LONG PERIOD GRATING-BASED PH SENSORS

FOR CORROSION MONITORING

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(ABSTRACT)

Corrosion related deterioration of aging aircraft has proven to cause reduced flight availability, service lifetime, costly repairs, and if undetected, can result in potentially unsafe operating conditions. The purpose of this research is to develop, fabricate and test optical fiber-based chemical sensors for monitoring corrosion from early stages through the entire corrosion event. Although there are several preventative methods under development to address the problem of corrosion degradation, new techniques are still needed that are cost-effective and reliable to ensure an acceptable health status determination of aging aircraft and civil infrastructure. In using optical fiber-based sensors to detect corrosion precursors such as moisture, pH, nitrates, sulfates, chlorates and corrosion related metal-ion by-products the severity of the corrosive environment can be determined allowing predictive health evaluation of the infrastructure. The long period grating (LPG) element is highly sensitive to refractive index changes and with appropriate design geometry a variety of target molecules can be detected. Optical fiber long period gratings are designed to act as spectral loss elements that couple a discrete wavelength out of the optical fiber as a function of the surrounding refractive index. By applying special coating that change refractive index with absorption of target molecules to the LPG surface, it becomes a transducer for chemical measurement. Presented in this research is the incorporation of pH-sensitive hydrogels with long period gratings for the development of a fiber optic-based pH sensor. Optical fiber-based pH sensors offer numerous advantages in wastewater monitoring, blood diagnostics, bioremediation, as well as chemical and food processing. Specifically this research focuses on pH sensors that can be multiplexed with other chemical sensors for a complete chemical analysis of the corrosive environment.

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CHAPTER 1 – INTRODUCTION

1.1 OBJECTIVES AND GOALS OF RESEARCH WORK

The primary objective of this research is to investigate, develop, fabricate and test optical fiber-based sensors for the detection of pH changes that are precursory to corrosion within aluminum alloy structures. The technical approach includes identification of the aluminum corrosion phenomena encompassing the chemical species that give insight into the corrosivity of the environment, pH sensitive coating development, optical fiber sensor progress, and optimization of coating/sensor performance. The developed sensors offer numerous advantages over conventional nondestructive evaluation (NDE) methods of corrosion monitoring in aging aircraft and other infrastructure as well as excellent chemical sensor candidates for medical, environmental, and food processing applications.

1.2 STATEMENT OF THESIS

Optical fiber sensors have been well demonstrated for determining chemical and physical parameters in a variety of harsh environments because they are resistant to attack by most chemicals and can withstand elevated temperatures. They are also immune to electromagnetic interference, light weight, inherently small and have a flexible geometry [1]. Performance characteristics such as these make optical fiber sensors ideal for the detection of corrosion in hidden and inaccessible regions of aircraft structures [2]. The application of fiber optic long period grating (LPG)-based sensors for the measurement of corrosion precursors and by-products will be demonstrated in this study by detailing the development, fabrication, and evaluation of these novel optical fiber sensors configured to perform as pH sensors. The LPG sensor element is highly sensitive to refractive index changes, and with the appropriate geometry can be designed to be sensitive to a variety of target molecules. For example, hydrogels that absorb water 1000 times their original weight can be formulated to be sensitive to pH. In particular, by applying unique pH-sensitive hydrogel coatings to the LPG sensor element, feasibility and sensor performance were investigated. Incorporating LPG-based pH sensors with other LPG-based

chemical sensors provides information about the surrounding environment for a better understanding of the corrosion state furnishing a complete tool for NDE of aluminum structures subject to corrosion.

1.3 TECHNIQUES APPLIED

The techniques discussed here include the use of pH sensitive coatings integrated with long period grating technology for the measurement of hydrogen ion (H^+) concentrations. The absorption of hydrogen ions produces a measurable change in the refractive index of the coating that can be measured by the LPG optical sensing platform. Initial evaluation of the pH-sensitive coatings was accomplished using planar substrates and various characterization techniques. Tools utilized for coating characterization include, use of an environmental scanning electron microscope (ESEM) for verifying coating uniformity on the optical fiber, weight analysis to determine swelling response of the hydrogel to various pH levels, and a refractometer for refractive index measurements in dry and hydrated states. Information gained from literature research and preliminary coating characterization was applied to the long period grating-based pH sensor development.

1.4 MAIN CONTRIBUTIONS

The research work presented in this thesis combines coating development, optical fiber sensor application, sensor/coating attachment methods and signal conditioning to develop a pH sensor system for informative evaluation of the corrosive state. The methodology for both the coating procedures and sensor evaluation presented for the development of an optical fiber-based pH sensor can be extended for the development of future LPG-based chemical and biochemical sensors.

The presented results demonstrate the potential for corrosion detection in aging aircraft by monitoring moisture, pH, metal-ions, sulfides, and nitrides with long period grating-based sensors. Other than corrosion detection, optical fiber-based pH sensors offer numerous advantages in wastewater monitoring, chemical and food processing, and medical diagnostics.

1.5 STRUCTURE OF THESIS

This thesis is organized into five sections that detail research work involved in optical fiber-based pH sensor development. Chapter 1 is an introduction that reviews goals, challenges, techniques and major accomplishments associated with the development of a highly sensitive, reliable optical fiber pH sensors for the detection of corrosive environments in aluminum alloy structures.

Chapter 2 provides the technical background on the corrosion process typically present within aluminum alloy lapjoint structures. Corrosion phenomena and mechanism causing structural degradation are reviewed, along with results from electrochemical analysis of corroded lapjoints. This crucial information is the basis for developing a sensor that is able to detect and quantify corrosion precursors and by-products to evaluate the extent of corrosion in inaccessible regions of civil infrastructures. Current methods of corrosion monitoring both optical and non-optical are also discussed. Chapter 2 covers long period grating (LPG) sensor theory, pH sensitive coating research, and methods used to blend the two together for the development of an optical fiber-based pH sensor. Included in this chapter is a list of pH-sensitive hydrogel candidates that can be applied to the LPG for sensor development.

Chapter 3 describes techniques used in the fabrication of the LPG-based pH sensors and coating development consisting of Polyvinylalcohol/ Polyacrylic acid (PVA-PAA) hydrogel preparation and coating procedures. By coating the LPG with a blend of PVA-PAA hydrogel, the LPG was capable of measuring pH. Several methods were used to characterize the hydrogels in order to anticipate the sensor performance and results from ESEM analysis, weight analysis, and refractive index measurements are presented here.

Chapter 4 details experimental results and sensor evaluation under various laboratory conditions. Sensor requirements are discussed and compared with experimental results that are presented with respect to sensor sensitivity, responsivitiy, reversibility, selectivity, repeatability and accuracy.

Chapter 5 summarizes research accomplishments along with future plans for development of expanded sensing capabilities using optical fiber long period gratings. Optical fiber sensor involvement in the medical, food processing and chemical industries are discussed with emphasis on pH monitoring of aqueous solutions and associated challenges.

CHAPTER 2–CORROSION PROCESS AND SENSING TECHNIQUES

2.1 INTRODUCTION

Corrosion related degradation of the aging aircraft fleet has proven to be costly to repair, cause reduced availability and service lifetime, and can result in potentially unsafe operating conditions. Although there are several preventative methods being developed to address this problem, the need for cost-effective and reliable methods for monitoring corrosion continue to exist to ensure an acceptable health status of aging aircraft and civil infrastructure. Currently the ability to reliably quantify corrosion in the field is limited to a threshold of about 10% loss of the original material thickness [3]. These methods generally consist of visual inspection first and later use of nondestructive techniques for further evaluation. It is preferable to detect corrosion in the earlier stages, because repairs are generally less expensive and corrosion tends to synergistically work together with other degradation mechanisms at an accelerated rate once it has begun. By developing continuous corrosion monitoring systems built into the structures, present system conditions of the aging structure can be determined and used for predictive model calculations and maintenance schedules.

The purpose of this research is to develop, fabricate and test optical fiber-based chemical sensors for monitoring corrosion from early stages through the entire corrosion event. Characteristics of optical fiber sensors such as, high strength, lightweight, small size, large bandwidth, low transmission loss, immunity to electro-magnetic interference, resistance to short term radiation damage, high sensitivity and dynamic range make them attractive candidates for nondestructive monitoring of corrosion in inaccessible regions [2]. By developing optical fiber sensors that can detect precursors to corrosion such as moisture, pH, nitrates, sulfates, chlorates and metal-ion corrosion by-products the severity of the corrosive environment can be determined and the predictive health of infrastructure can be evaluated. This chapter discusses the corrosion mechanism along with the chemical species that generally exist in aluminum alloy lapjoints to develop information for determination of pH levels and their significance in corrosion monitoring. The advantages and disadvantages of other related sensor developments that support pH measurement methods and corrosion monitoring are also discussed.

2.2 CORROSION IN ALUMINUM ALLOY STRUCTURES

Airframes are continuously subjected to corrosive environments as well as in-flight mechanical stresses. When airframe structures are adversely affected by the combined effects of corrosion and stress, the accelerated deterioration that occurs is referred to as corrosion fatigue [4]. Corrosion fatigue is most severe in those airframe parts that are most vulnerable to both stress and corrosion, such as fuselage skins, areas around steel fasteners, lower wing skin, pylon tank, horizontal and vertical stabilizers, and trailing edge flaps [5]. To protect aircraft structures from the initial onset of corrosion, organic coatings are applied to aircraft alloy parts. These coatings can successfully delay the onset of corrosion, but if the coating is compromised by cracking or UV degradation leading to water leaking into the aircraft joint the initiated corrosion can then spread extensively before being detected [6]. Some of these areas of the aircraft are often inaccessible and require costly disassembly for inspection placing emphasis on the prevention, detection, and understanding of the corrosion process.

The corrosion mechanism is an electrochemical reaction that is initiated by infiltrating moisture that results in a reduction oxidation process that breaks down compositional materials and degrades structural integrity. Environmental parameters that affect the corrosion process include: water quality and chemical concentrations, pH levels, temperature, and presence of suspended matter like dissolved salts [7]. Once water penetrates the aircraft lapjoints and corrosive precursors replace the existing environment, several forms of corrosion develop depending on the material, location, and structure of the airframe. Figure 1 illustrates the various types of corrosion: filiform, exfoliation, pitting, crevice, and 3rd layer corrosion indicating their typical location within an occluded lap joint [5,6]. These mechanisms are generally initiated under different circumstances and are almost never observed individually because they often work together to degrade the structural integrity of the host materials.

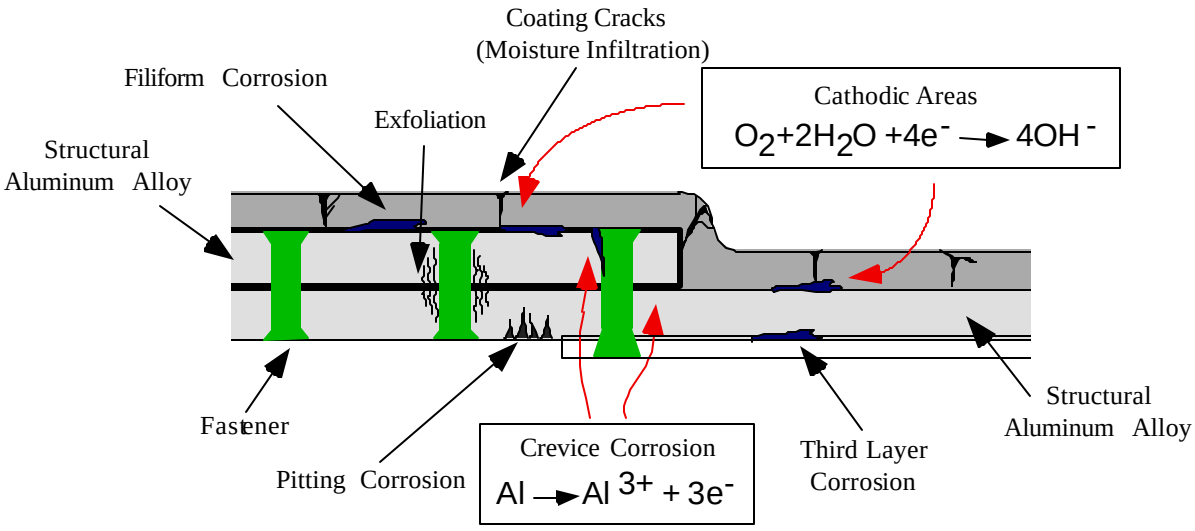

Figure 1. Types of corrosion and typical location within occluded aluminum alloy aircraft lapjoint [5,6].

Also illustrated in Figure 1 is the typical mechanism of the oxidation-reduction process. When water collects in crevices, it contains atmospheric components such as acids, salts, and other organics providing the electrolytes that lead to the initiation of corrosion. Moisture penetration into the airframe structure produces an aqueous electrolyte that causes anodic and cathodic reactions to take place. The main cathodic reaction stemming from atmospheric moisture infiltration is oxygen reduction. For localized corrosion such as pitting, crevice, and exfoliation, this cathodic reaction will tend to exist closer to the oxygen source than the anodic reaction and will cause an increase in the local pH [6]. In aluminum alloys, aluminum hydroxide, $Al(HO)_3$, is precipitated due to the formation of hydroxyl (OH-) groups initiating cracks and spreading from the areas where the original cracks were formed. Salts, that primarily consist of sodium and calcium, are present in the areas where these small cracks originate and continue to adsorb moisture from the atmosphere through osmosis [8]. Because of this process, conditions such as high humidity accelerate the propagation of corrosion and the original corrosive site continues to develop corrosion by-products as water is replenished by osmosis, continuing until complete degradation of the part [9,10].

A capillary electrophoresis (CE) laboratory test protocol has been used to identify the chemical species that are present in corroded lapjoints [3]. From samples removed from Al 2024-T3 fuselage lapjoints, it was determined that the presence of dissolved Cl^-, NO_X and/or SO_X anions catalyze the corrosion reactions which release Al^{3+} and Mg^{2+} ions from the aqueous-wet alloy surfaces [3]. These chemical indicators can be used to determine if the environment within a particular area of an airframe is conducive to corrosion or whether the corrosion process is active.

Traditional non-destructive detection methods rely on the pillowing of the underlying material caused by the corrosion process for detection that generally occurs when corrosion is already in an accelerated state with associated structural damage. Therefore detecting the onset of corrosion is crucial in cost-effective maintenance of aging aircraft and it has been proposed that detecting the precursors and by-products of the chemical reduction oxidation process is beneficial [1,2]. By measuring these precursor and by-product concentrations, determination of the level of corrosion damage can be evaluated. The intent of this research work is to ascertain early stage corrosion by detecting precursors and by-products of the corrosion process such as moisture, pH, chlorates, sulfate, nitrates and metal-ions. Specifically this research focuses on pH sensors that can be multiplexed with other chemical sensors for a complete chemical analysis of the corrosive environment. The following section discusses current methods of corrosion detection in aging aircraft structures and their limitations.

2.3 METHODS OF CORROSION DETECTION AND EVALUATION

Conventional methods of corrosion detection generally rely on substantial physical deterioration of the structure. Methods such as visual inspection, eddy current, dye penetrant, qualitative thermal wave imaging, imaging microwave spectroscopy, computerized tomography, ultrasonic, x-ray techniques, and neutron radiography offer several disadvantages when trying to successfully maintain the aging air fleet. These methods can be costly, time consuming, only allow access to the outer shell of the aircraft and often have a significant chance for human error where the consequence is not detecting corrosion in its early stages. Some of these techniques also make it difficult to discriminate between repaired sites, material dissimilarities, and the corrosion site [2]. To maintain an affordable aging air fleet,

onboard corrosion monitoring systems must be developed and installed in accessible and inaccessible regions of the aircraft along with models that correlate sensor output to the severity of corrosion. This system can be utilized for continuous monitoring of corrosive activity and will help reduce cost in maintenance as well as offer an overall health monitoring approach for future aircraft that require extended operation lifetimes.

Currently, there are several sensor design approaches that are being investigated for onboard corrosion monitoring systems. These sensors rely on electrical or optical transducers to measure either the physical or chemical changes within the designated corrosive site. One method of corrosion detection consists of a galvanic cell, that measures potential differentials upon corrosion of a sacrificial material [11]. Other optical sensor designs have been proposed using a sacrificial material. These sensors are generally pre-strained fiber optic strain gages with a sacrificial coating that upon corroding, release and cause a change in the optical path [12].

Optical and electrical strain gages that measure strain concentration as a result of pillowing displacement have been proposed for embedment during structure assembly. These sensors can be multiplexed with other strain gages that are employed for overall detection of strain and fatigue in critical locations onboard the aircraft. Although the fiber optic sensors, due to their inherent advantages, are the preferred method of sensing within the corrosive and electromagnetic aircraft environment, the electrochemical sensors are more established because they predate the fiber optic sensors, thus having more familiarity with the end users. For the detection of chemical species present within lapjoints, several electrochemical and optical sensor designs have been addressed [13].

Current types of chemical sensors can be described according to their transducer configuration, but generally the nature of the active material defines the transducer type and configuration. There are several classes of sensors, some of them include: electrical, optical, calorimetric, and piezoelectric. Although well established, electrical based sensors have limitation. These sensors show promise for chemical detection, but in many cases, optical fiber sensors offer greater performance due to their ability to withstand harsh environments in a wide temperature range without electromagnetic interference or

damage from corrosion. Section 2.4 discusses the advantages of optical fiber-based chemical sensors, and the current developments in sensor designs and their impact on pH measurement and corrosion monitoring.

2.4 PREVIOUS OPTICAL FIBER-BASED CHEMICAL SENSOR RESEARCH

By combining active materials with transducers and support instrumentation chemical sensors can be developed to detect target chemical species. The nature of the active material, along with the transducer configuration, and the support instrumentation define the type of sensor and its capabilities [14]. There are currently several optical fiber-based chemical sensors that surpass the limitations of electrical based sensors. Within the optical fiber-based chemical sensor platforms, sensor configurations can be classified as distal end, interferometric, and evanescent wave sensors [15].

Important factors used in the selection of an appropriate optical fiber sensor platform are ease of fabrication, multiplexing capabilities, signal demodulation, sensitivity, dynamic range, and cost. Many fiber optic methods are limited by complex sensor design, limited sensitivity to refractive index changes, and polarization sensitivity [16]. Intensity-based sensors operate by modulating the propagating power by an external perturbation [15]. A limitation of intensity-based sensors is that they require a reference signal to overcome any power variations due to fluctuations in the optical source or bends in the lead in/out fibers. Therefore, sensors that need a reference signal to extract the sensing output have limited use. Although these sensors are economical and easy to fabricate, they are difficult to multiplex and not suitable for large area distributed sensing applications such as corrosion monitoring. Until recently, optical fiber-based chemical sensors consisted mostly of intensity-based fluorescence, luminescence, and absorbency probe sensors that do not lend themselves to multiplexed operation and cost-effective large-scale manufacturing techniques. These sensors are often affected by ambient light resulting in low signal to noise responses.

More recent sensor designs consist of interferometric-based sensors that rely on an interference pattern or sensors that rely on the interaction of the evanescent field, propagating just outside the core of the

waveguide, with an interactive coating that changes refractive index upon absorption of target molecules. These include surface plasmon resonance (SPR) sensors, and long period grating (LPG) sensors [17,2]. By investigating the capabilities of other sensing platforms the impact and viability of long period grating-based pH sensors becomes better understood.

Distal end sensors are generally considered to be single fiber, dual fiber, or bundled fiber probes that measure intensity of light either reflected, fluorescing or luminescent from a coating applied to the distal end [15]. In all of these systems, chemical changes in the environment are monitored via the intensity of the returned optical signal. A disadvantage of such intensity-based sensing techniques is that the correctness of the system output may be compromised by unexpected changes in the intensity of the optical signal, such as those caused by source fluctuations, connector losses, ambient light influences or as a result of bend losses [18]. The fluorescence-based techniques are based on wavelength specific emissions from an electrochemically-active coating that fluoresces only in the presence of specific target molecules. For the fluorescence-based sensor, fluorescence indicator dyes are immobilized in a membrane. When light excites the molecules at one wavelength, the indicator dye emits light at a different wavelength if in the presence of the targeted chemical species. This specificity of the coating reduces the adverse effect of sensor cross-sensitivity to changes in other environmental parameters, however there are problems with ambient light and leaching of indicator reagants out of the sensing membrane. This leaching is generally due to the hydrophilic properties of an ionic form of the indicator [15]. For the absorption-based sensor, the absorbency changes as a function of target molecules absorbing into the coating. If the absorption is low, the light is reflected back. If the absorption increases, the intensity of the light reflected back to the detector will decrease.

Interferometric chemical sensors are based on a change in fringe pattern that is caused by the interference of two reflected light paths. As the optical path length changes, the fringe pattern changes can be monitored. This change in the optical path can be generated as a result of refractive index changes. By applying a coating that selectively absorbs target molecules and changes refractive index within the optical path region, chemical species can be quantitatively monitored. This sensor can be

configured with bulk optic instrumentation and with optical fiber. The main concern with this configuration is alignment issues and achieving an adequate active sensing area.

The third type of optical fiber-based chemical sensor incorporate active coatings that interact with the evanescent wave generated by the light transmitted through the optical fiber. This type of sensor includes surface plasmon resonance (SPR) sensors, and long period grating (LPG)-based chemical sensors. Surface plasmon sensors can be configured from bulk optics or optical fiber. The optical fiber configuration consist of an optical fiber with the cladding removed and coated with a metallic film such as silver or gold coated. When light travels through the optical fiber the internally reflected light generates an electromagnetic wave that propagates along the interface of the coating and the optical fiber. This effect results in spectral loss of certain wavelengths as a function of the refractive index directly contacting the sensor. By applying a coating that changes refractive index upon absorption of target molecules, chemical sensing can be accomplished. Unlike the long period grating (LPG) sensor, surface plasmon has a limited spectral loss dip profile that ultimately affects the ease of signal processing and interpretation. This is due to the fact that surface plasmon phenomena is excited by a restricted number of traveling modes in optical fiber [17].

The simple, low profile, flexible geometry and potential for low cost, repeatable manufacturing techniques make the LPG-based chemical sensor optimal for widespread corrosion monitoring. By coating the sensor elements with materials that change optical properties based absorption of target measurands, quantitative chemical measurements can be accomplished. Section 2.5 discusses principles behind long period grating-based chemical sensors, methods of fabrication, optical characteristics, and methods used to monitor refractive index changes.

2.5 LONG PERIOD GRATING -BASED SENSORS

First demonstrated by Vensarakar, et al. in 1995 for use in the telecommunication industry as a spectrally selective band rejection filter, the long period grating (LPG) has also been designed for strain, temperature, and refractive index sensing [19]. As a refractive index sensor, the LPG operates by

scattering light out of the core at a particular wavelength based on the grating period, the optical fiber index profile, and the surrounding refractive index [18]. Figure 2 shows a schematic of the uncoated LPG sensing element and the light coupling effect that occurs for certain wavelengths. By applying a coating that changes index of refraction based upon the pH of the environment to the surface of the LPG, quantitative pH measurements can be accomplished.

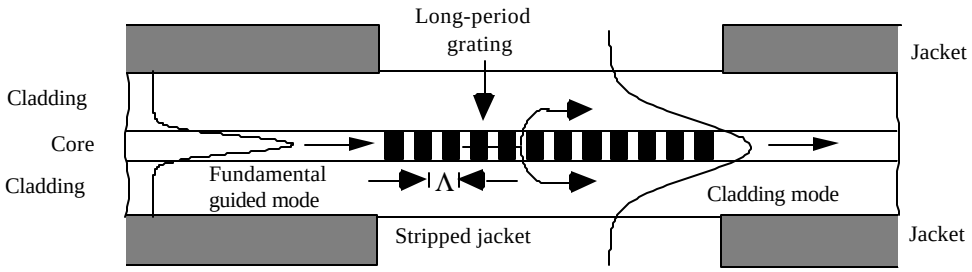

Figure 2. Schematic of long period grating (LPG) sensing element [24].

The long period grating is fabricated by permanently changing the refractive index periodically in the core of a photosensitive optical fiber. To accomplish this task, ultraviolet light is passed through an amplitude mask with a particular periodicity, usually on the order of hundreds of microns onto a stripped germanosilicate optical fiber that has been exposed to hydrogen under high pressure loading conditions. After diffusing hydrogen into the optical fiber, intense UV radiation causes the hydrogen to react with the Ge-O-Si sites resulting in the formation of Si-OH sites and oxygen deficient Ge sites that assist in a large change in the refractive index [20]. This results in a periodic change in the refractive index of the optical fiber core with the period determined by the amplitude mask period. After the grating is written into the fiber, unreacted hydrogen still exist in the fiber. As the hydrogen is released the spectral response of the LPG changes. It is therefore desirable to post anneal the LPGs before use. By annealing the fiber at elevated temperatures, unreacted hydrogen is released in a very short time, otherwise this hydrogen would release slowly over time.

Figure 3 is a representative spectrum plot resulting from passing white light through the long period grating and interrogating the output with an optical spectrum analyzer. The plot shows the various discrete resonance bands or spectral loss dips. The bands have different values of peak loss and

bandwidth due to the dissimilar coupling coefficients that are a function of modal overlap [18]. This particular long period grating has a 15 dB loss at 1582.5 nm wavelength as its highest resonant band. By focusing in on the highest resonant band and tracking its wavelength shift, the surrounding refractive index can be measured. The wavelength and the width of this resonance band can be tailored during the grating manufacturing process, resulting in highly tailorable sensors that can be used at a desirable operating wavelength for use with less expensive sources and detectors and can be multiplexed along a single fiber.

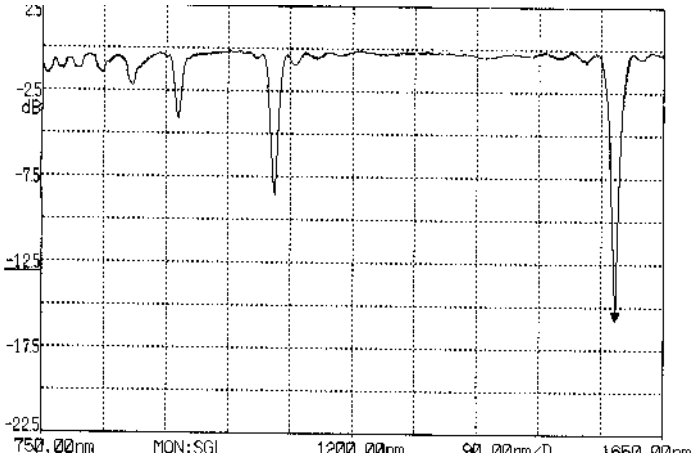

Figure 3. Representative long period grating (LPG) transmission spectrum showing wavelength in nanometers versus transmission loss in dB.

In designing LPG-based pH sensors, the coupling phenomena and resulting sensitivity to refractive index perturbations must be fully understood before selecting applicable coatings. It is important to note that the coating/LPG interaction occurs within the evanescent field that typically extends 700 nanometers radial from the cladding surface for this particular optical fiber index profile [21]. By applying a coating to this region, refractive index-based chemical measurements can be accomplished. The LPG sensor is operable as a refractometer as long as the refractive index of the solution or coating that surrounds the grating is less than the effective refractive index of the optical fiber cladding. For a refractive index greater than the cladding refractive index, the propagation constant of the cladding mode becomes complex and the mode becomes leaky with exponentially increasing radial field component [22] and therefore results in a loss of the resonant wavelength band. This loss of this resonant band is due to the

surrounding index being equal to the effective index of the cladding mode, causing the outer cladding interface to functionally disappear resulting in a non-occurring coupling of the guided mode. For the presented work, this cut off refractive index for sensor operation is approximately 1.436. By modifying the optical fiber index profile, this limitation can be overcome or shifted to a more desirable range. The refractive index design requirements are discussed further with respect to their interaction with coating properties in Chapters 3 and 4.

2.6 MEASUREMENTS OF PH

The percent hydrogen (pH) of an aqueous solution is the measure of the acidity or basicity and depends on the concentration of the free hydrogen(H+) ions and hydroxyl (OH-) ions present. The hydrogen ion concentrations are present in solutions in extremely small numbers, on the order of 1/10,000,000 moles/liter, and to avoid use of such cumbersome numbers the pH scale is used [23]. Equation 1 is used for the determination of pH with hydrogen ion concentration, where [H+] is in grams/liter. The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration [23]. Solutions with high concentrations of hydrogen ions have a low pH and solutions with low concentrations of hydrogen ions have a high pH.

$$pH = -\log10[H+] \quad (1)$$

Hydrogen-ion activity has now replaced ion concentrations in the measurement of pH. Thus Equation 2 is the present equation for pH, where a_{H+} is the activity of the hydrogen ion [23].

$$pH = -\log10[\ a_{H+}\ ] \quad (2)$$

Hydrogen ion activity is defined as the effective concentration of species in solution. It is usually expressed in the units of moles/liter. The distinction between effective concentration and actual concentration decreases as we move towards more dilute solutions when ionic interactions become progressively less important [23]. It should also be realized that the predominant form of the proton,

H^+, in aqueous solution is the hydronium ion, H_3O+, even though we find it convenient to speak of this as the "hydrogen ion" [24].

When designing analytical instrumentation, it is desirable for sensors to be capable of measuring the full pH range (0 to 14) with a 0.01 pH resolution, but there are very few sensors that measure pH values accurately with this dynamic range and sensitivity. Because of this, measurements are generally split into small pH ranges [25]. The next section considers unique hydrogel coatings and their capability of changing refractive index with pH changes in the surrounding environment. Many of these hydrogel coatings have a discrete pH response range that varies from the specific type of hydrogel.

2.7 PH SENSITIVE HYDROGEL COATINGS

A unique method for determining pH is through measurement of refractive index changes in pH-sensitive hydrogel coatings applied to a long period grating sensor element. In general, hydrogels are water swollen networks of hydrophilic homopolymers or copolymers. Hydrogels have been applied heavily as a biocompatible material and used in a variety of applications. Such applications are contact lenses, drug delivery systems, medical grafts, skin replacements, artificial cartilage, and several others waiting FDA approval. Because of the vast interest in this field and the strict FDA approval process, optical and physical properties of hydrogels have been studied and documented in depth. Therefore, to gain insight to the optical, mechanical, and pH sensitivity for hydrogel coatings, preliminary research was referred to contact lens and drug delivery system studies. Soft contact lenses require optical characterization, and have been studied under such environmental parameters as temperature and pH. A more in depth study on the swelling response of hydrogels to different pH levels can be gathered from hydrogel-based drug release systems. This section discusses material properties and water diffusion mechanism that will give insight to predicted sensor responses.

Hydrogels are water swollen, cross-linked polymeric structures produced by the simple reaction of one or more monomers or by associate bonds such as hydrogen bonds and strong vander Walls interactions between chains [26]. It has also been realized that with increased swelling there is a decrease in the

refractive index of the hydrogel coating. This refractive index change is due to the increase in scattering effects by expanding molecular domains and is the basis for the intended LPG-based pH sensor.

First referenced by Paul J. Flory in 1940s [27], the tremendous swelling behavior of ionic gels has been studied by Tanaka and other researchers and has led to applicable use of such gels in several applications. Polymer gels can exhibit abrupt volume changes in response to variations in their environmental conditions, shrinking and swelling up to 1000 times their original volume [28]. Swelling characteristics are very important in biomedical and pharmaceutical applications because equilibrium degree of swelling influences such properties as, solute diffusion coefficient through out the hydrogels, surface properties and surface mobility, optical properties, and mechanical properties. By investigating previously published work in these areas, insight is gained to enhance pH sensor development.

Responsive hydrogel networks may be formed by various techniques, however the most common synthetic route is the free radical polymerization of vinyl monomers in the presence of difunctional crosslinking agents and swelling agents [29]. The major disadvantage with hydrogels is their relatively low mechanical strength but this can be overcome by crosslinking, by forming interpenetrating networks, or by crystallization that induces crystallite formation and drastic reinforcement of their structure [29]. The water content of synthetic hydrogels is controlled by the structure of the polymer, and with appropriate constituent monomers, can be made responsive to environmental factors such as pH, salt concentrations, temperature, and electric fields [30]. If an ionic or hydrophobic monomer is incorporated into the hydrogel network, a responsive polymer is often created [29]. This responsiveness takes the form of volume phase transition characterized by a sudden change in the degree of swelling upon small changes in the environmental conditions [29]. In particular, the existence of the negative charged carboxyl ions can be accomplished through incorporating weakly acidic or basic groups into the copolymer network structure and enabled the gel to respond to pH changes [28].

2.7.1 Swelling Mechanism in Hydrogels

In order to understand the swelling phenomena in gels, forces exerted on the gel must be examined. These forces include polymer-polymer affinity, hydrogen-ion pressure, and rubber elasticity [27]. The total pressure is the sum of all these forces and is called the osmotic pressure. The osmotic pressure determines whether the gel tends to take up fluid or expel it. Polymer-polymer affinity is a result of interactions between the polymer strands and the encompassing solvent and is a function of solvent concentration and the volume of the gel [27]. In the case of pH-sensitive hydrogels, the solvent is considered to be the water or biological fluid surrounding the hydrogel. These forces can either be attractive or repulsive, depending on the electrical properties of the hydrogel molecule [27]. In an attractive interaction, the polymer can reduce its overall energy by surrounding itself with more solvent molecules, whereas if the interaction is repulsive the solvent is expelled [27]. This phenomena explains how hydrogen ion concentration of the solvent (water) affects the tendency of the gel to absorb or discharge the surrounding solvent. Hydrogen-ion pressure, associated with the ionization of the polymer network, releases an abundance of positively charge hydrogen ions (H^+) into the gel fluid. If these ions are the only charge present they will strongly repel each other. However, the positive ions are immersed in a sea of negative charges attached to the polymer network and therefore the gel as a whole maintains exact electrical neutrality [27]. The rubber elasticity of the hydrogel determines the ability of the hydrogel to expand and contract with the changing forces. This material characteristic is affected by the degree of cross-linking and temperature.

The changing balance of the three opposing forces result in the observed phase transitions. The concept that whenever possible the gels will adjust its volume so that the total osmotic pressure is zero, gives phase transitioning hydrogels the properties essential for pH sensing applications. If the osmotic pressure is initially positive, the gel takes up fluid and expands. If the pressure is negative, the gel expels fluids and shrinks. This course continues until the total of all three forces reach equilibrium. Time to reach equilibrium and mechanisms of dynamic swelling are affected by migration of residual ionic initiators and the difference between the inside and the outside of the gel [31]. Therefore thin films of such hydrogels undergo very rapid volume changes in comparison to thicker films. The time to reach equilibrium becomes critical when optimizing a sensor response of an LPG-based pH sensor. As discussed in Section 2.5, for this particular LPG, the evanescent wave only

exists within approximately the first 700 nanometers outside the cladding interface in the grating region of the optical fiber. Therefore any coating greater than this thickness is only adding to the time for the hydrogel to reach an equilibrium state decreasing the response time of the sensor.

Several rate processes should be taken it into account when investigating the swelling mechanism in pH-sensitive hydrogels. Ion diffusion, diffusional limited chemical reactions, ion migration, and consequently electrical and mechanical readjustments of the polymer network are some of the mechanisms that effect the swelling of a hydrogel [28]. The plot shown in Figure 4 illustrates the swelling of a Polyvinylalcohol and Polyacrylic acid (PVA-PAA) hydrogel sample to various pH buffers [28]. This plot only gives insight into the swelling response of this gel, but this information can be correlated to refractive index changes as will be demonstrated within this study. It is important to note that this hydrogel has a distinct expansion between pH 3 and pH 7. Later in Chapter 4, the relationship between this swelling response and refractive index change will be further discussed along with effects on the dynamic range of pH sensor operation.

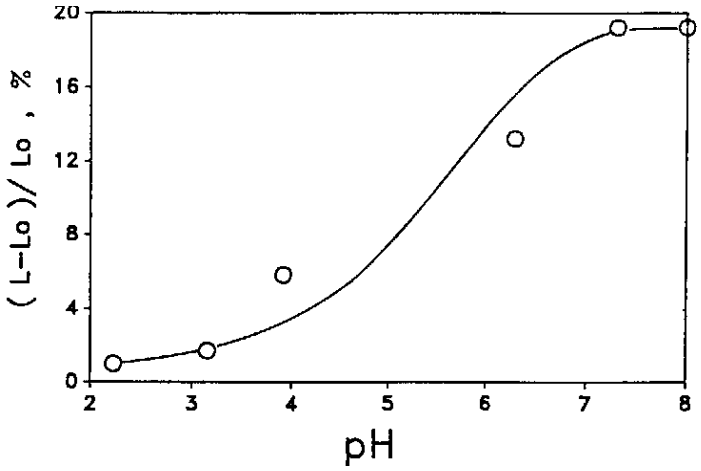

Figure 4. The linear equilibrium swellability of hydrogel in response to pH changes [28].

2.7.2 pH-Sensitive Hydrogels

The scientific push for hydrogel development in the biomedical field has resulted in numerous hydrogel blends that offer pH-sensitive swelling. A variety of co-monomers are easily incorporated into the system to alter the chemical or mechanical properties of the hydrogel. Although there are numerous hydrogel polymer blends that

have documented response to pH, for this study several types of hydrogel blends were selected as potential coating candidates for pH sensor development based on preparation procedures, documented optical properties and swelling sensitivity to pH changes. Table 1 is a list of hydrogel candidates for sensor development and related references. Although this thesis work concentrates on PVA-PAA coated long period gratings, the methodology for sensor fabrication and evaluation can easily be applied to future fiber optic and optical-based chemical sensor development.

Table 1. pH-Sensitive Hydrogel Coating Candidates.

PH-Sensitive Hydrogels	**Reference**
PVA-PAA - Polyvinylalcohol and Polyacrylic acid	[28,31,9]
PVA-MA – Polyvinylalcohol and Maleic acid	[32]
HEMA/DMA- 2-Hydroxyethyl methacrylate and Dimethylethylmethacrylate	[33,34,35]
PAN- Polyacrylonitrile	[31,9]

2.7.3 Hydrogel Coated Long Period Gratings

By coating an LPG element with pH-sensitive hydrogel coatings, water absorption will be determined by the pH of the surrounding aqueous solution. This absorption of water will result in a swelling of the hydrogel coating and thus a refractive index change and a shift in the LPG resonant band. Figure 5 illustrates LPG-based pH sensor operation and the direct relationship between critical parameters such as pH change in the environment, swelling response, and refractive index change. The pH of the solvent alters the osmotic pressure of the gel by reducing the ionization of the carboxyl groups on the polymer chains. As a result the hydrogen-ion pressure is reduced and the hydrogel collapses at a higher temperature than the neutral temperature. At equilibrium the total osmotic pressure reaches zero. As the coating swells with an increase in pH, the refractive index seen by the long period grating decreases. By injection a broad band source into the long period grating sensor the resonant band shift to the left with this decrease in refractive index can be monitored and by tracking this shift, real-time pH measurements can be obtained.

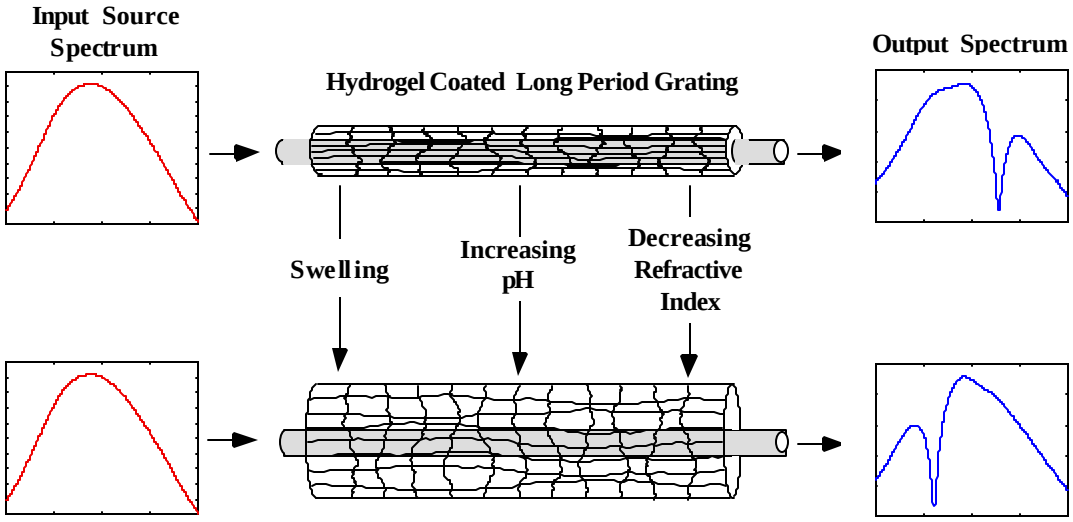

Figure 5. Schematic of anticipated sensor response to analyte pH changes.

For this study hydrogels derivatized from PVA-PAA were selected for sensor demonstration. Chapter 3 will discuss materials and methods used to prepare these hydrogels and apply them to the LPG sensor platform and Chapter 4 presents experimental results and discussion that support optical fiber-based pH sensor development.

CHAPTER 3 – RESEARCH METHODS AND MATERIALS

3.1 INTRODUCTION

As discussed in Section 2.4, the technical approach for optical fiber pH sensor development was to apply pH-sensitive hydrogel coatings to optical fiber long period grating sensors. This chapter discusses the fabrication and characterization methods used to accomplish this objective. The approach is divided into three parts that include long period grating fabrication and characterization, coating development and characterization, and application of coatings to the long period grating optical fiber surface and evaluation. The selection of pH sensitive coatings is highly dependent upon their compatibility with the LPG sensor element. The operating requirements are coating refractive index and coating adhesion. Other important considerations include coating robustness and permeability. Through weight analysis, use of an ABBE prism refractometer, and an environmental scanning microscope (ESEM), PVA-PAA hydrogel thin films were characterized, applied to the LPG sensing element, and evaluated under different laboratory conditions. Section 3.2 focuses on LPG fabrication and characterization while Section 3.3 discusses coating preparation and characterization. These results give preliminary information to better understand the compatibility of PVA-PAA hydrogel coatings with the long period grating (LPG) sensor element.

3.2 LONG PERIOD GRATING SENSOR CHARACTERIZATION

The ability of the long period grating to perform as a refractometer is highly dependent upon fabrication techniques. The LPG is tailorable to have different resonant band wavelengths and to be insensitive to temperature and strain by altering the optical fiber characteristics and fabrication parameters. Such parameters as the index profile of the optical fiber, the period of the grating mask, writing conditions, and the post processing govern the sensitivity, operating range and performance of the LPG. The data presented throughout this thesis is obtained by using LPGs that are fabricated in a similar manner, however the location of the resonance band varies slightly from LPG to LPG because of process variables but does not effect the objective of observing a relative shift in the resonant band.

3.2.1 Long Period Grating Refractive Index Calibration

To gain an understanding of the LPG performance for measuring refractive index change, the LPG is characterized with various refractive index calibration standards. From this data, LPG sensitivity, operation range, and expected response curves can be obtained. The LPG is calibrated by exposing it to silicone refractive index fluid standards and measuring the resulting wavelength location of the highest order spectral loss dip. As shown in Figure 6, the experimental setup includes injecting broad band light into the LPG and monitoring the spectral output with an optical spectrum analyzer (OSA) at the other end. The LPG is submerged into a selected refractive index fluid and the wavelength recorded. After each recorded measurement the LPG is cleaned thoroughly until the spectral response returns to the original state.

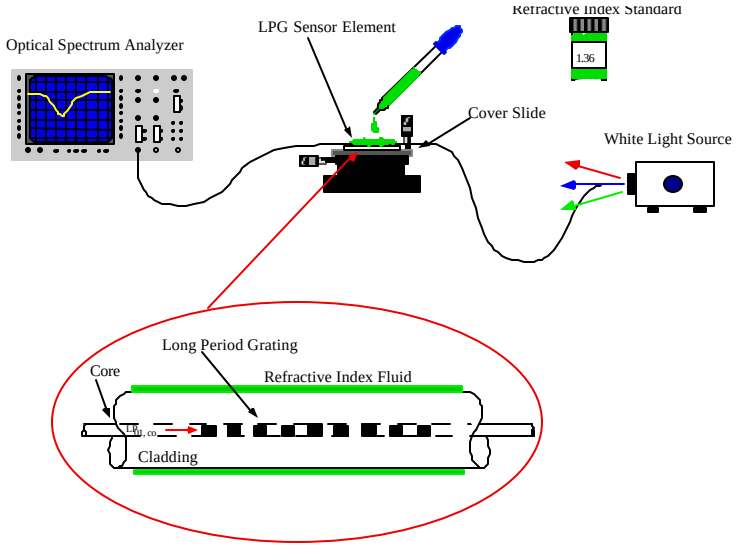

Figure 6. Experimental setup for refractive index calibration of a LPG sensor element.

Figure 7 is a plot of the spectral loss dip acquired by exposing the LPG to the various refractive index standards. The resolution of the OSA used for this test is 0.2 nanometers. By tracking the spectral loss dip, the LPG can be used to measure precise refractive index changes of the surrounding medium.

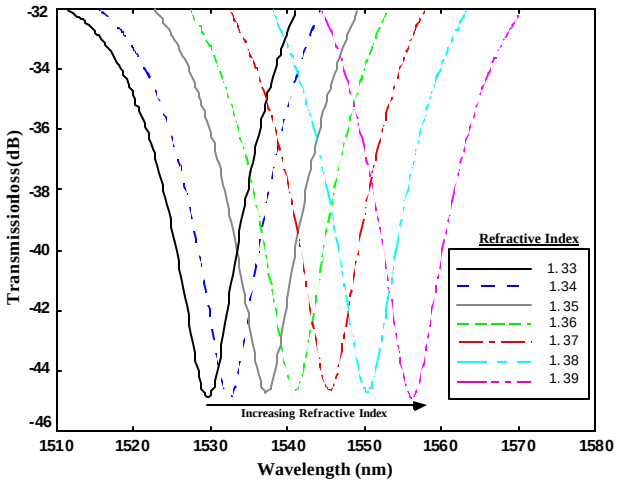

Figure 7. LPG spectral shift caused by refractive index changes.

For each spectral loss dip, the wavelength reported corresponds to the optical power minimum of the highest order spectral loss dip. Table 2 shows the corresponding minimum for each refractive index standard obtained during this experiment. For each calibration point, the LPG was submerged in the refractive index standard. There are no data points above 1.436 because the LPG spectral dip disappears above this refractive index. This is due to the characteristics of the optical fiber used to fabricate the long period grating.

Table 2. Calibration data for LPG sensor element.

Refractive Index	Wavelength (nm)
1.33	1529.6
1.34	1532.5
1.35	1537.4
1.36	1540.9
1.37	1545.5
1.38	1550.1
1.39	1556.8
1.40	1563.1
1.41	1573.1
1.42	1588.1
1.424	1596.5
1.426	1601.1
1.43	1617.8
1.434	1633.7
1.436	1642.9

As shown in Figure 8, when refractive index is plotted against wavelength, the resulting curve is asymptotic. The LPG response has its highest sensitivity to refractive index changes between 1.420 and 1.436. This information is critical when developing sensors for increased sensitivity to a desired environmental parameter. After 1.436 the refractive index of the solution is too close to the refractive index of the fiber cladding and the spectral loss dip disappears. By using a demodulation system with a resolution of 0.05nm, the sensitivity of the presented LPG to refractive index changes is determined to be 1.7×10^{-4} at the least sensitive region and 1.1×10^{-5} at the most sensitive region of the curve. The following section describes the integration of the LPG sensor element with the hydrogel coatings by covering coating preparation.

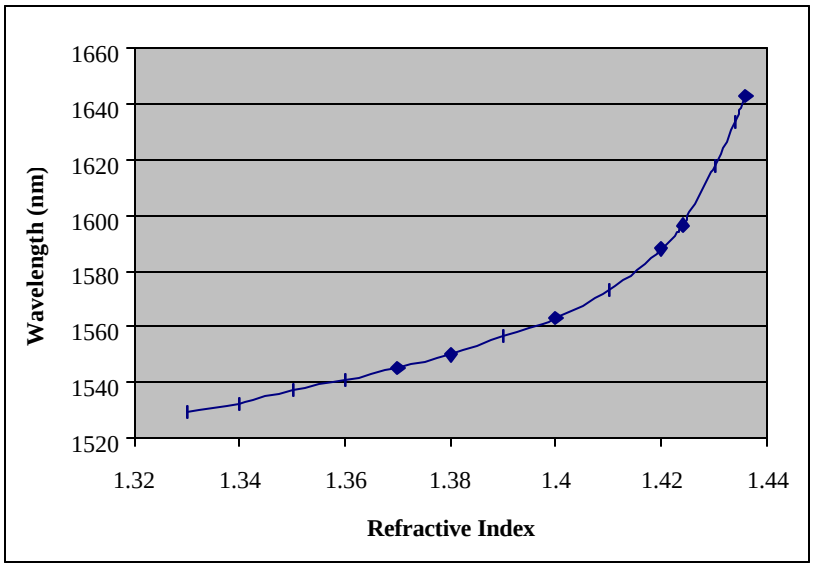

Figure 8. Plot of LPG wavelength shift with refractive index.

3.3 HYDROGEL PREPARATION AND COATING TECHNIQUES

Selection of coating material is an important consideration that warrants in depth analysis.
When choosing an appropriate coating for the optical fiber-based pH sensor, properties that need to be considered include: refractive index, adhesion to the optical fiber surface, method of coating, and coating robustness. Discussed here are polymer gel preparation procedures and characterization methods used to evaluate the resulting coating.

Polymeric network can be developed through bulk co-polymerization of the monomer with a cross-linking agent, cross-linking of the polymer in solution, or simultaneous co-polymerization and cross-linking of a monomer with a cross-linking agent [36]. The simultaneous co-polymerization and cross-linking of a monomer with a cross-linking agent solution is the preferred method because it results in very rapid processing at close to ambient conditions and the formation of the gels of a given shape can be readily obtained since the starting material is in a liquid form [36]. Crosslinking is accomplished using UV light in conjunction with photoinitiators, heat, gamma irradiation, and e-beam [37]. The properties that can be adjusted through coating synthesis include solubility, cross-link density, refractive index, hardness, selectivity, response time, and hydrophilicity. The following sections detail hydrogel preparation for LPG-based moisture and pH sensor development.

3.3.1 Preparation of Polyethylene Oxide

Long period grating sensors were first demonstrated with simple moisture absorbing hydrogels to understand sensor coating methodology. Samples of Polyethylene oxide (PEO) mixture formed from the polymerization of ethylene oxide monomers are dissolved into methanol at a 1:10 ratio. This coating is then applied to the long period grating and allowed to dry. By incorporation of PEO into a block co-polymer like polyurethane (PUU), the polymer can be modified to create a material which swells but does not dissolve in the presence of water [36].

3.3.2 Preparation of Polyvinyl Alcohol / Poly-acrylic Acid Hydrogel

Thermally cross-linked gel samples were prepared in thin sheet form using an 80/20% blend of Polyvinyl alcohol and Poly-acrylic acid (PVA-PAA). PVA with an average molecular weight of 78,000 (Polysciences, Inc.) and PAA with an average molecular weight of 450,000 (Polysciences, Inc.) were dissolved separately in deionized water and subsequently mixed in the relative proportions of 80% and 20% by weight, respectively. After 20 minutes of stirring at 60 °C, the homogeneous solution was dehydrated in a thermostatic oven at 40 °C under mild vacuum. The sample is then removed from the original container and thermally cross-linked at 130 °C for

60 minutes after which the samples are equilibrated with deionized water. Section 3.4 will specify characterization of the prepared hydrogel samples.

3.4 COATING CHARACTERIZATION

The methods used to characterize pH-sensitive hydrogel coatings included weight analysis, use of an ABBE prism refractometer, and an environmental electron microscope (ESEM). The characterization data along with knowledge acquired from sensor demonstrations offer valuable information for optimizing the long period grating-based pH sensor. All samples were fabricated as discussed above in Section 3.3.2 from the same batch of polymer solution. The following sections describe experimental characterization along with acquired results.

3.4.1 Refractive Index Determination through ABBE Measurements

For the LPG to measure refractive index changes, the applied coating must have a refractive index under 1.436, as determined experimentally in Section 3.2. To investigate the feasibility of various coatings, an ABBE refractometer with a resolution of +/- 0.001 was used to measure the refractive index of hydrogel coating candidates. Table 3 is the refractive index of the coating in the dry state and when hydrated with DI water. As shown in the table, all the coatings have refractive indices greater than 1.436 in the dry-state, therefore making them “invisible” to the LPG as discussed in Section 3.2.1. In the hydrated state, the PVA-PAA coating mixtures have a refractive index slightly higher than 1.336. The refractive index of the HEMA/DMA coating is in the 1.415 range, while the microspheres coating has a refractive index around 1.436. Because the long period grating responds to refractive index changes asymptotically, this information is critical in determining the sensitivity range of the coated LPG sensor to pH changes.

Table 3. Refractive index of potential hydrogel coating candidates.

Hydrogel Coating	Dry Refractive Index	Wet - Refractive Index
80/20 PVA-PAA	1.7280	1.3364
60/40 PVA-PAA	1.7602	1.3350
HEMA/DMA	1.7050	1.4149
Microspheres/HEMA	1.6880	1.4368

From these measurements, it was determined that the PVA-PAA coating and the HEMA/DMA coating refractive index meet the requirement of using a long period grating for the measuring refractive index changes from 1.33 to 1.436. It is important to note that refractive index measurements are highly user dependent and offer only a preliminary method of determining the refractive index of the coatings. A better method of evaluating the coating is to coat the LPG and measure the change in the spectral response.

3.4.2 Water Absorption Measurements through Weight Analysis

To determine the characteristic swelling and contraction response of PVA-PAA hydrogel coatings, samples were prepared and allowed to soak for 24 hours in buffer solutions ranging from pH 2 through pH 8. The weight of each sample was measured before and after a 24 hour soak period in the buffer. It was observed that as the pH of the buffer solution increased, both the size and the weight of the sample increased. This is to be expected when comparing with documented literature. Because the prepared samples did not have a defined geometry, percent weight change was used to give a good indication of water absorption and swelling. Table 4. details experimental results obtained from these measurements.

Table 4. Weight analysis of PVA-PAA samples before and after 24hr soak in pH buffers.

PH of Buffer Solution	Dry Weight (gms)	Hydrated Weight (gms)	Weight Percent Swelling(%)
2	0.1956	0.9291	4.75
3	0.204	1.0394	5.09
4	0.3467	2.1368	6.16
5	0.2511	2.4848	9.89
6	0.1351	1.558	11.53
7	0.1862	2.5551	13.72
8	0.2096	2.8535	13.61

By plotting this data a swelling characteristic curve can be determined. Figure 9 is a plot that illustrates a sudden increase in water absorption between pH 3 and pH 7. Because the index of refraction is very sensitive to swelling this experimental data can be used to verify performance of coating candidates that are responsive to pH and compatible with the long period grating sensor element.

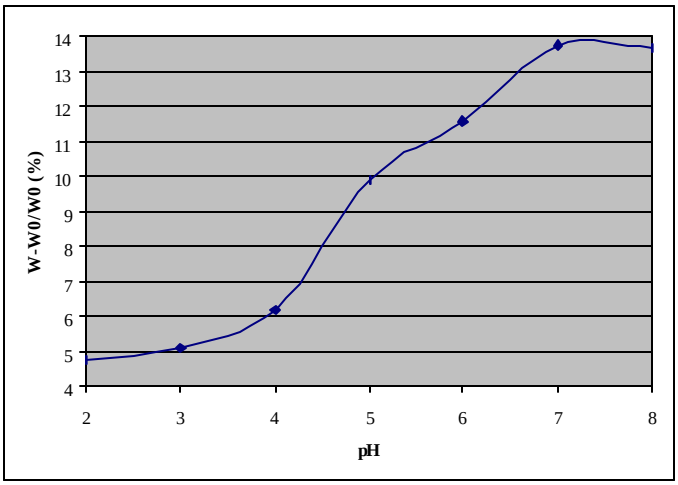

Figure 9. Plot illustrating pH dependent swelling of PVA-PAA hydrogel.

When comparing the data shown in Figure 9 with published data shown in Figure 4, there is a noticeable similarity in the sudden increase in size between pH 3 and pH 7.

3.4.3 Swelling and Drying Characterization Using ESEM

Because coating quality is very important in verifying sensor performance, a nice, fluffy, uniform coating with no pinholes is desirable. The evanescent wave only interacts with approximately the first 700nm of the coating thickness and any extra thickness, generally just increases the response time of the sensor. It is therefore desirable to determine the coating thickness, but this is often difficult to determine with ESEM micrographs due to the lack of resolution at very high magnifications. The following micrograph, shown in Figure 10, is a long period grating coated with an 80/20 (wt %) PVA-PAA hydrogel. This sensor was both operable and exhibited repeatable responses to different pH buffer solutions. The micrograph shows that the sensor is uniformly coated with no visible pinholes.

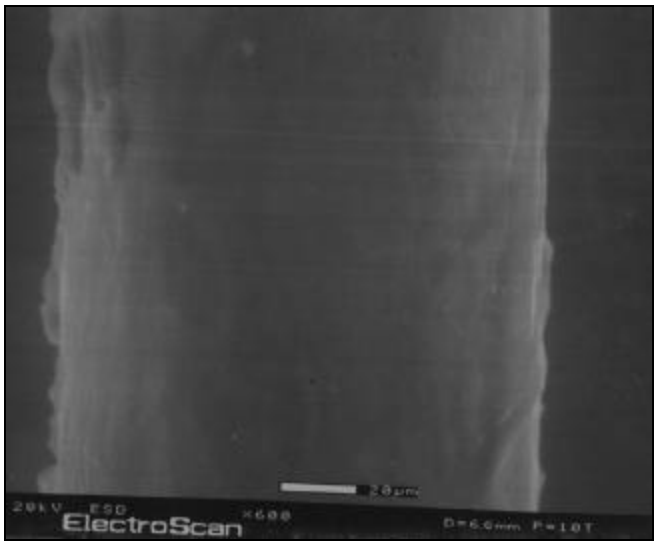

Figure 10. ESEM micrograph of hydrated and dehydrated PVA-PAA coatings.

CHAPTER 4 – EXPERIMENTAL RESULTS

4.1 INTRODUCTION

The following sections present experimental results that demonstrate optical fiber long period grating-based chemical sensors for moisture and pH monitoring of the surrounding environment. Initial sensor development consisted of coating the LPG with a PEO-based hydrogel that absorbs moisture upon exposure. Next, the LPG was coated with PVA-PAA, pH-sensitive hydrogel coatings and evaluated under laboratory conditions. As discussed in Chapter 3, the LPG was first demonstrated with a basic PEO-based hydrogel coating for the development of a LPG-based moisture sensor. This demonstration was also accomplished to illustrate the multiplexing capability of the LPG sensor element.

4.2 POLYETHYLENE OXIDE COATED LONG PERIOD GRATING SENSORS FOR MOISTURE DETECTION

The presented moisture sensor is fabricated by coating an LPG sensor element with polyethylene oxide (PEO), formed from the polymerization of ethylene oxide monomers. This PEO derivative is a water absorbing hydrogel coating that swells in the presence of moisture and is easily applied to the long period grating. While monitoring the spectral response, the LPG was dip-coated in a dilute mixture of PEO and methanol. After four dips the LPG peak disappeared indicating that the coating was thick enough to cover the evanescent field of the optical fiber. At this point the coating was allowed to air dry to be used for later evaluation.

The coating thickness is optimized for high responsivity and reversibility. When the coating is applied to the LPG, the spectral loss dip disappears due to the high refractive index of the coating. Figure 11 illustrates an experimental setup for two multiplexed sensors on a simulated lapjoint. In the presence of water the PEO hydrogel coating absorbs water and swells, leading to a decrease in the refractive index at the surface of the fiber, with a resulting shift in the LPG outcoupled wavelength.

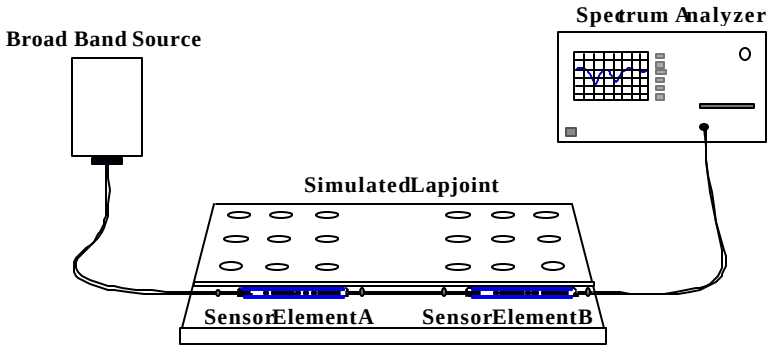

Figure 11. Experimental Setup for Moisture Sensor Demonstration.

The transmission spectrum of a dual multiplexed, PEO coated, LPG sensor was monitored by using a broadband source and an optical spectrum analyzer. The transmission spectrum obtained from the dual sensor in a dry coating state is shown in Figure 12a as a relatively flat line. As shown, no resonant bands are visible in the transmission spectrum, indicating that the index of refraction of the coating exceeds that of the fiber cladding. This high refractive index prevents the light from coupling out of the core mode into the higher-order cladding modes. However, once the sensor is submerged in water, the effective index is decreased and the familiar LPG resonant band returns to the spectrum. These sensors can be tailored to operate at various wavelengths to allow multiplexed operation, as shown in this sensor demonstration. The transmission spectrum of the hydrogel-coated LPG sensor Element A submerged in a water bath is shown in Figure 12b. Figure 12c illustrates the transmission spectrum with both sensor element A and B submerged in the water bath. To demonstrate reversibility of the sensors, the sensors were removed from the water bath, and the original flat transmission spectrum was observed almost instantaneously, as shown in Figure 12d. Hence, the PEO coated LPG sensors display short response time, reversibility and repeatability. This sensor demonstration also illustrates the multiplexing capability of long period grating-based chemical sensors.

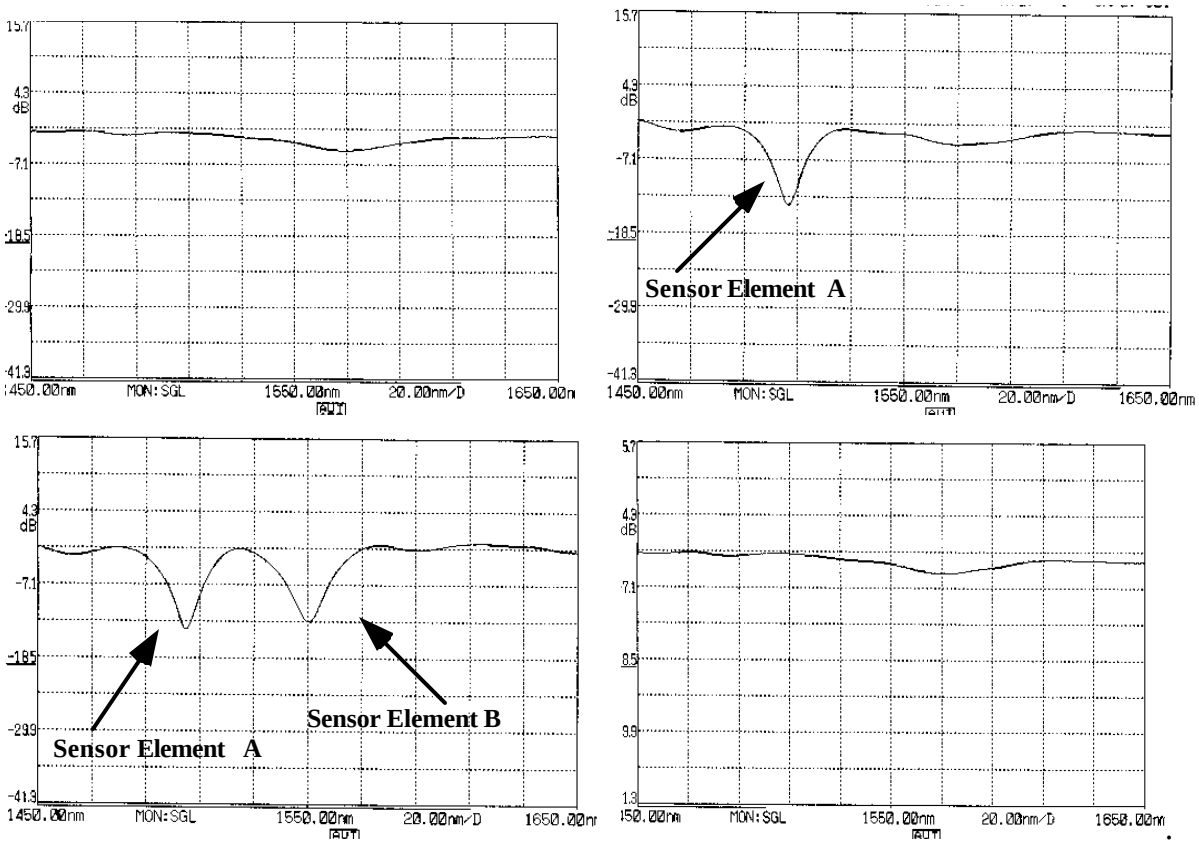

Figure 12. Transmission spectrum of dual multiplexed moisture sensors with wavelength on the x-axis and transmission power on the y-axis, a) in air b) spectrum after sensor element A is submerged in water bath, c) spectrum with sensor element A and B submerged in water bath, and d) spectrum returns to original flat base line when both sensor elements are removed from water bath.

4.3 POLYVINYL ALCOHOL / POLY-ACRYLIC ACID COATED LONG PERIOD GRATING

In a similar manner as the PEO coated LPG, the PVA-PAA coating was applied to the LPG and heat cured. This coating has a high refractive index in the dry state therefore no appearance of the spectral loss dip, but when the LPG sensor is hydrated in water the resonant band reappears due to a decrease in refractive index with water absorption. Coating preparation consists of procedures discussed in Section 3.3. The wavelength of the resonant band is dependent on the pH of the analyte. For this demonstration, LPG sensor elements were coated with an 80/20 (wt %) PVA-PAA polymer blend,

crosslinked with a heat gun, and a post cure at 130 °C for 60 minutes. The initial experimental setup is similar to the refractive index calibration set up, shown in Figure 6 and includes the use of a broad band source and an optical spectrum analyzer. By mixing various buffer solutions with various pH levels and observing the change in the spectral response, a relationship was acquired for later sensor calibration. The spectral response is shown in Figure 13. Table 5 gives the pH solutions and their respective location of the resonant band wavelength.

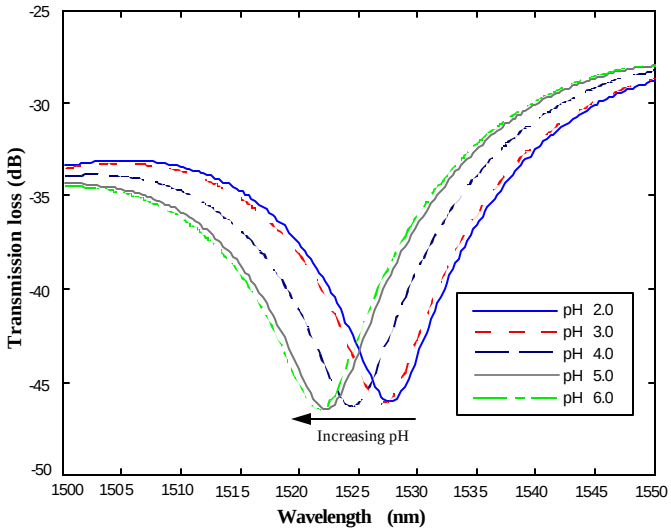

Figure 13. Spectral response of the PVA-PAA coated LPG with various pH buffer solutions.

Table 5. Spectral dip shift with various pH buffer solutions.

pH	Wavelength (nm) (+/- 0.2 nm)
2.0	1527.4
3.0	1526.9
4.0	1524.4
5.0	1522.4
6.0	1521.9
7.0	1521.9
8.0	1521.9

Figure 14 shows a plot of pH versus wavelength for the data presented in Table 5. According to this plot, the sensor response is linear between pH 3 and pH 5. The sensor shows a shift in wavelength

between pH 5.0 and pH 6.0 but as a nonlinear response, this requires complex curve fitting when incorporated into a demodulation algorithm.

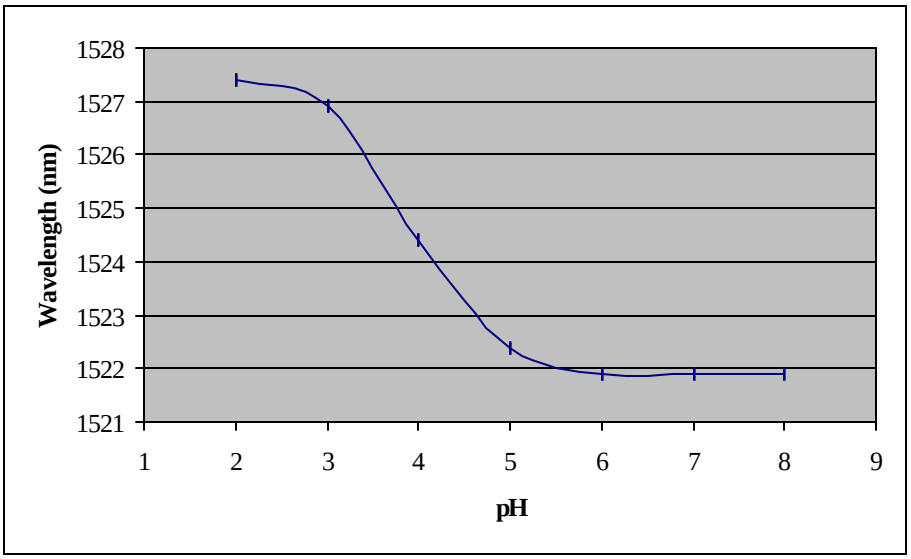

Figure 14. Plot of the data represented in Table 5.

The experimental results show the resonant band wavelength of the LPG shifts 4.5 nanometers between pH 3.0 and pH 5.0. Assuming the system used to track pH changes with this PVA-PAA coated LPG sensor can measure 0.05 nm wavelength shifts, then the possible resolution of the overall pH sensor system can be obtained by using

$$\frac{\Delta l}{\Delta pH} = \frac{l\_resolution}{pH\_resolution} \tag{3}$$

and using 4.5 for the change in wavelength, 2 for the change in pH, and 0.05nm for the system resolution to wavelength. By applying these numbers, the resulting equation is

$$\frac{4.50nm}{2} = \frac{0.05nm}{X}$$

and the calculated resolution to pH changes is $X = 0.022$.

To obtain refractive index measurements with time, sensogram plots were obtained utilizing an already developed LabView program that interfaces with a optical spectrum analyzer to obtain sensor response to various buffer solutions with time. The experimental method is similar to the one shown previously in Figure 8 except the demodulation system incorporates a broad band source and an optical spectrum analyzer along with supporting signal conditioning electronics. The system is programmed to track the minimum of the spectral loss dip and plot this data with time. This tracking system enables a time-based sensogram to be acquired and analyzed.

Figure 15 shows a sensogram taken by submerging the same pH sensor in pH 3.0 and pH 6.0 NIST standard buffer solutions. The sensor was submerged into each buffer solution, taken out and let dry until the original base line was obtained again. The sensogram illustrated excellent repeatability and reversibility of the PVA-PAA coated LPG-based pH sensor. The unusual peaks at the end of each cycle are due to timing differences between the signal conditioning system and the algorithm. When conducting the same experiment and monitoring the spectral data with the OSA there is no sudden increase in the wavelength as indicated. To ensure that the sensor is responding to a pH difference in the buffer solutions and not a refractive index difference. A sensogram, shown in Figure 16, was acquired using an uncoated LPG and exposing it to the various buffer solutions used in these experiments. This sensogram indicates that the PVA-PAA coated LPG is responding to the pH differences in the buffer solutions not differences in the refractive index of the buffers.

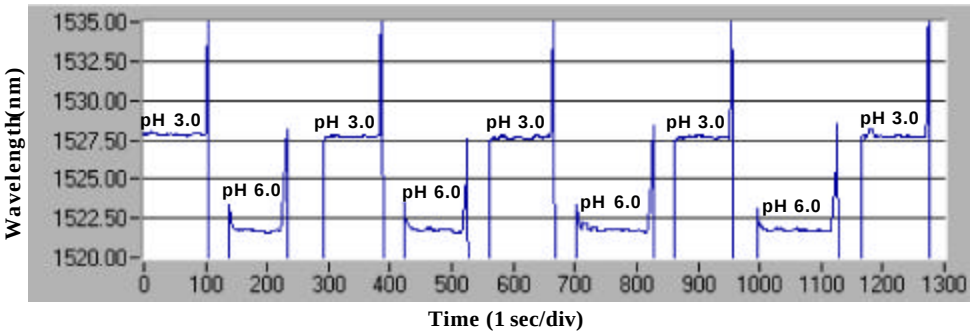

Figure 15. Sensogram of PVA-PAA coated LPG to various pH buffer solutions.

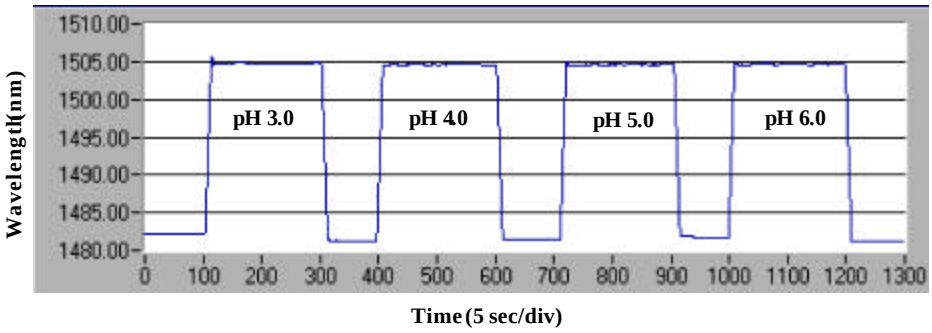

Figure 16. Sensogram of uncoated LPG to various pH buffer solutions.

4.3.1 Selectivity of Sensor Response

Because it is also important to test selectivity of the sensor to make sure it is responding to percent hydrogen concentration several other solutions with known pH values were tested on the PVA-PAA coated LPG sensor. The pH value of milk and grapefruit juice solutions were measured to be 6.5 and 3.0 respectively with a 0.1 resolution "pHastcheck" pH meter. The same PVA-PAA coated LPG was first exposed to the grapefruit juice with a resulting wavelength of 1533.00. The sensor was then washed with water and exposed to milk. The measurements taken with the milk and the grapefruit juice are repeatable, but the sensor response to water is not. This unrepeatable result is due to the water mixing with the previous sample in each case, but under each condition the sensor response is repeatable. The resonant band wavelength is located at 1527.50 when exposed to milk. The pH difference of 3.5 resulted in a total wavelength shift of 5.5 nm displaying a variance from the results in Table 5.

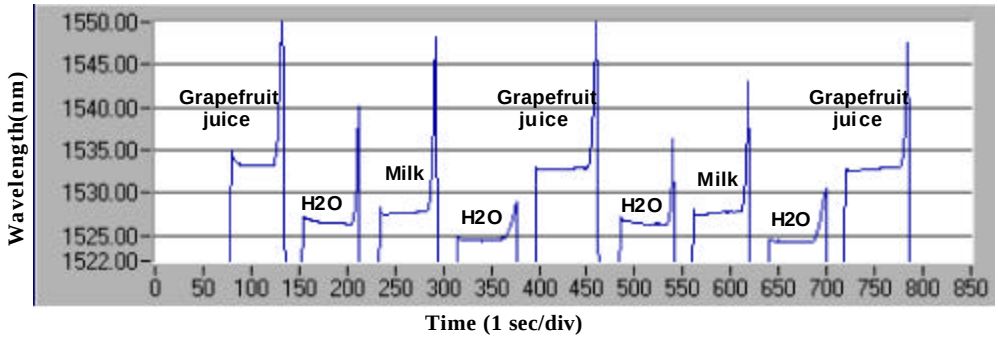

Figure 17. Sensogram of uncoated LPG to various analyte.

It was found that when comparing the resonance band wavelength for different analyte there is a discrepancy between the wavelength at the pH buffer 3.0 and the grapefruit juice (pH 3.0). This discrepancy is due to the difference in refractive index between the buffer solutions and the grapefruit juice. When the hydrogel coating swells the analyte is absorbed into the coating and if the analyte is a different refractive index from another there will be a difference in the sensor response. The ability to compensate for this refractive index difference can be accomplished by co-locating an uncoated LPG to measure the refractive index of the analyte to compensate the sensor response to different analyte pH. The following data, shown in Table 6, was collected by exposing an uncoated LPG to different refractive index oils and the grapefruit juice and milk. It was determined that the sensor refractive index response to the buffer solutions of pH 3.0 and 6.0 is around 1505 nm and the sensor refractive index response for the milk (pH 6.5) and grapefruit juice (pH 3.0) was approximately 1509 nm. These results give insight into the slight difference in the resonance band wavelengths when comparing sensograms presented in Figures 15 and 17. The pH sensor response is offset by the refractive index of the analyte.

Table 6. Wavelength vs. refractive index.

Refractive Index	Wavelength(nm)
DI water	1504.35
PH 3.0	1504.64
PH 6.0	1504.72
Grapefruit Juice	1509.07
Milk	1509.91

4.3.2 Resolution of pH Sensor Response

From Section 4.3, it was determined that theoretically the pH sensor system is sensitive to pH changes of 0.022 in the surrounding environment. To verify this, pH buffers were mixed and measured with an 0.001 resolution Accumet pH electrode. A 3.80 buffer solution and a 3.85 buffer solution were exposed to the sensor. Figure 18 illustrates the sensogram obtained during this experiment, verifying an at least 0.05 pH resolution. This plot shows that the sensor response is at least four times the noise

floor of the signal. The circled region is a transition region resulting from drying the sensor and rewetting the sensor with the next buffer solution.

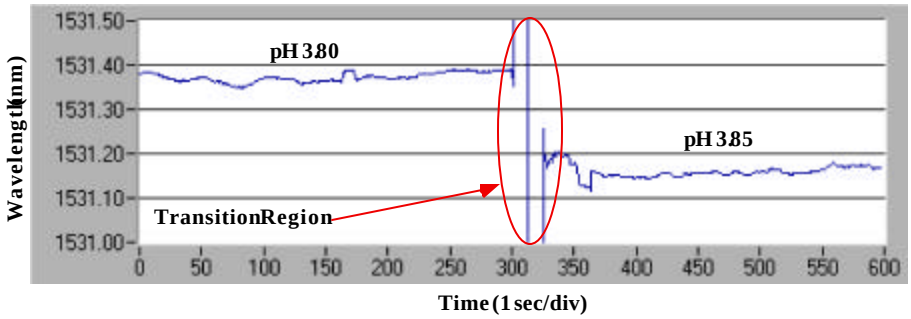

Figure 18. Sensogram showing a resolution of 0.05 and that the sensor response is 4 times the noise floor.

4.3.3 Repeatability of pH Sensor Response

It is often desirable to have a reusable sensor as opposed to a one time pH dosimeter, therefore sensor performance was evaluated under repeatable conditions. The plot shown in Figure 19 was acquired by exposing the same sensor to various pH buffer solutions ranging from pH 2.0 through pH 7.0 and repeating ten times. The response to each cycle shows excellent linearity and repeatability between pH 3.0 and 5.0. This range was therefore chosen as the sensor operating range for continued sensor evaluation.

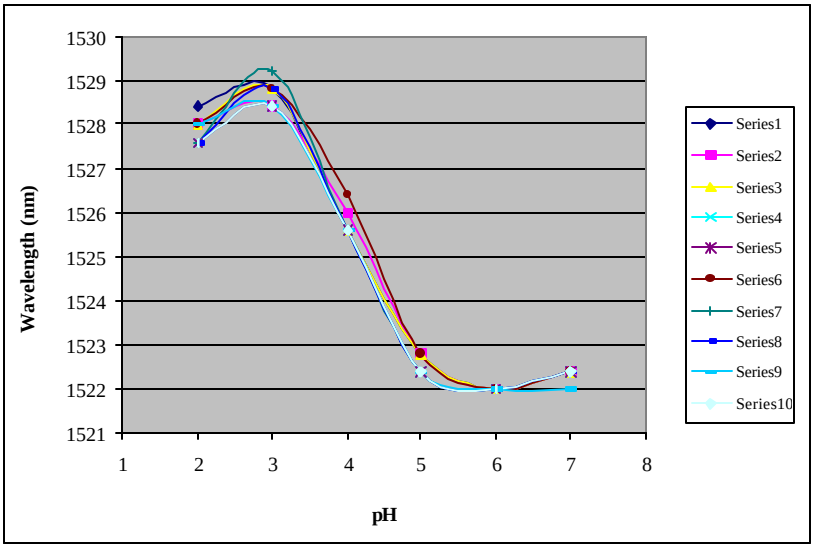

Figure 19. Repeatability plot for PVA-PAA coated LPG response to various pH buffers.

From this repeatability data shown in Figure 19, the statistical mean for each pH value was calculated and used to obtain a calibration curve. This curve is plotted below in Figure 20 along with 1-sigma error bars calculated from the repeatability data.

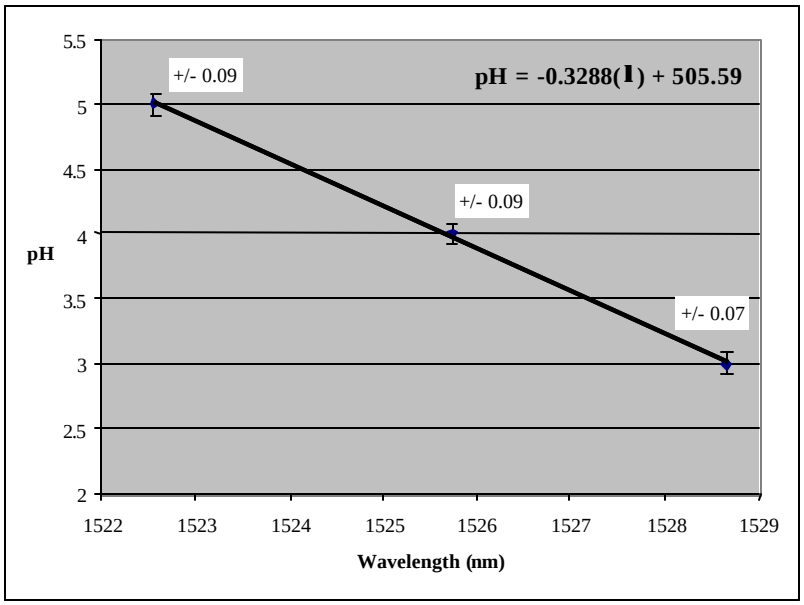

Figure 20. Calibration curve showing experimental accuracy.

Table 7 below illustrates the statistical data for a sample size of ten for each value between pH 3 and pH 5. This data was used to calculate the 95% confidence intervals shown in Figure 20. This data gives insight into the accuracy of the overall system to measure a given pH. For pH 3 through pH 4 the accuracy is +/-0.09. This accuracy gets better as the pH increases to pH 5 with a calculated accuracy of +/- 0.07.

Table 7. Experimental values for pH measurements.

	pH 3	pH 4	pH 5
Mean pH	2.97	3.93	4.97
St. Deviation	0.09	0.09	0.07

Errors shown in the data may be due to the accuracy of the long period gratings in refractive index measurements, the ability for the coating to respond in repeatable swelling when exposed to the same pH, the ability of the instrumentation to accurately measure the wavelength of the resonance band, or a calibration curve

that is slightly inaccurate. Other induced errors may result from not allowing enough response time for the coating to swell to equilibrium each time before documenting the wavelength. Although the buffers used were stored at room temperature, there may be variance as a result of temperature variations from buffer to buffer. Generally temperature is a critical factor in the measurement of pH and is often done simultaneously.

4.4 SUMMARY OF TEST RESULTS

In summary, the optical fiber long period grating is not only a highly sensitive refractometer, but by applying a pH-sensitive hydrogel coating it can be used to determine the pH of the surrounding environment. The presented data supports the use of long period gratings for use not only as a pH sensor, but as a sensor platform for a myriad of other chemical and biochemical sensors. These optical fiber-based sensors offer inherent advantages over traditional measurement techniques for harsh environments and within locations were electrical sparks are hazardous. The LPG is low profile with a cross-section diameter of approximately 125 microns, can be multiplexed for distributed measurements, and combined with other chemical sensors. Long period grating sensors enable repeatable, low cost, large-scale manufacturing needed for commercial market success. By incorporating a high resolution demodulation system, the sensing platform is capable of highly sensitive chemical measurements. The LPG coated with PVA-PAA demonstrated highly sensitive measurements between pH 3 and pH 5 with a resolution of at least 0.05 and an accuracy of +/- 0.09. Although this pH range may not be sufficient to totally characterize the pH levels present within a corrosive environment other sensors can easily be developed in a similar manner by applying other pH-sensitive coatings, such as, but not limited to, PVA-MA, HEMA/DMA, PAN. Preliminary studies that are not presented here indicate that pH-sensitive polystyrene microspheres incorporated into a HEMA coating when applied to the LPG extend the pH range from 7 through 9. The next chapter outlines the market potential for such sensors and future studies required to transition the presented sensors into these markets.

CHAPTER 5 – CONCLUSION

5.1 RESEARCH CONTRIBUTIONS AND COMMERCIAL APPLICATIONS

This thesis presented long period grating-based sensor results that demonstrate the potential for not only corrosion detection in aging aircraft by monitoring pH, but also, for a variety of other chemical sensing applications. The sensing platform shows great promise for corrosion by-product detection in, pipe networks, civil infrastructure, as well as applications in process control, and petroleum production operations. The measurement of pH is one of the most applied techniques in analytical chemistry. In addition to corrosion detection, other fields of application include medical diagnostics, industrial processes, and monitoring of water quality. With specific coatings the LPG platform has applications as biological sensors for in-vitro detection of pathogens, and chemical sensors for environmental and industrial process monitoring [2,3].

Within the medical diagnostic field, blood pH is a critical measurement. The pH of the blood and tissue are normally maintained within narrow ranges and even slight deviations from these values have great diagnostic value in critical care. Current pH measurement techniques rely on electrically monitoring the potential on the surface of pH sensitive oxides on glasses or by optically monitoring the degree of protonation of chemical indicators. The pH electrode has traditionally incorporated a thin glass membrane that encloses a reference solution and requires the use of a reference electrode that has a lifetime dependent on the volume of electrolyte it contains. This reference electrode is often a source of measurement error [23]. Electrical sensors also have the risk of interference from biologically important metal ions present in the blood [23]. Other optical fiber-based sensors based on fluorescence can be effected by fluorescence quenchers such as some inhalation general anesthetics [23]. The demonstrated long period grating-based pH sensor is a sensing method that offers a cost-effective, reliable solution to these current sensing limitations. The hydrogels utilized for sensor fabrication offer the added advantage of being biocompatible and thus lend themselves for *in-vivo* medical diagnostic applications. These sensors can also be multiplexed with similar LPG-based

pO_2 and pCO_2 sensors for hemoglobin monitoring or miniaturized for intercellular pH measurements [26].

The inherent small geometry and multiplexing capability of the LPG-based sensor offers advantages in batch and continuous monitoring of industrial processes for pharmaceuticals, chemicals, pulp and paper, food, and paints. The on-line monitoring of these processes will result in higher quality products with increased yield. The uniformity of product quality is often highly dependent on pH levels in processing and are often measured by batch testing methods [23]. By implementing on-line optical-fiber based pH sensors, product quality can be assured in a truly cost-effective manner.

Another area of interest for optical fiber-based pH sensors is in the geo-chemical and environmental fields. This includes the monitoring of our nations water quality. Currently available glass electrode pH sensors exhibit acid alkali errors, sensitivity to monovalent cations, mechanical fragility, undesirable impedance, and instability at temperatures greater than 100 °C [23]. Water quality measurements are required in industrial plants effluent, in rainwater, groundwater, and drinking water supply. Industrial facilities are currently held responsible for their effluent wastewater with pH being a critical indicator measurement. Other market applications include well water monitoring, sewage treatment compliance, biochemical, and fish industry for monitoring and control of dissolved oxygen in basins[23].

5.2 FUTURE STUDY

The presented results demonstrate the capability for optical fiber-based long period gratings to detect pH levels between pH 3 and pH 5. Typically the pH of corrosive environments range between pH 6 and pH 9, with a sudden change in pH indicating the onset of corrosion. By applying other pH-sensitive coatings that respond to changes in a higher pH range, the sensing capability can be expanded to be capable of monitoring the corrosive environment throughout its critical course.

The presented research study addresses initial feasibility studies for pH sensor development. In order for future implementation of these sensors aboard flight worthy aircraft and civil infrastructures several

issues must be addressed through further sensor evaluation. These issues include continued sensor evaluation with emphasizes on sensor repeatability, selectivity, reversibility, and stability. In order for these sensors to be implemented in future structures, sensor installation procedures, fight worthy components and an integrated implementation plan must be developed for acceptance of this state-of-the art technology. A critical question that needs to be addressed is what impact sensor installation will have on the structural integrity of the infrastructure in question. Also, incorporation of such corrosion monitoring systems should have no adverse effects on the structural integrity of the original structure. The detrimental effects of corrosion are not always due to corrosion alone but to the interaction of corrosion with fatigue, wear (including erosion and fretting), and stress resulting in premature fracture [5]. It will therefore be beneficial to explore compatibility and multiplexing capabilities of these sensors with other health monitoring sensors for aluminum alloy structures. In the area of medical diagnostics, industrial processing, and monitoring of water quality, similar extended sensor evaluation and application issues need to be addressed for acceptance within these industries.

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VITA

Jennifer Leith Elster was born in Bethesda, Maryland on July 21, 1971 the daughter of Jim and Carol Elster and soon moved with her parents and two older brothers to Guam where her father completed his duties as commanding officer in the United States Navy. Upon returning to the States, her family lived in Arlington Virginia where she completed her schooling at Washington-Lee High School. Jennifer matriculated at Virginia Polytechnic Institute and State University (VPI&SU) in 1989 and entered the Mechanical Engineering Department at Virginia Tech where she graduated with a Bachelor of Science in 1994.

During her undergraduate studies she participated as a research assistant in several fiber optic related research programs within the College of Engineering at Virginia Tech. Her interest in the multidiscipline sciences led Jennifer to a Master of Science program part-time in the Materials Science and Engineering Department at Virginia Tech. During her graduate studies in 1995 she began working full-time at F&S, Inc. in Blacksburg, Virginia. While completing her master's studies she made numerous contributions to research programs involving fiber optic sensor applications, and thin film usage for improving sensing techniques.