavior since the magnitude of $G''$ is greater than $G'$ and both are heavily frequency dependent, scaling as follows, $G' \sim \omega^2$ and $G'' \sim \omega^1$. Measurements of the solution without the tri-thiol at longer times (data not shown) revealed a lack of change in the dynamic moduli, indicating an absence of microstructure change within the sample.

When TMPTMP is introduced into the sample, the dynamic moduli change as a function of time, Figure 3.2. At 20 minutes after the introduction of TMPTMP into a sample of PETA with 34.2 mol% DEA, data for $G'$ has not changed when compared to the same sample without TMPTMP, indicating that at this point a microstructure large enough for detection has not yet formed and the applied stresses within the sample are able to relax to zero. As time progresses, an internal microstructure forms, indicated by the increase in $G'$, as depicted in Figure 3.2b. At 72 minutes after the introduction of TMPTMP, the dynamic moduli have increased by two orders of magnitude and are both frequency dependent. The data for $G'$ is less scattered, indicating the presence of a microstructure within the system large enough for detection. At a time of 150 minutes after adding the tri-thiol, the magnitude of $G'$ is greater than the magnitude of $G''$ and independent of frequency, typical of fully crosslinked systems. Throughout the duration of the polymerization, $G'$ has increased almost seven orders of magnitude, indicative of a highly crosslinked sample.

The previous data offer snapshots of the frequency dependence of the dynamic moduli at three different times without providing detailed information of their evolution. We monitored this sol to gel transition by applying a small stress at constant oscillatory frequency and measuring the change in the dynamic moduli over time. Figure 3.3 shows the
evolution of $G'$ and $G''$ for a representative sample, PETA with 34.2 mol% DEA, when applying a stress of 1 Pa at frequencies of 1 rad s$^{-1}$ and 10 rad s$^{-1}$. In the early stages of polymerization, $G''$ is much larger than $G'$, indicative of a sample in a sol state. At such low viscosities, the elastic character is difficult to detect, indicated by the noisy data for $G'$. However, around 60 minutes, $G'$ begins to significantly increase as the polymerized network begins to form. The period of time before the large increase in rate of change of $G'$ is known as the induction period. During this time, although the system is reacting, the small molecules are unable to form a network large enough to respond to the applied stress, as the system is still able to relax within the time of probing. It should be noted during the induction period, $G'$ slowly increases, indicating the growth of an elastic network. The length of the induction period was shown to correlate with the composition of DEA, as will be shown in later sections. After the induction period, $G'$ significantly increases as the smaller chains begin to connect and form a microstructure network. Near the point that the dynamic moduli are equal in magnitude, which is also near the gel point, a network of crosslinks forms between the top geometry and bottom plate. After this point, $G'$ dominates throughout the duration of the experiment as crosslinks continue to form between chains and the solution continues to polymerize. However, the rate of increase for $G'$ slows shortly after the cross over point due to a decrease in the number of available reactive sites as the reaction nears completion. Over the course of gelation, $G'$ is seen to increase by 7-8 orders of magnitude, revealing the complex nature of this material.
3.3.2 Gel Point Determination

The Winter-Chambon criteria can identify the time required for formation of the critical gel, the system at the gel point. A multiwave approach that generated time sweeps at frequencies of 1, 5, 10, and 20 rad s\(^{-1}\) and stress of 1 Pa in a single experiment were used for this purpose. Data within the window of interest from this technique matches within 5% with data from individual time sweeps at frequencies of 1 rad s\(^{-1}\) and 10 rad s\(^{-1}\) in Figure 3.3, thereby validating the use of this approach for this system.

Figure 3.4a shows tan δ values as a function of time for PETA with 34.2 mol% DEA obtained using the multiwave technique, for varying frequencies, 1, 5, 10, and 20 rad s\(^{-1}\). In this graph, according to the Winter-Chambon criterion, the point of intersection of tan δ represents the moment at which tan δ is independent of frequency corresponding to the gel point. For our sample we find the gel time to be approximately 75 minutes, corresponding to a tan δ value of about 20 and a relaxation exponent, n, of 0.97 as calculated using Equation 3.1.

In addition to the convergence of the loss tangent at the gel point, the dynamic moduli also show the same frequency dependence, i.e., both G’ and G” scales as ω\(^n\). This relationship is demonstrated by identical slopes for the moduli in a frequency sweep taken at a time equal to the gel point. As shown in Figure 3.4b, a frequency sweep at the gel point also shows the slope of the dynamic moduli to be equal to the calculated relaxation exponent. For systems with n > 0.5, the gel point has been shown to occur before the G’-G” crossover point in a time sweep, which is seen in this system.
Bonino et al. identified an alternative empirical method to characterize the onset of gelation by monitoring the sample strain during crosslinking for a photocrosslinkable alginate system. When the sample approaches the gel point, the strain rapidly decreases as a result of the growing modulus. The gel point is then estimated by a minimum in the derivative of log strain with respect to time. By slightly altering the aforementioned method, we are able to identify the gel point of the thiol-acrylate system. Figure 3.5 shows the change in sample strain over time of PETA with 34.2 mol% DEA for frequencies of 1, 5, 10, and 20 rad s$^{-1}$. At the onset of gelation, the rate of change of sample strain decreases rapidly. This region of change provides a window for determining the gel point of the system. Since polymerization begins once the tri-thiol is introduced the sample strain decreases over time. However, once the critical gel is formed, the rate of change in the sample strain decreases significantly. By extrapolating lines tangent to the various strain rates, a window is identified in which the gel point is located within the intersection of these lines, shown in Figure 3.5. Using this technique, we are within 10% error of the gel point identified using the Winter-Chambon criteria. Interestingly, Bonino et al. found the empirical approach only worked for low frequencies (< 1 rad s$^{-1}$), however, this altered approach properly identifies the gelation window for frequencies up to 20 rad s$^{-1}$. We find this technique provides a quick means of identifying a gelation window, while complementing the aforementioned tan δ method. This approach may thus be of further interest as we show it extends beyond photocrosslinkable systems.
3.3.3 Effect of *In Situ* Catalyst Concentration

Dynamic oscillatory rheology experiments and the Winter-Chambon method were employed on samples with varying amine concentrations in order to investigate the effects of the *in situ* catalyst concentration on the gel time and gel properties. Modulating the amount of DEA added into the system provides control over the concentration of *in situ* catalyst/comonomer formed by the reaction between DEA and PETA, which converts tri-functional acrylates into di-functional acrylates. The gel points as a function of DEA concentration identified by the Winter-Chambon method are shown in Figure 3.6.

A minimum in gel time is seen as a function of amine concentration consistent with the observation of Bounds et al.\textsuperscript{16} obtained using a crude bubble entrapment method for determining gel point. The time required for gelation decreases as the concentration of catalyst increases, up to 22.8 mol% DEA, which is expected. However, as the DEA concentration continues to increase, the time required for gelation increases as well. Bounds et al. attribute this change to a higher critical extent of conversion,\textsuperscript{16} which is the conversion required before a gel microstructure can form. The extent of reaction at the gel point (\(p_c\)) can be calculated using the statistical approach developed by Flory and Stockmayer.\textsuperscript{28} Since this system is comprised of a tri-functional acrylate, di-functional acrylate catalyst/comonomer, and tri-functional thiol, we use the following equation for a system with two functional groups that serve as branching units:

\[
p_c = \frac{1}{\left[ r \left( f_{w,\text{acrylate}} - 1 \right) \left( f_{w,\text{thiol}} - 1 \right) \right]^{\frac{1}{2}}}
\]  \( (3.2) \)
where \( r \) is the stoichiometric ratio of the thiol to acrylate functional groups, \( f_{w,\text{acrylate}} \) represents the weight-average functionality of the monomers containing acrylate functional groups, and \( f_{w,\text{thiol}} \) represents the weight-average functionality of the thiol monomer. We find that the concentration of DEA and the critical extent of reaction are directly proportional, Figure 3.7, which is in agreement with previous reports.\(^{16}\)

This relationship is due to a decrease in acrylate functionality caused by the increase in DEA concentration and can be used to explain the minimum observed in gel time (Figure 3.6). As the amine concentration increases, a higher percentage of PETA molecules react to form di-functional acrylates, decreasing the overall acrylate functionality of the system. Thus, a higher percent conversion is required before a significant gelled network can form. The decrease in overall acrylate functionality and increase in the percent conversion required for gelation is directly reflected in the time required for gelation. For samples containing catalyst concentration less than 22.8 mol\%, the gel point decreases due to an increase in catalyst concentration. However, at catalyst concentrations greater than 22.8 mol\%, the benefit gained from an increase in catalyst concentration is negated by the decrease in acrylate functionality. For these samples, greater than 75\% of the thiol functional groups in the system must react before a gelled microstructure can form. Thus, the time required for gelation increases.

We are able to verify the theoretical critical conversion predicted by Flory and Stockmayer using rheological techniques to identify the gel point and Fourier transform infrared spectroscopy (FTIR) to monitor the thiol conversion. FTIR data shows propagation of the thiol-acrylate reaction over time, Figure 3.8. The conversion at the gel point for PETA
with 16.1 mol% DEA and 29 mol% DEA is 0.55 and 0.71, respectively. Both values match well with the theoretical critical conversion at the gel point, predicted as 0.57 and 0.76 for PETA with 16.1 mol% DEA and 29 mol% DEA, respectively. Slight discrepancies in the theoretical and experimental values may be attributed to the assumption that all functional groups of the same type are equal in reactivity and error in the FTIR conversion calculations as the reaction may propagate during initial measurements. This agreement further validates the accuracy of the Winter-Chambon criteria for gel point detection in a polymerizing system with an in situ catalyst species.

Using rheological techniques and FTIR, we are able to correlate the thiol conversion with the elastic modulus of the system, providing a means to analyze the growth of the microstructure not only in terms of time but also in terms of degree of conversion. Figure 3.8a shows the thiol conversion, adapted with permission from Bounds et al., and G’ as a function of time for PETA with 16.1 mol% DEA. In the initial stages of the reaction, the percent conversion of thiol increases rapidly, reaching a conversion of roughly 0.55 within 30 minutes after the addition of TMPTMP. However, during this period of time, the elastic modulus has no appreciable value. Shortly after the gel point, the magnitude of G’ increases rapidly. This delay in growth of G’ can be explained by recalling the theoretical value of \( p_c = 0.57 \). This value indicates that the reaction must proceed to a critical conversion before G’ is detectable, as seen in Figure 3.8c. G’ is negligible at conversions less than \( p_c \). However, after this point, G’ increases roughly 2.5 orders of magnitude as the thiol conversion sees only a 10% increase. The same trend is shown for PETA with 29 mol% DEA in Figure 3.8b and 3.8d. Until the critical conversion of 0.71 is reached, G’ has no appreciable value but grows
very rapidly after the critical conversion. This data verifies our previous hypothesis that the minimum in gel point is related to an increase in percent conversion required for gelation. Relating the magnitude in G’ and percent conversion has also been shown for a PDMS system\textsuperscript{29} and a thiol-allyl system.\textsuperscript{30} Additionally, these features are indicative of the suggested step-growth mechanism, where polymerization proceeds by forming many small clusters, which grow into a crosslinked network by sequentially adding chain segments. At lower conversions, small clusters are able to relax within the time scale of the experiment. At the critical conversion, $p_c$, the larger microstructure is unable to relax fully during the time scale of the experiment and G’ can be detected. G’ will then continue to grow rapidly as the reaction proceeds to completion.

We have demonstrated that modulating the amine concentration can affect the time required for gelation, but it is also important to analyze the state of the crosslinking system at the gel point. Winter and Chambon have shown that rheological data, particularly the relaxation exponent, $n$, can be used to investigate the microstructure of the critical gel.\textsuperscript{22} The relaxation exponent for systems of varying amine concentration can be calculated using Equation 3.1. Previous literature calculated relaxation exponents of 0.8 and 0.81-0.82 for tri-functional and tetra-functional thiols, respectively, in a photo-initiated thiol-allyl reaction.\textsuperscript{25} However, no in-depth rheological gelation studies have been performed for thiol-acrylate systems, specifically systems incorporating an \textit{in situ} catalyst comonomer. The exponent values observed for this system are very high, ranging between 0.97 and 0.98 for all samples. It is typical to find values of $n \geq 0.5$ for crosslinked systems with $n = 0.5$ found only for systems in specific stoichiometric conditions, corresponding to a gel time occurring at the
time of the $G'$ and $G''$ crossover.\textsuperscript{23,31} Winter has shown for systems where $n > 0.5$ such as ours, the gel point occurs before the $G'$, $G''$ crossover point,\textsuperscript{21} indicating a critical gel with a greater viscous modulus than elastic modulus. Results for our system are consistent and expected due to the lack of elastic character in the pre-gel state. Some researchers have attempted to establish a definitive relationship between the relaxation exponent and molecular weight of the pre-polymer. Izuka et al. showed that the relaxation exponent increased as the pre-polymer molecular weight decreased for end linking poly-caprolactone (PCL). A relaxation exponent value as high as 0.91 was calculated for PCL of number average molecular weight equal to 2000.\textsuperscript{32} Additionally, Scanlan et al. calculated a relaxation exponent of 0.92 for a system of end-linking medium chained PDMS with excess diluents.\textsuperscript{33} We believe the high value of $n$ may be due to low molecular weight prepolymer. Since the molecular weight of monomers in our system is extremely low, approximately 300 - 400 g/mol, resulting in a pre-gel with negligible elastic character, the high relaxation exponent is not unexpected.

Another parameter used to analyze the microstructure of the critical gel is the fractal dimension, $d_f$. It has been shown that the power law relationship demonstrated between $G'$, $G''$ and frequency at the gel point is due to the self-similar nature of the critical gel.\textsuperscript{34} The self-similar nature refers to the fact that if a portion of the critical gel were magnified, the overall structure would resemble the original piece, no matter the magnification or size of the original portion. This self-similarity is quantified using the fractal dimension which has been shown to relate the radius of gyration (spatial size, $R$), and molecular weight of the polymer as follows:
\[ R^{d_f} \sim MW \]

Assuming excluded volume effects are screened, the fractal dimension can be calculated using the following equation:

\[
n = \frac{d \left( d + 2 - 2d_f \right)}{2 \left( d + 2 - d_f \right)}
\]  

(3.3)

where \( d \) is the space dimension 3.\textsuperscript{23,35} The same fractal dimension of 1.3 was calculated for all systems investigated. Although such low fractal dimensions have not been reported for polymeric systems, a fractal dimension of 1.3 has been observed in nature to represent tree branches, root systems, and clouds.\textsuperscript{34} Low fractal dimensions, yet values higher than our system, have been associated with open structures,\textsuperscript{33} the polymerization of small molecules, and systems with many crosslinking defects.\textsuperscript{20,35,36} All reactants in the system are small molecules and the \textit{in situ} catalyst comonomer contains an amine functional group which truncates chain growth in that direction, as the polymerization proceeds between the acrylate and thiol groups. These factors may promote defects in the crosslinked network. Considering these attributes, a low fractal dimension should not be unexpected.

Utilizing the Boltzmann inversion\textsuperscript{37} coarse graining method along with DMD\textsuperscript{38} simulations in the EMBLEM package developed by Curtis and Hall,\textsuperscript{39} we are able to qualitatively verify the state of the critical gel of PETA containing 16.1 mol\% DEA, and further, quantitatively verify the fractal dimension and theoretical critical extent of reaction (\( p_c \)). The model uses the Boltzmann inversion coarse graining method to obtain realistic geometry configurations and interactions between coarse grained functional groups. To mimic the step growth polymerization of PETA, thiol functional groups were labeled as
reactive if they had an excluded volume reaction with the nitrogen from the amine group on
the *in situ* catalyst, thereby mimicking the deprotonation of the thiol group by the catalyst. If
a specific thiol and acrylate group had an excluded volume interaction and had been
previously designated as reactive, a permanent bond was formed between the two sites. At
low conversions, the simulation shows the formation of small clusters, agreeing well with
previously discussed rheological data, shown in Figure 3.9a. As the reaction approached the
theoretical critical extent of reaction, calculated as 0.57 using Flory-Stockmayer’s statistical
approach, larger chains began to form. It is apparent in Figure 3.9b that the polymer chains
have begun to span into a three dimensional area, characteristic of the critical gel. When the
reaction nears completion the system contains primarily cross-linked polymer chains, Figure
3.9c.

Using the relationship between the radial distribution function and fractal dimension
established by Kieffer and Angell,\textsuperscript{40} we are able to calculate the fractal dimension of the
simulated system at the gel point as 1.34, which is in agreement with the experimental
values. The computer simulations allow for the capturing of a transient state, such as the gel
point and critical gel, allowing for the validation of experimental characteristics.
Interestingly, the relaxation exponent and the fractal dimension remain unaffected by
changes in the amine concentration.

Figure 3.10 contains rheological time sweeps for all systems investigated. As can be
seen, the elastic modulus plateaus at approximately the same value despite changes in amine
concentration. The only change observed is the length of the induction period, which relates
back to the previous discussion regarding the trade-off between an improvement in reaction
speed due to increased catalyst concentration and higher critical conversions required for gelation. Since the relaxation exponent is also independent of the amine concentration, we conclude that the crosslinking mechanism remains unaffected by changes in the concentration of in situ catalyst.\textsuperscript{41} This provides the ability to tune the gel time of the system by modulating the amine concentration without affecting the formation mechanism or spatial size of the critical gel.

3.4 Conclusions

We have demonstrated the applicability of dynamic rheology together with a multiwave technique and the Winter-Chambon criteria for examining the gelation of a novel thiol-acrylate system where an in situ catalyst is incorporated into the crosslinked network. Using this approach, we were able to probe the evolving rheological properties and relate the macroscopic properties to the gel time and characteristics of the critical gel, such as the fractal dimension. We also investigated the effect of amine concentration from 7.8 mol\% DEA to 34.2 mol\% DEA on the gelation mechanism, properties of the critical gel, and gel times.

The gel times for all systems investigated ranged from as short as 30 minutes for 16.1 mol\% DEA to as long as 75 minutes for 34.2 mol\% DEA. Initially, the time required for gelation decreased as the amine concentration increased up to 22 mol\% DEA. At concentrations greater than 22 mol\% DEA, the time required for gelation increased. We attribute this trend to a decrease in the overall acrylate functionality, requiring a higher thiol conversion for gelation to occur. Rheological techniques in combination with FTIR were
used to calculate the conversion at the gel point for PETA with 16.1 mol% DEA and 29 mol% DEA. The experimental thiol conversion of 0.55 and 0.71 at the gel point matched well with the theoretical conversions calculated using the statistical approach developed by Flory and Stockmayer.

The value of the relaxation exponent, $n$, for all systems investigated was approximately 0.97, yielding a fractal dimension of 1.3. The high value of $n$ can be attributed to the low molecular weight of the prepolymer materials, resulting in a lack of any significant elastic character in the pregel state. As such, the gel time occurring before the $G'$-$G''$ crossover point was not unexpected. Such low fractal dimensions have not been reported for polymeric systems, but have been observed in nature. Interestingly, we found the final elastic modulus to be equal for all systems investigated as well. Since the relaxation exponent was independent of changes in the amine concentration, we conclude that the reaction mechanism remained the same for all systems. Changes in the amine concentration, and thus the $in situ$ catalyst concentration, seem to only affect the rate of reaction and time required for gelation. Altering the amine concentration changes the time required for gelation without affecting the crosslinking mechanism or development of the critical gel. This provides facile control over the gelation time without sacrificing the integrity of the critical gel, which would be imperative for applications such as $in situ$ gelation in the biomedical field.

### 3.5 Acknowledgements

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3.6 References


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Figure 3.1. Polymerization reaction for tri-acrylate and tri-thiol monomers containing an in situ amine catalyst. Adapted from Bounds et al.\textsuperscript{16}
Figure 3.2. Frequency spectra of (A) PETA with 34.2 mol% DEA with and without TMPTMP approximately 20 minutes after initial sample preparation and (B) of PETA with 34.2 mol% DEA at varying times after the addition of the tri-thiol.
Figure 3.3. Time sweeps depicting the evolution of $G'$ and $G''$ of PETA with 34.2 mol\% DEA for frequency ($\omega$) of (A) 1 rad s$^{-1}$ and (B) 10 rad s$^{-1}$ showing data from FTMS experiments match well with individual time sweeps.
Figure 3.4. (A) Variation of \( \tan \delta \) over time for PETA with 34.2 mol\% DEA measured at frequencies of 1, 5, 10, and 20 rads\(^{-1}\) using the multiwave technique, showing the gel point occurs at 75 min. (B) Frequency spectrum at the gel point for PETA with 34.2 mol\% DEA showing parallel slopes for \( G' \) and \( G'' \).
Figure 3.5. Strain on PETA with 34.2 mol% DEA over time at 1, 5, 10, and 20 rad s$^{-1}$. At the onset of gelation (75 min), the relationship between strain and time changes dramatically, indicated by changes in slopes. The gel point can be estimated by the intersection of the lines tangent to the slopes.
Figure 3.6. Calculated gel points, from Winter-Chambon method, as a function of mol% DEA, where mol% DEA is calculated as the ratio of moles of amine groups to moles of acrylate groups.
Figure 3.7. Theoretical thiol conversion at the gel point calculated using Flory-Stockmayer statistical approach as a function of mol% DEA. As the amine concentration increases, a higher conversion is required for the system to gel.
Figure 3.8. Percent thiol conversion and evolution of $G'$ for PETA with (A) 16.1 mol% DEA and (B) 29 mol% DEA. $G'$ plotted against percent thiol conversion for PETA with (C) 16.1 mol% DEA and (D) 29 mol% DEA. Percent conversions of 55% and 68%, respectively, are required before the elastic moduli have any appreciable value.
Figure 3.9. Simulation snapshots of PETA with 16.1 mol% DEA at (A) 0%, (B) 57%, and (C) 95% thiol conversion. As the reaction continues, the prepolymer monomers can be seen reacting together, forming a crosslinked network.
Figure 3.10. Evolution of the elastic ($G'$) and viscous ($G''$) moduli over time at frequency ($\omega$) of 1 rad s$^{-1}$ and stress ($\tau$) of 1 Pa of samples with 7.8, 16.1, 22.8, 29, and 34.2 mol% DEA.
CHAPTER 4

Real-Time Rheological Characterization of the Two-Step Crosslinking Mechanism of Photoinitiated Alginate Hydrogels

Chapter 4 is essentially a manuscript by Alina K. Higham, Srinivasa R. Raghavan, and Saad A. Khan submitted to *Langmuir*.
Real-Time Rheological Characterization of the Two-Step Crosslinking Mechanism for Photoinitiated Alginate Hydrogels

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Abstract

We examine the gelation of alginate undergoing ionic crosslinking upon ultra-violet (UV) irradiation using in situ UV dynamic rheology. Hydrogels are formed by combining alginate with calcium carbonate (CaCO₃) and a photoacid generator (PAG), which is photolyzed upon UV irradiation, resulting in the release of free calcium ions for ionic crosslinking. The material properties, such as the viscous and elastic moduli, and gel points of the hydrogels are analyzed as a function of UV irradiation intensity, exposure time, alginate concentration, and the ratio between alginate and calcium carbonate. Gel time decreases as irradiation intensity increases because a larger concentration of PAG is photolyzed. Interestingly, dark curing, the continuing growth of microstructure in the absence of UV light, is observed and believed to be due to the two-step crosslinking mechanism. In some instances, the sample transitions from a solution to a gel during the dark curing phase. Additionally, when exposed to constant UV irradiation after the dark curing phase, samples reach the same plateau modulus as samples exposed to constant UV without dark curing,
implying dark curing does not affect the gelation mechanism. A wide range of gel moduli may be obtained by modulating the process parameters rather than changing polymer systems, allowing this system to be used in applications with a wide range of requirements.
4.1 Introduction

The fabrication of hydrogels from biocompatible materials is of interest since these malleable systems are excellent candidates for biomedical and tissue engineering applications. Hydrogels are formed from polymer networks spanning in three dimensions and have the ability to swell in aqueous solutions. Additionally, the shape, mechanical stability, and rates of degradation can be tailored, making them promising materials for applications such as drug delivery and regenerative medicine. As demands for less invasive procedures and smart materials grow, research focusing on the development of novel hydrogels has surged, specifically light responsive systems comprised of biocompatible materials.

Alginate, a polysaccharide derived from various species of brown algae, has been used extensively in applications such as tissue scaffolding, the encapsulation and delivery of biological moieties (i.e. cells, proteins, drugs), wound healing, and photopatterning to interface biological moieties with hard surfaces. Alginate hydrogels can be constructed via chemical crosslinking (reaction with gluteraldehyde or bonding of chemically modified methacrylated alginate) and physical crosslinking mechanisms (ionic bonding with divalent cations such as Ca$^{2+}$ and Mg$^{2+}$). Alginate hydrogels formed from these two mechanisms have shown promise, however both possess inherent drawbacks, as chemical crosslinking requires the use of chemical reagents which present cytotoxicity concerns, while control over the gelation mechanism is difficult for typical physically crosslinked alginites.

Recently, the development of photoinitiated alginate hydrogels has been reported to garner better control over alginate gelation. Photoinitiated alginate hydrogels present benefits such as targeted, controlled, and minimally invasive gelation, which may be useful in
biomedical or photopatterning applications, since light can be directed at a precise location from a distance, avoiding direct contact. To date current approaches for the fabrication of photoinitiated alginate hydrogels include: the synthesis of chemically modified alginate containing reactive methacrylate side groups, the release of CaCl$_2$ from phototriggerable liposomes, and the release of Ca$^{2+}$ from photoresponsive Ca$^{2+}$ chelators or cages. Unfortunately, these alternate techniques require additional chemical synthesis steps and the use of chemical reagents that may pose cytotoxicity concerns or the use of expensive materials (caged Ca$^{2+}$ and liposomes).

Javvaji et al. have reported a novel system for the fabrication of photoinitiated alginate hydrogels via physical crosslinking, based on the release of calcium ions from dispersed calcium carbonate nanoparticles. Using inexpensive, commercial materials, alginate is dissolved with a photoacid generator (PAG) and dispersed calcium carbonate (CaCO$_3$) particles. Upon ultra-violet (UV) irradiation, the PAG is hydrolyzed, releasing acid (H$^+$). The release of acid triggers the dissociation of the CaCO$_3$ particles, releasing Ca$^{2+}$ ions capable of combining with alginate to form the widely accepted “egg-box” junctions between alginate chains, creating a gel, Figure 4.1. Since the calcium ions and alginate form ionic bonds, the sample may be reversed into the sol state upon removal of the cation from the “egg-box” junction. Alginate is comprised of β-D-mannuronate (M) and α-L-guluronate (G) residues which arrange in non-regular blockwise patterns along the linear chain. Residues can form three types of sequential blocks: alternating sequence (MG), repeat M residues (M-block), and repeat G residues (G-block). Interestingly, paired G-sequences form a buckled structure in the shape of an “egg-box” whose cavity can accommodate divalent cations (e.g.
Ca\(^{2+}\)) forming an ionic bond between G-blocks on adjacent alginate chains and the cation, schematic shown in Figure 4.1.\(^{21}\) As the sequence patterns and lengths of the varying blocks heavily depend on the biological source, alginate hydrogels may possess a wide range of gel properties, such as final modulus and crosslinking kinetics. An understanding of the relationship between the system components and time required for gelation would be beneficial for instances such as avoiding the irradiation of a sample for a longer duration of time than necessary.

Small amplitude dynamic oscillatory rheology is an established technique for monitoring the gelation mechanism of crosslinking samples, as information regarding the magnitude of material properties such as the elastic (G’) and viscous (G’”) modulus can be attained without disrupting the fragile internal microstructure.\(^{22-24}\) Rheological characterization of gelation mechanisms is critical for developing an understanding of the relationships between microstructure and product properties. Reported work has focused solely on the rheological characterization of photoinitiated hydrogels undergoing chemical crosslinking mechanisms, the majority of which propagate via free-radical polymerization rather than physical gelation. Furthermore, most of these studies do not report \textit{in situ} characterization of the gelation process, focusing only on characterization of the gelled samples.\(^{13,25-27}\) Recently, \textit{in situ} UV rheological techniques have been established to examine the kinetics of photocurable gels.\(^{28-32}\) \textit{In situ} techniques are advantageous in that real-time quantitative information of the changing properties (G’,G’”) can be gathered as a function of time. Although a rheological \textit{in situ} characterization has been performed for chemically modified methacrylated alginate,\(^{31}\) there is a lack of rheological understanding for UV
initiated alginates undergoing physical crosslinking gelation. In this study, we present a rheological study of UV initiated physically crosslinked alginate hydrogels, investigating the effects of UV intensity, irradiation exposure, and chemical composition on the gelation kinetics and final gel properties. We determine the relationship between gel point and UV intensity, as well as probe the role of PAG in this crosslinking system. Other parameters investigated include the role of alginate concentration and the ratio of alginate and CaCO$_3$ concentration, as modulating the number of available G-blocks and/or Ca$^{2+}$ ions will play a major role in the gel strength. We also investigate the role of UV exposure time on final elastic modulus as dark curing is observed for this two-step mechanism. This phenomenon provides a means for tailoring the final gel properties by simply modulating UV exposure time without altering the sample composition.

4.2 Materials and Methods

4.2.1 Materials

A photoacid generator, diphenyliodonium nitrate, (henceforth abbreviated as PAG) and sodium alginate (molecular weight: 12-40 kDa, originating from *Macrocystis pyrifera*) were purchased from Sigma Aldrich. Alginate originating from this specific source has been shown to have the following composition: alternating MG block 42%, M-block 40%, and G-block 18%.$^{33}$ Precipitated calcium carbonate particles, mean particle radius of 70 nm, were obtained from Specialty Minerals from Birmingham, U.K.
4.2.2 Solution Preparation and Characterization

Solutions were prepared by mixing sodium alginate, PAG, and CaCO₃ particles in de-ionized water. Samples used in this study contain 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO₃ unless otherwise stated. Mixtures were stirred by a magnetic stir bar at room temperature for approximately 6 hours until dissolved. Before use, samples were sonicated for 10 minutes. Stock solutions of 10 mL were prepared to enable multiple experiments.

The pH of the system was measured (accumet Basic AB15 pH meter) before, during, and after UV irradiation from a 200 W mercury lamp (Lumens Dynamic, Omnicure S2000, filter 320-500 nm) with a fiber glass optical light guide. Samples were gently stirred by a magnetic stir bar while irradiated to ensure homogeneity.

4.2.3 Rheological Characterization

All rheology experiments were conducted using a stress-controlled Discovery Hybrid Rheometer HR-2 rheometer (TA Instruments) and 20 mm parallel plate geometry. All UV experiments were performed with the UV Light Guide accessory (TA Instruments) connected to a 200 W mercury arc bulb UV source (Lumens Dynamic, Omnicure S2000, filter 320-500 nm) with UV intensity equal to 175 mW/cm², unless otherwise stated. Solution gelling behavior was monitored using small amplitude dynamic oscillatory time and frequency sweeps, where time zero represents the start of UV irradiation. The stress applied to the sample was kept constant at 1 Pa, which was within the linear viscoelastic regime (LVR).
4.3 Results and Discussion

4.3.1 Evolution of Crosslinking Reaction

The photogelling response of a system containing alginate, a photoacid generator (PAG), and calcium carbonate (CaCO₃) particles, was characterized before and after ultra-violet (UV) exposure using small amplitude dynamic oscillatory rheology, so as not to disturb the fragile developing microstructure. The frequency spectra can be seen in Figure 4.2A. Our experiments used an aqueous solution of 4 wt./vol.% alginate and 60 mM PAG containing 30 mM CaCO₃ particles dispersed in solution exposed to 175 mW/cm² UV irradiation, unless otherwise stated. Sample behavior prior to irradiation shows typical solution behavior. The viscous modulus, G″, has a strong dependence on frequency, G″ ~ ω¹, while the magnitude is higher than the elastic modulus, G′. Data shown for G′ before irradiation is noisy due to a lack of elastic character since the majority of the system is water. However, after 2000 seconds of UV exposure, the sample shows gel-like behavior, as G′ is independent of frequency. Additionally, the magnitude of G′ has increased by several orders of magnitude, surpassing G″. This change is indicative of the development of a complex microstructure, able to hold its own weight upon inversion as previously shown.¹³ Upon UV irradiation, the PAG is photolyzed, releasing acid (H⁺) into the system. The acid release triggers the dissociation of CaCO₃, releasing Ca²⁺ ions, which have been shown to ionically bond with consecutive α-L-guluronate (G) residues (G-blocks) along the alginate chain. The bonding of Ca²⁺ with G-blocks on adjacent alginate chains form “egg-box” junctions, resulting in a crosslinked network.¹⁴,¹⁹,²⁰
In addition to characterizing samples before and after UV irradiation, we have monitored the transition from the sol state to the gelled state in situ during constant UV irradiation, as shown in Figure 4.2B. At time less than 200 seconds, the magnitude of $G'$ is less than $G''$, with $G'$ dramatically rising. Eventually, $G'$ surpasses $G''$, with the $G'$-$G''$ crossover occurring at 150 seconds, and continues to grow, reaching a final value of 450 Pa. The initial sharp rise in $G'$ can be attributed to the physical linking of Ca$^{2+}$ ions with available G-blocks on adjacent alginate chains. Although $G'$ continues to increase after the $G'$-$G''$ crossover, the rate of growth slows as demonstrated by a change in slope. Interestingly, the change in slope corresponds with the gel point, approximately 200 seconds, (determination of which is explained in subsequent sections). This trend is also observed for samples exposed to varying UV intensities, shown later. Although gelation kinetics have been shown to slow over time for many gelation systems, the change in slope corresponding to the gel point seems to be unique to this system. We believe that this change in kinetics is due to diffusion rate limitations from the growing microstructure. Alginate chain mobility significantly decreases when free Ca$^{2+}$ ions and available G-blocks from adjacent chains combine to form crosslinks. Free Ca$^{2+}$ ions must diffuse through the developing microstructure to bond with unoccupied G-blocks, furthering microstructure growth. As the crosslinked network becomes more complex, the free Ca$^{2+}$ ions have more barriers to diffusion, leading to a decrease in the rate of growth for $G'$. 
4.3.2 Gel Point Determination

An important factor to consider when dealing with systems transforming from a solution to a gel is determination of the gel point (GP), the point in time at which the molecular weight increases to infinity or where the first complete chain reaches from plate to plate in the rheometer. Typically, gel points are rheologically detected using the Winter-Chambon criteria.\textsuperscript{24,34-39} This criteria states that at the gel point, $G'$ and $G''$ depend on frequency in the same manner, which can be graphically depicted as the time at which the point of intersection occurs when plotting $\tan \delta$ (the ratio of $G''$ to $G'$) versus time for varying frequencies, as depicted in Figure 4.3A for a representative sample. In this case, the gel time corresponds to 200 seconds.

Although the Winter-Chambon criteria is a well-documented method for determining the gel point, it may require multiple experiments and it may occasionally be difficult to identify the point of intersection due to weak signals from $G''$ resulting in scattered data. Previously, our group reported the use of an empirical method for pinpointing the gel point for photoinitiated hydrogels comprised of chemically modified alginate by monitoring the percent strain over time.\textsuperscript{31} Monitoring the strain can be advantageous for systems with weak $G''$ signals after gelation or systems that experience rapid gelation, as both scenarios result in a narrow observation window for monitoring $\tan \delta$. When the sample approaches the gel point, the strain rapidly decreases as a result of the increasing modulus, Figure 4.3B. The gel point can be pinpointed by a minimum in the derivative of the log strain with respect to time. We find that using both the Winter-Chambon criteria and the empirical approach reveal the same gel point for our system (200 seconds), indicating that the empirical approach works...
well for UV initiated alginate systems undergoing physical gelation. Using this empirical approach, the gel point may be quickly determined without the need for multiple time sweeps at varying frequencies, as required by the Winter-Chambon method.

4.3.3 Effect of UV Intensity

It has been shown that gelation kinetics and final gel properties are directly affected by the UV intensity for photocurable systems. Thus, it is imperative to fully investigate the effects of UV intensity for this system, as UV sources typically vary in wattage. Data for the evolution our system from a solution to a gel over time for varying intensities and corresponding frequency spectra of the final gels are shown in Figure 4.4. Note only data for G’ is shown for clarity. Time sweeps containing both G’ and G” can be found in supplemental information, Figure S4.1.

For all UV intensities investigated (75 mW/cm² to 275 mW/cm²), time sweeps show G’ is initially less than G”, but with continuing UV exposure, G’ increases significantly, eventually surpassing G”, indicating the formation of an internal microstructure. Although the same general trend is seen for all samples, greater UV intensity shows an increase in the rate of microstructure growth, Figure 4.4A inset. For instance, G’ for a sample exposed to 275 mW/cm² equals 80 Pa at 500 seconds, while G’ for a sample exposed to 75 mW/cm² has only reached 10 Pa. The delay in gelation kinetics is also observed when pinpointing the gel point (GP), as determined by the previously discussed empirical method. It is observed that the gel point is inversely proportional to UV intensity (I), scaling GP~I⁻⁰.₆₅, Figure 4.4C, providing a means to predicting the gel point based on UV intensity. Decreasing the UV
intensity diminishes the amount of energy emitted from the UV source, providing less energy to enter the system in a specific period of time. This provides a delay in the release of acid from PAG, and subsequently, the release of $\text{Ca}^{2+}$ for crosslinking. The microstructure develops more slowly due to fewer available $\text{Ca}^{2+}$ ions for crosslinking and diffusion rate limitations due to the forming microstructure. Thus, a longer period of time is required before gel point. It should be noted that although the gel point occurs after the $G'$-$G''$ crossover for all samples, this should not be unexpected. Systems possessing gel points that occur after the $G'$-$G''$ crossover are associated with large fractal dimensions ($>2$), representative of a closely packed system. Hydrogels formed by the physical crosslinking of alginate and calcium have been shown to create compact networks.\textsuperscript{40}

Interestingly, despite the delay in gelation kinetics, all samples show $G'$ plateaus at approximately the same magnitude given ample irradiation time. For instance, the plateau modulus for 275 mW/cm$^2$ is reached at 1000 seconds, compared to 3000 seconds for 75 mW/cm$^2$. Frequency spectra of samples after UV irradiation show $G'$ is independent of frequency and equal to the same magnitude (~400 Pa) for all gelled samples regardless of UV intensity, Figure 4.4B. This was not observed for chemically crosslinked methacrylated-alginate, which reported decreases in plateau modulus as UV intensity was lowered due to a higher concentration of intramolecular crosslinks compared to intermolecular crosslinks.\textsuperscript{31} For our physically crosslinking system, independence of the plateau modulus from UV intensity infers that the crosslinking mechanism is unaffected by UV intensity. The plateau modulus for this system is reached when all available G-blocks in the system have bonded with $\text{Ca}^{2+}$ ions. Thus, the magnitude in plateau modulus is more likely dependent on the
composition of the sample rather than intensity of UV exposure. For this photoinitiated alginate system, modulating the UV irradiation intensity alters the gelation kinetics without changing the crosslinking mechanism or final gel properties, thus the rate of formation may be tailored depending on the desired application without sacrificing final gel strength.

4.3.4 Effects of UV Exposure Time and Dark Curing

Alginate hydrogels are beneficial for a variety of applications, requiring a wide range of final gel properties, especially gel modulus. For example, many alginate hydrogels are used in tissue engineering applications, but tissues have a broad range of moduli (~a 1 kPa for the liver to ~40 GPa for bone).\(^4\) Since the gelation kinetics are dependent upon UV intensity during constant exposure, a means to modulate the final gel modulus may lie in altering the UV exposure time. Interestingly, evidence of dark curing, defined as the continuing formation of an internal microstructure in the absence of UV light exposure, is prevalent for this system. Dark curing is not usually observed, since most UV initiated systems propagate via free radical polymerization and radicals quickly self-terminate by recombination upon the removal of UV irradiation. However, as our system does not propagate by free radical polymerization, we probed the dark curing phenomenon further, identifying the effects of UV exposure time on the gelation and plateau modulus, as well as quantifying the dark curing effects.

The effects of dark curing are demonstrated for our system in Figure 4.5A by monitoring G’ and G” over time after a specified duration of UV exposure at 175 mW/cm\(^2\) ranging from 20 seconds to 240 seconds. Note that G” is not shown for clarity, but time
sweeps containing G’ and G” can be found in supplemental information, Supplemental Figure S4.2. A single exposure of 20 seconds yields no change in G’, even over 2500 seconds. Frequency spectra of the final sample after 20 seconds of UV irradiation show solution behavior as G” is greater than G’ and both moduli are frequency dependent, Figure 4.5B. However, for exposure times greater than 20 seconds, an increase in G’ is quickly detected, with both moduli increasing in magnitude over time after the removal of UV light. Dark curing from exposure times greater than 45 seconds yield completely gelled samples, as frequency spectra show G’ independent of frequency, Figure 4.5B. As expected, the rate of microstructure growth and the magnitude of the final gel modulus increase as the exposure times lengthen. Longer durations of exposure to UV irradiation allow more energy to enter the system, photolyzing a higher concentration of PAG and releasing a greater quantity of Ca\(^{2+}\) for crosslinking. The lack of change in microstructure after 20 seconds of UV exposure and the gelation of samples after UV exposure greater than 45 seconds infers that an activation energy must be reached in order to release ample H\(^+\) to form a microstructure larger enough for detection.

In order to further probe this issue, we performed a single time sweep with multiple UV exposures of 20 seconds in duration, Figure 4.6. After each UV exposure (presented by the shaded regions in the time sweep), G’ and G” were monitored over time in the absence of UV light, dividing the time sweep into four regions, each consisting of UV exposure, a dark curing phase, and corresponding frequency spectra, Figure 4.6. In region 1, the sample shows solution like behavior and no change is observed for G’ or G”. However, in region 2 (i.e. after the second UV exposure), G’ is detectable and shown to grow over time during the dark
curing phase. This demonstrates that the activation energy has been reached upon subsequent UV exposure and an adequate amount of Ca\(^ {2+} \) ions are released to form a microstructure large enough for detection. It should be noted that the activation energy does not need to be reached by continuous UV exposure, but may be attained by discrete UV exposure steps. In region 3 (i.e. after the third UV exposure), G’ surpasses G” during the dark curing phase and frequency spectra of the sample after region 3 shows G’ is greater than G” and independent of frequency, indicative of a gelled sample. Note that the transition from a sol to gel occurs in the absence of UV light. After the fourth 20 second dose, the microstructure continues to grow, with the magnitude of G’ rising to 5 Pa.

We believe the presence of dark curing is a result of the two-step crosslinking method. When irradiated, UV energy is absorbed in the system photolyzing the PAG and releasing H\(^ + \) ions in the form of an acid. Although the UV sample is no longer exposed to UV light, the acidic environment within the sample persists, allowing CaCO\(_3\) to dissociate, thereby releasing free Ca\(^ {2+} \) ions capable of binding with available G-blocks. The growth of microstructure is then detected if the activation energy has been reached (ample Ca\(^ {2+} \) ions have been released). Additionally, dark curing could also be a result of the time required for Ca\(^ {2+} \) ions to diffuse towards available G-blocks. The continuation of gelation is therefore dependent on the presence of acid and Ca\(^ {2+} \) ions, not the constant exposure to UV light as is the case for most crosslinking systems. This hypothesis was confirmed by monitoring the pH of the system before, during, and after timed exposures to UV light. A plot of the change in pH over time can be found in supplemental information, Supplemental Figure S4.3. During UV exposure, the pH drops from an initial value of 8 to 6.5 as a result of the release of acid...
from the photolyzed PAG. However, after UV irradiation is removed, the pH remains unchanged for a few minutes demonstrating a persistent acidic environment in the absence of UV light. The pH then slowly increases as the acid is consumed in the dissociation reaction of the CaCO$_3$ particles, creating Ca$^{2+}$ ions and CO$_2$. It is interesting to note that the pH after UV exposure plateaus at a pH value lower than the initial solution prior to UV exposure, most likely due to the consumption and resulting decrease in concentration of CaCO$_3$ particles, whose presence creates a more basic environment (higher pH). This trend persisted for subsequent exposures to UV irradiation. Since exposure to UV light quickly photolyzes PAG and drops the pH, we can infer that dark curing is due to the dissociation of CaCO$_3$ and the diffusion of free Ca$^{2+}$ ions to available G-blocks, even after UV irradiation is removed.

While understanding the mechanism responsible for dark curing in this system is important, it is also necessary to quantify the dark curing effects. Samples exposed to UV irradiation for a varying duration of time show a plateau in the magnitude of $G'$ after the dark curing phase. This plateau in $G'$ possibly relates to the integration of all Ca$^{2+}$ ions freed during initial UV exposure into the microstructure. Since the magnitude of the plateau modulus relates to UV exposure time, the following equation is used to quantify the dark curing effects:

$$\text{Extent of dark curing} = \frac{G'_{\text{final}} - G'_{t=\text{UVOFF}}}{G'_{t=\text{UVOFF}}}$$  \hspace{1cm} (4.1)$$

where $G'_{\text{final}}$ represents the magnitude of the elastic modulus when plateaued at the end of dark curing, and $G'_{t=\text{UVOFF}}$ represents the magnitude of $G'$ at the end of UV exposure.
A plot of the extent of dark curing as a function of UV exposure duration can be seen in Figure 4.7A for our system. As stated previously, UV exposure of 20 seconds was not long enough to initiate the formation of a detectable microstructure, thus there is a lack of dark curing. As the UV exposure time increases from 45 seconds to 90 seconds, the change in magnitude of $G'$ (i.e., extent of dark curing) grows from 40 times $G'_{t=\text{UV off}}$ to 162 times $G'_{t=\text{UV off}}$ during the dark curing phase. As more energy is added into the system via longer exposure times, a larger concentration of PAG is photolyzed, thereby allowing for the dissociation of a larger quantity of CaCO$_3$ particles and thus free Ca$^{2+}$ ions available for crosslinking. Interestingly, a maximum in the extent of dark curing is seen to occur around 90 seconds, even though the magnitude of $G'_{\text{final}}$ continues to increase with lengthened UV exposure time. At UV exposure times greater than 90 seconds, microstructure formation occurs during the initial exposure, thus increasing the value of $G'_{t=\text{UV off}}$. Many of the Ca$^{2+}$ ions are released during UV exposure and bond with available G-blocks before the UV light is removed. Thus, the extent of dark curing decreases for prolonged exposure times as the microstructure grows minimally after the removal of UV light.

As mentioned previously, the magnitude of $G'_{\text{final}}$ increases as exposure time is lengthened, inferring that there is a relationship between $G'_{\text{final}}$ and UV exposure time. Plotting $G'_{\text{final}}$ as a function of energy input, $E_{\text{input}}$, which is the product of power and time, shows a linear trend modeled by an empirical mathematical equation, Figure 4.7B. It should be noted that this equation yields a negative value for $G'_{\text{final}}$ for energy input less than 30 J. This value represents the activation energy required to release ample Ca$^{2+}$ ions to form a microstructure large enough for detection. The relationship between $G'_{\text{final}}$ and energy input
can be used to predict and tailor the final magnitude of $G'$ for a sample by simply modulating the duration of UV exposure without having to alter the sample composition.

Another factor to consider is whether the energy input has a direct effect on the crosslinking kinetics. The phenomenon of reciprocity, whether the final modulus is dependent upon the UV exposure procedure, is investigated by performing rheological experiments where UV intensity and exposure times are varied, while maintaining an equivalent energy input. Two scenarios exist where the energy input is maintained. One scenario varies the UV exposure procedure for constant UV intensity (e.g. 120 second dose at 175 mW/cm$^2$, a 90 second and subsequent 30 second dose, or two doses each lasting 60 seconds in duration). Time sweeps monitoring $G'$ and $G''$ during these UV exposure procedures can be found in Figure 4.8A, with corresponding frequency spectra in Figure 4.8C. At the end of each experiment, the total energy emitted equals 66 J. It is interesting to note that initial doses of 120 seconds, 90 seconds, and 60 seconds emit ample energy for the sample to transition from a solution to a gel during the dark curing phase, however microstructure growth is not detected until the second dose when emitting in 20 second increments (shown previously). This can be attributed to the fact that a dose of 20 seconds at 175 mW/cm$^2$ equals an energy input of 11 J, which is less than the calculated activation energy of 30 J. Thus, an inadequate amount of Ca$^{2+}$ ions to form a microstructure large enough for detection have released. Interestingly, the magnitude of $G'$ after dark curing for each sample is equal, suggesting that the mechanism for crosslinking remains unaffected by UV exposure procedure and reciprocity is maintained when comparing samples irradiated with the same intensity. The second scenario for maintaining equal energy input is by
altering both the intensity and the dosage time during continuous UV exposure. Our system was exposed to UV intensities ranging from 75 mW/cm$^2$ to 175 mW/cm$^2$ for varying exposure times, while maintaining a total energy input of 133 J. The samples were characterized via time sweeps and frequency sweeps of the resultant gel, Figure 4.8B and 4.8D, respectively. A delay in the gelation kinetics is seen when the UV intensity decreases and microstructure growth occurs in the absence of UV light as a result of dark curing, as was previously discussed. After ample time has elapsed, $G'$ is shown to plateau as all free Ca$^{2+}$ released during UV exposure have bonded with G-blocks on the alginate chains. Interestingly, frequency spectra of the resultant gels show the magnitude of $G'$ to be equal for all experiments of energy input 133 J, showing that reciprocity is also maintained when modulating both UV intensity and exposure time. Knowledge of this phenomenon is advantageous in predicting processing procedures for the formation of gels with equal moduli despite variation in UV intensity from different UV sources. Reciprocity, in combination with the relationship between final gel modulus and energy input discussed previously, provide a means to tailor the final modulus by modulating the energy input, independent of UV intensity.

One important factor to note is that the crosslinking mechanism, driven by the formation of egg-box junctions, remains unaffected during the dark curing phase, as illustrated in Figure 4.9. A representative system is first exposed to UV irradiation for 180 seconds and then monitored during the dark curing phase for 2000 seconds, as shown in Figure 4.9A in region 1. During the dark curing phase, the magnitude of $G'$ increases to 45 Pa. Interestingly, upon subsequent exposure to constant UV irradiation after the dark curing
phase (time of 2000 to 4000 seconds, region 2), $G'$ is shown to increase, eventually reaching the magnitude of 400 Pa which seems to be equal to the plateau modulus for a sample exposed to continuous UV irradiation, Figure 4.9A. In figure 4.9B, we show the frequency spectra for a sample from region 1 (after 180 seconds of UV exposure and the dark curing phase), region 2 (after 180 seconds of UV exposure, dark curing, and subsequent constant UV irradiation), and a sample exposed to continuous UV irradiation with no dark curing phase. The magnitudes of $G'$ and $G''$ of the sample from region 1 increase upon subsequent constant UV exposure (region 2). Additionally, the frequency spectra from region 2 show both dynamic moduli to be equal to that for a sample exposed to continuous UV irradiation with no dark curing phase. This effect is also shown for samples exposed to constant UV irradiation after exposure times of 240 seconds and 450 seconds and their respective dark curing phases, Figure 4.9C. After exposure to constant UV irradiation, all samples show a final modulus of 400 Pa. This equality infers that the crosslinking mechanism during the dark curing phase is the same mechanism used to form a microstructure under constant irradiation. The ability to pause at a specific magnitude of $G'$ and subsequently continue microstructure growth upon additional UV irradiation may prove to be beneficial for applications where varying moduli are required at specific times.

4.3.5 Composition Effects

Although processing effects are important to investigate, it is also imperative to understand the relationship between sample composition and properties of the resultant gel. One such factor is the ratio of G-blocks in the alginate chain to the number of available Ca$^{2+}$
ions. The theoretical maximum amount of calcium ions the system is able to accommodate (henceforth referred to as the theoretical maximum) can be calculated by assuming a 2:1 G-block to Ca$^{2+}$ ion ratio (from one “egg-box” junction) and using the reported composition percentage of alginate derived from *Macrocystis pyrifera* (42% alternating MG-block, 40% M-block, and 18% G-block). Time sweeps and frequency sweeps of irradiated samples containing concentrations of CaCO$_3$ varying from 0.25 times the theoretical maximum to 1.5 times the theoretical maximum can be found in Figure 4.10A and 10B, respectively. Time sweeps containing G” are not shown for clarity, but can be found in supplemental information, Supplemental Figure S4.4. It should be noted that the alginate concentration (4 wt./vol.%) and the ratio of PAG to CaCO$_3$ of 2:1 remained constant. As expected, samples containing 0.25 and 0.5 times the theoretical maximum are unable to form microstructures large enough for detection, as an insufficient amount of calcium is available. Frequency spectra of these systems after 2800 seconds of UV irradiation, Figure 4.10B, show solution behavior as G’ is heavily dependent on frequency. However, as the amount of calcium is increased to 0.75 times the theoretical maximum, the solution shows microstructure growth upon irradiation with G’ increasing to a value of 50 Pa. As the concentration of CaCO$_3$ is further increased to the theoretical maximum and 1.5 times the theoretical maximum, samples show faster microstructure growth as the plateau modulus is reached in a shorter period of time. Samples containing increasing concentrations of CaCO$_3$ are able to reach the plateau modulus more quickly as a larger amount of calcium ions are available for crosslinking, which reduces the amount of time required for the ions to diffuse through the microstructure and find available G-blocks. Frequency spectra of samples containing greater
than 0.5 times the theoretical maximum show gel behavior as $G'$ is independent of frequency and of magnitude greater than $G''$, Figure 4.10B, inferring that a minimum quantity of crosslinks, and thus available Ca$^{2+}$ ions, is required for the formation of any detectable microstructure. Increasing the number of crosslinks produces stronger gels, as $G'$ increases from 50 Pa to 400 Pa when the concentration of CaCO$_3$ is raised from 0.75 times the theoretical maximum to 1.5 times the theoretical maximum. An increase in the concentration of CaCO$_3$, and thus available Ca$^{2+}$ ions, allows for a greater quantity of crosslinks between G-blocks on adjacent alginate chains to form, creating stronger microstructures with a larger magnitude of $G'$. Interestingly, samples containing the theoretical maximum and 1.5 times the theoretical maximum have equal plateau moduli (400 Pa). The final modulus remains unaffected since all of the available G-blocks on the alginate chain are occupied by calcium ions, despite there being excess Ca$^{2+}$. Although gelation kinetics and gel strength are improved with excess CaCO$_3$, the maximum gel modulus remains unaffected, as this value is determined by the quantity of G-blocks in the system when calcium is in excess. These findings are consistent with previous literature stating that the gel strength is directly related to the fraction of G-blocks within the sample.$^{42}$

Additionally, the concentration of alginate can be modulated while maintaining the calcium concentration to be 1.5 times the theoretical maximum. It must be noted that the theoretical maximum amount of calcium was adjusted for each sample, since this value depends upon the quantity of G-blocks which is directly affected by the concentration of alginate. A minimum alginate concentration is required for the formation of a microstructure large enough for detection as time sweeps of systems containing 1 wt./vol.% alginate during
constant UV irradiation show no change in G’, Figure 4.11A. Frequency spectra after 1800 seconds of UV irradiation for this system show solution behavior as G’ and G” are dependent upon frequency, Figure 4.11B. Time sweeps of samples containing alginate concentrations ranging from 2 wt./vol.% to 4 wt./vol.% during constant UV irradiation show growth in G’ over time, indicating the formation of an internal microstructure. The concentration of alginate is directly proportional to the magnitude of the final gel modulus, depicted via frequency spectra, Figure 4.11B. Increasing the alginate concentration introduces a higher quantity of G-blocks, which presents a larger number of potential crosslinking sites, creating an intricate and stronger microstructure. This provides another means of altering the final gel properties dependent upon the desired magnitude of G’ which is usually application dependent.

4.4 Conclusions

We have performed an in situ rheological study of a two-step physical crosslinking method for the fabrication of UV initiated alginate hydrogels. UV irradiation is used to photolyzed a photoacid generator, which releases acid causing the dissociation of dispersed CaCO₃ particles and liberation of Ca²⁺ ions to form egg-box junctions with adjacent alginate chains. Gel points for a system of 4 wt./vol.% alginate with 60 mM PAG and 30 mM CaCO₃ were determined using an empirical approach which monitors strain over time and was shown to correlate well with the Winter-Chambon criteria for gel point determination. Time required for gelation decreases as the UV intensity increases, since a larger amount of energy is emitted into the system, thereby photolyzing a larger quantity of PAG molecules and
further allowing a larger concentration of Ca\(^{2+}\) ions to release. Most interestingly, evidence of microstructure growth in the absence of UV light, also known as dark curing, was observed. Some samples even transition from the sol state to the gelled state during the dark curing phase. For our system irradiated at an intensity of 175 mW/cm\(^2\), the extent of dark curing increases with UV exposure time up to 90 seconds. Longer durations of exposure allow ample time for the sample to crosslink during UV irradiation, causing the extent of dark curing to decrease. Dark curing is a direct result of the two-step crosslinking mechanism, specifically the time required for Ca\(^{2+}\) to diffuse to available G-blocks and a persistent acidic environment which allows for the release of Ca\(^{2+}\) ions in the absence of UV light. A relationship between the final gel modulus and energy input provides a means to tailor the final elastic modulus by modulating the energy input. As reciprocity is exhibited by this system, the final elastic modulus can be predicted by energy input, providing a means to tailor samples despite differences in UV intensity for varying UV sources by simply modulating the duration of UV exposure and irradiation intensity. The crosslinking mechanism remains unaffected by dark curing, as samples exposed to UV irradiation for a short period of time and then subsequent continuous UV irradiation produce gels with the same modulus as a sample continuously exposed to constant UV irradiation. Lastly, the effects of composition such as alginate concentration and the ratio of alginate and CaCO\(_3\) on gelation kinetics and final gel modulus were investigated. A minimum concentration of calcium (0.5 times the theoretical maximum) and alginate (2 wt./vol.\%) were both required for the formation of a microstructure large enough for detection. Increases in CaCO\(_3\) and alginate concentrations enhance the gelation kinetics and gel strength. Interestingly, the final
elastic modulus is highly dependent upon the quantity of G-blocks since the final elastic modulus remains unchanged when the CaCO$_3$ concentration is greater than the theoretical maximum. In this case, once all available G-blocks have bonded with Ca$^{2+}$ ions, excess calcium ions are unable to form any further crosslinks. Additionally, the final gel modulus increases as the alginate concentration increases since the quantity of G-blocks available for crosslinking has increased. Overall, this system provides a means for fabricating alginate hydrogels upon UV irradiation, but specifically, the dark curing phenomenon provides a means to tailor the final elastic modulus by modulating the energy input into the system without having to alter the gel composition. This alginate hydrogel system would be suitable in a plethora of applications as a wide range of elastic moduli magnitudes are easily attained by simply modulating composition and processing parameters.

4.5 Acknowledgements

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4.6 References


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Figure 4.1. Conformations of β-D-mannuronate (M) and α-L-guluronate (G) residues found in alginate and the possible block sequences along the alginate backbone. Visual representation of the two-step UV initiated alginate crosslinking reaction with PAG and CaCO$_3$. Adapted from Javvaji et al.$^{13}$
Figure 4.2. (A) Frequency spectra of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM of CaCO₃ before and after UV irradiation of 175 mW/cm². (B) Time sweep at 1 rad/s of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO₃ during constant UV irradiation at 175 mW/cm².
Figure 4.3. (A) Tan δ versus time for 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO₃ at varying frequencies, showing the gel point occurs at 200 seconds at constant UV irradiation of 175 mW/cm². (B) Monitoring of samples strain over time at frequency of 1 rad/s. The gel point occurs at the minimum of the derivative of strain with respect to time. Both methods match very well.
Figure 4.4. (A) Time sweeps and (B) frequency spectra of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$ at varying UV intensities of 75 mW/cm$^2$ to 275 mW/cm$^2$. (C) The gel point scales as $GP \sim I^{-0.65}$, providing a means to predict the gel point for different UV intensity.
Figure 4.5. (A) Time sweep of $G'$ for samples of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$ after varying durations of UV exposure (20 seconds to 240 seconds) and continuous UV exposure at an intensity of 175 mW/cm$^2$. (B) Frequency spectra for samples after dark curing phase for samples subjected to UV irradiation for 20 seconds, 90 seconds, 240 seconds, and continuous UV exposure.
Figure 4.6. Time sweep for 4 wt/vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$ subjected to four 20 second doses of UV irradiation at 175 mW/cm$^2$, indicated by the shaded areas. Frequency spectra show the state of the sample in region 1, region 3, and region 4.
Figure 4.7. (A) The extent of dark curing as a function of UV exposure time for 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$ at UV intensity of 175 mW/cm$^2$. (B) Plot of $G'$ after the dark curing phase as a function of energy input for 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$.
Figure 4.8. Time sweeps and corresponding frequency spectra of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$ for energy inputs of (A,C) 66 Joules and (B,D) 133 Joules.
Figure 4.9. (A) Time sweep and (B) frequency spectra of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$ exposed to UV irradiation at 175 mW/cm$^2$ for 180 seconds and then subsequent continuous UV exposure, shown by the shaded regions. (C) Frequency spectra showing the magnitude of $G'$ for a gel exposed to constant UV irradiation can be obtained with continuous UV exposure after short durations of UV exposure equals to 180 seconds, 240 seconds, and 450 seconds.
Figure 4.10. (A) Time sweeps and (B) frequency spectra of 4 wt./vol.% alginate with varying concentrations of CaCO$_3$, ranging from 0.25 to 1.5 times the maximum theoretical amount.
Figure 4.11. (A) Time sweeps and (B) frequency spectra of samples containing varying concentrations of alginate, while maintaining a calcium concentration of 1.5 times the maximum theoretical amount, subjected to UV irradiation of 175 mW/cm².
4.7 Supplemental Information

Figure S4.1. Time sweeps of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO₃ exposed to UV irradiation at varying intensities. The $G'$-$G''$ crossover is delayed as the irradiation intensity decreases.
Figure S4.2. Time sweeps of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO₃ subjected to UV irradiation for varying durations of exposure.
Figure S4.3. A plot of the change in pH of 4 wt./vol.% alginate, 60 mM PAG, and 30 mM CaCO$_3$ over time during and after exposure to UV irradiation, shown by the shaded regions. The pH is shown to drop when the sample is irradiated, but then increases as the acid is consumed in the dissociation reaction of CaCO$_3$. 
**Figure S4.4.** Time sweeps monitoring $G'$ and $G''$ over time for 4 wt./vol.% alginate containing varying concentrations of CaCO$_3$ when exposed to UV irradiation.
CHAPTER 5

Conclusions and Recommendations
5.1 Conclusions

In the preceding chapters, we explored the process-structure-property relationships for two classes of functional materials: electrospun nanofibers and gels (both chemically and physically bonded). We investigated the effects of modulations in processing parameters on the fabrication and final properties of electrospun nanofibers from foam electrospinning, a novel, needle-less electrospinning technique. Furthermore, we used rheological techniques to characterize the evolving microstructures of a thiol-acrylate polymerizing system and a photoinitiated alginate hydrogel. Some of the major findings are summarized below.

Chapter 2. We developed and characterized a novel, needle-less electrospinning setup capable of simultaneous fabrication of multiple nanofibers. In this foam electrospinning process, the electric charge must be distributed through the polymer solution in order to facilitate electrospinning. Other processing parameters such as collection distance, electric field strength, and polymer concentration (polymer chain entanglement) follow similar trends seen in syringe electrospinning. A minimum collection distance and electric field strength are required for adequate solvent evaporation and uniform fiber fabrication. Interestingly, the empirical correlation between polymer entanglement and electrospinnability used to predict the concentration required for uniform fiber fabrication in syringe electrospinning also applies to the foam electrospinning setup for poly vinyl alcohol (PVA) and poly-ethylene oxide (PEO). This implies that solutions shown to syringe electrospin would also fabricate uniform fibers in the foam electrospinning setup without the need for additional experiments to identify the “electrospinning window.” Lastly, the polymer throughput and crystallinity
within the electrospun fibers increased when comparing foam electrospun with syringe electrospun fibers.

Chapter 3. Using dynamic oscillatory experiments coupled with a multiwave rheological technique, we were able to determine the evolving rheological properties (e.g., viscous and elastic modulus) as a function of time and further relate the macroscopic gel properties with the microstructure for a thiol-acrylate system. In addition, the gel points were determined using the Winter-Chambon criteria as a function of in situ catalyst concentration. The time required for gelation initially decreased as catalyst concentration increased, but after 22 mol% DEA, the time for gelation lengthened as the catalyst concentration continued to increase. This minimum in gel time was attributed to a decrease in overall acrylate functionality, which was confirmed via FTIR. The microstructure of the critical gel was also characterized and a fractal of 1.3 was calculated, referring to an open microstructure with defects which can be attributed to the amine functional groups on the in situ catalyst. The open microstructure and fractal dimension were confirmed using molecular simulations.

Chapter 4. The gelation kinetics and characterization of a photoinitiated alginate hydrogel undergoing physical crosslinking with calcium ions were analyzed in real-time using in situ UV rheology. Calcium ions were successfully released upon UV initiation using a photoacid generator and calcium carbonate. Gel time, which was determined using an empirical method where strain is monitored over time, as a function of UV intensity was shown to decrease as UV intensity increased. This was attributed to a larger amount of
energy entering the system, thereby photolyzing a larger quantity of PAG and releasing more calcium ions in a certain period of time. Dark curing was observed in the system as the acidic environment persisted in the absence of UV light, allowing the sample to continue crosslinking as calcium ions still released. In some instances, the sample transitioned from solution to gel in the dark curing phase. Reciprocity was observed in the system, which led to the development of an empirical relationship that relates energy input to final gel modulus. Additionally, decreasing the concentration of alginate resulted in weaker hydrogels as the number of available crosslinking sites decreased. Changes in the ratio between calcium carbonate and alginate showed a minimum calcium concentration is required for gelation, while concentrations at and above the theoretical maximum concentration of calcium the system may accommodate formed gels with the same final modulus.

5.2 Future Recommendations

In this dissertation, we have discussed the process and solution parameter effects on final properties of electrospun nanofibers from foam electrospinning, a novel thiol-acrylate polymerization scheme, and a photoinitiated alginate hydrogel. The scope of this work can be expanded and some future recommendations are summarized below.

5.2.1 Expansion of foam electrospinning process: foam electrospinning specific process parameters, continuous process, alternate electrospinning systems

In Chapter 2, we discussed the effects of key electrospinning process parameters on fiber properties for foam electrospun fibers. A natural extension of this work would be to
investigate how modulations in parameters specific to foam electrospinning, such as compressed gas type, gas flow rate, gas pressure and funnel porosity, affect the final fiber properties and electrospinnability. Knowledge of the relationship between foam electrospinning specific parameters and their effects on electrospun fiber properties open new avenues for facile control over fiber properties in foam electrospinning. In addition, expansion of this work to the development of a continuous process would also be beneficial. Currently, the system acts as a batch system, but by adding a polymer tank and means of controlling the flow rate of solution entering the process, the electrospinning setup allow for the continuous electrospinning of nanofibers. Work in this area could lead to scaling-up the foam electrospinning process, thereby providing an alternate means for commercialization of electrospun nanofibers. Alternatively, electrospinning literature consists of nanofibers fabricated from a myriad of polymer/solvent systems (e.g. polyacrylonitrile,\textsuperscript{1-4} chitosan,\textsuperscript{5,6} nylon,\textsuperscript{7,8} etc.). We have demonstrated that foam electrospinning is capable of fabricating nanofibers from aqueous systems, but it would be interesting to analyze the electrospinning window for non-aqueous polymer systems. Research into this endeavor would provide a means for fabricating electrospun nanofibers at increased production rates for applications where water-soluble polymers may not be used.

5.2.2 Distribution of nanoparticles and/or other solution components within electrospun/composite fibers from foam electrospinning

Currently, interest in the fabrication of electrospun nanofibers containing nanoparticles,\textsuperscript{4,9} conductive platelets,\textsuperscript{10} or other biological moieties\textsuperscript{11-13} has gained
momentum in applications such as energy storage, wound dressings, and drug delivery.\textsuperscript{1,14} For example, nanofibers containing silver nanoparticles provide antimicrobial qualities for exceptional wound healing,\textsuperscript{15} while fibers containing carbon nanotubes or graphene have been used as cathodes for batteries.\textsuperscript{16} It has been shown that the distribution of these added moieties, especially when conductive or charged, may be affected by the electric field during the electrospinning process. For instance, gold nanoparticles have been shown to align within PEO nanofibers.\textsuperscript{17} In addition, it has also been shown that depending on the charge on biological moieties such as enzymes, their location in the nanofiber can be adjusted to either the surface or interior core of the fiber.\textsuperscript{12} Although, a small number of papers have been published on the distribution of functional moieties within nanofibrous structures, all of these studies have focused on syringe electrospun fibers. It would be interesting to investigate the distribution of nanoparticles on or within foam electrospun fibers. It should be pointed out that in syringe electrospinning, the jet initiates from a point source while in foam electrospinning, the jets initiate from the curved surfaces of bubbles, which we expect would lead to a different electric field. Additionally, as the electric field would depend on the surface of the foam, it may be possible to control the deposition or placement of the functional moieties on the electrospun nanofibers by modulating the bubble sizes within the foam.

5.2.3 Alginic hydrogels with multiple crosslinking methods

Hydrogels from crosslinking alginate are typically either formed by physical crosslinking or chemical crosslinking. Both methods possess advantages and disadvantages,
mainly the tradeoff between strength, controlled degradation, and cytotoxicity. Physically crosslinked gels are widely accepted as more biocompatible compared to their counterparts, since chemically crosslinked gels require toxic chemical reagents for chain modification or initiation.\textsuperscript{18-20} However, physically crosslinked gels are generally weaker with unpredictable degradation rates. Interestingly, chemical crosslinking gels are shown to produce stronger gels with more controlled degradation rates.\textsuperscript{18,20} Research has expanded into producing systems able to chemically and physically crosslink to combine the advantages of both methods in one product.\textsuperscript{21,22} Robb et al.\textsuperscript{23} and Lee et al.\textsuperscript{24} reported the combination of chemical and physical crosslinking for hydrogels composed of poly(NIPAAm-co-cysteamine) improved mechanical properties compared to gels created by physical crosslinking alone. Developing an alginate system capable of both chemical and physical crosslinking is a natural extension of the work presented here, as it may provide a means to fabricate strong, biocompatible alginate gels with controlled degradation rates. One example could be combining the photoinitiated system presented here with the methacrylated alginate previously reported in our group.\textsuperscript{18,25}

5.2.4 Rheology of alginate hydrogels with on-demand reversible gelation mechanism

The ability to form hydrogels possessing triggered gelation from external stimuli (e.g. temperature, UV light) is very beneficial for in situ gelation applications, more specifically biomedical applications. Many hydrogels are used for the release of biological moieties such as cells and drugs, thus degradation rate is an important aspect as well.\textsuperscript{20,26,27} The alginate system discussed in this dissertation has been shown to reverse from a gel to a
solution upon the addition of a chelating agent. The calcium ions preferentially bond with the chelator over the alginate chains, thus destroying the bonds of the microstructure. Future work in this area could include the development of a system with triggered release of chelating agents. Some methods used to trigger release are changes in temperature or pH, as well as shear-induced release. A rheological study of the gel degradation would also be beneficial to characterize the process and gather a better understanding of the mechanism. Lastly, if a means to release the calcium ion could be obtained, it would be interesting to characterize the transition from a solution to a gel, the degradation of the gel back to the solution, and gelation of the microstructure again. This system could be used as a drug delivery vehicle with slow controlled release of drug and then an on-demand burst release as the microstructure decomposes.

5.2.5 Rheology of alginate hydrogels containing biological moieties

Alginate hydrogels are heavily used for drug delivery and biomedical applications due to its biocompatibility, ease of crosslinking with divalent cations, among others. In addition, alginate hydrogels are great candidates for cell or enzyme encapsulation as their high water content can allow for movement within the microstructure. Research has typically focused on the incorporation of enzyme/cells within the microstructure and maintaining cell viability for tissue engineering applications. The Mooney group in particular has reported an increase in modulus from cells attaching to peptide-modified polymer chains. The rheological properties during the crosslinking reaction would be heavily affected by the attachment/presence of cells within the system and would be of interest to
investigate. In addition, it would be interesting to analyze the viability of the cells during any steady shear experiments. This type of study would be beneficial for analyzing the effects of processing parameters on hydrogel properties containing cells or enzymes.
5.3 References


APPENDICES
Appendix A

Progress Report Towards Melt Electrospinning With Supercritical Carbon Dioxide
Abstract

The purpose of this study is to successfully construct a melt electrospinning process able to fabricate sub-micron diameter fibers, and then investigate relationships between key process parameters and nanofiber characteristics. Industrially relevant polymers such as poly(ethylene terephthalate), poly-(ε-caprolactone), polypropylene, will be used as model electrospinning systems. This technique may also incorporate the plasticization effects of supercritical carbon dioxide or other additives in order to lower the polymer melt viscosity and fabricate fibers with decreased diameters.

A.1 Introduction

Electrospinning is a technique currently employed to produce nonwoven mats composed of fibers with diameters less than 500 nm (nanofibers). The setup is typically composed of three main parts: power supply, spinneret, and collection plate. A direct current (DC) is applied to the system in which a polymer solution is simultaneously pumped through the spinneret. The protruding pendant drop is subjected to a high voltage field and as a result of the induced charge, the droplet distorts into a conical shape known as a Taylor cone. With increasing electric field, the droplet ejects towards the collector plate, undergoing a whipping instability and solvent evaporation which both greatly diminish the jet diameter. The jet is then deposited on the collector plate, resulting in a nonwoven nanofiber mat.

Although a promising technique, electrospinning typically requires the use of toxic solvents and is also a low throughput process. In order to improve upon these drawbacks, this project focuses on developing a high throughput electrospinning process capable of
fabricating fibers from the melt phase, thereby negating the use of toxic solvents. The use of polymer melts also provides a more diverse selection of electrospinnable polymers, such as polyethylene and polypropylene, which do not have suitable solvents at room temperature. However, polymer melts have higher viscosities than polymer-solvent solutions which impede the formation of fibers during electrospinning. We propose that supercritical carbon dioxide (scCO\textsubscript{2}) can be used as a plasticizing agent to lower the viscosity of the melt. It is also proposed that a mathematical model be developed to further understand the dynamics of melt electrospinning.

The specific objectives of this project include the following:

- Designing and constructing a high throughput melt electrospinning process
- Investigating various process parameter effects on electrospun fiber morphology and characteristics
- Study the effects of spinning atmosphere on formed fibers
- Extend process to more advanced methodologies such as core-sheath electrospinning and other industrially relevant polymer melts

### A.2 Extrusion Based Melt Electrospinning Process

A melt electrospinning setup has been designed and constructed using a single screw extruder, collection drum, and power supply. A schematic of the setup can be seen in Figure A.1. Polymer pellets are deposited into the hopper and distributed throughout the extruder barrel. Band heaters are placed around the extruder barrel allowing control over the temperature in four separate heating zones. The pressure and temperature of the spinneret are monitored and controlled via pressure transducers and additional band heaters. The screw rotations per minute (RPM) are controlled on the extruder, which further allow us to control the flow rate of the polymer melt out of the spinneret. A power supply is used to charge the
collector plate, which has the geometry of a rotating cylinder. Once an electric field is applied between the spinneret and rotating cylinder, polymer jets eject towards the charged collector plate, resulting in electrospun fibers. The rotating cylinder used in this setup also provides an additional tensile force which may further diminish the fiber diameter.

During preliminary experiments, low screw RPMs result in a high polymer flow rate with a single-holed spinneret. The higher flow rates do not allow ample time for the induced charges from the electric field to collect upon the droplets of polymer melt, resulting in an inability to electrospin. A spinneret containing twenty holes of (150 micron diameters each) was constructed in order to decrease the flow rate of polymer melt exiting the apparatus. This distributes the extruder flow rate across the face of the spinneret, resulting in an overall lower flow rate per hole. This also provides the added advantage of electrospinning several fibers simultaneously. The addition of the multiple-holed spinneret allows ample time for the electric field to induce charges great enough to pull the polymer jet towards the collection roller.

A.3 Preliminary Results

Once the overall setup was constructed, experiments commenced using bottle-grade virgin PET pellets donated from Voridian. Characteristic data of the pellets can be found in Table A.1. Several experiments were performed to investigate the effect of spinneret to collector distance in the melt electrospinning setup on the fiber formation, morphology, and structure. Table A.2 lists the parameters of each PET experiment performed with the collection roller standing still. It should be noted that the spinneret pressure consists of a
range of values. This is due to the fact that the RPMs used are near the limitations of the machine. As a result of these limitations, the extruder would surge, producing a change in pressure as the amount of polymer being pushed out would fluctuate slightly.

During these experiments, the collection roller did not rotate and electrospun fibers were collected on the face of the roller. The polymer jets experience a whipping instability similar to that observed in polymer-solvent solution electrospinning. However, due to the higher viscosity of polymer melts compared to polymer-solvent solutions, the whipping is suppressed. As a result, the polymer jets move in a circular motion and collect on the face of the roller in a nonwoven formation. In Figure A.2, is a picture of the polymer jets whipping as they are collected on the surface of the collection roller.

Scanning electron microscopy (SEM) was used to further investigate the morphology and structure of the collected electrospun fibers, shown in Figure A.3. Using ImageJ software to measure the fiber diameters, we found that the average diameter is greatly affected at closer distances to the spinneret. The average diameter and the standard error for each collection distance investigated can be found in Table A.3, while Figure A.4 contains the fiber diameter distribution at each collection distance.

As can be seen in Figure A.4, the range of fiber diameters in each sample, represented by the gray area in the graph, stays relatively constant for collection distances between 6 cm and 10 cm. However, at distances greater than 10 cm, the diameter range begins to broaden. From this, we conclude the diameter of the as-spun fibers are significantly affected by tip to collector distances between 6 and 10 cm. The main drawing mechanism in melt electrospinning is the drawing force exerted on the filament from the electrostatic charges,
which are directly proportional to the strength of the electrical field applied to the system. The electrical field is a function of applied voltage and spinneret to collector distance. As the collector distance decreased, the strength of the electrical field increased, thus the drawing force was able to reduce the diameter of the filament further. However, as the tip-to-collector distance increases, the fiber diameter distribution broadens, while the diameters remain unaffected. We believe this to be due to the solidification of the filament. As the filament exits the extruder and flies towards the collection roller, heat dissipates from the jet, further limiting the mobility of the fiber chains. When the temperature drops below the solidification temperature (260°C for PET), the polymer chains are no longer mobile, rendering the electrostatic drawing forces ineffective. Zhou et. al. found similar findings in their study with melt electrospinning poly-lactic acid.\(^1\) For this specific system, this effect occurs at 10 cm. This implies that the time taken for the filament to travel 10 cm from the extruder is the same amount of time needed for the jet to cool to a temperature below the solidification temperature. It should also be noted that interference amongst adjacent fibers in the whipping instability region may also be contributing to the broad diameter distributions (ranging from 60 – 120 micron). This has been reported in several articles that have previously researched the use of multiple spinnerets.\(^2\)-\(^4\)

In an attempt to obtain smaller diameter fibers, the collection roller was added to the system, as it would provide additional tensile force to help attenuate the fiber diameter and serve as a means to collect the fibers. Parameters for these experiments can be found in Table A.4.
After each experiment, the fibers were removed from the collection roller and imaged in order to characterize the fiber morphology and properties. Final fiber diameters remain relatively unchanged, ranging between 10 and 20 µm for all collection distances investigated (6-20 cm). This is significantly lower than fiber diameters fabricated from our setup without the rotating cylinder. The decrease in fiber diameter is attributed to the additional tensile force from the collection roller. The standard error, maximum, minimum, and average fiber diameters are listed in Table A.5. SEM micrographs can be seen in Figure A.5. By graphing the average diameter versus the collection distance, as shown in Figure A.6, it is clear that the diameter does not change dramatically with collection distance when a rotating cylinder is employed. We believe that the diameter remains relatively unchanged due to the tensile force exerted on the polymer jet from the rotating collection roller. Although, the fiber diameter is greatly reduced when the collection roller is rotating at 350 RPM compared to 0 RPM. The attenuation from the tensile force is much greater than that experienced due to the whipping instability characteristic of electrospinning. This implies that the external tensile force is the main drawing mechanism, which is comparable to melt spinning. In this process, the fibers are attenuated and collected by rotating drums in the absence of an electric field. However, it should be noted that fiber formation occurs only when an electric field is applied. During experiments with no applied voltage, the polymer remains on the face of the spinneret.

It should also be noted that not all orifices were capable of producing electrospun fibers. In most experiments, the inner most orifices on the multiple-holed spinneret were unable to form filaments that stretched towards the collection plate since the molten polymer
would remain on the face of the spinneret. We believe this may be due to a lack of uniformity of the electrical field on the face of the spinneret. Niu et. al. \(^5\) investigated the electrical field profile on the surface of a rotating cylinder and a rotating disk electrode for solution electrospinning using poly vinyl alcohol (PVA). They discovered that the electrical field profile for a disc electrode was uniform in all directions. Additionally, the profile for a rotating cylinder electrode showed a peak on the two ends of the cylinder, but a diminished strength along the length of the cylinder, showing a lack of uniformity along the electrode. When applying the same voltage to each system, the strength was also compared. The strength of the electric field was consistently stronger using the disk electrode when compared to the peaks on the rotating cylinder electrode, when applying the same voltage. As a result, a lower voltage can be applied to the disc collector system to induce electrospun fiber formation since the electrical field strength is stronger. We believe the electrical field distribution on the spinneret face is similar to that seen on the rotating cylinder.

### A.4 Project Challenges

Despite the ability to produce submicron fibers, the processing window for the fabrication of such fibers is still relatively small, and challenges relating to competing factors between the electrospinning process and the extruder still remain. A list of the main challenges associated with the extruder is listed below:

- **Viscosity conflicts:** The extruder requires the use of relatively viscous polymer melts in order to sufficiently propel the melt through the barrel. The electrospinning process is most successful with less viscous solutions/melts. The electrostatic charges serve as
the main drawing force, and more viscous solutions cannot stretch or whip as readily as less viscous solutions, resulting in larger fiber diameters.

- **Flow rate conflicts:** Due to the large dimensions of the extruder, the flow rate exiting the spinneret holes can be relatively large. Electrospinning typically requires a lower flow rate. This allows the induced charges to congregate on the solution/melt droplet, concentrating the electrostatic charge per gram of solution/melt. The concentrated electrostatic charges tend to reduce the fiber diameter greater.

- **Spinneret issues:** A multiple holed spinneret was manufactured in order to reduce the flow rate per hole, so that submicron fibers could be fabricated. However, the design of the spinneret with the extruder does not allow for all holes to receive the same pressure. Thus, the flow rate of each hole is not the same. Additionally, every hole does not produce a fiber (this may be a cause of too low of electric field).

- **Polymer degradation issues:** Due to the lower flow rates necessary for the electrospinning process, the polymer pellets would remain the melt phase at high temperatures for prolonged periods of time, resulting in polymer degradation within the barrel.

**A.5 Summary**

Experimental work has found that the collection distance plays an important role in extrusion based melt electrospinning up to a critical distance, whereupon at further distances, the diameter remains relatively unchanged. This is most likely due to the temperature of the fiber dropping below the solidification temperature, preventing further attenuation. As such,
the heat transfer dissipating from the fiber filament will be an important parameter to investigate and predict when utilizing melt electrospinning. We have also discovered that the addition of a rotating collector drum can decrease the electrospun fiber diameters to below 20 μm. While this is still not in the nanometer range, the fiber diameter is still reduced over an order of magnitude.

Our findings from electrospinning with PET can be summarized by the following bullets:

- At close collection distances (< 12 cm), the fiber diameter is significantly affected. The diameter is directly proportional to collection distance, due to an increase in electrostatic charges (the major drawing force).
- At larger distances (> 12 cm), the fiber diameter remains unaffected. As heat transfers from the molten filament to the atmosphere, the fiber cools to a temperature below the solidification temperature, inhibiting translational movement of the polymer chains. The electrostatic drawing forces are unable to further reduce the diameter of the fiber.
- With the collection roller rotating at 350 RPMs (max RPM available), fibers of diameters ~10 microns can be fabricated since the drawing force from the collection roller overpowers the electrostatic drawing forces.
A.6 References


**Figure A.1.** Extrusion based melt electrospinning setup

<table>
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<tr>
<th>Table A.1. PET pellet characteristics</th>
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<p>| Table A.2. PET experimental parameters without the collection roller |
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Figure A.2. Poly (ethylene teraphthalate) polymer jet, redrawn for emphasis, whipping instability with an electric voltage of 35 kV, collection distance of 20 cm, and a spinneret temperature of 290°C.

Figure A.3. SEM micrographs of extrusion based melt electrospun fibers with applied voltage of 35 kV and extruder screw speed of 1 RPM, at a) 6 cm collection distance, and b) 16 cm collection distance.
Table A.3. Average, maximum, and minimum fiber diameters, along with standard error at varying collection distances for electric field voltages of 35 kV, screw RPM of 1, and no collection roller

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<th>Sample</th>
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Figure A.4. Diameter distribution for electrospun PET fibers at varying collection distances with a voltage of 35 kV, screw RPM at 1, and no collection roller.
### Table A.4. PET experimental parameters with the collection roller

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### Table A.5. Average, maximum, and minimum fiber diameters, along with standard deviation at varying collection distances for electric field voltages of 35 kV, screw RPM of 1, and collection roller at 350 RPMs.

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Figure A.5. SEM micrographs of extrusion based melt electrospun fibers with applied voltage of 35 kV, collector speed of 350 RPM, extruder screw speed of 1 RPM, at a) 6 cm collection distance, and b) 16 cm collection distance.

Figure A.6. Average diameter with standard deviation at varying collection distances with an applied voltage of 35 kV, a collector take-up speed of 350 RPM, and screw RPM of 1.
Appendix B

Progress Report Towards Melt Electrospinning With Adhesive Polymers
Abstract

The purpose of this project is to investigate the relationship between polymer properties (viscosity, hydrophobicity, conductivity, etc.) and the electrospinnability of the polymer, as well as fiber properties (adhesive strength, mechanical strength, uniformity, average fiber diameter, etc.). We first present a single capillary process as a small scale melt electrospinning setup. Then we utilize a melt-on-demand system which possesses interchangeable application nozzles and provides facile control over polymer flow rate and 4 distinct temperature zones. This allows us the ability to investigate the polymer-fiber property relationships without hindrances experienced when melt electrospinning using a single barrel extruder. This study includes investigating effects of electrostatic forces, melt viscosity, and the incorporation of compressed air on the average fiber diameter of electrospun fibers fabricated from adhesive polymers (DHM 2442 and DHM 1314). Due to the low electric conductivity of polymer melts, the electrostatic force remains ineffective in decreasing fiber diameter. However, decreasing melt viscosity by increasing operating temperature can decrease the fiber diameter by about 35% to 60 μm. Degradation is also not an issue at high operating temperatures, as shown by thermal gravimetric analysis data. Lastly, inclusion of compressed air can attenuate the diameter of the polymer jet significantly. Combination of higher operating temperatures and compressed air may lead to further decreases in fiber diameter.
B.1 Introduction

We hope to use adhesive polymers to modulate polymer properties and investigate their effects on fiber uniformity and properties such as diameter distribution and adhesion properties. Electrospinning fibers directly from adhesive polymers decreases the amount of processing steps by removing the need for surface modification for the production of composite nonwovens in a variety of applications.

Our goal is to relate macroscopic and microscopic polymer properties with the quality and properties of the fibers produced. In particular, we focus on melt electrospinning polymers currently used for adhesive applications, provided by DHM Adhesives. Fabricating fibers directly from adhesive polymers provides a single step process for the production of nonwoven composites, rendering surface modification an unnecessary step.

Instead of focusing on a novel process and polymer systems that are typically not used for fiber fabrication, we propose to transition to a more manageable, existing technology that is easily scalable. The smaller dimensions of the existing technology will allow us to focus more predominantly on the materials used in the melt electrospinning process. We plan to characterize industrially relevant polymer systems and relate macroscopic and microscopic polymer properties with fiber quality and properties. In particular, we hope to focus on melt electrospinning polymers currently used for adhesive applications. We hope by fabricating fibers directly from adhesive polymers, modification of fiber surfaces may be unnecessary, resulting in fewer processing steps for the production of nonwoven composites for various applications. The specific objectives of this project include the following:
• Designing and constructing a melt electrospinning process comprised of a melt on demand system and means to finitely control polymer melt flow rate.
• Investigating various polymer property effects on electrospun fiber morphology and characteristics
• Investigate various process parameter effects on electrospun fiber morphology and characteristics.

B.2 Single Capillary Melt Electrospinning Process

A glass syringe is wrapped with electrical heating tape, in order to control the temperature of the adhesive polymer within the syringe. As the polymer pellets melt, gravity forces the polymer through the capillary at a slow rate. A charge is applied to a metal collection plate located below the syringe, producing melt electrospun fibers from a single capillary, Figure B.1. Initially, the experiments were performed inside of a fume hood. However, air streams within the hood pulled fibers away from the nozzle and collection plate. Additionally, when increasing the applied voltage above 40 kV, arcing and charging in the system was observed, and as a result, the single nozzle set up was moved inside of an electrospinning chamber constructed for the melt-on-demand electrospinning process. In order to control degradation issues in the single nozzle apparatus, aluminum foil was wrapped around the glass syringe to act as a heat sink so that the system could heat a slower rate, thereby not overshooting the setpoint temperature of 177°C.
B.3 Preliminary Results – Single Capillary Set Up

Initially, the single capillary setup was used to preliminarily investigate effects of melt electrospinning parameters on final fiber properties for melt adhesives. The first parameter investigated was the effect of electric field strength at a collection distance of 10 cm and temperature of 177°C for adhesive DHM 2442 (DHM Adhesives, used as received), the specifications of which can be found in Table B.1. SEM micrographs and corresponding fiber diameter distributions at varying electric field strengths can be found in Figures B.2 and B.3. Preliminary experiments show a slight indication that the average fiber diameter decreases with increases in the applied voltage. Continued research should be performed on this system to better understand the melt electrospinning process dynamics.

B.4 Melt-on-Demand Melt Electrospinning Process

In order to resolve the degradation and flow rate control issues associated with the extruder, we focused on using an existing melt-on-demand technology. Melt-on-demand technology uses drop-in grids to melt the specific amount of polymer necessary for operation rather than having large batches of pellets in the melt phase in reserve. The specific melt-on-demand system used in this study is the Dynatec Dynamelt S Series Adhesive Supply Unit (ASU) paired with Dynatec multiple holed dies, Figure B.4. This specific piece of equipment provides several benefits. The machine allows for facile control over four distinct temperature zones: pre-melt hopper, hopper, hose, and application head. The degradation issues are resolved by using the melt-on-demand process, while the flow rate issues are resolved by using a high accuracy pump capable of pumping a low volume of melt per
revolution. Additionally, the geometry of the applicator die can be modulated by using Dynatec dies with different orifice sizes and number of orifices, which can be used to lower the flow rate per hole even further if flow rate issues occur. Similar to the melt electrospinning set up utilizing the single barrel extruder, the system is grounded while a positive charge is applied to the collector plate. As a safety precaution to prevent arcing in the system, we wanted to isolate the electric field as much as possible. As a result, a plastic chamber was constructed to enclose the electrospinning area, Figure B.4. In order to change the tip to collector distance, the application head was mounted to a bar which was further mounted to metal bars with slots allowing us to raise or lower the application head. Additionally, nonconductive supplies can be used to raise the charged collection plate towards the application head in order to analyze small tip to collector distances.

**B.5 Preliminary Results – Melt-on-Demand Setup**

**B.5.1 Apparatus Configuration**

Experiments were also performed using the Dynamelt ASU setup. Polymer flow rate emerging from the melt-on-demand system was calculated using the following equation:

\[
\text{Flow rate (g/min)} = \left[ \text{Pump rate (cm}^3/\text{rev}) \right] \times \left[ \text{RPM (rev/min)} \right] \times \left[ \text{specific gravity (g/cm}^3) \right]
\]

with pump rate equal to 2.92 cubic centimeters per revolution (cm\(^3\)/rev). The flow rate per hole is calculated by dividing the overall flow rate by the number of orifices in the die. Electrospinning with DHM 2442 and a multiple-holed die containing 17 holes results in
molten polymer streams exiting the die when operating at 2 RPMs, Figure B.5A. However, the flow rate per hole using a 17-orifice die and the 2.92 cm\(^3\)/rev pump calculated to be around 0.3 g/hole-min even when operating at 2 RPMs. This flow rate per hole is too high to electrospin, as polymer filaments collect on the charged collector plate before the electrostatic charges are able to accumulate on the filament. In order to alleviate this issue, a smaller capacity high accuracy pump capable of operating at 0.297 cm\(^3\)/rev was used. When operating the smaller pump at 1.7 RPM, a flow rate equal to 0.1 g/hole-min was obtained for a 5-hole die, Figure B.5B.

Once the flow rate issues were resolved, we began an exploration to characterize a few process parameters and their effect on the electrospinnability and quality of fibers produced with this new setup. However, electrospinning with the 5-holed die results in problems with polymer coagulation on the surface of the die. We believe this to be a result of the orifice holes being flush with the die plate. In order to alleviate this issue, we switched to a die which contained polymer orifice holes that protruded from the die plate. The die which we found suitable was a 2-holed die with orifice holes of 16x16 mils. All subsequent experiments use the 2-holed die, a pump rate of 0.8 RPM, flat collection plate geometry, and vertical electrospinning orientation.

From the collected data, it appears that an increase in collection distance (while maintaining constant electric field strength) decreases the average fiber diameter when electrospinning from the Dynamelt ASU, which was also observed with the single capillary setup. The molten filament can elongate for a longer duration of time when the tip to collector distance is increased, resulting in smaller diameter fibers. When looking at the
effect of electric field strength, we see that generally, the fiber diameter decreases when the electric field strength is increased. This would correlate with the thought that the electrostatic drawing force attenuates the fiber diameter. As the applied electric field strength is increased, the electrostatic drawing force should increase as well, thereby pulling the fiber with a stronger force, decreasing the resulting fiber diameter. It should be noted that the experiment performed with no applied voltage (0 kV) was still able to produce fibers of finite length. As the polymer melt exits the die nozzle, gravity pulls the droplet towards the collection plate. As the droplet falls towards the collection plate, the droplet would elongate into a filament, eventually breaking and collecting on the plate. Scanning electron micrographs show smaller diameter fibers are formed with 0 kV compared to experiments when 50 kV is applied at the same collection distance, although, the quality of the collected nonwoven mat is not comparable, Figure B.6.

Unfortunately, a large amount of coagulated adhesive collects directly under the Dynatec nozzle when 0 kV is applied compared to a mat collected when applying 50 kV, when operating in a vertical orientation. Reconfiguration of the apparatus allows electrospinning in a horizontal orientation, as shown in Figure B.7. Results from experiments using horizontal and vertical orientation with similar parameters can be found in Figure B.8. The average fiber diameter remains unaffected by electrospinning orientation, with reduced standard deviations seen for some experiments using horizontal orientation compared to vertical orientation. Although average fiber diameter measurements remain unaltered by orientation, overall mat quality is improved using a horizontal orientation, as only fibers are visible in the mat, Figure B.9. Since the average fiber diameter and overall mat quality
improves using the horizontal orientation, this configuration was used for subsequent experiments.

After reconfiguration, we characterized the quality of fibers produced at various collection distances and applied voltages, in particular examining the effects of electrical field strength. All experiments used polymer adhesive DHM 2442, operating temperature of 177°C, as suggested by the manufacturer, 2-hole die (with hole diameter 16x16 mils), and a polymer flow rate (calculated from the previous equation) of 0.12 g/hole-min, where the pump flow rate is 0.297 cm³/rev, operating at 0.8 rotations per minute. In order to examine the effects of electrical field strength, the applied voltage was modulated while keeping all other parameters constant.

Fiber diameters were measured using ImageJ software and average diameter was calculated from at least 50 fiber diameter measurements. We define electrical field strength as the applied voltage divided by the collection distance. From Figure B.10, we see that the average fiber diameter remains statistically unaffected by changes in electrical field strength. The adhesive polymer is a poly-α olefin, which is structurally similar to low molecular weight polyethylene. The conductivity of polyethylene is reported as $10^{-20}$ S/cm to $10^{-18}$ S/cm, which is at least 10 orders of magnitude lower than values typically seen for polymer solutions used in electrospinning. We believe the fiber diameter remains unaffected by electric field strength as a result of low melt conductivity.
**B.5.2 Polymer Adhesive Characterization at Varying Temperature**

It has been reported that viscosity greatly impacts fiber diameter during melt electrospinning using poly-ε-caprolactone and the melt extruder. Viscosity of polymer melt is known to scale inversely with temperature. In order to take advantage of this relationship, we employed rheological tests to characterize DHM 2442 and DHM 1314 at various temperatures, Figure B.11. Rheology data shown represents at least two trials within a 5% tolerance, error of which is depicted by the size of the data. Polymer pellets were placed on a stress controlled AR2000 rheometer by TA Instruments using 25 mm parallel plate geometry and an environmental temperature chamber (ETC) to control the experiment temperature. When the sample was placed on the rheometer, nitrogen was used at a flowrate of 10 L/min in order to prevent degradation. Once the pellets melted into a single phase, bubbles were removed from the sample, if present, and stress sweeps were conducted from 0.8 Pa to 300 Pa at temperatures ranging from 165°C to 225°C.

Stress sweep data for all temperatures show Newtonian behavior over all applied stresses for both samples. Viscosity also decreases with temperature, as expected. Viscosity is reduced by 50% by increasing the temperature from 177°C to 225°C for DHM 2442 and from 177°C to 205°C for DHM 1314. It should be noted that the viscosity for DHM 1314 at 205°C is approximately equal to the viscosity for DHM 2442 at 225°C, indicating that lower viscosities can be attained at lower temperatures for DHM 1314. By graphing the natural log of the zero shear viscosity as a function of temperature, Figure B.12, the data can be fitted to the following Arrhenius relationship for both samples:

\[
\eta(T) = \eta_0 e^{(E/RT)}
\]
where $\eta(T)$ represents the zero shear viscosity as a function of temperature, $\eta_0$ represents a fitting constant, $E$ is an activation energy, more specifically the heat of motion in an amorphous melt, and $R$ represents the ideal gas constant. From the graphed data, linear fits are used to generate the following equations:

DHM 2442: $\ln \eta(T) = \ln \eta_0 + \left(\frac{E}{R}\right) \cdot \left(\frac{1}{T}\right)$

$\ln \eta(T) = -10.3 + \left(\frac{4757}{T}\right)$

DHM 1314: $\ln \eta(T) = \ln \eta_0 + \left(\frac{E}{R}\right) \cdot \left(\frac{1}{T}\right)$

$\ln \eta(T) = -11.6 + \left(\frac{5102}{T}\right)$

where we obtain the values for $\eta_0$ and activation energy as $3.3 \times 10^{-5}$ and $40$ kJ/mol for DHM 2442 and $9.2 \times 10^{-6}$ and $42.4$ kJ/mol for DHM 1314, respectively. This relationship allows us to predict the viscosity of the polymer at any operating temperature.

In addition to quantifying the viscosity as a function of temperature, degradation rates of the polymer while in the melt phase at elevated temperatures must be addressed. The degradation temperature for each polymer was identified using thermal gravimetric analysis (TGA) using a ramp rate of $10^\circ C/min$ to $900^\circ C$, Figure B.13. Significant degradation does not occur until approximately $400^\circ C$, with $100\%$ mass loss occurring around $500^\circ C$ for both samples. Both temperatures exceed the ASU operating temperature range. Therefore degradation should not play a role when operating between $165^\circ C$ and $250^\circ C$. However, degradation also occurs as a result of long residence times at elevated temperatures. To investigate this phenomenon, TGA was used to study the degradation rate over time at isothermal conditions for temperatures ranging from $165^\circ C$ to $215^\circ C$ for both adhesives, Figure B.14 and B.15. Significant degradation, which we define as greater than $10\%$ loss in mass, is not seen in either sample for temperatures investigated at isothermal conditions over $10$ hours. Additionally, when operating the ASU, the operating temperature is applied only to
the applicator head block, while the other temperature zones are not raised to temperatures significantly above the recommended temperature profile. We assume the residence time in the applicator head block does not exceed 4 hours, even at low operating flow rates. Future work should focus on obtaining the dimensions of the pipes inside the applicator block in order to accurately calculate the residence time of the melt in the applicator head to verify this assumption.

**B.5.3 Effects of Operating Temperature on Fiber Properties using DHM 2442**

By electrospinning at various operating temperatures ranging from 165°C to 195°C, we can analyze the effects of melt viscosity on the electrospinnability and quality of fibers produced. Fibers produced remain relatively uniform, with smooth surfaces, Figure B.16. The average fiber diameter, measured from at least 50 fibers, scales proportionately to viscosity, which correlates to an inverse relationship with operating temperature, Figure B.17. This trend is to be expected. As viscosity of the melt increases, the whipping instability experienced attenuates the fiber to a lesser extent than a less viscous sample. This phenomenon was also witnessed macroscopically as the polymer jets fabricated at an operating temperature of 165°C experienced less movement than those formed at 195°C. It should be noted that at a collection distance of 5 inches and applied voltage of 50 kV, electrospun fibers could not be collected at an operating temperature of 165°C, which correlates to a zero shear viscosity around 1.7 Pa.s. We also believe an inverse relationship between fiber diameter and operating temperature occurs due to heat dissipation from the polymer jets. As the polymer temperature decreases below the softening temperature, which
is reported to be 140°C, attenuation of the jet cannot occur. As the operating temperature is elevated, and consequentially, the viscosity decreased, the temperature of the jet can remain above the softening temperature for a longer duration of time, resulting in more attenuation. When comparing fibers electrospun from DHM 1314 and DHM 2442, the fiber diameter decreases as viscosity decreases, Figure B.18.

**B.5.4 Compressed Air Attenuation Effects**

The Dynamelt ASU is also equipped to include compressed air into the system, Figure B.19. Air enters into the back of the applicator head and exits through air orifices in the face of the Dynatec die. The location and diameter of the air orifices depend on the specific die being used. In this case, each polymer outlet contains two air streams on either side. In order to decrease the fiber diameters further, we equipped the system to comprise compressed air at a pressure of 10 psi and temperature of 177°C. Experiments were performed with and without an applied electric field to analyze potential differences.

The addition of compressed air reduces the fiber diameter by an order of magnitude in some instances, while electrostatic forces seem negligible compared to the attenuation effects from the compressed air, Figure B.20. When utilizing compressed air, the average fiber diameter ranged between approximately 10 and 15 μm, depending on the electrospinning parameters. Additionally, the diameter distribution narrows significantly, which is represented by the height of the whiskers on the boxes. Fiber diameters of this size are comparable to fibers created via spunbond process. However, further attenuation is possible, as shown in an SEM micrograph in Figure B.21. We also note bonding between the fibers,
producing a self-bonded mat in a one step process. This process still continues to show promise in producing uniform nonwoven mats in a one-step melt electrospinning method.

**B.6 Summary**

This project has shifted focus away from developing a successful melt electrospinning process towards identifying polymer properties that can facilitate melt electrospinning by investigating melt electrospinning with adhesive polymers. Adhesive polymers may be interesting to study since we can easily tailor macroscopic properties of the adhesives by modulating microscopic properties of the polymers, such as viscosity, hydrophobicity, polymer type, chain length, etc. which will help us better understand the dynamics of melt electrospinning. We began developing a single capillary melt electrospinning setup utilizing a glass syringe and investigating the effects of applied voltage on average fiber diameter. As the applied voltage increases, the average fiber diameter decreases as well. Additionally, a new melt electrospinning apparatus capable of melting polymer on demand was constructed, thereby negating degradation issues seen in a single barrel extruder. This new apparatus provides facile control over the polymer flow rate and the ability to modulate the number and size of orifices on the applicator nozzle. Using the new Dynamelt ASU apparatus, we have begun investigating the ability to melt electrospin two types of adhesive polymer, DHM 2442 and DM 1314 (amorphous poly alpha-olefin) and the effects of collection distance and applied voltage on the average fiber diameter and diameter distribution. An increase in collection distance or electrical field strength helps elongate the fiber and results in smaller diameter fibers, as was demonstrated with the single
capillary process. We also investigated the effects of electrospinning orientation, electrical field strength, operating temperature and melt viscosity, and incorporation of compressed air into the process on the average fiber diameter and quality of nonwoven mats fabricated. The electrospinning orientation does not significantly affect fiber diameter, however a horizontal orientation improves overall mat quality. When electrospinning horizontally, no change in fiber diameter is seen when modulating the electric field strength. We assume this to be a result of low electrical conductivity, yielding little effect from electrostatic forces. The zero shear melt viscosity was also characterized at several temperatures. An Arrhenius equation was fitted to the data, where the activation energy was calculated as 40 kJ/mol and 42 kJ/mol for DHM 2442 and DHM 1314, respectively. These values are comparable to values reported for low molecular weight polyethylene. Using thermal gravimetric analysis, degradation of the polymer samples were also examined, showing excellent thermal stability at elevated temperatures for durations up to 10 hours, as less than 10% weight loss is observed. Lower melt viscosities, obtained by electrospinning at higher operating temperatures, were shown to strongly impact the final fiber diameter. A reduction of 35% in fiber diameter was seen with an increase of operating temperature from 177°C to 195°C. Lastly, compressed air was incorporated into the system with two heated air jet streams per polymer orifice. The shearing force from the air streams reduced the fiber diameter significantly, with average diameters ranging between 10 and 15 μm, depending on the electrospinning parameters. Additionally, SEM micrographs showed evidence of self-bonding between fibers, eliminating the need for thermal bonding steps.
**Figure B.1.** Schematic of single capillary melt electrospinning setup.

**Figure B.2.** SEM micrographs of melt electrospun fibers using DHM 2442 adhesive and varying applied voltage from single nozzle electrospinning setup with a collection distance of 10 cm: (A) 25 kV, (B) 30 kV, (C) 40 kV, (D) 45 kV, (E) 50 kV, (F) 55 kV, (G) 60 kV.
Figure B.3. Fiber diameter distributions for collected melt electrospun fibers of DHM 2442 utilizing single nozzle electrospinning setup at varying applied voltages.

Figure B.4. Schematic and flow diagram of Dynatec Dynamelt S Series Adhesive Supply Unit with enclosed electrospinning chamber, using vertical electrospinning orientation.
### Table B.1. DHM 2442 and DHM 1314 polymer specifications

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<td>Viscosity at 350°F</td>
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<td>Heat stability at 350°F</td>
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<td>Application Temperature</td>
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<td></td>
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**Figure B.5.** Photos of DHM 2442 polymer exiting Dynamelt ASU at (A) 2.92 cm³/rev pump operating at 2 RPM using a 17-holed die and (B) 0.297 cm³/rev pump operating at 1.7 RPM using a 5-holed die.
Figure B.6. Photographs of collected melt electrospun nonwoven mats compared at different applied voltages (A) side by side comparison of 0 kV at 5” CD and 50 kV at 5” CD, (B) close up of 0 kV at 5” CD, and (C) close up of 50 kV at 5” CD.

Figure B.7. Schematic and flow diagram of Dynatec Dynamelt S Series Adhesive Supply Unit with enclosed electrospinning chamber, using horizontal electrospinning orientation.
Figure B.8. Graphical representation of average fiber diameter and standard deviation for melt electrospun fibers fabricated at an operating temperature of 177°C and flow rate of 0.12 g/min-hole using a horizontal and vertical orientation.

Figure B.9. Photographs of electrospun mats using DHM 2442 fabricated using Dynatec’s ASU operating at 177°C, flow rate of 0.12 g/min-hole, 50 kV applied voltage, and 5 inch collection distance with (A) vertical orientation and (B) horizontal orientation.
Figure B.10. (A) Average fiber diameters as a function of applied voltages ranging from 25 kV to 60 kV at a collection distance of 3.5 inches, operating temperature of 177°C, and flow rate of 0.12 g/min-hole and (B) representative SEM micrograph of melt electrospun fibers.

Figure B.11. Steady shear sweep data for (A) DHM 2442 and (B) DHM 1314 polymer adhesives at temperatures ranging from 165°C to 225°C.
Figure B.12. Natural log of zero shear viscosity as a function of inverse temperature with a linear fitted Arrhenius equation for (A) DHM 2442 and (B) DHM 1314.

Figure B.13. Thermal gravimetric analysis data (TGA) for (A) DHM 2442 and (B) DHM 1314 using a ramp rate of 10°C/min ranging from 25°C to 900°C.
Figure B.14. Thermal gravimetric analysis (TGA) data for DHM 2442 at isothermal conditions for various temperatures over a ten hour period, with a magnified view of the initial 30 minutes.

Figure B.15. Thermal gravimetric analysis (TGA) data for DHM 1314 at isothermal conditions for various temperatures over a ten hour period, with a magnified view of the initial 140 minutes.
Figure B.16. SEM micrographs of melt electrospun fibers at flow rate of 0.12 g/min-hole, 3.5 inch collection distance, 60 kV applied voltage and operating temperature of (A) 165°C and (B) 195°C.

Figure B.17. Average fiber diameter as a function of zero shear melt viscosity at a flow rate of 0.12 g/min-hole and (A) 3.5 inch collection distance and 50 kV applied voltage, (B) 3.5 inch collection distance and 60 kV applied voltage, (C) 5 inch collection distance and 50 kV applied voltage, and (D) 5 inch collection distance and 60 kV applied voltage.
Figure B.18. Fiber diameter plotted as a function of viscosity for melt electrospun fibers from DHM 1314 and DHM 2442.

Figure B.19. Schematic of Dynamelt Adhesive Supply Unit (ASU) by Dynamelt with compressed air incorporated into the process.
Figure B.20. Fiber diameter distributions at varying parameters, operating at 177°C and flow rate of 0.12 g/min-hole, (B, C, D, F) with and (E, G) without compressed air at 177°C and 10 psi, where the boxes represent the average diameter +/- the standard deviation, and the whiskers represent the maximum and minimum fiber diameters.

Figure B.21. SEM micrograph of fibers produced at 177°C, flow rate of 0.12 g/min-hole, collection distance of 5 inches, applied voltage of 60 kV, and compressed air at 177°C at 10 psi.
Appendix C

Recorded Data for Melt-on-Demand Electrospinning with DHM 2442
Table C.1. Melt electrospinning using the Dynamelt ASU at 0.8 RPM and 2 hole die without compressed air

<table>
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<th>Collection Distance (in)</th>
<th>Applied Voltage (kV)</th>
<th>Polymer Temp. (°C)</th>
<th>Avg. Fiber Diameter (μm)</th>
<th>St. Dev. (μm)</th>
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Table C.3. Melt electrospinning using the Dynamelt ASU at 0.8 RPM with compressed air at 177°C and 10 psi for varying number of die holes

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<th>Air Pressure (psi)</th>
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Appendix D

Recorded Data and Graphs for Melt-on-Demand Electrospinning with DHM 1314
Table D.1. Melt electrospinning data using the Dynamelt ASU at 0.8 RPM and 2 hole die without compressed air.

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Table D.2. Melt electrospinning data using the Dynamelt ASU at 0.8 RPM and 2 hole die at collection distance 5 inches with compressed air.

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Figure D.1. SEM micrographs of electrospun fibers fabricated from the Dynamelt ASU operating at 0.8 RPM and 2 hole die without.
Figure D.2. SEM micrographs of electrospun fibers fabricated from the Dynamelt ASU operating at 0.8 RPM and 2 hole die with compressed air at 160°C and 10 psi.
Figure D.3. SEM micrographs of electrospun fibers fabricated from the Dynamelt ASU operating at 0.8 RPM and 2 hole die with compressed air at 177°C and 10 psi.
**Figure D.4.** Electrospun fiber diameters as a function of operating temperature for DHM 1314 using a 2 hole die and 0.8 RPM for various process parameters.

Average fiber diameter of samples fabricated using the Dynamelt ASU at 0.8 RPMs, 5 hole die, collection distance of 5 inches and compressed air at 160°C and 10 psi are smaller for experiments where there is no applied voltage. However, the laydown was significantly affected. When applying a voltage equal to 60 kV the sample would spread over the collection plate rather than collecting in a mound, allowing for longer collection times. This process would be improved with the addition of a moving conveyor belt for fiber collection.
Table D.3. Melt electrospinning data using the Dynamelt ASU at 0.8 RPM and 5 hole die at collection distance 5 inches with compressed air at 160°C and 10 psi.

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Figure D.5. Micrographs of fibers fabricated from the Dynamelt ASU at 0.8 RPM and 5 hole die at collection distance 5 inches with compressed air at 160°C and 10 psi.
Figure D.6. Fiber diameter as a function of operating temperature for varying process parameters.