Examining Regional Weather Effects on Single Ply Roofing Membranes

by

Gisica N Abdallah

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science in Engineering

in the

Chemical Engineering

Program

YOUNGSTOWN STATE UNIVERSITY

May 2018

Examining Regional Weather Effects on Single Ply Roofing Membranes

Gisica N Abdallah

I hereby release thesis to the public. I understand that this thesis will be made available from the OhioLINK ETD Center and the Maag Library Circulation Desk for public access. I also authorize the University or other individuals to make copies of this thesis as needed for scholarly research.

Signature:

_____

Gisica N Abdallah   Date

Approvals:

_____

Dr. Holly J. Martin, Thesis Advisor   Date

_____

Mr. Jeffrey Meyers, Thesis Advisor   Date

_____

Dr. Pedro Cortes, Committee Member   Date

_____

Dr. Salvatore A. Sanders, Dean of Graduate Studies

Date

Abstract

Weather across the different regions in the country can variably influence the performance of roofing membranes, affecting the long-term stability and function of single ply roofing membranes, such as Thermoplastic polyolefin (TPO), Polyvinyl chloride (PVC), and Ethylene-propylene-diene monomer (EPDM). Different weathering factors, such as humidity, salinity, UV exposure, and freezing and thawing cycles, were simulated under lab conditions to mimic diverse weather conditions across the various regions in the United States. Using the different lab conditions, the aging effects can be associated with different regions based on specific weathering patterns. Therefore, a more accurate prediction of roofing performance can be predicted and applied to enhance the choice for appropriate roofing systems and warranty plans in the roofing industry. The research presented here details the effects of various environmental exposures over 1000 or more hours on three different single ply roofing membranes to establish specific weathering behavior. To test different weathering effects, weight, puncture resistance, and thickness were measured for all three membranes after each aging cycle. TPO lost weight, puncture resistance, and thickness, indicating material degradation and oxidation of the membranes after the different aging cycles. PVC lost puncture resistance, but gained weight and thickness throughout the experiment. Measurements demonstrated water retention,

oxidation, and degradation of the polymer due to UV. EPDM gained weight, puncture resistance, and thickness. EPDM absorbed water but was more UV stable than both PVC and TPO. The negative effects of all three membranes were highlighted after the freeze-thaw conditions, where temperature changes caused thermal stress on the membranes and caused a decrease in puncture resistance. QUV effects were increased after extended hours of exposure (2000 hours), and were less prominent when membranes were initially exposed to 1000 hours. UV stabilizers in the membranes were able to withstand 1000 hours of exposure, but began to degrade when tested after 2000 hours. Salt and humidity presented similar results to QUV effects, and isolated humidity effects were more apparent on EPDM membranes, where water retention was a clear effect.

Acknowledgments

I want to dedicate this thesis to Simon Roofing and the faculty at Youngstown State University for their help and support. I would like to dedicate this specifically to Jeff Meyers at Simon Roofing for giving me the support and flexibility with my research. I would also like to dedicate this specifically to Dr. Martin at YSU, who supported my research and guided me in the right direction. A big thanks to Dr. Pedro Cortes for his input and time as well. I would also like to dedicate this to my family and friends for their help and support.

Table of Contents

List of Figures

List of Tables

1.0 Introduction and Literature Review

Roofing is an important aspect of building codes and construction, since every enclosed building needs one. Depending on the type of construction, a building may require a different type of roof. There are two major types of roofing: flat to no slope roofs and residential, or high-sloped roofs. High-sloped roofs are intended to shed water, with a slope of more than 25 percent of a completely horizontal roof. Low-slope roofs are intended to be watertight, to be used on systems that lead to a drain but only sloped at 25 percent or less compared to a flat, horizontal roof (1).

For cost effective measures and low geometrical problems, low-slope roofs are used on commercial buildings, which are more problematic in nature due to the lack of drainage available. There are two types of low-sloped roofs: built-up roofs, and single-ply roofs. A built-up roof consists of multiple layers of membranes or plies (typically three or four). Alternating layers are made of felts and molten bitumen, and require a protective surface, such as stone aggregates or gravel, for protection against UV rays and cracking (2). Single-ply roofs are typically elastomeric or thermoplastic roofing materials that are applied as a sheet on the roof (3). They were first introduced in the US in the 1960s to make roofing easier and more "foolproof" (4). Single-ply membranes are manufactured in rolls that are laid out and fastened on the roof via metal fasteners. Seams are often

attached with seam tape, adhesives, or heat welding. Depending on the adhesion

mechanism, some of the sheets are fastened using fasteners to the deck (2). The

unrolling, fastening, and seam sealing makes their application fast and easy,

requiring less labor than built-up roofs (2).

There are three major types of single-ply membranes in the market today:

Thermoplastic polyolefin (TPO), Polyvinyl chloride (PVC), and Ethylene-

propylene-diene monomer (EPDM). TPO's polymer backbone is composed of

polypropylene or polyethylene, supplemented with pigments, fillers, UV light

stabilizers, antioxidants, and containing polyester or glass fabric reinforcement

(1). There are many different manufacturers of TPO, and the typical thickness of

the membrane varies between 40-100 mil sheets (1.016 – 2.54 mm) (5). PVC is

made up of vinyl chloride monomers, and in roofing, the polymer is plasticized, to

provide flexibility and durability (6, 7). Current plasticizers used are complex

phthalates and other copolymers, and the reinforcement is made out of polyester

and/or glass fibers (1). Currently, the only PVC available in the market is

reinforced, with a thickness of typically 45, 60, or 90 mils (1.143, 1.524, or 2.286

mm), and available in white, tan, or gray (6). EPDM is an ethylene-propylene-

diene monomer, composed of rubber polymers, carbon black, oils and plasticizers,

and other fillers. There are two types of EPDM roofing membrane: non-reinforced

and reinforced with polyester, which can be white or black, with a thickness that

typically varies between 30 and 60 mils (0.762 and 1.524 mm) (5). Although it is

available, white EPDM roofing is not recommended due to the lack of carbon

black in the formulation, which adds UV protection properties to the membranes

(1). TPO and PVC are both thermoplastic polymers, which are polymers that

become liquid as heat is applied (7). Unlike TPO and PVC, EPDM is

thermosetting, meaning it will burn without melting (1). In addition, the rubber

does not crosslink until it is cured, after extrusion into thin sheets. .

All three types of single-ply membranes improved roofing due to shorter

roofing application time and ease of use. However, when all three were

introduced into the market, problems arose and the membranes were altered to

improve their service life.

TPO is the newest single-ply to be introduced, with the first demonstration

project in 1986 (Taylor). They were manufactured to be superior to PVC due to

their flexibility without plasticizer addition. This flexibility is said to be achieved

by the polymer's "internal flexibilization" (8), and plasticizer migration would not

be an issue. Primary issues with TPO revolved around premature aging, whether

from ultraviolet (UV) or heat exposure. Initially, TPO formulas contained

brominated fire retardants that caused premature weathering and degradation (8).

Flame retardancy is very important in roofing systems, and each membrane alters

its formulation to meet industry standards (9). With UV rays, the membranes aged

quicker than anticipated, leading to research of new flame-retardants. The TPO

membranes would be intact until they underwent accelerated weathering, at which

point they would quickly deteriorate and fail (10). As a result, TPO membranes manufactured after 1994 use magnesium hydroxide as the flame retardant, which stopped the sudden failures (10).

Heat was also a cause of failure, not just UV. As a result, formulations were further altered and different stabilizers were used to fix the issue of premature aging (10). Further studies with heat aging were conducted, due to the large volume of premature failure issues that were discussed during the 2009 American Society for Testing and Materials (ASTM) TPO task group meeting. It became apparent that the sun was not the only source of heat for failure; heat was conducted through the walls, heating ducts, ventilation equipment, air conditioning units, and reflected from sand or solar panels (10). As a result, a change to standard D6878 was proposed to double the heat exposure time under lab conditions, and increase the temperature at which TPO is to be exposed. Standard D6878 was established in 2003, and after multiple updates, it called for heat aging of TPO at 240 degrees Fahrenheit, for 28 days (11). A new proposal also suggested 275 degrees Fahrenheit for 56 days to account for the extra heat on TPO membranes. Heat and UV rays were also believed to exhaust anti-aging compounds in the formulations, such as antioxidants, UV absorbers, and stabilizing components (10). This could also lead to failure of the membrane at temperatures above 160 degrees Fahrenheit and at elevated heat loading. Taylor and other researchers argued that degradation of membranes are also present in

areas where UV rays are blocked by dirt and debris, and they argued that aged TPO membranes were continually stable up to 190 degrees Fahrenheit (10). Taylor also emphasized that TPO performance differed between manufacturers (10). In response to industry concerns and research data, ASTM raised the standard exposure time to 224 days at 240 degrees Fahrenheit, and published in 2011 (12).

Increasing the surface temperature of a membrane can significantly reduce its service life, if predicted using the Arrhenius law (8). The law states that for many chemical reactions at room temperature, when the temperature is increased by 10 degrees Celsius, the reaction rate is doubled (13). If the assumption holds that heat and UV rays break down polymer chains, then every 10 degree temperature increase doubles the aging of the membranes, hence decreasing its service life (8). Deaton and Martin conducted a study in which they compared methods of predicting service life of single ply membranes (12). Unlike built-up roofs that are aged in black ovens, single ply membranes are aged for longer periods of time to establish trends (12). They focused on thermal aging to determine effects on service life, in which they correlated weight loss to heat aging of TPO from 240 to 275 degrees Fahrenheit (12). In their study, they found that as TPO shows weight loss after heat aging, there is a direct correlation with an increase in cracking of the membranes (12).

Like TPO, PVC had its own issues to resolve pertaining to the formulations. When PVC was first introduced to the market, it was non-reinforced. As the temperatures plummeted at night and dropped below the glass transition temperature of the polymer, the membranes shattered, causing catastrophic failures (14). Since then, PVC is manufactured with polyester reinforcement. Polyester reinforcement is of high strength, and adds mechanical resistance and dimensional stability to the existing PVC (15). In addition, plasticizers used in PVC were fugitive, which quickly migrated out of the membranes, leaving PVC to be brittle and unable to withstand any weathering conditions (1). A loss of plasticizer causes the material to harden and it directly affects the mechanical properties of the membrane (16). In his study, Gerhard Patuska discusses the physical property effects of plasticizer loss, which include loss of thickness, hardness, shrinkage, and loss of elasticity modulus. To detect loss of plasticizer in aged PVC, thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and other thermal analyses have also been widely used (17). These tools are useful in understanding how the material properties change to predict weathering behavior on the roof (17). In a study about aging of PVC membranes, Lys used weight loss as a valid indicator of plasticizer loss (15). In the field, loss of plasticizer was directly correlated to shrinkage of the membrane, particularly around the flashings (18). Flashings are barriers that seal the roof between the membrane and penetrations, such as chimneys, vent pipes, or

drains (1). It can be easier to detect shrinkage of membrane around the flashings due to increased stress around the area (18). Furthermore, Koontz used specific gravity of field samples, compared those samples to samples that were not exposed, also known as laps, and used the difference as an indicator of plasticizer loss. He explained that as plasticizers migrate out of the membrane (and age), the membrane becomes more dense and would have a higher specific gravity than an unaged sample (18).

In his study about the effects of plasticizers, Patuska mentions that plasticizers are typically 36% of the formulation of PVC (16). A loss of 10-12% of that 36% indicates damage or failure of the membrane (16). He used liquid chromatography to extract plasticizers and used that as a method of analysis, focusing on the effect of plasticizer migration on PVC surface (16). In a study done by Jim D Koontz in 1997, his data showed how a loss of plasticizer (or aging) in PVC significantly increased damage caused by hail (18). Thus, he developed a standard in his study where he categorizes loss of plasticizer between the lap and field, to determine plasticizer presence before and after weathering. Similar to Patuska, he used extraction to measure the level of plasticizer (18). His numbers were slightly higher than Patuska's, where he categorizes shatter of membrane at 17.25% plasticizer loss, and damage around 10%, if exposed to hail (18).

Once the problems about early plasticizers were improved, membranes began to last longer. In 2005, Capocci and Hubbard researched a new UV stabilizer that was found to increase the life of the membrane drastically (6). In comparison to traditional UV stabilizers, this amine derivative sustained PVC elongation, kept PVC color more stable in harsh weathering conditions, and extended the life of the membrane (6). The white color of PVC is reflective, which gives an energy-saving advantage in roofing (6). Maintaining color under direct sunlight is difficult to achieve without any UV stabilizers.

Initially, industry specifications of the material were emphasized, and private data was publicized. However, in the early years of PVC, long term weathering effects were not addressed by the industry (15). The typical PVC membrane did not pass 5000 hours of accelerated weathering (15). If it passed, it only lasted six to eight years after installation if ponding water existed (15). Ponding water is a phenomenon that many roofs exhibit (15). It is "basically a slurry of water, minerals, and algae containing dissolved salts and acids" (15) . With the addition of UV rays, ponding water can be detrimental to the life of the polymer (15) . The water and salts add weight and stress on the membrane, eventually accelerating deterioration (15) . It is also known that water contributes to hydrolytic disintegration reactions, to further deteriorate the materials (15) . ASTM methods have been established since then to ensure that PVC membranes pass certain weathering criteria prior to installment (15).

Since UV rays increase the decay of polymers, different additives, such as UV absorbers, are added to formulas to decrease UV effects. EPDM has also improved over the years since its initial formulation in the 1960's, and changes have been made to the color, fillers and additives, and reinforcement of the membrane. When EPDM was introduced into the market in the 1960s, there was an issue with shrinkage (19). The plasticizers, or oils, used in the formulations were too volatile, leaving the membranes to shrink when weathered (19). This caused EPDM manufacturers to change their formulations to include less volatile components (19). However, not all formulation changes have been benevolent. One manufacturer altered the catalyst in the formulation from a lead to magnesium catalyst, causing major water swelling of the membrane and seams, flooding, and great damage to the buildings (1).

In EPDM, the main additive is carbon black, averaging at 30 to 40 percent of the total formulation (20). Hence, when white EPDM was formulated, it did not contain carbon black, and its ability to absorb UV rays was lower, causing the white roofs to fail faster (1). Studies have been done to compare both white and black EPDM roofs, and surface deterioration was more prevalent in the white membranes, not the black (21). Experimentation with white EPDM was done because, under hot heat, the temperatures of black EPDM can rise up to the temperature of boiling water. In general, the temperature of black membranes can rise 40 to 50 degrees Celsius above ambient temperatures (22). White EPDM was

an attempt at decreasing roof temperatures, not accounting for the decrease of UV absorption.

Thermal aging of EPDM has been studied and tested using TGA, DMA, differential scanning calorimetry (DSC), and thermomechanical analysis (TMA) (23). In 1993, Penn and Paroli took two different manufacturers of EPDM and studied heat aging of the membranes (23). Their research was done at 130 degrees Celsius and they aged the membranes for 7 and 28 days (23). As a result, they concluded that EPDM composition varies between manufacturers, and heat aging and performance is reliant on how plasticizers migrate (23). Their conclusion ties to the importance of slow-volatilizing oils in formulations.

One of the major issues of EPDM roofing is puncture and tearing when aged, which were about 25% of EPDM issues in the early 1990's (14). Initially, EPDM was non-reinforced, but over the years, a reinforced sheet with polyester was made to improve puncture resistance of the sheet (14). The sheet added strength to the EPDM, and it has been shown that polyester improves tear resistance and increases tensile strength of single-ply membranes (14). A study done by Gish and Jablonowski verified that aging of EPDM roofing decreased its tensile strength (21). In EPDM, tensile strength was one of the biggest factors in field aging of the membranes (24). With the addition of a polyester reinforcement, such issues could be improved.

Collectively, all three types of single-ply membranes are presented with two disadvantages. The main problem with application is the seam adhesion, which is the overlap between two individual rolls. In TPO and PVC, the seams are typically heat sealed or solvent welded (1). In EPDM, the seams are adhered using seam tape or solvents. This is problematic because EPDM has an inert surface that makes it difficult for good adhesion (25). As a result, seams are not very durable in comparison to the rest of the roll. The second main problem is membrane attachment to the roof. Single-ply membranes can be attached mechanically via fasteners, fully adhered using adhesives, or ballasted using rocks or pavers (1). All of these methods present separate membrane issues and limitations. Concrete decks on the roof cannot be directly fastened, because it would compromise the integrity of the entire roof system (1). Fasteners are mainly problematic because they can rupture, or pop out, creating holes in the membranes that progress to leaks and failure (1). When membranes are fastened, or glued using a strong adhesive, their elongation, or extension, is limited. Any shrinkage or movement in the membranes can force a tear around the fastened area (1).

Since initial developments, other issues began to arise, and the different manufacturers have addressed these issues separately. One of the biggest issues in roofing is the different weathering conditions to which the membranes can be exposed, such as the weather and exposure differences between the northeast and

the southwest. Subsequently, different regions in the country present different problems and conditions that must be accounted for when choosing an appropriate roofing membrane. Some of the weathering conditions are sunlight, temperature changes, wind, moisture, rain, hail, frost, and dew. The conditions are summarized below.

Sunlight, or ultraviolet (UV) rays: UV rays can degrade roofing materials; cause chemical reactions, such as oxidation, and can soften polymers (20). These problems may be more prevalent in southern states with strong sun exposure, such as Florida. As a result, UV stabilizers (such as hydroxy- phenylbenzotriazole and hydroxybenzophenone) and UV absorbers are added to formulations to improve their resistance to UV rays (6).

Temperature fluctuations: Temperature changes can alter the thermal expansion of the membranes. Whether these changes are caused by freeze-thaw cycles, gradual, or sudden temperature changes, these changes create extra stress on roof membranes (20). Additionally, freeze-thaw cycles can propagate cracks, since water has different properties and expands when it freezes. One of the theories studied regarding crack propagation of roof membranes is the introduction of water into the membrane followed by the expansion of ice (20). Freeze thaw cycles with the combination of leaking and water soaking of the roofing components can also cause a reduction in tensile strength, leading to its inability

to withstand heavy loads on the roof (26). These problems are more prevalent in northern states, where temperatures cycle below and above freezing, frequently.

Wind: External forces are applied to the roof via high wind velocities, in high-rise buildings and in high wind regions, such as south Florida during hurricane season (20).

Rain: Although rain cleans the roof from dirt, it can be problematic when cracks are present, which the water can permeate, and temperatures plummet below freezing, where any water absorbed into the membrane can expand into ice.

Hail: Hail causes mechanical damage, cracks, and tearing of the membranes. In single-ply membranes, fasteners are mostly affected by hail, since they provide a weak point on the membrane (27). This is mainly a problem where dangerous thunderstorms carrying and dropping hail occur, including in southern states and those associated with tornado alley.

Snow: Snow increases weight on the roof, and provides another source of water for crack propagation (20). This is mostly a problem in northern states, where several inches to several feet of snow can fall in any given year.

Humidity, dew, and frost: When there is high humidity during the night, dew and frost are formed overnight, causing expansion of water if they freeze, and shrinking when the water melts, contributing to crack propagation as well (20).

The service life of a roof is predicted to be about twenty years, plus or minus seven years, depending on the occupancy of the building and proper

installation of the roof (1). It is unknown how the different weathering conditions affect the number of years a roof is predicted to last. In order to link weathering cycles with aging of different single ply systems, this study focuses on individual effects of UV, temperature changes, and salt and humidity. TPO, PVC, and EPDM samples were weathered in the lab and tested to determine individual and combined effects of weathering cycles.

Three weathering cycles were used in this experiment: UV and humidity cycle, salt and humidity cycle, and a freeze-thaw cycle. In order to isolate humidity effects, an additional humidity cycle was used. The membranes were then tested to derive the weight, puncture resistance, and thickness for comparison. Data was compiled and used to bring correlations to the different weathering conditions.

2.0 Materials and Methods

2.1 Materials

TPO, PVC, and EPDM were analyzed in this study. Although there are multiple manufacturers available, only one proprietary manufacturer was used for each type of single ply membrane. Additionally, only one roll (each at 100 feet long) was used per roofing membrane, due to cost constraints. Samples were taken from three different locations from each roll and analyzed.

2.2 Instrumentation

2.2.1 QUV accelerated weathering tester (Model LE 10)

A QUV accelerated weathering tester provides cyclic corrosion due to the combination of sunlight, rain, and dew (Q-Fog, Cleveland, OH). It was used to expose the different roofing membranes to UV light through fluorescent UV lamps and humidity cycles for rain and dew simulation. Each cycle consisting of 8 hours of UV light exposure and 16 hours of humidity was used to determine the effect of the combination of the two conditions on the membranes (28). Although there are different ASTM methods for exposure on each membrane, they were all exposed to the same conditions to obtain direct comparison. Figure 1 below is an image of a similar QUV model.

Figure 1. QUV Accelerated Weathering Tester

2.2.2 Q-fog Cyclic Corrosion Tester - Model CCT

A cyclic corrosion tester was used to apply humidity and salt to the samples (Q-Fog, Cleveland, OH). Figure 2 below is a model similar to the one used for experimentation (28). Areas labeled 1 and 4 are the reservoir and lid, where the chamber was filled every 2-5 days. Area labeled 2 is where the samples were placed. Area 3 is a fiberglass lid with low thermal conductivity, used to enhance temperature control in the chamber. Area 5 is the control panel, where cycle was controlled and aging method was selected.

Figure 2. Q-Fog Cyclic Corrosion Test

As seen in figure 3, the water (salted and unsalted), is dispensed from the reservoir into the pump, sending the solution to the fog nozzles. Concurrently, air is compressed through the bubble tower and is sent to the fog nozzles via the same pump. The solution and air are distributed onto the samples as fog mist (29).
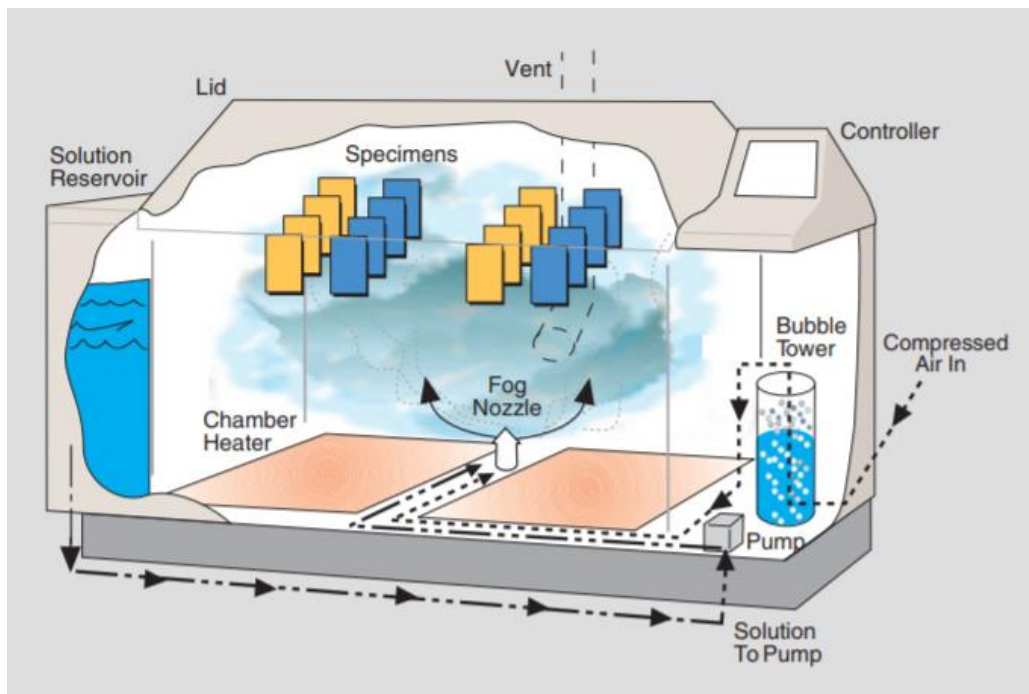
Figure 3. Cyclic Flow in a Corrosion Tester

2.2.3 Futura Silver Series - Refrigerator and Freezer

      Samples were placed on shelves in the refrigerator, freezer, and ambient temperatures to simulate freeze-thaw conditions (LabRepCo, Horshem, PA). In the refrigerator, samples were placed in containers immersed in water and temperatures ranged between 1 and 10°C. The temperature was kept between 2 and 4°C during the experiment. The refrigerator contains a glass door and three shelves for samples to be placed, and it has a cyclic defrost. In the freezer, temperatures ranged between -15 and -25°C, but were kept between -21 and -23°C. The construction of the freezer consists of a solid door and three shelves for samples to be placed, and it auto defrosts. Figure 4 below shows a similar model as the one used in this experiment.

Figure 4. Refrigerator and Freezer

2.3 Aging Methods

2.3.1 QUV cycle

Samples were 3 x 6 inch each and were placed in aluminum holders, held in place by flat aluminum panels, and secured with snap rings. The QUV was filled with 25 samples for the duration of the test, as suggested by the operating manual; 24 membrane samples and 1 blank sample holder. One cycle consisted of 24 hours, where the samples underwent UV exposure for eight hours, and a

humidity cycle for sixteen hours. The temperature was cycled from 45 to 80°C during UV exposure, and from 45 to 60°C during humidity hours (29). The first aging period was intended for 1000 hours; actual hours were 1010 hours. The second aging period was intended for 2000 hours; actual hours were 2008 hours.

2.3.2 Cyclic Corrosion Tester

The samples were suspended in the sample holders and hung in place using plastic hangers. They were inclined from the hanging rod at approximately 15 degree angle. This was done to ensure that the samples were uniformly exposed to the fog released from the different nozzles. To further ensure proper exposure, samples were constantly being readjusted and replaced in the sample holders. Sample size was 9.5 inches by 7.5 inches. Samples included three PVC, three EPDM, and three TPO samples. The samples were left uninterrupted in the chamber unless the reservoir was being replenished, or the samples were adjusted for proper exposure.

This test was continuous for the duration of the time (roughly 1000 hours) for the salt and humidity cycles, as described in ASTM B117 (30), which is a standard practice for operating salt spray (fog) apparatus. The method was used as a guide to imitate salt and humidity weathering conditions, such as those exhibited in South Florida. The method calls for an apparatus with a reservoir that

is capable of dispensing salt/unsalted water through nozzles onto the samples (30).

The roofing membranes were exposed to two different cycles. The first cycle was 1000 hours of salt and humidity exposure. The first cycle used 0.32 grams of salt per liter of water, to imitate air salt concentration conditions in regions such as South Florida. An article about the salinity of the Florida Bay discusses the salinity of ocean water versus air salt concentrations. Levels in the South Florida Bay can average around 32 Practical Salinity Units (PSU) (31). 1 PSU can be defined as one gram of salt per 1000 grams of water (or 1 liter) (32). Depending on the region of the bay, the salinity can vary between 20 and 39 PSUs. 32 PSUs were used for this study to correlate to an average air salt concentration. An estimated relationship of 10% of air to bay salt concentration was used and 0.32 grams of salt were added per liter of deionized water. The second cycle was only a humidity cycle for 1000 hours; actual hours were 1008 hours. The purpose of the second method was to isolate the effects of salt and UV from humidity. The temperature for both the salt fog and humidity cycle combination as well as the isolated humidity cycle was controlled at 35°C.

2.3.3 Freeze-thaw cycles

In order to simulate freeze and thaw conditions, samples were placed in the freezer, refrigerator, and on shelves at ambient temperatures. Sample size was

9.5 inches by 7.5 inches. Samples included three PVC, three EPDM, and three TPO samples.

On freeze-thaw cycle consisted of the following, with each constituting a step in the cycle:

- o Room temperature (~23°C) for 3 hours - Samples were placed on shelves in the laboratory at ambient temperatures. Temperatures often varied between 21 and 23°C.

- o Refrigerator temperature (~3°C) for 3 hours - Containers were placed on the shelves in the refrigerator, and samples were immersed in the containers filled with spring water. Temperatures often varied between 2 and 4°C.

- o Freezer temperature (~ -22°C) for 15 hours. Samples were taken out of the water and placed directly on the shelves in the freezer. They were not physically dried off before placing in the freezer; the water was allowed to drip off before replacement on the freezer shelves. Temperatures often varied between -21 and -23°C.

- o Refrigerator temperature (~3°C) for 3 hours. Same procedure was followed as the first 3 hours in the refrigerator. Samples were in containers with spring water at a temperature range of 2 and 4°C.

The following freeze-thaw control sequence was used as a guide on testing freeze-thaw conditions on insulation boards (33). The method is outlined in Figure 5. Temperatures were imitated, but freeze-thaw cycles were done manually and at different time intervals.

STEP	STEP TIME	TOTAL TIME	OPERATION
	(HR - MIN)	(HR - MIN)	
1.	1 - 10	1 - 10	Specimens submerged in circulating water maintained at 16°C (60°F).
2.	0 - 17	1 - 27	Water pumped from test chamber. All specimens now thawed.
3.	0 - 30	1 - 57	Freezer on with fan circulating cold air around test chamber. Chamber temperature ramped down to -23°C (-10°F).
4.	1 - 25	3 - 22	Freezer and fan on with chamber temperature ramped up to -18°C (0°F). All specimens frozen.
5.	0 - 10	3 - 32	Water at about 16°C (60°F) pumped into test chamber.

Figure 5. Example of Freeze-Thaw sequence

Samples were cycled Monday morning through Friday. On the weekends and holidays, samples were placed in the refrigerator, immersed in spring water. Samples were left to air dry before testing at ambient temperatures.

The first set of trials consisted of 20 freeze-thaw cycles. After initial data analysis, a second set of trials were conducted at double the cycles (40 freeze-thaw cycles) to further explore the effects. Studies have been done on freeze-thaw cycles of insulation boards, and a chart of the average cycles were determined based on location. Figure 6 is also taken directly from the article "Freeze-Thaw Durability of Common Roof Insulations" and it is used a basis for the number of initial freeze thaw cycles used (33). Number of cycles was chosen based on the average of the lowest number of national cycles, to imitate initial weathering behavior change.

Location	Cycles per year
San Francisco, CA	0
Portland, OR	15
Macon, GA	15
Baker Lake, NWT	28
Boston, MA	42
Winnipeg, Manitoba	46
Juneau, AK	52
Yarmouth, Nova Scotia	52
Akron, OH	63
Millinocket, ME	71
Elkins, WV	85
Garden City, KS	96
Elko, NV	137

Figure 6. Average Freeze-Thaw Cycles in North American Cities

2.4 Testing methods

Each aged membrane was tested against a baseline. Measurable test
methods include weight, dynamic puncture, and thickness. The following section
provides an explanation of the test methods used, the instruments used to measure
them, and the significance of each test.

2.4.1 Weight

Research has found that the percentage of weight loss in plastic industries
can be directly correlated to the degradation of the material. There has also been a
strong correlation with weight loss and cracking of materials membranes (12). A
negative change in weight indicates loss of material, leaving less material to
withstand weathering conditions and more essential volatiles escaping the
membranes (20). As a result, weight of the membranes is considered to be an
affected factor. It was measured using a Symmetry PT -213 E PT series precision
top loading balance, in grams (Cole-Parmer, Vernon Hills, IL). Samples measured
were cut out of the larger samples using a 3 inch diameter die, with precision of
+/- 0.005 inches. Three 3-inch round samples were cut using the specified die
from each aged sample and weighed, with the mean and standard deviation then
calculated.

2.4.2 Dynamic Puncture

Puncture is done to test the ability of the membrane to withstand puncture under a specified force. It is important to test whether a roof would be able to withstand hail damage, or any blunt fallen objects (1). ASTM D5602 was used as the background for testing. This standard provides a basis for comparing static puncture resistance of the different single ply roofing membranes (34).

There are two types of puncture tests, a static and a dynamic puncture test. Static puncture is when the force applied through a flat-ended plunger onto a sample and held until puncture is achieved over the course of 24 hours. Dynamic puncture is when the force is continuously applied and increased until a puncture is formed. Only dynamic puncture is explored in this study.

Samples were cut out using the same die used for weight, which were 3 inches in diameter. Samples were tested using an in-house testing apparatus (Made in House, Boardman, OH). During the test, the sample is sandwiched between two steel plates. Both the top and bottom plates have a hole in the center of them to allow a mandrel to be pushed through. The plates are secured together using vice grips. Once the sample is between the plates and the plates are secured together, a pneumatic hand pump is used to drive a mandrel up through the hole in the plates, passing it through the roof sample that is between them. The mandrel used for puncturing has a 10 mm ball on the tip. The force exerted on the membrane is recorded using a load cell (Made in House, Boardman, OH). Figure 7 below is an Autocad drawing of the test, without the hand pump and vice grips.

The black represents the roofing membrane, sandwiched between two steel plates,

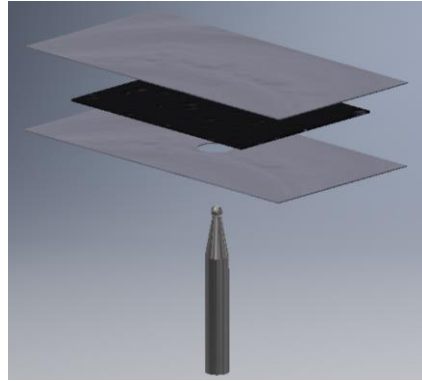with a mandrel driven through the bottom until the membrane is punctured.

Figure 7. Autocad drawing of the puncture test

2.4.3 Thickness

Thickness of the samples was measured using a Mitutoyo micrometer. The unit of measurement is a mil, which is a thousandth of an inch (1 mil is 0.0254 mm), and it is the common unit throughout the industry.

The thickness of each sample was measured from stamped dog bones, as specified by the test method ASTM D412 (35). Thickness was taken at three different locations, and the mean and standard deviation of the three samples was determined. Thickness was measured using a micrometer at the center and at each end of the thin area of the dumbbell specimen. Each aged sample was measured three different times, with a mean and standard deviation determined for all three. Each aging mechanism contained three samples, with three different means and standard deviations from three different samples.

2.5 Data analysis

All data was compiled and compared to baselines. Each test average, standard deviation, and percent change were computed per sample polymer and compared. Standard deviation was established using three separate measurements from each sample, and three different samples were used per aging mechanism. Furthermore, the percent deviation from the baseline was calculated. They were calculated using the formula (Baseline – Aged sample)/ Baseline X 100. The measurements and standard deviations were all compared in a graph against one

another, with standard deviation bars. One graph was used per test, along with a table of the results. Additionally, a statistical t-test was done on the puncture resistance data, as seen in section 3.2. Three values were computed to determine the significance of the results: p-value, t stat, and a t critical. A p-value less than 0.05 and a t stat less than the t critical value determined if the results obtained were significant, rejecting the null hypothesis (which states that the change is equal to zero).

3.0 Results

3.1 Weight

Table 1 - Summary TPO Weight (grams)			
Aging Method	**Average**	**Standard Deviation**	**Percent change from baseline (%)**
Baseline	5.07	0.05	0.00%
1000 hours QUV	5.08	0.04	0.15%
2000 hours QUV	4.94	0.03	-2.51%
1000 hours humidity and salt at 0.32g/L salt in water	4.87	0.03	-3.97%
1000 hours humidity	5.05	0.04	-0.32%
20 freeze-thaw cycles	5.00	0.13	-1.33%
40 freeze-thaw cycles	5.03	0.12	-0.82%

Table 1 is the numerical summary of weights obtained for the TPO samples. The first column is a list of the aging methods. The second column is the average weights in grams of all samples tested after each aging cycle. The third column is the standard deviation of each category. The fourth column is the percent change from the baseline, expressed in percentage. Negative change is indicative of weight loss, and positive change is weight gain.

The first category represents the baseline weights, with a weight of 5.07 ± 0.05 grams. The biggest decrease seen was for those exposed to the 1000 hours of humidity and salt exposure, with an ending weight of 4.87 ± 0.03 grams. The smallest decrease seen was for those exposed to 1000 hours of only humidity exposure, with an ending weight of 5.05 ± 0.04 grams. Interestingly, the samples

exposed to 1000 hours of QUV exposure ended up gaining weight, with a final weight of 5.08 ± 0.04 grams. In addition, while the weights for the freeze-thaw cycles did not decrease as much as some of the other methods, the standard deviations for the two techniques are much larger than the other techniques.
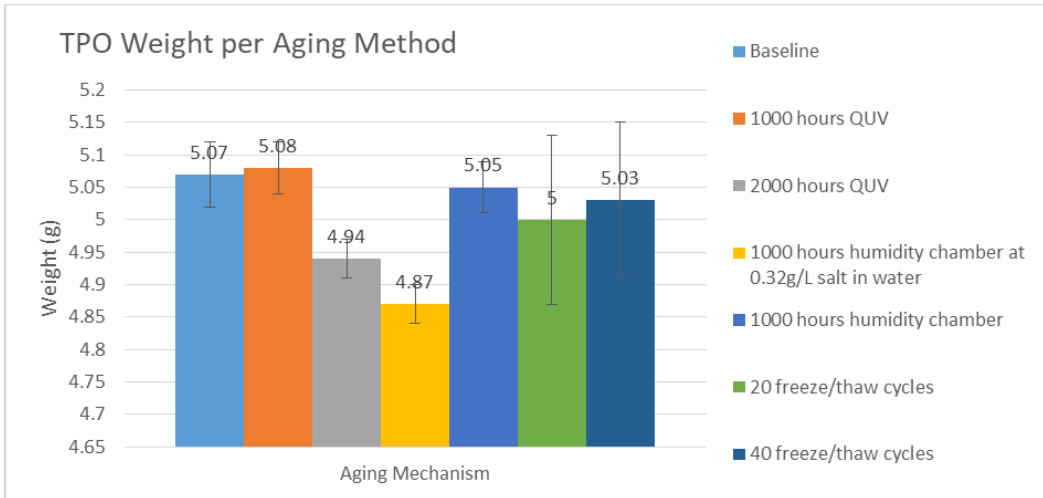
Figure 8. Weight of TPO Samples After Each Aging Mechanism

Figure 8 is a graphical representation of Table 1, in the form of a bar graph. The different aging cycles were compared against the weight in grams. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. For all of the graphs presented, the same colors are used throughout this paper to represent each aging mechanism. Light blue represents the baseline results. Orange represents the 1000 hours in the QUV. Gray represents 2000 hours in the QUV. Yellow represents the salt and humidity. Bright blue represents the 1000 hours of the humidity cycle. Green represents 20 freeze-thaw cycles. Dark blue color represents the 40 freeze-thaw cycles.

When looking at Figure 8, one can see that there is a drastic decrease between the baseline and the 2000 hours QUV and 1000 hours of humidity and

salt spray. While all of the other techniques caused weight loss, with the

exception of 1000 hours of QUV, the weight loss was ultimately minimal, with

the largest percent decrease being 3.97%. The 1000 hours of QUV did experience

weight gain, but with the standard deviations, the weight comparison between

1000 hours of QUV and the baseline is basically equal.

Table 2 – Summary PVC Weight (grams)			
Aging Method	Average	Standard Deviation	Percent change from baseline (%)
Baseline	6.37	0.03	0.00%
1000 hours QUV	6.55	0.04	2.83%
2000 hours QUV	6.58	0.04	3.34%
1000 hours humidity and salt at 0.32g/L salt in water	6.64	0.05	4.24%
1000 hours humidity	6.78	0.05	6.39%
20 freeze-thaw cycles	6.49	0.06	1.87%
40 freeze-thaw cycles	6.55	0.05	2.84%

Table 2 is the numerical summary of weights obtained for the PVC samples. The first column is a list of the aging methods. The second column is the average weights in grams of all samples tested after each aging cycle. The third column is the standard deviation of each category. The fourth column is the percent change from the baseline, expressed in percentage. Negative change is indicative of weight loss, and positive change is weight gain.

The first category represents the baseline weights, with an average of 6.37 ± 0.03 grams. All the different cycles produced higher weights than baseline. The greatest weight change is seen after 1000 hours in the humidity cycle, with average weight of 6.64 ± 0.05 grams. The smallest amount of increase is seen after the two freeze thaw cycles, as well as both QUV cycles.

Figure 9. Weight of PVC after each Aging Mechanism

Figure 9 is a graphical depiction of Table 2 in the form of a bar graph. The different aging cycles were compared against the weight in grams. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. There is a distinct increase in weight of 6.39% after 1000 hours in the humidity cycle, followed by the salt and humidity cycle with an increase of 4.24%. All of the other aging cycles are similar in weight gain, with the largest remaining increase being 3.34%.

Table 3 - Summary EPDM Weight (grams)			
Aging Method	Average	Standard Deviation	Percent change from baseline (%)
Baseline	6.17	0.03	0.00%
1000 hours QUV	6.22	0.02	0.84%
2000 hours QUV	6.38	0.06	3.52%
1000 hours humidity and salt at 0.32g/L salt in water	6.36	0.06	3.08%
1000 hours humidity	6.29	0.02	2.02%
20 freeze-thaw cycles	6.16	0.07	-0.07%
40 freeze-thaw cycles	6.22	0.11	0.95%

Table 3 is the numerical summary of weights obtained for the EPDM samples. The first column is a list of the aging methods. The second column is the average weights in grams of all samples tested after each aging cycle. The third column is the standard deviation of each category. The fourth column is the percent change from the baseline, expressed in percentage. Negative change is indicative of weight loss, and positive change is weight gain.

The first category represents the baseline weights, with an average of 6.17 ± 0.03 grams. All the different cycles produced higher weights than baseline, except for the 20 freeze-thaw cycles where the weights were on par with the baselines. The greatest weight change is seen after 2000 hours in the QUV, with average weight of 6.38 ± 0.06 grams. The greatest deviation of weights is seen after the 20 and 40 freeze-thaw cycles.
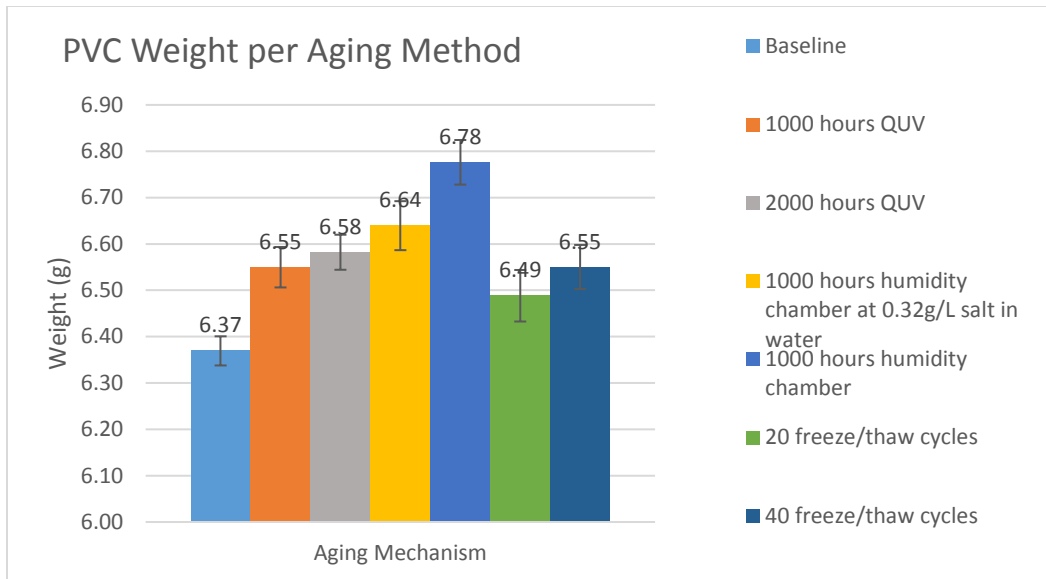
Figure 10. Weight of EPDM after each Aging Mechanism

Figure 10 is a graphical depiction of Table 3 in the form of a bar graph. The different aging cycles were compared against the weight in grams. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. There is a clear increase between the two different hours in the QUV weathering tester, with an increase of 0.84% for 1000 hours and 3.52%% for 2000 hours. Most of the weights did not exhibit a large increase from the baseline, with the largest increase of 3.08%% for the salt and humidity environment, not including the two UV cycles.

3.2 Puncture

Table 4 - Summary TPO Puncture (N)			
Aging Method	**Average**	**Standard Deviation**	**Percent change from baseline (%)**
Baseline	891.11	35.19	0.00%
1000 hours QUV	873.56	46.90	-1.97%
2000 hours QUV	830.00	39.76	-6.86%
1000 hours humidity and salt at 0.32g/L salt in water	856.00	19.29	-3.94%
1000 hours humidity	839.33	72.87	-5.81%
20 freeze-thaw cycles	768.89	44.40	-13.72%
40 freeze-thaw cycles	755.44	48.90	-15.22%

Table 4 is the numerical summary of puncture tested of the TPO samples. The first column is a list of the aging methods. The second column is the average puncture in Newtons (N) of all samples tested after each aging cycle. The third column is the standard deviation of each category. The fourth column is the percent change from the baseline, expressed in percentage. Negative change is indicative of puncture resistance loss, and positive change is puncture resistance gain.

The first category represents the baseline puncture, with an average of 891.11 ± 35.19 N. All the different cycles produced samples with lower puncture than the baseline. The lowest puncture is seen after the two freeze-thaw cycles, with a puncture of 768.89 ± 44.4 N for the 20 cycles and 755.44 ± 48.90 N for the 40 cycles. The higher number of cycles led to lower puncture. Subsequently, more

time in the QUV resulted in lower puncture. Humidity cycle alone resulted in

more puncture loss than humidity and salt cycle, but with greater standard
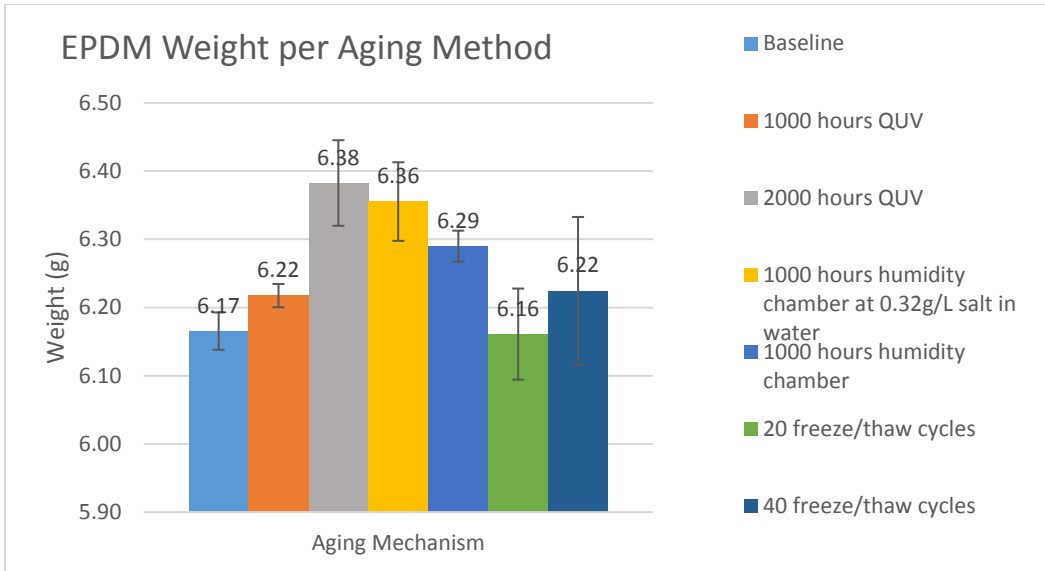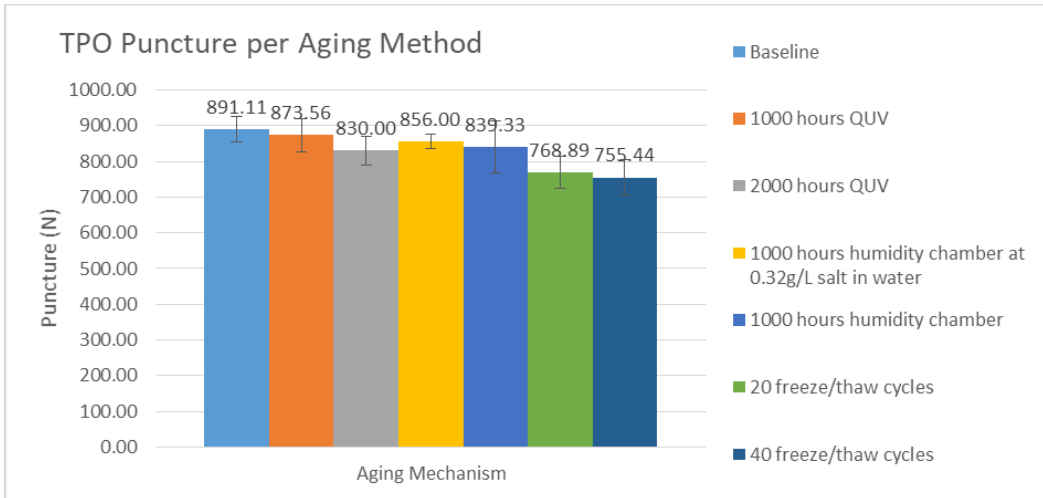
deviation.

Figure 11. Puncture of TPO Samples after Each Aging Mechanism

Figure 11 is a graphical representation of Table 4, in the form of a bar graph. The different aging cycles were compared against the puncture in Newtons. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. It is apparent how the puncture resistance of all the aged membranes decreased after each aging cycle, with the lowest puncture resistance seen at the end of the graph after the freeze-thaw cycles. From this graph, it can be seen that the puncture resistance decreased after being exposed to 1000 hours of humidity cycle, but with great deviation. The 1000 hours in the QUV has a negative impact on puncture with a decrease of 1.97%, but not as high as the one caused by the humidity cycle, with a decrease of 5.81%. The humidity cycle caused a greater decrease in puncture of 3.94% as compared to the combination of salt and humidity with a decrease of 3.94%. There is a direct negative correlation

between increased time in the QUV and puncture resistance. As time increases in the QUV, the puncture of the TPO samples is lowered by 6.86%. After only 20 cycles, there is a loss of puncture resistance of 13.72% as compared to the baseline, but with some deviation. As the number of freeze-thaw cycles increased, the puncture resistance decreased, but at a lower rate than the 20 freeze-thaw cycles.

Table 5 - T-test on the Puncture of TPO				
Comparison	t Stat	t Critical two-tail	P(T<=t) two-tail	Result
Baseline: 1000 hours in the QUV	0.995	2.306	0.349	Not significantly different
Baseline: 2000 hours in the QUV	5.823	2.306	0.000	Significantly different
Baseline: 1000 hours salt and humidity	2.153	2.306	0.063	Not significantly different
Baseline: 1000 hours humidity	2.436	2.306	0.041	Significantly different
Baseline: 20 freeze thaw cycles	6.111	2.306	0.000	Significantly different
Baseline: 40 freeze thaw cycles	5.412	2.306	0.001	Significantly different

Table 5 above displays the results of a statistical t-test done on the values

derived after the puncture test of TPO. The first column identifies the comparison

being tested, which tests all of the aging methods to the baseline. The second,

third, and fourth columns give the values derived directly from the t-test. The fifth

column states whether or not the results are significant or insignificant, based on

the t and p values obtained. After the analysis was done, it can be determined

based on the p-values (>0.05) and t-values (t stat < t critical) that the 1000 hours

in the QUV and 1000 hours of salt and humidity exposure caused insignificant

change from the baseline. Aging methods that had p-values less than 0.05 and a t

stat larger than the t critical were significantly different. In TPO, the significant

difference was seen in 2000 hours in the QUV, 1000 hours of humidity, and the

20 and 40 freeze-thaw cycles.

Table 6 – Summary PVC Puncture (N)			
Aging Method	Average	Standard Deviation	Percent change from baseline (%)
Baseline	1086.00	23.87	0.00%
1000 hours QUV	1068.89	68.35	-1.58%
2000 hours QUV	1014.89	15.46	-6.55%
1000 hours humidity and salt at 0.32g/L salt in water	1022.00	36.15	-5.89%
1000 hours humidity	1046.67	28.53	-3.62%
20 freeze-thaw cycles	976.22	68.25	-10.11%
40 freeze-thaw cycles	1020.67	59.63	-6.02%

Table 6 is the numerical summary of puncture tested of the PVC samples.

The first column is a list of the aging methods. The second column is the average

puncture in Newtons (N) of all samples tested after each aging cycle. The third

column is the standard deviation of each category. The fourth column is the

percent change from the baseline, expressed in percentage. Negative change is

indicative of puncture resistance loss, and positive change is puncture resistance

gain.

The first category represents the baseline puncture, with an average of

1086 ± 23.87 N. All the different cycles produced samples with lower puncture

than the baseline. The lowest puncture is seen after the 20 freeze-thaw cycles with

an average of 976.22 ± 68.25 N, compared to 1086 ± 23.87 N of the baseline.

Subsequently, more time in the QUV resulted in lower puncture, changing from

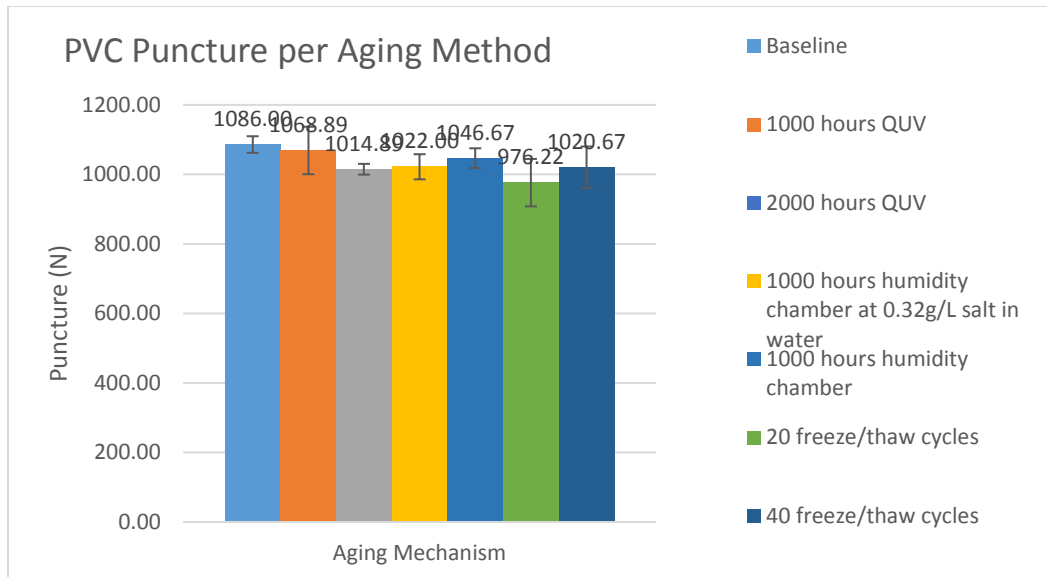1068 ± 68.35 N to 1014.89 ± 15.46 N.

Figure 12. Puncture of PVC after each Aging Mechanism

Figure 12 is a graphical representation of Table 6, in the form of a bar graph. The different aging cycles were compared against the puncture in Newtons. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. It is apparent from the graph how the puncture of PVC decreases after aging mechanism, with emphasis on the lowest puncture value after 20 freeze-thaw cycles (green), with a decrease of 10.11%%. The 1000 hours in the QUV has a negative correlation to puncture resistance with a decrease of 1.58%, but not as high as the one caused by the humidity cycle, which decreased by 3.62%. The combination of humidity and salt cycle caused a greater decrease, of 5.89%, in puncture resistance compared to the humidity cycle alone. There is a direct negative correlation between increased time in the QUV and puncture

resistance. 2000 hours in the QUV produced the second lowest puncture

resistance measurement, with a decrease of 6.55%. The 20 and 40 freeze-thaw

cycles produced the lowest puncture resistance in this study, accompanied with

high deviations.

Table 7 - T-test on the Puncture of PVC				
Comparison	t Stat	t Critical two-tail	P(T<=t) two-tail	Result
Baseline: 1000 hours in the QUV	0.711	2.306	0.497	Not significantly different
Baseline: 2000 hours in the QUV	7.826	2.306	0.000	Significantly different
Baseline: 1000 hours salt and humidity	5.042	2.306	0.001	Significantly different
Baseline: 1000 hours humidity	3.180	2.306	0.013	Significantly different
Baseline: 20 freeze thaw cycles	4.208	2.306	2.306	Significantly different
Baseline: 40 freeze thaw cycles	4.334	2.306	0.002	Significantly different

Table 7 above displays the results of a statistical t-test done on the values

derived after the puncture test of PVC. The first column identifies the comparison

being tested, which tests all of the aging methods to the baseline. The second,

third, and fourth columns give the values derived directly from the t-test. The fifth

column states whether or not the results are significant or insignificant, based on

the t and p values obtained. After the analysis was done, it can be determined

based on the p-values (>0.05) and t-values (t stat < t critical) that the 1000 hours

in the QUV caused insignificant change from the baseline. Aging methods that

had p-values less than 0.05 and a t stat larger than the t critical were significantly

different. In PVC, the significant difference was seen in 2000 hours in the QUV,

1000 hours of salt and humidity, 1000 hours of isolated humidity, and the 20 and

40 freeze-thaw cycles.

Table 8 – Summary EPDM Puncture (N)			
Aging Method	Average	Standard Deviation	Percent change from baseline (%)
Baseline	640.22	15.60	0.00%
1000 hours QUV	655.33	22.18	2.36%
2000 hours QUV	661.11	31.51	3.26%
1000 hours humidity and salt at 0.32g/L salt in water	637.33	14.59	-0.45%
1000 hours humidity	715.11	36.11	11.70%
20 freeze-thaw cycles	599.78	36.99	-6.32%
40 freeze-thaw cycles	633.56	31.43	-1.04%

Table 8 is the numerical summary of puncture tests of the EPDM samples. The first column is a list of the aging methods. The second column is the average puncture in Newtons (N) of all samples tested after each aging cycle. The third column is the standard deviation of each category. The fourth column is the percent change from the baseline, expressed in percentage. Negative change is indicative of puncture resistance loss, and positive change is puncture resistance gain.

The first category represents the baseline puncture, with an average of 640.22 ± 15.60 N. The different cycles presented variable puncture data among the EPDM membranes; some samples presented higher puncture resistance, such as 1000 hours of humidity while others exhibited lower puncture resistance, such as the 20 and 40 freeze-thaw cycles. The highest increase in puncture resistance is

seen after 1000 hours in the humidity cycle at 715.11 ± 36.11 N, while the

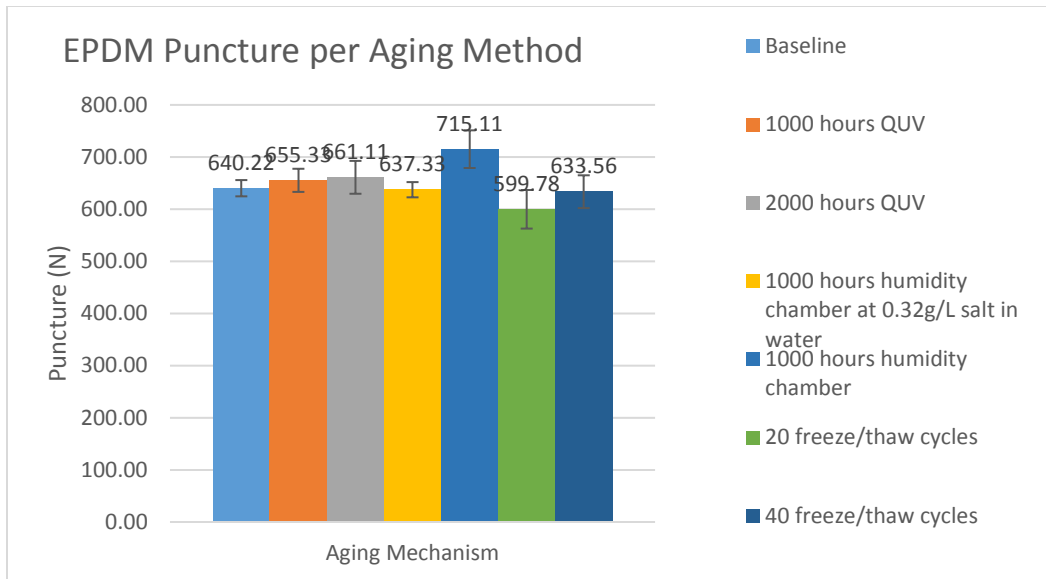greatest decrease was seen after 20 freeze thaw cycles at 599.78 ± 36.99N.

EPDM Puncture per Aging Method

Figure 13. Puncture of EPDM after each Aging Mechanism

Figure 13 is a graphical representation of Table 8, in the form of a bar graph. The different aging cycles were compared against the puncture in Newtons. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. It can be seen that the humidity cycle caused the highest increase in puncture resistance in the EPDM membranes, with an increase of11.7%, whereas the salt and humidity combination cycle resulted in an overall decrease of puncture resistance of 0.45%%. The 1000 hours in the QUV resulted in a slight increase in puncture resistance of 2.36%, whereas the humidity cycle causes a much higher increase of 11.7%. After 2000 hours in the QUV, the samples increased slightly in puncture resistance, with some deviation, by 3.26%. After only 20 cycles of freeze-thaw, there is a loss of puncture resistance compared to

the baseline of 6.32%, but with some deviation. After 40 cycles, the puncture

resistance stayed consistent with the baseline samples, only changing by 1.04%.

Table 9 - T-test on the Puncture of EPDM				
Comparison	t Stat	t Critical two-tail	P(T<=t) two-tail	Result
Baseline: 1000 hours in the QUV	-1.414	2.306	0.195	Not significantly different
Baseline: 2000 hours in the QUV	-2.970	2.306	0.018	Significantly different
Baseline: 1000 hours salt and humidity	0.325	2.306	0.754	Not significantly different
Baseline: 1000 hours humidity	-5.417	2.306	0.001	Significantly different
Baseline: 20 freeze thaw cycles	3.255	2.306	0.012	Significantly different
Baseline: 40 freeze thaw cycles	0.558	2.306	0.592	Not significantly different

Table 9 above displays the results of a statistical t-test done on the values

derived after the puncture test of EPDM. The first column identifies the

comparison being tested, which tests all of the aging methods to the baseline. The

second, third, and fourth columns give the values derived directly from the t-test.

The fifth column states whether or not the results are significant or insignificant,

based on the t and p values obtained. After the analysis was done, it can be

determined based on the p-values (>0.05) and t-values (t stat $<$ t critical) that the

1000 hours in the QUV caused insignificant change from the baseline. After the

analysis was done, it can be determined based on the p-values (>0.05) and t-

values (t stat $<$ t critical) that the 1000 hours in the QUV, 1000 hours of salt and

humidity exposure, and the 40 freeze-thaw cycles caused insignificant change

from the baseline. Aging methods that had p-values less than 0.05 and a t stat

larger than the t critical were significantly different. In EPDM, the significant

difference was seen in 2000 hours in the QUV, 1000 hours of humidity, and the

20 freeze-thaw cycles.

3.3 Thickness

Table 10 - Summary TPO Thickness (mil)			
Aging Method	Average	Standard Deviation	Percent change from baseline (%)
Baseline	42.39	0.49	0.00%
1000 hours QUV	42.50	0.00	0.26%
2000 hours QUV	40.83	0.35	-3.67%
1000 hours humidity and salt 0.32g/L salt in water	41.33	0.25	-2.49%
1000 hours humidity	42.28	0.26	-0.26%
20 freeze-thaw cycles	41.33	1.09	-2.49%
40 freeze-thaw cycles	42.03	1.19	-0.85%

Table 10 is the numerical summary of thickness of the TPO samples. The

first column is a list of the aging methods. The second column is the average

thickness in mils of all samples tested after each aging cycle. The third column is

the standard deviation of each category. The fourth column is the percent change

from the baseline, expressed in percentage. Negative change is indicative of

thickness loss, and positive change is thickness increase.

The first category represents the baseline thickness, with an average of

42.39 ± 0.49 mils.

Most of the thicknesses of the samples are lower than the baseline, with the

lowest thickness seen after 2000 hours in the QUV, measuring at 40.83 ± 0.35

mils. 1000 hours in the QUV produced slightly higher thicknesses than the

baseline, at 42.50 mils, but with no calculated standard deviation, as all samples

measured at the same thickness. Humidity cycle produced higher thickness samples than samples placed in a humidity and salt cycle. Freeze-thaw cycles produced the highest standard deviation, with thickness increase as the number of cycles increased.
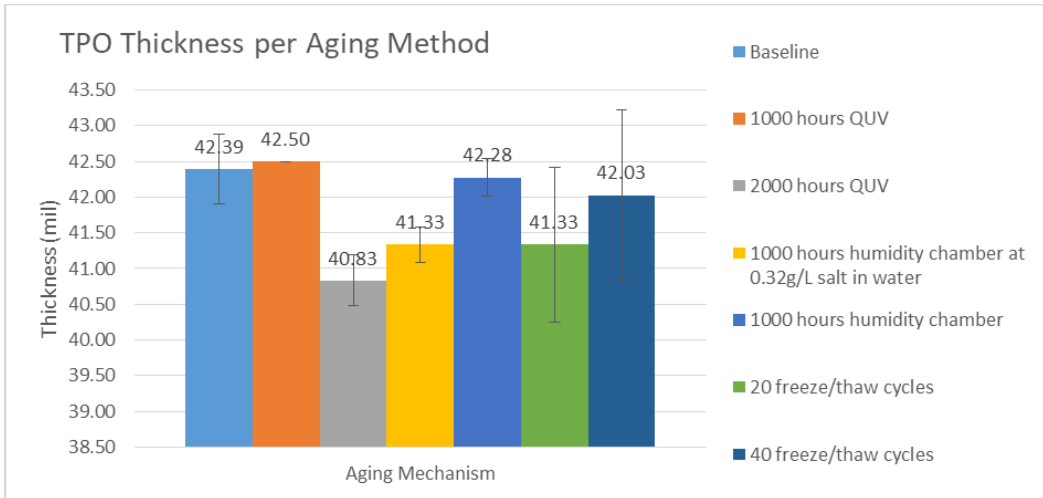
Figure 14. Thickness of TPO Samples after Each Aging Mechanism

Figure 14 is a graphical representation of Table 10, in the form of a bar graph. The different aging cycles were compared against the thickness in mils. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. It can be seen how the thickness of most of the samples are decreased, distinctly after the 2000 hours in the QUV, with a decrease of 3.67%, and 1000 hours of salt and humidity exposure, with a decrease of 2.49%. The samples from the QUV increased in thickness by 0.26%, but the sample thicknesses decreased in the humidity chamber by 0.26%. The first 1000 hours in the QUV caused minor thickness increase of 0.26% as compared to the baseline, but more time in the QUV (2000 hours) caused a more drastic decrease in thickness of 3.67%. After 20 cycles of freeze-thaw, the thickness decreases by 2.49%, but with more cycles, the

thickness increased from the 20 cycles. The standard deviation on the thicknesses

after the freeze-thaw cycles are high.

Table 11 – Summary PVC Thickness (mil)			
Aging Method	Average	Standard Deviation	Percent change from baseline (%)
Baseline	41.61	0.42	0.00%
1000 hours QUV	43.50	0.00	4.54%
2000 hours QUV	43.22	0.26	3.87%
1000 hours humidity and salt at 0.32g/L salt in water	43.50	0.43	4.54%
1000 hours humidity	44.94	0.68	8.01%
20 freeze-thaw cycles	42.06	0.46	1.07%
40 freeze-thaw cycles	42.22	0.55	1.47%

Table 11 is the numerical summary of thickness of the PVC samples. The first column is a list of the aging methods. The second column is the average thickness in mils of all samples tested after each aging cycle. The third column is the standard deviation of each category. The fourth column is the percent change from the baseline, expressed in percentage. Negative change is indicative of thickness loss, and positive change is thickness increase.

The first category represents the baseline thickness, with an average of 41.61 ± 0.42 mils. Thickness of the samples are all higher than the baseline, with the highest measurement after 1000 hours of humidity cycle at 44.94 ± 0.68 mils. The lowest thickness increase was seen after the 20 freeze-thaw cycles, with a value of 42.06 ± 0.46 N. Regardless of the aging method, all thicknesses increased.
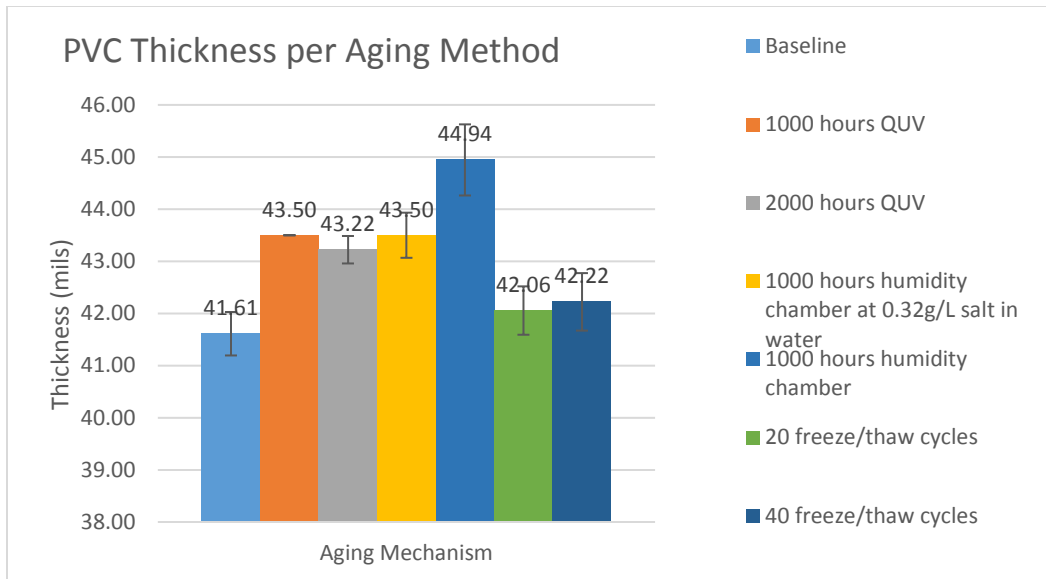
Figure 15. Thickness of PVC after each Aging Mechanism

Figure 15 is a graphical representation of Table 11, in the form of a bar graph. The different aging cycles were compared against the thickness in mils. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. The increase in thickness can be seen, especially after the 1000 hours of humidity exposure, with an increase of 8.01%. The lowest increase is seen after the freeze-thaw cycles, with an increase of 1.07% for the 20 cycles and a slightly higher increase of 1.47% for the 40 cycles. Salt and humidity cycle caused a 4.54% increase in thickness, where 1000 hours resulted in a 4.54% increase, whereas the 2000 hours resulted in a 3.87% increase from the baseline.

Table 12 – Summary EPDM Thickness (mil)			
Aging Method	Average	Standard Deviation	Percent change from baseline (%)
Baseline	42.78	0.51	0.00%
1000 hours QUV	43.83	0.25	2.47%
2000 hours QUV	44.11	0.33	3.12%
1000 hours humidity and salt at 0.32g/L salt in water	44.75	0.22	4.61%
1000 hours humidity	45.89	0.33	7.27%
20 freeze-thaw cycles	42.67	0.50	-0.26%
40 freeze-thaw cycles	43.14	1.75	0.84%

Table 12 is the numerical summary of thickness of the EPDM samples. The first column is a list of the aging methods. The second column is the average thickness in mils of all samples tested after each aging cycle. The third column is the standard deviation of each category. The fourth column is the percent change from the baseline, expressed in percentage. Negative change is indicative of thickness loss, and positive change is thickness increase.

The first category represents the baseline thickness, with an average of 42.78 ± 0.51 mils. Thickness of the samples increased from the baseline after all of the aging cycles except for the 20 freeze-thaw cycles, which decreased slightly to 42.67 ± 0.50 N. The highest increase is seen after the 1000 hours of humidity cycle with a final value of 45.89 ± 0.33 N. The highest deviation is seen after the 40 freeze-thaw cycles, with a standard deviation of 43.14 ± 1.75 N, as compared to the baseline standard deviation of 42.78 ± 0.51 N.
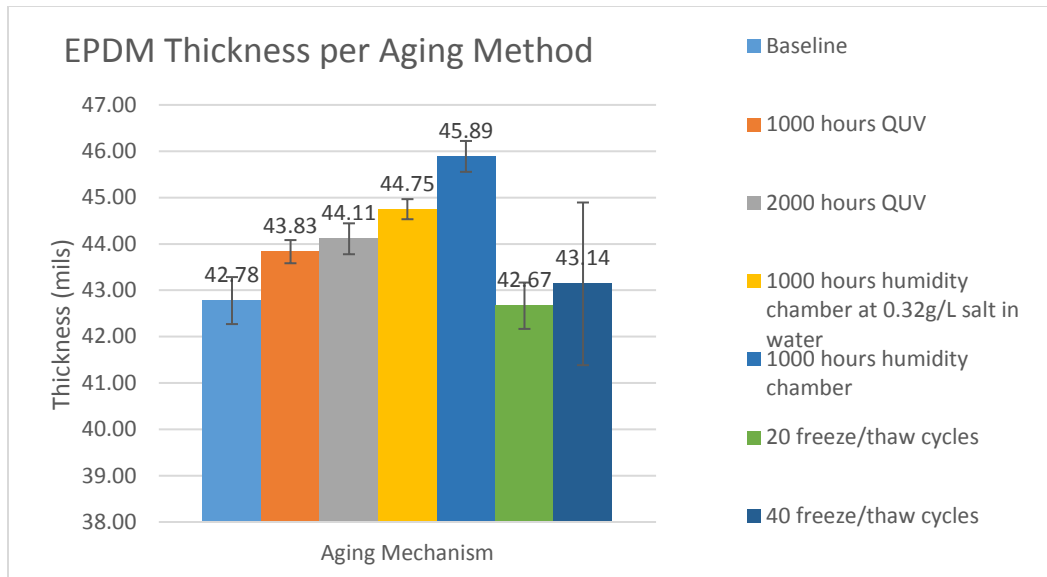
Figure 16. Thickness of EPDM after each Aging Mechanism

Figure 16 is a graphical representation of Table 12, in the form of a bar graph. The different aging cycles were compared against the thickness in mils. Standard deviations bars are above each aging cycle. Each age mechanism is represented by a different color, with the legend on the right for identification. The thickness of the samples increased linearly, through the 1000 hours in the humidity chamber, which increased by 7.27%. 1000 hours of salt and humidity exposure caused an increase of 4.61%. After 1000 hours in the QUV, sample thickness increased by 2.47%, whereas 2000 hours caused an increase of 3.12%. For both the freeze-thaw cycles, the linear trend did not exist, with a decrease of 0.26% in the 20 freeze-thaw cycle and an increase of 0.84% in the 40 freeze-thaw cycle.

4.0 Discussion

4.1 Weight

There is no effect on the weight of TPO samples after being exposed to 1000 hours of controlled humidity (Fig. 8). As the samples were subjected to humidity, they exhibited little to no weight loss, concluding that small additions of water on TPO samples during short term exposure had little effect. TPO is composed of a polypropylene or polyethylene polymer backbone, supplemented with fillers and stabilizers. Without any chemical reactions or higher pressures, polypropylene or polyethylene are not affected by small water additions. When the cycle was combined with salt, a greater decrease of weight was seen compared to the isolated humidity cycle, even short term. The salt environment made the polymer more susceptible to attack and possible hydrolysis. By the weight decrease, salt is associated with chemical polymer degradation and potential oxidation. The samples experience different effects when they were immersed in water and introduced to freezing conditions. The membranes were compromised during the freeze-thaw cycles and lost more weight than during the humidity cycle alone when the water was sprayed in small quantities, but with higher deviations. The fluctuations in temperatures during the freezing and thawing cause stress on the membranes due to the differential in thermal expansion (20). The freezing of water further propagated any impurities in the membranes, resulting in more

detrimental effects on the integrity of the membranes, and in the case of TPO, there was direct weight loss. The effect of UV rays on the weight of TPO samples for 1000 hours are isolated from Figure 8, by comparing baseline weight, the weight of the samples after 1000 hours of QUV (which includes UV heat and humidity), and samples after 1000 hours of isolated humidity cycle. There is little to no effect of 1000 hours of QUV exposure on the weight of TPO samples, which can be associated with the UV stabilizers present in TPO formulations. However, as the time increases in the QUV, sample weights decreased by 2.51% after 2000 hours. UV from the QUV introduces photons onto the aged samples, resulting in breaking of chemical bonds. In the case of the TPO samples, the bond breakage is most likely associated with the oxidation of the polymer. When oxidized, the material begins to lose weight as a result of losing hydrogen atoms from the polymer backbone, either polypropylene or polyethylene. Since the weight decreased, it can be inferred that UV stabilizers are effective for 1000 hours of UV exposure, and have started to degrade at 2000 hours. UV degradation is a big problem on the aging of polymers, such as TPO, and it can be seen that as time increases, degradation increases, and UV stabilizers become less effective.

There is a positive correlation with weight increase on all of the PVC samples in this study. As the samples were subjected to humidity, they exhibited weight gain (Fig. 9). The humidity cycle caused a total of 6.39% increase to the weight of PVC samples. Humidity, or introduction of water intermittently,

resulted in high PVC water retention. PVC is capable of absorbing 0.50 weight%

of the water it is exposed to (36). The top layer of PVC roofing membranes is

polymerized from vinyl chloride monomers, and supplemented with plasticizers,

UV stabilizers, and other additives and pigments. When the humidity is combined

with UV in the QUV for 1000 hours, weight is also increased due to water

retention, but at a small 2.83%, compared to the high 6.39% for humidity. This

change could have been due to the loss of some of the UV stabilizers, which

correlates with the weight decrease. However, with the presence of a water spray,

water uptake by the membranes can be responsible for the slight weight increase

from the baseline. UV could have also caused a shift in plasticizer, resulting in

plasticizer migration out of the membrane. Plasticizers present in the membranes

are not chemically bound to the backbone structure. Thus, when the membranes

are weathered, plasticizers migrate, leaving the membranes to be more brittle and

susceptible to weight loss. Longer exposure in the QUV resulted in higher

increase in weight, at 3.34%, which could be due to the higher water intake from

the 1000 hours. The longer the samples sat in the QUV, the higher the loss of UV

stabilizers and plasticizers, and the more water they retained. When humidity

effects are combined with salt spray, the samples increased in weight, but only at

4.24% from the baseline. The salt could have also forced plasticizer migration,

and more water retention from the humidity cycle. In the membranes, salt could

have replaced the plasticizers, which are not chemically bound to the polymer

backbone, and through diffusion, it drove water into the membranes. This water retention was also seen after the freeze-thaw cycles, which also increased in weight over time. The freezing of the membranes could have also caused migration of the plasticizer, leading to more water retention, and essentially the compromise of the membranes. Increasing the number of cycles increased the weight from the water retention, since the immersion of water increased.

After all of the aging cycles, EPDM exhibited a weight increase except after the 20 freeze-thaw cycles, where the weight did not change (Fig. 10). EPDM was less susceptible to the weight gain than PVC due to natural flexibility of the polymer and the addition of beneficial additives and fillers. In addition to UV stabilizers and plasticizers, EPDM contains carbon black in the formulations, which is a filler that further protects the membrane from UV. After the samples were placed in the QUV, over time, they increased in weight, indicating that some of the membrane began to breakdown due to the high exposure to UV. Plasticizers and carbon black begin to migrate to the surface after UV exposure, which can be depicted in the change of properties of the membranes. During the QUV cycle, the humidity rotation introduces water to the membranes, causing a weight increase. Humidity alone caused a weight increase, but at a much lower rate compared to the combined humidity and UV cycles. The combination of salt and humidity also caused a great increase in weight, insinuating that salt also began to chemically affect the polymer, resulting in higher weight retention. When the

membranes were immersed in water, they exhibited the least amount of weight change. This clarifies that EPDM weight is mostly affected by UV, and degradation becomes a problem when UV is combined with a water cycle.

Out of the three membranes, TPO is the only one that exhibited weight loss after all of the aging cycles (Fig. 8). Similar to PVC, EPDM also has a positive weight correlation after the different aging cycles, but at a lower rate (Fig. 10). For example, humidity presented the highest weight increase on PVC by 6.39%, whereas 2000 hours of QUV caused the highest increase in weight on EPDM at 3.52%. PVC retained water easier than EPDM (Figs. 9-10); EPDM needed to be chemically affected by either UV or salt first in order to retain water. Contrary to both PVC and EPDM, TPO did not retain any water during any of the cycles, and consistently lost weight. This can be more detrimental on the roof, where the cycles are further exacerbated by the combination of the weathering cycles. Out of the three membranes, EPDM behaved the best, followed by PVC, and TPO last, based on the weight loss and gain. The more the weight loss or gain, the more damage occurred, so EPDM exhibited the least amount of damage and TPO exhibited the most amount of damage.

The three membranes behaved differently after each aging cycle, though there were general trends that were followed. The effect of weight after 1000 hours of aging is minimal, under 1%, in TPO and EPDM but it presented a larger

deviation in PVC with a 2.83% increase from the baseline. Extended aging in the QUV for 2000 hours caused a greater change in EPDM and TPO, but a smaller increase in PVC. UV stabilizers in TPO and EPDM can be slightly different than the ones present in this specific PVC membrane. UV stabilizers in TPO and EPDM stabilizers also behaved differently, since TPO was affected negatively and lost weight, while EPDM gained weight. This is also dependent on the formulations, type of pigment used, and the quality of the polymer backbone. The presence of an intermittent water source, as seen in the humidity cycle, affected TPO differently than both PVC and EPDM. TPO lost a small amount of weight, while PVC and EPDM gained weight. Although the same effect was seen, PVC gained more weight than EPDM; PVC is more likely to absorb water, as previously mentioned. The same pattern was seen when the membranes were exposed to a combination cycle of salt and humidity. TPO lost weight, while PVC and EPDM gained weight, with PVC gaining more weight than EPDM. The freeze-thaw cycles followed the same pattern as the other cycles: TPO lost weight while PVC and EPDM gained weight. The amount of weight gained or lost increased with the increasing number of cycles. Overall, the membranes followed similar patterns during each aging cycle: TPO lost weight while PVC and EPDM gained weight, with PVC gaining weight a greater rate than EPDM.

4.2 Puncture

The puncture resistance of TPO decreased after each aging method (Fig. 11). The most significant decrease is seen after the 20 and 40 freeze-thaw cycles, at 13.72% and 15.22% respectively (Fig. 11, green and dark blue). The percentage increased with the increasing number of cycles. The temperature fluctuations evidently compromised the membranes due to the thermoplastic nature of the polymer, resulting in potential polymer degradation. Thus, when stress was applied onto the membranes, their ability to withstand the stress was lowered by a high percentage. The water from the refrigerator cycle could have also expanded during the freezing cycle, resulting in more polymer damage and weakening of the TPO membranes. The degradation effects were also seen when the membranes were exposed to small amounts of water, via the humidity cycle, but to a lesser degree. The puncture resistance loss averaged 5.81% from the baseline. When the humidity cycle was combined with UV for 1000 hours, initial results showed insignificant puncture resistance loss, at 1.97%, which can be correlated with the presence of UV stabilizers in the formulations of TPO. However, extended UV and humidity at 2000 hours resulted in a large decrease in puncture resistance, insinuating that at 2000 hours, UV stabilizers were becoming ineffective resulting in compromised membranes. This can be due to the migration or breakdown of the stabilizers, from UV and humidity. When humidity was combined with the salt spray for 1000 hours, puncture resistance decreased by 3.94%, which was determined as insignificant change by the t-test results. It is unclear how the

membranes will behave after 2000 hours of salt exposure, but 2000 hours of QUV was more detrimental to the puncture resistance of the membranes than 1000 hours of QUV.

Similar to TPO, PVC membranes lost significant puncture resistance after all of the aging methods except for the 1000 hours of QUV exposure (Fig. 12). The most significant decrease was seen after 20 freeze-thaw cycles, measuring at 10.11% loss ($p<0.05$ and t stat>t critical). When weighed, the PVC membranes gained weight during the cycles, due to water retention. This initial water retention made the membranes more susceptible to puncture, especially when combined with freezing and expansion of ice in the membranes. The 40 freeze-thaw cycles caused a decrease of only 6.02%. This increase is superficial, since the membranes did not improve; these numbers could be a result of experimental error and are accounted for in the standard deviation. Water retention could have also been the cause of puncture resistance decrease when analyzing the effects of humidity spray onto the samples. However, the effects were more apparent when humidity was combined with a salt spray or UV. Salt and humidity caused a 5.89% loss, whereas humidity alone caused a 3.82% decrease. Salt could have forced important additives such as plasticizers out of the membranes, resulting in more brittle and puncture prone PVC. With the combination of humidity with UV, initially, the membranes were able to withstand puncture closely with the baseline, as verified by the insignificant change from the t-test ($p>0.05$ and t

stat<t critical). As time progressed in the QUV to 2000 hours, the membranes

exhibited 6.55% decrease of puncture resistance. Like TPO, membranes could

have lost some of the UV stabilizers at 2000 hours, resulting in decreased ability

to resist UV degradation effects described earlier.

Unlike TPO and PVC, EPDM membranes exhibited variable effects of

puncture resistance (Fig. 13). The most dramatic change was seen after 1000

hours of humidity exposure, where EPDM gained a significant 11.7% of puncture

resistance ($p<0.05$ and t stat>t critical). Humidity caused weight gain in the

membranes, concluding that water retention could have been the cause of the

increase. The uptake of water by thermosets results in the increase of their

mechanical properties. In EPDM, the uptake of water was seen in the increase of

puncture resistance of the membrane. When humidity was combined with salt, the

change was seen as a small decrease of puncture resistance at 0.45%, and verified

as insignificant ($p>0.05$ and t stat<t critical). Thermosets, like EPDM, are less

susceptible to corrosion and have high heat resistance. The second phenomenon

explains the small change of puncture resistance after QUV aging compared to

TPO and PVC. EPDM experiences an insignificant change of puncture resistance

($p>0.05$ and t stat<t critical) after only 1000 hours. The combination of the

thermoset polymer and the addition of carbon black makes EPDM less susceptible

to UV effects. Temperature fluctuations, like freeze-thaw conditions, caused an

overall decrease in puncture resistance, with a higher decrease after 20 freeze-

thaw cycles. The effects of the 40 cycles are less prominent and determined to be insignificant (p>0.05 and t stat<t critical), which could also be due to experimental error and standard deviation. The weight of the membranes after the temperature fluctuations was not affected, which can be the result of the thermoset properties of the membrane. Hence, the membranes were less likely to retain water, but more likely to have been compromised or fatigued when exposed to water and freezing conditions. These results can be further verified by increasing the number of freeze-thaw cycles on the membranes.

After comparison, the two thermoplastic membranes, TPO and PVC, exhibited significant puncture resistance decreases after all aging methods except for 1000 hours of QUV and humidity and salt cycles for TPO (Figs. 11-12). EPDM was the only thermoset and its behavior varied based on the aging environment (Fig. 13). TPO and PVC behaved similarly after 2000 hours in the QUV, which suggests that the type of UV stabilizers such as the white pigment (Titanium Dioxide) used in both formulations have similar efficacy. Due to the nature of the thermoset polymer and the addition of carbon black to the formulations, EPDM behaved better when it was exposed to UV than both thermoplastic membranes. The polymer also behaved better after temperature fluctuations in the freeze-thaw cycles than TPO and PVC. The decrease in puncture was the greatest in TPO, followed by PVC, then EPDM. Corrosion from the salt environment affected PVC more than TPO, and EPDM was affected the

least. Repeatedly, the puncture resistance of EPDM was better than the thermoplastic membranes, and in some cases, increased instead of decreased as expected.

All the aging cycles presented different effects on the puncture of the membranes. After 1000 hours of QUV exposure, none of the membranes exhibited any significant puncture resistance change ($p > 0.05$ and t stat < t critical). The same pattern was followed after 2000 hours of QUV exposure, but EPDM showed a positive change. EPDM behaved better after QUV aging, which can be associated with the presence of carbon black with the combination of UV stabilizers in the formulations. Both TPO and PVC contain Titanium Dioxide, and both showed a more prominent negative trend after 2000 hours of aging. When the membranes were exposed to a humidity cycle, TPO and PVC continued to lose puncture resistance, while EPDM gained a large percentage. The combination of salt and humidity caused insignificant changes on the puncture of EPDM and TPO, while decreasing the puncture resistance of PVC. Freeze-thaw conditions caused all of the membranes to lose puncture resistance. It is clear that the freezing, thawing, and immersion of the membranes in water compromises their integrity and ability to withstand puncture. The thermoplastic membranes were more affected by the temperature fluctuations, whereas the thermoset was the least affected. Although all three were negatively affected, TPO lost the highest amount of puncture resistance, followed by PVC, then EPDM.

4.3 Thickness

Similar patterns, as expected, were seen after weighing and measuring the thicknesses of the single ply membranes; with loss of mass, there is a loss of thickness. For TPO, the greatest decrease was seen after extended hours in the QUV (Fig. 14). After the first aging cycle of 1000 hours, the TPO membranes lost no membrane thickness, which is expected since the formulations of TPO include UV stabilizers that are present for UV protection. However, these UV stabilizers lost efficacy after extended hours in the QUV, and when finally tested at 2000 hours, the thickness of the membranes had decreased by 3.67% from the baseline. This change is substantial since single ply membranes are known to decrease by less than a mil a year. A 3.67% decrease is equivalent to a loss of 1.5 mils, and 2000 hours in the QUV are equivalent to only 9 months of normal aging on the roof (1 hour in the QUV is representative of 3 hours on the roof). This type of TPO was more susceptible to aging from UV and humidity effects. When humidity was isolated, the decrease of thickness was less prominent, resulting in a 0.26% decrease. Under no high pressures or increase in temperatures, polypropylene and polyethylene are less likely to be affected by small additions of water. When humidity was combined with a salt spray, the membranes lost more thickness, averaging at a loss of 2.49%. This decrease is also substantial and representative of 1.06 mils, which is directly proportional to the loss of mass. Salt

in the cycle could have attacked the polymer backbone, resulting in cross-linking and hence the thickness decrease. When TPO was immersed in water, a 2.49% decrease was seen after the freeze-thaw cycles. Temperature fluctuations and the freezing of water is detrimental to the life of TPO membranes, as seen by the decrease in weight and drastic decrease in puncture resistance.

Similar to the change seen in PVC weight calculations, PVC increased thickness throughout the experiment, regardless of aging method (Fig. 15). The most drastic increase was seen after the humidity cycle, averaging at 8.01% increase from the baseline. Similar to the weight increase, PVC was more likely to retain water than TPO, which is responsible for the thickness increase seen. When the humidity cycle was combined with a salt spray, there was a less prominent increase. Salt was more likely to slow down the water retention of the polymer by attacking additives such as plasticizers in the membranes, causing them to shift or migrate. In theory, as the plasticizers migrate to the surface, the membranes were able to retain less water. Plasticizers are like oils and repel water, which correlates to the less water retention of the membranes. This decrease in water retention was also seen when combined with UV or freeze-thaw conditions. From the baseline, the first 1000 hours of QUV presented a 4.54% increase, whereas 2000 hours resulted in 3.87% increase. As seen by the puncture results, UV stabilizers in PVC were more effective for 1000 hours of QUV aging, and less effective as time increased. The first 1000 hours could be the start of the

aging of PVC under these conditions, and as time progresses, thickness begins to fall. Instead of resulting in a straight linear decreasing relationship, the two aging methods could related by a polynomial or exponential relationship, and more data is required to establish the actual trend. When the membranes were exposed to water and temperature fluctuations, the membranes gained a small increase in thickness after the freeze-thaw cycles. When the membranes were immersed in water, they retained a small amount of water. When they were frozen, the water expanded, causing propagation of any impurities, resulting in only a small increase of thickness. However, this compromise is apparent when evaluating the puncture resistance of the membranes after the freeze-thaw conditions, which was substantial compared to the humidity cycle alone.

Similar to PVC increase in thickness, EPDM membranes increased in thickness after all the aging cycles, except for the 20 freeze-thaw cycles, where the thickness fluctuated below the baseline (Fig. 16). The highest thickness was also seen after the isolated humidity cycle, with an average of 7.27% increase from the baseline. EPDM allowed for water retention, which also is the likely cause of the increase of weight in the membranes. When humidity was combined with UV or salt, the change was less substantial. In the QUV, the membranes gained 2.47% and 3.12% of thickness at 1000 hours and 2000 hours of exposure, respectively. The UV effects were mostly blocked by the use of carbon black, UV stabilizers, and plasticizers in EPDM membranes. The higher the exposure, the

higher the effects of UV on the membranes due to additive shift or loss, making

the membranes more susceptible to water retention. Similar effects were seen

after salt exposure, which lessened the amount of water retention in the

membranes, resulting in thinner thicknesses than the ones caused by isolated

humidity exposure. The freeze-thaw cycles caused little change in thickness of the

membranes, indicating little water retention during immersion and freezing of the

membranes. However, when combined with the puncture results, these

thicknesses are not an indication of unaffected membranes. The freeze-thaw

conditions worsened the membranes, resulting in the loss of puncture resistance

compared to the baseline. Temperature fluctuations combined with the

introduction of water and freezing of water compromised the membranes,

although these results are not apparent through the small thickness change.

Once again, TPO behaved differently than PVC and EPDM after the aging

cycles (Figs. 14-16). The thickness of TPO decreased after all of the aging

methods, except for the 1000 hours of QUV exposure, where it fluctuated slightly

above the baseline. PVC and EPDM gained weight after the cycles, except when

EPDM was introduced to 20 freeze-thaw cycles. Overall, TPO behaved the

poorest because it started to lose thickness from the initial conditions. Once again,

when these membranes are placed on the roof, they exhibit one or more of these

cycles, indicating worse conditions long term than the lab environment. Since

TPO was not able to withstand initial trials in the lab, it is likely that it will

behave poorly on the roof compared to PVC and EPDM. PVC continued to exceed TPO measurements but did roughly 1% worse in thickness than EPDM during all of the cycles. The presence of carbon black in the formulations allows EPDM to exceed the white membranes that have a different color pigment. Thus, as a conclusion from the thickness results, EPDM behaved the best, followed by PVC, followed by TPO. The more the membranes gained thickness, the more water retention is allowed into the membranes, resulting in poor physical testing, such as puncture. Losing thickness indicates loss of mass, and that correlates to less material to withstand weathering conditions and physical testing. EPDM results fluctuated near the baseline thickness, indicating the least amount of damage by the aging cycles.

After 1000 hours of aging in the QUV, the thickness of all three membranes increased, with the smallest deviation seen in TPO. After 2000 hours of aging, the thickness of TPO began to decrease, while PVC and EPDM continued to increase. Once again, TPO lost thickness, while PVC and EPDM gained thickness, with PVC increasing at a higher rate. EPDM behaved better over time, which is a function of the formulations and color of the membrane. The humidity cycle for 1000 hours resulted in thickness decrease of TPO, and thickness increase in PVC and EPDM. The thickness decrease in TPO is minimal, deviating slightly below the baseline. PVC and EPDM, however, increased thickness at a higher rate than TPO lost thickness. This can be due to the

assumption that PVC and EPDM gained water during the water cycles, and TPO did not accept any water, verified by the weights. When the humidity cycle was combined with salt, TPO lost thickness, while PVC and EPDM gained thickness. Once again, TPO retained no water, and lost thickness at a slower rate than PVC and EPDM gained millage. The freeze-thaw cycles resulted in thicknesses of the membranes near the baseline. However, similar to the other aging methods, TPO lost thickness, while PVC and EPDM gained a small percentage of thickness.

Overall, the aging environments affected the three membranes distinctly. QUV aging caused a loss of weight, puncture resistance, and thickness of TPO. The higher the hours in the QUV, the higher the loss of properties of TPO, which can be correlated to polymer cross-linking by UV. PVC increased in both weight and thickness, and the increase was further exaggerated with increasing number of hours in the QUV, as the membranes retained more water. Although weight and thickness increased, the puncture resistance of PVC decreased after QUV aging, which could be linked to plasticizer migration or even cross-linking. QUV effects were more detrimental on the white thermoplastic membranes, since EPDM was only positively affected in weight, puncture resistance, and thickness. As the membranes spent more time in the QUV, EPDM test results continued to increase. EPDM is more UV stable due to the presence of carbon black and its thermoset properties. The humidity cycle resulted in similar effects on the three membranes. TPO lost weight, puncture resistance, and thickness. PVC membranes

demonstrated large weight and thickness increases, mostly due to water retention. However, as seen in the QUV results, the puncture of PVC decreased slightly after the humidity cycle, which can also be linked to plasticizer migration. EPDM saw a high increase in both puncture and thickness, with a small increase in weight, indicating water retention. As the humidity cycle was combined with salt, TPO lost a large percentage of its weight and a small amount of puncture and thickness, since there was no apparent retention of water. PVC increased in weight and thickness, but once again, lost puncture resistance after salt and humidity cycle. Similarly, EPDM increased in weight and thickness, but the membranes demonstrated small changes in puncture resistance. There was water retention to affect weight and thickness, but not enough to influence the puncture resistance. Freeze-thaw conditions caused similar results in all three membranes with respect to puncture resistance. In TPO and PVC, there was a large decrease in puncture resistance, and EPDM showed a smaller decrease. TPO and PVC are more affected by temperature fluctuations due to their thermoplastic nature, whereas the thermoset EPDM was able to withstand the thermal stress better. TPO continued to lose weight and thickness, PVC continued to slightly increase in weight and thickness, while EPDM saw a very small change.

5.0 Conclusion

The three membranes used for experimentation in this study were TPO, PVC, and EPDM. The objective was to identify the effects of regional weathering patterns on the life of the membranes. Six different aging cycles were used to represent isolated weathering patterns in the country. The six patterns imitated were 1000 hours of QUV, 2000 hours of QUV, 1000 hours of combined salt and humidity cycle, 1000 hours of isolated humidity cycle, 20 freeze-thaw cycles, and 40 freeze-thaw cycles. All membranes were cycled and tested against the baseline. The weight, puncture resistance, and thickness were measured after each cycle of each membrane.

The weights of the membranes varied depending on the type and the aging cycle. Overall, TPO lost weight after each aging cycle, whereas PVC and EPDM gained weight. TPO membranes were degrading, whereas PVC and EPDM were retaining water. The puncture resistance of EPDM was mostly increased after the cycles, whereas PVC and TPO puncture resistance decreased. Additionally, the thicknesses of the membranes varied after each aging cycle. TPO thickness consistently decreased throughout the experiment, whereas PVC and EPDM increased in thickness. Overall, TPO lost weight, puncture resistance, and thickness after the majority of the aging methods. Although PVC did not lose any weight or thickness during the cycles, the puncture resistance of the membranes

decreased in comparison to EPDM. EPDM weight and thickness increased, and most of the aging cycles produced membranes with higher puncture resistance than the baseline.

To better understand how regional weather affected the membranes, they were further analyzed by aging cycle. Humidity alone resulted in weight and thickness increase in EPDM and PVC and a decrease in TPO. When exposed to UV and humidity, the weight of EPDM fluctuated the least, mostly due to the coloration of the membrane with carbon black with the use of plasticizers. It would be safe to conclude that in regions with high humidity and UV, EPDM would excel compared to PVC and TPO. In regions with high salt and humidity, like South Florida, EPDM would also excel compared to TPO and PVC. Although EPDM was more stable, it absorbed more water than TPO and PVC, which could become problematic in areas with low heat. In regions with freeze-thaw conditions, such as the ones seen in Ohio, EPDM was the least affected by weight, puncture, and thickness. The puncture of PVC and TPO was highly compromised after the freeze-thaw conditions, losing 10-15% of puncture resistance in TPO and 6-10% in PVC. Temperature fluctuations were more detrimental on the thermoplastic membranes, TPO and PVC, than the thermoset EPDM.

6.0 Future Work

Further analysis is required to confirm the conclusions made about the different membranes. First, more physical tests need to be conducted on the membranes in order to verify mode of failure, especially after some of the more detrimental aging cycles. Two important tests used on roofing membranes are tensile strength and elongation using ASTM D412. Although tensile strength is mostly a product of the reinforcement used, it typically gives an indication of the brittle behavior of the membranes. Elongation is used to test how long the polymers can be stretched when a force is applied. It is unclear how the membranes will behave after these tests, but it would be beneficial to tie the results to the conclusions drawn in this study to confirm the assumptions made. Second, chemical analysis should be conducted using Fourier Transform Infrared Spectrometer (FTIR) in order to confirm water retention, oxidation, plasticizer migration, and polymer degradation. The spectroscopy can be used to confirm such assumptions by analysis of the spectrum transmitted or absorbed. In addition, more mechanical tests like a dynamic mechanical analysis (DMA) can be done to determine the molecular weight distributions of the polymers to determine the mechanical properties of the membranes and their elasticity.

Once the additional three tests are conducted, the process of including these trends into a service life formula at Simon Roofing (SR) can be initiated. At

SR, a homegrown program is used to test the service life of a roof. With these trends, the testing process can be improved with regional aging effects on the membranes, improving the age of the roof that is calculated.

Furthermore, it would be beneficial to include longer aging cycles of the membranes. For example, the weight and thickness of PVC and EPDM were increased after aging of the membranes from 1000 to 2000 hours. In order to determine the tipping point to loss of material and thickness, the membranes need to be aged for longer than 2000 hours in the QUV and salt and humidity chambers, and for more than 40 freeze-thaw cycles. The results will confirm the rate of decomposition of the membranes in order to draw a complete life cycle of the membranes.

In order to get a clear understanding of the different formulation effects, more manufacturers need to be compared, and more than one roll needs to be used from the same manufacturer. That will help demonstrate the intensity of the effect that each manufacturer has on the life of the membrane, and the quality of the membranes coming out of the manufacturing facility.

In the long run, field data should be used to create an aging model of the membranes. This field data can be used to confirm the trends and to tighten the error in the model predicted. The model can be a more detailed version of the following equation:

$$\frac{dAg}{dt} = f\{W, Th, E, TS, Ox, Pm\}$$

Where dAg/dt is the rate of aging as a function of W, Th, E, TS, Ox, and Pm. W is weight, Th is thickness, E is elongation, TS is the tensile strength, Ox is oxidation, and Pm is plasticizer migration.

7.0 References

1. **Cash, Carl G.** *Roofing Failures.* London : Taylor & Francis, 2003.

2. **Weiler, Susan and Scholz-Barth, Katrin.** *Green Roof Systems: A Guide to the Planning, Design, and Construction of Landscapes Over Structure.* Hoboken, NJ : John Wiley & Sons, 2009.

3. **Gumpertz, W. H.** *Single-Ply Roofing Technology.* s.l. : ASTM International, 1982.

4. *Failure Investigation and Testing of Single-Ply Roofing Membranes.* **Nelson, Peter E.** 1985, Second International Symposium on Roofing Technology, pp. 86-88.

5. **Ramsey, Charles George and Sleeper, Harold Reeve.** *Architectural Graphic Standards: Student Edition.* Hoboken, NJ : John Wiley & Sons, 2011.

6. *A radically new UV stabilizer for flexible PVC roofing membranes.* **Capocci, G. and Hubbard, M.** 2005, Journal of Vinyl and Additive Technology, pp. 91-94.

7. **Young, Robert J and Lovell, Peter A.** *Introduction to Polymers.* Boca Raton, FL : Taylor & Francis Group, 2011.

8. *Longevity and Ecology of Polyolefin Roofing Membranes.* **Beer, Hans-Rudolph.** Gaithersburg, MD : NRCA, 1997. Fourth International Symposium on Roofing Technology. pp. 14-20.

9. *Heat Release Rate: The Single Most Important Variable in Fire Hazard.* **Babrauskas, V. and Peacock, R. D.** 1992, Fire Safety Journal, Volume 18 Issue 3, pp. 255-272.

10. *Accelerated Aging of Thermoplastic Polyolefin Membranes-Prediction of Actual Performance.* **Taylor, T. J and Xing, L.** 2015, Roofing Research and Standards Development: 8th Volume, pp. 139-152.

11. **ASTM International.** ASTM D6878, Standard Specification for Thermoplastic Polyolefin Based Sheet Roofing. West Conshohocken, PA : ASTM International, 2011.

12. **Deaton, K., Martin, N.** Putting Membranes to the Test: A Comparison of Methods for Predicting Long-Term Performance of Commercial Roofing Membranes. *Roofing Contractor Magazine.* 2013.

13. **Clark, Mark M.** *Transport Modeling for Environmental Engineers and Scientists.* Hoboken, NJ : John Wiley & Sons, 2009.

14. *Shattering of Unreinforced PVC Roof Membranes: Problem Phenomenon, Causes and Prevention.* **Paroli, R., Smith, T. and Whelan, R.** Gaithersburg, MD : NRCA, 1993. 10th Conference on Roofing Technology: Problem: Issues and Answers. pp. 93-107.

15. *Aging Criteria for PVC Roofing Membranes.* **Lys, H.P.** Washington, D. C. : NRCA, 1985. Second International Symposium on Roofing Technology. pp. 270-274.

16. *Roofing Coverings Made of PVC Sheetings: The Effect of Plasticizers on Lifetime and Service Performance.* **Patuska, Gerhard.** Rosemont, IL : National Roofing Contractors Association, 1985. Second International Symposium on Roofing Technology. pp. 173-176.

17. *Dynamic Mechanical Properties of Single-Ply Roof Coverings for Low-Slope Roofs and the Influence of Water.* **Oba, K. and Bjork, F.** 1993, Polymer Testing 12, pp. 35-56.

18. *Field Evaluation and Laboratory Testing of PVC Roof Systems.* **Koontz, Jim D.** Gaithersburg, MD : NRCA, 1997. Fourth International Symposium on Roofing Technology. pp. 22-27.

19. *Shrinkage of EPDM Roof Membranes: Phenomenon, Causes, Prevention, and Remediation.* **Paroli, R. M., et al.** Gaithersburg, MD : NRCA, 1995. 11th Conference on Roofing Technology. pp. 90-110.

20. *Weathering of roofing materials – An overview.* **Berdahl, Paul, et al.** 2008, Construction and Building Materials 22, number 4, pp. 423-433.

21. *Weathering Tests for EPDM Rubber Sheets for Use in Roofing Applications.* **Gish, B. D. and Jablonowski, T. L.** Gaithersburg, MD : NRCA, 1987. 8th NBS/NRCA Conference on Roofing Technology. pp. 54-68.

22. *Outdoor Exposure of EPDM Roofing Membrane.* **Strong, A. G. and Puse, J.W.** Gaithersburg, MD : NRCA, 1985. Second International Symposium on Roofing Technology. pp. 376-382.

23. *Evaluating the Effects of Aging on Thermal Properties of EPDM Roofing Materials.* **Penn, J. and Paroli, R.** 1993, Thermochimica Acta, pp. 77-84.

24. **Rosenfield, M. J., Folrz, S. D. and Bailey, D. M.** *Long Term Field Results of Experimental EPDM and PUF Roofing.* Champaihn, ILL : Construction Engineering Research Lab (Army), 1990.

25. *Effect of Temperature and Stress on the Time-to-Failure of EPDM T-Peel Joints.* **Martin, J. W., Embree, E. and Bentz, D. P.** Gaithersburg, MD : NRCA, 1988. 8th Conference on Roofing Technology. pp. 69-74.

26. *A Theory to Explain Roof Splitting By Ice.* **Riedel, Roger G.** Gaithersburg, MD : NRCA, 1985. Second International Symposium on Roofing Technology. pp. 112-115.

27. *Developing a Test Method for a Very Severe Hail Rating for Low Slope Roofing Assemblies.* **Boardman, D. A. and Brown, D. E.** 2015, Roofing Research and Standards Development: 8th Volume, pp. 1-13.

28. **Q-fog.** *Cyclic Corrosion Testers: Q-fog brochure.* Westlake, OH : s.n., 2011.

29. —. *Q-lab Corporation: Q-lab Products and Services Summary.* Westlake, OH : s.n.

30. **ASTM International.** ASTM B117-16, Standard Practice for Operating Salt Spray (Fog) Apparatus. West Conshohocken, PA : ASTM International, 2016.

31. ***Salinity and Hydrology of Florida Bay: Status and Trends 1990-2009.* Homestead, Florida : South Florida Natural Resources Center Everglades National Park, 2012. SFNRC Technical Series.**

32. **Taylor, Jessica E. Practical Salinity Unit (PSU).** *MyNASAData.* **[Online] November 7, 2017. mynasadata.larc..nasa.gov.**

33. ***Freeze-Thaw Durability of Common Roof Insulations.* Tobiasson, W., Young, B. and Greatorex, A. Gaithersburg, MD : NRCA, 1999. Fourth International Symposium on Roofing Technology. pp. 252-259.**

34. **ASTM International. ASTM D5602 / D5602M-11, Standard Test Method for Static Puncture Resistance of Roofing Membrane Specimens. West Conshohocken, PA : ASTM International, 2011.**

35. **ASTM International. ASTM D412-16, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension. West Conshohocken, PA : ASTM International, 2011.**

36. **GEHR Plastics PVC-C.** *Material Property Data.* **[Online] MatWeb, LLC, 2018.**