ANALYSIS OF PREMATURE DEGRADATION TO HIGH PERFORMANCE AEROSPACE MILITARY COATINGS

by

Nickolaus K. Weise A Dissertation Submitted to the Graduate Faculty of George Mason University in Partial Fulfillment of The Requirements for the Degree of Doctor of Philosophy Chemistry and Biochemistry



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Dedication

This is dedicated to the women in my life: Sarah, Linna, and Brianne. Linna and Brianne, I love you more than you will ever comprehend... that is, until you have kids of your own. Sarah, you are my life, my love, my everything. Thank you for always believing in me, for encouraging me, and for picking me up whenever I was down. Without your help I would never have completed this part of my journey. I am grateful for every day I get to spend with you.

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List of Abbreviations

ATR - attenuated total reflectance

CPVC – critical pigment volume concentration

DBTDL - dibutyltin dilaurate

DMA – dynamic mechanical analysis

DSC - differential scanning calorimetry

E' - elastic modulus

E* - complex modulus

FT-IR – Fourier transform infrared spectroscopy

HDI – hexamethylene diisocyanate

LSCM – laser scanning confocal microscopy

PABE – poly(tetramethylene ethylene adipate)

PLA - polylactic acid

PU – polyurethane

PS – polystyrene

PVC - pigment volume concentration

RH – relative humidity

TDI – toluene diisocyanate

TGA – thermogravimetric analysis

T_g – glass transition temperature

VOC – volatile organic compound

XPS – X-ray photoelectron spectroscopy

Abstract

Analysis of Premature Degradation to High Performance Aerospace Military Coatings Nickolaus K. Weise, Ph.D.

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High performance aerospace coatings are intended to protect the substrate from the effects of sunlight and humidity, ensuring an airframe lasts its intended lifespan. The coating systems that are applied to the airframe are intended to last for 12-15 years, with minor periodic touch ups or "rework". However, when the applied coating system degrades prematurely, the U.S Navy is forced to spend a great deal of money and man hours repairing the defective coating. Currently, the Navy employs a coating system that is experiencing premature degradation from hot and humid environments. To explore what is causing this degradation and ways to prevent it, analogue coating systems were synthesized and exposed to accelerated weathering conditions. The study focused on manipulating three (3) separate variables: 1) the blending of poly(ether) and poly(ester) macrodiol; 2) the – NCO:-OH mole ratio; and 3) the pigment volume concentration. This work describes the results from the accelerated weathering study. Surface analysis, bulk mechanical analysis and spectroscopic analysis were used to understand how variables were affected due to

accelerated weathering. When the macrodiol was blended, the mechanical properties of weathered coatings more closely resembled the T_0 mechanical properties after 2000 *h* of weathering. When the –NCO:-OH mole ratio was manipulated, the urea linkages formed from the excess isocyanate did not adversely affect coating performance. Finally, when the PVC was manipulated, the blended polyol coating systems performed better than the single polyol coating systems. This work furthers the knowledge base contributing to the development of the next generation of high performance military coatings.

Chapter 1: Introduction

1.1 Polymeric Materials

Polymeric materials can be viewed simplistically as large organic molecules composed of repeating units, also known as "mers". Different classes of polymers are named after the type of monomer employed, preceded by the prefix "poly".¹⁻² The development of polymeric materials has created the potential for limitless products through the manipulation, order, and chemistry of the employed monomers. The dramatic increase in the development of new polymeric products has resulted in a reduced dependence on natural products, such as natural rubber.³ Today, polymeric materials can be found in many aspects of daily living. Polymers can be processed into various forms to include fibers, films, castables, coatings, and paints.⁴

The vast majority of polymeric materials manufactured today are plastics, which can be organized into two categories: thermoplastics and thermosets. Thermoplastics are polymeric materials that can be repeatedly processed by the application of heat and pressure. Common thermoplastics include polyethylene, polypropylene and polyvinyl chloride. Thermosets are polymeric materials that incorporate a covalently cross-linked three-dimensional network upon polymerization. Once formed, thermoset polymers, will not soften upon heating. The three-dimensional cross linked network in thermosets provides durability and resistance to thermal and chemical degradation of the material.⁴ The increased resistance makes thermosets desirable for long-term applications. Inclusion of additives and the development of different polymers have led to a large increase in the availability of polymeric materials and to increased use in various applications, to include coatings.⁵⁻⁶

The word "coatings" is a general term that applies to anything that coats or covers a substrate. Coatings are applied to: (1) protect the substrate from physical damage (corrosion, abrasion; (2) enhance appearance by adding color or gloss to the substrate. A commonly used synonym for this type of coating is the word *paint*. Paints are often polymers dissolved in solvent. When solvent-based paints are applied, the solvent evaporates and results in a polymeric coating over a substrate.

Recently, water-based systems have become state-of-the-art in coatings technology. The most commonly known water-based system is latex paint. Latex paint is formed from an emulsion of polymer micelles in water.⁷ As the coating dries, water evaporates, causing particles in the latex paint to become closer in proximity to each other. The shrinking proximity of the paint particles eventually causes disruption of the micelles, which were originally formed by surfactant molecules, allowing the paint particles to coalesce into a continuous polymer film.⁸ While the largest benefit to using latex paint remains the absence of volatile organic compound (VOC) emissions, latex paints have certain shortcomings. As such, conventional latex coatings have poor resistance to abrasion and organic solvents. These shortcomings are the primary reasons for using monomer solutions that react to form a polymer, such as polyurethanes, for applications that require high performance coatings.

High performance coating systems must possess several different physical properties that can be tuned for a specific application. For example, the elastic modulus, storage modulus, glass transition temperature (T_g) , tack, air permeability, and degradation onset temperature can be modulated for a specific application by manipulating the chemistry of the coating. The storage modulus of the coating is a measure of its flexibility. A low storage modulus indicates that a coating is more easily deformed. The elastic modulus, also known as Young's modulus, is a ratio of tensile stress to tensile strain of a material over the elastic portion of a material's stress-strain curve (*i.e.*, the range of strain over which the material will return to its original length). A low elastic modulus is indicative of a material that can be easily deformed. The T_g of a material is the temperature at which a polymer transitions from a semi-crystalline to a rubbery state. Each of these properties may be tuned to a desirable range to yield a coating that is optimal for a specific application.

1.2 Polyurethanes

Polyurethane (PU) materials have been in production on an industrial scale since the early 1940s. PUs were first discovered in Germany by Otto Bayer and coworkers in 1937 while developing alternatives to Carother's work on polyamides at Dupont. Initially, the reaction of isocyanates with diamine was investigated. This reaction formed polyureas which resulted in a hydrophilic material that would not melt. Bayer continued his research into isocyanates, next attempting a reaction with aliphatic isocyanate with glycol resulting in PUs, a new material with interesting properites.⁹

Over the years, advances in this material class, availability, and use of PU coatings have increased across a wide variety of applications. Further, the development of low-cost materials has enabled PUs to be used in a wider variety of products.¹⁰ Due to the ease of use and availability of polyurethane materials, global use was estimated at 16.9 million tons in 2017 and is estimated to reach 21.3 million tons by 2022. The market share for polyurethane materials was estimated at 12.47 billion USD in 2017 and is expected to grow to 16.63 billion USD by 2022, with a common annual growth rate of 5.9% from 2017 to 2022.¹¹

Today, PU coatings are found on a multitude of different substrates to improve not only their appearance, but also, the product's lifespan. For example, several building materials, such as steel trusses and concrete supports, are spray-coated with PU material to improve durability in varied environmental conditions.¹² The automobile industry uses PU coatings for the high gloss exterior, color retention, and scratch and corrosion resistance of automobile exterior coatings. Rigid PU foams are extensively utilized for seat cushions, as well as insulating materials.¹² When compared to traditional materials such as wood or metals, PUs have uniquely desirable properties that include low density, low thermal conductivity, high strength to weight ratio, and high dimensional stability.¹³

Generically, PUs are composed of an interconnected arrangement of a hard segment (isocyanate), soft segment (macrodiols), and chain extender if applicable¹⁴. Chain extenders are generally short chain diols. Both the isocyanate or alcohol can be monomeric molecules or polymers with a wide range of molecular weights.^{4, 15} The diversity of PU starting materials allows a wide variety of potential applications. The chemistry involved

in the synthesis of these materials is initiated by the reaction of an isocyanate functional group with a polyol, which results in the formation of a urethane bond.¹⁶⁻¹⁷ The reaction is detailed in Figure 1-1. The polymerization proceeds through a step-growth mechanism: monomer units react with different functional groups on either the same monomer or (more commonly) another monomer to form dimers, trimers and eventually large polymer chains.



Figure 1-1: Urethane bond formation via the reaction of an isocyanate and alcohol functional groups.

Urethane bond formation can be monitored through Fourier-transform infrared (FT-IR) spectroscopy by observing the disappearance of the characteristic isocyanate peak near 2270 cm⁻¹.¹⁸⁻¹⁹ The reaction proceeds through polyaddition into a high molecular weight molecule.³ Once formed, PUs are exceptional commercial polymers due to their physical properties, including robust strength, rigidity, elasticity, solvent resistance, and hydrolytic stability.²⁰ The polyol component of the resulting polymer plays a dominant role in the mechanical properties of the material. For example, PUs employ poly(ether) polyol afford coatings that are flexible and resistant to hydrolysis, whereas poly(ester) polyols produce more rigid and oil-resistant coatings.²¹

There are two different classes of isocyanate used to prepare PU coatings: aliphatic and aromatic²². Aromatic-based PUs are generally employed in areas where weather resistance, particularly sunlight or ultraviolet radiation, is of concern. However, aromatic isocyanates have the undesirable property of yellowing under such conditions. Purely aesthetic, the yellowing process does not affect the mechanical properties of these coating employed aromatic isocyanates systems. The two commonly are 4.4'methylenebis(phenyl isocyanate) (MDI) and toluene diisocyanate (TDI) (Figure 1-2). Because of the negative effects sunlight has on aromatic isocyanate-based polyurethane coatings, aliphatic isocyanates are used. While these aliphatic variants are more expensive, they do not yellow when exposed to sunlight, making them excellent candidates for use on outdoor products. Common aliphatic isocyanates include hexamethylene diisocyanate (HDI) and 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) (Figure 1-2).



Figure 1-2: Common aromatic and aliphatic diisocyanates used in polyurethane synthesis. A) toluene diisocyanate, B) 4,4'-methylenebis(phenyl isocyanate), C) hexamethylene diisocyanate, and D) 4,4'-methylenebis(cyclohexyl isocyanate)

The isocyanate functionality readily reacts with active nucleophilic groups, i.e., -OH, -NH₂, -NH, -COOH, and -SH groups. In general, four main types of polyols are employed when synthesizing PUs, including poly(ether), poly(ester), polyacrylic, and hydrocarbon (Figure 1-3). These polyols are available with a variety of functionalities as well as molecular weights. The reactivity of these polyols depends on the functionality of the reactive hydrogen-containing group. As expected, primary groups react more rapidly than secondary groups, which, in turn, react more rapidly than tertiary groups.



Figure 1-3: Common polyols used in the synthesis of polyurethane materials. A) poly(ether), B) poly(ester), C) polyacrylic, and D) hydrocarbon polyol.

1.3 Qualification Standards for Military Coatings

Coating systems comprised of PU have emerged as a useful material due to their advantageous properties discussed in Section 1.2.¹² The use of these coatings for military applications demand extremely robust systems in order to withstand unique physical challenges. Namely, military coatings need to inhibit corrosion, provide visual camouflage, and withstand rigorous physical abuse.²³ To ensure coatings can withstand

these conditions, any potential coating is subjected to harsh environmental testing through a set of performance inspections.

Military coatings must adhere to a specific set of standards before the coating can be applied to an asset. The materials used to make the coating are not limited to a specific vendor, yet the resulting coating must pass all requirements of the coating specification. As stated, these coatings are typically 2- or 3-component systems, depending on the class. For example, in Military Performance Standard 85285 (MIL-PRF-85285), the components can be broken down as follows: Component A consists of a pigmented poly(ester) polyol resin and solvents; Component B contains a clear aliphatic isocyanate and solvents, while Component C is optional and contains organic solvents for class H coatings.²⁴

The MIL-PRF-85285 specification sheet outlines how each component must appear during storage, and must include the guidelines for product shelf life. Component A must be smooth, homogeneous, and pourable. Additionally, Component A may not exhibit pigment flotation or settling that cannot be reincorporated into the resin through mixing with a hand paddle. Component B must be clear, homogenous, and exhibit no gelation or detectable particulate matter, either suspended in solution or settled at the bottom of the container.

During the qualification process, films are cast and a conformance inspection is performed on cured coatings. Inspections range from examining coating flexibility, impact resistance, and adhesion, to measuring the fluid resistance, solvent resistance, and soiling of test panels. The majority of required tests are governed by an American Society for Testing and Materials (ASTM) standard for reproducibility. For example, the ASTM G155 standard outlines weathering resistance and specifies that the weathering be performed with a Xenon-arc light and water apparatus.²⁵ The standard is intended to reproduce the weathering effects that occur when a material is exposed to sunlight and rain or moisture. The protocol calls for weathering cycles of 102 minutes of light and only 18 minutes of light and spray. Weathering conditions regarding temperature, humidity, and light intensity can be found in Table 1-1. Upon completion of the weathering protocol, the 60° specular gloss and coating color are tested in accordance with the respective ASTM standard for each characteristic.

Cabinet temperature:	$42 \pm 3 \ ^{\circ}C \ (108 \pm 5 \ ^{\circ}F)$
Black body temperature in cabinet:	$63 \pm 3 \ ^{\circ}C \ (145 \pm 5 \ ^{\circ}F)$
Relative humidity in cabinet:	50 ± 5 percent
Intensity (spectral irradiance):	0.35 to 0.5 $W/m^2 \cdot nm$ at a wavelength of 340 nm

Table 1-1: Weatherometer Temperature, Humidity, and Light Intensity Conditions as Outlined in ASTM G155.

The use of weathering chambers has been employed to qualify new coating systems quickly to enable researchers to keep up with environmental policies, such as low VOC coatings. The shift to low VOC coatings was the result of a constant need to rework/repaint assets, frequently due to premature weather-induced degradation. Such premature degradation has spurred the recent study of degradation in PU systems. Zhang *et al.*²⁶

developed a step scan phase modulation photo-acoustic FT-IR peak fitting method to analyze degradation. This method allows for the study of PU coating degradation, as well as the harshness of natural exposure sites. Zhang *et al.*²⁶ were able to correlate these natural exposure sites to accelerated weather degradation. Likewise, Yang *et al.*²⁷ used X-ray photo-electron spectroscopy and FT-IR to characterize an increase in urea concentration during exposure to a Q-panel ultra violet (QUV) chamber. The group also observed blistering on the topcoat surfaces upon QUV exposure.

Other groups have utilized FT-IR spectroscopy to characterize degradation through observation of changes in the carbonyl, amide II, or amide III stretching frequencies.²⁸⁻³⁰ Keene *et al.*²⁸ demonstrated that a reduction in the amide II stretching frequency, as well as a broadening of the carbonyl peak within FT-IR, is indicative of photooxidation of polyurethanes. Additionally, the mechanical properties of weathered coatings have been studied by means of dynamic mechanical analysis (DMA). Thermal evaluation of the coating was shown to provide insight on changes in glass transition temperature, crosslink density, and modulus due to accelerated weathering. From DMA studies, an increase in T_g was observed after exposure to QUV weathering indicating significant molecular changes.³¹

1.4 Polymer Blending

Polymer blends are defined as a mixture of two or more macromolecular substances, polymers, or copolymers.³² Polymer blending is an attractive approach that has the potential to generate coatings with new and/or better properties derived from two existing polymers, possibly eliminating the process of synthesizing new polymers.³³⁻³⁵

Blending is usually less expensive and less time-consuming than developing new monomers and polymerization techniques. One significant drawback to blending polymers is the potential for decreased recyclability. Generally, neat or reinforced polymers are easier to recycle than blended materials. Morphology and miscibility are key factors that affect the mechanical properties of a newly formulated polymer blend.^{18, 32, 36-37} With miscibility especially, the difficulty arises due to the high viscosity of many macromolecular species.³⁸

Polymer blends are either homogeneous or heterogeneous. In homogenous blends, both components lose some portion of their properties and the properties of the final product represent an average of the components. Heterogeneous blends retain all properties of the components utilized. A weakness of one component can be overcome to a certain extent by the other component in the mixture. Furthermore, heterogeneous blends appear in a variety of morphologies. The best known morphologies are: 1) a dispersion of one polymer in the matrix of the other polymer; and 2) a co-continuous two-phase morphology.³⁹

When two polymers are successfully blended, in some cases improvements can be observed in mechanical properties.⁴⁰⁻⁴¹ For example, Hamad *et.al.*⁴² composed blends of polylactic acid (PLA) and polystyrene (PS). Polymer blends ranging from neat PLA to neat PS in 25 *wt%* increments were extruded for the purpose of examining tensile strength and elongation of the various blends. It was found that blends containing 50 and 75 *wt%* PLA improved mechanical properties compared to PS only. Malinowski *et al.*⁴³ studied blends of polylactide and polycaprolactone that were crosslinked with isocyanurate. From

this study, it was found that addition of isocyanurate hindered phase separation. Furthermore, Malinowski *et al.* found that addition of isocyanurate to the blend caused an increase in strength and elastic modulus, while elongation at break and impact strength decreased.

1.5 Manipulating Stoichiometry of Isocyanate to Hydroxyl Groups

The addition of isocyanate to the polyurethane network causes changes to the mechanical properties of the synthesized polymer. These changes correlate with the amount of isocyanate added. Adding isocyanate to a system can cause crosslinking, further increasing mechanical properties, such as T_g , storage modulus, and yielding strength.

While the reaction between isocyanate and hydroxyl groups are preferred for PU materials, the isocyanate group can undergo several different reactions. If the nucleophile group is composed of -NH₂, the urea linkage is formed. Further, if an isocyanate group reacts with water, an unstable carbamic acid is formed, which quickly decomposes to an amine and carbon dioxide. The afforded amine group can react with an isocyanate group to form a urea linkage (Figure 1-4).



Figure 1-4: Mechanism for urea formation from reaction of isocyanate with atmospheric moisture.

Hydrogen atoms on urethane groups are still available to react under specific conditions. For example, allophanate and biuret linkages form favorably between 120-150° C and 100-150° C, respectively. The formation of these linkages promote polymer crosslinking. In the presence of a basic catalyst, the isocyanate group can react with itself to dimerize or trimerize, thereby affording uretdione and isocyanurate species, respectively.⁴⁴

Modulating the relative amount of isocyanate and polyol or "indexing," as it is referred to in industry, is a standard practice used in industrial coatings: excess isocyanate is added to ensure complete reaction with the incorporated polyol. The index ratio refers to the relative amount of –NCO to –OH contained in the coating. Generally, solvent-based coating systems are indexed at 1.1:1.0 –NCO: –OH. The addition of excess isocyanate has the ability, for those functional groups, to form urea linkages within coating systems.⁴⁵ The additional urea linkages due to overindexing cause an increase in hard segment percentage within the coating. Increased hard segment, in turn, raises the glass transition temperature of the cured films.⁴⁶⁻⁴⁷ This effect was studied by Levin *et al.*²³ when the group used two different polyurethane formulations and manipulated the –NCO:-OH stoichiometry. In Figure 1-5 a plot of –NCO:-OH *vs* T_g is presented for the two different polyurethane formulations that have also been cured two different ways. Both coatings were cured at ambient temperatures for one month, then a post-cure was performed on test films at 102 °C for 1 *h*. The ambient temperature cure and post cured samples were then analyzed using DMA. The results from Levin *et al.*²³ in Figure 1-5 indicate that as the – NCO:-OH index increased, the T_g of the material also increased. The authors believed this was likely due to the increase in urea linkages relative to the urethane linkages.²³



Figure 1-5: Glass transition temperature of cured films with different -NCO:-OH index ratios.

Additionally, the group found that, in general, an increase in –NCO:-OH ratio improved tensile strength and elastic modulus was observed for the cured coatings. Also the elongation at break and film toughness decreased slightly with increased index ratios.

Overindexing also had an effect on barrier properties of the coating system. Barrier properties are an important characteristic of performance depending on the specific application, for example, use on military vehicles. Coatings with improved barrier properties are better able to block the absorption of chemical agents, improving asset decontamination. Improved barrier properties additionally block moisture from reaching the substrate which could cause substrate corrosion and eventually require repair or replacement. In the study performed by Levin *et al.*²³, increasing the isocyanate index caused the permeability of dimethyl methylphosponate (DMMP) to decrease. Barrier properties were studied by experimentally measuring permeability and solubility, then calculating diffusivity through the following relationship $P = S * D.^{23}$ Where P is equal to permeability, S is the solubility and D is the diffusivity. By increasing the index ratio, both coating systems studied displayed an increased resistance to penetration by DMMP. However, when the coatings were tested against water, they found that increasing the isocyanate index had no effect.²³

1.6 Effects of Pigments

The word "pigment" is derived from the Latin word *pigmentum*. Today, pigment is defined as a substance consisting of small particles that are insoluble and used to account for coloring, light scattering, protective, or magnetic properties.⁴⁸ These substances differ from dyes due to their low solubility in solvents and binders. Pigments can be classified

as organic or inorganic, depending on their chemical makeup.⁴⁹⁻⁵⁰ Another common additive to paints are fillers. Fillers are generally granular solids that are incorporated to impart toughness or texture. Fillers can impart other special properties to the paint.

Pigments have been used for generations, yet an actual pigment industry was not started until the 18th century with the development of pigments such as Berlin blue, cobalt blue, Scheel's green, and chromate yellow.⁵¹ By the 20th century, pigments became a subject of scientific research. New synthetic pigments were created, *i.e.*, cadmium red, titanium dioxide (with anatase or rutile structures), and luster pigments.⁵² Today, pigments are widely employed in paints, varnishes, plastics, printing inks for paper and textiles, leather decoration, building materials, floor coverings, rubber, paper, cosmetics, ceramic glazes, and enamels.

Pigments, or fillers, are added to coating systems to provide either aesthetic appearance or functionality, such as spectral reflectance or magnetic properties. Additives also play a role in controlling the physical properties of a coating. There is a finite amount of pigment that can be incorporated into the polymer matrix. This amount is governed by the ability for the paint to encapsulate the pigment. The effects that pigments have on the mechanical properties of a coating can be monitored by a variety of techniques such as DMA, DSC, and TGA. By monitoring changes in mechanical properties, it is possible to investigate how increasing pigment loading affects coating performance.⁵³

When the Pigment Volume Concentration (PVC) reaches or surpasses the Critical Pigment Volume Concentration (CPVC), the interplay between the polymer and pigment begins to have negative effects on performance. When the PVC exceeds CPVC, there is

no longer enough polymer to form a continuous polymer network, causing pigment to not be completely encapsulated. This effect can cause voids or cracks to form in the film, thereby allowing excess water or other contaminants to enter the matrix.⁵³ Furthermore, the mechanical properties of the coating are affected. For example, a recent work studied the thermal and mechanical properties of an epoxy primer with increasing PVC⁵⁴. It concluded that elastic modulus increased with increasing PVC, leading researchers to believe that the films were more adverse to deformation, while rupture and strain limit exhibited an inverse relationship with PVC concentration.⁵⁴

Chapter 2: Coating Analysis

In the data presented below, analysis of coating properties was performed to characterize the accelerated weathered coatings in order to understand how the manipulated variables affected coating degradation. Surface characterization was utilized to observe visible changes to the coatings as well as changes to surface chemistries. Thermal and mechanical analyses were performed to understand and characterize the changes to the polymer matrix that occurred due to exposure to accelerated weathering.

2.1 Laser Scanning Confocal Microscopy (LSCM)

Laser scanning confocal microscopy (LSCM) was used to provide information on surface characteristics of the sample coatings. LSCM measurements were performed on an Olympus LEXT OLS4000 using the LEXT software package. Images were acquired using a laser source at 405 *nm* with 20x optics providing 108x magnification of the coating surfaces. Surface roughness parameter measurements were performed using the LEXT software package using the following equation:

$$S_q = \sqrt{\frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [z(x_k, y_l)]^2}$$

Equation 2-1

2.2 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) provided thermal stability data of the polymer films analyzed. TGA analysis shows the sample degradation with increasing temperature at a given rate under controlled conditions. TGA experiments were performed on a TA Instruments Discovery TGA instrument using a platinum sample pan. The analyses were carried out in a nitrogen environment. Nitrogen was also used as the purge gas for the balance. Thermal stability experiments were recorded from ambient temperature to 700 °C at 10 °C *min*⁻¹. Plots of percent weight loss *versus* temperature were generated in order to analyze the data.

2.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the polymer films. The T_g is the temperature at which a polymer transitions from a glassy state to a rubbery state. DSC measurements were performed using a TA Instruments Discovery DSC instrument equipped with the DSC Refrigerated Cooling System (RCS) and a purge gas of nitrogen set to 50 *mL/min*. Samples of approximately 1-2 mg were placed into TA Instrument TzeroTM Aluminum pans, and an empty TzeroTM aluminum pan was used as reference. Powder and free film samples were analyzed using a cyclic method, including two consecutive cycles from -70 °C to 150 °C at 10 °C/*min*. DSC experiments were used to monitor the changes of the glass transition temperature. The T_g values for the samples were determined from data present in the second ramp cycle. Based on this data, glass transition temperatures were found using the TA Universal Analysis program.

2.4 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) provided complementary thermal and mechanical data for fully cured films. DMA analysis was performed using a TA Instruments Q800 Dynamic mechanical analyzer equipped with a gas cooling accessory (GCA) and film tension clamp. Free film samples were analyzed from -70 °C to 150 °C at a ramp rate of 3 °C/*min* to thoroughly analyze the mechanical properties before and after the glass transition. Mechanical data was collected at an oscillation frequency of 1 Hz.

2.5 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transformed infrared spectroscopy was used to provide broad chemical information of control (non-weathered / T_0) and weathered films. FT-IR spectra were recorded on a Thermo Scientific Nicolet 6700 with the Omnic software package. The Nicolet 6700 was equipped with a Smart Performer Attenuated Total Reflectance (ATR) attachment, and a diamond crystal was used. Air was employed as the background and each sample was subjected to 32 scans for each ATR-FT-IR spectra.

2.6 Contact Angle Analysis

Studying the water contact angle of a polymer surface can provide insight to changes in surface chemistry on PU coatings. The contact angle of triple distilled water provided useful information in changes to the hydrophobicity/hydrophilicity of the weathered coatings. Contact angle measurements were performed utilizing a VCA 2500 video contact angle system by AST Products, Inc.
2.7 Weathering Conditions

Accelerated weathering of the PUs was performed in an Atlas Suntest XXL+ flatbed Weatherometer, which conformed to the ASTM G155 standard. The weathering exposure occurred in 2-hour cycles consisting of UV-light irradiation ($0.35 W/m^2$ at $\lambda_{max} \cong$ 340 nm) at 50% relative humidity (RH) for 102 min, followed by 18 min of spraying with deionized water. The chamber temperature was kept at 48 °C and the chamber black panel at 63° C. Samples were exposed for time intervals of 0, 250, 500, 750, 1000, 1500, and 2000 h.

Chapter 3: Project Goals

The lifespan of coating systems is of tremendous importance to the United States military, the U.S. Navy in particular. A well-designed coating can save a tremendous amount of money and time.

The primary goal of this study was to understand the effects that individual components have on the degradation of military coating systems. In this work, three distinct variables of coatings were analyzed: 1) the blending of poly(ether) and poly(ester) macrodiol; 2) the –NCO:-OH mole ratio; and 3) the pigment volume concentration.

Free films varying the above components were synthesized and subjected to accelerated weathering. The data presented in the following section summarily describe the results from the experiments performed to evaluate the effects of manipulating these components.

Chapter 4: Manipulation of Poly(ester) to Poly(ether) Macrodiol Ratio

4.1 Overview

The goal of this portion of the project was to evaluate how the mole ratio of the macrodiol(s) used in this study affected the degradation process of the coatings subjected to accelerated weathering. In general, a poly(ether) macrodiol is added to coating systems to allow more flexibility. The importance of this section is born out of an engineering investigation that stated the poly(ether) macrodiol would uptake moisture, but would not cause any negative reactions. To study this, the mole ratio was varied between 0, 33, 66 or 100% poly(ether) to poly(ester) macrodiol. The coatings were then subjected to 2000 h of accelerated weathering. The following details the findings from this portion of the study.

4.2 Film Preparation

The poly(ester) macrodiol, Polymac® HS 220-2015 (Polynt Company, Chatam, VA, USA), was used as received. The poly(ether) macrodiol, ARCOL® PPG 425 (Covestro, Pittsburg, PA, USA) was dried under vacuum (2 Torr) at 23 °C for 24 h prior to use. The isocyanate crosslinker, Desmodur® N3390 BA/SN (Covestro, Pittsburg, PA, USA), was used as received. The polymers were cured in 2-heptanone (Fisher Scientific, 99%), which was dried on 3 Å molecular sieves for 24 h prior to use. The catalyst, dibutyltin dilaurate (DBTDL, Sigma-Aldrich, 95%) was used as received.

The poly(urethane) films were synthesized with a –NCO:–OH 1.1:1 *mol* ratio to ensure complete reaction of the macrodiol component. Coatings were synthesized with poly(ester) to poly(ether) macrodiol ratios of 1/0, 0.66/0.33, 0.33/0.66 and 0/1. A typical PU synthesis is described below in detail. Desmodur 3390 (27.2 g, 127 *mmol*), Arcol® PPG425 (24.3 g, 116 *mmol*), and 2-heptanone (12 *mL*) were added to a disposable polypropylene beaker and stirred for 30 *min* using an overhead mechanical mixer. Next, DBTDL (0.01 *mol*%) was added to the mixture and stirring was continued by hand until the reaction vessel became warm. Once warm, the solution was cast onto an aluminum pan and allowed to cure for 2 weeks at 23° C.

4.3 PU Characteristics

The cured PU samples made by reaction of diol terminated poly(ether) and/or poly(ester) with a trifunctional isocyanate crosslinker appear as transparent 'rubbery' pucks. Their general characteristics before weathering are listed in Table 1.

Sample	Macrodiol Mole Ratio Poly(ester) / Poly(ether)	$E^*(MPa)^a$	T _{g,/DSC} (°C)	Tan δ
PU1	1/0	73.1	10.1	23.8
PU2	0.66 / 0.33	55.2	8.2	21.7
PU3	0.33 / 0.66	41.3	1.4	21.3
PU4	0 / 1	12.3	-2.2	14.0

Table 4-1: Characteristics of Prepared PUs Before Weathering.

^{*a*}Measurements taken at 23 °C.

The PUs were allowed to cure at room temperature for two weeks. During this time the characteristic isocyanate peak at 2270 cm^{-1} disappeared (Figure 4-1). The spectra in Figure 4-1 indicate the coatings had completely cured after 2 weeks.⁵⁵



Figure 4-1: FT-IR-ATR spectra of the PUs. Virtually complete reaction of isocyanate is indicated by the absence of the –NCO peak around 2270 cm^{-1} . Spectra were collected by averaging of 32 scans with a resolution of 4 cm^{-1} .

The PUs behaved as elastic rubbers at room temperature with Young's moduli (E^*) in the MPa range. All of the PUs tend to soften by approximately a factor of ~10³ upon heating through their glass transition temperature. The thermal analyses by DSC yielded narrow T_g ranges, which seemed to increase with the amount of ester content in the sample. The assignment of T_g can be done in several ways, such as the inflection point in the DSC thermogram, locating the maximum of the loss tangent or the loss modulus, or locating the onset of the storage modulus decrease in mechanical analyses. The mechanical analyses revealed uniform Tan δ curves, which is consistent with networks that have high uniformity and homogeneity (Figure 4-2).



Figure 4-2: Complex modulus and Tan δ curves for PUs before weathering. Data collected from DMA with a heating rate of 3 °C *min*⁻¹.

The TGA plots (Figure 4-3) show that decomposition of the PUs does not occur until ca. 300° C. Further, formulations with poly(ester) incorporated stabilized the coatings in terms of onset of thermal degradation temperature, through 2000 h of weathering. This indicates that the PUs examined here (prior to weathering) are ideal for vibrationally damping coatings where UV-light, moisture, and significant temperature variability may be experienced.



Figure 4-3: Thermogravimetric analysis of PUs at various weathering intervals. The scans were collected at a heating rate of 10 °C min^{-1} .

The prepared PUs were placed in an environmental chamber, Figure 4-4 for the artificial weathering to determine how the ester and ether moieties of the macrodiols influence degradation of the PUs with respect to the surface characteristics and mechanical properties. The ASTM G155 method of artificial weathering was selected because it reproduces environmental conditions that are similar to those experienced by PU coatings when applied to aerospace and automobile vehicles.⁵⁶⁻⁵⁹



Figure 4-4: Representational image of the weatherometer employed (left) and the inside of the weathering chamber (right).

4.4 Surface Characterization

The surfaces of the PU coatings were investigated by laser confocal microscopy for 0 h and 2000 h are shown in Figure 4-5. The PU coatings at 0 h were smooth to the touch and flexible when manipulated by hand. The surfaces of the PUs appeared to have very small, but visible, bubbles as a result of solvent evaporation during the curing process; no

other distinct surface features could be detected. Calculations of the surface roughness for each sample confirmed that the samples were smooth.



Figure 4-5: Confocal Microscopy Images of PUs before $(0 \ h)$ and after $(2000 \ h)$ Weathering. Note that weathering of PU4 ended at 1500 h. (Scale bars = 500 μ m)

After 2000 *h* of weathering, the surface of PU4 had small cracks that were visible to the eye, but the appearance of the other PUs did not change (Figure 4-5). However, confocal microscopy revealed that the surfaces of all of the PUs were markedly different. The surfaces had a 'wave-like' appearance which tended to increase from PU1 to PU4 and, is more apparent when greater ether content is in the PU coating. It is believed that these 'waves' are caused by: (1) the formation of new crosslinks, (2) changes in how molecular fragments are arranged in the network, and (3) de-swelling of the PU after weathering,

which may cause strain on newly crosslinked chain segments that were in more stable conformations when the PU was in a swollen state. In support of this statement, is the observation that the locations of the bubbles in the PUs either disappear or change, indicating that the locations of various molecular fragments or chain segments must be somewhat different after weathering. These considerations are critical for understanding how the PUs change during weathering and have important consequences on the mechanical properties of the weathered PUs.

The percent change in surface roughness for each of the PUs, along with their confocal images, are found in and Figure 4-6 and Table 4-2. Each of the samples show an increase in surface roughness, where the smallest changes were found for the two macrodiol PUs (PU2 and PU3). The PUs containing the single macrodiol, poly(ester) (PU1) or poly(ether) (PU4), showed the largest changes in surface roughness. Note that the two macrodiol PUs had better mechanical stabilities (as evidenced by a smaller change in their Tan δ) after weathering than the single macrodiol ones and this can be partially attributed to the changes in surface roughness. These changes will be discussed in terms of the mechanical stabilities of the PUs after weathering.



Figure 4-6: Confocal microscopy images of the PUs showing their surface roughness before (0 h) and after (2000 h) weathering. Note that weathering of PU4 ended at 1500 h.

Table 4-2: Surface Roughness Obtained from Laser Confocal Microscopy

Sample	$0 h (\mu m)$	$2000 h (\mu m)$	Percent Change
PU1	1.93	3.50	81%
PU2	2.50	3.65	46%
PU3	2.02	2.84	41%
PU4	2.38	21.24	792%

The changes in the surfaces of the PUs was furthered examined by water contact angle analyses. The coatings applied to aerospace and automobile vehicles must be hydrophobic because, if not, changes in humidity will affect their damping performance. Because the macrodiols used here are mostly hydrophobic, changes in the water contact angle can indicate the types of functional groups (*e.g.*, hydrophilic or hydrophobic) that are generated during weathering. Initially, the PU coatings have a high water contact angle (~90°) and

are mostly hydrophobic. During the weathering, the water contact angle for each PU decreased and indicates that the degradation products are more hydrophilic (Figure 4-7). Clearly, the water contact angle of PU1 is much less than PU4, making PU4 a more hydrophobic material. Note that a larger standard deviation was observed in the water contact angle measurements of PU4 and is attributed to the greater surface roughness after weathering than the other PUs. However, the hydrophobicity of PU4 allows the coating to be more resistant to water than PU1 because its ether groups are less susceptible to hydrolysis than the ester groups of PU1. The rapid decrease of the water contact angle for PU1 is attributed to the formation of carboxylic acid degradation products during weathering and is found via FT-IR. These degradation products occur to a lesser degree in PU4 because a different primary degradation pathway is operative.



Figure 4-7: Contact angle of water on the PUs at different weathering intervals.

The contact angle of water on the two macrodiols PUs (PU2 and PU3) follow trends more similar to the PU1 than PU4. Interestingly, at weathering intervals less than1500 h, it appears that the water contact angles of PU2 and PU3 are still higher than PU1. The higher contact angles indicate that the two macrodiol PUs are more stable than PU1 in the presence of water. Although the water contact angles are still highest for PU4, the cracks that formed in its surface and its 'gel-like' feel severely limited its mechanical stability after weathering. Perhaps, these surface changes lead to the larger jumps (less steady decrease) in the values of the water contact angles during weathering. Additionally, it was believed that the cracks formed in the PU4 surface will facilitate water entering in the polymer matrix and increase the rate of degradation over longer periods of weathering than those used here.

4.5 Bulk Properties

DMA in the tensile mode was used to examine how the bulk mechanical properties of the PUs were affected by weathering. The control PUs (T₀) (Figure 6-6) all exhibit a Young's modulus (E^*) that decreases by about 3 orders of magnitude and is similar to the storage modulus (E') during heating. Also, the loss modulus (E'') and viscoelastic loss tangent (tan δ) both display a local maxima (Figure 4-8).



Figure 4-8: Storage modulus, loss modulus, complex modulus, and Tan δ curves for control (T₀) coatings. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹.

The Tan δ is directly indicative of the damping performance of the PUs because it is proportional to the ratio of energy dissipated to the maximum elastic energy within an

oscillatory cycle.⁶⁰ The Tan δ peaks are all above 1, except in the case of PU1, and the breadths of the peaks are all relatively sharp (Figure 4-8). These observations are consistent with the networks of the PUs being highly uniform. Further, the two macrodiol PUs (PU2 and PU3) have the highest Tan δ values. Therefore, the damping properties of the PUs increase when two macrodiol components are used instead of a single one. The difference in peak height with respect to the dual marocdiol formulations are attributed to packing considerations. Because networks consisting of both poly(ether) and poly(ester) macrodiols will be unable to pack as efficiently as their single macrodiol networks.⁶¹

A decrease in packing efficiency also leads to larger free volume within the polymer matrix, which enhances its vibrationally damping ability. This observation is confirmed by measurements of the free volumes of the PU films via water weight gain experiments (Table 4-3). When the PUs were soaked in water, the water uptake was found to be larger for the two-macrodiol PUs (3.99% and 3.53% for PU2 and PU3, respectively) than the single macrodiol ones (3.11% for PUs 1 and 4) and indicates that the two macrodiol PUs have larger free volumes.

Sample	Volume Swell (%)	Water Weight Gain (%)
PU1	3.36	3.11
PU2	4.31	3.99
PU3	3.20	3.53
PU4	3.10	3.11

Table 4-3: Volume Swell and Water Weight Gain for Control Samples.

As can be seen in Figure 4-9, the weathering of the PUs at 2000 h was found to affect the loss tangent peak in several ways: (1) the height of the loss tangent peak decreased; (2) a second peak appeared; (3) the peaks were found to be broader; and (4) the symmetry of the peaks decreased. Clearly, a reduction in the loss tangent peaks indicate that the elastic responses are increased and the samples become stiffer. It could also be expected that the loss tangent peak would lose symmetry as some dynamic heterogeneity is introduced into the system during swelling and degradation. An example of the heterogeneity could be from the changes to the surface of the film that were observed through confocal microscopy, surface roughness, and water contact angle analysis. It is also possible that hydrophobic segments of the polymer aggregate to the center of the film and away from the surface since it has been in contact with water. However, the presence of a new loss tangent peak altogether is quite surprising and is attributed to the formation of new crosslinks during weathering.⁶² Interestingly, the magnitudes of the new loss tangent peaks are very low for a damping material (~ 0.25) and indicate that the mobilities of portions of the networks are stiff. Perhaps, the formation of crosslinks while the PU was in a swollen state caused the networks to stiffen once the PU was allowed to contract to its original state; the new crosslinks that formed during weathering may have been more stable and perhaps more elastic when the polymer was swollen. Note that the new Tan δ peak in PU4 is the least distinct and is a manifestation of its 'gel-like' surface. Due to this attribute not being observed in other PU formulations, it was believed that the absence of the poly(ester) macrodiol led to significant mechanical instabilities when compared to the other PU formulations with distinct Tan δ peaks.



Figure 4-9: Tan δ curves for 0 *h* and 2000 *h*. The data were acquired at an oscillation frequency of 1 *Hz*, 15 µm amplitude, and a heating rate of 3 °C *min*⁻¹

A clearer indication of the damping properties of the PUs after weathering is presented by examining changes in elasticity. The examination was accomplished by plotting the complex and Young's moduli. The complex modulus (Figure 4-10) of PU1 displays a large shift to higher temperatures while the PU4 samples remain tight to the T₀ curve. The shift to higher temperatures displayed in PU1 is indicative of polymer stiffening and was attributed to the degradation of poly(ester) macrodoil due to the absences of this stiffening in the poly(ether) sample. When dual macrodiol samples are examined (PU2 and PU3) the 2000 *h* curves remained tight with the 0 *h* curves below ~37 °C. Above ~ 37 °C the slope of the complex modulus curve changed indicating the samples were stiffer above these temperatures. Further, the deviation from the T₀ curve is much smaller in the PU3 sample. This was attributed to the fact that the PU3 formulation contained the least amount of poly(ester) macrodiol in the formulation.



Figure 4-10: Complex moduli for 0 *h* and 2000 *h*. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹.

The Young's moduli were plotted by examining the linear portion of the stress strain curve. The average of three curves can be found in Figure 4-11. In general, as the films are weathered, the elasticity increased as well as the initial slope. This indicated an increase in Young's modulus.



Figure 4-11: Stress-strain curves of the PUs at various weathering intervals. Stress-strain curves were collected at a strain rate of $1 N \min^{-1}$ until 18 N at 25 °C.

Examining the Young's modulus (Figure 4-12) reveal that the PUs containing more poly(ester) content become stiff during weathering. The increase in stiffness is correlated with larger increases in the T_g values and indicates that the crosslink density has increased.⁶³⁻⁶⁴ The increase in the degree of crosslinks is also evidenced by the rubbery plateau regions via DMA analyses because they increase and become steep after weathering. The changes in the rubbery plateau regions are more pronounced for the PUs with more poly(ester) content than those with more poly(ether) content.

The increase in new crosslinks can be expected to occur to a greater extent for the PUs containing more poly(ester) because the ester groups can more easily undergo hydrolysis than can the PUs containing more poly(ether). The hydrolysis of ester groups yields carboxylic acids, which provide new and rigid, ionic crosslinks. Still the other single macrodiol PU, PU4, containing only the ether macrodiol, became slightly more mechanically stiff up through 1000 h and then weakened to the point of fracture after 1500 h. This indicates that, although shorter and more ridged crosslinks were formed during weathering, the sum of the degradation ultimately weakened the mechanical properties of PU4. Additionally, the surface of PU4 was sticky and 'gel-like' and not smooth as was the case for the other PUs. By assessing a combination of mechanical analysis and surface properties, it was concluded that PU3 contains an ideal ratio of poly(ester) to poly(ether) macrodiol for the enhancement of mechanical stability.



Figure 4-12: Young's moduli of the PUs taken at various weathering intervals. The data were acquired using a ramp rate of $3 N \min^{-1}$ at 25 °C.

4.6 Analysis of Degradation Pathways

Although degradation of PUs (that are linear and not crosslinked) by photooxidation has been studied previously,⁶⁵⁻⁶⁷ the influence of water on their degradation is relatively unexplored. FT-IR has been previously employed to monitor functional group changes from photooxidation.^{63, 66-69} The absorption of UV-light by PUs is known to generate radicals, which tend to form at the urethane linkages, or other functional groups and subsequently react with the polymer backbone. By monitoring specific regions of the FT-IR spectrum, the degradation products can be monitoring by following the loss (or gain) in intensity of those functional groups. The FT-IR spectra for each formulation are plotted, along with their difference spectra. The difference spectra was calculated by taking the difference between the IR intensities at 0 h and 2000 h (or 1500 h for PU4). The several bands in the IR difference spectrum show either positive or negative intensities. The negative absorbances reflect functional groups that were formed during irradiation, while positive absorbances mark groups that were lost. The following paragraphs discuss the spectral changes for single macrodiol PUs because changes in their IR intensities are more easily separated when compared to dual macrodiol formulations. However, the two macrodiol PUs will be discussed in terms of their degradation pathways.

The weathering of PU1 (Figure 4-13) resulted in changes to several peaks in the spectra. Most notable are the peaks in the region at $3700 - 3125 \text{ cm}^{-1}$ (-NH/-OH stretches), 2950 - 2850 cm⁻¹ (CH₂ stretching), 1760 – 1650 cm⁻¹ (carbonyl stretching), 1538 and 1273 cm⁻¹ (-N-H stretching), and 1125 cm⁻¹ (C-O stretching). The increase in peak intensity at 3700 - 3125 cm⁻¹, especially with the presence of two maxima, indicate that new primary amide and carboxylic acid functionalities are being formed; this observation is attributed to cleavage of both the ester and urethane linkages. The decrease in stretching at 2950 - 2850 cm⁻¹ is consistent with CH₂ oxidation, specifically at the carbon atoms adjacent to the nitrogen of the urethane linkages.⁶⁶⁻⁶⁷ The region of carbonyl stretching is quite complex because of several changes in the intensities and make their attributions somewhat difficult. However, the largest increase in intensity at 1746 cm⁻¹ can be ascribed to the formation of

carboxylic acids via ester hydrolysis. Additionally, the amide II (1529 cm^{-1}) and amide III (1277 cm^{-1}) peaks decrease in intensity because of urethane cleavage. The decrease in the peak intensity at 1125 cm^{-1} is indicative of the C-O of the ester undergoing hydrolysis.



Figure 4-13: FT-IR spectra at various time intervals and difference spectra of PU1 during weathering. The difference spectra were taken as the difference between the IR intensities at 0 h and 2000 h.

The weathering of PU4 (Figure 4-14) led to slightly simpler changes in the regions from 3700 - 3125 cm^{-1} (-NH/-OH stretches), 2970 - 2825 cm^{-1} (CH₂ stretching), 1780 -

 cm^{-1} (carbonyl stretching), 1480 cm^{-1} (-N-H stretching), and 1125 cm^{-1} (C-O stretching). Again, the increase in peak intensity in the region at 3700 - 3125 cm^{-1} is because of new amide and carboxylic acid functionalities. Additionally, the CH₂ region of PU4 is similar to PU1, except for a noticeable spike in the difference spectrum at (2980 cm^{-1}), which suggests that some CH₂ groups adjacent to the oxygen in the ester moieties have crosslinked in the polymer matrix.^{63, 66} Although the intensity of the peak at 2980 cm^{-1} is rather small, it is absent in PU1, and begins to increase in intensity as more ether groups are introduced into the PU; it becomes visible in PU2, increases in PU3, and reaches a maximum in PU4. The region of the carbonyl stretching is much simpler and is the most probable degradation route that leads to the formation of carboxylic acids and amides, and oxidation of the some of the ether moieties to esters. The decrease in intensity at 1110 cm^{-1} , coupled with an increase in peak intensity at 1205 cm^{-1} , is indicative of the oxidation of aliphatic ether linkage to formate groups.⁶⁶



Figure 4-14: FT-IR spectra at various time intervals and difference spectra of PU4 during weathering. The difference spectra were taken as the difference between the IR intensities at 0 h and 2000 h.

Therefore, several different pathways of PU degradation are possible.^{63, 66-67} FT-IR spectra indicate that degradation pathways that lead to hydrolysis are the important pathways due to the presence of water and its reactions with the PU. Again, note that the studies to date on PU degradation do not include the presence of water. Some of the important degradation pathways, especially those that include the presence of water shown in Scheme 4-1, are addressed in the following discussion.



Scheme 4-1: Important Degradation Pathways and their Simplified Mechanisms.

Both PU1 and PU4 experience degradation of the urethane linkage as shown by pathway **1U**. The **1U** pathway proceeds through the oxidation of the carbon atom adjacent

to the -NH functionality of the urethane linkage: a hydrogen atom on the carbon atom adjacent to the nitrogen is extracted and yields a radical which can eventually lead to carboxylic acid and amide products after hydrolysis. Additionally, the FT-IR spectra of PU1 suggest that significant hydrolysis of the ester groups (**1Es**) occurs in PU1 because of the broadening of the peak at 1746 cm^{-1} . The hydrolysis of the ester groups lead to carboxylic acid and hydroxyl products, which form ionic, rigid crosslinks. It has also been shown by Gardette and co-workers that new crosslinks can occur in linear, non-crosslinked, ester containing PUs⁶⁷ by photooxidation (and in the absence of water) in **2Es**; however, the large increase in hydrophilicity of the surface of PU1, given by the large decrease in the water contact angle during weathering (Figure 4-7) indicates that **1Es** is instead the dominant pathway during weathering in the presence of water. Recall that the T_g values and the Young's moduli increase the most for the PUs containing more poly(ester) content because of the increase in stiffness from these rigid, ionic crosslinks.

The important degradation pathways of PU4 via weathering are shown in Scheme 4-1. The degradation of the ether functional groups in PU4 initiates from the formation of hydroperoxides at the carbon adjacent to the oxygen atom of the ether group. In the presence of UV-light alone (without water), Gardette and co-workers found that the predominate degradation pathway of linear, non-crosslinked, ether containing PUs⁶⁶ is oxidation of the ether groups to esters and the subsequent formation of formates (**E1**).⁶⁶⁻⁶⁷ However, the presence of water during weathering and the shape of the C=O stretch in the difference spectra of Figure 4-14 suggests that **2E** and **3E** are the dominant degradation pathways instead. The hydroperoxide groups oxidize to esters, while a smaller population of the hydroperoxides react with the water to form carboxylic acids and alcohols. The carboxylic acid functional groups also have the ability to form new crosslinks and can increase the stiffness of the PU. Because the elastic modulus does not significantly change in the PU4 samples, it supports the observation that the majority of the ether groups will oxidize to esters within 1500 h of weathering.

When dual marocdiol formulations were examined with FT-IR, similar stretching frequencies were effected when compared to single marodiol formulations. Due to the similarities it is logical to conclude that the dual macrodiol formulations undergo a combination of degradation pathways described in Scheme 4-1.



Figure 4-15: FT-IR spectra at various time intervals and difference spectra of PU2 and PU3 during weathering. The difference spectra was taken as the difference between the IR intensities at 0 h and 2000 h

The proposed degradation pathways in Scheme 4-1 support the results from the FT-IR analyses and water contact angle measurements; the FT-IR signals that are indicative of the formation of acids, esters or amide groups increased in intensity and these moieties have greater hydrophilicity than their non-degraded counterparts as evidenced by the changes in the water contact angles. The enhancement in the mechanical stabilities of the two macrodiol PUs was attributed to competition among the different degradation pathways. Clearly, multiple important degradation pathways operate during degradation of the two macrodiol PUs because of the presence of both of the poly(ether) or poly(ester) components. However, for degradation of the macrodiols to occur, photons of UV-light and molecules of water must be present. These 'degradation reagents' are distributed in an equilibrium among the different degradation pathways of the macrodiols. This equilibrium limits the degree to which a single pathway may occur. A single degradation pathway will lead to rapid degradation and, in turn, mechanical instabilities. However, the presence of macrodiols with various functional groups introduces several different pathways and reduces the extent to which a single pathway will reach 'completion' and lead to significant mechanical instabilities.

Importantly, the UV-Vis absorbance spectra of the components used to synthesize the PUs are shown in Figure 4-16. A 'model urethane', methyl carbamate, was included to represent a urethane linkage because Desmodur was in its isocyanate form. The urethane, Desmodur, and ester absorb UV-light at wavelengths longer than 210 *nm* and their absorbances partially overlap. The high concentration of ester moieties will absorb more of the UV-light emitted on the PU and provide a 'sunscreen-like' effect to protect the

urethane linkages and Desmodur. Although the ester groups undergo hydrolysis and impart some degree of brittleness into the PUs, their utility is substantiated by their ability to protect the urethane linkages; this is especially important because the crosslinks occur at these urethane linkages and are also nearby to the Desmodur component.



Figure 4-16: UV-Vis Absorbance spectra of the components of the PUs and methyl carbamate (10 wt%) in acetonitrile.

4.7 Conclusions

Heavily crosslinked PUs consisting of ester and/or ether macrodiols were prepared and subjected to accelerating weathering (*i.e.*, introduction of UV-light and water). Their mechanical stabilities and surface morphologies were characterized over the course of 2000 hours of weathering using optical microscopy, thermal analysis, mechanical methods, and FT-IR analysis. The single macrodiol PUs, which were comprised of either poly(ester) or poly(ether), were mechanically more unstable than the two macrodiol PUs. A combination of the two macrodiol PUs led to a 'synergistic effect' where their damping abilities given by Tan δ increases and their mechanical stabilities after weathering increased. The increase in the damping abilities of the blended PUs is attributed to a decrease in the packing efficiency of the macrodiol chains by combining the two different functional groups. Further, the increase in the mechanical stabilities after weathering were found to be a function of the competing degradation processes and 'protection' of the urethane group by the ester.

Degradation analyses of the PUs had shown that the surfaces become much more hydrophilic, which resulted in new functional groups such as carboxylic acids, amides, amines, and hydroxyls and could be attributed to the presence of water. The single macrodiol PU1, comprised of poly(ester), indicated that significant degradation of the ester groups occurred and resulted in carboxylic acid and hydroxyl group containing products. The formation of carboxylic acids created new rigid, ionic crosslinks and led to large increases in the Young's moduli and T_g values. The PU4, containing the poly(ether) macrodiol, indicated that the ether groups could either crosslink or oxidize into ester functional groups. Further, the two macrodiol PUs demonstrated an increase in their mechanical stabilities during weathering. This increase is attributed to: (1) the occurrence of multiple degradation pathways that remain in an overall equilibrium with the total degradation, limiting the degree to which a single degradation pathway ages a PU to where the mechanical differences are apparent and (2) the overlap in the UV-Vis absorbance between the ester and urethane moieties; the overlap and high concentration of ester groups may protect the urethane linkages by absorbing the majority of UV-light.

Overall, the examples presented here show that the damping abilities and mechanical stabilities of vibrationally damping PUs, especially those used in coating systems, can be enhanced by combining macrodiols that contain different functional groups. The results also provide a clear 'blueprint' for developing weather resistant, vibrationally damping PU's with improved mechanical stability.

Chapter 5: Effects of Manipulating the Isocyanate to Hydroxyl Mole Ratio

5.1 Overview

Varying the mole ratio of isocyanate to hydroxyl units has the potential to increaes the crosslink density of a thermoset PU. When the the mole ratio (or indexed level) is increased, the excess isocyanate functional groups react to afford urea linkages (Figure 5-1).



Figure 5-1: Mechanism for urea formation from the reaction of isocyanate with atmospheric moisture of an isocyanate and alcohol functional group.

These urea likages could undergo degradation through either photooxidative or hydrolysis processes. Therefore, it was important to determin the effect of manipulation of isocyanate to hydroxyl mole ratio and subject these coating to accelerated weathering. To determine the effect these linkages had on the coating system, four polyurethne coating formulations were prepared. In each formulation, the isocyanate to hydroxyl mole ratio was given a different value. The values of the mole ratios were as followed; 1.1, 1.3, 1.5 and 2 isocyanate groups to 1 hydroxyl group. Once cured, the coatings were placed under accelerated weathering conditions. Post weathering, the coatings were analyzed and the results are detailed below.

5.2 Film Preparation

The poly(ether) macrodiol used was ARCOL® PPG 425 (Covestro, Pittsburg, PA, USA) and was dried under vacuum (2 Torr) at 23 °C for 24 h prior to use. The isocyanate crosslinker, Desmodur® N3390 BA/SN (Covestro, Pittsburg, PA, USA) was used as received. The polymers were cured in 2-heptanone (Fisher Scientific, 99%) which was dried on 3 Å molecular sieves for 24 h prior to use. The catalyst, dibutyltin dilaurate (DBTDL, Sigma-Aldrich, 95%) was used as received. Methyl carbamate (Aldrich, 98%) and acetonitrile (Sigma, 99%) were used as received.

The poly(urethane) films were synthesized with a –NCO:–OH index ratio of 1.1:1, 1.3:1, 1.5:1, and 2:1. A typical PU synthesis is described below in detail. Desmodur 3390 (27.2 g, 127 mmol), Arcol® PPG-425 (24.3 g, 116 mmol) and 2-heptanone (3 mL) were added to a disposable polypropylene beaker and stirred for 30 min using an overhead mechanical mixer. Next, DBTDL (0.1 mol %) was added to the mixture and stirring was continued by hand until the reaction vessel became warm. Once warm, the solution was cast onto an aluminum sheet and allowed to cure for 2 weeks at 23 °C under ambient conditions.
5.3 PU Characteristics

The PUs were synthesized by reacting a tri-isocyanate with a hydroxyl terminated macrodiol. Verification of complete polymerization was ensured by observing the dissaperance of the characteristic isocyanate peak near 2270 cm^{-1} (Figure 5-2).⁷⁰⁻⁷¹



Figure 5-2: Stacked FT-IR ATR spectra of prepared PUs indicating complete reaction by the absence of the -NCO stretching frequency at 2270 cm^{-1}

Frequently, paint formulators will add excess isocyanate into polyurethane coatings to ensure complete reaction of the employed macrodiol. This is called overindexing and the overindex ratio refers to the ratio of -OH: -NCO functional groups. The PUs mechanical and thermal properties varied as the index ratio was increased. Some general thermal and mechanical properties of the prepared PUs are listed in Table 5-1. In general, the complex modulus, and T_g all increase with isocyanate mole ratio. Also, the Tan δ peak height decreases with increased isocyanate content, which is indicutive of polymer stiffening. These trends aggree with a PU system that is increaseing in crosslink density.⁷²⁻ 74

	$E^*(MPa)^a$	Tg (°C) ^{b}	Tg (°C) ^c	Tan δ peak height
PU1.1	8.1	5.2	2.2	0.96
PU1.3	10.9	8.9	2.3	0.69
PU1.5	12.5	5.2	6.0	0.54
PU2	19.1	6.8	8.0	0.54

Table 5-1: Characteristics of Prepared PUs Before Weathering.

^{*a*}value taken at 25 °C

^bmeasurement taken using loss tangent peak through DMA ^{*c*}measurement taken using the inflection point from DSC

From the Table 5-1, it is observed that as the isocyanate to hydroxyl mole ratio is increased, the elastic modulus and glass transition temperature increased. This trend can be attributed to the increase in crosslink density.⁷⁵⁻⁷⁷ Additionally, as the crosslink density increased a decrease in the Tan δ is observed due to the samples increaseing in elasticity. This increase in elasticity is also attributed to the increase in crosslink density.

The increase in index ratio caused a corresponding increase in crosslink density by reaction of the -N=C=O groups with atmospheric water to create amine groups which further reacted with isocyanate groups to afford urea linkages. To illustrate this, the difference spectra of PU1, a stoichiometric ratio of isocyanate to hydroxyl group, was subtracted out of each formulation in Figure 5-3. There are several stretching frequencies that change as the index ratio is increased. An increase at 1695 cm^{-1} is due to the increase in isocyanate causing imide carbonyl peak to gain in intensity. A shoulder near 1640 cm^{-1} develops due to the formation of urea linkages.⁷⁸⁻⁷⁹ Further, the FT-IR streatch at 1538 cm^{-1} shifts to higher wavenumbers due to additional -N-H stretching from the presence of urea linkages.



Figure 5-3: Carbonyl and fingerprint regions of the prepared PUs and their difference spectra. Difference spectra was obtained by subtracting PU1 from each of the remaining PUs.

At room temperature, the indexed PUs behaved as rubbery pucks, with Complex Modulus (E^*) in the *MPa* range, which increased as the isocyanate to hydroxyl ratio increased. The Tan δ became broader with increased index ratio, indicating crosslinking became heterogeneous with increased isocyanate amount. This outcome was expected due to the increase in urea linkages (Figure 5-4).



Figure 5-4: Storage modulus, loss modulus, complex modulus, and Tan δ curves for control (T₀) coatings. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹

TGA analysis yielded onset degradation temperatures of above 300 °C for control (T₀) coatings, indicating the prepared PUs were thermally stable (Figure 5-5). From the thermograms in can be observed that the onset in degradation occurs near 310 °C for all formulations.



Figure 5-5: Thermographic analysis of PUs at various weathering intervals. The scans were collected at a heating rate of 10 °C min^{-1}

The indexed PUs were placed in an environmental chamber for artificial weathering (*i.e.*, introduction of UV-light and then water in timed cycles) to determine how the urea linkages influence degradation of the PUs with respect to the surface characteristics and

mechanical properties. The ASTM G155 method of artificial weathering was selected because it reproduces environmental conditions that are similar to those experienced by PU coatings when applied to aerospace and automobile vehicles.⁵⁶⁻⁵⁹



Figure 5-6: Representational image of the weatherometer employed (left) and the inside of the weathering chamber (right).

5.4 Surface Characterization

The surfaces of the PU coatings were investigated with laser confocal microscopy and the 0 h and 1500 h images are shown in Figure 5-7. The PUs at 0 h were smooth to the touch and flexible when manipulated by hand. The appearance of small bubbles at the surface were attributed to solvent evaporation during the cure process. No other distinct surface features were visible.



Figure 5-7: Confocal Microscopy Images of PUs before $(0 \ h)$ and after $(1500 \ h)$ Weathering. (Scale bars = $500 \ \mu m$).

After 1500 *h* of accelerated weathering, the surface of PU1.1 had several small blisters and cracking were visible at the surface. The blistering of the coating was not observed in higher indexed coatings, however surface cracking was more extensive. While these cracks may be due to sample manipulation, it is apparent that changes to the surface chemistry (from contact angle analysis) contributed to the mechanical integrity (DMA analysis) of the surface. These surface features are attributed to changes in molecular fragments rearranging in the network and de-swelling of the PU after weathering. Further, de-swelling of the polyurethane network could cause strain on the rearranged molecular fragments in addition to any new crosslinks that may have formed during accelerated weathering.

The surfaces of weathered PUs were further examined using water contact angle analysis. In general, coatings that are exposed to outdoor environments would, under ideal circumstances, remain hydrophobic so that they remain environmentally robust. Changes in water contact angle can provide insight into the types of functional groups (hydrophilic or hydrophobic) that are formed post-weathering. Initially the indexed PUs are relativly hydrophobic, with high water contact angles (~85°) (Figure 5-8). Clearly PU1.1 remains the most hydrophobic post weathering. When the isocyanate content was increased the coatings became more hydrophilic after 2000 h of weathering. This may be due to the degradation of the extra urea groups that are incorporated into the coatings from increasing the mole ratio of isocyate to hydroxyl groups. This would cause more primary amines during degradation generating more hypophilic functional groups.



Figure 5-8: Water-contact angle for weathered PUs at different time intervals.

5.5 Bulk Mechanical Properties

Dynamic mechanical analysis, in multifrequency strain mode, was used to analyze the viscoelastic properties of a polymer while holding the oscillation amplitude constant. The selection of this mode was used to examine how the bulk mechanical properties of the PUs were affected by accelerated weathering. The Complex modulus of control (T₀) exhibit sharp transitions and decrease three orders of magnitude, which was similar to the storage modulus (E') during heating. The maxima of the Tan δ decreases with higher index ratios, indicating that the elasticity of the PUs increased as the isocyanate content increased. These observations are indicative of a polyurethane network that increases in crosslink density as the index ratio increased.

The weathering of the PUs through 1500 *h* influence the loss tangent peak in several different ways (Figure 5-9). Interestingly, it appears that the PUs underwent additional curing, judging by the changes in the Tan δ peak. Clearly from Figure 5-2, the isocyanate peak is not present in any of the control, 0 *h*, spectra. However, FT-IR-ATR can only penetrate the sample approximately 2 μ m, making this technique ineffective for examining the bulk of the material. While DMA is not a spectroscopic technique, it does allow us to understand what is occurring to bulk properties of the PUs. From 0 *h* to 250 *h* of weathering the Tan δ peak increases in intensity and becomes sharper like the Tan δ curve of PU1.1 at 0 *h*. The sharpness of the peak is indicative of a polymer network that is more homogenous, indicating that polymer crosslinks are more uniform. Further, the fact that the maxima of the Tan δ peak gains in intensity indicates an increase in sample elasticity. The additional curing may have been facilitated due to the increase in temperature as well as polymer

swelling during accelerated weathering. However, after 1500 h of weathering, several additional changes were observed in the indexed PUs Tan δ peak: (1) the maxima of the Tan δ peak became smaller; (2) the peaks became broader; (3) a shoulder developed at higher temperatures. Clearly, the decrease in the Tan δ peak maxima can be attributed to sample stiffening. Interestingly, despite samples becoming stiffer, there is no large shift of peak maxima to higher temperatures in any of the index formulations. It appears that the increase in stiffness is due to an increase in crosslink density from shorter ionic bonds that are formed during acclerated weathering.^{62, 80} Polymer swelling also allowed the entry of water into the polymer matrix, facilitating the potential for hydrolysis. The formation of ionic bonds within the polymer matrix also account for the formation of the shoulder at higher temperatures. While it appears that the Tan δ curve is broadest in the PU1.1 sample, it is believed that the sample lost mechanical integrity near 50 °C. This conclusion was attributed to the sharp changes in slope above 50 °C. In the remaining formulations, the shoulder was broadest in the PU2 sample. This was attributed to the PU2 formulation having the greatest amount of isocyanate incorported in the formulation, subsequently having the greatest crosslink density.

The complex modulus (E^*), Figure 5-10, of the indexed sample also indicates sample stiffening. In PU1.1, there is a slight divergence of the 1500 h curve from the 0 hcurve. However, when the index value is increased, there is a shift in complex modulus to higher temperatures in all samples indicating an increase in crosslink density due to weathering.



Figure 5-9: Curves of Tan δ of the PUs. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹



Figure 5-10: Curves of complex moduli of the PUs. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹.

Plotting the Complex modulus at 25 °C over time displayed changes to the elasticity of the formulations due to weathering (Figure 5-11). Clearly, the largest change is observed in PU2 after 1500 *h* of artifical weathering due to the amount of isocyanate in the coating formulation. Predictably, the complex modulus decreased with the isocyanate mole ratio. However, it is interesting that PU1.3 (142 *MPa*) and PU1.5 (165 *MPa*) at 1500 *h* of weathering have complex modulus values that are similar at 25° C. Monitoring the complex modulus with time displays a gradual increase in index values of PU1.1 through 1.5 when compared to PU2. In addition to the presence of new ionic bonds created during the weathering process, the PU2 samples also benefit from an increase in hydrogen bonding due to the increased amount of urea functional groups. The extent to which increased hydrogen bonding affected the complex modulus scaled with the index value, which was expected.



Figure 5-11: Values of complex modulus at 25 °C for PUs at various time points. Data was acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹.

5.6 Analysis of Degradation Pathways

The accelerated weathering of PUs (that are linear and not over-indexed) by photooxidation has been studied previously.⁶⁵⁻⁶⁷ The absorption of UV-light by PUs is known to generate radicals, which tend to form at the urethane linkages, or other functional groups, and subsequently react with the polymer backbone. FT-IR is a powerful technique that can depict changes to chemical functional groups from degradation of PU coatings.

This was accomplised by observing the loss (or gain) of specific functional groups. In Figure: 5-12, the FT-IR spectra are shown for the indexed PUs, along with their difference spectrum. The difference spectrum was calculated by taking the difference between the IR intensities at 0 h and 1000 h and displays several functional groups have changed by showing a negative absorbance (growth) or a positive absorbance (loss).



Figure: 5-12: FT-IR spectra at various time intervals and difference spectra of indexed PUs during weathering. The difference spectra were taken as the difference between the IR intensities at 0 h and 1000 h.

The weathering of poly(ether) based PUs led to several changes to functional groups, namely, the region at 3700 - 3125 cm^{-1} (-NH/-OH stretches), 2970 - 2825 cm^{-1} (CH₂ stretching), 1780- 1630 cm^{-1} (carbonyl stretching), 1480 cm^{-1} (-C-H stretching), and 1125 cm^{-1} (C-O stretching). The increase in peak intensity in the region of 3700 - 3125 cm^{-1} is because of new amide and carboxylic acid functionalities. The decrease in intensity at at 2950 - 2850 cm^{-1} is consistent with CH₂ oxidation, specifically at the carbon atoms adjacent to the nitrogen of the urethane linkages.⁶⁶⁻⁶⁷ The region of the carbonyl stretching is much simpler in the PU1.1 sample ,but quickly becomes more complex as the index ratio is increased to PU2. However, the most probable degradation routes lead to the formation of carboxylic acids and amides, there are also some ether moieties that oxidize to esters. The peak in the difference spectra at 1480 cm^{-1} is the gain of amine and amide groups from urethane degradation. The decrease in intensity at 1110 cm^{-1} coupled with an increase in intensity at 1205 cm^{-1} is indicative of the oxidation of aliphatic ether linkage to formate groups.

From changes in the FT-IR spectra, there are several different functional groups that can degrade under accelerated weathering conditions. Possible degradation pathways are outlined in Scheme 5-1. Previous studies on photooxidation have been performed on linear poly(ether) based polymers. However, the degradation of thermoset poly(ether) with varying isocyanate to hydroxyl ratios is relatively unexplored. Herein a thermoset poly(ether) based system that was not only exposed to artificial sunlight but also a water spray cycle to simulate rain and humidity is discussed. From the spectra of the various samples it is clear that the urethane linkage is degraded during the weathering process and is schematically shown in pathway **1U**. Degradation begins through the oxidation of the carbon atom adjacent to the -NH functionality of the urethane linkage: a hydrogen atom on the carbon atom adjacent to the nitrogen is extracted and yields a radical which can eventually lead to carboxylic acid and amide products after hydrolysis.

The ether group is particularly affected from the effects of photooxidation and in the presence of UV light alone. Gardette and co-workers found that the predominant degradation pathway of linear, non-crosslinked, ether-containing PUs is oxidation of the ether groups to esters and the subsequent formation of formates (**E1**).⁶⁶⁻⁶⁷ However, the presence of water during weathering and the shape of the carbonyl region in the difference spectra suggest that **2E** and **3E** are the dominant pathways. Causing the hydroperoxide groups oxidize to esters while a small population react with water to form carboxylic acids and alcohols.

The effects that accelerated weathering had on the urea linkage are less certain. Firstly, a literature search provided no background information to the effects of photooxidation of polyurea polymers. Due to the similarities of the urethane linkage, it would seem logical that the carbon atom in the position α to the –NH functionality is oxidized, initiating a similar degradation process to U1. Following the scheme in U1, the products of the oxidation undergo hydrolysis, thereby generating a carboxylic acid and primary amide. However, it was believed that because urea is easily dissolved, polyurea would be easily susceptible to hydrolysis. The work of Ying *et al.*⁸¹ highlights that the urea bond is actually an extremely stable chemical bonds against further reactions. This includes hydrolysis and is attributed to the conjugation effect of its duel amide structure.

Because there is little change in the difference spectra near the typical FT-IR stretching frequency of 1630 cm^{-1} it was postulated that the presence of excess urea linkages does not significantly impact the degradation of the PU coatings.

Scheme 5-1: Important Degradation Pathways and their Simplified Mechanisms.



5.7 Conclusions

Poly(ether-urethane)s with varying isocyanate to hydroxyl ratios (overindex) values were prepared and subjected to accelerating weathering (i.e., introduction of UV-light and water). Their mechanical stabilities and surface morphologies were characterized over the course of 2000 h of weathering using optical microscopy, thermal analysis, mechanical methods, and FT-IR analysis. The addition of excess isocyanate and the resulting urea linkages were found to not cause adverse effects to PUs. The mechanical properties of the PUs increased due to the increase in crosslink density. Upon weathering it was found that more heavily crosslinked PUs were stiffer than lower indexed PUs.

The degradation analysis of the PUs have shown that the surfaces become more hydrophobic due to new functional groups such as carboxylic acids, amides, amines, and hydroxyls. The formation of these functional groups was attributed to the presence of water from the accelerated weathering protocol. These functional groups are able to form new ionic crosslinks which contributed to sample stiffening which was displayed in the increase in complex modulus as well as the loss in magnitude in the loss tangent curve. Further analyzing the degraded samples via FT-IR indicated that the urethane and ether functional groups were severely affected, while the urea linkage did not clearly show adverse effects.

Overall, the this work demonstrates that the use of overindexing did not adversely affect the weathering of PUs. Further, this work reinforces the ability to increase the mechanical properties of a PU by increasing the isocyanate to hydroxyl ratio.

Chapter 6: Manipulation of Pigment Volume Concentration

6.1 Overview

In this chapter, the effects on the pigment volume concentration (PVC) due to weathering are presented. It is known that, as the PVC increases above the critical pigment volume concentration (CPVC), negative interactions between polymer and pigment arise. Other researchers have studied the effects of weathering on pigmented films. However, there is a gap in knowledge on the effects of increasing the PVC and how increased PVC affects coating properties after weathering. In this study, polyurethane films that incorporated 10%, 20% or 30% v/v were synthesized and subjected to accelerated weathering. The weathered films were then analyzed with a variety of analytical techniques, which are detailed below.

6.2 Film Preparation

The poly(ester) macrodiol was Polymac® HS 220-2015 (Polynt Company, Chatam, VA, USA) was used as received. The poly(ether) macrodiol was ARCOL® PPG 425 (Covestro, Pittsburg, PA, USA) and was dried under vacuum (2 Torr) at 23 °C for 24 hours prior to use. The isocyanate crosslinker was Desmodur® N3390 BA/SN (Covestro, Pittsburg, PA, USA) and was used as received. The polymers were cured in 2-heptanone (Fisher Scientific, 99%), which was dried on 3 Å molecular sieves for 24 *h* prior to use. The catalyst, dibutyltin dilaurate (DBTDL, Sigma-Aldrich, 95%) was used as received.

Carbonyl iron pentachloride (CIP) was obtained from Osprey Metals, LTD (Neath, UK) and used as received.

Films were synthesized using the functional weights of the respective reactive groups. A –NCO: –OH ratio of 1.1:1 was used to ensure complete reaction of polyol. Generally commercial coatings are also indexed at this isocyanate to hydroxyl ratio. Coatings with polyol ratios of 0, 33, 66 and 100% ester to ether ratios were synthesized. Coatings were synthesized with poly(ester) to poly(ether) macrodiol ratios of 1/0, 0.66/0.33, 0.33/0.66 and 0/1. Coatings were pigmented at 10, 20, and 30% v/v without taking solvent volume into account. A typical PU synthesis is described as follows: 127.1 *mmol* (27.199 *g*) of Desmodur N3390, 111.5 *mmol* (24.264 *g*) of PC270, 12 *mL* of 2-heptanone, and iron pigment, were added to a disposable polypropylene beaker and stirred for 30 *min* with an overhead mechanical mixer. Upon which, 0.1 *mol*% of DBTDL was then added and the mixture was stirred gently, by hand, until the reaction vessel was warm to touch. The warm pre-polymer was then cast into aluminum weigh boats and allowed to cure for 2 weeks at 23 °C.

6.3 PU Characteristics

The cured PU samples were made by reaction of diol terminated poly(ether) and/or poly(ester) with a trifunctional isocyanate crosslinker. The PUs were allowed to cure at room temperature for two weeks. The disappearance of the characteristic isocyanate (-N=C=O) IR absorbance at approximately 2270 cm^{-1} ensured coatings were fully cured (Figure 6-1).⁸²



Figure 6-1: FT-IR spectra of the PUs Indicating complete reaction of isocyanate through the absence of the -NCO peak around 2270 cm^{-1}

General characteristics for the control (T₀) PUs before weathering are listed in Table 6-1. The PUs behave as elastic rubbers at room temperature with Young's moduli in the *MPa* range. Thermal mechanical analyses of the control samples displayed an increase in the complex moduli with respect to PVC and poly(ester) content. Additionally, the loss tangent peak decreased with increased poly(ester) content, indicating that the poly(ether) component led to increased elasticity in those samples. Furthermore, the T_g generally increased with more poly(ester) content or greater loading of pigment. When the PVC is increased there is a subsequent increase in the complex modulus, indicating the samples became stiffer with more pigment incorporated. The T_g of the samples was impacted more on the macrodiol(s) that are incorporated. For example, the T_g is highest in single macrodiol poly(ester) formulations, this is most likely due to the rigid bonds associated with the ester linkage of the macrodiol.

Sample	Macrodiol Ratio Poly(ester)/ Poly(ether)	%vol pigment (PVC)	E* (MPa)	$T_g (^{\circ}C)^a$	$T_g (^{\circ}C)^{b}$	Tan δ peak height
PU1-10	1 / 0	10	80.3	17.9	29.1	0.67
PU1-20	1 / 0	20	289.7	15.8	33.5	0.95
PU1-30	1 / 0	30	332.9	15.9	30.9	0.90
PU2-10	0.66 / 0.33	10	16.4	7.4	18.9	0.99
PU2-20	0.66 / 0.33	20	44.1	6.5	34.4	1.11
PU2-30	0.66 / 0.33	30	50.5	2.7	20.3	1.08
PU3-10	0.33 / 0.66	10	7.0	-6.4	10.2	1.13
PU3-20	0.33 / 0.66	20	10.2	-4.1	11.4	1.24
PU3-30	0.33 / 0.66	30	20.1	-1.3	12.1	1.20
PU4-10	0 / 1	10	7.7	-8.4	6.8	1.25
PU4-20	0 / 1	20	9.1	-8.7	5.9	1.26
PU4-30	0 / 1	30	16.1	-5.9	7.8	1.20

Table 6-1: Characteristics of Prepared PUs Before Weathering.

^aT_g measured with DSC. ^bT_g measured with loss tangent peak through DMA.

Thermogravimetric analysis was performed on the prepared PUs (Figure 6-2). From the plots, it can be seen that the PUs are thermally stable to 300 °C, at which point the onset in degradation begins. In addition, the remaining mass scaled with the PVC content incorporated into the coating formulation. As expected, the coatings that contained 30% PVC yielded the highest remaining % mass.



Figure 6-2: Thermographic analysis of PUs at various weathering intervals. The scans were collected at a heating rate of 10 °C min^{-1} .

The prepared PUs were placed in an environmental chamber (Figure 6-3), for the artificial weathering to determine how the PVC influenced degradation of the PUs with respect to the surface characteristics and mechanical properties. The ASTM G155 method of artificial weathering was selected because it reproduces environmental conditions that are similar to those experienced by PU coatings when applied to aerospace and automobile vehicles.⁵⁶⁻⁵⁹



Figure 6-3: Representational image of the weatherometer employed (left) and the inside of the weathering chamber (right)

6.4 Surface Characterization

The surfaces of the PU coatings were investigated by laser confocal microscopy at each time interval and are shown in Figure 6-4. As described in Section 2.1, LSCM utilized a 405 *nm* laser source utilizing 20x optics. Images were processed using the LEXT software package to stitch together 16 magnified images. Images were collected every .06 μm along the Z-axis to create a 3 dimensional image. The PU coatings at 0 *h* were smooth to the touch and flexible when manipulated by hand. While the samples were easy to manipulate, film stiffness noticeably increased with the content of PVC. The surfaces of the PUs appeared to have very small, but visible, air bubbles as a result of solvent evaporation during the curing process; no other distinct surface features could be detected.

After 2000 h of accelerated laboratory weathering, various changes occurred to the surface of the pigmented films. In general, the appearance of pigment at the surface of the

films was more evident via confocal microscopy (Figure 6-4). From the images, as the PVC increased, more pigment was observed at the coating surface after weathering. Attempts were made to confirm the presence of pigment utilizing SEM-EDS but were unsuccessful. This was likely due to sample thickness and charging from the SEM microscope. The presence of pigment at the surface is likely due to polymer erosion that occurred during weathering⁸³⁻⁸⁵; the most obvious case of this appearance is in the PU4 series of coatings. In the 10 vol% PVC coating, the surface lost all smooth features and the morphology appears to have changed vastly after 2000 h of weathering. As the PVC of the formulation increased, the surface of the polymer appeared to erode, which allowed for more pigment to become visible. This is also observed in the PU1 series; however, the extent to which pigment is visible is far less than in the PU4-10 coating. While the erosion of the surface is not as drastic as the PU4 series, the PU1 images clearly illustrate the erosion that occurred at the surface, which is exacerbated as the PVC is increased. The PU2 and PU3 coating series more closely follow trends observed in PU4 series. All of the PU formulations exhibited some degree of polymer erosion that influenced the mechanical properties and will be discussed in Section 6.5.



Figure 6-4: Confocal Microscopy Images of PUs before (0 h) and after (2000 h) of weathering. (Scale bars = $500 \ \mu m$)

Variations of the PUs surfaces after weathering were further examined by water contact angle analysis (Figure 6-5). Changes in the film's hydrophobicity can provide insight into the types of functional groups that are generated from accelerated weathering. Initially, the PU coatings had a high water contact angle (~85°). During accelerated weathering, the contact angle decreased for each PVC formulation and indicates that the functional groups of the degradation products are more hydrophilic. Figure 6-5 clearly shows that the water contact angle for PU1-10 is much lower than PU4-10 and indicates it is more hydrophilic than PU4-10 after weathering. Dual macrodiol coatings, PU2-10 and PU3-10, are also more hydrophobic than PU1-10 after weathering, indicating that the hydrophobicity of the poly(ether) component has an influence on the pigmented coatings to a greater degree than the poly(ester) component. Additionally, the similarity between the contact angles of PU2-10 and PU3-10, after weathering, indicates that the ratio of macrodiols used did not have a large impact on coating hydrophobicity. This observation suggested that more hydrophilic polymer segments may have migrated to the surfaces as the coatings are in a swollen state during weathering or the presence of pigment at the surface has affected the contact angle. X-ray photoelectron spectroscopy (XPS) could be used to perform a surface analysis to test this hypothesis. This method would provide the means of determining the relative counts of a certain element that are present at the airpolymer interface.



Figure 6-5: Water contact angle measurements of pigmented PUs at different weathering intervals.

A decrease in water contact angle was observed when the pigment volume concentration increased. However, the extent to which the contact angle decreased is not as large as the 10% PVC formulations. In fact, as the PVC increased, the hydrophobicity of the PUs had less of an impact on water contact angle. This was attributed to the increase in pigment at the surface of the coating after weathering. It appeared that as more pigment was observed at the surface, either through erosion of the polymer or pigment migration, the hydrophobicity of the coating became less impactful on the water contact angle. The increase of pigment at the surface due to accelerated weathering created cracks and voids. The appearance of voids or cracking from accelerated weathering has been reported in other works.^{53, 86-88} The appearance of voids or cracking would increase the surface area, facilitating hydrolysis.

6.5 Mechanical Properties

DMA in the multi-frequency strain mode was used to observe the viscoelastic properties of the pigmented films. The complex modulus (E^*) in the control (T₀) films displayed sharp transitions from the glassy state below the T_g to the rubbery state above the T_g (Figure 6-6). Additionally, the magnitude of the loss tangent peak increased as the amount of poly(ether) was increased. The decrease in Tan δ magnitude is attributed to a decrease in elasticity from the poly(ether) component. These observations are true for all non-weathered coatings with increasing PVC. The control DMA plots for the 20% and 30% coatings can be found in the appendix. The 20% and 30% formulation plots display the same trends as found below in Figure 6-6.



Figure 6-6: Storage modulus, loss modulus, complex modulus, and Tan δ curves for control (T₀) coatings incorporating 10% PVC. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μ m amplitude, and a heating rate of 3 °C min⁻¹.

After 2000 h of weathering, the loss tangent curve of the 10% PVC PUs (Figure 6-7) exhibited several changes after the accelerated weathering protocol; (1) the height of

the loss tangent peak decreased; (2) a second peak appeared; (3) the peaks were found to be broader; and, (4) the peaks lost symmetry. The reduction in the loss tangent peak indicates that the elastic response of the materials increased due to sample stiffening. Further, the decrease in symmetry of the loss tangent peak and the appearance of the secondary peak indicate that some heterogeneity was introduced during the swelling and degradation of the samples. The secondary transition is most prevalent in samples with poly(ester) macrodiol incorporated in the formulation. The secondary loss tangent peak, when compared to the parent peak, is at a much higher temperature and is smaller in magnitude. The secondary peak is indicative of additional crosslinks that formed during weathering.⁶² Due to the fact that this feature occurred at higher temperatures it can be concluded that these new crosslinks have shorter molecular weight chains between crosslinks. Also, because the secondary transition only occurred in samples that contained the poly(ester) macrodiol, it was concluded that these new crosslinks are formed from the hydrolysis of the poly(ester) macrodiol. The poly(ether) macrodiol, which is much less susceptible to hydrolysis.

When the complex modulus (Figure 6-8) of the 10% PVC formulation was examined, an increase in sample stiffness is observed in all but one formulation. All samples that incorporated the poly(ester) macrodiol displayed a shift to higher temperatures after 2000 *h* of accelerated weathering. The single component poly(ether) sample (PU4-10) remained tight to the T₀ complex modulus curve and displayed a significant loss of modulus in the rubbery plateau. This indicated a decrease in crosslink density was observed in the PU4-10 sample after 2000 *h* of weathering.⁴⁵


Figure 6-7: Curves of Tan δ for 10% PVC coatings at various weathering times of the PUs. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹



Figure 6-8: Curves of complex modulus for PUs incorporating 10% PVC. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C min^{-1}

When the loss tangent curve for the 20% PVC samples are analyzed (Figure 6-9) similar trends were observed from the 10% PVC formulations: (1) the height of the loss tangent peak decreased; (2) a second peak appeared; (3) the peaks were found to be broader; and, (4) the peaks lost symmetry. These trends are all exhibited in samples that incorporate the poly(ester) macrodiol and are absent in the single component poly(ether) formulation. It was noted that there appears to be a small secondary peak at higher temperatures in the PU4 sample. However, it is believed that that is a feature of the sample becoming mechanically unstable at higher temperatures as the material responds to the stress applied from DMA. The secondary transitions observed at higher temperatures indicated that shorter stiffer crosslinks had formed in the samples. As the secondary transition did not occur in the single macrodiol poly(ether) formulation, the shorter crosslinks were attributed to the degradation of the poly(ester) macrodiol. It is believed that once chain scission occurred in the poly(ester) macrodiol, shorter ionic crosslinks formed which caused the secondary transition at the elevated temperature.⁶³

The complex modulus for the 20% PVC coatings can be found in Figure 6-10. In these samples there is again a shift to higher temperatures as observed in the 10% PVC coatings. However, these samples remain tight with the T₀ curves and only deviated at slightly elevated temperatures. The PU4-20 sample displayed the same large decrease in rubbery plateau as the 10% PVC sample indicating a decrease in crosslink density occurred in this formulation after 2000 *h* of accelerated weathering.⁴⁵



Figure 6-9: Curves of Tan d for PUs incorporating 20% PVC. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C *min*⁻¹



Figure 6-10: Curves of complex modulus for PUs incorporating 20% PVC. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C min^{-1} .

The Tan δ curves for the 30% PVC PUs display the same trends that were observed in lower PVC compositions (Figure 6-11). These plots indicate that the increase in PVC did not change the trends observed in lower PVC compositions. The loss tangent peak displayed the following trends: (1) the height of the loss tangent peak decreased; (2) a second peak appeared; (3) the peaks were found to be broader; and, (4) the peaks lost symmetry. The secondary transition is again not observed in the PU4-30 formulation however, the peak does become broader than the T₀ curve. The secondary transitions observed at higher temperatures indicated that shorter stiffer crosslinks had formed in the samples. As the secondary transition did not occur in the single macrodiol poly(ether) formulation, the shorter crosslinks were attributed to the degradation of the poly(ester) macrodiol. It is believed that once chain scission occurred in the poly(ester) macrodiol, shorter ionic crosslinks formed which caused the secondary transition at the elevated temperature.⁶³

The complex modulus for the 30% PVC (Figure 6-13) coatings also displayed similar trends observed in lower PVC formulations. The complex modulus shifts to to higher temperatures as observed in the 10% and 20% PVC coatings. The 2000 *h* curves remain tight with the T₀ curves and only deviated at slightly elevated temperatures. The PU4-30 sample displayed the same large decrease in rubbery plateau as the 10% and 20% PVC sample indicating a decrease in crosslink density occurred in this formulation after 2000 *h* of accelerated weathering.⁴⁵



Figure 6-11: Curves for Tan d for PUs incorporating 30% PVC. The data were acquired at an oscillation frequency of 1 H_z , 15 μm amplitude, and a heating rate of 3 °C min^{-1} .



Figure 6-12: Curves of complex modulus for PUs incorporating 30% PVC. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μm amplitude, and a heating rate of 3 °C min^{-1}

A clearer picture of how the elasticity of these coatings changes with weathering is presented by their Young's moduli in Figure 6-13. First, it is important to understand how the Pigment Volume Concentration (PVC) and Critical Pigment Volume Concentration (CPVC) interact with each other. For a PU with PVC below the CPVC, the cured PU is a continuous coating with particles (pigments) randomly dispersed throughout a continuous polymer matrix. As the PVC increased above the CPVC, voids in the polymer matrix begin to appear due to insufficient polymer to completely encapsulate pigments.⁸⁹⁻⁹⁰ The presence of voids in the polymer matrix causes a decrease in mechanical properties due to negative interactions between pigment and polymer.^{54, 91} The presence of voids do to pigment-polymer interactions change with different pigments or polymer systems employed.

In the studied coating formulation, an increase in Young's modulus is observed as the PVC is increased. Because a subsequent decrease is Young's modulus is not observed after an increase, this indicates the pigment is sufficiently encapsulated with polymer. From this observation it was concluded there were no negative interactions between the polymer and pigment in these formulations.



Figure 6-13: Young's modulus of the PUs taken at various weathering intervals. The data were acquired using a ramp rate of $3 N \min^{-1}$ at 25 °C.

After 2000 h of weathering, single component poly(ester) coatings displayed a general increase in Young's modulus. However, changes in the Young's modulus of the PU1-20 coatings (Figure 6-13) are far greater than the 10% or 30% PVC formulations. This trend indicated that the interactions between polymer and pigment became negative from increasing the PVC from 20% to 30% after 2000 h of weathering.

The decrease in Young's modulus in the PU1-30 formulation was attributed to the erosion that was visualized from confocal microscopy (Figure 6-4). This erosion may have caused new voids to develop within the polymer matrix that would have allowed an increase in moisture to the bulk of the coating facilitating hydrolysis of the poly(ester) macrodiol.

Conversely, the Young's modulus for the PU4 coatings did not increase with time as observed in the PU1 coatings. Like the PU1 series, the Young's modulus increased with PVC in T_0 samples. After 2000 *h* of weathering however, the Young's modulus for PU4-10 did not display significant changes. When the PVC is increased, a loss in Young's modulus was observed, with the greatest loss occurring in PU4-30. The decrease was attributed the lack of poly(ester) macrodiol to form new crosslinks.

Further, the decrease in Young's modulus seems to be due to negative interactions between polymer and pigment, similar to what was observed when the PVC in PU1 samples, increased from 20% to 30%.

When the dual macrodiol PUs were examined, again the control coatings, the Young's modulus increased with PVC. Clearly the Young's modulus for the PU2 series increased to a greater extent than the PU3 series coatings. This was attributed to the greater amount of poly(ester) macrodiol in the PU2 series than the PU3 series.

The Young's modulus did not continue to increase through 2000 h like PU1 series nor did it decrease like the PU4 series. Rather, an equilibrium between the degradation of the two macrodiols caused the Young's modulus to level out through 2000 h of accelerated weathering. Additionally, the surface erosion that was observed in laser confocal microscopy did not affect polymer pigment interactions in these formulations

6.6 Analysis of Degradation Pathways

The absorption of UV-light by PUs, due to chromophoric defects ⁹²⁻⁹⁵, is known to generate radicals that tend to form at the urethane linkages or other functional groups and subsequently react with the polymer backbone. Through FT-IR experiments, the degradation processes of the pigmented PUs were analyzed by monitoring changes in specific functional groups.

The following paragraphs describe degradation routes for single macrodiol formulations. Compared to the two macrodiol PU formulations, changes these IR intensities are more apparent and more easily separable. As a result, degradation route analysis is based on these formulations.

The spectra have been normalized at 765 cm⁻¹ due to the isocyanurate peak of the tri-functional isocyanate and has been reported to not be affected by phootooxidation⁹⁶. Difference spectra between 0 *h* and 750 *h* for PU1-10 and 0 *h* and 1000 *h* for PU4-10. This is due to inconsistencies in the FT-IR spectra that was attribute to excess pigment at the surface of the coating after weathering.

The weathering of the PU1-10 led to changes in several FT-IR peaks (Figure 6-14), namely, the region at 3700 - 3125 cm^{-1} (-NH/-OH stretches), 2950 - 2850 cm^{-1} (CH₂ stretching), 1760 - 1650 cm^{-1} (carbonyl stretching), 1538 and 1273 cm^{-1} (-N-H stretching), and 1125 cm^{-1} (C-O stretching).

The increase of the peaks at $3700 - 3125 \text{ cm}^{-1}$, especially with the presence of two maxima, indicate that new primary amide and carboxylic acid functionalities were formed. This was attributed to cleavage of both the ester and urethane linkages. The decrease in stretching at 2950 - 2850 cm⁻¹ is consistent with CH₂ oxidation, specifically at the carbon atoms adjacent to the nitrogen of the urethane linkages.

The region of carbonyl stretching is quite complex due to several changes in the intensities and make their attributions somewhat difficult. However, the increase at 1745 cm^{-1} can be ascribed to the formation of carboxylic acids via ester hydrolysis. Additionally, the amide II (1553 cm^{-1}) and amide III (1252 cm^{-1}) peaks decrease in intensity because of urethane cleavage. The decrease in the peak at 1120 cm^{-1} is indicative of the C-O of the ester undergoing hydrolysis.



Figure 6-14: FT-IR spectra at various time intervals and difference spectra of PU1-10 after weathering. The difference spectra were taken as the difference between the IR intensities at 0 h and 750 h.

The weathering of PU4 led to slightly simpler changes being, the region at 3700 -

3125 *cm*⁻¹ (-NH/-OH stretches), 2970 - 2825 *cm*⁻¹ (CH₂ stretching), 1780 - 1630 *cm*⁻¹ (carbonyl stretching), 1480 *cm*⁻¹ (-N-H stretching), and 1125 *cm*⁻¹ (C-O stretching).

Again, the increase in the region at $3700 - 3125 \ cm^{-1}$ is because of new amide and carboxylic acid functionalities. The CH₂ region is also the same as in PU1, with the exception of a small peak in the difference spectrum at 2980 $\ cm^{-1}$. This difference is an indication that some CH₂ groups adjacent to the oxygen in the ester moieties have crosslinked in the polymer matrix.^{63, 66}

Although the intensity of this peak is rather small, it is absent in PU1, appears in PU2, and increases with more poly(ether) introduced in the formulation. The region of the carbonyl stretching is much simpler. In fact, the most to probable routes are the formation of carboxylic acids and amides, and oxidation of the some of the ether moieties to esters. The decrease in intensity at 1110 cm^{-1} coupled with an increase in intensity at 1205 cm^{-1} is inductive of the oxidation of aliphatic ether linkage to formate groups.



Figure 6-15: FT-IR spectra at various time intervals and difference spectra of PU4-10 after weathering. The difference spectra were taken as the difference between the IR intensities at 0 h and 1000 h.

Therefore, multiple different pathways of PU degradation are possible. Some of those can include in-cage and out-of-cage radical reactions.^{63, 66-67} The FT-IR studies indicate that the prepared PUs follow similar degradation pathways, but the primary ones include water as a reactant.

Below the important degradation pathways, especially those that include the presence of water, are presented in Scheme 6-1. Correlating FT-IR data with the degradation pathways, it is clear that PU1 and PU4 experience degradation of the urethane linkage as shown by pathway **1U**. This process proceeds through the oxidation of the carbon atom adjacent to the -NH functionality of the urethane linkage: a hydrogen atom on the carbon atom adjacent to the nitrogen is extracted and yields a radical which can eventually lead to carboxylic acid and amide products after hydrolysis.

Additionally, the FT-IR spectra of PU1 suggest that significant hydrolysis of the ester groups (**1Es**) occurs in PU1 due to changes of the peak at 1746 *cm*⁻¹. The hydrolysis of the ester groups leads to carboxylic acid and hydroxyl products, which form ionic, rigid crosslinks. It has also been shown by Gardette and co-workers that new crosslinks can occur in linear, non-crosslinked, ester containing PUs⁶⁷ by photooxidation (and in the absence of water) in **2Es**; however, the large increase in hydrophilicity of the surface of PU1, given by the large decrease in the water contact angle during weathering (Figure 6-5), indicates that **1Es** is instead the dominate pathway during weathering in the presence of water. Recall that the Young's moduli (Figure 6-13) increase the most for the PUs containing more poly(ester) content because of the increase in stiffness from these rigid, ionic crosslinks.

The important degradation pathways of PU4 via weathering are also shown in Scheme 6-1. The degradation of the ether functional groups in PU4 initiates from the formation of hydroperoxides at the carbon adjacent to the oxygen atom of the ether group. In the presence of UV-light alone (without water), Gardette and co-workers found that the predominate degradation pathway of linear, non-crosslinked, ether containing PUs⁶⁶ is oxidation of the ether groups to esters and the subsequent formation of formates (**E1**).⁶⁶⁻⁶⁷ However, the presence of water during weathering and the shape of the carbonyl stretch in the difference spectra of Figure 6-14 suggest that **2E** and **3E** are the dominate degradation pathways.

The hydroperoxide groups oxidize to esters while a smaller population react with the water to form carboxylic acids and alcohols. It is possible that the carboxylic acid functional groups also have the ability to form new crosslinks and can increase the stiffness of the PU. Because the elastic modulus does not significantly change in the PU4 samples, it supports the observation that the majority of the ether groups will oxidize to esters within the 2000 h of weathering.





When the FT-IR spectra for the dual macrodiol PUs were examined similar IR stretching frequencies were affected (Figure 6-16). Namely the region at $3700 - 3125 \text{ cm}^{-1}$

(-NH/-OH stretches), 2970 - 2825 cm^{-1} (CH₂ stretching), 1780 - 1630 cm^{-1} (carbonyl stretching), and 1125 cm^{-1} (C-O stretching). Similarities in changes in these functional groups leads to the belief that the dual macrodiol formulations are undergoing a combination of the proposed degradation pathways.



Figure 6-16: FT-IR spectra at various time intervals and difference spectra of PU2-10 (Top) and PU3-10 (Bottom) during weathering

Examining the products in the degradation pathways proposed in Scheme 6-1, these products support the proposed results from FT-IR analysis as well as the water contact angle measurements. The results of the FT-IR and water contact angle analyses that are indicative of the formation of acids, esters, or amide groups increased in intensity. These moieties are less hydrophobic than their non-degraded counterparts as evidenced by the changes in the water contact angles.

Further, the enhancement in mechanical stabilities of the two component PUs was attributed to competition among the different degradation pathways. Clearly, multiple important degradation pathways occur during degradation of the two component PUs due of the presence of both of the poly(ether) or poly(ester) components. However, for degradation of the macriodiols to occur, photons of UV-light and molecules of water must be present. These 'degradation reagents' are distributed in an equilibrium among the different degradation pathways of the macrodiols. The equilibrium limits the degree to which a single pathway may occur. A single degradation pathway will lead to rapid degradation and, in turn, mechanical instabilities. However, the presence of macrodiols with various functional groups introduces several different pathways and reduces the extent to which a single pathway will reach 'completion' and lead to significant mechanical instabilities.

When the PVC is increased the base line of the FT-IR, the functional groups previously discussed were similarly affected. However, the intensity of the FT-IR peaks begins to decrease in the PU4-20 coating then gets worse when the PVC is increased to 30% PVC (Figures 6-17 and 6-18). It was believed that the increase in PVC allowed more

pigment to migrate to the surface through erosion of the PUs. The increased pigment at the surface would cause a decrease in the amount of PU to perform FT-IR with, subsequently accounting for the decrease in intensity of the spectra.



Figure 6-17: FT-IR for 20% PVC coatings at various time points during weathering.



Figure 6-18: FT-IR for 30% PVC coatings at various time points during weathering.

6.7 Conclusions

Pigmented PU films with varying PVC, and poly(ether) to poly(ester) macrodiol ratios were synthesized and subjected to accelerated weathering (*i.e.*, UV-light and water). The mechanical properties and surface effects were characterized over 2000 h of weathering through techniques which include optical microscopy, thermal, mechanical, and FT-IR analysis. Using the above techniques, it was found that the single component PUs of either poly(ester) or poly(ether) macrodiol were more mechanically unstable. The mechanical instabilities were exacerbated with increase in PVC in different ways. The poly(ester) samples displayed a large increase in Young's modulus with increasing PVC from 10% to 20% then a subsequent decrease from 20% to 30% PVC. The decrease in mechanical properties was attributed to the creation of voids in the polymer matrix due to erosion of polymer resin, subsequently causing negative interactions between the polymer and pigment

Single component poly(ether) coatings displayed a decrease in mechanical stabilities with increased PVC, not only due to negative interactions with pigment and polymer resin, but also due to the lack of ester groups to create additional crosslinks. The two component PUs led to a 'synergistic effect' between the degradation of the two macrodiols in which the stiffening of the PUs showed an increase then subsequent leveling off with respect to the Young's modulus. Furthermore, the increase in PVC did not cause subsequent decreases in Young's modulus after 2000 h of weathering indicating that the polymer was still able to encapsulate the pigment maintaining positive interactions between the components. Overall, this work suggests that PVC not only effects the mechanical properties of non-weathered samples but also contributes to changes to mechanical properties of coatings subjected to accelerated weathering.

Chapter 7: Conclusions

In summary, this work takes a systematic approach to studying key variables that may influence accelerated degradation of military aircraft coatings. While all coating systems do suffer from degradation, the coating in question was particularly susceptible to hot and humid environments. To study this phenomenon, the polyol ratio, isocyanate to hydroxyl mole ratio, and pigment volume concentration of an analogous coating system were analyzed. This was accomplished by synthesizing coatings and subjecting them to accelerated weathering. The accelerated weathering was performed in accordance to an ASTM standard to ensure continuity between changes in the aforementioned variables.

When the polyol ratio was examined, dual polyol systems were least affected by accelerated weathering. The Young's and complex modulus values through 2000 h of weathering were closer to the T₀ values than either single polyol coating. When the single polyol coatings were examined, the poly(ester) based coating became exceedingly stiff and brittle. The poly(ether) based coating became mechanically weakened, as evidenced by DMA and stress strain experiments. It is believed that additional crosslinking occurred during the degradation of the poly(ester) coating that did not occur in the poly(ether) coating. When the two polyols are incorporated into the same coating, a synergistic effect occurred: the stiffness of poly(ester) was offset by the degradation of the poly(ether)

component. This allowed the coating to remain more flexible through 2000 h of accelerated weathering.

The manipulation of the isocyanate to hydroxyl mole ratio was studied next, by synthesizing coatings with varying mole ratios and subjecting these coatings to accelerated weathering. It was found that lower indexed coatings (-NCO:-OH 1.1:1 and 1.3:1) displayed little changes to mechanical properties, while higher ratios (-NCO:-OH 1.5:1 and 2:1) increased in complex modulus. It is proposed that the increase in mechanical stiffness in higher ratios is due to the degradation of the additional urea linkages and their ability to form new ionic crosslinks. It appears that for this system, the additional isocyanate did not adversely affect the accelerated weathering, but it did enhance the mechanical properties of the coatings.

Finally, the effects of PVC on the coatings were studied. Coating systems with PVCs of 10%, 20% and 30% v/v with varying polyol ratios were synthesized and and subjected to 2000 h of accelerated weathering. This study found that the single polyol systems performed unfavorably, when comparing their mechancial properties to dual polyol systems. Yet, while the single polyol systems became mechanically unfavorable, the dual polyol systems were able to mitigate large increases in Young's and complex modulus through a synergistic effect of the two polyols.

Evaluating the work holistically, it seems likely that the major variable contributing to premature degradation is the polyol(s) employed in the coating system. Increasing the urea likeages through isocyanate/hydroxyl mole ratio manipulation created more crosslinks that are susceptible to hydrolysis or photooxidation. However, the increase in crosslink density

only improved the mechancial properties. This indicates that it may act more as a tool for tuning a coating system for a specific application. Further, the PVC of a coating system can also play a role in premature degradation. However, this seems to be the easiest variable to correct, by either increasing or decrasing the pigment volume.

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Appendix



Figure 9-1: Storage modulus, loss modulus, complex modulus, and Tan δ curves for control (T₀) coatings incorporating 20% PVC. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μ m amplitude, and a heating rate of 3 °C min⁻¹.



Figure 9-2: Storage modulus, loss modulus, complex modulus, and Tan δ curves for control (T₀) coatings incorporating 30% PVC. The data were acquired at an oscillation frequency of 1 *Hz*, 15 μ m amplitude, and a heating rate of 3 °C min⁻¹
Biography

Nickolaus K. Weise is a materials chemist working at the Naval Research Laboratory, researching novel polymeric coatings and the analysis of premature coating degradation. Mr. Weise was born in Honolulu, HI and moved to Kent, WA in 1995. After graduating from high school, he enlisted in the United States Navy, where he was deployed on the USS Harry S. Truman, supporting Operation Iraqi Freedom and Operation Enduring Freedom. After completing six years of active duty service, he attended Northern Virginia Community College, then George Mason University. He earned a B.S. in Chemistry in 2010 and a M.S. in Chemistry in 2013. Mr. Weise has worked at the Naval Research Laboratory since 2010.