POLYMER BLENDS, COMPOSITES AND AEROGEL MODIFICATION

BY INNOVATIVE APPROACHES

by

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proprietary material contained therein.
To my family,

Through you I have become the man I am today, and

without you I would never have gotten as far as I have come.

I owe it all to you.
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Chapter 2 discusses the advances in oxygen barrier materials through innovative approaches to modifying the refractive index change induced by biaxial orientation by simple melt blending procedures. Chapter 3 discusses an approach to developing 3D data storage devices by the blending of common optical polymers with inorganic chalcogenide glasses. Chapter 4 discusses the vast mechanical improvement of a polymer/clay aerogel composite material by a simple dip coating procedure. Chapters 5-7 involve the use of biomineralization for various purposes. In Chapter 5 a polyethylene imine/clay aerogel is coated by a silica layer to impart vastly superior mechanical properties, while a layering approach modestly improves mechanical performance. In Chapter 6 a polyacrylic acid/clay aerogel is subjected to CaCO₃ deposition, showing the ability to grow large amounts of CaCO₃ in relatively short times. Chapter 7 discusses an electrophoretic mineralization approach to collagen hydrogels.
Chapter 1: Introduction

The field of polymer science and engineering covers a broad range of study, being one of the truly interdisciplinary fields in modern science. Ranging from the birth of a polymer in its synthetic stages to the deployment in a range of applications, polymer integration in the physical sciences is widespread. Polymers play a large role in chemistry, physics, biology, medicine, engineering, etc. and pursuits in one field can often lead directly into other. This dissertation covers a wide array of polymer science, from investigating the barrier properties of polymer blends for commercial products and their specifications to using novel approaches to incorporate glassy inorganic materials within a polymer matrix for high density data storage materials to using common materials in new ways to increase the use range of low density clay aerogels to using bioinspired chemistry to develop reinforcement of current materials and bone replacement materials.

In Section 1.2 the basics of packaging and related barrier properties will be described along with the current progress towards high barrier materials. Section 1.3 will discuss the basics of data storage, current technology and next generation approaches. Section 1.4 will discuss aerogels, focusing on clay aerogels and the state of the art in that field. Section 1.5 will discuss the basics of biomineralization and current attempts at mimicking what biology produces. Section 1.6 will outline the dissertation's content, providing scope and objectives for each body of work.
1.1 Plastics in Packaging and Recent Trends Towards High Barrier Materials

The packaging market is one of the largest materials consumers for protecting products from handling, transportation and environmental elements. First modern packaging materials were primarily glass, metal and paper products. Oddly enough food packaging made major strides during times of war, with World War II serving as the first major use of plastic food packaging.\(^1\) Afterwards, food and beverage packaging gained much momentum as the developing world turned their focus on having year round access to high quality foods and beverages. In 1957, the first roll to roll sandwich bag was produced, and by 1966, all bread sold was packaged in polyethylene bags.\(^1\) The plastic packaging industry was well on its way, but not without major improvements to the process. While many plastics were being used to help store the food for transport, most applications of longer term food storage demanded lower permeability of oxygen, carbon dioxide and aromatics in the food. One major step towards solving the high permeability of polymers was metallized plastic, in which a plastic film was exposed to metal vapors, collecting a metal film on the outside which lowered permeabilities of the materials up to 40-fold.\(^2\)

Although metallized films offered very low permeability over traditional unmodified plastics, this approach is not acceptable in many applications where transparency is desired. Traditional commodity polymers offered marginal barrier properties, and the desire for more complex systems arose. The packaging industry moved more towards materials with higher selectivities in barrier properties, such as EVOH polymers and their high moisture barriers and PET with its high oxygen barrier properties.\(^3\) Multilayer co-extrusion technology developed by Hercules in the late 1960’s introduced more
innovative ways of reducing permeabilities by producing materials with combinative properties in one processing step.\textsuperscript{2} In this fashion one could produce a packaging material with two or more layers with, for example, the high oxygen barrier of PET and the high moisture barrier of EVOH.\textsuperscript{1} Another example of barrier improvements has been the development of oxygen scavengers that can be dispersed within an existing polymer to improve barrier properties, although these have only been moderately successful.\textsuperscript{4}

In more recent studies, there have been innovations in packaging ranging from simple to complex approaches. For simplicity and low cost, many approaches look to improve the barrier properties by blending two high barrier polymers, dispersing one in small amounts within another. The dispersed polymer is spherical, and through biaxial orientation, a process that mimics bottle blowing, the disperse spheres stretch into large aspect ratio discs.\textsuperscript{5-10} These discs of low permeability dispersed are well in the polymer, and dramatically lower the permeability of the composite material by introducing a tortuous path to the permeating gas, lengthening the diffusion time. Many polymer blends have been produced to attempt to induce this effect, one of the most common being blending small amounts of nylon into PET.\textsuperscript{5-10} While nylons have a much higher barrier to gasses than PET, water absorption by common aliphatic nylons induces plasticization causing the barrier properties to be lost.\textsuperscript{9} A way around this is using aromatic nylons that are, while more expensive, much less influenced by water absorption. The main problem in this approach is that during biaxial orientation the refractive index of the PET changes, creating a refractive index mismatch between the nylon and polyester and introducing a large reduction in transparency.
Chapter 2 of this dissertation will focus on efforts to reduce the permeability of oxygen through PET by blending with aromatic nylons. Certain compatibilizers are investigated to determine ways to reduce particle size and increase transparency of the blends. Other approaches to increase transparency are focused on modifying the refractive index of either material to decrease the mismatch in refractive index after orientation.

1.2 Optical Data Storage in Current Technology and Material Research Towards Higher Density Data Storage

Modern digital media has been undergoing a consistent development over the past century that began with data storage needs of the first computers. Since the invention of the compact disc, optical data storage has been of extreme importance for portable media playback applications. Such applications began with the compact disc capable of storing about 700 MB of information which is written as “pits” and “lands” in polycarbonate coated with a reflective layer of aluminum and is limited in density based on the reading laser technology (red laser, 780 nm). Digital versatile discs (DVDs) were created shortly thereafter, originating as being similar to CD technology with “pits” and “lands” but capable of much higher data storage due to a lower wavelength reading laser (650 nm) and smaller bits of data. The next commercially successful ODS technology was Blu-ray® discs, capable of storing much higher data densities due to using a blue laser light (405 nm) and smaller “pits” and “lands.”

A large focus of the optical data storage development has focused not only on the production of “read-only” disc media, but also on writeable and rewritable mediums. Most common systems employ a phase change material as the active reading and writing
layer of the disc that is capable of non-linear light absorption, specifically two-photon absorption. TPA materials can absorb 2 photons of light at the same time which can result in fast excitation of the molecules which, along with other phenomena, cause rapid heating of these materials.\textsuperscript{11} Chalcogenide glasses are currently used as the writeable layers and are surrounded on each side by a dielectric layer to protect the polycarbonate from the rapid heating and cooling that the glass undergoes during the heat absorption.\textsuperscript{12-15} This heat causes the glasses to undergo a phase transition from amorphous glass to crystalline material with a higher refractive index.\textsuperscript{15} This refractive index change causes a change in the reflectivity, creating the “pits” and “lands” that would be found in conventional read-only discs.

Much of the next generation optical data storage media will focus on expanding the physical limitations of the single layer disc by construction of a three dimensional data storage material. These are materials that can be written on throughout the thickness of the material instead of a single layer. Much of this work focuses on either holographic data writing which cross-links monomers dispersed in polymeric material of multi-layer disc construction. Holographic data storage is currently very promising, although rewrite capabilities are non-existant because the cross-linking is an irreversible reaction.\textsuperscript{11} Multilayered systems are currently being developed, most notably by Pioneer Corporation\textsuperscript{16} who in 2008 unveiled a 16 layer read only Blu-ray disc that can store up to 400 GB. Current multilayer materials have limited practicality though because the current process of layering one material at a time is a severe hindrance to production speed.
Chapter 3 of this thesis will address an attempt towards the fast production of multilayered materials with dispersed layers of rewritable chalcogenide glass within an optical polymer. Issues address will be the feasibility of finding a glass that has low enough processing temperature and still presents crystallinity. Mainly optical and rheological properties are important in blends of these material. This type of material would be subjected to biaxial orientation and produce high aspect ratio discs of crystallizable glass within the polymer matrix that could then be written upon via two photon absorption if successful.

1.3 Clay Aerogels and Recent Progress in Developments

Aerogels are a class of materials that are typically known for their exceptionally low densities, the lowest of any known material. The first aerogel materials were developed in the 1930’s\textsuperscript{17-18}, and the much of the work since then has focused on silica aerogels that eventually made their way into the NASA and enjoyed great success in bringing back comet dust to earth.\textsuperscript{19-20} While silica is one of the most widely known aerogel materials, many other materials have been converted into aerogels. Carbon and carbon nanotube aerogels, metal oxide aerogels and cellulose aerogels have all found a moderate amount of success, but perhaps the most promising of the group are clay aerogels. These clay aerogels were first discovered in the early 1950’s, described as “gel skeletons” based on the way the materials were processed, being frozen while in gel form and the ice being sublimated from the material, leaving only the solids in the expanded gel orientation behind.\textsuperscript{21-23}
More recently, the processing of clays into clay aerogels have made a dramatic comeback because of the environmentally friendly way of processing. Sodium montmorillonite is the most common clay used for these purposes, with high availability in the environment and the aerogels are produced from simply forming a clay gel in water and freeze drying the material, involving no environmentally harmful solvents. A robust process for the production of organically modified clays was developed in 2006 and since then has been expanded to a large focus of research.\textsuperscript{24} Unmodified aerogels have very low densities and thermal conductivities, making them prime candidates for insulation materials, but suffer from a lack of substantial mechanical reinforcement.

Much of the research undertaken on clay aerogels in recent history involves different approaches to reinforce the clay aerogels by various means. The most common way to reinforce the clay is to make a clay/polymer composite by including a water soluble polymer in the clay gel. The first such material incorporated poly(N-isopropyl acrylamide) with the clay gel, imparting a temperature sensitive swelling and contraction in aqueous environments.\textsuperscript{25} Other water soluble polymers that have been incorporated are poly(vinyl alcohol), poly(ethylene imine), poly(acrylic acid), and cross-linked epoxy systems.\textsuperscript{26-28} Some of the more influential composites may prove to be formed with polymers that are biologically available or biodegradable, such as casein or polyhydroxybutyrate.\textsuperscript{29} Another very successful way of mechanically reinforcing the clay aerogels has been the incorporation of fibers, acting as a small scale “rebar.”\textsuperscript{30}

Clay aerogels will be discussed in much more detail in chapter 4-6, where different methods of reinforcement or modification will be attempted. Chapter 4 discusses the attempt to use commercially available coating technologies to improve the mechanical
integrity of an epoxy aerogel. Chapter 5 deals with reinforcement of the aerogel by the approach of depositing silica mimicking a diatom’s cell wall formation. Chapter 6 discusses the attempt to mineralize calcium carbonate in an aerogel to mimic seashell nacreous materials.

1.4 Biomineralization in Nature and Attempts to Mimic in Biomaterial Research

Biomineralization is the natural process that hundreds of biological systems use to make complex organic/inorganic composites that serve structural reinforcement, sensory perception, gravity sensors and optical imaging functions within plants and animals. Humans bone and teeth are composites consisting of calcium phosphate deposited within collagen matrices. In other natural systems, these types of materials make cell walls, seashells, eye lenses and even the calcium stores found in leaves. Structural and biomedical applications have been of high interest because these natural composite structures present unique materials with unusually high strength to weight ratios. The integration of hard mineral phases in high interaction with soft organic phases lead to materials that have the high stiffness properties of the inorganic material and the flexibility of the organic polymeric backbones.

Because of the characteristically high strength to weight ratio of biomineralized materials there has been ongoing research in mimicking the way biology directs mineral formation within polymer matrices for defense and aerospace applications. Mineralized systems generally consist of complex hierarchical structures with alternating layers of minerals surrounded by a polymer. Silica mineralization in diatoms involves the formation of a silica exoskeleton on an amine rich protein outer layer. Many polyamines have been
investigated to determine their silica forming ability including polylysine, poly(allyl amine) and poly(ethylene imine) to varying degrees of success.\textsuperscript{35-39} Mimicking of this type of system has proven to be relatively simple with quick silica deposition by alkoxy silanes.

Seashell nacre is one of the more complex hierarchical materials in biological systems and helps to protect the organisms inside by offering very high impact strength. The high impact strength is achieved by a “brick and mortar” structure induced by depositing calcium carbonate as the brick on a complex polymer structure comprising of β-chitin, silk-like proteins, and aspartic acid rich glycoproteins.\textsuperscript{40-41} The strong adhesion between the two types of minerals creates a cooperative strength when it is impacted, the flexible polymers dissipating the force through the material and the calcium carbonate providing the strength to keep the material together. Many have tried to directly synthesize nacre from organic macromolecules by growing calcium carbonate crystals from solution on an organic substrate. One such approach by Germaine Fu, et al. was to deposit calcium carbonate crystals onto a Kevlar® substrate fiber by dissolving calcium carbonate in a poly(vinyl Alcohol) (PVOH) solution with various nacre proteins.\textsuperscript{42} Another approach taken by many who mimic nacre structure is the use of a polymer induced liquid precursor (PILP) that keeps the calcium carbonate in the amorphous form while developing the crystals on a substrate.\textsuperscript{43} Tang, et al. uses a layer-by-layer assembly of clay platelets and oppositely charged polyelectrolytes to develop the nacre-like structure.\textsuperscript{44} While all are interesting approaches, no approach has come close to commercializable production scales.
Human bones and teeth, a complex composite made of collagen proteins and hydroxyapatite (a calcium phosphate polymorph), present equally interesting possibilities in biomedical applications. Many needs to replace bone with a material that acts as a support for new bone growth or integrates itself with bone have arisen in the medical field. There are multiple requirements for bone substitute materials such as: the material should have the same mechanical stability as the bone it is replacing, biodegradability to allow natural dissolution and regrowth, high porosity to allow integration to the existing bone and tissue around it, the ability to be formed into complex shapes to accommodate the replacement site dimensions and biological similarities to reduce rejection or scarring around implantation sites. Many approaches have been taken to make bone substitute materials, the simplest of cases being a mix of blood and bone chips with hydroxyapatite to promote new bone growth in the area. Another method of replacing bone defects with a temporary solution is bone cement, which is usually hydroxyapatite mixed in a NaCl solution that is injected into the site needing reinforcement and hardens. A similar approach has been undertaken by making a nano-hydroxyapatite paste that does not harden because the paste does not dry under biological conditions. Porous scaffolds have also been introduced that can fill the space and let bone growth continue in the area while providing structural support.

Biomineralization is heavily discussed within the latter half of this dissertation. Chapter 5 investigates the combination of clay aerogel production with silica mineralization. Chapter 6 is an investigation of the mineralization behavior of calcium carbonate on a poly(acrylic acid)/clay aerogel substrate. Chapter 7 involves the use of electrical current
to “seed” a collagen hydrogel with calcium phosphate and subsequent mineralization by an alternate soaking procedure.

1.5 Research Objectives

This dissertation covers a wide range of polymer science and engineering presenting many various applications of research to new technologies. Chapter 2 documents research concerning the blending of small amounts of aromatic polyamides into poly(ethylene terephthalate). The main objectives of this research was to:

1.) Create transparent high barrier films by blending polyaramides into PET.
2.) Use biaxial orientation to simulate bottle blowing and measure refractive index changes and barrier properties in the materials.
3.) Modify the blend by compatibilization or other means to increase transparency of biaxially oriented films.

Chapter 3 describes research into creating high density data storage materials by the simple method of blending active TPA materials dispersed within a polycarbonate matrix. The active material that will record data should be of chalcogenide glass composition that crystallizes and disperses well in PC. The main objectives of this study were:

1.) Discover low T_g chalcogenide glass compositions and work with collaborators to obtain these materials.
2.) Perform complete thermal characterization to find compositions that are most likely suitable to be processed with polycarbonate.
3.) Create film of polycarbonate filled with chalcogenide glass by melt blending.

Chapter 4 describes the use of coating to reinforce clay/polymer aerogel composites. Coating should provide vertically oriented aerogels to undergo flexure to improve the range of applications that these low density/thermal conductivity materials can be used in. The main objectives of this research were to:

1.) Find an ideal polymer to create a strong and flexible aerogel.
2.) Explore different commercially available coatings to determine the properties the coating should impart to the aerogel composite.
3.) Coat aerogels and determine physical property enhancements by testing in compression and flexure.
4.) Determine how large of an effect the coating would have on thermal conductivity.

Chapter 5 discusses a biomimetic approach to mechanically enhancing a clay/polymer aerogel by developing a silica exterior on the material. Subsequent mechanical reinforcement was achieved by developing a layer-by-layer approach to build successive layers of silica, strengthening the material further while retaining the low density. The main objectives of this research were to:

1.) Develop polyamine/clay aerogel composite that would be highly likely to mineralize by silicic acid.
2.) Determine optimum method of mineralization.
3.) Determine mechanical property enhancement by testing in compression.
4.) Further enhance mechanical properties by layering the silica and polyamine.
Chapter 6 discusses the mineralization of calcium carbonate on a poly(acrylic acid)/clay aerogel composite. The material should then undergo analysis to determine the chemical structure of the mineral deposited and subsequent property changes from mineralization should be tested. The objectives in this project were to:

1.) Find a water soluble polymer that interacts strongly with clays and forms a hydrogel after processing into aerogel that had proper functionality to induce calcium carbonate deposition.

2.) Develop mineralization method to mineralize calcium carbonate on and within the aerogel composite.

3.) Analyze the mineralized material to determine mineral properties and extent of mineralization

Chapter 7 discusses the electrophoretic mineralization of calcium carbonate within a collagen hydrogel. The mineralized hydrogel was then freeze dried to inspect mineral formation with an intact gel network structure. The objectives for this project were:

1.) Develop method for electrophoretic mineralization of a small sample of hydrogel to limit collagen use.

2.) Optimize electrophoretic parameters to find quick and efficient mineralization method.

3.) Further mineralization by employing an alternate soaking procedure.

4.) Analyze materials to determine type of calcium phosphate created and extent of mineralization.
1.6 References


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Chapter 2: Blends of Poly(ethylene terephthalate) and Poly(m-xylylene adipamide) for High Barrier Films Utilizing Compatibilization and Refractive Index Modification to Increase Transparency in the Blends.

2.1 Abstract

In this investigation, poly(ethylene terephthalate) (PET) and poly(m-xylylene adipamide) (MXD6) were blended to determine the usefulness of such a blend in high barrier applications. Copolymers of MXD6 and MXDI were also blended to determine the reduction in average domain size that could be achieved with additions of isophthalamide in the aromatic nylon backbone. Biaxial orientation was employed to determine the material properties after orientation, notably the change in the refractive index of PET. Compatibilization of the PET and MXD6 based copolymers was investigated through the use of polymers and copolymers that show possible compatibilities with PET or MXD6, the most useful compatibilization being a sulfonated PET copolymer that introduced an acid-base interaction with the aromatic nylons. Another approach was to blend with a refractive modifying polymer, and the most positive result was a commercial PBT/PBI copolymer that effectively delayed refractive index changes in biaxially oriented PET blends. This approach may lead to the use of similar approaches that, instead of traditionally try to compatibilize PET and MXD6, effectively reduce the refractive index mismatch between the two materials after orientation.
2.2 Introduction

Poly(ethylene terephthalate) (PET) is one of the most common polymers used in food and beverage packaging for many of its advantageous properties.\(^1\) Common properties important for beverage packaging in particular include being optically transparent and colorless, a high barrier to oxygen and carbon dioxide, and free from harmful side products such as bisphenol A at the lowest price point possible for the application. PET not only fits all these criteria, but also undergoes structural alignment under the biaxial orientation conditions of blow molding which further reduces its permeability. While PET has been commonly used for many applications in bottling and “clam shell” containers, certain products are more sensitive to oxygen and carbon dioxide permeation, creating a large demand for higher barrier packaging applications.\(^2\)

One approach to increasing the barrier of PET in the packaging industry has been thin metal coatings that create a virtually impassable barrier, but due to demand for transparency in liquid packaging this approach is not acceptable.\(^2\) Another approach that is moderately successful in liquid beverage packaging presently is multilayered coextrusion of PET with high barrier polymers, such as poly(m-xylylene adipamide) (MXD6), an aromatic nylon with very high barrier properties.\(^3\) While sufficient barrier values are achieved the cost of such composites, considering the higher cost of MXD6 and extra machinery needed to produce such composites, limits the use of this solution. A significant need is apparent for using much lower amounts of polyaramides and technology using the same production lines in current bottle manufacturing.
Polymer blends have been studied in many different applications and technologies to put polymers with vastly different properties together and achieve synergistic results. There are few compatibilities between PET and non-polyester polymers, but advances have been made in enhancing the miscibility of PET with various polymers. Recent studies have shown partial miscibility with poly(trimethylene terephthalate) and polycarbonate due to transesterification creates a compatible blend by reactive compatibilization, but neither would improve barrier properties of the blend further than homogeneous PET. Reactive compatibilization has also been achieved in polyamide/polyester blends with the use of an epoxy resin, but the high degrees of crosslinking involved can negatively impact rheological properties in melt extrusion. Other studies have investigated the use of a liquid crystalline polyester for high barrier improvements, but the nature of the changing crystalline phases makes these materials brittle and birefringence in the LCP would inherently inhibit transparency. While these approaches help to understand some key factors to the ability to compatibilize PET, none provide a simple melt extruded polymer blend with high barrier and transparency properties.

Nylons in general have very good gas barrier properties when dry but absorb much water, leading to a large loss in barrier properties in aliphatic nylons. Aromatic nylons such as MXD6 have shown much lower effects from water absorption on barrier properties. Recent studies have shown that while PET and MXD6 are incompatible, introducing irregularities in the polymer chain by simple substitution of isophthalamide in place of adipamide (making MXDI) can lead to the reduction of particle size in blends. Further studies have shown that introducing a small concentration of sodium-5-isophthalic acid (SIPE) for terephthalic acid (making PET-co-SIPE) in PET can partially compatibilize
MXD6/PET blends by disrupting PET regularity and introducing an ionic interaction between the sulfonate and amide groups, lowering the surface tension between the two polymers and increasing miscibility.\textsuperscript{15-17} This reduction in particle size can lead to very transparent films with higher barrier properties than PET alone in the extruded state. In further processing as the blend is processed into bottle form, the high draw ratios of blow molding biaxially orient the blend, stretching the dispersed particles into high aspect ratio platelets. By increasing the surface area of MXD6 and introducing a tortuous path to gas diffusion the barrier properties are improved drastically, but orientation leads to an increase in the refractive index of PET. This creates a mismatch in refractive index that lowers the transparency of the material, an undesirable result. Despite this limitation, the PET/SIPE/MXD6 product does enjoy some commercial volume at the present time.

The present study aims to explore PET/MXD6 blends and possible compatibilizations to increase transparency of the polymer blends. The nature of blending these materials will be explored by determining morphological links to transparency and barrier properties of MXD6 at different viscosities and with various amounts of isophthalamide substitution. PET-co-SIPE will be introduced to determine compatibilization standards and other possible compatibilizers will be tested. Refractive index modifiers will also be tested to determine the possibilities of creating non-compatible blends with high transparency and high barrier properties. Blended material will undergo biaxial orientation to determine what effects the compatibilization and refractive index modification can have on the blended materials.
2.3 Experimental

Materials

Polyethylene terephthalate (PET), grade 9921 W, was obtained from Eastman Chemical Company, experimental aromatic nylons (MXD6 and MXDI series), Griltex® (co-polyester) and Grilon® (co-polyamide) were supplied by EMS-Chemie, polyethylene terephthalate with 2.29 mol% sodium-5-sulfoisophthalate replacing terephthalic acid (PET SIPE) was obtained from INVISTA, high $M_w$ phenoxy resin (PKFE) was obtained from InChem, Ultem® 1000 polyether imide (PEI), was obtained from Sabic Innovative Plastics and polyethylene naphthalate (PEN) was obtained from Teijin Dupont Films and all polymer resins were used as received. Coupling compounds Irgacor® L190 and Irgamod® 195 were obtained from BASF and used as received. Kapton® film was purchased from McMaster-Carr and used as received.

Compounding

All polymer resin was dried at 100 °C under vacuum for at least 3 days prior to melt blending. All compounding work performed on a DACA twin screw micro-extruder at 100 rpm for 4 min. at 280 °C unless otherwise noted. Aromatic nylons were always added at 10 wt. %, with PET and modifiers being added to make up the remaining 90 wt. %. Extrudate was collected and cut into pellets manually, then dried for 3 days at 100 °C under vacuum. Extrudate was then molded into films using a model C Carver Press heated to 280 °C between pieces of Kapton® film to ensure low surface roughness.
Stretching

Square films measuring 85 mm × 85 mm were cut from the compression molded sheets, marked with a grid pattern, and stretched in a Bruckner Karo IV biaxial stretcher. The films were simultaneously and equi-biaxially drawn at various temperatures at an engineering strain rate of 400 % s⁻¹ based on the original specimen dimensions. The uniformity of the drawn specimen was determined from the even deformation of the grid pattern. The preheat time before drawing was 60 s.

Analysis

Thermogravimetric analysis (TGA) was performed to determine degradation point for all polymer resins on a Mettler-Toledo TGA model 851e. All samples were heated at 10 °C/min to 350 °C. Differential scanning calorimetry (DSC) was performed on all resins to determine glass transitions and crystallization/melting behavior on a Mettler-Toledo DSC model 822e/700. Samples were run at 5-10 °C/min from 25 °C to a 280 °C and back to 25 °C for 2 cycles. Samples from each blend were mounted in epoxy and microtomed at -75 °C to reveal cross-section morphology. To examine the morphology of the blend by atomic force microscopy (AFM), a Veeco Instruments Dimension 3100 equipped with a NanoScope IIIa controller was used. Simultaneous images of height and phase imaging were recorded in 10x10 µm areas. Oxygen flux J(t) at 0% relative humidity, 1 atm and 23 °C was measured with a MOCON OX-TRAN 2/20. An Ocean Optics UV-Vis spectrometer was used to determine transmission values for films, an average of 5 different points on the films. A Metricon Model 2010 Prism-Coupler was used to measure the refractive index of the oriented films at a wavelength of 1544 nm.
The measurements were performed at 23 °C and 5 points were averaged for the measurements.

2.4 Discussion

The structures of the PET and polyaramides are given in Figure 1, with the MXDI segments incorporation into the MXD6 backbone being labeled according to the wt. % of MXDI in the copolymer in the notation. For example, MXD6 with 2 % MXDI in the backbone of the copolymer is labeled MXD6-2I. There were 3 different MXD6/MXDI copolymers considered to evaluate the effect of isophthalamide substitution in the MXD6 backbone. There were also 2 MXD6 polymers of different molecular weight to determine the effect of viscosity on blending and compatibilization labeled as MXD6-ηL and MXD6-ηH to indicate low and high molecular weight. Early studies by Taylor in the 1930’s suggested that the major factors in dispersed particle size in mixed fluids are interfacial tension between the two phases, shear rate in mixing and the difference in viscosity between the two fluids. This suggests that if all other factors are constant, mixing polymers with similar viscosities will provide smaller dispersed domains. By introducing a compatibilizer hopes are that the interfacial tension will decrease, resulting in smaller particle size.

Thermal properties of the polymers of interest needed to be determined before blending. Differential scanning calorimetry (DSC) was employed to determine these properties, the results being given in Table 1. The PET selected for this study was chosen to represent common bottle resin, and PET thermal values were close to literature values for glass transition temperature (T_g), melting temperature (T_m), and cold crystallization
temperature (T_{cc}) as expected. The high and low viscosity MDX6 resins showed little deviation, sharing a T_g = 84 °C and T_m = 240 °C and having slightly different T_{cc}. Incorporating MXDI in the MXD6 lowered the T_g incrementally from 83 °C at 12 % MXDI to 79 °C at 2 % MXDI. In these copolymers, the melting temperature decreases and cold crystallization temperature increases from pure MXD6 as well, indicating that the isophthalamide substitution inhibits preferred orientation because of the kinks in the chain that the irregularity presents. This is the purpose of using isophthalamide in the polymer backbone, and further isophthalamide inclusion would be expected to continue this trend.

Blending the PET and MXD6 polymer and copolymers is necessary to determine initial incompatibilities, what effect the MXDI inclusion has on blend morphology and what type of properties trends develop. For comparison purposes, the level of polyaramide inclusion was set at 10 wt. % in the final composites. All polymers were blended at 280 °C in a corotating twin screw micro-compounder for 4 minutes to ensure proper dispersement of the minor phase (MDX6/MXDI) in the PET. Atomic force microscopy (AFM) is a powerful tool that can be used to observe morphology in heterogeneous polymer blends because of the minor differences in elasticity between two different materials. AFM images were produced of the 5 different 90/10 wt. % blends of PET/MXD6 and are shown in Figure 2. The first observation can be that across all blends, the two materials are incompatible with large dispersed domains of polyaramide in PET. Average dispersed domain size of the polyaramide can be seen in Table 2. The viscosity of the MXD6 seemed to play a minor role in the avg. domain size of the dispersed minor phase, with the higher viscosity MXD6 showing improvement with ~400
nm lower domain size and much better dispersion of spherical domains. MXDI inclusion in the MXD6 backbone was not very advantageous at only 2 %, but at 6 % the domain size was reduced by about half of the original domain size and an increase in dispersion is also observed. An inclusion of 12 % MXDI slightly reduces domain size to 500 nm, but it should not be understated that any decrease in domain size is large when approaching the lower limits of the visible light spectrum. At sufficiently low domain size, the particles should not be visible by the human eye.

The transparency seems quite good in the initial blends, but during the processing involved in bottle production the material will undergo biaxial orientation. To simulate the bottle blowing process a biaxial orientation was induced by using an instrument specifically designed to draw films in two directions simultaneously. Since dramatic effects are expected from orientation of PET, the refractive index and permeability of the oriented films were tested. Figure 3 shows the results of biaxial orientation on the films of each sample indicating the problem most prevalent in blends of PET and aromatic nylons. The PET has a drastic change in RI from n=1.57 as extruded up to 1.63 when stretched to 4X4 its original size. In contrast, the refractive indexes of the polyaramides remain relatively constant. This large mismatch introduced by biaxial orientation is the main reason for the introduction of unacceptably low transparencies in blends of the materials. Biaxial orientation can impart positive changes as well, especially in permeability. Figure 4 displays the O₂ permeability changes imparted by biaxial orientation. PET starts out at close to two orders of magnitude more permeable than MXD6 and MXDI copolymers. The permeability reduces by about half in PET, while small reductions are observed in the aromatic nylons.
Multiple approaches were used to reduce the difference in transparency between the polyester and polyaramide and mainly consist of partial compatibilization and influencing the change in refractive index. The chemicals and polymers used for these attempts can be seen in Figure 5. All of these chemicals and polymers were added at 5 wt. %, changing PET to 85 wt. % and the initial 10 wt. % polyaramide remained constant, the resultant morphology inspected by AFM and displayed in Figure 6. Figure 5A shows the structure of sodium-5-sulfoisophthalate which was incorporated into PET by substituting for terephthalic acid in synthesis and is referred to as PET-co-SIPE. This simple substitution serves to partially compatibilize the two polymers by introducing an acid-base interaction between the sulfonate groups of the PET-co-SIPE and the amide groups in MXD6. Table 3 summarizes the results of PET-co-SIPE addition into the polymer blend and the relationship between dispersed particle size and resultant transparency. The PET copolymer proved to be a powerful compatibilizer, reducing the particle size in every instance with the final average domain size in the 250 nm - 500 nm range. These dramatic results have been observed in similar systems in previous studies13-17, but the refractive index mismatch that result from biaxial orientation leads to large drops in transparency.

To further reduce average domain size in the polymer blends, other approaches to compatibilization were explored. PKFE is a phenoxy resin based on the reaction of bisphenol A and epichlorohydrin that has been investigated as a reactive compatibilizer. In this study, the phenoxy resin created a third phase as seen in the AFM imaging that surrounds and encapsulates the polyaramide. While this does reduce domain size of the dispersed domains, the reduction is not large enough and the introduction of a third phase
would present even more refractive index issues. Two coupling compounds traditionally used to increase the molecular weight of polymer resin, Irgacor® L19 and Irgamod® 195, were investigated, the structures shown in Figure 5B and 5C. The purpose of using these coupling compounds was an attempt at reactive compatibilization and resultant domain size was affected, although the domain size reduction was again not large enough to be of promise in increasing transparency. Polyether imide (PEI), shown in Figure 5E, was investigated as a possible compatibilizer, but high processing temperatures and the original orange color of the PEI cause the film to gain an unacceptable amount of orange color.

Another way to affect the transparency of the blended films is to modify the refractive index of the polyester or polyaramide. Polyethylene napthalate (PEN), shown in Figure 5D, was used effect the refractive index of the PET by interrupting the regularity of chain stacking in orientation, and the results of biaxial orientation on PET/PEN blends can be seen in Figure 7. The blending of PET and PEN actually raises the refractive index of the blended material due to PEN’s higher refractive index and does not reduce the orientation of PET, making it an unsuitable approach towards lowering the refractive index mismatch. Grilon®, a PA66/PA6,10/MXDI/MXD10 copolymer was used to attempt to raise the refractive index of the polyaramides, shown in Figure 8. The resultant refractive index of blends of Grilon® and polyaramides is lower than the original refractive indexes, increasing the refractive index mismatch between the two polymers. Griltex®, a copolymer of polybutylene terephthalate (PBT) and polybutylene isophthaltate (PBI) shown in Figure 5F, was used to alter the refractive index behavior of PET as well, the results shown in Figure 9. The Griltex® actually affected the PET in a
desired way, delaying the refractive index change present in PET biaxial orientation, possibly to a level that could lead to no refractive index difference at biaxial orientations close to 4 X 4. In between a draw ratio of 3.5 X 3.5 and 6 X 6 though the refractive index goes through its usual behavior, although the final refractive index value is lower. This tends to be the most promising of the RI modifying polymers used in this study. Unfortunately, because of the proximity of the refractive index to the target draw ratio of 4 X 4, transparency was still too low in these blends.

2.5 Conclusions

A systematic approach towards high transparency blends of PET and MXD6 based polymers was tested. Previous studies showed PET-co-SIPE as the most desirable compatibilizer presently available, and this study confirmed those findings. Modification of the refractive index of MXD6 and PET is possible through a third polymer that interacts with the orientation behavior of the polymers. PEN would be useful if attempting to raise the refractive index of PET, and Grilon® would be a good copolymer to reduce the refractive index of MXD6. The most promising result is the refractive index modification effect that Griltex®, a copolyester, has on delaying the onset of the orientation induced changes in the refractive index of PET. Although low transparency was still a considerable issue because of the proximity of the delay to the desired draw ratio, an approach to making other RI altering copolymers based on Griltex® could provide the RI alteration needed to blend PET and MXD6 with no transparency issues after 4 X 4 biaxial orientation.
2.6 Acknowledgements

We would like to thank Dr. Yijian Lin, Dr. Eric Baer and Dr. Anne Hiltner for their collaboration in this project.

2.7 References


2.8 Tables and Figures

Figure 1: Chemical structures of A.) PET, B.) MXD6 and C.) MXDI
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**Table 1:** Thermal properties of PET and MXD6/MXDI polymers
Figure 2: Morphology of PET/MXD6 or PET/MXDI blends. All blends are 90/10 wt.% PET/Nylon.
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<thead>
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<td>PET/ MXD6- η L</td>
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Table 2: Average domain diameter of PET/Nylon blends.
Figure 3: Refractive index changes that occur because of biaxial orientation.
Figure 4: Top table shows permeability values for PET and Polyaramides as a result of biaxial orientation, the plot visualizing this data.
Figure 5: Chemical structures of compatibilizers and RI modifiers:

A.) Sodium-5-sulfoisophthalate, B.) Irgacor ® L90, C.) Irgamod ® 195

D.) PEN, E.) PEI, F.) Griltex®, G.) Grilon®
Figure 6: AFM images showing morphology of modified blends with 5 wt. % modifier, 10 wt. % polyaramide and 85 wt. % PET.
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Table 3: The relationship of particle size to transparency and the effect of PET-co-SIPE.
Figure 7: The RI behavior of PET/PEN blends.
Figure 8: The RI behavior of blends of MXD6-6I and Grilon®.
Figure 9: The RI modification of PET by Griltex® incorporation.
Chapter 3: Towards 3 Dimensional Data Writing Materials through the Melt

Blending of Polycarbonate and Chalcogenide Glasses

3.1 Abstract

Chalcogenide glasses represent a wide array of inorganic glasses with very different properties based on the material composition. Low $T_g$ chalcogenide glasses were chosen, two commercial and three synthetic, to determine material parameters for successful melt blending of these materials with polycarbonate. Like the organic polymer family, some compositions crystallize with input of light or heat, this behavior serving as the optical data writing observed in current rewritable CD’s. It was found through extensive testing that materials for this purpose should have a $T_g$ close to that of the organic polymer it is being compounded with and $T_m$ lower than degradation temperatures in the organic polymer. Successful blends were made, although very poor miscibility between the two materials was observed. A high difference in refractive index between the two materials ultimately proved to be too high for multilayer data storage applications.

3.2 Introduction

Data storage applications are increasingly demanding on storage capacity as high definition media continues to increase the amount of material put onto optical storage discs. Conventional optical data storage is currently limited to two dimensional forms in CD and DVD writable and rewriteable formats. Current rewritable formats usually consist of a chalcogenide glass within a polycarbonate matrix that is writable and
erasable through a photocrystallization method aided by the two photon absorption (TPA) of these glasses.\textsuperscript{1-4} Increasing the amount of data storage on these media will require either higher resolution reading and writing lasers, which would be quite expensive, or creating a three dimensional data storage system where the data could be stored throughout the material.

Previous attempts at 3D data storage have given mixed results, and have usually been limited in production value. The first demonstration of a data storage device in this manner was by Rentzepis, et al. in which excitation of a photochromic dye was performed utilizing TPA.\textsuperscript{5} Gu, et al. have shown 3D rewritable storage with polarization sensitive photorefractive dye in a liquid crystal polymer, also utilizing TPA.\textsuperscript{6} Another approach to writable materials has been shown by Hawker et al., in which holographic photopolymerization of a monomer dispersed in a polymer matrix created a 3D data storage network\textsuperscript{7}, although it could not be rewritten. Other attempts have been shown to work equivalently with these systems, but most suffer from limited written stability, processibility and erasibility.\textsuperscript{8-10}

Chalcogenide glasses present a unique class of materials, much like the organic polymer family. These materials are inorganic glasses primarily consisting of Group XVI elements S, Se and Te excluding oxygen and are characterized as highly optically active materials. Most chalcogenide glasses exhibit strong two photon absorption, are highly transparent in the IR region of light, exhibit non-linear optical properties and can exhibit a photo-generated change in refractive index.\textsuperscript{11-13} Depending on composition many of their properties can be tailored to meet certain criteria such as processing temperatures and presence of crystallization.\textsuperscript{14-16} Current rewritable CD and DVD technologies use
chalcogenide glass, mainly GeSbTe, as the active write/erase material because of the ultrafast crystallization and the high rewrite capability of these materials.\textsuperscript{12} While useful in single layer media, the very high processing temperatures and crystallization temperatures of this particular chalcogenide glass makes it unsuitable for mass production of high density multilayered storage devices. Many glasses in this class though have much lower processing temperatures that would allow them to be processed with polymers for 3D storage applications.\textsuperscript{15,16} By using a glass with low processing temperature, a composite with an optically inert polymer could create a writable medium, and by using multilayer co-extrusion, this system could create an industrially feasible 3D data storage network with high recording densities and rewritability.

Previous work by Gupta, et. al, has shown the feasibility of such a study.\textsuperscript{17,18} By incorporating a low $T_g$ phosphate glass and using partial compatibilization techniques the glass was dispersed very efficiently in a polypropylene based composite structure. By reducing the dispersed particle size and inducing biaxial orientation, the well dispersed spheres were stretching into impermeable discs throughout the material. Using multilayer co-extrusion technology, a film with hundreds of layers could be continually produced, and after biaxial orientation would have small, almost impermeable glass layers of very high aspect ratio. Using this type of approach, a crystallizable chalcogenide glass could theoretically be incorporated into a polymer and form a highly layered system with much higher rewritable data storage density than currently possible.
3.3 Experimental

Materials

Polycarbonate (Calibre® 200-14) was obtained from Styron (formerly Dow Chemical Company) and used as received. Commercial chalcogenide glasses (AMTIR-6 and C-1) were obtained from Amorphous Materials and used as received. All other glasses were prepared by the Morgan Research Group at Fisk University and were used as received. All compounding was performed on a DACA corotating twin screw extruder at 100 rpm for 4 min at various temperatures based on the individual material properties.

Characterization

Thermogravimetric analysis (TGA) was performed to determine degradation point for PC and chalcogenide glasses on a Mettler-Toledo TGA model 851e. All samples were heated at 10 °C/min to varying maximum temperatures. Differential scanning calorimetry (DSC) was performed on all materials to determine glass transitions and crystallization/melting behavior on a Mettler-Toledo DSC model 822e/700. Samples were ran at 5-10 °C/min from 25 °C to a maximum temperature based on their TGA decomposition temperature and back to 25 °C for 2 cycles. Rheological testing was performed on an Anton Paar MCR501. Scanning Electron Microscopy (SEM) was performed on Pd coated samples using a FEI Quanta 200 3D ESEM/FIB system. Vis/FTIR measurements preformed on a Cary 500 UV-VIS-NIR Spectrophotometer from 600 nm – 2000 nm.
3.4 Discussion

Chalcogenide glasses have similarities with organic polymers, both sharing relatively low glass transitions and the ability in some distinct cases to form crystallized structures. The main difference between the two classes of materials is the nature of transitions and stability of intermolecular bonding, most notably in crystallization and degradations.\textsuperscript{12,19} Organic polymeric materials have long range covalent bonding with relatively low energies required for bond destruction and crystallization in comparison to chalcogenide glasses. This usually puts inorganic phase change materials out of the temperature range of most polymers in direct contact, which is why a dielectric layer sandwiches the chalcogenide glass layer in most optical media. For a direct polymeric blend, glasses should be chosen that have thermal properties both close to organic polymers and with the ability to crystallize in a workable range in direct contact with polymeric materials.

Because chalcogenide glass compositions can vary as much as those of the organic polymer family, certain criteria should be met when choosing the chalcogenide glass composition to use in our experiments. Five chalcogenide glass compositions were chosen, two commercially available glasses manufactured for optical fibers and IR filters and three glasses supplied by our collaborators at Fisk University, covering a range of high and low glass transition temperatures that could be blended with polycarbonates. The composition of these glasses are given in Table 1. C-1 and AMTIR-1 are commercial glasses with low $T_g$’s and specifically produced for highly precise optical equipment and have a low chance of being highly crystallizable, but are equally important for comparison and choice of appropriate glasses to manufacture synthetically.
F1, F2 and F3 were all chosen based on the work of Chen al. based on their reported $T_g$ and presence of crystallinity.$^{14}$

An extensive study of thermal properties was needed to find the correct criteria for a combination of polycarbonate and chalcogenide glass suitable in blending and co-extrusion. The glasses should have similar melt flow properties and glass transitions to the polycarbonate, and to determine the thermal transitions differential scanning calorimetry was used. **Figure 1** shows the first heating curves and the first cooling curves of polycarbonate in comparison to a commercial glass, C1, and the lower $T_g$ glass F1. While the $T_g$ of the polycarbonate follows similar heating and cooling curves, the chalcogenide glass curves are vastly different from the first heating to the subsequent cooling. The dramatic shift in $T_g$ in the chalcogenide glasses can be attributed to thermodynamic effects based on the much slower cooling rates and the reversing of aging in the material. This dramatic shift in $T_g$ is present in all the chalcogenide glasses tested, but is most prevalent in the synthesized glasses due to residual stress from synthesis not being relieved by the processing that the commercial glasses undergo.

To be a suitable material in this study, the chalcogenide glasses must display a good crystallizability at lower temperatures than result in polycarbonate degradation. Crystallization is necessary for writing and reading data and crystallizing the material above these temperatures would damage the matrix polymer and limit the rewritability of the medium. Glasses were tested for crystallization using differential scanning calorimetry. The commercial glasses, shown in **Figure 2** and **Figure 3**, behaved as expected showing little, if any, crystallization. In both C1 and AMTIR-6 slight peaks could be repeatedly observed in cooling, but all testing shows that any crystallization is
not significant enough to produce a rewritable medium. As for the synthetic glasses F1 showed no crystallization, while F2 and F3 showed very significant crystallization. **Figure 4** shows the second heating and cooling curves for F2 and it is apparent that the material crystallizes readily, although the melting point of 410 °C is higher than desirable for these materials.

Rheology of the glasses in comparison to the polycarbonate is extremely important for many reasons. In the blending of the material before considerations of compatibilization to get homogenous dispersion of the minor phase, the materials need to have similar viscosities. Even more important are viscosity matches in multilayered materials. The multilayer co-extruder has a viscosity and heat limit (upper limits are around 1000 Pa*s and 300 °C) and the materials need to have very similar viscosities in this range for the scope of this project. Materials were tested under 300 °C on a parallel plate melt rheometer for determination of viscosity matches. **Figure 5** shows results for 3 materials (polycarbonate, C1 and F1) that did not crystallize for simplicity of testing. F1 had a much lower T_g than PC or C1, and a rheological match was not possible for this material. PC and C1, with matching T_g’s had very close viscosities at the upper limit of the temperature window, leading to the conclusion that similar T_g’s make good rheological matches. While F2 and F3 had similar T_g’s to polycarbonate, they do not fully melt until 400 °C because of crystallization and are assumed to be unfit for co-extrusion purposes.

To determine the possibility of making a suitable composite, the melt blending of C1 and polycarbonate was performed; this pair of materials was chosen because of their similarities in viscosities at co-extrusion temperatures. If disperse particles of small diameter can be achieved by melt blending, the possibility of making a chalcogenide
A glass/polycarbonate blend would be much more feasible. The materials were blended at a 95/5 wt. % mixture of polycarbonate/C1. The material was compression molded into a film at 300 °C, and produced a flexible black material. SEM imaging was performed to determine the morphology of the blend, shown in Figure 6. The glass did not disperse well and substantial voiding was observed around particles, indicating very poor compatibility. The blend of polycarbonate and glass could likely be improved lowering the surface tension of the glass, which is likely much higher than the polycarbonate, or adding a compatibilizer.

Determination of optical properties of the glasses also needed to be undertaken to determine the correct combination of glass and polymer for a multilayered data writing application. FTIR analysis was performed on some of the glasses, the results shown in Figure 7. Polycarbonate is mostly transparent in visible regions, so the main absorption processes would involve chalcogenide glasses absorbing visible light with inexpensive commercial lasers. While the AMTIR-1, an arsenic trisulfide commercial glass, showed very high transparency in the visible region the Ge-based glasses all of the glasses exhibited high levels of absorbance in the visible region, making them suitable for these applications. The refractive index of these materials, however, did not match up well. Polycarbonate has a refractive index of n=1.585, while chalcogenide glasses have refractive indexes of n=2.4 or higher. This difference would not be a huge issue in single layer data storage medium, but using two photon processes involve angled incidental light and writing through multiple layers, as shown in Figure 8, would be very difficult to control. Given this barrier to success, a decision was made to move on to two-photon absorbable dyes that could display rewritability through light based heating.
3.5 Conclusions

Creating a three dimensional medium for data storage with rewrite capabilities shows significant promise for next generation portable storage, such as replacing DVD and Blu-Ray technologies. Combining current technologies such as current rewritable discs and extending their capacity by a productivity friendly process such as multilayer co-extrusion would be extremely advantageous. Chalcogenide glasses are very similar to organic polymers in general flow properties and could make good candidates for this type of approach if not for insurmountable differences in refractive indexes, preventing multilayer data writing and reading with current laser technology. Composites of these materials are possible by simple melt blending, although good composites would need significant compatibilization to achieve adhesion between the two materials. Given these major obstacles, the decision was made to adjust the focus of high density 3D data storage to systems based on light assisted thermal aggregation and dispersion of a TPA dye in a polymer matrix.

3.6 Acknowledgements

We would like to thank Dr. Steve Morgan and his research group for continued collaboration in this project and the synthesis of the experimental chalcogenide glasses.
3.7 References


### 3.8 Tables and Figures

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**Table 1:** Materials, composition and basic thermal properties of glasses used in study.

Degradation temperatures were not evident in some chalcogenide glasses in this study.
Figure 1: DSC first heating (top) and cooling (bottom) curves.
Figure 2: Second heating and cooling curves for C1.
Figure 3: Second heating and cooling curves for AMTIR-6.
Figure 4: Second heating and cooling curves for F2.
Figure 5: Viscosity profiles for glasses compared to polycarbonate.
Figure 6: SEM image of 95/5 wt % blend of polycarbonate/C1.
Figure 7: FTIR spectra for 3 chalcogenide glasses. AMTIR-6 has relatively little absorption in visible range, but Ge based glasses C1 and F1 absorb strongly.
Figure 8: Schematic of data writing in single disc or layer (top) and multiple layers (bottom). Because of the difference in index of refraction, writing and reading in subsequent layers is much more difficult.
Chapter 4: Improving Mechanical Properties of Clay/Polymer Aerogels by a Simple Dip Coating Procedure

4.1 Abstract

Clay aerogels have many advantages as one of the lowest density materials current technology can provide, having very low thermal conductivities, high porosity and high surface area. Although the mechanical properties of native clay aerogels are somewhat low, incorporating water soluble polymers into the clay gel before processing into aerogel form can easily form a much stronger composite. Various processing modification and incorporations can be employed to strengthen the aerogel material but currently the materials have some notable weaknesses in abrasion resistance, water absorption and flexural weakness. The present study employs a low cost rubber coating material to quickly and efficiently solve all three problems. After coating, the aerogels gain significant mechanical reinforcements of 20 x in flexural modulus and 15x in yield stress, while exhibiting a decrease of only 8% in thermal conductivity. Improvements such as this makes the clay/polymer aerogels much more attractive as thermal insulation materials.

4.2 Introduction

Sodium montmorillonite has been extensively used as a cheap, renewable resource for addition in polymer composites.\textsuperscript{1-3} Over the past 10 years, it has also been used as an environmentally friendly source for making aerogel materials.\textsuperscript{4-18} The process for producing these materials involves the freezing of an exfoliated clay gel in water with the ice growth pushing the clay into sheets and the subsequent lyophilizing of this frozen
material to leave only the “house-of-cards” clay structure behind. These materials are very attractive because of their extremely low densities, low thermal conductivities, high surface areas and high porosity. With only clay in the suspension though, these aerogels lack the mechanical properties, solution resistance and recoverability to make them broadly useful beyond the academic landscape.

Many successful attempts to increase the mechanical performance of clay aerogels have been reported recently, with the most widespread success being the incorporation of water soluble polymers in the original water and clay suspension prior to freeze drying. Fiber reinforcement has also proven to be a highly successful way of reinforcing the aerogel composites, with much more improvement in multi-directional stresses. Reactive mixtures have been successful in crosslinking the polymers or monomers in the original solution post-lyophilizing to impart a great deal of recovery, making these materials act much like polymer foams. Even more recently there have been efforts to develop silica layers on the surface of the clay/polymer composites that can increase the mechanical values by a factor of one. It has been shown that these reinforcement methods will slightly increase density of the aerogels, while still retaining a very low thermal conductivity, making these materials very attractive as more eco-friendly replacements for traditional polymer foams.

Thermal conductivity aside, one of the other reasons that clay aerogels are inherently important is the ease of molding the aerogels into any shape desired. The clay gel freezes to the shape of whatever container it is in, giving the materials a distinct advantage over materials that need to be shaped into their desired part after formation. Lateral and vertical orientation of the structural layers in clay aerogels have previously been studied
The results of these studies show higher strength in the oriented direction, but without further modification the aerogel can be weak in the layer perpendicular to orientation. Coating technology, in all various forms, has been one of the principle applications in polymer science. The application of coating technology to aerogel technology hopes to address the problems posed by vertical orientation by adding a flexible outer layer that gives the material flexural stability and abrasion resistance while minimally affecting the density of the aerogel.

4.3 Experimental

Materials

Sodium montmorillonite (PGW grade) was obtained from Nanocor Inc. and used as received. Deionized (DI) water was obtained using a Barnstead Nanopure low pressure, reverse osmosis purification system. Triethylenetetraamine (TETA) and 1,4-Butanediol diglycidyl ether (BDGE) were obtained from Sigma Aldrich Co. and used as received. Liquid Tape® made by Performix, a dispersion of synthetic rubber in organic solvent, was purchased from a local vendor and used as received. Urethane RTV Mold-Making System® was obtained from TAP Plastics and used as received. The aerogel sample for thermal conductivity measurements was provided by Aeroclay Inc. and was produced from 5 % clay, 2.5 % PVOH, and 1 % PVOH fibers content in the original aqueous mixture prior to freeze drying.
**Materials and Preparation of Polymer/Clay Solutions**

16.115 g BDGE was added to 100 mL DI H₂O and mixed thoroughly by hand until dissolved. 5.000 g of sodium montmorillonite was mixed in slowly with an electric hand mixer, carefully avoiding bubble formation. 3.885 g TETA was added slowly and mixed in thoroughly by hand. Samples were transferred directly to a freeze drying molds, which was transferred immediately in a VirTis AdVantage@ EL-85 freeze-dryer. The shelf was cooled down to -30 °C until they were completely frozen, then freeze dried for 96 hrs. After freeze drying, samples were placed in a vacuum oven at 80 °C for 24 hrs to complete curing reaction.

**Coating**

Samples were cut into desired shape for testing using a band saw when needed. Copper wire was pushed through the sample to hold during coating. The samples were then dip coated with the Liquid Tape and hung to dry. Any holes from removing the copper wire were sealed afterwards with an additional spot coating of exposed areas using a brush. The panel provided for thermal conductivity measurements was coated by brush and left to dry overnight.

**Testing**

All samples were measured and weighed to obtain densities before and after coating. Mechanical testing was conducted using an Instron model 5500 Universal Testing Machine equipped with a 1kN load cell. All compression testing was performed at a
constant strain rate of 1 mm/min, with 3 replicate tests for each set of samples. All data analysis was performed in Microsoft Excel. Thermal analysis testing was performed using a LaserComp Fox 314 Heat flow meter.

4.4 Discussion

Initial studies to form clay aerogels found that at 5 wt. % in the initial solution could give densities close to 0.05 g/cm$^3$ and a compressive modulus as high as 10 kPa.$^{12}$ While that density is very low, the associated mechanical properties were far too low to be of significant value, by this method alone. Attempts to increase the mechanical values have been exhaustive, and most commonly employ the use of a water soluble polymer with some sort of interaction with clay to get the best results while keeping the density low. Poly(vinyl alcohol) has been one of the most studied systems within the Schiraldi group’s aerogel program, and can lend much mechanical improvement, while still providing very low densities and thermal conductivities.$^{16}$ With a 5 wt. % addition of polyvinyl alcohol at a modest $M_w$ of 85,000 – 124,000 g/mol, for example, the initial compressive modulus rose an order of magnitude to 1.6 MPa relative to pure clay aerogels.$^{17}$ The inclusion of natural and synthetic fibers has also pushed the boundaries of mechanical robustness by acting as a sort of rebar for the system, transferring load to the continuous fiber to lower stresses on the individual clay/polymer sheets.$^8$

Most aerogels reinforced only by water soluble polymer gain a significant amount of mechanical integrity with a higher addition of polymer, but only become useful materials around 2.5 - 5 wt. % addition. A 20 wt. % addition of the epoxy starting material was
needed to increase the initial modulus to ~0.5 MPa, which slightly lower than a 5 wt. %
addition of poly(vinyl alcohol) (~1.5 MPa) but with much more starting material. The
density rose to 0.2 g/ cm³, which is close to that of similar composites and still very low.
The main advantage in using the epoxy system is the ability to cross-link, lowering the
water solubility to negligible amounts. Also, with such high cross-link density the
elasticity and recovery of the aerogel should be much higher than normal methods of
reinforcement.

To further improve this technology, it is important that the material to coat aerogels be
tough, easily obtainable and low cost. Commercially available synthetic rubber coating
material commonly known as Liquid Tape® covered all of the previous requirements
while also having a quick drying time and easy application. Epoxy aerogel samples were
dip coated and dried overnight, giving a relatively uniform coating of 0.38 mm in all
samples, as measured with a digital caliper. Samples before and after coating, as well as
a cross-section of the coating on the aerogel can be seen in Figure 1. Samples were cube
shaped for compression testing and custom shaped bars for flexural testing.

The initial properties of the coated aerogels were much better than the uncoated original
materials. The average density of cube shaped aerogel samples rose from 0.22 g/ cm³ to
0.35 g/ cm³, while the smaller flex bars density rose from 0.24 g/ cm³ to 0.39 g/ cm³.
Since these are smaller samples and the average coating thickness of all samples was
fairly uniform at 0.38 mm, one can assume the density changes would be less important
with larger samples. Compression testing was then performed to evaluate the practical
improvements that the coating offered. Seen in Figure 2 are common stress-strain curves
for the coated material compared to the original epoxy aerogel, showing a marked
improvement in all aspects of mechanical performance. Figure 3 clearly shows that the initial modulus has risen from 0.41 MPa in this specific sample set to 1.6 MPa. Since the initial modulus can have large variations from sample to sample, with these materials it is better in some circumstances to compare the working modulus, taken after initial modulus and within the elastic region of deformation, that gives a better indication of performance during use. The working modulus rises from 3.2 MPa in the original epoxy aerogel to 6.4 MPa in the coated materials, improving the performance by double. The toughness values almost double as well, rising from 5.2 MPa to 9.2 MPa. Overall, the boost in mechanical values in compression rise somewhat from a small application of coating layer on the outside of the material.

Flexural testing on unreinforced clay aerogels is somewhat difficult as samples tend to break at relatively low strains due to weak cohesion between the layers of the material. That behavior was indeed the case with epoxy aerogels, seen in Figure 4; the samples broke cleanly at low levels of displacement. This type of behavior is a severe limiting factor in aerogel applications, as even in low flexure applications such as thermal insulation these materials still need to have some flexural integrity. By coating the aerogels with a synthetic rubber layer the samples not only gain mechanical performance but the coating prevents the samples from breaking, the data from these experiments shown in Figure 5. Figure 6 shows a comparison of the flexural testing between the 2 samples with an image showing the samples after testing. The coated samples outperform the original aerogels, raising the flexural modulus from 0.82 MPa in the original epoxy aerogels to 17.0 MPa in the coated material. The yield strength of the
coated aerogels similarly increased from 0.95 N to 15 N, netting an order of magnitude increase in mechanical properties over the starting, uncoated aerogels.

The coated aerogel is what is considered to be a classic sandwich composite, the rubber coating reinforcing the aerogel material, specifically in flexure, to retain low density while increasing the use of such a material. Gibson and Ashby expounded on the theory and optimization of such a structure, in particular to a coating being applied to a foam core.\textsuperscript{18} When mechanical properties are measured in flexure, one common property in coated foams is equivalent flexural rigidity ($R_{eq}$) that can be obtained by the following equation\textsuperscript{18}:

$$E_{tot}I = \frac{E_f b t^3}{6} + \frac{E_c b c^3}{12} + \frac{E_f b d^3}{2} = R_{eq}$$

In this equation, $R_{eq}$ = equivalent flexural rigidity, $E_{tot}$ = flexural modulus of coated composite, $I = 2^{nd}$ moment of inertia, $E_f$ = flexural modulus of the coating/face, $E_c$ = flexural modulus of the core, $b$ = width of coated material, $t$ = thickness of coating, $c$ = core thickness and $d$ = total sample thickness. The first term accounts for the contributions of the coating, while the second term accounts for contributions from the core, while the third term accounts for the contributions of the coating to the whole sample. Using this method to solve for the modulus of the rubber coating the expression is reduced to $E_f \sim 92$ MPa. When compared to the core flexural modulus and composite flexural modulus ($E_c = 0.82$ MPa, $E_{tot} = 17$ MPa) it becomes apparent that the coating significantly reinforces the material.
A significant increase in mechanical properties has been fully demonstrated for coating the aerogels with a synthetic rubber material, but this advantage can come with some trade-offs, mainly in thermal conductivity. If the thermal conductivity for the coating is much higher than the aerogel, which given aerogels very low thermal conductivity is assumed to be the case, then conductive thermal transfer could occur throughout the coating and short circuiting the aerogel’s insulative structure. Because the coatings used in this study are very thin in relation to the aerogel samples, this conductive concern might not be problematic, but needed to be tested. For this experiment, an external sample was received from Aeroclay Inc. with known thermal conductivity values that were very low for good comparison. Thermal conductivity values for the original and coated samples are given in Table 1. It is clear that thermal conductivity does increase but not by an appreciable amount, and these coated materials are well in the range of other low thermal conductivity insulators.

4.5 Conclusions

Through a study with a common coating material a method was established for coating aerogel materials with a thin uniform coating. Coating the materials with this specific synthetic rubber coating gave great increases in all performing aspects of the aerogel material, perhaps the most important impact was on flexural properties, an improvement of 20x in flexural modulus and 15x in yield stress. With this coating, the flexural performance of aerogel materials can compete with more traditional insulating materials such as fiberglass or polymer foams. The thermal properties do not change significantly with this coating, only reducing by 8% of the original aerogel, so this technology would be highly advantageous to aerogel applications in the insulation field. It can be assumed
that other coatings with different chemistries could impart characteristics, such as selective absorption, hydro/olio-phobicity, tailored mechanical reinforcements, etc.

4.6 Future Outlook

The main success in this study was finding an easy way to strengthen the materials in flexure. To further develop this success, many other coatings should be tried to determine the types of properties one can gain. From early trials in finding the preferred coating used in this study, it was found that other coatings such as polyurethane and 2 part epoxy materials commercially available could impart much different properties on the exterior of the aerogel. Such investigations should continue, especially in the area of smart coatings and biodegradable rubber-like coatings. These types of coating would be very beneficial to the “green” effort that is currently being undertaken in most production facilities in the country.
4.7 References


(15) Schiraldi, D. A.; Pojanavaraphan, T.; Magaraphan, R.; Chiou, B. S. 
_Biomacromolecules_ **2010**, *11*, 2640.


(18) Gibson, L. J.; Ashby, M. F. _Cellular solids : structure & properties_; 1st ed.; 
4.8 Tables and Figures

Figure 1: Aerogels with coating applied. Top figure shows a cube shaped aerogel sample before and after coating. The bottom image shows a cross section of the material after coating.
Figure 2: Compression behavior for epoxy aerogel with (top) coating and without (bottom) coating.
Figure 3: Mechanical properties for epoxy aerogels before and after coating.
Figure 4: Force-displacement curves for flexural testing of epoxy aerogels (3 replicate samples).
Figure 5: Force-displacement curves for flexural testing of coated epoxy aerogels (3 replicate samples).
Figure 6: Comparison of mechanical behavior before and after coating (top) with an image of complete failure without coating (bottom).
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**Table 1:** Thermal conductivity measurements of coated and uncoated materials.

5.1 Abstract
Clay aerogels, ultra-low density materials made via a simple freeze drying technique, have shown much promise in broad applications due to their low densities, often in the same range as silica aerogels (0.03-0.3 g/cm³), but suffering from low mechanical strength. A bio-inspired approach to mineralize an active polymer/clay aerogel composite is inspected, showing marked improvement of the mechanical properties with increasing modification. Further property improvement was achieved using a layer-by-layer approach to produce alternate layers of polymer and silica on the surface.

5.2 Introduction
Layered silicates have been used extensively over the past 20 years as an affordable and renewable source of reinforcement in nanocomposites, clays such as sodium montmorillonite being at the forefront of these efforts.¹⁻³ Recently it has been found that the layered silicates, through a simple and environmentally friendly process, can be converted into aerogels with ultra low densities (0.05-0.1 g/cm³).⁴⁻¹⁰ Their unique house of cards structure, generated by a rearrangement of the clay during freeze drying, offers many different benefits ranging from thermal insulation properties to an extremely large surface area for efficient catalysis reactions. Although these materials can be very beneficial, most suffer from a lack of mechanical strength without reinforcement.
Incorporation of organic materials into the inorganic framework of clay aerogel materials has been used as a means of enhancing mechanical properties. A variety of water soluble polymers in the original solutions before freezing so that the polymers are included in the rearranged house of cards structure. Many porous composites, clay aerogels included, have also benefitted from reinforcement from natural and synthetic fibers. Another method of reinforcement has been the cross-linking of organic precursors within the template of the material, imparting low hysteresis loss behavior in the reinforced composite material subjected to repeated stress application. All these efforts have yielded success to a degree, and all retained the low density that gives this material its most valuable attribute.

Biomineralization is a natural process of building intricate inorganic-organic composites for improved structural integrity, sensory perception and other biological functions. Mineralized systems generally consist of complex hierarchical structures with alternating layers of minerals surrounded by a polymer. Silica mineralization in diatoms employ lysine based proteins to selectively uptake silicic acid from seawater and condense this to an amorphous silica exoskeleton. Many polyamines have been investigated to determine their silica forming ability including polylysine, poly(allyl amine) and poly(ethylene imine). Similar approaches have been used to increase the chemical and mechanical stability of polyesters as well. Of these systems, poly(ethylene imine) (PEI) has shown the ability to direct silica formation from pure alkoxy silanes with the help of a catalytic amount of water almost instantaneously, requiring little time in
solutions for systems sensitive to water. PEI has also been shown to have strong interactions with 2:1 layered silicates such as sodium montmorillonite.

The present work describes the production of PEI/Clay aerogel and the subsequent mineralization of this composite by condensation of tetramethyl orthosilicate (TMOS) with the polymer backbone, and the resultant enhancement of the mechanical properties of the aerogels. The effects of layering PEI and silica were also investigated.

5.3 Experimental

Materials

Tetramethyl orthosilicate (>98%, TMOS), lithium chloride (>99%), acetone (≥99.5%) and methanol (≥99.8%) were purchased from Sigma Aldrich Co. and used as received. Branched poly(ethylene imine) (B-PEI) with $M_w = 1,800$ and linear poly(ethylene imine) (L-PEI) with $M_w = 2,500$ were purchased from Polysciences, Inc. and used as received. Sodium montmorillonite (PGW) was obtained from Nanocor Inc. and used as received. Deionized (DI) water was obtained using a Barnstead Nanopure low pressure, reverse osmosis purification system.
Preparation of Aerogels, Silicification and Subsequent Layering

5.00 g of sodium montmorillonite (PGW) was slowly added to 45 g DI water while mixing by hand to wet clay, then the mixture was transferred to a Waring model MC2 mini laboratory blender and mixed at high speed for approximately 1 min. 5.00 g of B-PEI was added to 50 ml of DI water to produce a readily soluble mixture. The B-PEI solution was slowly added to the clay gel for a final 1:1 ratio of 2.5 wt. % clay : B-PEI. The resulting hydrogels were then transferred to 2 cm diameter cylindrical vials and immediately frozen in an ethanol-dry ice mixture. Frozen samples were transferred to a VirTis AdVantage® EL-85 freeze-dryer and subjected to very high vacuum to sublime the ice for 5 days. Resulting aerogels were cut into similar dimensions using a band saw and placed in dessicator until silicification.

Samples were taken out of dessicator and placed in a ~80% relative humidity chamber prepared by dissolving 17.73 g LiCl in 100.00 g H₂O, sealed and left for 3 days to equilibrate. Aerogels were removed from the humidity chamber and placed in small vials which were then filled with neat TMOS and allowed to react for 30 sec. After reaction, further reaction was limited by immediate and thorough rinsing with acetone. Samples then were allowed to dry in air overnight and placed back in the dessicator for further drying until characterization or subsequent layer.

For layering of the silicified aerogels, 2 g linear PEI (L-PEI) was dissolved in 200 ml methanol to produce a 1% solution. Samples were taken out of the desiccator and immediately placed in small vial with 10 ml of the 1% PEI solution and allowed to soak
for 20 min. Samples were taken out of the solution and placed in a vacuum chamber heated at 60°C to drive the solvent off and leave the adsorbed L-PEI. Samples were then placed in the humidity chamber for 3 days and subsequently silicified in the same conditions with TMOS. Subsequent layers were deposited in the same method.

**Characterization of Materials**

Compression testing was conducted using an Instron 5500 Universal Testing Machine equipped with a 1kN load cell. All compression testing was performed at a constant strain rate of 1 mm/min with \( n=3 \) for each set of samples. Imaging was performed on Pd coated samples using Philips XL-30 Environmental Scanning Electron Microscope.

**5.4 Discussion**

In the investigation of mineralization as a method of a reinforcement of clay aerogels it is useful to have the mechanical properties of virgin aerogels along with some standards in reinforcement. Previous studies have shown clay aerogels produced from a 5 wt. % solution in water without reinforcement to have an initial modulus of 10 kPa and have a density close to 0.05 g/cm\(^3\).\(^3\)\(^{-9}\) Reinforcement of a clay aerogel by addition of a polymer to the architecture should ideally incorporate a clay-interactive polymer, but also should be water soluble to be processed into an aerogel in the same manner. Poly(vinyl alcohol) with a \( M_w = 85,000 \) – 124,000 g/mol has been shown to exhibit strong interactions with montmorillonite,\(^6\) and was quite advantageous when added to the initial mixture, raising the initial modulus more than one hundredfold to 1.6 MPa.
Poly(ethylene imine) has been demonstrated to strongly adsorb to clay surfaces and strongly influence the rheology of clays in water mixtures. Branched PEI was initially used in the present work to reinforce the clay aerogels because of the tendency of linear PEI to crystallize into fibers while cooling in a water solution. Branched PEI showed the ability to reinforce the aerogel while retaining the low density desired of the material, increasing the initial compressive modulus to 270 kPa and the density to 0.075 g/cm³ when 2.5% PEI was incorporated in the starting clay/water mixture. While these values indicate lower interaction of PEI with clay than PVOH, the molecular weight of the B-PEI was much lower and the initial solution had half the clay loading, leading to the difference in mechanical properties.

Diatom silicification has been exhaustively studied over the past 50 years providing much information on the process, and has subsequently been mimicked often with similar material. The initial formation of amorphous silica within the organism begins by the uptake of silicic acid and the deposition along silacin protein segments. Many studies of the deposition of silica on natural and synthetic proteins of this nature have isolated the most easily reproducible segment of the proteins to be a polyamine type subunit. Being one such type polymer, poly(ethylene imine) has an advantage over other polyamines because, with water present, it exhibits an almost instantaneous silicification directly from alkoxy silanes, such as TMOS. This reaction occurs with a catalytic amount of water that helps in the initial hydrolysis of the alkoxy silane, followed by a condensation into amorphous silica. Because the PEI aerogels in this study are soluble in
water, the reaction would necessitate an instantaneous mineralization prevent the aerogel from deforming.

For silicification of the PEI aerogel to occur, a catalytic amount of water must be present in the aerogel without physically being in water. To prevent too much water uptake the aerogels were placed in sealed humidity chambers on a platform over LiCl solutions giving relative humidities of 60% and 80%. When kept at 60% RH, the initial modulus only rises from 270 kPa to roughly 870 kPa and upon visual inspection the sample was slightly deformed from its original dimensions. The sample kept at 80% RH and silicified had an initial modulus of roughly 2.8 MPa, while maintaining its original dimensions, an increase in modulus of over 1 order of magnitude. These findings suggest that an ideal catalytic amount of water was present at a relative humidity of 80%.

Further inspection of these materials under SEM shows the aerogel maintains its lamellar structure, while adopting a rougher surface on the individual sheets, shown in Figure 1. The silicification changed not only the initial modulus, but the behavior of the aerogel undergoing compression, shown in Figure 2. Most clay aerogels tested in compression to date, along with other low density materials such as polymer foams, undergo an initial loading response followed by a leveling off while the material collapses and once all the voids have been collapsed the stress-strain behavior quickly transitions into work hardening.5, 7-9 This behavior is seen in the PEI/clay aerogel stress strain behavior in compression. After silicification though, the material undergoes a series of localized fractures, avoiding total yield until a critical amount of fractures occurs. This behavior is believed to be because of the increased toughness of the supporting layers along with a
decrease in flexibility. Supporting layers can absorb more load but will undergo brittle fracture systematically, one connection at a time.

In many biomineralized systems, such as seashell nacre, additional reinforcement comes not from just a coating of minerals, but a layered system that can absorb and transfer more load through the alternating soft organic phase and hard inorganic phase. This natural approach leads to very tough materials that can withstand much more impact than either material alone through cooperative stress dissipation. Since PEI has such a strong interaction with silicates, an alternative soaking process can be performed where after one silica layer has been deposited, the PEI can be adsorbed to the surface in solution and another layer of silica can be added. This layering approach is summarized in Figure 3. For this approach linear PEI was used for enhanced mobility throughout the aerogel. Instead of using water, which LPEI can readily crystallize in, methanol was used as the solvent because this crystallization does not occur in methanol. Because of methanol’s low vaporization temperature, the LPEI could be assured to stay in the aerogel by flashing the solvent off at 70 °C under vacuum.

Table 1 shows the results of layering up to 5 layers of silica, zero layer indicating the PEI/clay aerogel material before silicification, and Figure 4 shows SEM images of the layering at layer 3 and layer 5 of silica. Because of small variations in the architecture of each different aerogel, some samples underwent initial yield at various points, many different aspects of the mechanical data were interpreted. The initial modulus is an indication of the material response before any permanent damage is done to the sample.
and, shown in Figure 5A, the initial modulus of the layered material improved up to the fourth layer of silica, where a small drop was observed. At its highest level of reinforcement with 4 layers of silica, the initial modulus was improved over the original PEI/clay aerogel by over twenty fold. The secant modulus at 5 % was taken as a measure of the materials response after small amounts of permanent damage, where the material would more than likely be used. This measurement followed the same behavior as the initial modulus, with the fourth layer having the highest reinforcement at roughly 20 times higher modulus, shown in Figure 5B. The toughness of the material was calculated as more of an indication as to how well the material would perform, and was calculated at 10 and 20 % strain. At 10 % strain, the toughness of the material followed the same trend as both modulus values, maxing out in the fourth layer and slightly digressing in the fifth, with the maximum toughness being close to twenty fold higher than the original PEI/clay aerogel, shown in Figure 5C. At 20 % strain the toughness of the 5th layer was the highest, indicating at these high strain values that the material could absorb more load, and was again close to twenty times the original toughness at 20 %, shown in Figure 5D. These improvements in each area of mechanical integrity occurred with a minimal increase in the density of the material.

Values in each category of mechanical properties, except toughness at 20%, seem to indicate a loss in mechanical integrity after 4 layers, but most of the data for the fifth layer of each set lies within the error of the fourth layer, indicating a leveling off of beneficial reinforcement. Further inspection of SEM images of the 5th layer indicate that a layer is forming on the outside of the material which would prevent as much PEI, and
therefore silica, from adsorbing inside the material. This behavior would limit the amount of silica buildup and limit the reinforcement of the composite system in general.

5.5 Conclusions

Low density clay aerogels were successfully produced with incorporation of poly(ethylene imine) polymer layers showing marked improvement in compression than clay aerogels of similar clay content. These polymer-modified aerogels provided an effective platform for biomimetic mineralization of silica with tetramethyl orthosilicate, providing silica-encapsulated structures. These materials showed an increase in compressive properties of over ten-fold while still maintaining their structure and low density. Repeated treatment with PEI and orthosilicate resulted in up to five layers of silica/PEI, with progressively enhanced mechanical properties up to 20X better than the unmodified aerogel. As is the case with biomineralized structures which can be found in nature, these synthetic materials exhibit exceedingly high strength:weight ratios, likely resulting from the alternating polymer/inorganic hierarchical structure.

5.6 Acknowledgements

We would like to thanks Dr. Patrick Mather and Dr. Pritesh Patel for helpful discussions in the initial stages of this work.
5.7 References


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### 5.8 Tables and Figures

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**Table 1:** Property changes due to the alternate layering of PEI and silica. 0 Layer indicates initial, unmodified PEI/Clay aerogel.
Figure 1: Effect of Silicification: SEM images showing the PEI/Clay aerogel before (left) and after (right) silicification.
**Figure 2**: Compressive stress-strain behavior of unmodified PEI/Clay aerogel (grey) and silicified PEI/Clay aerogel (black). The inset visualizes the theoretical behavior of the silicified aerogel in the initial elastic region (A) and the stepwise failure because of brittle ties between layers.
Figure 3: Schematic of layering process. Silicified aerogel is put in a 1% PEI/MeOH solution, the solvent being quickly evaporated under vacuum. The sample is then put in a 80% RH chamber for 3 days and immersed in pure TMOS for 60 sec. This process accounts for 1 additional PEI/silica layer.
Figure 4: Effects of Layering on Structure: SEM images of silicified aerogels. A-B show different magnifications after 3 layers and C-D show different magnification after 5 layers.
**Figure 5:** Changes in Mechanical Properties of Layered PEI/Clay Aerogels: Layering silica and PEI shows initial modulus increases (A), secant modulus increases at 5% strain (B) and toughness of the material at 10% (C) and 20% (D) strain.
Chapter 6: Calcium Carbonate Mineralization on Clay/Polymer Aerogels by CO$_2$

Diffusion in CaCl$_2$ Solutions

6.1 Abstract

Poly(acrylic acid) (PAA) is known to have strong interactions with ionic silicates, such as sodium montmorillonite, along with functionality allowing for calcium carbonate mineralization. In this study, the feasibility of biomineralization on PAA/Clay aerogels was investigated. PAA formed strong bonds with the clay, and after aerogel formation the interaction acted as a physical crosslink allowing for the previously water-soluble clay/polymer solution to retain its physical structure, absorbing water without dissolving. This material was placed in a mineralizing apparatus containing Ca$^+$ ions in a CaCl$_2$ solution and CO$_2$ vapor from ammonium bicarbonate breakdown. CaCO$_3$ was formed on the surface of the aerogel, leading to mass increases of up to 300% in 2 days. XRD, FTIR and SEM observations all indicated that the CaCO$_3$ deposits on the surface as vaterite, then changes over time to the more stable calcite polymorph. The mass increases showed no improvement on the mechanical properties of the mineralized aerogel, indicating primarily surface mineralization, although at the longest mineralization trials CaCO$_3$ was observed growing on the interior of the aerogel.

6.2 Introduction

Nature produces some of the finest hierarchical composite materials in existence, and structural biomineralized composites represent some of the most elegant of the natural composites. These materials are made up of organic and inorganic elements, drawing from the strengths of each to make highly organized composites that range from cell wall
protection to highly sensitive sensory perception organs in animals.\textsuperscript{1-5} Biomineralization is very prolific in nature, occurring in most plants and animals down to microorganisms in amounts that make up for a significant uses of the base materials. This method of composites of inorganic minerals built onto organic matrices produces some of the strongest and toughest materials known.\textsuperscript{1}

Of the biomineralized materials that act as structural support mammalian bone and seashell nacre are some of the most well-known. Mammalian bone has been studied rigorously over the past century and consists of a network of collagen fibrils with hydroxyapatite, a calcium phosphate mineral, deposited within the collagen framework giving the material the very strong properties of hydroxyapatite but the flexibility that bones need to become very tough materials through the biopolymer integration.\textsuperscript{3} Nacre is the inner layer of seashells, providing the protective function of the shell itself through an incredible hierarchy formed by biological direction.\textsuperscript{1-5} It forms a “brick-and-mortar”-like structure using calcium carbonate as the hard brick layer a complex of naturally occurring polymers as the mortar layers.\textsuperscript{6} Calcium carbonate is formed within the organic framework and the hierarchy present appears, at microscopic levels, to resemble a brick wall. This has many advantages, first and foremost the cooperative nature of the brick and mortar network, much like in other biomineralized materials, gives the seashell very high impact strength because of the flexibility of the organic layer and the hardness of the inorganic bricks.\textsuperscript{7,8}

The morphology of nacre is of considerable interest when compared to clay/polymer aerogels. Inorganic “bricks” of calcium carbonate are typically platelets 5-10 µm across and 0.2-0.4 µm, lined on all sides by a thin 10 nm organic matrix.\textsuperscript{9,10} Clay aerogels and
analogous composites with polymers are very low density materials, typically in the range of 5–10 % solid and 90–95 % air. Unlike other classic aerogels where the network is formed during processing, the clay/polymer aerogels prepared via lyophilization are mechanically forced into a “House-of-Cards” structure by the freezing of the aqueous medium the gel is formed in. Processing and gel properties directs the morphology of the solid with freezing rate with the main contributors being solid content, freezing rate, polymer/clay attractions, rheology of the gel and electrolyte content. This “House-of-Cards” structure left behind by extraction of the frozen solvent is very close in resemblance to the organic framework of nacreous materials if the inorganic minerals are dissolved out, with intercalated layers of clay and polymer on the nanoscale and large micrometer scale pores.

Starting with a relatively similar morphology to nacre, clay aerogels also have the advantage of forming composites with any water soluble polymer. This gives great flexibility in choosing a polymer that not only helps form a more stable final material, but choosing a polymer with the right functionality for studying the biomineralization process. It is widely known that the formation of calcium carbonate develops on polymers with certain functional groups, in particular those having carbonate, silanol or sulfonate functionalization. While such a design motif keeps many selections open, the biomineralization process is aqueous in nature, and finding the right polymer for aerogel formation that will go into solution with clay yet soak water up after formation without dissolving can prove challenging. Poly(acrylic acid) (PAA) has been found to form strong interactions with clay minerals across the pH range due to the anionic nature of PAA and clays’ anionic and cationic nature and actually actively helps disperse and
exfoliate clay by preferably interacting with the surface over other clay sheet.\textsuperscript{22,23} This strong interaction can act as a physical cross-linking agent to help the PAA/clay aerogel act as a hydrogel after aerogel formation for use in the study of biomineral formation. Using freeze drying to produce the organic framework that strongly resembles nacreous organic framework is invaluable in understanding the natural process of biomineralization.

6.3 Experimental

Materials

Poly(acrylic acid) (M\textsubscript{w}=750,000 g/mol), CaCl\textsubscript{2} and (NH\textsubscript{3})\textsubscript{2}CO\textsubscript{3} were purchased from Sigma Aldrich and used as received. Sodium Montmorillonite (PGW grade) was obtained from Nanocor and used as received. Deionized water (DI H\textsubscript{2}O) was obtained using a Barnstead Nanopure lo pressure, reverse osmosis purification system.

Sample Preparation

15 g PGW was added to 150 mL DI H\textsubscript{2}O and blended in a small blending vessel. To obtain 5 wt\% clay/ 0.5 wt.% PAA solution, 75 mL of 1 wt.% PAA solution was mixed into 82.5 g of clay gel. Resulting hydrogels were then transferred to 2 cm diameter cylindrical vials and immediately frozen in an ethanol-dry ice mixture. Frozen samples were transferred to a VirTis AdVantage\textregistered EL-85 freeze-dryer and subjected to very high vacuum to sublime the ice for 5 days. After water removal, resultant PAA aerogel composites were cut into discs using a band-saw for ease of testing.
CaCO$_3$ Mineralization

Mineralization was achieved by placing the aerogel discs in a CaCl$_2$ solution of different molarities and exposure to CO$_2$ by decomposition of (NH$_3$)$_2$CO$_3$ in a sealed desiccator. Samples were removed at intervals of 2, 4, 8, 32 and 56 hours to observe mineral formation over time. After removal, aerogel samples were soaked in DI H$_2$O for 24 hours and rinsed thoroughly to remove any surplus ions from the mineralized aerogel material. A second lyophilization was used to remove excess water while preserving the porous structure. The final masses of the samples were recorded.

Characterization of Materials:

Compression testing was conducted using an Instron 5500 Universal Testing Machine equipped with a 1kN load cell. All compression testing was performed at a constant strain rate of 1 mm/min with n=3 for each set of samples. A Perkin Elmer Spectrum system was used to obtain FTIR analysis. X-ray diffraction (XRD) measurements were performed using a Rigaku diffractometer (RINT 2000 series) with CuK$\alpha$ source (1.5418 Å$^\circ$). Scanning Electron Microscopy (SEM) was performed on Pd coated samples using a FEI Quanta 200 3D ESEM/FIB system.

6.4 Discussion

A relatively low PAA Mw of 750K g/mol had to be used at lower concentration in water than is usual for aerogel composite formation to produce solutions instead of hydrogels (because of the ability of PAA to form hydrogels). Most aerogels reinforced only by water soluble polymer gain a significant amount of mechanical integrity with a higher addition of polymer, but only become useful materials around 2.5-5 wt. % addition. A
0.5 wt. % addition of polyacrylic acid was found to be the lowest practical addition possible, raising the density to 0.05 g/cm³, very close to aerogels with no polymer inclusion. In traditional clay aerogel composites this low level of polymer incorporation would leave the sample with severely limited mechanical reinforcement; in this specific case PAA/clay aerogels were produced with an initial modulus of 2.80 MPa, a value close to that of much higher additions of other polymers used in aerogel reinforcement. The high strength for such a small addition can be attributed to the high Mw (low for PAA, but higher than what typical is used for aerogel composites) and degree of interaction between polymer and clay. When tested for water absorption, the samples swelled to almost double their original volumes and weights without leaching out of PAA, indicating again that the high level of interaction between the two materials creates physical cross-links.

Mineralization was performed in a traditional system shown in Figure 1. Samples were cut to their desired dimensions and placed in vials with 1.5 M, 2.5 M and 5 M CaCl₂ solutions. After soaking the samples were placed in a desiccator with ammonium carbonate which decomposes creating CO₂ and NH₃. As the CO₂ dissolves into the CaCl₂ solution it can form a complex with Ca⁺ and form calcium carbonate (CaCO₃). Figure 2 tracks the weight change over time in the solution for 1.5 M and 2.5 M CaCl₂ solutions, indicating that during the primary stages of CaCO₃ formation the samples in the higher molarity solution gain more calcium carbonate. Over the course of the 56 hour experiment though the differences between the carbonate building of the 2 solutions had leveled off to more equal levels. Although a mass gain of 350% was seen in some
samples, a very appreciable level of mineral evolution in such porous samples, there was no notable change in the density of these samples indicating a filling in of these pores.

Mechanical testing was performed on the mineralized samples to determine the ability of the calcium carbonate testing to reinforce the material. Even with up to 350% weight gain, the samples did not tend to get stronger, with most samples having decreased initial moduli compared to the original PAA/clay aerogels. This behavior is summarized in Figure 3, showing that the modulus decreasing as the mass rises with time in the mineralization apparatus. This decrease in moduli with further processing is most likely indicative of the materials overall lower density due to swelling and subsequent freeze drying in the swollen state and not of the role calcium carbonate plays in the structure. Figure 4 compares two stress-strain curves for the compression of a PAA/clay aerogel with and without mineralization. These are typical stress-strain curves for both materials, and there was not large increase in initial modulus, toughness or strength that would be indicative of densification due to mineralization. This behavior could be explained by the swelling of the PAA aerogels in water, but it also could indicate surface mineralization.

To determine the chemical composition of the minerals developed on the surface, and to confirm that the weight gain seen was not residual CaCl₂, Fourier-Transform Infrared Spectroscopy (FTIR) was performed on samples. FTIR is an analytical method of investigating the chemical structure and composition of samples by exposing the samples to infrared light and monitoring the amount of light transmitted over the IR spectrum. Compounds absorb IR light at particular frequencies due to the compounds’ individual bonds either stretching, bending or vibrating at certain wavelengths. This absorption can generally reveal information about the structure of a compound, and in the case of CaCO₃
the absorption bands are well defined. The characteristic peaks of calcium carbonate, a broad peak centered at 1430 cm\(^{-1}\) and sharp peaks at 1795, 876 and 712 cm\(^{-1}\) were all clearly present in the final samples for all concentrations of calcium chloride seen in Figure 5. Evolution of these characteristic peaks confirms that calcium carbonate was present and the main chemical change brought on by the mineralization process.

Scanning electron microscopy (SEM) is one of the most useful tools in visualizing the surface of substrate by scanning the area with an electron beam in a rastering fashion. SEM imaging is essential for monitoring the changes in the mineral growth over time both on the surface and within the aerogel. Figure 6 tracks the changes on the surface of mineralized PAA aerogels at short and long times in the duration of the mineralization in a 2.5 M CaCl\(_2\) solution. Initially small spheres of calcium carbonate appear on the surface along with small blocks in some areas, which over time grow larger and eventually, at 48 hours, appear to envelop the entire surface. Calcium carbonate is known to be a polymorphic mineral, appearing most frequently in the highly unstable vaterite form that generally takes on the appearance of spheres, the crystalline calcite form which is a stable block-like mineral that usually develops at lower temperatures and crystalline aragonite with a needle-like morphology that tends to be formed at higher temperatures. The spherical formation of vaterite is difficult to see and has relatively few images in literature, but is seen clearly because of the immediate freezing of the aerogel in short mineralization times and can be thought of as a precursor to the block-like presumed calcite we observe on the surface over time. Calcite is formed instead of aragonite because of the ambient mineralization temperature, but literature suggests this can easily be made into aragonite by starting the mineralization experiment closer to 75
°C or above. Figure 7 compares the 3 CaCl$_2$ molarities used in the mineralization experiments after 8 hours of exposure to CO$_2$ via the decomposition of (NH$_3$)$_2$CO$_3$. At 1.5 M and 2.5 M, the evolution of calcium carbonate seems to follow the same pattern of crystal growth with 2.5 M showing more spherical growths, but both seeming to have high crystal growth and vaterite conversion. At 5 M, however, much more vaterite is seen, along with disc-like growths that can be assumed to be ill-formed halves of vaterite particles. This suggests that the higher Ca$^{+2}$ concentration sustains the vaterite form for longer periods of time.

Most SEM imaging to this point has shown the surface only, because no mineralization was found inside the samples during imaging. This would indicate that surface mineralization could potentially be preventing mineralization of the interior. To investigate this, a closer look was taken at a sample in the 2.5M CaCl$_2$ solution after 48 hours of mineralization, shown in Figure 8. The cross section of this sample clearly shows a large amount of mineralization on the surface of the aerogel, with very large calcite crystals and vaterite spheres, but mineralization on the inside of the aerogel is not apparent. A closer inspection of the cross-section shows many very small crystals starting to form. The most interesting of the observed crystal formations may be the crystals growing from the aerogel wall, growing much like one would expect a seeded mineral growth to. This indicates that although significant mineralization was not achieved in this particular experiment, it is possible to grow CaCO$_3$ inside the aerogel and perhaps a change of mineralization conditions or duration may lead to significant growth.
X-ray diffraction is the most common tool used to analyze crystal structure in solid materials both organic and inorganic. Wide angle x-ray diffraction was used to investigate the crystal structure of the mineralized aerogels, the results of which are shown in Figure 9. Calcite, vaterite and aragonite show very distinct XRD patterns when measured in pure forms, but mixed crystal forms complicates the spectra greatly. Montmorillonite also shows distinct XRD patterns indicating the d-spacing of clay layers from each other. Factors changing the spectrum from the addition of PAA to clays has also been shown to greatly vary the d-spacing as PAA replaces Ca$^{2+}$ ions in between layers. All these factors will greatly influence the simplicity of the spectrum and subsequent analysis, but pure crystal forms should still be easily distinguished. The spectrum after 2 hours has a great number of competing peaks, the low angle peaks being indicative of d-spacing in the clay/PAA composites. Most of the peaks are hardly distinguishable, indicating a great deal of polymorphism in the sample, but a peak at 27° corresponds to vaterite, peaks around 29° and 35° are indicative of calcite. After 4 hours there still seems to be a great deal of polymorphism, with peaks in the same range with the 2 hour sample. After 48 hours a large difference is seen, this spectrum very closely resembling that of pure calcite with trademarks peaks at 23°, 29°, 36°, 39°, 43°, 47° and 48°. The XRD data then is consistent with the SEM imaging data, indicating that spherical vaterite first deposits on the aerogel then is converted to the more stable calcite crystal form.

6.5 Conclusions

Poly(acrylic acid) is an ideal choice for clay aerogel experiments involving aqueous medium as it provides a water soluble system that forms physical cross-link to make it a
hydrogel after freeze drying. Biomineralization of this system occurs quickly to form calcium carbonate, first in the unstable vaterite form, then converting quickly into calcite at ambient temperatures. FTIR spectroscopy experiments confirm the presence of CaCO₃, while XRD and SEM confirmed that vaterite was converted to calcite over time. CaCO₃ deposited rather quickly on the surface of the aerogel but left no real improvements in the mechanical properties, indicating little buildup inside the material. Although mineralization on the interior of the aerogel was not abundant, it was observed in longer mineralization trials. It is assumed that if experimental procedure was modified to accommodate longer mineralization time and higher temperatures, the aerogel could be filled more efficiently and be closer to the structure of naturally occurring nacre.

6.6 Future Outlook

This study shows the possibility of a simple method for mineralizing a clay/PAA aerogel, and the methods should receive further consideration in future experiments. A major need in this study would be to carry out the mineralization studies for a much longer trial time to determine the ability of this type of system to develop interior mineralization more fully. One problem in the approach of this work was the density of the aerogel being less than the CaCl₂ solution, causing the aerogel to float in the solution and the CO₂ to hit the surface of the material first, which caused mineralization to occur first. A modification of this approach could have a different method of CO₂ diffusion where the CO₂ is directed to the bottom of the solution first with a needle or pipet. Another method for determining how much mineralization occurred on the surface is to find a way to keep the aerogel submerged physically without affecting the CO₂ diffusion into the solution.
Another possibility to continue PAA/clay aerogel mineralization research is to investigate other mineralization methods, in particular the polymer induced liquid precursor (PILP) method that forms an amorphous crystalline phase that preferably attaches to mineralization functional groups.\textsuperscript{24} To promote interior mineralization, two methods could be employed to determine the possibility. One would be to use nanoparticles of calcium carbonate in the original PAA/clay gel before freezing, which could serve as seeded mineralization sites in the aerogel. Another would be to develop a very strong hydrogel system from these materials, maybe even cross-linking the PAA, and attempt an electrophoretic approach to the mineralization.
6.7 References


(20) Schiraldi, D. A.; Finlay, K.; Gawryla, M. D. Ind Eng Chem Res **2008**, *47*, 615.


6.8 Tables and Figures

**Figure 1:** Set-up of mineralization by placing the aerogel disks in CaCl₂ solutions with NH₄HCO₃ powder free to decompose into CO₂ vapor and dissolve in the solution.
Figure 2: Weight changes per time in mineralization apparatus for 1.5 M and 2.5 M CaCl₂ solutions
Figure 3: Increase in mass in comparison with initial modulus of samples.
**Figure 4:** Typical stress-strain curves for mineralized and unmineralized samples.
Figure 5: FTIR spectroscopy of mineralized and unmineralized PAA aerogels.
Figure 6: Surface of the mineralized surface at 2, 4, 24 and 48 hrs for a 2.5 M CaCl₂ solution.
Figure 7: Mineralized surface of aerogels after 8 hrs in (clockwise) 1.5 M, 2.5 M and 5 M CaCl$_2$ solutions.
Figure 8: Showing mineralization after 48 hrs in a 2.5 M solution. A.) Showing top surface edge B.) Middle of the top surface C.) Closer on the edge D.) Inside of aerogel where minerals are beginning to form E.) Closer look at one of the minerals inside the aerogel.
Figure 9: XRD spectra for samples in 2.5 M solutions.
Chapter 7: Electrophoretic Calcium Phosphate Mineralization of Collagen

Hydrogels towards Bone Substitute Materials

7.1 Abstract

Natural human bone is a very complex hierarchical material made of hydroxyapatite and collagen fibrils. For bone substitute materials, one needs high porosity and bio-friendly materials to encourage the living tissue to repair itself faster and supply mechanical reinforcement of the area. In this study, collagen hydrogels were formed and subjected to electrophoretic mineralization procedures that force the calcium and phosphate ions into the material very quickly. In 1 hour a large amount of calcium phosphate was formed within the hydrogel, and an alternating soaking procedure was employed to further mineralization of the “seeded” hydrogel. Freeze drying these materials after mineralization provided a very porous network of mineralized collagen, similar to what can be found in natural bone and a step towards bone replacement materials. SEM, EDX and XRD confirmed this mineral growth and indicate that hydroxyapatite is being formed within the hydrogels.

7.2 Introduction

Calcium phosphates biomineralization is one of the most important processes in the mammalian kingdom, contributing to the structural supports and living tissues such as bone, teeth and enamel. Collagen is a naturally occurring group of proteins found mostly in mammalian connective tissue and bone, most notably in humans, and the integration of calcium phosphates and collagen give rise to one of the most interactive biological composites. In biological systems, bone tissue cooperates with its
environment in a highly interactive manner, directing the level of calcium phosphate
levels necessary to match the specific function needed.\textsuperscript{5} Hence, less mineral is found in
the more elastic bones of animals, such as deer, in comparison to the high mineral content
found in large whales. Mammalian bone is an ever-changing living tissue that grows,
dissolves and replenishes itself over time. Sometimes though, biologically mediated self-
replication and repair is not enough. Certain illnesses and injuries require bone
replacement or temporary substitution to allow the body to integrate new bone into the
body.

Bone replacement carries many risks and requirements to be successful, stressing the
importance of replacing bone with materials that closely resemble the natural material
biologically and mechanically. Ideally, the material should have the same mechanical
stability as the bone it is replacing, biodegradability to allow natural dissolution and
regrowth, high porosity to allow integration to the existing bone and tissue around it, the
ability to be formed into complex shapes to accommodate the replacement site
dimensions and biological similarities to reduce rejection or scarring around implantation
sites.\textsuperscript{4} Collagen, being the common naturally occurring organic polymer in bone,
presents itself as an ideal polymer for this application because it is biologically identical
and can integrate into new bone growth easily.

Despite many attempts to use collagen as a bone substitute, relatively little success has
been achieved due to the low rate of calcium phosphate uptake or the poor mechanical
properties. To increase the mechanical performance of such systems, water soluble
polymers have been employed as a reinforcing agent.\textsuperscript{6-8} More promising is the addition
of calcium phosphate directly to collagen gels to achieve greater mechanical stability,
although the properties fall short to those of bone.\textsuperscript{9-11} Liu et al., used phase separation to make a porous collagen/hydroxyapatite composite, and while good mechanical values were present in the composite and cell proliferation behavior was encouraging, phase separation techniques does not provide materials at a high enough rate.\textsuperscript{12} Eglin et al., introduced a composite based on collagen and employing bioactive glass to collagen hydrogels to induce osteoconductive and osteoinducive processes that encourage bone regeneration.\textsuperscript{13} While calcium phosphate precipitation was observed, the morphology of the calcium phosphate was negatively affected because of a change in the collagen structure, in turn altering the polymorph of calcium phosphate deposited. This result indicates a need for a purely biological system containing only collagen and calcium phosphates that retains the original collagen structure and the growth of calcium phosphate within the collagen fibril spacing to gain the morphology of hydroxyapatite.

Electrophoresis has been successfully demonstrated in many systems to induce fast development of calcium carbonate or calcium phosphate within the interior of a hydrogel.\textsuperscript{14-18} The advantages presented by electrophoresis are using a highly porous system and considerably speeding up mineralization times by using an electrical current to drive the positive and negative ions into the hydrogel interior to from minerals first within a material. This approach also solves the problem of surface mineralization dominating many direct mineralization routes while also giving large flexibility to the physical dimensions of the mineralized hydrogel. Presently, there have been no reports of using electrophoresis in collagen mineralization, but such a process could result in a biomineralized hydrogel that is seeded with calcium phosphate and highly porous composite materials that could be used for direct bone substitutes. An alternate soaking
approach\textsuperscript{17} takes such a hydrogel with formed calcium phosphate phases on the interior, then soaks the hydrogel in alternating baths of calcium and phosphate ions to evenly develop calcium phosphates within the material and further reinforce the material. An alternate soaking study on one such material is reported herein with the objective to determine if further mineralization could be easily and quickly accomplished.

7.3 Experimental

Materials

Lyophilized collagen (semed S, acid-soluble), principally collagen type I with ca. 5% type III, from bovine dermis was kindly provided by the Kensey Nash Corporation. Ethanol, 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), potassium chloride, sodium chloride, monobasic potassium phosphate and dibasic sodium chloride heptahydrate were purchased from Sigma-Aldrich Co. and used without further purification. Calcium chloride and dibasic sodium phosphate heptahydrate were purchased from Fisher Scientific and used without further purification. TAP Urethane RTV Mold-Making System was obtained from TAP Plastics and used as received. Deionized water (DI H\textsubscript{2}O) was obtained using a Barnstead Nanopure low pressure, reverse osmosis purification system.

Collagen Hydrogel Preparation

The collagen hydrogel was prepared by dissolving Type-I collagen into the cross-linker solution. PBS 20X buffer was prepared according to the literature.\textsuperscript{19} 16 wt. % of Type-I collagen was dissolved in PBS buffer (20x) and ethanol with the volume ratio of 1:1.
Prior to adding the buffer the cross-linkers EDC and NHS were added to the ethanol to equal 200 mM of EDC and 400 mM of NHS in the solution. Samples were prepared directly into 1 mL B-D plastic syringes at a target volume of 0.2-0.3 mL solution per syringe, and then stored for 3 days in to allow full crosslinking to occur. The syringes were cut at both ends and placed in DI water for an additional 3 days to replace ethanol and buffer solutions with DI water for hydrogel formation.

*Electrophoretic Mineralization*

For electrophoretic mineralization, a FisherBiotech® Horizontal Electrophoresis System with a 7 X 10 cm gel size was used in conjunction with a 120 V FisherBiotech® Power Supply. A mold of the well was made using the TAP Urethane Mold Making System and cut with a band saw to accommodate the 1 mL syringes without leakage from one side to the other. 0.1 M CaCl$_2$ solution was made in DI water and placed in the anode reservoir, along with a 0.1 M Na$_2$HPO$_4$ solution that was placed in the cathode reservoir. The voltage was set to 100 V and the amperage was set at 50 mAmp, with the electrical current running for various times, up to 4 hr. If further mineralization was to be performed using an alternate soaking approach, the samples were then placed in a 0.1 M solution of CaCl$_2$ for 1 hour. The second step is to transfer the hydrogel directly to a 0.1 M solution of Na$_2$HPO$_4$. The process was repeated 4 times and then the sample placed in DI water for 3 days. All other samples were placed in DI water to wash any free ions out and cut to expose the inside of the samples, then frozen in liquid N$_2$ and transferred to a VirTis AdVantage® EL-85 freeze-dryer and subjected to very high vacuum to sublime the ice for 5 days.
Characterization

Digital photographs obtained using a Nikon D80 DSLR camera with a Nikon Micro-Nikkor 55mm lens. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) elemental mapping was performed on Pd coated samples using a FEI Quanta 200 3D ESEM/FIB system. X-ray diffraction (XRD) measurements were performed using a Rigaku diffractometer (RINT 2000 series) with CuKR source (1.5418 Å).

7.4 Discussion

While collagen is relatively abundant, it is currently obtained from animal sources, making the conservation of such samples important when determining the best mineralization approach. For this reason, a traditional electrophoresis system was modified to be able to use amounts of collagen hydrogel less than the 700 mL gel volume available. A common 2-part polyurethane mold making system was obtained that filled the original gel volume, with sections in the middle being modified to insert a syringe filled with the hydrogel that could lower the amount of hydrogel needed from 700 mL to 2-3 mL, detailed in Figure 1. The polyurethane mold formed a tight fit around the syringe so that the mineralizing solutions were isolated to their respective wells. This approach also allowed for demonstrating the ease of customizing the material to a desired shape, fulfilling one requirement for bone substitution.

The electrophoretic mineralization process is relatively simple, using an electrical charge to force ions into the interior of opposite charges. While initial electrophoretic
mineralization attempts used very low times for mineralization, longer times were desired in this approach to more evenly disperse. The collagen hydrogels started as very transparent materials, and the change over time in transparency can be documented in Figure 2. Shown in the trial ran at 30 min, the initial responses were good, exhibiting very white areas on one side of the hydrogel which then spread into the interior of the gel. It can also be observed that the second 30 min sample has more buildup on the interior. This second sample was about half the size of the rest of the samples, indicating that smaller distances could be more beneficial for mineralizing the interior of the hydrogel more efficiently. At one hour of electrophoresis time, a marked improvement could be seen in the penetration depth of the white mineral formation on the interior; more general opaqueness was observed throughout the sample indicating that a greater amount of the material had built up inside of the gel. The 4 hour trial shows relatively similar results as the 1 hour trial, indicating a limit that could be achieved by this particular approach. Further visual investigation indicated that the buildup at one end could have solidified, blocking diffusion of ions after this period. Watanabe’s studies with electrophoretic mineralization have shown an alternating current could help to prevent this type of buildup.14-18 The alternate soaking approach was carried out on a 30 min sample, and after only 4 cycles of Ca$^{2+}$ and HPO$_4^{-}$ exposure the sample turned very white and bone-like, with a large increase in mechanical properties to the touch.

To determine the extent of mineralization in the hydrogels, the samples were dissected and freeze-dried for SEM analysis. Energy dispersive x-ray (EDX) spectroscopy was also employed to examine the chemical nature of any particulate inside the dried gels and
construct an elemental map of the material to determine if particulates are calcium phosphate. SEM analysis of the freeze dried collagen hydrogel, shown in Figure 3, shows a very large open network of collagen in Figure 3A, enlarged in 3B to show no particulate detected in the dried collagen hydrogel. This alone is important, giving a very porous structure of collagen with minimal manipulation. Elemental mapping shows regions of carbon and oxygen, and little calcium or phosphorous were detected that would be indicative of insufficient mineral dissolution in the collagen used.

SEM and EDX analysis of mineralized hydrogels showed completely different results. Figure 4 presents an analysis of a sample mineralized for 30 minutes. Figure 4A shows the SEM analysis of the interior of the dried hydrogel, with many small particles being revealed. Figure 4B investigates a piece of the sample with what appears to be mineral deposits on a thread of collagen, which would be an analogous precursor to bone-like mineralization. Figure 4C shows a similar region where mineral-like deposits are found on a thread; these deposits correspond with Ca mapping. Figure 4D shows the overlay of the Ca map on the SEM image, indicating that it is calcium phosphate materials (the reasonable assumption that calcium is coordinated with phosphate is made here). These images indicate calcium phosphate deposition is slowly developing at 30 minutes of electrophoresis, but that the mineralization is already deeply integrated with the collagen material.

Figure 5 shows similar images taken of a sample that underwent 1 hour of electrophoretic mineralization. Figures 5A and 5B indicate that the surface has much
more mineralization present. Also shown are exposed edges of collagen with integrated calcium phosphate in the collagen, indicating that the mineralization is not limited to the surface of the hydrogel, but occurs within the collagen during the electrophoresis. This important discovery shows that the biomineralization is occurring much like natural bone growth. Figures 5C and 5D show the mineral growth to be composed of calcium and phosphorous, with an overlay of Ca and P elemental maps on the SEM image showing perfect correspondence with the particles on the surface.

In Figure 6 SEM imaging shows a sample after 4 hours of electrophoretic mineralization with similar particle buildup to samples undergoing only an hour of processing. Figures 6A and 6B are SEM images of the interior of the hydrogel with similar buildup of particles to that is seen in the previous sample, albeit with slightly larger particles. Figures 6C and 6D confirm that the particles are indeed calcium phosphate. From initial indication and further inspection, it can be concluded that additional time beyond an hour of electrophoresis under direct current is not beneficial to mineral buildup.

To further mineralize the “seeded” hydrogel, a sample was subjected to 30 min of electrophoretic mineralization and then subjected to an alternate soaking approach detailed in other studies. Previously, it was mentioned that a strong visible change was detected after this approach, indicating a higher degree of mineralization which is further reinforced in Figure 7. Parts of the hydrogel, shown in Figures 7A and 7C, were completely enveloped by this particulate. Shown at higher magnification in Figure 7C, the material had taken on a vastly different morphology than previously seen, appearing
much like other images of calcium phosphate. Other areas had less mineralization, as shown in 7B, but these areas still had much more significant mineralization than was previously seen. Figures 7D and 7E further confirm that these are calcium phosphate minerals. This alternate soaking approach demonstrates that the seeded materials respond quite well to further mineral growth, and such a fast and easy method could be employed if mechanical properties needed to be enhanced.

To determine the collagen and minerals packing and crystal structure, if present in the material, X-ray diffraction (XRD) was employed. Shown in Figure 8 are the results from XRD measurements on the initial collagen, freeze dried collagen and samples at the 30 min, 1 hr. and 4 hr. mineralization times along with a sample that was treated with the alternate soaking approach. The collagen powder shows the characteristic peak at 2θ=7.383 corresponding to a d-spacing of 1.19 nm indicating a dried collagen matrix that is packed very closely together.4 The freeze dried collagen hydrogel displays an amorphous halo throughout the material, indicating that the structure had disrupted structure from cross-linking. After 30 minutes of electrophoresis, the d-spacing had grown to 1.61 nm, which is close to a low density hydrated collagen form with room for mineralization. A slight peak at 2θ=32°, which is one of the more prominent peaks of hydroxyapatite12,13,20, was also observable after 30 minutes of processing. After 1 hour of electrophoresis the d-spacing remained the same, retaining the peak at 2θ=32° and with a new peak arising at 2θ=26° (another peak related to hydroxyapatite). At 4 hours the peak at 2θ=26° had all but disappeared, looking much like the same spectra from the 30 min sample. This finding would not be inconsistent with previous findings by Watanabe that
mineralization can reverse under long periods of electrophoresis. The alternative soaking approach led to very prominent changes, the low angle peaks being broadened most likely indicating that the collagen structure varied greatly and a new peak at $2\theta=9.5^\circ$ indicating that d-spacing below 1 nm. This result suggests very closely packed collagen and calcium phosphate, indicating that the material is hardening. The crystal peaks at $2\theta=26^\circ$ and $31^\circ$ again are indicative of the hydroxyapatite form of calcium phosphate. Hydroxyapatite formation is desired, so the tendency of the calcium phosphate to convert to hydroxyapatite is encouraging.

### 7.5 Conclusions

While there is much more that needs to be done, this initial study indicates that an electrophoretic approach to mineralization can provide many advantages to existing systems and could be a viable approach to bone replacement with further refinement. Collagen was cross-linked and converted to a hydrogel, which was subjected to electrophoretic mineralization that substantially seeded the hydrogel with calcium phosphate. Combining this approach with alternate soaking methods has been shown to significantly increase the calcium phosphate content. XRD analysis indicates that the collagen is forming the bone-like hydroxyapatite form of calcium phosphate, which would make the material very useful in bone substitution uses.
7.6 Acknowledgements

We would like to thank Dr. Gary Wnek and Linhui Ming for collaborations in this work, specifically for providing us with the collagen hydrogels and working with us to design the best hydrogel for our purposes.

7.7 Future Outlook

While great success in the initial electrophoretic approach to mineralizing collagen hydrogels for bone replacement materials, much still needs to be investigated. Narrowing down the electrophoresis optimization was of great importance, and now the materials need to have a systematic study to determine how much HA is grown in the material and how much can later be deposited by alternating soaking. Other mineralization approaches should be considered as well, such as using simulated body fluid to deposit the minerals after electrophoretic seeding. A study needs to be carried out using the same exact optimized approach of this study and explore the mechanical properties of the gel after electrophoresis and alternate soaking procedures.

An even greater impact may arise if this same approach is applied to cross-linked collagen fiber mats produced by electrospinning. Mineralization will occur much faster due to the smaller size, and theoretically disks of highly mineralized hydroxyapatite on a dense collagen fiber network could be achieved. In this way the possibilities of a “bone tape” could be explored by varying the amount of HA that is deposited on the fiber mat. This material could be used to mechanically support injuries such as spiral fractures while promoting bone growth better than leading approaches.
To determine the possibilities of actual implantation additional studies are needed. Samples should be tested in vivo and in vitro to determine the cell attachment and proliferation within the material, and biocompatibility studies should be undertaken to determine the body’s response. If these steps are taken this may enable this material to be used as a medical material and be of greater impact.
7.8 References


7.9 Figures

Figure 1: Picture of customized electrophoresis gel reservoir.
Figure 2: Collagen hydrogels before (left) and after (right) electrophoretic mineral deposition. Time of electrophoresis are noted in white.
Figure 3: Collagen hydrogel after freeze drying. SEM imaging (A and B) show no particulates on surface indicating prior mineral residue. EDX analysis (C) indicates C and O as the primary detected elements.
Figure 4: SEM images of collagen hydrogel after 30 min of electrophoretic mineral deposition (A and B). EDX elemental analysis (C) and Ca⁺ map overlay on the SEM image is shown (D).
**Figure 5:** SEM images of collagen hydrogel after 1 hr. of electrophoretic mineral deposition (A and B). EDX (C and D) elemental mapping and subsequent overlay image are shown as well.
Figure 6: SEM images of collagen hydrogel after 4 hrs. of electrophoretic mineral deposition (A and B). EDX (C and D) elemental mapping and subsequent overlay image are shown as well.
Figure 7: SEM imaging after alternative soaking approach (A-C). Large mineral block (A) and less dense mineralization (B) are shown with a higher magnification of the mineral block (C). EDX imaging (D and E) shows analysis of the particles.
Figure 8: XRD of mineralized collagen hydrogels.
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