

EFFECT OF POLYMER DESIGN AND COATING FORMULATION ON THE WATER UPTAKE  
AND SENSITIVITY OF ACRYLIC WATER-BORNE FILMS

A Thesis

presented to

the Faculty of California Polytechnic State University,

San Luis Obispo

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Polymers and Coatings

by

William Zachary Thompson

June 2020

© 2020

William Zachary Thompson

ALL RIGHTS RESERVED

## COMMITTEE MEMBERSHIP

TITLE: Effect of Polymer Design and Coating Formulation  
on the Water Uptake and Sensitivity of Acrylic  
Water-Borne Films

AUTHOR: William Zachary Thompson

DATE SUBMITTED: June 2020

COMMITTEE CHAIR: Erik Sapper, Ph. D  
Assistant Professor of Chemistry

COMMITTEE MEMBER: Karl Booth, M.S.  
Research and Development Group Leader  
Sherwin-Williams Co.

COMMITTEE MEMBER: Howard Killilea, M.S., M.B.A, J.D.  
Global Technical Director  
Sherwin-Williams Co.

## ABSTRACT

### Effect of Polymer Design and Coating Formulation on the Water Uptake and Sensitivity of Acrylic Water-Borne Films

William Zachary Thompson

Water-borne latex coatings represent a safer, more user-friendly, and environmentally responsible alternative to solvent-borne coatings, and are growing in popularity each year. However, these coatings often exhibit unfavorable performance when exposed to water for extended periods of time. This prolonged exposure often results in water uptake, which may give rise to other detrimental effects such as a decrease in modulus, blushing or water-whitening, reduced serviceable life, and softening of the film. In this study, various polymer composition latex design spaces are studied to develop an understanding of how water uptake can be modulated and minimized using common synthetic approaches. Factors including monomer selection, particle size, polymer molecular weight, crosslinking density, surfactant choice and particle stabilization, processing variables and  $T_g$  are considered. In addition, some formulation modifications including PVC, film thickness, and choice of coalescent package are explored to gain a more comprehensive understanding of final product performance. In quantifying the total water uptake of the films, gravimetric analysis tends to be the preferred method employed in the coatings industry. However, other analytical approaches can be used to better understand the effect that water has on the properties of the film. These methods may include differential scanning calorimetry, electrochemical impedance spectroscopy, immersion testing using dynamic mechanical analysis, and others.

In the work, it has been shown that interparticle crosslinking, surfactant, and monomer selection can have an extreme influence on the water uptake of free films. Film samples exhibit a range of water uptake values from nearly 200% to less than 5% over a one-week soak in deionized water. It is thought that the surfactant may provide hydrophilic channels that allow water to

penetrate the film and form heterogenous domains within the coating. These domains then grow and scatter light, leading to water-whitening and an increase in mass when compared to the dry film. Utilizing monomers with differing relative solubilities in water, such as methyl methacrylate and styrene, further allow control of this effect. Interparticle crosslinking via keto-hydrazide crosslinking, which is achieved during the film formation process, can also prevent the formation and growth of these large water domains, thus resulting in better performing films.

Keywords: Polymer, Coating, Water, Absorption, Latex, Film, Water-Based, Emulsion, Paint

## ACKNOWLEDGMENTS

I would like to express my gratitude to Engineered Polymer Solutions and the Sherwin-Williams Company for sponsoring my work over the past year. In particular, I would like to thank Karl Booth for being an incredible advisor and providing a tremendous amount of direction throughout the duration of my project, while also allowing me the ability and agency to steer it in a direction that I thought was important. Thanks also to Ashley Rodgers, Matthew Andersson, Christopher Savittieri, Dr. Robert Sandoval, Mary Jane Hibben, and everyone else in Marengo for all of your support, guidance and free food during my time at EPS. My appreciation also extends to Howard Killilea for helping make this opportunity at EPS possible. I also thank the members of the Valspar Applied Science and Technology Center for providing support with data acquisition that could not be completed on site at EPS.

My appreciation also extends to all of my professors at California Polytechnic State University San Luis Obispo, namely Dr. Erik Sapper and Dr. Raymond Fernando. Thank you, Dr. Sapper, for helping guide my project and develop my thesis as it is presented here today, and for all of the direction you have provided me during my time at Cal Poly. And thank you Dr. Fernando for guiding my peers and myself through the Polymers and Coatings Science program.

Finally, thank you to my family for all of your support, love, and acceptance during not only my time at Cal Poly, but my entire life. My love for you grows each and every day, and your encouragement of my pursuits has, and always will be paramount to my success.

# TABLE OF CONTENTS

<b>LIST OF TABLES .....</b>	<b>ix</b>
<b>LIST OF FIGURES .....</b>	<b>x</b>
<b>1. INTRODUCTION .....</b>	<b>1</b>
1.1 Statement of Problem and Purpose of Study.....	1
<b>2. LITERATURE REVIEW AND BACKGROUND INFORMATION.....</b>	<b>4</b>
2.1 Polymer Basics .....	4
Polymer Structure .....	4
Molecular Weight .....	6
2.2 Free Radical Polymerization .....	8
Process .....	8
Raw Materials and Processing .....	11
2.3 Emulsion Polymerization.....	12
Background.....	12
Process .....	12
Surfactants .....	14
2.4 Thermal Properties of Polymers .....	17
Glass Transition Temperature .....	17
Fox Equation.....	18
2.5 Latex Film Formation and Coalescence .....	18
Film Formation Process .....	18
Minimum Film Formation Temperature.....	19
Coalescent Utilization .....	20
Water Based Coating Formulation Basics .....	21
PVC and CPVC.....	21
2.6 Emulsion Polymer Crosslinking .....	23
Interparticle Crosslinking (Keto-Hydrazide Crosslinking) .....	23
Intraparticle Crosslinking (Difunctional Monomer Crosslinking) .....	25
2.7 Water Whitening and Blushing.....	26
2.8 Current Mechanistic Understanding of Water Uptake .....	27
<b>3. MATERIALS AND METHODS.....</b>	<b>30</b>
3.1 Materials.....	30
3.2 Methods.....	30
Emulsion Polymerization.....	30
Film Preparation and Water Uptake Gravimetric Analysis .....	34
Film Preparation and Permeability Testing .....	35
Electrochemical Impedance Spectroscopy .....	36
Contact Angle Measurements.....	39
Differential Scanning Calorimetry .....	39
<b>4. RESULTS AND DISCUSSION.....</b>	<b>40</b>

4.1 Effects of Coating Formulation and Formation .....	40
PVC .....	40
Coalescent Level.....	41
Ratio of ADH to DAA.....	42
Film Thickness .....	44
Film Curing Conditions.....	45
4.2 Effects of Polymer Design.....	46
T <sub>g</sub> Effect.....	46
Polymer Synthesis DOE #1 .....	47
Surfactant Type and Concentration (Anionic vs. Non-Ionic vs. Reactive Anionic vs. Dialysis) & PAM Monomer .....	54
Phosphate Adhesion Monomer (PAM A vs. PAM B).....	57
pH of Monomer Emulsion .....	58
Initiation Method.....	59
Crosslinking (Keto-Hydrazide, Di-Functional Monomer).....	60
Core/Shell Designs .....	61
Polymer Synthesis DOE #2 .....	62
4.3 Effects of Testing Methods.....	67
Water Temperature .....	67
Caustic Solution .....	68
4.4 Effects on Blushing and Surfactant Leaching .....	69
Blushing .....	69
Surfactant Leaching .....	73
4.5 Considerations and Future Work .....	74
Mechanical Stability .....	74
Alternative Stabilization.....	75
Additional Crosslinking Methods .....	76
Permeability .....	76
Effect on Other Properties .....	76
<b>5. CONCLUSION.....</b>	<b>78</b>
<b>6. REFERENCES .....</b>	<b>80</b>



## LIST OF TABLES

Table	Page
<b>Table 1.</b> Sample composition including molar and stoichiometric ratios of DAA and ADH. Note that 2.0% ADH results in a 1:1 stoichiometric ratio of ADH to DAA based on molecular weight and functionality. ....	43
<b>Table 2.</b> These polymers are compositionally identical and were processed using the same methods. Unless otherwise noted, the polymers were prepared using redox initiation, grown on a seed, and are all acrylic. ....	45
<b>Table 3.</b> Polymer samples with $T_g$ values and required coalescent loading. $T_g$ was measured using a TA instruments DSC of neat polymer. ....	46
<b>Table 4.</b> DOE #1 designed to assess the effect of crosslinking, molecular weight, monomer hydrophobicity, and $T_g$ on water uptake. Crosslinking is achieved with DAA monomer and ADH, molecular weight is decreased by addition of 0.5% DDM chain transfer agent, the hydrophobicity is altered by using either styrene or methyl methacrylate as the bulk monomers, and finally the $T_g$ is controlled by changing the ratio of EHA & BA to Styrene or MMA. ....	48
<b>Table 5.</b> DOE data overview. The samples provide a large response range, allowing for easy identification of important factors. The min/max/mean indicate a broad range of performance was achieved. The large variation should permit good differentiation between sample conditions. ....	49
<b>Table 6.</b> DOE samples used for EIS testing. PAM is a 50/50 mixture of PAM A and PAM B. ....	65
<b>Table 7.</b> Samples chosen for water whitening (blushing) tests. ....	70
<b>Table 8.</b> Surfactant leaching results from experimental polymers. ....	74

## LIST OF FIGURES

Figure	Page
<b>Figure 1.</b> Styrene and polystyrene. ....	4
<b>Figure 2.</b> Initiation and propagation reactions. First some initiator molecule (such as a peroxide) will decompose to form two radical species (either thermally driven or using a redox coupling). This radical can then add rapidly to a monomer molecule, resulting in a larger molecule with another radical. This chain reaction then continues to add monomers to the growing molecule, eventually resulting in a polymer chain. ....	9
<b>Figure 3.</b> Termination by combination and disproportionation. Combination occurs when two radical species add to one another, resulting in radical consumption. Disproportionation occurs when one hydrogen is transferred from one molecule to the other, forming a double bond, and again resulting in radical consumption. Radical species that may participate in these termination reactions can include growing polymer chains or newly formed initiator radicals. ....	10
<b>Figure 4.</b> Diacetone acrylamide (left) & adipic acid dihydrazide (right).....	24
<b>Figure 5.</b> During film formation ADH reacts with DAA that has polymerized into the backbone, resulting in a crosslink between two polymer chains. This reaction is acid catalyzed and thus occurs upon evaporation of volatile base (usually ammonia) during film drying. As the reaction proceeds, water is produced as a byproduct and evaporates, further driving the equilibrium to the right. ....	25
<b>Figure 6.</b> The proposed three step process by which water uptake occurs. The film which is clear and applied to a black substrate is initially submersed in DI water. Upon initial contact with water, water molecules penetrate into the film where there are more hydrophilic functional groups or areas of the polymer. These may include areas where there is a high concentration of surfactant, acid monomer or other polar functional groups. Following this hydration, certain areas continue to absorb more water up to and past the point of saturation. Finally, as these domains grow large enough, they begin to scatter light and the coating slowly turns opaque due to the heterogenous domains of water within the clear coating. Forces acting inside the water “pocket” expand the film, swelling it beyond its starting size and shape, this force is opposed by the polymer matrix resisting expansion. ....	28
<b>Figure 7.</b> Reactor charged with latex seed and water (left). Reactor hot water bath setup (right). Redox initiators are fed from the graduated cylinders located in the rear of the hood in the left-hand picture. ....	31
<b>Figure 8.</b> Monomer pre-emulsion building process (left). Monomer pre-emulsion complete and ready for reactor feed (right). ....	32
<b>Figure 9.</b> Monomer pre-emulsion, redox co-feed, and redox charge ready for synthesis. Initiator charge (front beakers) is added to the reactor, at which point monomer and initiator co-feeds are initiated. This particular setup is for a two-stage polymer, where the second larger emulsion will be fed following the completion of the first. ....	33
<b>Figure 10.</b> A finished emulsion reaction with polymer still in the reactor. At this point the product is filtered through a 100-micron filter into the jugs (left). A series of completed polymer resins (0.5 gallons) awaiting testing (right). ....	34

<b>Figure 11.</b> Resins are formulated and then drawn down on release liner or polypropylene sheets. Following the drying of the film, 1" x 2" samples are cut out and tested. ....	35
<b>Figure 12.</b> After test samples are prepared, they are placed in a jar of DI water and left at room temperature for the duration of the testing time. Periodically the samples are pulled out of the water and patted dry before being weighed and placed back into the jar (left). Samples may absorb varying amounts of water, resulting in variable swelling. ....	35
<b>Figure 13.</b> Films are cut out and placed in the BYK permeability cups. Note that these cups have slightly different designs but perform identically. ....	36
<b>Figure 14.</b> EIS potentiostat. ....	37
<b>Figure 15.</b> Diagram of sample with three electrode setup for EIS. ....	37
<b>Figure 16.</b> Three electrode setup for EIS measurements and depiction of Randles cell circuit. ....	38
<b>Figure 17.</b> PVC effect on the water uptake of a roof coating. Samples are cut out into 1" x 2" coupons, weighed, and submerged in 500mL DI water at room temperature (21 °C) for the duration of the experiment. At each data point the films are removed from the jar, patted dry to remove excess surface moisture, weighed, and returned to the jar. ....	40
<b>Figure 18.</b> The effect of a low VOC coalescing aid on the water uptake of a roof coating. ....	41
<b>Figure 19.</b> The effect of a VOC coalescing aid on the water uptake of a roof coating. ....	42
<b>Figure 20.</b> Water uptake of samples with varying molar ratios of ADH and DAA. ....	43
<b>Figure 21.</b> The effect of coating thickness on the water uptake of a roof coating. ....	44
<b>Figure 22.</b> Water uptake values after a one-week soak at 21 °C. Low temperature film formation was done at 21 °C, slightly above the polymer $T_g$ , and high temperature film formation was done at 50 °C, well above the $T_g$ of the polymer. ....	45
<b>Figure 23.</b> The effect of polymer $T_g$ on the water uptake of a coating. ....	47
<b>Figure 24.</b> Xbar-R chart for one-week water uptake values of DOE polymers. Evaluating the range data (lower graph), where the within subgroup is replicate soak test, outliers have already been removed (n=2 or 3) the measurement system is in control (no points outside the control limits). The mean within-subgroup range is 2.5% which is historically the expected replicate variation. The X-bar graph (upper) shows the ability for the measurement system to detect the between subgroup variation (polymer treatment). Because there is a large range in responses (122%), and a small range in replicate (avg 2.5%) there is a very strong ability to detect performance differences in the samples tested. ....	49
<b>Figure 25.</b> Polymers were synthesized in the run order shown here. There does not appear to be any run order dependence. Films were prepared and measured simultaneously and run order dependence could not be assessed. ....	50
<b>Figure 26.</b> Pareto chart identifying that crosslinking and monomer choice are the main effects of interest. Two-way interactions between monomer choice/crosslinking and crosslinking/molecular weight are also of interest. The plot identifies the other two main effects and two-way interactions as being statistically significant, however they are not nearly as influential, and definitive conclusions relating to them could not be confidently drawn. ....	50

**Figure 27.** The effect of monomer polarity (MMA vs Styrene) is shown in this main effect plot. As the samples become more non-polar and heavily styrenated, they tend to uptake less water. .... 51

**Figure 28.** The effect of crosslinking is shown in this main effect plot. As the samples are crosslinked, they tend to uptake less water than their non-crosslinked counterparts ..... 51

**Figure 29.** The effect of molecular weight is shown in this main effect plot. DDM is shown to have very little impact on the water uptake of these samples. .... 52

**Figure 30.** The effect of  $T_g$  is shown in this main effect plot, where samples with higher  $T_g$  values tended to perform worse. .... 52

**Figure 31.** The predicted DDM\*XL interaction does not seem to be active in the way predicted, where lower MW was predicted to facilitate better crosslinking, and uptake resistance. MW data would need to be collected to confirm that this conclusion can be drawn. .... 53

**Figure 32.** An interaction between monomer polarity and crosslinking was not predicted, however may be justified due to more similar solubilities of MMA and DAA monomer, resulting in more uniform incorporation of crosslinkable moieties. .... 53

**Figure 33.** Effect of surfactant amount and type. Non-ionic surfactants resulted in an increase in performance, similar performance increases were seen when the overall level of surfactant was decreased. .... 54

**Figure 34.** Polymer before and after dialysis. This serves to further support our conclusion that higher amounts of surfactant are detrimental to performance. .... 55

**Figure 35.** Effect of surfactant type and PAM monomer. Non-ionic surfactants performed the best, followed by reactive anionic, and finally anionic surfactants. And polymers that lack PAM monomers also perform much better than those that contain them. .... 56

**Figure 36.** Polymer samples with varying loadings of PAM A and PAM B to determine their contribution to water uptake performance in waterborne resins. .... 57

**Figure 37.** pH of the monomer pre-emulsion was changed before the polymerization begun. pH values of 7.0, 5.5, and 4.0 were used respectively as high, mid, and low pH levels. Below pH of 4.0 the monomer emulsion loses stability due to the reduced effectiveness of the anionic surfactant. .... 58

**Figure 38.** Effect of initiation method on water uptake after 1-week soak in DI water. The 6 samples differ in their mode of initiation, type of surfactant used, and the loading of phosphate adhesion monomer (PAM). Besides these variables all other compositional and processing variables are kept constant. .... 59

**Figure 39.** Effect of crosslinking chemistry on water uptake. A difunctional monomer HDODA was assessed alongside DAA, an intramolecular crosslinking agent that utilizes ADH to form covalent bonds between polymer chains of adjacent particles during the coalescence process. .... 60

**Figure 40.** Effect of core/shell polymer design on water uptake. Due to its inability to film form, the hard core/soft shell sample was only able to be assessed with a 5% loading of DPnB coalescent. The other two samples were then loaded and assessed with the same level of DPnB. .... 62

**Figure 41.** This result is identical to those found previously that PAM is detrimental to performance. .... 63

**Figure 42.** This result is identical to those found previously that anionic surfactant is worse for performance than non-ionic surfactant. .... 63

**Figure 43.** This result is identical to those found previously that styrene drives improved water uptake performance. .... 64

**Figure 44.** This result is identical to those found previously that higher degrees of crosslinking drive improved performance. .... 64

**Figure 45.** Higher capacitance values here correspond to higher water uptake values. Sample 86 was not recorded as the sample failed upon initialization of the test. .... 65

**Figure 46.** Increased resistance values correlate to increased barrier properties of the coating. The commercial product samples are fully formulated paint coatings and are not ideal candidates for sample comparison. .... 66

**Figure 47.** Static water contact angles have a loose correlation with uptake values, where larger contact angles drive higher water uptake values. Presumably this is due to waters unfavorable interaction with more hydrophobic polymers as they exhibit higher contact angles. .... 67

**Figure 48.** Variable water temperature of test samples. .... 68

**Figure 49.** 5% NaOH caustic water uptake testing. .... 69

**Figure 50.** Films at 6 wet mils after 24 hours. .... 70

**Figure 51.** Films at 6 wet mils after 120 hours. .... 70

**Figure 52.** Films at 6 and 7 wet mils after 24 hours. .... 71

**Figure 53.** Films at 6 and 7 wet mils after 120 hours. .... 72

**Figure 54.** Films at 6 and 7 wet mils after 24 hours. .... 73

# 1. INTRODUCTION

## 1.1 Statement of Problem and Purpose of Study

Prior to the mid-20<sup>th</sup> century, nearly all coatings that were used both at home and industrially were solvent-borne. This included paints, lacquers, and other coatings which were used in nearly every part of the coatings industry. However, with the development and release of Super Kem-Tone latex paint in the 1940s, Sherwin-Williams introduced the homeowner to a water-based paint with myriad advantages over its oil-based counterparts. These paints, as their name suggests, are based on a chemistry centered around using water rather than oil to produce and form a coating.<sup>1</sup> The binder that these coatings use are known as latexes or latex resins. The latex is a dispersion of polymer particles in water. Most commonly these polymers are synthesized using free radical polymerization, also known as chain-growth polymerization. However, step-growth polymerization can also be used to synthesize these aqueous dispersions. Polyurethane dispersions, also known as PUDs, are created in this way.<sup>1</sup>

These coating systems exhibit some limitations when compared to their solvent-borne counterparts. Limitations include but are not limited to film formation, adhesion to certain substrates, resistance to mechanical and chemical degradation, and sensitivities to moisture. This sensitivity to water can result in coating failures in the form of blistering, delamination, drop in modulus, blushing, reduced service-life, and softening.<sup>2</sup> One example of the need for water resistance in water-based coatings can be seen in industrial roof coatings. These coatings, often seen on the roofs of large box stores and commercial buildings, must be able to endure changing weather and standing water for prolonged periods of time. Since the roofs are often low sloped and may have poor drainage systems, the chance that water will pool and sit until it evaporates is quite high. A coating that exhibits poor water resistance will suffer the adverse effects of multiple wet weathering cycles and require repeated recoats to maintain and protect the underlying structure from water damage. After multiple seasons of wet weather, and a coating that exhibits poor resistance to the adverse effects of water, a roof may have to be recoated, water damage to the

underlying structure might need to be repaired, and a dissatisfied owner will be on the search for a coating from a different manufacturer.

The purpose of this work is to develop an understanding of what drives water sensitivity and, more specifically, water uptake or absorption in waterborne coatings. Nearly all coatings will encounter water at some point throughout their service life and having some resistance to water is an important factor for end use applications. Water uptake is of interest to coatings and polymer manufacturers for these reasons. Some roofing coatings must meet standards set forth in ASTM D6083 and D471 where a coating free film cannot uptake more than 20% of its mass in water. Many industrial polymers may be used in roofing coatings; however, this is one very important specification that must be met.

There are many factors and variables that can be changed during the synthesis and production of latex resins, as well as formulation of the coatings themselves. Some of these factors are understood, however many are not, and it is the purpose of this study to obtain a more comprehensive understanding of how polymer composition and processing affect water uptake. Acquiring a better understanding of water uptake in latex coatings will allow future development of commercial resins to occur with much more ease and purpose. These conclusions and findings should aid in the evolution of resins used in architectural, industrial, and construction applications.

From a business standpoint the work will serve to advance waterborne acrylic coatings performance in numerous commercial applications and in the development of products for EPS and the Sherwin-Williams Company. A coating's interaction with water affects many properties of importance to the coatings industry, including corrosion resistance, adhesion, blister resistance, blush resistance, and water absorption. Innovative polymers must be able to demonstrate advancements in these attributes to be successful in the marketplace. Research into the fundamental factors that contribute to water uptake contributes to advancement of these properties. Resins that demonstrate water resistance (and other qualities related to water resistance) will provide a more profitable and marketable product to the coatings community and coatings manufacturers. It is for these reasons that it is important to invest time and resources into

developing this technology and gaining a more comprehensive understanding of the water uptake phenomenon.

The project is separated into three main stages: understanding the effect of coating formulation, polymer synthesis and design, and the characterization and understanding of the water uptake mechanism and other properties of interest to coatings manufacturers.

**Coating formulation-** Polymers are tested primarily in neat “formulation-free” systems. However, a series of formulation effects are studied within the scope of roofing formulas, such as pigment loading, coalescent, coating thickness, curing conditions, and non-uniformities in the finished film.

**Polymer design-** Polymer design is the main focus of the study. Polymers are designed, manipulated, and synthesized to provide an accurate understanding of how compositional and processing parameters affect the performance of the coating. Parameters include  $T_g$ , monomer selection, hard/soft dual stage polymers, molecular weight, crosslinking, initiation method, surfactant level/type, and others. The control polymer used for manipulation and study is an altered, simplified version of a current product offered by EPS.

**Characterization-** In quantifying the water uptake, a simple gravimetric method is employed. However, EIS, AFM, and other techniques are also used to obtain a deeper understanding of the uptake phenomenon, and factors that affect it. Other performance attributes are measured using current and developing test methods. These methods include surfactant leaching testing, blushing tests, contact angle measurements, and water vapor transmission.



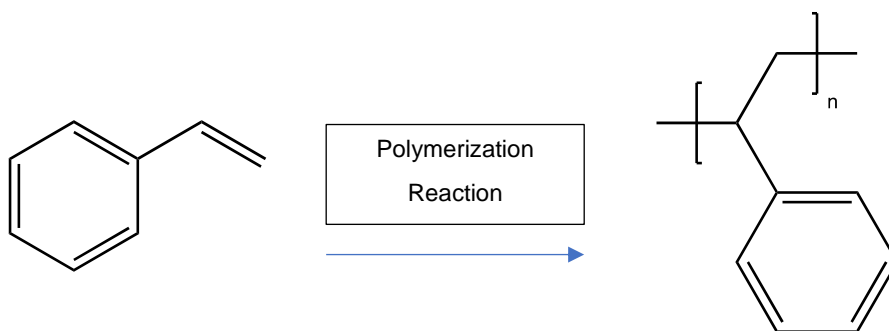
## 2. LITERATURE REVIEW AND BACKGROUND INFORMATION

### 2.1 Polymer Basics

#### *Polymer Structure*

Polymers are large molecules composed of small building blocks called monomers. The final properties of the polymer are dependent on two things: what the monomeric repeat units are, and how they are put together in the larger structure of the polymer. As one might expect, there are nearly an infinite number of possible monomer combinations, resulting in a vast array of final properties. These polymers are arguably the most important component of coatings and are the driving factor behind many coating properties. They can be synthesized in the lab, as well as found naturally nearly everywhere we look. The former will be the focus of this work, but it is important to understand how abundant these macromolecules are in our day-to-day lives. Oftentimes, polymers are thought only to be rubber and plastic materials; people are very familiar with polystyrene and polyethylene, but the connection is rarely made between the label of “polymer” and everyday things such as cotton, cellulose, protein, and DNA. Some of the most interesting and useful materials human civilization has ever created are polymers, and the field of research pertaining to these materials is immense and growing.

An example is presented below of a simple monomer and resulting polymer structure.



*Figure 1. Styrene and polystyrene.*

The repeat unit or monomer in Figure 1 is styrene, and the resulting polymer is polystyrene, where  $n$  represents the number of repeat units, which can practically range from 100-200 to upwards of 100,000. This is a particularly simplified presentation of a polymer, but it serves to show

that the structure of the final product relies nearly entirely on the structure of the monomer. If the monomer is changed, the polymer changes with it.

One of the most fundamental ways to classify polymers is based on chain design and how the chains are oriented in the molecule itself. We can classify most polymers into three categories: linear, branched, and crosslinked polymers. Linear polymers, as the name suggests, are linear macromolecules. The monomer units are joined one after the other and there are no junctions or deviations from the linearity of the chain. The monomer units may be all the same (homopolymers), they may be random combinations of two or more chemically different monomers (random or statistical copolymers), they might be alternating one after another (alternating copolymers) or they may consist of regions of one monomer followed by regions of another, also known as a block copolymers. Branched polymers have periodic branching from the main linear chain. These molecules may have long linear regions but every so often there exists a “fork in the road” where a secondary chain may extend from the primary one. There exist many forms of these polymers, such as graft or comb polymers, but the principle of multiple branches of chains from other chains remains constant. The third class of polymers are known as crosslinked or network polymers. These chains not only have branching, but also covalent bonding of these chains to other molecules in the system. In theory, each and every chain in a crosslinked system may be covalently bound to each other, resulting in one large interconnected molecule. This last class is of extreme importance in coatings applications and is the basis of much research in the field of coatings.

These crosslinked polymers are often referred to as thermoset polymers. In theory these polymers will not soften or turn rubbery when heated, but instead remain rigid and keep their form. Conversely, non-crosslinked polymers are known as thermoplastic polymers, as they will soften and lose their form when heated above a certain temperature known as the glass transition temperature. The glass transition temperature or  $T_g$  will be discussed later, however it is important to draw the connection between polymer chain design and  $T_g$  early.

## *Molecular Weight*

One of the most integral and important properties that influence the properties of polymers is their molecular weight (MW). The molecular weight is dependent upon two things: the number of monomeric repeat units that are part of the polymer chain and the type of repeat unit that is used to build the polymer chain. One of the most important characteristics of polymer molecular weights, and something that differs drastically from molecular weights of typical small molecules such as water (H<sub>2</sub>O: 18.02 g/mol) or glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>: 180.16 g/mol), is that since there is a distribution of polymer chains in the sample, there is a corresponding distribution of molecular weights.

Naturally, chemists are used to the understanding that a MW is a discrete value dependent upon the number of atoms in the molecule. Each molecule of styrene contains 8 carbon and 8 hydrogen atoms, each having a mass of 12.01 g/mol and 1.01 g/mol respectively (ignoring the effect of isotopes). The sum of these 16 atoms is 104.16 g/mol; the MW of a styrene molecule. However, during a typical polymerization process polymer chains don't all grow at the same rate. This results in a distribution of long molecules with varying lengths and MWs, centered around some mean value. We refer to this distribution of MWs as a molecular weight distribution. One consequence of this MW distribution is the presence of different average values: the number average molecular weight and the weight average molecular weight. These are defined below:

$$\text{Number average:} \quad \bar{M}_n = \frac{\sum N_x M_x}{\sum N_x}$$

$$\text{Weight average:} \quad \bar{M}_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

Here x represents the degree of polymerization (DP<sub>n</sub>), N<sub>x</sub> equals the number of molecules with length x, M<sub>x</sub> is the molecular weight of a molecule with degree of polymerization x. The degree of polymerization is equal to the number of repeat units in the polymer chain and is, in this case, synonymous with chain length. The M<sub>n</sub> is the statistical average molecular weight of all the chains in the sample, compared to the M<sub>w</sub>, which takes into account the molecular weight of the chain in determining contributions to the average molecular weight. This means that the presence of a few large chains, or a right skewed distribution of polymer MW will have a larger impact on the M<sub>w</sub> than

on the  $M_n$ . Furthermore, the  $M_w$  will always be equal to or larger than the  $M_n$  for this reason. There exists a relationship between these two values which helps us understand this right skewed distribution of polymer chains: the polydispersity index.<sup>3</sup>

$$\text{Polydispersity Index (PDI):} \quad PDI = \frac{M_w}{M_n}$$

Notice that since  $M_w \geq M_n$ , the value for PDI will always be greater than 1 in real world samples of polymer. The larger the PDI, the broader the distribution of polymer molecular weights and the more polydisperse the sample is. True monodisperse samples are rare in synthetic polymer chemistry; however, they do exist. A sample of isolated proteins could have a PDI of 1, however carefully controlled synthetic polymers might only be able to achieve PDI values of 1.02 to 1.10. Commercial chain reaction polymers typically have PDIs in the range of 1.5 to 20.<sup>3</sup> For samples with exceptionally narrow distributions (and thus small PDI) the  $M_p$  value is often reported. This is known as the peak molecular weight and is essentially the mode of the molecular weight distribution.<sup>4</sup>

It should be noted that there are numerous ways of measuring and reporting molecular weights, such as Z-average molecular weight, viscosity average molecular weight, and using light scattering to measure MW. Some are more accurate, and some are more easily determined experimentally, however a true comprehensive understanding of molecular weight is not paramount to the understanding and execution of this research.

Gel permeation chromatography is a type of size exclusion chromatography or SEC. There are many intricacies to GPC, but the underlying goal is to separate molecules of differing MW and elute them from a column or set of columns. The sample of polymer that is to be analyzed is first dissolved in solvent and injected into the instrument column. The sample of polymer chains is pumped with a continuous flow of solvent over tiny beads of media. These beads have microscopic pores and crevices that allow small molecules to enter, but exclude large molecules based on their size. This results in small molecules becoming “captured” along their tortuous path through the column, as they are pushed into every nook and cranny along the way. The larger molecules cannot enter these tight spaces, and instead flow through the media and through the column much faster.

As these molecules flow through the column, the larger ones eventually outpace the smaller ones and elute out of the column and onto the detector before than the smaller chains. Hydrodynamic volume is the technical factor that drives these elution profiles, and here we correlate this hydrodynamic volume to chain length and MW.<sup>5</sup>

SEC requires much calibration, elution of standards, understanding of sample preparation, and column selection. Branching of the polymer sample will change how the sample behaves and elutes, and effectiveness of the media and solvent also affect how the sample will flow through the column.<sup>6</sup> Highly crosslinked samples tend to be nearly impossible to run using these conventional methods due to their low solubility in the solvents used.

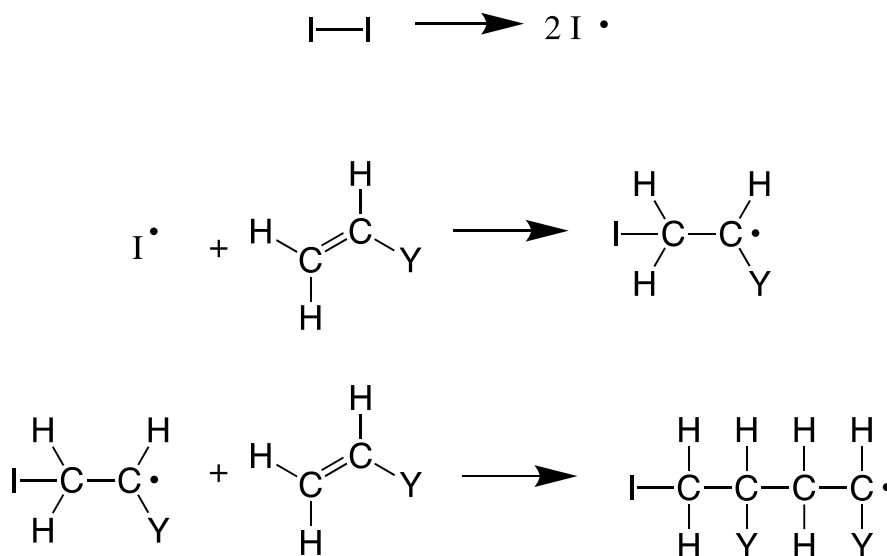
## 2.2 Free Radical Polymerization

### *Process*

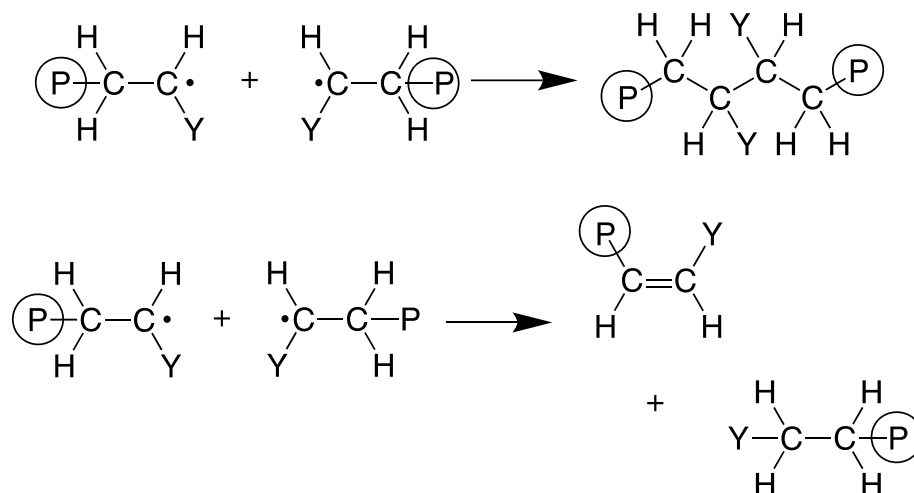
There are two commonly accepted classifications of polymerization reactions; *step-growth* and *chain-growth polymerization*. The former will not be discussed at length in this paper, though it does account for a large portion of polymers produced and used extensively in our day-to-day lives. Many of our clothing products are constructed from nylon polymers, which are synthesized using a step-growth polymerization reaction.

In chain-growth polymerization, the reactions are chain reactions, meaning that one reaction leads to another and so on. Here the monomers must have either unsaturated bonds such as the case with various olefins, dienes, and acetylene, or they may have certain ring structures such as caprolactam and ethylene oxide. The two most commonly used chain-growth polymerization processes for coatings polymers are initiated with free radicals and are known as *solution* and *emulsion polymerizations*. Both systems are initiated with free radicals. Solution polymerizations are marked by a reaction in an organic solvent, where all processes occur within a homogenous solvent system. In emulsion polymerization, the process occurs in a heterogenous system where non-polar monomer/polymer particles are suspended within an aqueous phase.

There are three main steps during the free radical polymerization (FRP) process: *initiation*, *propagation*, and *termination*. A fourth reaction known as chain transfer also takes place that can impact the product of the polymerization. During the initiation phase, the initiating molecule (I) reacts to form one or more free radicals (I·). A free radical then reacts with an available monomer molecule (M), combining the two and forming a new free radical on the monomer (I-M·). The subsequent reactions of this free radical on the monomer molecule with other monomer molecules are called propagating reactions. These reactions grow the polymer chain and take place very fast, resulting in the growth of polymer chains hundreds of units long in a fraction of a second. At any moment during the polymerization process the concentration of monomer and polymer greatly exceed the concentration of growing polymer chains, due to the limited solubility of initiator molecules into the non-polar phase. Since initiation occurs at independent monomer molecules, it is believed that growing polymer particles contain just a few growing chains at any given time. This results in high molecular weight chains being produced very quickly with FRP.<sup>7</sup>



**Figure 2.** Initiation and propagation reactions. First some initiator molecule (such as a peroxide) will decompose to form two radical species (either thermally driven or using a redox coupling). This radical can then add rapidly to a monomer molecule, resulting in a larger molecule with another radical. This chain reaction then continues to add monomers to the growing molecule, eventually resulting in a polymer chain.



**Figure 3.** Termination by combination and disproportionation. Combination occurs when two radical species add to one another, resulting in radical consumption. Disproportionation occurs when one hydrogen is transferred from one molecule to the other, forming a double bond, and again resulting in radical consumption. Radical species that may participate in these termination reactions can include growing polymer chains or newly formed initiator radicals.

The third and final step of the FRP process is termination. Termination reactions are broken down into two categories: *combination* and *disproportionation*. A combination reaction occurs when two free radicals, either from initiator molecules, growing polymer chains, or both react together to form a covalent bond. This reaction results in the destruction of two active propagating sites, and the formation of a single “dead” polymer chain. Disproportionation is similar and occurs when two propagating chains meet. Here, the two chains don’t combine, but rather a proton is transferred, and a double bond is formed resulting in the cannibalization of both free radicals. There exists an extensive discussion into the kinetics of FRP, however the content of this discussion extends beyond the scope of this research.<sup>3,4</sup>

The chain transfer reaction is a side reaction that takes place in nearly all FRP processes. These reactions result in a free radical on the end of a propagating chain, abstracting a hydrogen atom from some molecule X·, and transferring the propagating radical to Y-H. The result is the termination of the first propagating chain, X-H, and the start of propagation reactions off of the molecule Y·. X may be another polymer chain, initiator, monomer, solvent or *chain transfer agent* (CTA). These CTAs are purposefully added to the reaction mixture in order to facilitate an increased

number of chain transfer reactions. Chain transfer reactions usually result in two outcomes: a higher ratio of  $M_w$  to  $M_n$  (or an increase in PDI), as well as an overall decrease in molecular weight.<sup>3</sup>

### *Raw Materials and Processing*

As was mentioned briefly, monomers must have either unsaturation or ring structures containing at least one hetero atom such as oxygen or nitrogen. Most of the monomers used in the coatings industry fall into the first category. Most of these monomers which contain unsaturations are alkenes with an electron withdrawing group such as a methyl acrylate and methyl methacrylate. Polymers composed of predominantly acrylic and methacrylic ester monomers are known as *acrylic polymers* or just *acrylics*. Styrene is another common monomer used in these reactions.

Initiator molecules or *initiators* are typically used in the 0.1-4.0 wt.% range. Two main classes of initiators are used in coatings polymers: *azo compounds* and *peroxides*. These initiators will decompose to form two radicals when subject to high temperatures or a reducing agent. Initiator selection will depend heavily on the polymer processing that is desired, for example in emulsion polymerization the initiator should be soluble in water and are oftentimes persulfate salts. Persulfate salts such as ammonium persulfate (APS) are very common, and in the case of APS, cleave thermally in water to produce sulfate anion radicals, this is known as *thermal initiation*.

This initiation requires a high temperature (oftentimes these reactions are run around 80 °C) to achieve radical production at a substantial rate. For initiation at lower temperatures, a reducing agent is often used to help drive the decomposition reaction and radical formation. This initiation via the use of a redox reaction is known as *redox initiation*. Redox initiation can be used to initiate polymerization at room temperature. The resulting exotherm and heat production from the polymerization process can be removed using a cooling jacket or water bath. In the later stages of the polymerization when nearly all of the monomer is reacted, a *chaser* or *clean-up* redox feed is often added to the reaction vessel. This redox couple should be more lipophilic to help push the conversion of monomer to polymer to near 100%. The peroxide *t*-butyl-hydroperoxide (tBHP) and erythorbic acid ("e-acid") are a common redox pair used for this chase. This oxidizer is more soluble



in the polymer particles and will help react the remaining monomer that is found inside these particles. The other advantage to using *t*-butyl hydroperoxide is that there are no remains of persulfate ions following the reaction. It is for this reason that a tBHP redox pair is commonly used as the sole initiator for FRP systems.

## 2.3 Emulsion Polymerization

### *Background*

One of the most common polymer synthesis processes that utilizes FRP is *emulsion polymerization*. As one might expect, emulsion polymerization relies on the emulsification of monomer droplets into water throughout the process. This polymerization method can be used with a variety of chemistries, such as acrylic free radical polymerization and polyurethane synthesis to create polyurethane dispersions or PUDs. These systems have many names of varying technical accuracies, such as colloidal dispersions, polymer colloids, latexes, aqueous dispersions, latex emulsifications, etc. We will use the common terms *emulsion* or *latex* for the purposes of this paper.

One defining characteristic of latex polymers is that they tend to have relatively high MW when compared to polymers prepared by other means. Polymers exhibiting  $\overline{M_w}$  values of 1,000,000 g/mol or higher is quite common. Interestingly enough, the viscosity of the resulting emulsion is not highly dependent on the molecular weight of the polymer, but rather by the volume fraction of polymer to aqueous media in the sample. This is further influenced by particle packing in the emulsion and the size of the individual latex particles. This is key when attempting to create polymers with high molecular weight. Solution polymers with the same MW and solids content as emulsion polymers would be much more viscous. These high molecular weights can result in an increase in durability of the final coating.<sup>1</sup>

### *Process*

The process of emulsion polymerization requires water, monomer, surfactant, and a water-soluble initiator. The FRP reaction process outlined above is the same *chemical* reaction process

in emulsion polymerization, however the physical circumstances of this polymerization are much different than the FRP of a solution polymer. There are countless parameters and variables that heavily affect both the processing and final product of the polymerization. Temperature, reaction time, pH, feed rate, concentration of surfactant/monomer/initiator, type of surfactant, monomer, initiator, agitation, and solubility of those compounds are just a few of the many important and diverse set of parameters that are variable in this process. The extreme customizability of each component means that it is very difficult to predict the final characteristics of the latex, and that there are innumerable possibilities for both successful and unsuccessful latex products.<sup>3</sup>

There are two common ways of carrying out an emulsion polymerization process: batch polymerization and semi-continuous polymerization (it is true that continuous reactions are possible as well, but they are not the focus or purpose of this study). Batch polymerization is typically used primarily on small-scale situations, such as in the lab. Here, all of the components necessary are placed into the reaction vessel simultaneously and reacted at once. This method is rarely used on a large scale due to the uncontrollable exotherm and evolution of heat during the reaction. Consequentially, semi-continuous reactor setups are usually the first choice for large-scale production of latex resin. Miniature versions of these industrial-scale reactors are easy to setup in the lab, on a 0.5 to 4-gallon scale, and serve as a good model for eventual production-scale processes. In a semi-continuous reactor, the monomers and other components are added or fed into the reactor at a controlled rate so as to facilitate expeditious polymerization. This is referred to as monomer-starved conditions and allows for very good control of the overall reaction, especially heat production. Furthermore, the composition of the polymer product should theoretically reflect the composition of the monomer feed, all but negating the influence of varying monomer reactivity ratios. This means that the composition of the polymer particle can be influenced by altering the composition of the monomer feed throughout the span of the feed process.<sup>8</sup>

Traditional emulsion polymerizations are started when an initiator molecule and monomer molecule react together. The subsequent propagation reactions occurring on this growing molecule eventually yield a small particle which continues to grow into the final product. This is known as *in-*

*situ* seeding. Chemists have used *in-situ* seeding to produce resins with tight particle size distributions and allows them more control over the average particle size.

A seed is oftentimes used at the outset of the polymerization process to further control variability in the product from one reactor to another. Industrially, a seed is used to minimize batch variability and botched runs, since it is all on the “same” pre-made seed. This seed is essentially a previously prepared infant emulsion, where a small amount of monomer had been initiated and grown into a resin with very small and controlled particle size. These particles then provide the monomer in the main reaction a place to begin the propagation reactions. The utilization of a seed helps control particle size and morphology of the final product for subsequent batches.<sup>1,9</sup>

### *Surfactants*

Surfactants are molecules not inherently required for FRP, but rather for the physical process of emulsion polymerization. Surfactant molecules contain both a polar head group (hydrophilic) and a non-polar tail group (hydrophobic), and schematically resemble a tadpole. These surfactants are typically non-ionic or anionic, but there exists a vast number of different surfactants, depending on what properties the chemist is looking for. A common example of an ionic surfactant would be sodium lauryl sulfate. Here we can see the anionic head group  $\text{SO}_3^-$  as well as the long hydrophobic hydrocarbon chain.

Non-ionic surfactants must still provide a polar region without the use of a charged group. These surfactants provide water solubility mainly via hydrogen bonding. These also exhibit a reduction in water solubility as temperature is increased (driven by a reduction in hydrogen bonding effectiveness) but are less sensitive to water hardness or quality. Ionic surfactants can be affected greatly due to water chemistry.<sup>1</sup>

The emulsion polymerization process begins with the formation of an emulsion. This is achieved by mixing water, monomer, and surfactant together. Surfactant molecules will form micelles once their concentration reaches the critical micelle concentration or CMC. This orientation has the polar head groups associating with the water, and the non-polar tail groups associating

with themselves. These micelles typically resemble spheres or rods, with either one or two layers of surfactant molecules. When the monomer is added to this system, the non-polar tails of the surfactant associate freely with the monomer, placing monomer molecules inside the micellar surfactant aggregate. This means that small monomer droplets will be stabilized by the surfactant, resulting in a monomer/water emulsion. The size of the monomer droplets is dependent upon stirring rate, surfactant concentration, and monomer/water ratio.<sup>10</sup>

Once this emulsion is formed, the initiator can be fed into the system. It is very important that the initiator be *water soluble*. The initiator will initiate polymerization as it comes into contact with one of the monomer molecules that happens to be in the aqueous phase. Since the monomer is very insoluble in water, this process is slightly hindered. As the polymer chain grows, surfactant molecules begin to stabilize the chain, and form a small polymer particle. As the process continues, monomer will diffuse out of the monomer droplets and into the growing polymer particle, which grows with each addition of monomer. Surfactant will also join the growing polymer particle to help with stabilization. The monomer droplets shrink until they are gone, at which point all monomer has been converted to polymer, and all surfactant is now associated around the polymer particles, stabilizing the final emulsion product. Termination occurs when a radical, which typically comes from the initiator in the aqueous phase, diffuses into the polymer particle and ends the propagation reaction. This is one of the main reasons that the MW can grow to such great values with emulsion polymerization. It is also beneficial in polymerizing monomers which tend to be much less reactive or terminate too quickly in solution polymerization.<sup>8</sup>

The emulsion polymerization process results in polymers with relatively high MW, low viscosity, high solids, and advantageous processing considerations. Their 0.1-3.0 micron (typically) diameter and ease of handling makes them nearly immediately ready for substrate application, or formulation into paints, caulks, adhesives, etc. Unfortunately, the surfactant will always be a part of the latex resin, which can have detrimental effects such as a reduction in adhesion, durability, and an increase in water sensitivity. Traditionally the surfactant will always be found on the outside of the polymer particle, however if a polymerizable surfactant is used, it will be able to participate in the FRP process and become part of the polymer backbone.<sup>11</sup> The stability of the polymer emulsion

relies heavily on the surfactant. With poor stability, the polymer particles will approach each other and become held together due to the strong van der Waals forces. This is known as *flocculation*, which raises the viscosity of the resin, changes the flow to shear thinning and reduces the effectiveness of the resin to be used in coatings. Some systems can be synthesized with surfactant-free systems, however this is atypical and not traditionally used in industrial applications.<sup>1,12,13,14</sup>

The surfactant stabilizes the particles using two main mechanisms: charge repulsion and outer layer repulsion (comprised of steric, osmotic, and entropic repulsion). Anionic surfactants will be adsorbed along the surface of the particle and orient their anionic salt group outwards toward the aqueous phase. This essentially covers the particle in anions that are then associated with a cation. The layer of cations is known as the Stern layer and behaves as if it were part of the particle itself. The Stern layer then induces the formation of a *second* layer of anions surrounding it. This double layer of anionic charges causes a repulsive force between any two particles than come near each other. As one might imagine, the presence of salts, especially multivalent ions, can heavily impact the effectiveness of this electrostatic double layer by screening or dampening electronic interactions, which is why water chemistry is more important when anionic surfactants are utilized in the emulsion process.<sup>15,16</sup>

The hydrophilic nature of the particle surface also results in the adsorption of water, which causes the surface to swell. The thicker this swollen layer of water and surfactant is, the more *steric* repulsion there will be between two particles, reducing the chance of flocculation.

Additionally, when the water swells these hydrophilic domains of the particles, there exists a large area for the molecules to adopt varying conformations, as water molecules can adsorb and desorb freely. As another particle begins encroaching on this large area, the molecules are limited in the number of conformations they can readily assume. This reduction in entropy results in a resistance to flocculation and a repulsive force known as *entropic repulsion*.

Similarly, as the water is expelled from the space between particles, many argue that there is an *osmotic driving force* that pushes water back into the space between particles. This helps return the system to the equilibrium concentration in the outer layer, and hence is why the

phenomenon is called *osmotic repulsion*. The exact contribution of these three phenomena to the stabilization of the particles is a topic of debate, however, contribution to varying extents of all three is usually accepted.<sup>1</sup>

## 2.4 Thermal Properties of Polymers

### *Glass Transition Temperature*

The molar ratio of monomers used in a polymer determine one of the most important properties of the final polymer: the glass transition temperature or  $T_g$ . When the temperature of a polymer is raised above its  $T_g$ , the polymer transitions from a hard and glassy state to a soft and rubbery state. This is a result of long-range motion of the polymer backbone becoming enabled, meaning that in addition to small vibrations, portions of the polymer chain can move around or slip past one another. The viscosity of thermoplastic polymers falls sub-exponentially as the temperature is further increased above this temperature.<sup>17</sup>

When an amorphous (non-crystalline) polymer increases in temperature, there is a steady increase in specific volume, however at no point is there an abrupt (non-differentiable) change to the volume of the sample. In crystalline polymers there would be a sharp change in volume which would be associated with the samples melting temperature. Instead, there is a temperature at which the rate of increase of specific volume will change. Above this temperature, the rate of increase of thermal expansion is greater than it would be below that temperature. Many refer to this phase change as a *pseudo second order* phase change because the derivative of the volume change as a function of temperature is discontinuous at the  $T_g$  value. This phenomenon is unique to amorphous polymers, as crystalline polymers exhibit the *first order* phase change: melting at temperature  $T_m$ . Semi crystalline polymers will exhibit both a  $T_g$  as well as a  $T_m$  value. Generally speaking, polymers that exhibit melting points are known as thermoplastic polymers, and polymers that do not melt are known as thermoset polymers.<sup>1</sup>

### *Fox Equation*

Being able to estimate the value of a copolymer  $T_g$  is of great importance in polymer development. It is most common to use the *Fox equation* to derive these theoretical values. Here,  $w_1$ ,  $w_2$ ,  $w_3$ , etc. are the weight fractions of the monomers present in the copolymer product. Similarly,  $T_{g1}$ ,  $T_{g2}$ ,  $T_{g3}$ , etc. are the  $T_g$  values of their high MW homopolymers.<sup>1</sup>

$$\frac{1}{T_{g(\text{copolymer})}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} + \dots$$

A value derived for a copolymer  $T_g$  is a theoretical estimation and will vary based on many other factors of the polymerization. It is important to check the actual  $T_g$  value following the polymer synthesis, in order to be sure of the  $T_g$  value for the sample.

## **2.5 Latex Film Formation and Coalescence**

### *Film Formation Process*

Film formation of latex-based coatings is a much more complicated process than it seems, in fact when paint dries (as exciting as the process may sound), there are many different changes taking place in the coating itself that facilitate the formation of a robust and continuous film. This is a result of the interaction between insoluble polymer particles and the water phase of the system.

Film formation takes place in three discrete steps: evaporation, deformation, and finally inter-diffusion or coalescence. Beginning immediately after the coating is applied to the substrate, the water component (or any volatile compound present in the wet coating) begins to evaporate. As the water leaves, the relative solids content in the coating begins to rise, and the polymer particles start to become packed together. As this process continues and more of the water leaves the system, the particles have nowhere to go and begin to deform as they come into contact with each other. This deformation of particles is the second stage in the film formation process and is driven by surface tension and capillary forces. Finally, when nearly all the water is gone and the particles are neatly packed together, the individual polymer chains begin to diffuse out of one particle and into adjacent ones. Additionally, the ionic repulsion is lost as the salt content becomes

more concentrated, so the ionic double layer stability fails at some point during this process. This interdiffusion of polymer chains is the final step in film formation and arguably the most important. If there is poor or no chain diffusion between particles, there is no way for a continuous film to form on the substrate and all coating properties will be either compromised or absent. This chain diffusion is based heavily on the  $T_g$  of the polymer but is also influenced by other factors as well, such as the presence of any plasticizer molecules and crosslink density.<sup>3,17,18</sup>

A drawback to this film formation by particle coalescence is that very high gloss values are typically difficult to achieve, especially when compared to solvent-borne polymers. This is due to two things: first, an accumulation of surfactant on the surface of the film post-coalescence, and second, a non-uniform surface from the remains of polymer particles left behind after non-complete particle flattening. For high gloss values to be achieved, specular reflection is required. Specular reflection occurs when light reflects off of a surface at an angle to the surface normal that is equal to the angle of incidence. The surface roughness resulting from incomplete particle deformation of emulsion-based coatings limits their ability to reach the same level of specular reflection as solution-based coatings.<sup>17</sup>

#### *Minimum Film Formation Temperature*

Temperature is a tremendously important driving factor for many natural phenomena. In the case of film formation, it is arguably the most important variable that controls the effectiveness of a coatings ability to form a continuous film. So important is temperature that each waterborne coating has a corresponding physical property known as the minimum film formation temperature or MFFT. The MFFT is the temperature below which the polymer chains in each individual polymer particle cannot diffuse enough to form a continuous film, due to a lack of thermal and kinetic energy within the chains of the particle. The MFFT is based heavily on the  $T_g$  of the polymer, but not entirely on this property. Other factors such as polymer type, surfactant, and the presence of any other compounds in the coating can have an influence on the MFFT. As the temperature of the substrate and environment that the coating is drying in is increased above the MFFT, formation and complete



coalescence of the film will be achieved. However, at temperatures below the MFFT of the coating, film formation will not be achieved and after drying, the coating will most likely flake off and provide no protection or desired properties due to poor particle interdiffusion.<sup>17,1</sup>

### *Coalescent Utilization*

The film formation paradox is one of the main challenges that chemists and formulators face when developing coatings using latex resins. On one hand, the  $T_g$  must be low enough to achieve good coalescence at room temperature, but on the other hand, these low  $T_g$  values result in soft films that are often tacky, susceptible to scratches, and suffer additional performance requirements. So, the question becomes how does one achieve a film that is hard enough to withstand abuse, but will also form a continuous film at room temperature?

One of the most effective ways to satisfy both of these requirements is to incorporate a *plasticizer* or *coalescing aid* to allow the polymer chains to more easily move past one another and artificially lower the  $T_g$  of the polymer. Typically, these coalescing solvents are volatile so after they facilitate coalesce, they evaporate out of the coating leaving behind a hard, durable finished product with a  $T_g$  that is higher than room temperature. One of the most widely used coalescent solvents in both industry as well as literature is 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, or TPM, also known as Texanol™. The pronounced effect of this coalescing solvent on diffusivity of the film has been shown to increase diffusivity by nearly 4 orders of magnitude when 12 weight percent Texanol™ is added to coatings with MFFT values moderately above room temperature. Three weight percent additions increase the diffusivity factor by one order of magnitude.<sup>17</sup>

There are three factors one must take into consideration that are vital to the effectiveness of the coalescent. The rate at which the solvent evaporates from the coating is extremely important. If the coalescent evaporates faster than water, then it will have little to no effect on the film formation. If the solvent takes a long time to leave the coating, then the film will be softened for the duration of the evaporation. Even a small amount of coalescent leftover can soften a film a noticeable amount. And if the coalescent is non-volatile (which is important if coating VOCs must

remain low), it must still allow the coating to harden enough for it to perform as intended. The glass transition temperature of the coalescing aid is also important; the lower the  $T_g$  the more effective the coalescent will be. Many accept the estimation of coalescent  $T_g$  to be  $2/3$  that of the melting temperature, though this is by no means universally true. And finally, the solubility of the coalescent is also very important. If the solvent is mainly soluble in water (insoluble in the polymer) then it will take much longer for it to diffuse into the particles to effectively encourage coalescence. On the other hand, if the solvent is very soluble in the polymer, then it will readily diffuse into the particle and aid in coalescence, but may remain in the polymer as a plasticizer.<sup>17,1</sup>

### *Water Based Coating Formulation Basics*

Formulations for water-based coatings can vary greatly, but many of them have very similar components in order to achieve the desired final film properties. These coatings will commonly include pigment, biocide, rheology modifiers, surfactants, dispersants, defoamers, other small additives, and binders. As discussed previously, MFFT and coalescence is a common hurdle for latex based coatings and requiring a coalescent is very common for this reason. Surfactant and dispersant aid in the stabilization of the coating and incorporation of pigments and other additives. Rheology modifiers grant the wet coating desirable flow and leveling properties, pigments provide aesthetic and body to the film, biocides reduce the tendency for biological degradation of the coating both before and after application, and defoamers help with processing of the product. The binder is the polymer which provides many of the final properties of the film, and is the main focus of this report.<sup>19,1</sup>

### *PVC and CPVC*

Pigmentation is one of the most important formulation parameters that coatings formulators account for when designing targeted systems. Pigments have a profound effect on the final properties of both the paint/coating and the performance of the finished film. From viscosity, to hiding, to stain resistance, pigments can affect many performance characteristics.

Traditionally, weight relationships are what formulators use when designing paints and coatings, but volume relationships with respect to pigments are of more value and fundamental importance. One of the most popular and important ways of quantifying a pigment loading in any system is using the calculated pigment volume concentration, or PVC. The PVC is merely the volume percent of pigment in a *dry* film. It is important to remember that the PVC should be expressed as a percent, not a volume fraction, and that the PVC of a *wet* coating is of no interest.

The development of this understanding is credited to Asbeck and Van Loo<sup>20</sup>, who go on to observe a stark change in film properties above certain PVC values in different coating systems. They called this PVC level the *critical* pigment volume concentration, or CPVC. The CPVC is defined as the PVC where there is just sufficient binder to provide a completely adsorbed layer around each and every pigment particle. At this PVC, any additional pigment added to the system would not have enough binder to surround the particles, and there would be void spaces in the film. These void spaces will be composed of air, increasing the porosity and affecting other film properties. The CPVC depends on many factors including binder type, pigment type, solids percentage, dispersant usage, and others.<sup>20,18</sup>

The hiding effect of coatings relies on two main factors: the dry film thickness (DFT) and the refractive index (RI) differences between polymer and pigment. It is easy to understand that the larger the DFT, the more difficult it is for light rays to penetrate the film, reach the substrate, and reflect back out through the film. Refractive index is also very important, and is the main reason hiding of a coating increases sharply above CPVC. The RI of rutile  $\text{TiO}_2$  is 2.7, the RI of polymer is typically around 1.5, and the RI of air is 1.0. As we pass through the CPVC, air-pigment and air-polymer interfaces are created in addition to the already existing polymer-pigment interfaces. These interfaces between regions of differing RI values scatter light with great efficiency, disallowing light to be reflected off of the substrate through the coating. Other authors discuss CPVC in more detail, and is not the focus of this report.<sup>1,21,22</sup>

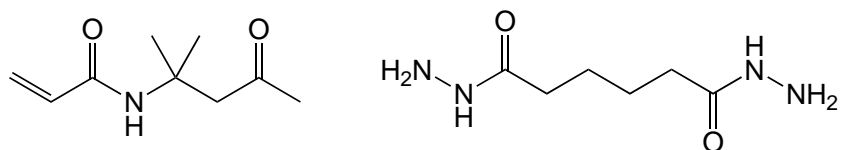
## 2.6 Emulsion Polymer Crosslinking

There are many methods and available chemistries that can be used to crosslink polymer systems. The decision to use one over the many other options is the prerogative of the chemist or formulator doing the work. These decisions can be driven by innumerable reasons, some of which may include toxicity, efficacy, performance requirements, cost, regulatory concerns, and most importantly, compatibility with the given polymer system. The two crosslinking methods that are used in this study are based on techniques that are both industrially and commercially relevant. There are other methods that could be explored; however, the following are of most immediate interest with respect to the scope of the project.

### *Interparticle Crosslinking (Keto-Hydrazide Crosslinking)*

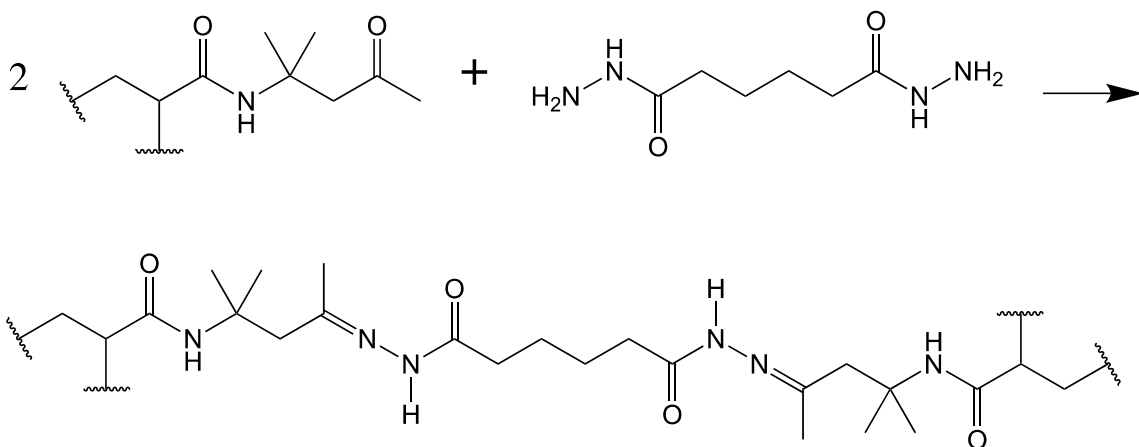
The development of many mechanical properties for waterborne coatings can usually be enhanced by creating covalent bonds between the polymer chains. We call these bonds between chains crosslinks, and they provide both benefits and considerations when it comes to the overall performance of the film. For example, the film formation process is known to rely heavily on the interdiffusion of polymer chains into adjacent polymer particles. This phenomenon is known as coalescence. If the polymer chains are covalently bound together, it profoundly inhibits the chains' ability to diffuse and coalesce into a uniform film. Ideally, the crosslinking reaction would take place soon *after* chain diffusion and coalescence occur, allowing the formation of a film, followed by the hardening and final development of properties.<sup>22</sup>

Diacetone acrylamide (DAA) is a monomer commonly used in acrylic emulsion polymers that contains a pendant carbonyl group that can undergo a crosslinking reaction with strong difunctional nucleophiles such as, adipic dihydrazide (ADH). The reaction between the ketone and hydrazide groups results in either an imine, enamine, or more likely a mixture of both. The precise mechanism of this reaction has not been reported but is non-essential in understanding the impact that the reaction has on the coating properties.



**Figure 4.** Diacetone acrylamide (left) & adipic acid dihydrazide (right)

Polymers containing DAA for the purpose of crosslinking with ADH, are first neutralized to slightly basic conditions with ammonium hydroxide before adding ADH and mixing until dissolved. ADH is a water-soluble compound and thus should remain in the aqueous phase of the emulsion. Upon drying of the film, water evaporates along with ammonium hydroxide resulting in film formation/coalescence and a reduction in pH. As the coating turns acidic, the rate of the crosslinking reaction between the ketone and hydrazide moieties increases. Since the ADH is water soluble and mostly found outside the particle, the vast majority of crosslinking occurs on the outside of the particles and between adjacent particles that have outwards facing DAA rich regions. This is referred to as interparticle crosslinking. Some ADH will have penetrate into the polymer particle and result in intraparticle crosslinking as well, but not on the same scale as interparticle crosslinking. The crosslinking reaction, shown below in Figure 5, is acid-catalyzed and produces water as a reaction by-product. The water continues to evaporate along with ammonium hydroxide as the film finishes curing, and the crosslinking reactions reach completion.<sup>22,23</sup>



**Figure 5.** During film formation ADH reacts with DAA that has polymerized into the backbone, resulting in a crosslink between two polymer chains. This reaction is acid catalyzed and thus occurs upon evaporation of volatile base (usually ammonia) during film drying. As the reaction proceeds, water is produced as a byproduct and evaporates, further driving the equilibrium to the right.

#### *Intraparticle Crosslinking (Difunctional Monomer Crosslinking)*

FRP relies on having an acrylic unsaturation, usually an alkene that can undergo radical attack and subsequent propagation reactions with similar monomer molecules. These monomers are usually monofunctional, meaning that they have only one moiety on the molecule that can participate in this reaction. However, multi-functional monomers with two or more of these alkene unsaturations exist and are used to create polymers with branches, crosslinks, and higher molecular weights. Typically used at very small amounts (1% POM), the addition of these monomers can result in huge performance swings of the polymer. However, any benefits offered to the film must be balanced with the reduction in chain mobility and poorer film forming capabilities of the resin. Since these crosslinks are built into the backbone of the polymer throughout the synthesis process, the entire particle will achieve full crosslink density before being applied to the substrate and allowed to coalesce. This also results in a lack of crosslinking bonds between neighboring particles and can lead to poorer final film qualities. An increase in stiffness and strength are commonly seen in these systems, but without chain entanglements will lack cohesion.<sup>8</sup>

## 2.7 Water Whitening and Blushing

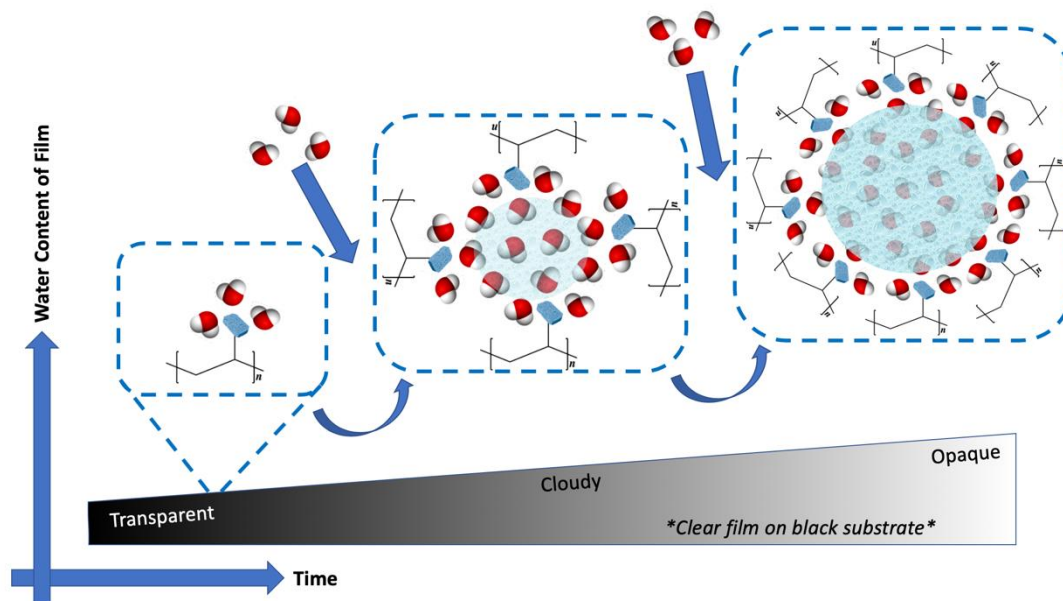
Coating plasticization is caused by small molecules such as water intercalating themselves between the polymer chains in a coating. These small molecules facilitate the movement of polymer chains around one another, aiding in coalescence before and during film formation, but detract from beneficial mechanical properties post film formation. Water often plasticizes films, especially after having been submerged for extended periods of time. Water will tend to associate with polymer films in one of three ways: either as freezing free water, freezing bound water, or as non-freezing bound water, the latter being heavily associated with water that contributes to plasticization of a polymer sample.<sup>24</sup> These three water-polymer interactions can be studied using DSC, and developing an understanding of the relationship between the polymers  $T_g$ , waters  $T_g$ , and the plasticized or wet  $T_g$  of the polymer with non-freezing bound water. The plasticization of polymer films is a direct result of this non-freezing bound water associating with polar moieties along the backbone of the polymer chain. This artificially lowers the  $T_g$  of the polymer by allowing the chains to move past each other with more ease.<sup>25,26,27,28</sup>

Past this plasticization point, additional water infiltration results in the growth of heterogenous domains of water and soluble residues. These domains will locate themselves around either polar moieties of the polymer chains, or more likely, in areas of the film that contain pockets of increased surfactant concentration. During film formation the adsorbed surfactant molecules will tend to migrate toward substrate-film interfaces, film-air interfaces, or localized regions within the film.<sup>29</sup> Throughout the duration of the films contact with water, it will also tend to leach out surfactant molecules that are able to migrate out of the film.<sup>30</sup> This phenomenon is significantly reduced when polymerizable surfactants are used, as they become part of the polymer backbone after having participated in the FRP process.<sup>11</sup> Once the water domains grow large enough, they begin to scatter light due to the refractive index difference between the polymer binder and the water in the film. This results in an effect known as water whitening or blushing. Somewhere between hydroplasticization and water whitening of the film, freezing bound water can be detected by using DSC.<sup>25</sup> Water is driven into the film by a number of forces, namely osmotic pressure and surface tension.<sup>29,31</sup>

## 2.8 Current Mechanistic Understanding of Water Uptake

The water uptake mechanism proposed is merely an extension of the same phenomenon that drives the blushing effect. This is believed to occur in three stages: first the film is hydroplasticized quickly when in contact with water. Hydroplasticization results in a softening of the film as water molecules associate along polar moieties in the polymer chain, as well as within surfactant rich domains within the film.<sup>32</sup> This water is known as non-freezing bound water, as it is non-detectable as a water glass transition peak in a DSC thermogram, however a reduction in polymer  $T_g$  can be observed (this is known as the polymers *wet*  $T_g$ ). Following the association of water molecules in the film, domains form where heterogenous pockets of water are created. These areas are large enough to scatter light due to the RI difference between binder and water, resulting in an opaque film. At this point water will be detectable using DSC and will appear as freezable water on the thermogram. The polymer will still appear to have been hydroplasticized as its  $T_g$  value will be artificially lower than if it were dry. Finally, these domains will continue to grow, being driven by osmotic pressure and capillary forces, the film may exhibit intense blushing and even the formation of micro blisters and large blisters. Eventually the film will reach equilibrium with its surrounding aqueous environment and cease to uptake any more water. This water uptake process is shown below in Figure 6. As expected, the more water the film absorbs, the worse performance is expected to be.<sup>33</sup>





**Figure 6.** The proposed three step process by which water uptake occurs. The film which is clear and applied to a black substrate is initially submersed in DI water. Upon initial contact with water, water molecules penetrate into the film where there are more hydrophilic functional groups or areas of the polymer. These may include areas where there is a high concentration of surfactant, acid monomer or other polar functional groups. Following this hydration, certain areas continue to absorb more water up to and past the point of saturation. Finally, as these domains grow large enough, they begin to scatter light and the coating slowly turns opaque due to the heterogenous domains of water within the clear coating. Forces acting inside the water “pocket” expand the film, swelling it beyond its starting size and shape, this force is opposed by the polymer matrix resisting expansion.

There have been studies relating to polymer design and its effect on water uptake, but these studies tend to be very targeted and less applicable to the products and technology used at EPS. Incorporation of increased acrylic acid onto the outside of the polymer particle has been shown to increase film porosity, increasing water uptake and water vapor transmission. This is attributed to the increase in colloidal surface charge on the particle, as well as the film structure itself.<sup>34</sup> Other papers attribute an increase in blushing resistance to keto-hydrazide crosslinking in fluorinated polymers. This system contains perfluoroethyl groups in the second-stage of the polymer, and exhibited increased water-repellency, but poorer resistance to blushing and uptake.<sup>35</sup> The majority of studies into the effect of surfactant on the water uptake, focus their effort on developing surfactant free methods of polymer synthesis. These methods include clay stabilized systems<sup>14</sup>, polymers supported by RAFT copolymerization<sup>36</sup>, fluorinated surfactant<sup>37</sup>, reactive

surfactant<sup>29,10,11,15</sup>, and other surface active monomers<sup>12</sup>. Results show increasing evidence to support a surfactant free system for use in a water-resistant film.  $T_g$  has been correlated to blushing where researchers found higher  $T_g$  values led to increased resistance to blushing. These results fail to take into account the effect of actual polymer composition as the monomer ratios are altered. Instead they attribute the blushing to the tendency for surfactant to migrate out of the film due to decreased adsorption strength to softer polymer particles.<sup>28</sup>

### 3. MATERIALS AND METHODS

#### 3.1 Materials

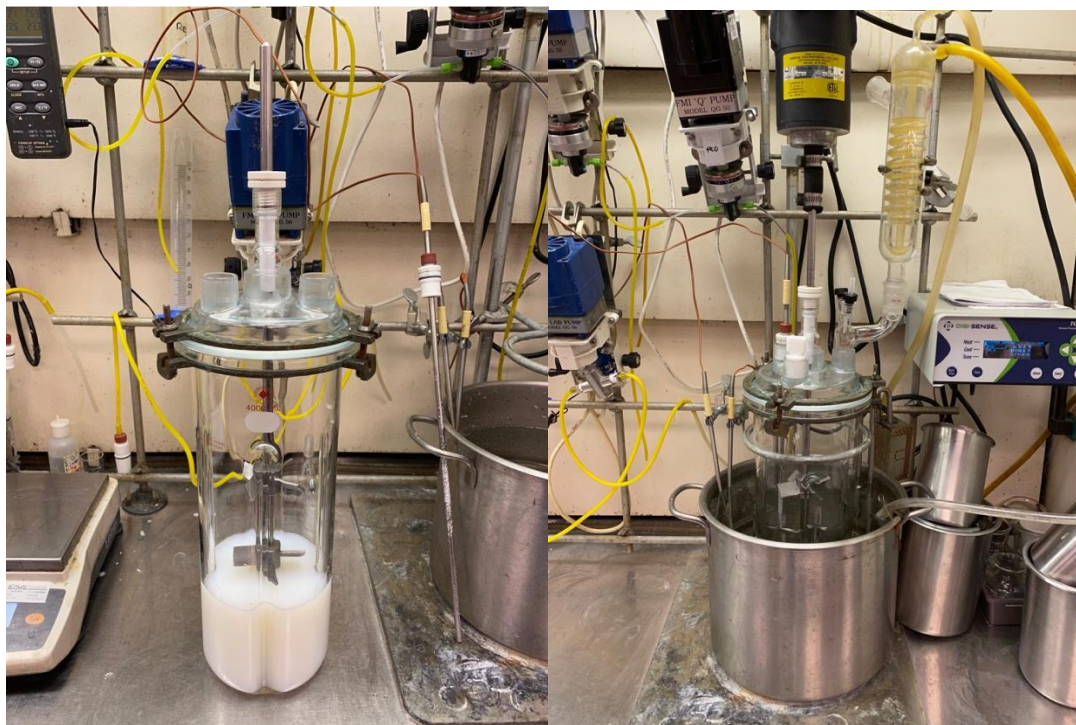
All materials and precursors are provided by Engineered Polymer Solutions and The Sherwin-Williams Company. All materials are used as provided from the manufacturer without any further processing unless noted in the methods or results sections. These materials are sourced from many suppliers, all of which are not to be listed in this paper. The films and polymer test specimens are all prepared using a semi-continuous emulsion polymerization process. Monomers used include styrene, methacrylic acid, acrylic acid, *n*-butyl acrylate, methyl methacrylate, butyl methacrylate, ethyl hexyl acrylate, diacetone acrylamide, 1,6-hexanediol diacrylate, acetoacetoxyethyl methacrylate, phosphate adhesion monomers (PAM monomers A and B), and other un-disclosed monomers. Crosslinking is facilitated using adipic acid dihydrazide. Initiators used include erythorbic acid, *t*-butyl hydroperoxide, sodium persulfate, and ammonium persulfate. A proprietary iron catalyst solution is also used during polymerization. Surfactants include anionic phosphate ester, non-ionic alcohol ethoxylate, and a reactive anionic co-polymerizable surfactant. Dodecyl mercaptan is the chain transfer agent used. Thickener used is Acrysol RM-12W, a non-ionic urethane thickener for development of low-shear viscosity. Acticide MV, Acticide MBS, and Acticide M 20 S are used as biocide additives. A 30.0 wt.% seed latex of undisclosed composition and ammonium hydroxide are also used.

#### 3.2 Methods

##### *Emulsion Polymerization*

A semi-continuous emulsion polymerization is used to produce polymer resins at 50% solids for nearly all samples. The reactor is initially charged with water and a small amount (2.5% on monomer solids or POM) of seed latex. This is then placed in a water bath and stirred until brought up to temperature as shown in Figure 7. All redox polymerizations are run at 60-65 °C using erythorbic acid and TBHP as the redox initiator package. Thermally initiated emulsions are

run between 80-85 °C using ammonium persulfate as the charge and co-feed initiator, and erythorbic acid and TBHP are used as the chase initiators.



*Figure 7. Reactor charged with latex seed and water (left). Reactor hot water bath setup (right). Redox initiators are fed from the graduated cylinders located in the rear of the hood in the left-hand picture.*

The monomer pre-emulsion shown in Figure 8 is then prepared by adding water, surfactant, ammonia, and specialty monomers to a pot and beginning agitation. To this, the bulk monomer is added slowly to create a stable oil-in-water emulsion. The more hydrophobic monomers are added first to begin the process and create the most stable emulsion. After a few minutes of stirring, the pH of the mixture is taken and recorded. If the pH is not within the target range, adjustments are made by adding additional ammonium hydroxide. The initiator solutions are then prepared by adding a desired amount of reducing and oxidizing agents to beakers and mixing with water. The actives of each initiator feed used is kept at about 0.3% for redox batches and 0.1% for thermal batches. Initial redox charge is 0.1% POM and the charge for thermal batches is 0.35%.



**Figure 8.** Monomer pre-emulsion building process (left). Monomer pre-emulsion complete and ready for reactor feed (right).

After all solutions are prepared, a small charge of initiator is added to the reactor and the monomer and initiator feeds are started. Temperature and feed rates are recorded and adjusted throughout the duration of the feed process. The initiator feed continues for 1 hour after the monomer feed finishes (3-hour monomer feed) to facilitate reaction completion and nearly full conversion of monomer. If the polymer is intended to be two-stage, the secondary monomer feed will begin immediately after the primary feed ends, and the initiator feed will have been set to ensure a 1 hour overrun of the second monomer feed. At the conclusion of each monomer feed, a 30-gram rinse of DI water will be added to the pot and fed through the pump to ensure any remaining pre-emulsion is added.





**Figure 9.** Monomer pre-emulsion, redox co-feed, and redox charge ready for synthesis. Initiator charge (front beakers) is added to the reactor, at which point monomer and initiator co-feeds are initiated. This particular setup is for a two-stage polymer, where the second larger emulsion will be fed following the completion of the first.

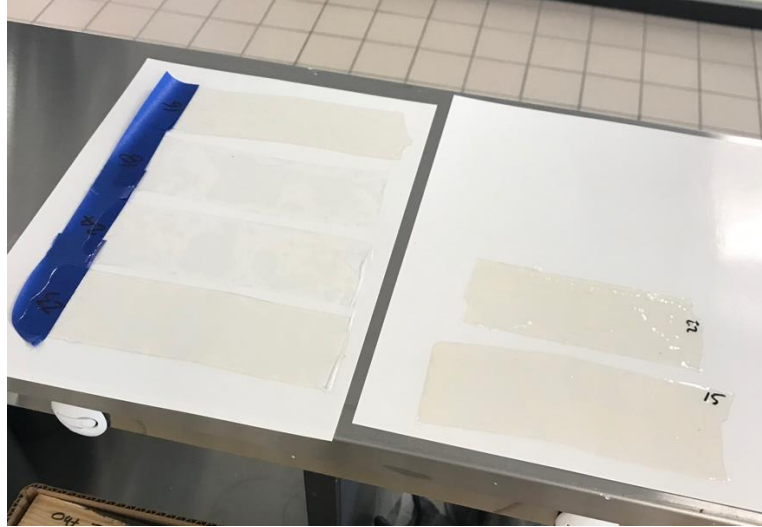
After all initiator is added at the end of the fourth hour, the water bath is cooled, and the final ammonia/biocide charge is added once the reactor temperature falls below 35 °C. If the formulation calls for the addition of ADH, it is added 10 minutes after the ammonia. The ADH is mixed for 15 minutes before filtering the product through a 100-micron filter bag into a 0.5-1.0-gallon jug for storage.



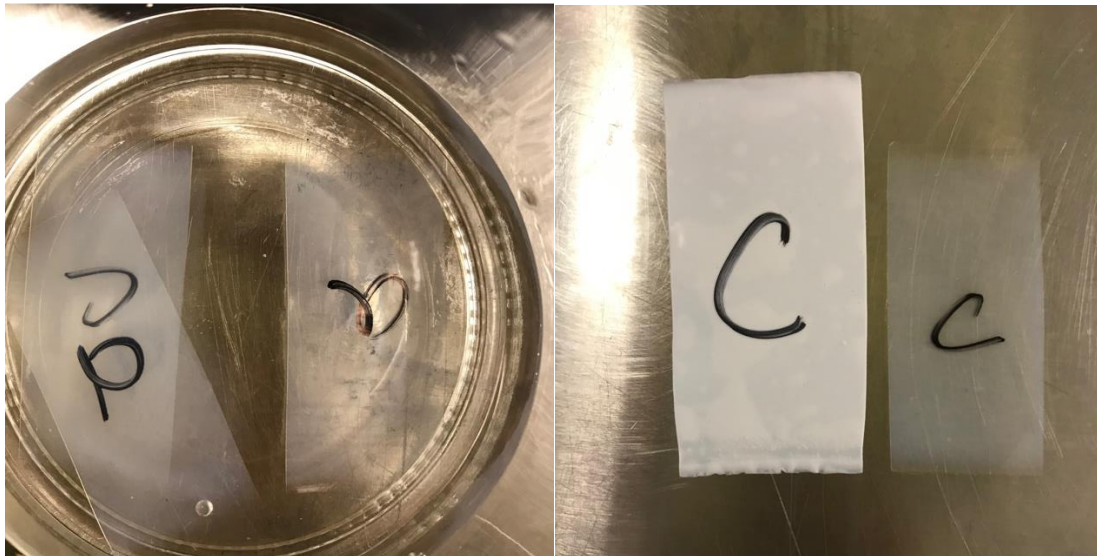
**Figure 10.** A finished emulsion reaction with polymer still in the reactor. At this point the product is filtered through a 100-micron filter into the jugs (left). A series of completed polymer resins (0.5 gallons) awaiting testing (right).

#### *Film Preparation and Water Uptake Gravimetric Analysis*

Polymer product is mixed with Acticide MV at 1% (biocide), BYK 024 at 0.5% (defoamer), and Acrysol RM-12W at 0.5% (thickener) on polymer solids by mass. This is then mixed for 1 hour to ensure uniform and complete incorporation of the thickener. The coating is then drawn down at 30 wet mils on polypropylene sheets and allowed to dry at room temperature (21 °C) and 50% RH for one week, resulting in the films shown in Figure 11. Following the one week dry, the films are peeled off the substrate and cut into 1" x 2" sample coupons (in triplicate), weighed on a Sartorius Entris 64-1S analytical balance, and put into a jar with 500 mL of DI water at 21 °C. The films are periodically pulled out of the water, patted dry to remove any excess water, and weighed before being submerged again. They are measured every 3-5 days for 10-14 days in order to develop a mass change curve. Figure 12 shows a set of three films during this test. After the final measurement the films are discarded, and a new round of data collection is started with the next set of polymers. This is a slightly modified and simplified version of the method outlined in ASTM D471<sup>38</sup>, which is an important test method for any roof coatings that must pass ASTM D6083<sup>39</sup>. Error between triplicate samples is accepted if below 5%.



**Figure 11.** Resins are formulated and then drawn down on release liner or polypropylene sheets. Following the drying of the film, 1" x 2" samples are cut out and tested.



**Figure 12.** After test samples are prepared, they are placed in a jar of DI water and left at room temperature for the duration of the testing time. Periodically the samples are pulled out of the water and patted dry before being weighed and placed back into the jar (left). Samples may absorb varying amounts of water, resulting in variable swelling.

#### **Film Preparation and Permeability Testing**

Polymer product is mixed with Acticide MV at 1%, BYK 024 at 0.5%, and Acrysol RM-12W at 0.5% on polymer solids by mass. This is then mixed for 1 hour to ensure uniform and complete



incorporation of the thickener. The coating is then drawn down in triplicate on polypropylene sheets and allowed to dry at room temperature (21 °C) and 50% RH for one week. Following the one week dry, the films are peeled off the substrate and cut into circles the diameter of the BYK permeability cups. After filling the cups with 10 mL of DI water, the film is placed on the cup between two gaskets and sealed tightly with the threaded cover ring. After weighing the cup, it is placed in a temperature humidity-controlled chamber at 20 °C and 50% RH for 24 hours before being reweighed using a Sartorius Entris 64-1S analytical balance. From the DFT and 24-hour mass difference the specific moisture vapor permeability can be determined.



**Figure 13.** Films are cut out and placed in the BYK permeability cups. Note that these cups have slightly different designs but perform identically.

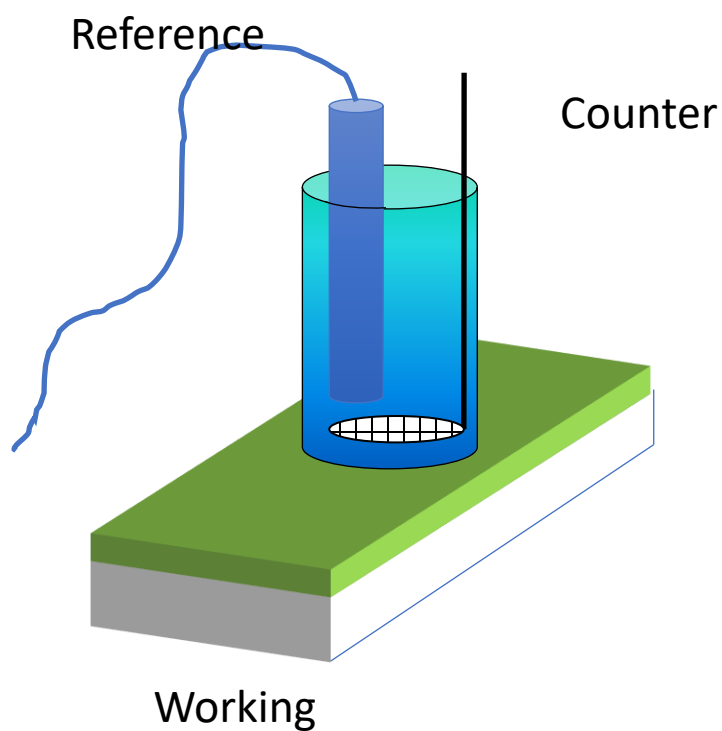
#### *Electrochemical Impedance Spectroscopy*

The polymer sample is drawn down in triplicates on 4" x 8" aluminum Q-Panels at a wet film thickness of 4 mil. The coatings are 50% solids resulting in a ~2 mil DFT. These samples then dry for 7 days at room temperature (21 °C) and 50% RH for one week. All measurements were taken on a Gamry Instruments, Reference 6002 Potentiostat / Galvanostat ZRA (Zero Resistance Ammeter).



*Figure 14. EIS potentiostat.*

The samples are then prepared by placing a small column of 0.5% NaCl solution on the coating and connected to working, reference, and counter electrodes. Here a three-electrode setup is used for the measurement: the metal substrate to which the coating is applied acts as a working electrode, a platinum mesh in the solution is a counter electrode, and a silver/silver chloride electrode is used as the reference electrode. The frequency range for the measurements was 100,000-0.01 HZ, collecting 10 points/decade using 10 mV RMS of AC perturbation potential.



*Figure 15. Diagram of sample with three electrode setup for EIS.*

A small sinusoidal potential of 5-10 mV is applied to the open circuit potential at varying frequencies. Phase lag and the current response for varying applied frequencies is measured by the instrument. The data is then modeled using Randles cell circuit to obtain values of coating resistance and coating capacitance.

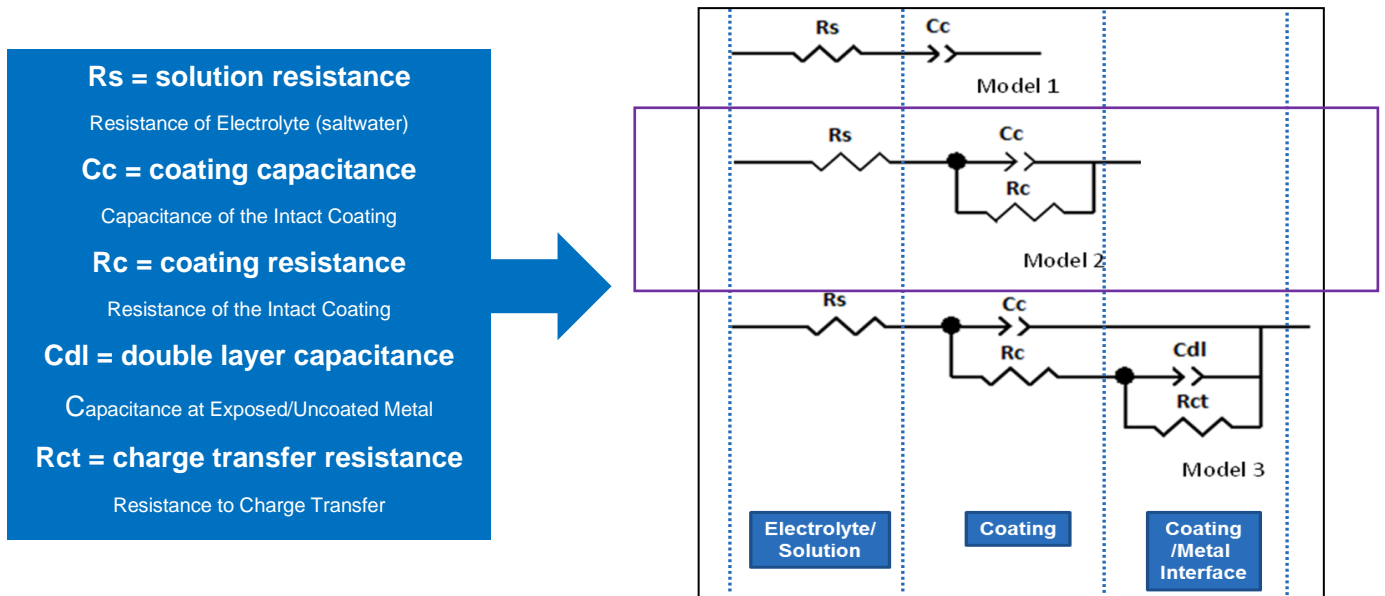


Figure 16. Three electrode setup for EIS measurements and depiction of Randles cell circuit.

The two parameters of interest are coating resistance (also known as pore resistance) and the coating capacitance. Coating resistance is the resistance of the coating to uptake incoming water and ions. The magnitude of this resistance is indicative of the coatings state of degradation at any given time. The three timepoints used for data collection are 30 minutes, 24 hours, and 1 week after exposure. Coating capacitance relates to the total amount of water currently in the coating. Due to the solution's increased conductivity than the coating binder, as the water uptake increases, the capacitance will increase. The following formula is used to help calculate a value for coating capacitance or  $C_c$ .

$$C_c = \epsilon \epsilon_0 A / d$$

Here,  $\epsilon$  is the dielectric constant of the coating, and  $\epsilon_0$  is the permittivity of free vacuum.  $A$  is the exposed area of the coating to the salt solution and  $d$  is the thickness of the coating. Any

step changes or rapid increases in the coating capacitance value indicates that delamination of the coating may have occurred.

#### *Contact Angle Measurements*

The polymer sample is drawn down in triplicates on 4" x 8" aluminum Q-Panels at a wet film thickness of 4 mil. The coatings are 50% solids resulting in a ~2 mil DFT. These samples then dry for 7 days at room temperature (21 °C) and 50% RH for one week. Following sample preparation, the static water contact angle of the coating is measured using a Kruss DSA-30 instrument.

#### *Differential Scanning Calorimetry*

One gram of the polymer is put into an aluminum weigh pan and allowed to dry for 24 hours at room temperature (21 °C) and 50% RH. Approximately ten milligrams of the polymer sample is then cut off and placed into a tared DSC pan. This value is recorded into the TA Instruments Trios software. The sample is then run using the following procedure on a TA Instruments Discovery DSC25 with an RCS90 cooling system in order to obtain the  $T_g$  value of the polymer.

1. Equilibrate to -75 °C
2. Ramp to 150 °C at 10 °C/min (serves to reset any thermal history of the polymer)
3. Equilibrate to -75 °C
4. Ramp to 150 °C at 10 °C/min

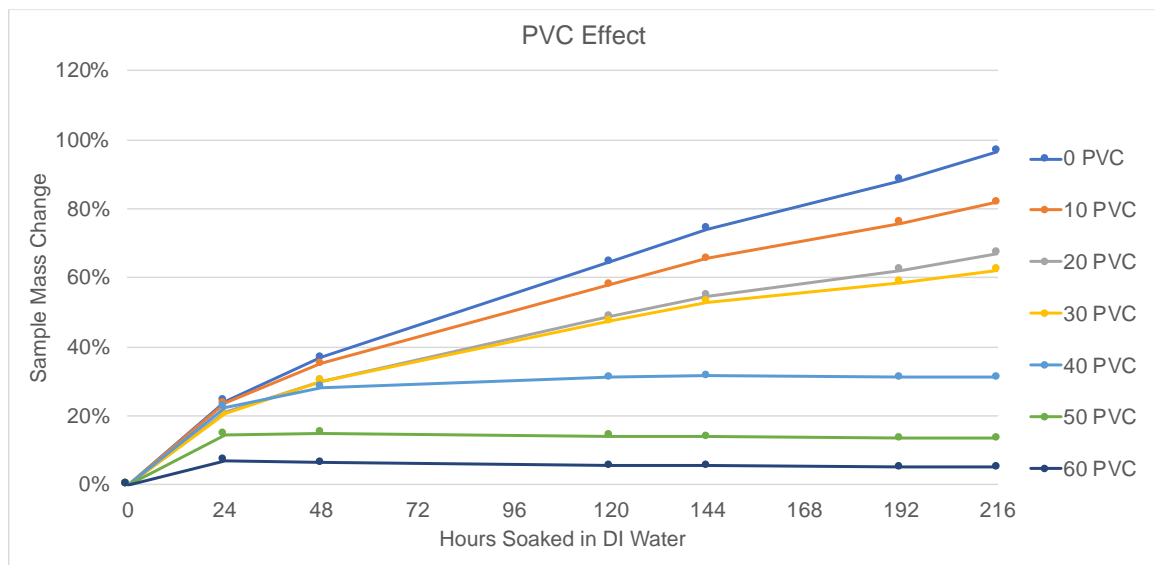
The software is then used to determine the  $T_g$  of the sample on the second heating cycle, following thermal history reset of the polymer.

## 4. RESULTS AND DISCUSSION

### 4.1 Effects of Coating Formulation and Formation

#### PVC

The same control polymer was used to prepare 7 coatings with the same formulation but varying PVC levels. The coatings all used a 1/7 ratio of TiPure R-960 (titanium dioxide pigment) and Drikalite (calcium carbonate pigment). The 7 coating samples had PVC levels of 0, 10, 20, 30, 40, 50, and 60 PVC, with all formulation factors remaining constant. A master grind paste was made and added to 7 letdowns in different amounts before being drawn down at 40 wet mils. It was seen that water uptake decreased uniformly as the PVC was increased, and these results are plotted in Figure 17.



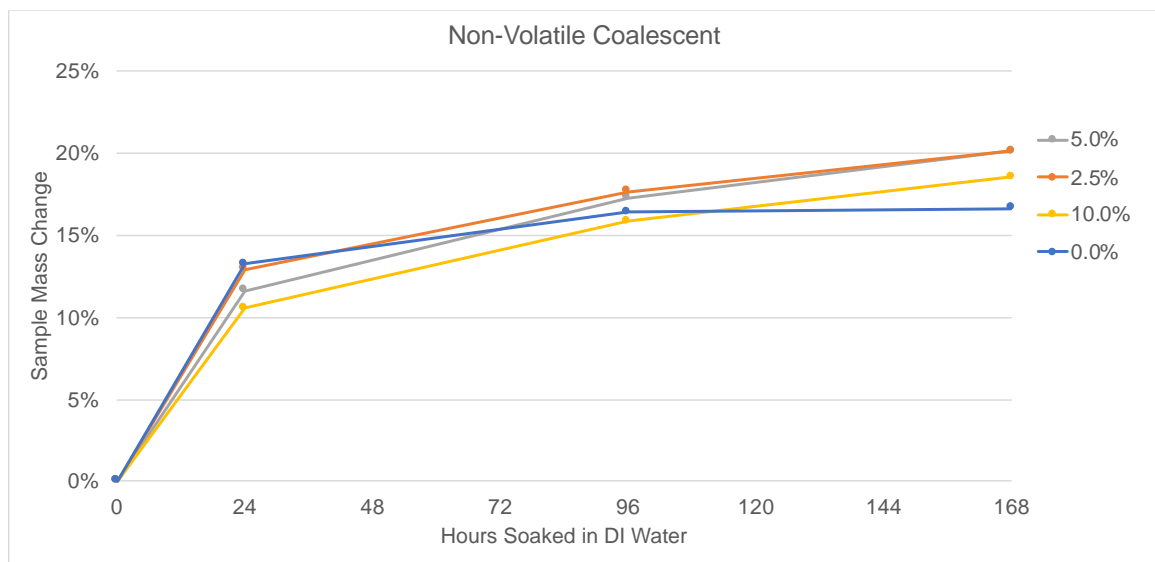
**Figure 17.** PVC effect on the water uptake of a roof coating. Samples are cut out into 1" x 2" coupons, weighed, and submerged in 500mL DI water at room temperature (21 °C) for the duration of the experiment. At each data point the films are removed from the jar, patted dry to remove excess surface moisture, weighed, and returned to the jar.

The decrease in water uptake here is attributed to the decreased volume fraction of polymer in each sample with higher pigment loading levels. The pigment particle is not able to expand and absorb water in the same way that the polymer matrix in the coating can. Water molecules instead adsorb onto the surface of the pigment particle, where polymer adsorption is

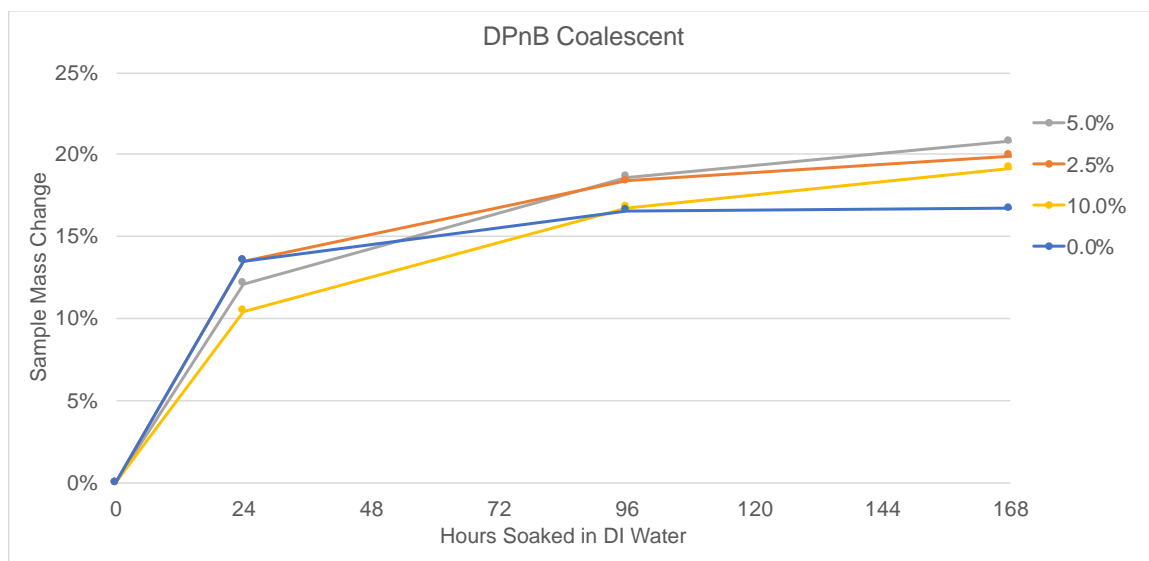
less favorable. Since the polymer matrix is the only domain in the film that can expand and uptake water, increased PVCs displace polymer that could otherwise uptake water. This effect is seen in all samples that were assessed and remains constant even above the CPVC of the coating which is estimated to be below 60 PVC.

### *Coalescent Level*

In studying the effect of coalescent, the same roof coating formula as above was used. Here, a single polymer formulation was used to prepare 8 samples using two different coalescent solvents at 4 different levels, plotted in Figures 18 and 19. EPS 9147 which is a low VOC coalescent designed for acrylic emulsions was loaded at 0%, 2.5%, 5.0%, and 10.0% based on polymer solids. These formulations were then used in a water uptake assessment as described in the methods. The same procedure was employed to prepare and study the effect of a volatile coalescing aid, dipropylene Glycol *n*-Butyl Ether (DPnB) at the same loading levels.



**Figure 18.** The effect of a low VOC coalescing aid on the water uptake of a roof coating.



**Figure 19.** The effect of a VOC coalescing aid on the water uptake of a roof coating.

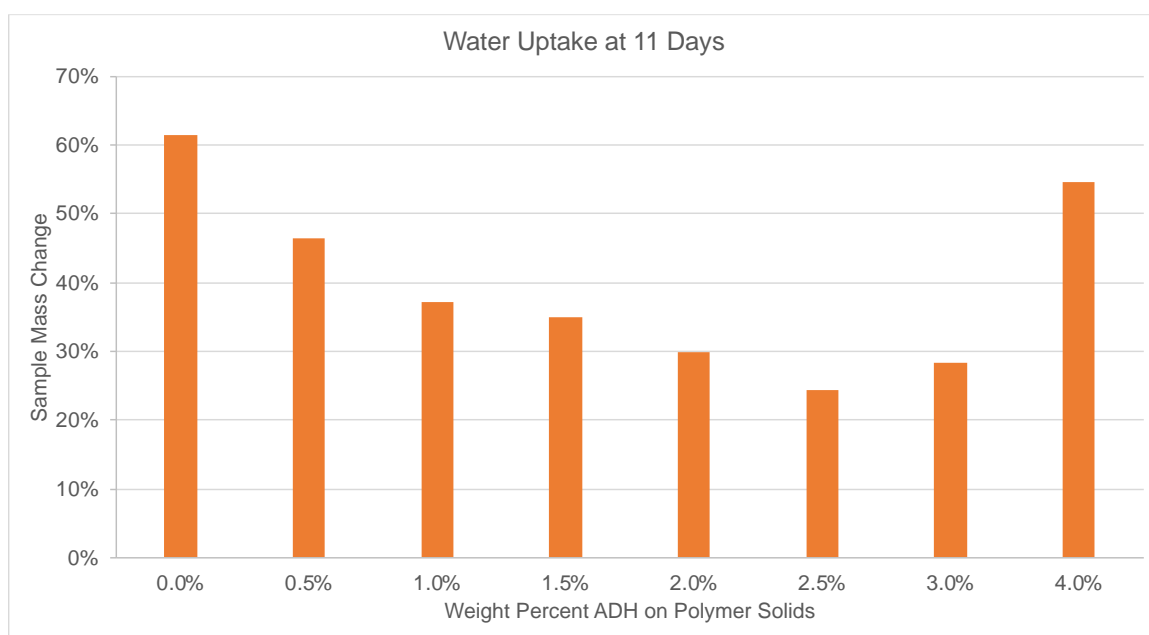
The same trend was observed using both types of coalescing solvents. The addition of coalescing solvents to a coating resulted in slightly elevated water uptake values. This may be due to the plasticization that the coalescent causes in the polymer, allowing water to migrate into the film with more ease. The presence of the coalescent should also increase the osmotic pressure within the coating as well. This would force water into the coating. The increased rate of water uptake at the outset of the experiment may be attributed to the improved film formation of the film. The coalescent should enhance film formation and particle coalescence, lowering the rate of water ingress, however this does not result in lower overall water uptake values.

#### *Ratio of ADH to DAA*

The reaction between ADH and DAA during film formation and coalescence of particles results in crosslinks between polymer chains both within the same particles, and between adjacent particles. A polymer with 4% DAA by polymer mass was loaded with varying levels of ADH. These levels correspond to stoichiometric ratios encompassing an excess of ADH or DAA. A more detailed description of their composition is outlined in Table 1, with results shown in Figure 20.

**Table 1.** Sample composition including molar and stoichiometric ratios of DAA and ADH. Note that 2.0% ADH results in a 1:1 stoichiometric ratio of ADH to DAA based on molecular weight and functionality.

% ADH	% DAA	ketone/hydrazide	mol DAA/ADH
0.0%	4.0%	-	-
0.5%	4.0%	4.1	8.2
1.0%	4.0%	2.1	4.1
1.5%	4.0%	1.4	2.7
2.0%	4.0%	1.0	2.1
2.5%	4.0%	0.8	1.6
3.0%	4.0%	0.7	1.4
4.0%	4.0%	0.5	1.0



**Figure 20.** Water uptake of samples with varying molar ratios of ADH and DAA.

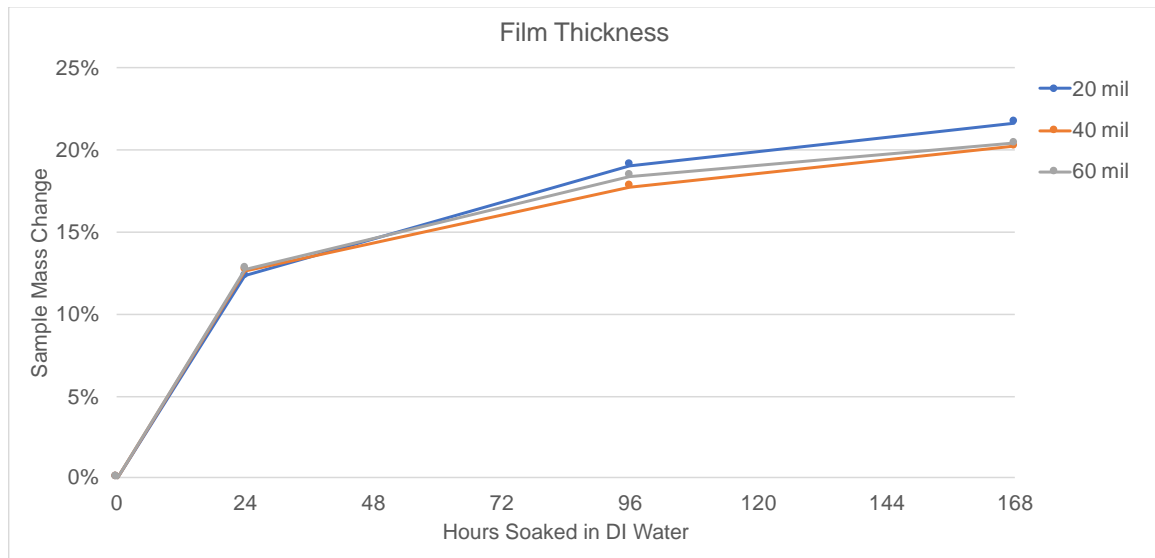
A stoichiometric equivalent of ADH and DAA in these formulations corresponds to 2.0% ADH. The data shows that a slight excess of ADH provides the polymer with optimal water uptake properties. During the crosslinking reaction, the bifunctional ADH molecules must react with two different DAA moieties of the polymer. When the ratio of ADH/DAA is lower than this ideal proportion, there are free DAA functional groups not participating in any crosslinking. This leads to a decrease in performance due to the hydrophilic nature of that monomer. When a large excess of ADH is used in the coating, there will be free ADH in the coating, which leads to a sharp decrease



in coating properties. A slight excess of ADH ensures that crosslinking density is maximized, and that the coating system has been optimized.

### *Film Thickness*

Film thickness is an easily controlled parameter, and one that has many effects on the final coating performance. In preparation for this experiment, the same control coating formulation that was used previously was drawn down at 20, 40, and 60 wet mils. These coatings were then assessed using the same method outlined above. Dry film thicknesses were half that of the wet film thickness, due to the coatings volume solids being 50%.



**Figure 21.** *The effect of coating thickness on the water uptake of a roof coating.*

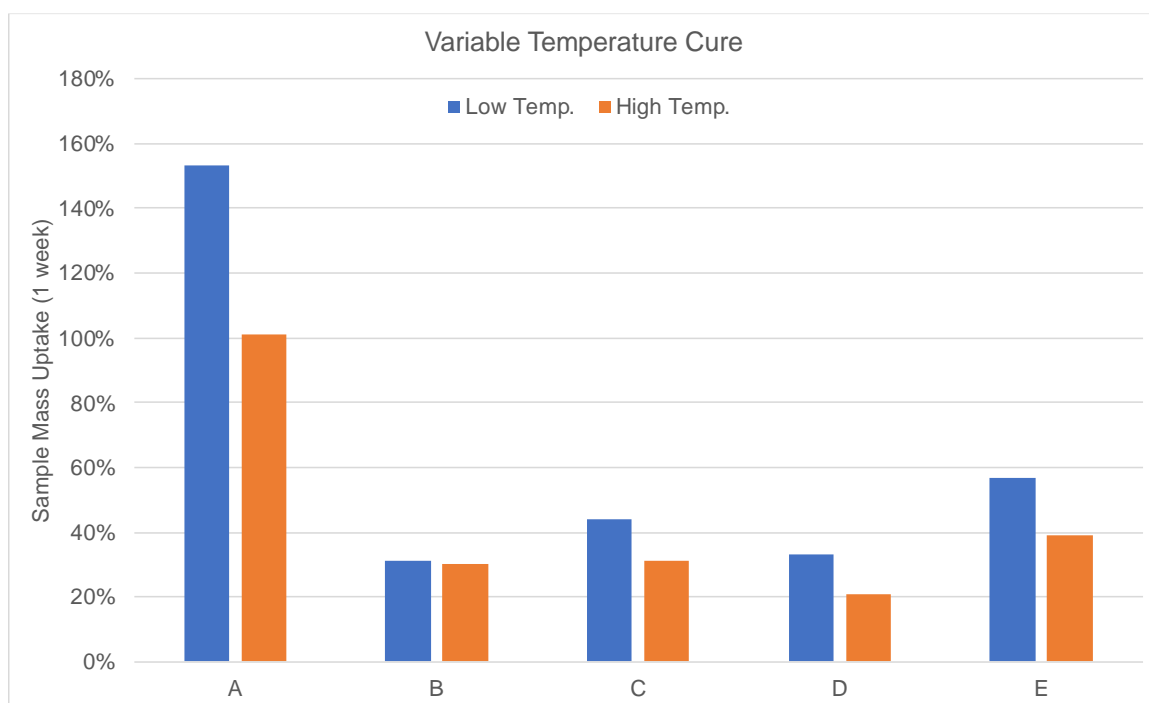
It appears from Figure 21 that the film thickness has little to no impact on the water uptake of the coating. The film is porous and susceptible to water penetration, meaning that the film in its entirety will become saturated relatively quickly. The samples will swell an amount that is proportional to their starting size and will gain mass in this same proportion.

### Film Curing Conditions

The degree of film formation has always been something that coatings chemists believe to be important to the final properties of the film. In order to qualitatively study the effect of water uptake, films with varying compositions shown in Table 2 were cured both at room temperature and at an elevated temperature in an oven for 7 days. These samples were then tested and compared against each other.

**Table 2.** These polymers are compositionally identical and were processed using the same methods. Unless otherwise noted, the polymers were prepared using redox initiation, grown on a seed, and are all acrylic.

Sample	Description
A	4% Anionic surfactant
B	2% Non-ionic surfactant
C	2% Non-ionic surfactant, no PAM
D	Reactive ionic surfactant, no PAM
E	Sample D; <i>in-situ</i> seeded



**Figure 22.** Water uptake values after a one-week soak at 21 °C. Low temperature film formation was done at 21 °C, slightly above the polymer  $T_g$ , and high temperature film formation was done at 50 °C, well above the  $T_g$  of the polymer.

The results in Figure 22 indicate that film forming the coating at an elevated temperature has a positive impact on the water uptake performance. As the temperature is raised the particles are able to deform and coalesce more effectively. Some samples showed greater variation between high/low temperatures depending on their composition. Table 2 is included to highlight the key differences between each sample, which are otherwise identical in composition and processing. Interestingly, sample B shows very little improvement. This may be due to the non-ionic surfactant having less of a barrier effect on film formation during coalescence than anionic surfactant, even at ambient temperatures.

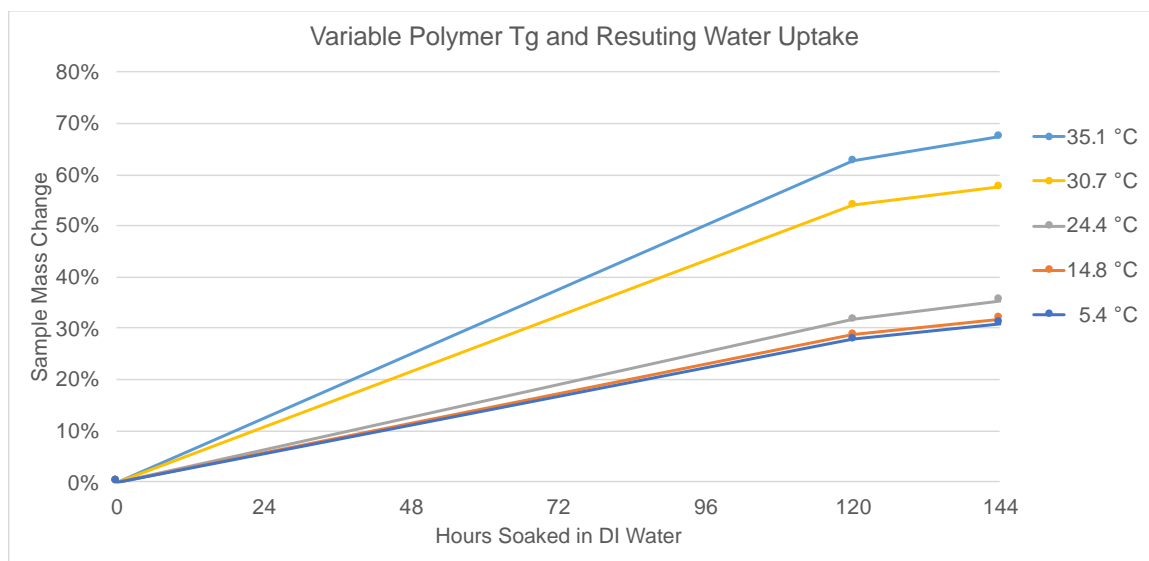
## 4.2 Effects of Polymer Design

### *T<sub>g</sub> Effect*

$T_g$  is an important and easily controlled parameter of a polymer. Reduced  $T_g$  values are commonly associated with better film formation but at the cost of reduced durability. Here, 5 polymers were prepared with a range of  $T_g$  values. The  $T_g$ s were manipulated by changing the ratio of styrene and EHA monomer. For polymers with higher  $T_g$ s, more styrene was used in the polymerization. The difficulty with associating  $T_g$  values and performance parameters, is that the value as well as the polymer composition changes simultaneously.

**Table 3.** Polymer samples with  $T_g$  values and required coalescent loading.  $T_g$  was measured using a TA instruments DSC of neat polymer.

Measured Polymer $T_g$	Coalescent Loading for RTFF
5.4 °C	0%
14.8 °C	4%
24.4 °C	8%
30.7 °C	12%
35.1 °C	16%



**Figure 23.** The effect of polymer  $T_g$  on the water uptake of a coating.

Figure 23 shows a trend opposite to what was initially hypothesized. As the  $T_g$  values increase, the water uptake of the polymers is seen to increase as well. One explanation is that this result was driven by coalescent loading, rather than the  $T_g$  itself. As seen in a previous result, coalescent tends to have a negative impact on water uptake. In addition, this result could be driven by a change in polymer composition.

#### *Polymer Synthesis DOE #1*

To efficiently assess the effects of various polymer compositions, a DOE was designed to study how molecular weight, glass transition temperature, hydrophobicity of bulk monomer, and crosslinking density alter the water uptake of the resulting polymer. The DOE is a half fractional factorial with a midpoint and four factors, resulting in an experiment with 9 runs. These polymers were synthesized in the following run order and tested at the same time, using identical methodology as outlined in the methods. Table 4 outlines the factors, their levels and other physical

**Table 4.** DOE #1 designed to assess the effect of crosslinking, molecular weight, monomer hydrophobicity, and  $T_g$  on water uptake. Crosslinking is achieved with DAA monomer and ADH, molecular weight is decreased by addition of 0.5% DDM chain transfer agent, the hydrophobicity is altered by using either styrene or methyl methacrylate as the bulk monomers, and finally the  $T_g$  is controlled by changing the ratio of EHA & BA to Styrene or MMA.

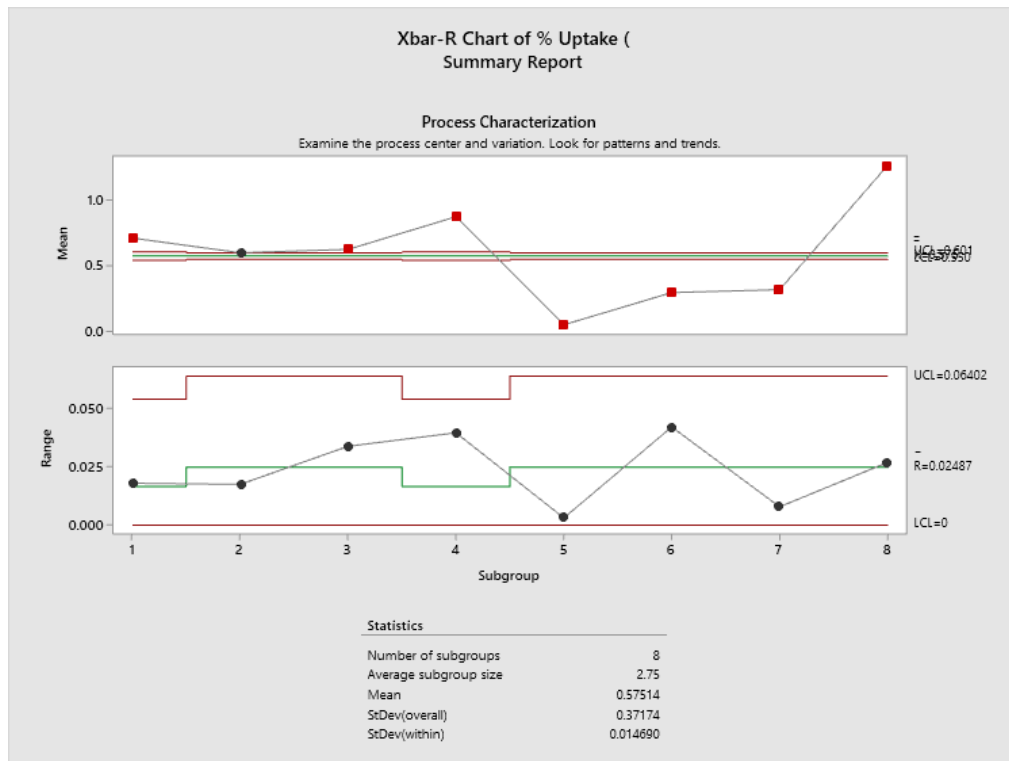
<b>Crosslinking %</b>	<b>0%</b>				<b>4%</b>				<b>2%</b>
<b>Molecular Weight</b>	<b>High</b>		<b>Low</b>		<b>High</b>		<b>Low</b>		<b>Mid</b>
<b>Hydrophobicity</b>	<b>MMA</b>	<b>Sty</b>	<b>MMA</b>	<b>Sty</b>	<b>MMA</b>	<b>Sty</b>	<b>MMA</b>	<b>Sty</b>	<b>Blend</b>
<b><math>T_g</math> (Fox) (°C)</b>	-5	20	20	-5	20	-5	-5	20	7.5
<b>Page #, Book 266</b>	24	19	17	22	21	23	18	20	16
Std. Order	1	2	3	4	5	6	7	8	9
Run Order	9	4	2	7	6	8	3	5	1
$T_g$ (DSC) (°C)	12	41	35	13	31	15	6	35	22
MFFT (°C)	17	44	38	16	28	18	17	37	19
pH	8.4	8.6	8.6	8.8	8.6	8.7	8.6	8.7	8.4
Particle Size (nm)	120	107	122	109	121	111	113	109	109
Solids %	50%	50%	49%	51%	48%	51%	50%	50%	50%
1-week uptake	126%	63%	71%	30%	5%	32%	60%	87%	18%

Unless noted above, the polymers in the experiment are processed using the same method and compositional variables. These are redox initiated at 60 °C and reacted over 3 hours with a 1 hour clean up. EHA and BA amounts are kept the same (ex. 20% EHA and 20% BA), and the ratio of these two monomers to the high  $T_g$  monomer (styrene or MMA) adjusted to achieve the target Fox  $T_g$ . Styrene and MMA were compared to determine the effect of hydrophobicity, as MMA is ~10 times more water soluble and therefore more hydrophilic than styrene. These monomers also result in polymers with similar  $T_g$  values, meaning that swapping MMA for styrene (and vice versa) will have minimal effect on  $T_g$  and eliminate any unwanted variation in composition. Chain transfer agent was added at 0.5% to the monomer emulsion to reduce the molecular weight of certain samples: high molecular weight refers to samples with no chain transfer.

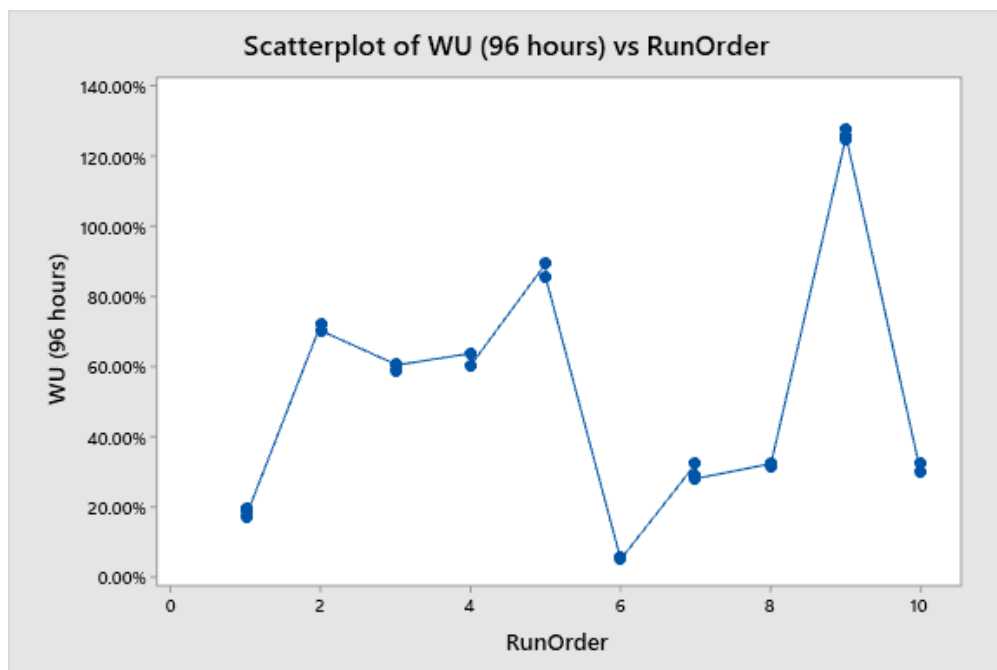
The results were then analyzed to identify the main effects and any 2-way interactions. The analysis is included in the figures and discussion below.

**Table 5.** DOE data overview. The samples provide a large response range, allowing for easy identification of important factors. The min/max/mean indicate a broad range of performance was achieved. The large variation should permit good differentiation between sample conditions.

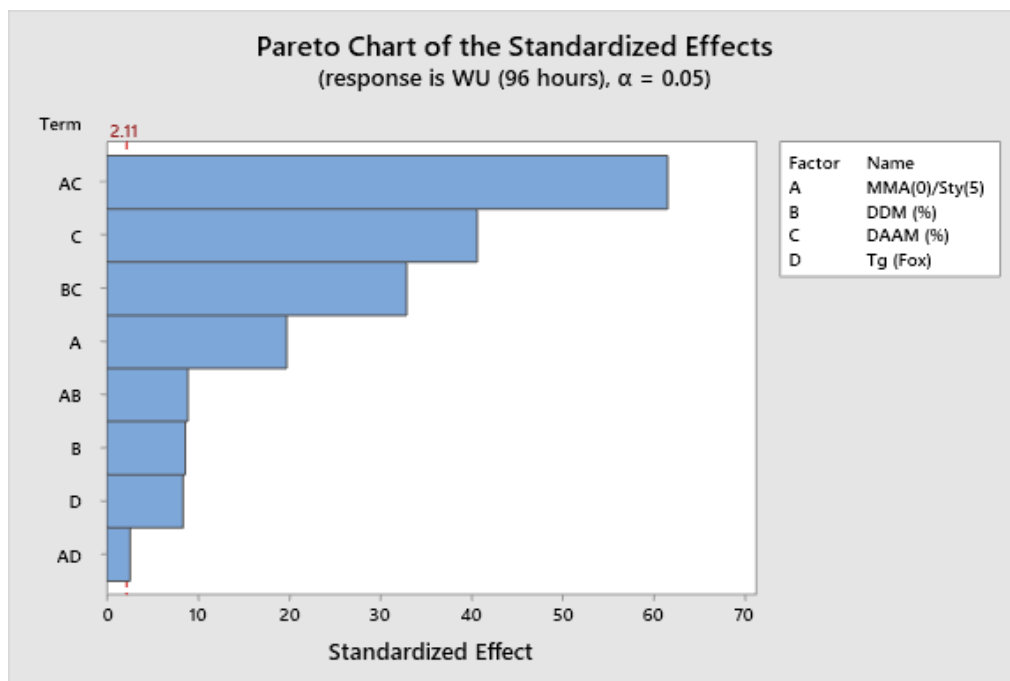
% Water Uptake at 1 week	
Mean	51%
Min	5%
Max	128%
Range	123%
Std Dev	36%



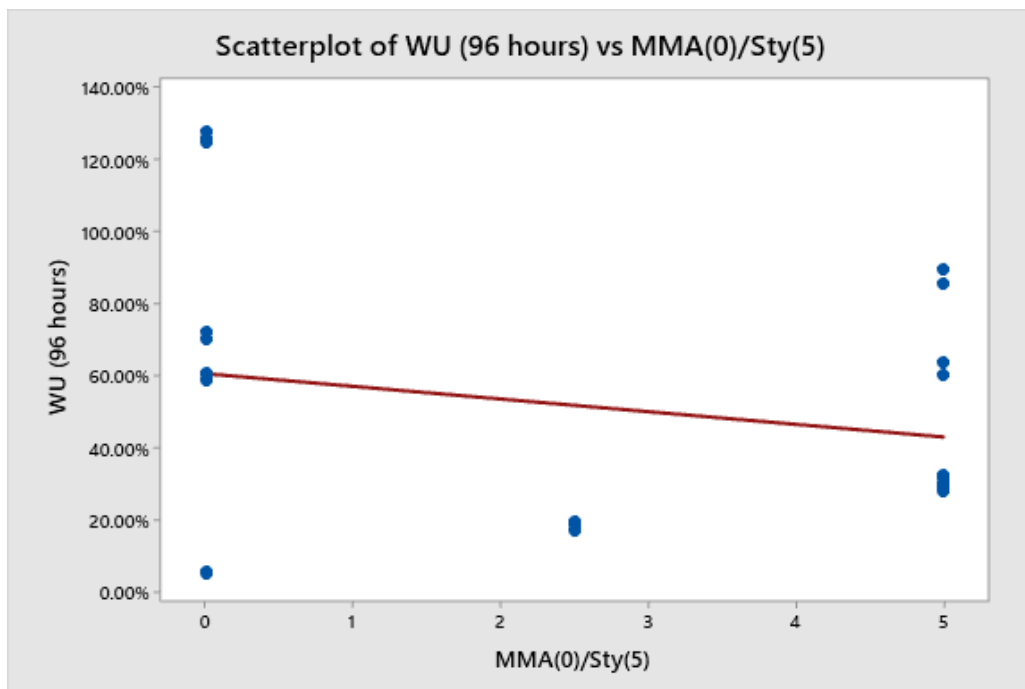
**Figure 24.** Xbar-R chart for one-week water uptake values of DOE polymers. Evaluating the range data (lower graph), where the within subgroup is replicate soak test, outliers have already been removed ( $n=2$  or  $3$ ) the measurement system is in control (no points outside the control limits). The mean within-subgroup range is 2.5% which is historically the expected replicate variation. The X-bar graph (upper) shows the ability for the measurement system to detect the between subgroup variation (polymer treatment). Because there is a large range in responses (122%), and a small range in replicate (avg 2.5%) there is a very strong ability to detect performance differences in the samples tested.



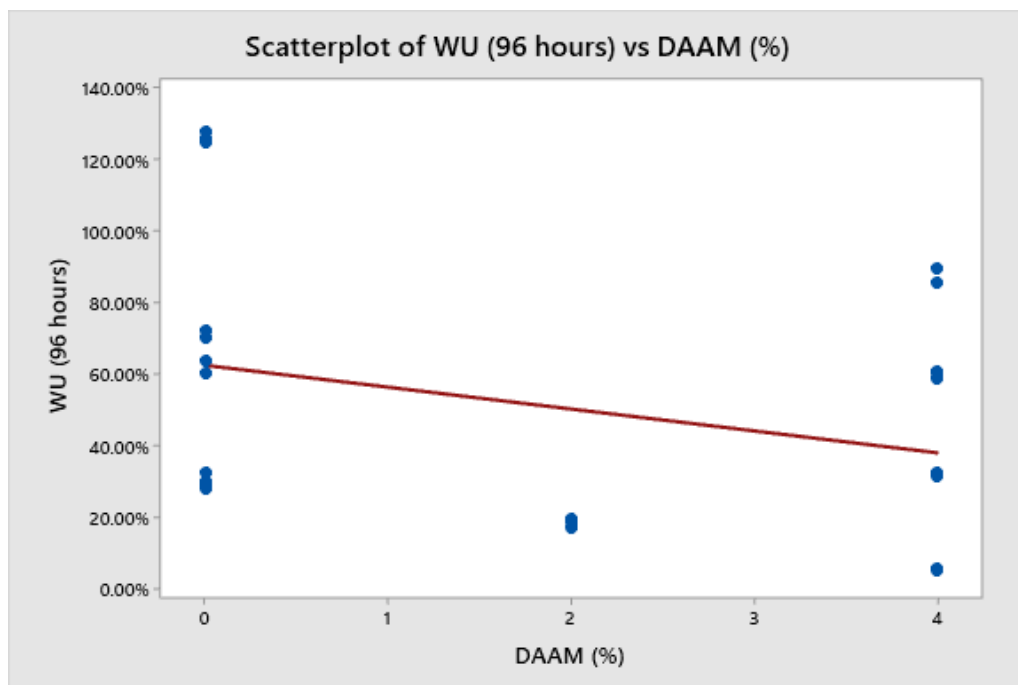
**Figure 25.** Polymers were synthesized in the run order shown here. There does not appear to be any run order dependence. Films were prepared and measured simultaneously and run order dependence could not be assessed.



**Figure 26.** Pareto chart identifying that crosslinking and monomer choice are the main effects of interest. Two-way interactions between monomer choice/crosslinking and crosslinking/molecular weight are also of interest. The plot identifies the other two main effects and two-way interactions as being statistically significant, however they are not nearly as influential, and definitive conclusions relating to them could not be confidently drawn.

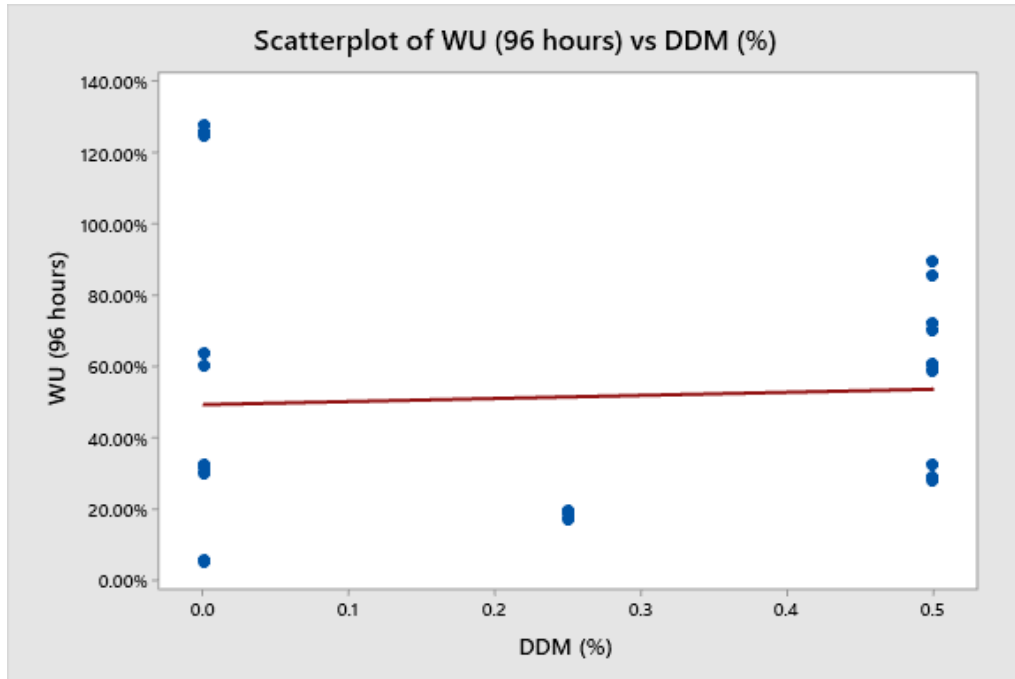


**Figure 27.** The effect of monomer polarity (MMA vs Styrene) is shown in this main effect plot. As the samples become more non-polar and heavily styrenated, they tend to uptake less water.

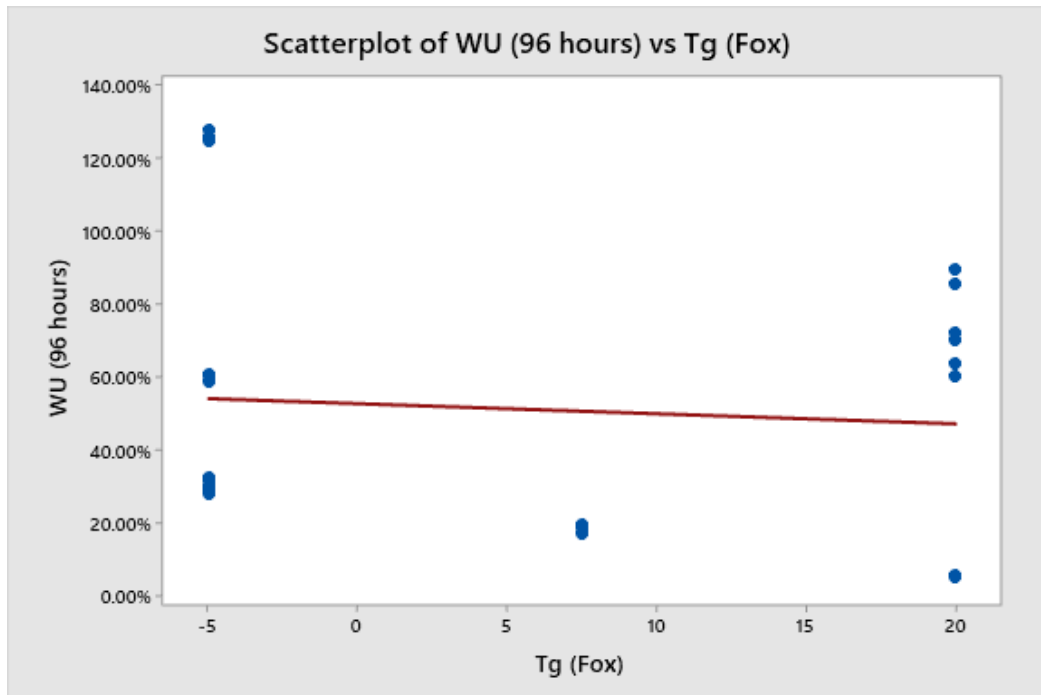


**Figure 28.** The effect of crosslinking is shown in this main effect plot. As the samples are crosslinked, they tend to uptake less water than their non-crosslinked counterparts

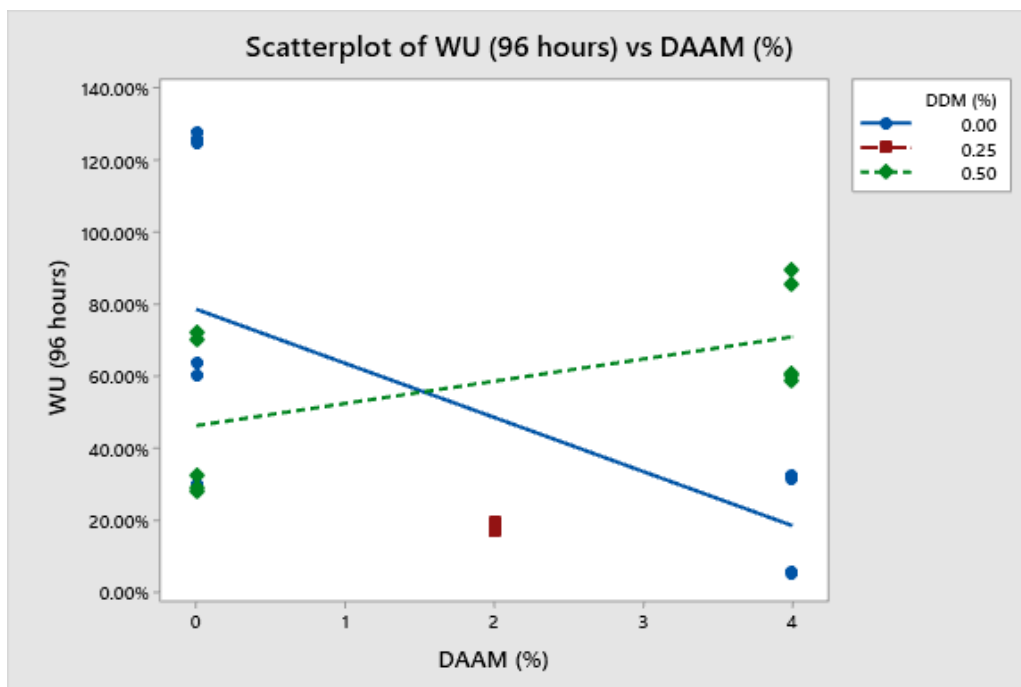




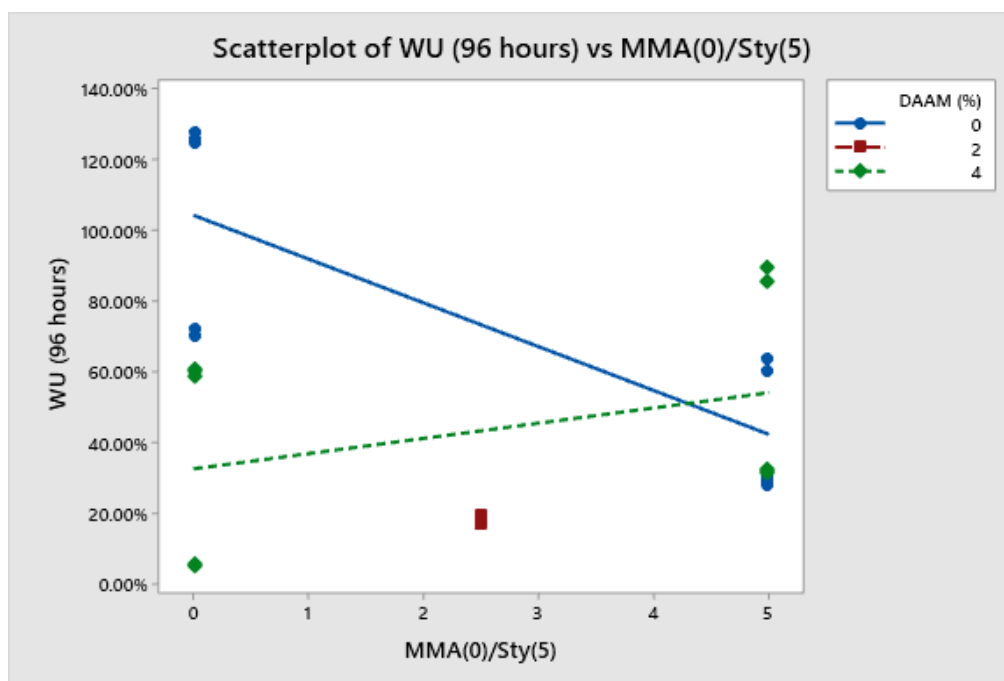
**Figure 29.** The effect of molecular weight is shown in this main effect plot. DDM is shown to have very little impact on the water uptake of these samples.



**Figure 30.** The effect of  $T_g$  is shown in this main effect plot, where samples with higher  $T_g$  values tended to perform worse.



**Figure 31.** The predicted DDM\*XL interaction does not seem to be active in the way predicted, where lower MW was predicted to facilitate better crosslinking, and uptake resistance. MW data would need to be collected to confirm that this conclusion can be drawn.

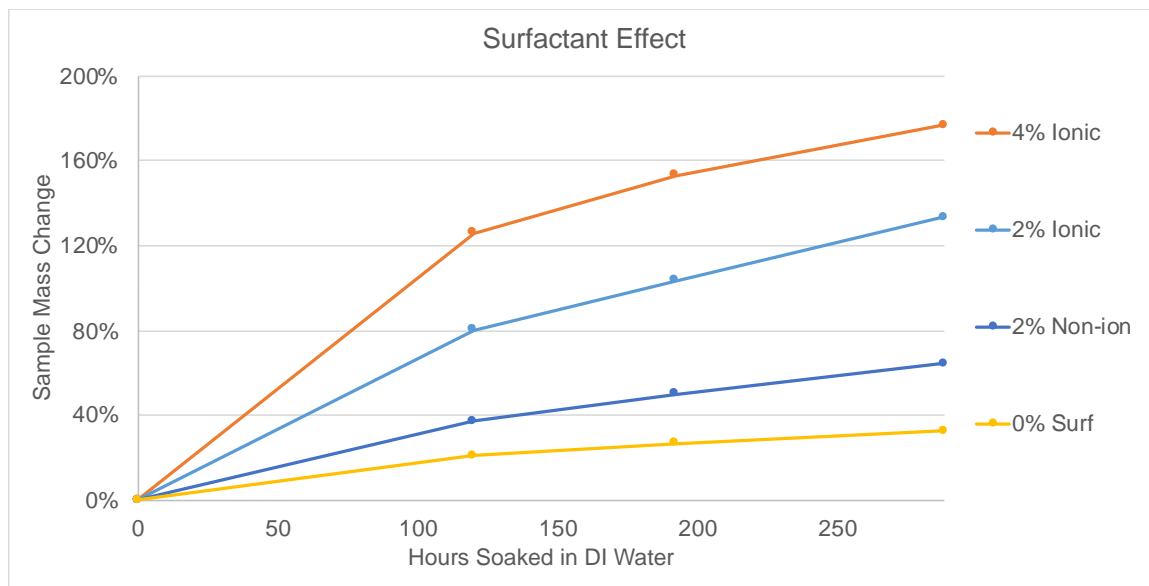


**Figure 32.** An interaction between monomer polarity and crosslinking was not predicted, however may be justified due to more similar solubilities of MMA and DAA monomer, resulting in more uniform incorporation of crosslinkable moieties.

The results show that monomer selection and crosslinking are of utmost importance, and definitively have large impacts on the water uptake of resulting polymers. However, MW and  $T_g$  are not shown in this experiment to have a large influence on the performance. The interactions between monomer-crosslinking and MW-crosslinking do appear to have a significant effect on the performance, though further analysis and experiments should be performed to develop a more confident conclusion.

#### *Surfactant Type and Concentration (Anionic vs. Non-Ionic vs. Reactive Anionic vs. Dialysis) & PAM Monomer*

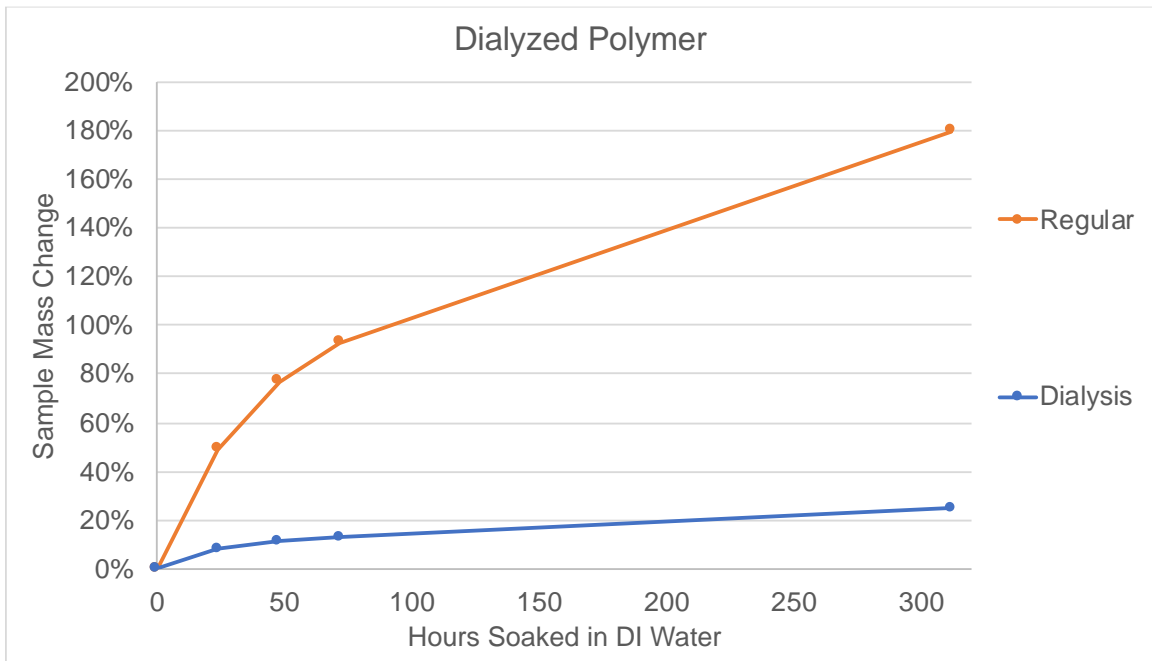
Surfactant is one of the most important factors in traditional emulsion polymerizations. Here the effect of both surfactant type and concentration is assessed in multiple ways. First a series of polymers were prepared using 0%, 2%, and 4% anionic surfactant, and a separate sample with 2% non-ionic surfactant. Surfactant-free polymers rely on ionic monomer and methacrylic acid monomer to help stabilize the emulsion.



**Figure 33.** Effect of surfactant amount and type. Non-ionic surfactants resulted in an increase in performance, similar performance increases were seen when the overall level of surfactant was decreased.

The data in Figure 33 support the hypothesis that less surfactant yields more favorable performance with respect to water uptake. Furthermore, anionic surfactant performed worse than non-ionic surfactant at the same levels, presumably due to increased hydrophilicity of the ionic head group. The surfactant free polymer was extremely unstable and processed in the reactor poorly. The polymer could not be produced on an industrial scale, but this does confirm the association between water uptake and surfactant type.

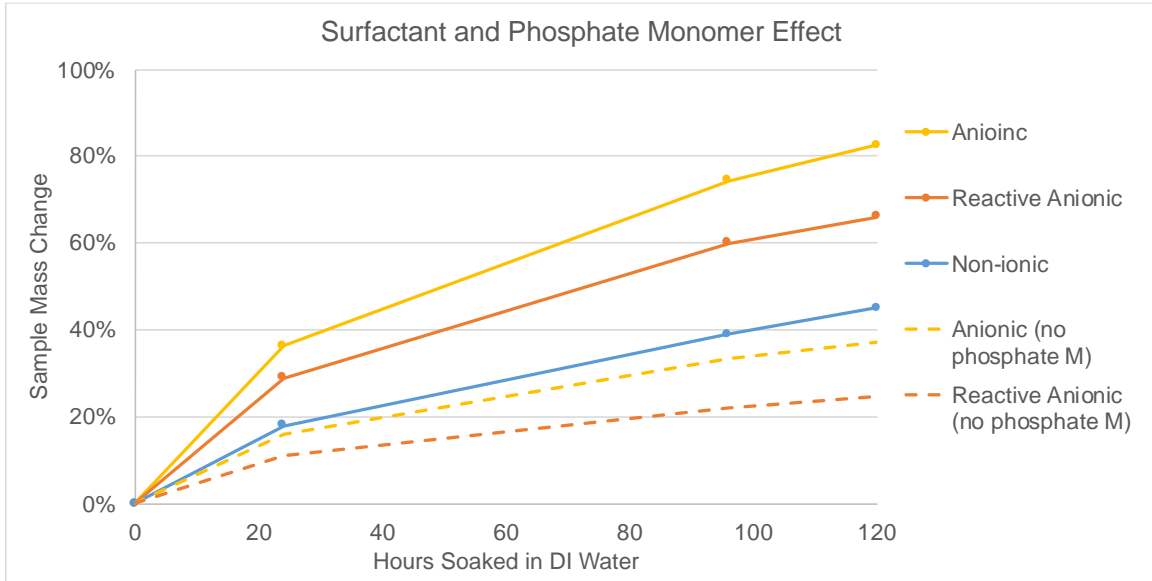
Next, the 2% anionic sample was added to dialysis tubing and dialyzed for 1 week in DI water, the water was changed daily in order to aid in the removal of surfactant from the resin. Following the dialysis, the polymers solids were measured, and the control was adjusted to reflect the same solids. These two samples were tested for water uptake using the same procedure.



**Figure 34.** Polymer before and after dialysis. This serves to further support our conclusion that higher amounts of surfactant are detrimental to performance.

The significant difference between these two samples shown in Figure 34 highlights the importance of surfactant with respect to water uptake performance. Other water-soluble

components may have also been able to leave the resin; however, none could be justified as having such a large impact on the performance of the film. As the surfactant leaves the polymer, the resin becomes more unstable, as the double layer is diminished. During the subsequent film formation process, particle coalescence and interdiffusion of polymer chains can occur with less hinderance.

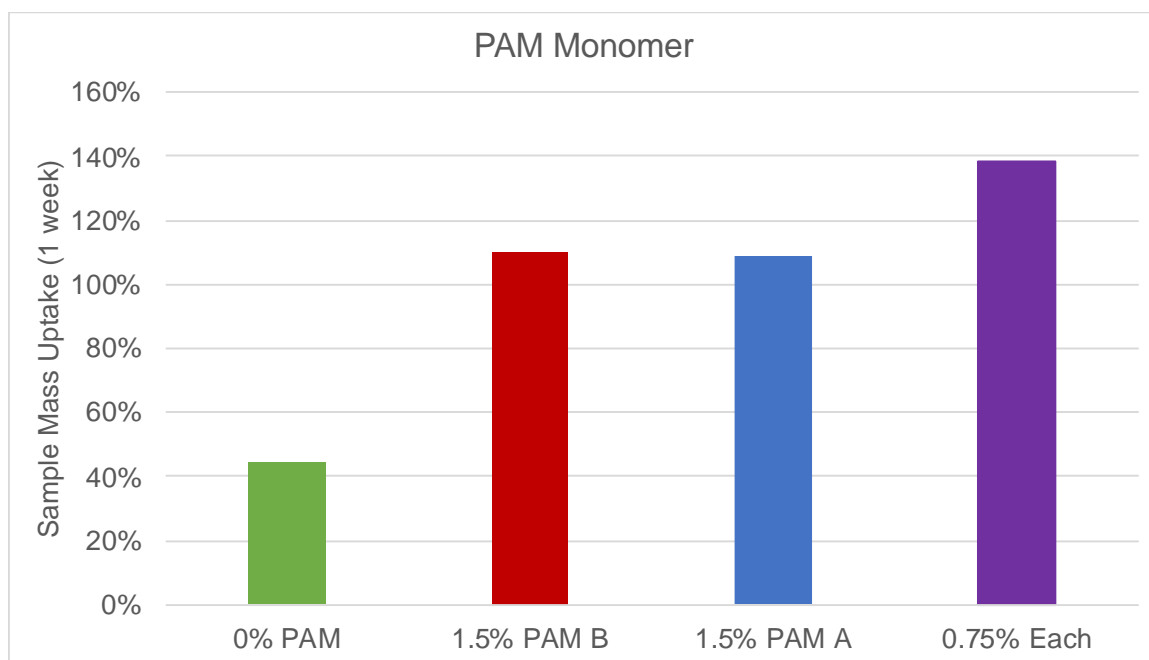


**Figure 35.** Effect of surfactant type and PAM monomer. Non-ionic surfactants performed the best, followed by reactive anionic, and finally anionic surfactants. And polymers that lack PAM monomers also perform much better than those that contain them.

The data presented in Figure 35 confirms the hypothesis that charge-free surfactants perform better than anionic ones, however giving the surfactant reactivity allowing it to polymerize into the backbone results in enhanced performance as well. These surfactants are not allowed to leach out of the film during its soak in water, reducing the formation of channels that water can use to penetrate into the film. This reduces both the rate and ultimate value of water uptake. These surfactants retain their anionic qualities, meaning that there is still a very hydrophilic component surrounding the polymer particles and causing them to perform worse than their non-ionic counterparts.

### Phosphate Adhesion Monomer (PAM A vs. PAM B)

It was determined in the previous experiment that PAM monomer contributed to poor water uptake performance. Each of the previous polymers with these PAM monomers contained 0.75% of each PAM A and PAM B. Four polymers were prepared with either 0% PAM, 1.5% PAM A, 1.5% PAM B, or 1.5% of a 50/50 blend.

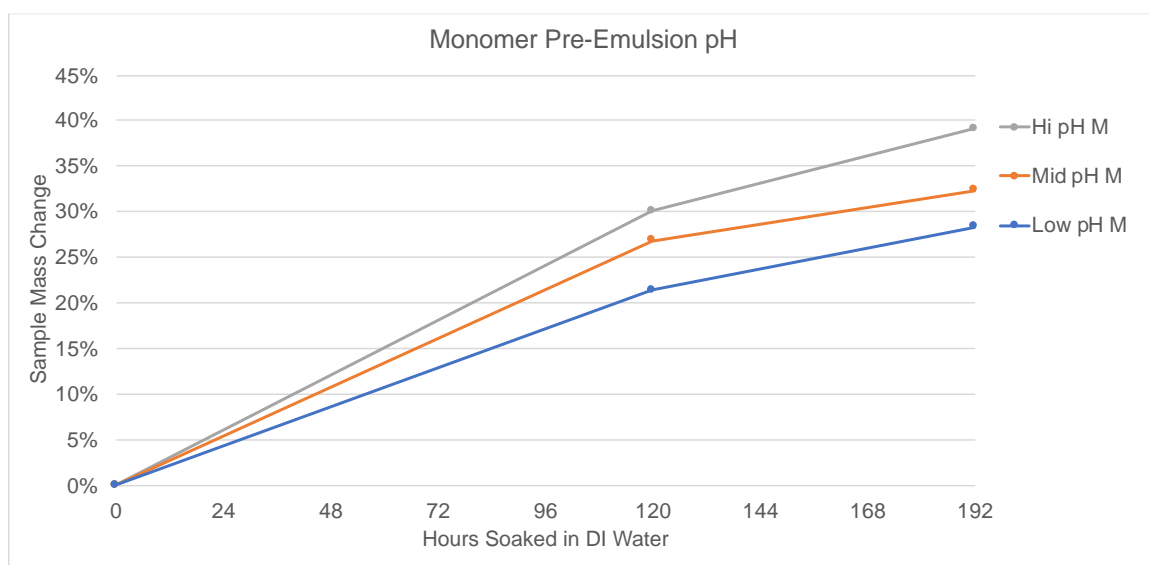


**Figure 36.** Polymer samples with varying loadings of PAM A and PAM B to determine their contribution to water uptake performance in waterborne resins.

It seems from Figure 36 that neither PAM A nor PAM B has a more dominant impact on the polymers performance with respect to water uptake. Both samples with identical loadings of these monomers performed nearly identically, though when a 50/50 blend of the two were used, performance decreased further, perhaps due to increased packing efficiency on the surface of the particle. The phosphate functionality of these monomers contributes to the overall hydrophilicity of the polymer particle and enhances the ability of the polymer chains themselves to associate with water. This drives colloidal stability of the system, while decreasing water uptake performance.

### *pH of Monomer Emulsion*

Adjusting the pH of the monomer pre-emulsion is a critical step in emulsion polymer synthesis. This is known to influence both the surfactant effectivity and the polymerization of the acidic monomers into the polymer. Ionic surfactants rely heavily on pH selection to work properly, as their ionic characteristics can dissipate rapidly at low pH. Similarly, it is hypothesized that monomer such as methacrylic acid (MAA), which has a pKa of 4.7 will exist primarily in its anionic form under typical reaction conditions (ph 5-7).<sup>40</sup> As the pH of the reactor and emulsion is brought below this pKa value, MAA can become neutralized and less water soluble, encouraging polymerization with the growing non-polar chain. If these polar monomers are stimulated to polymerize more readily and found deeper within the polymer particle of the resulting resin, then their interaction with water molecules on the surface of the particle will be reduced.



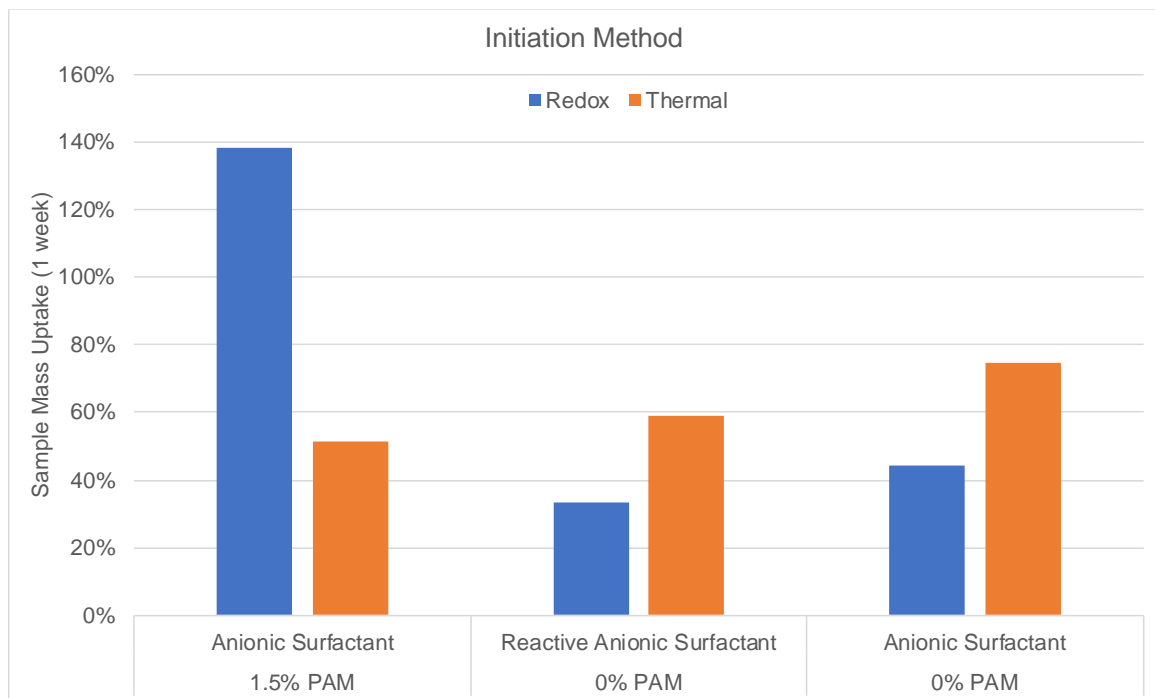
**Figure 37.** pH of the monomer pre-emulsion was changed before the polymerization begun. pH values of 7.0, 5.5, and 4.0 were used respectively as high, mid, and low pH levels. Below pH of 4.0 the monomer emulsion loses stability due to the reduced effectiveness of the anionic surfactant.

Though more acidic monomer pre-emulsions ultimately produced better performing polymers, the improvements were not sizable according to data plotted in Figure 37. A ~5% improvement on the standard resin is good, but ultimately not worth the reduction in stability of the emulsion. However, the results do support the hypothesis that more hydrophilic monomer (MAA)

may be expressed less on the surface of the particle during these conditions. Additionally, at these conditions the surfactant will have less anionic characteristics, thus reducing the double layer surrounding the particles and enhancing film formation.

*Initiation Method*

Emulsion polymerizations are initiated using either a redox coupled reaction, or by using a thermal system in which an oxidizer is thermally decomposed to form the reactive radical species. Redox initiators used are TBHP and e-acid. In thermal systems APS is used and the reaction is carried out at 85 °C. Upon completion of the monomer and APS feeds, a “chase” or “clean-up” redox pair (TBHP & e-acid) are fed for 30 minutes to ensure near full conversion of monomer.



**Figure 38.** Effect of initiation method on water uptake after 1-week soak in DI water. The 6 samples differ in their mode of initiation, type of surfactant used, and the loading of phosphate adhesion monomer (PAM). Besides these variables all other compositional and processing variables are kept constant.

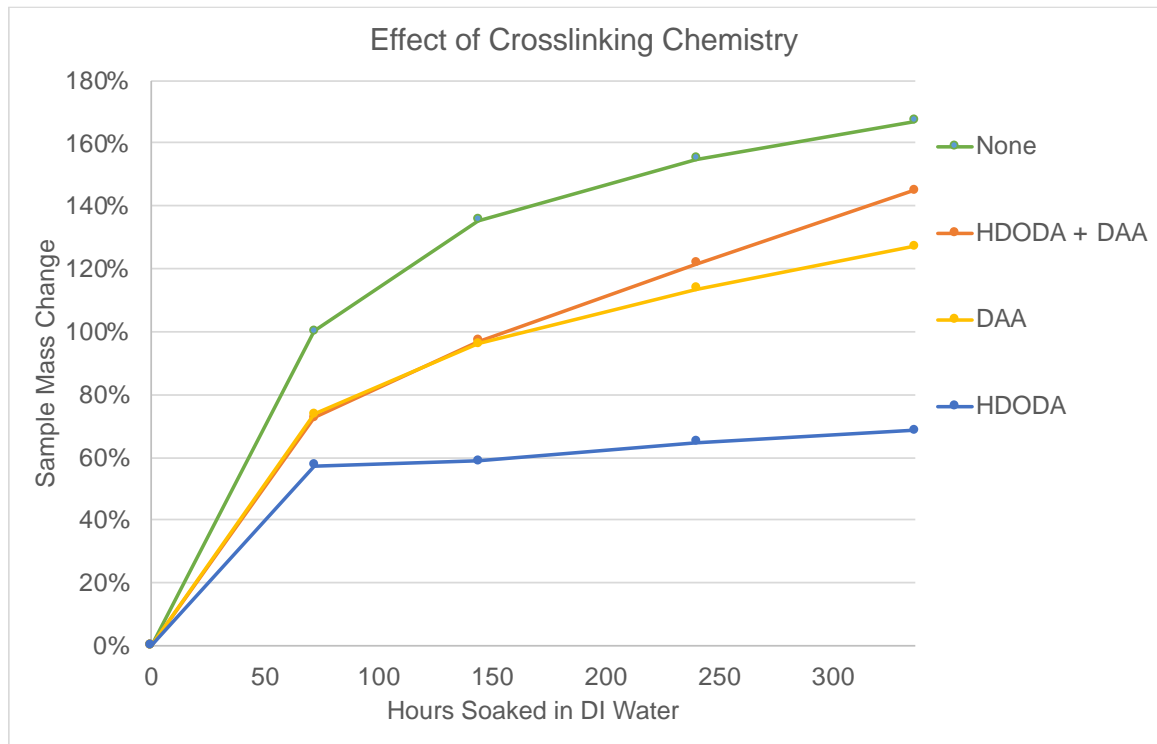
The results in Figure 38 are striking, however difficult to rationalize. In the system using a polymerizable surfactant, a thermal initiation results in decreased performance. Similarly, anionic



surfactant with 1.5% PAM monomer exhibits the same behavior. When PAM monomer is excluded from this reaction, the thermal system performs vastly better. To gain further insight and develop a more confident understanding of the way that initiation affects water uptake, additional work should be done.

#### *Crosslinking (Keto-Hydrazide, Di-Functional Monomer)*

Four polymer samples were prepared, using either 2% DAA, 1% HDODA, or both. It is thought that the DAA molecules crosslink along the surface of the particle, reducing the water uptake where there is a higher concentration of water sensitive moieties. The polymers are compositionally identical besides the crosslinking monomers and added ADH. Processing variables are also kept the same between samples.

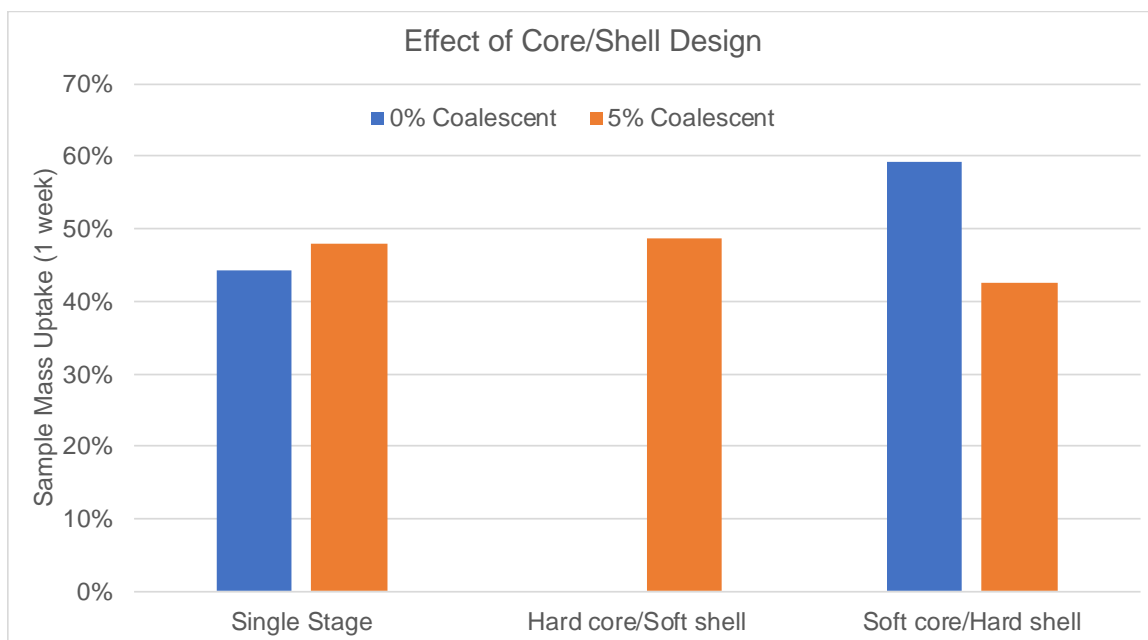


**Figure 39.** Effect of crosslinking chemistry on water uptake. A difunctional monomer HDODA was assessed alongside DAA, an intramolecular crosslinking agent that utilizes ADH to form covalent bonds between polymer chains of adjacent particles during the coalescence process.

In this experiment, the polymer with HDODA performed much better than samples with DAA. Although all crosslinked samples were better performing than the control, the result is unexpected. The sample with both DAA and HDODA performed worse than the sample without DAA. Previous studies suggested that DAA would have a larger impact on the water uptake of these films than is presented here. HDODA performing this well is an indication that further investigation should be completed into this method of crosslinking. Crosslinking seems to be a primary element that chemists can use to drive the water uptake of polymers towards an acceptable level.

### *Core/Shell Designs*

Synthesis of core/shell or dual stage polymers is simple, though the effect on properties can be pronounced. The second stage monomer is fed into the reactor after the first stage, theoretically resulting in a polymer particle with a core composition reflective of the first monomer feed, and the shell composition reflective of the second. Here, a “hard” stage is referring to a compositional Fox  $T_g$  of 20 °C and a “soft” stage refers to a composition with a  $T_g$  of -26 °C. Each stage is 50% (resin solids) of the final composition, resulting in a polymer with an “overall” Fox  $T_g$  of -5 °C, the same as all other samples in this project. These  $T_g$  values are varied by changing the ratio of hard and soft monomer (styrene, and EHA/BA respectively).

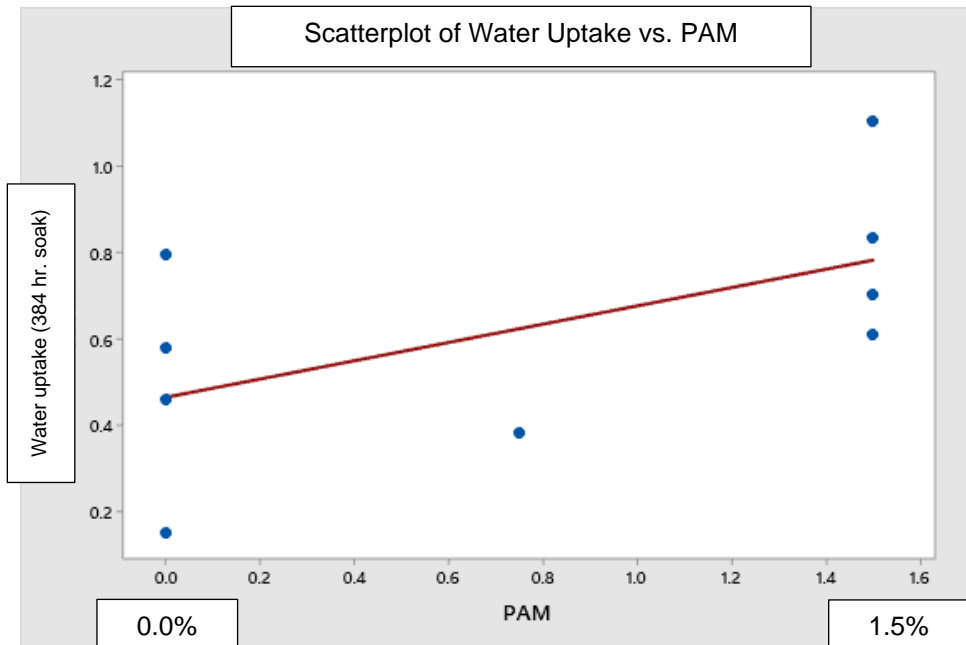


**Figure 40.** Effect of core/shell polymer design on water uptake. Due to its inability to film form, the hard core/soft shell sample was only able to be assessed with a 5% loading of DPnB coalescent. The other two samples were then loaded and assessed with the same level of DPnB.

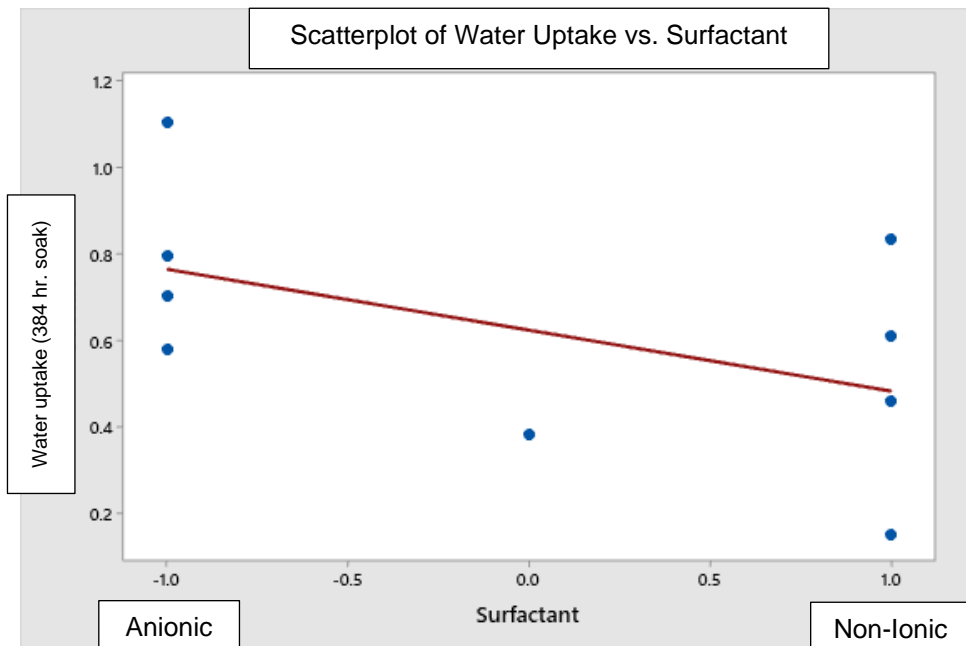
According to Figure 40, there is minimal difference between the samples with 5% coalescent. This indicates that the two-stage design has little impact on the water uptake performance of these polymers. However, we do see a slight improvement with the soft/hard sample when 5% coalescent is added, which is attributed to improved film formation.

#### *Polymer Synthesis DOE #2*

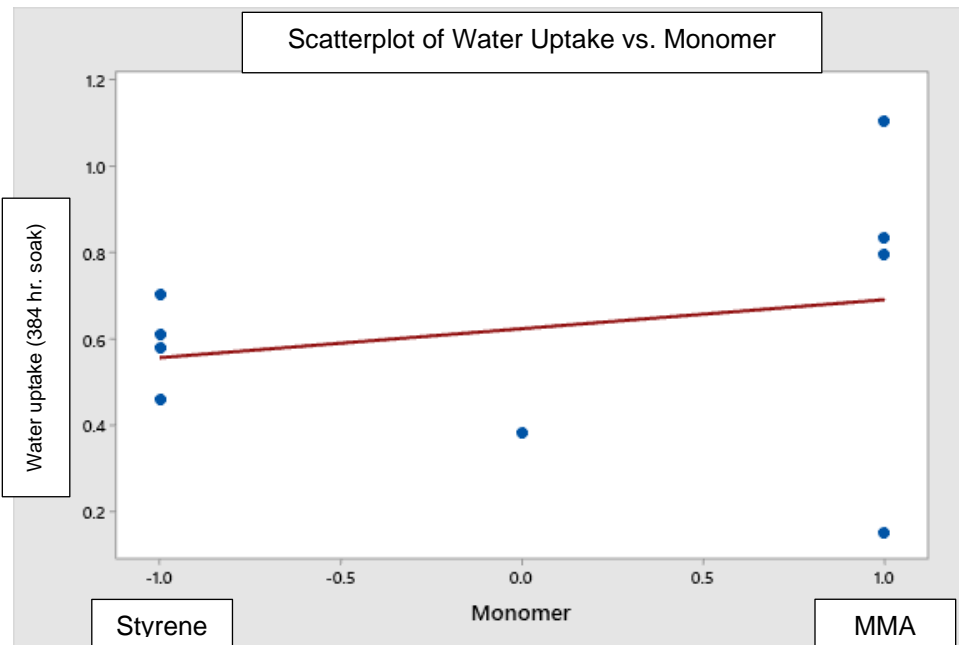
Upon developing an understanding around how some of these factors influence water uptake, a second DOE was prepared to confirm how surfactant choice, crosslinking, monomer selection, and PAM monomer work together to impact the polymer performance. The purpose of this experiment is primarily to confirm our understanding of these main factors, but to also see how they work together. The following data was obtained from samples that were soaked for 384 hours, or just over two weeks.



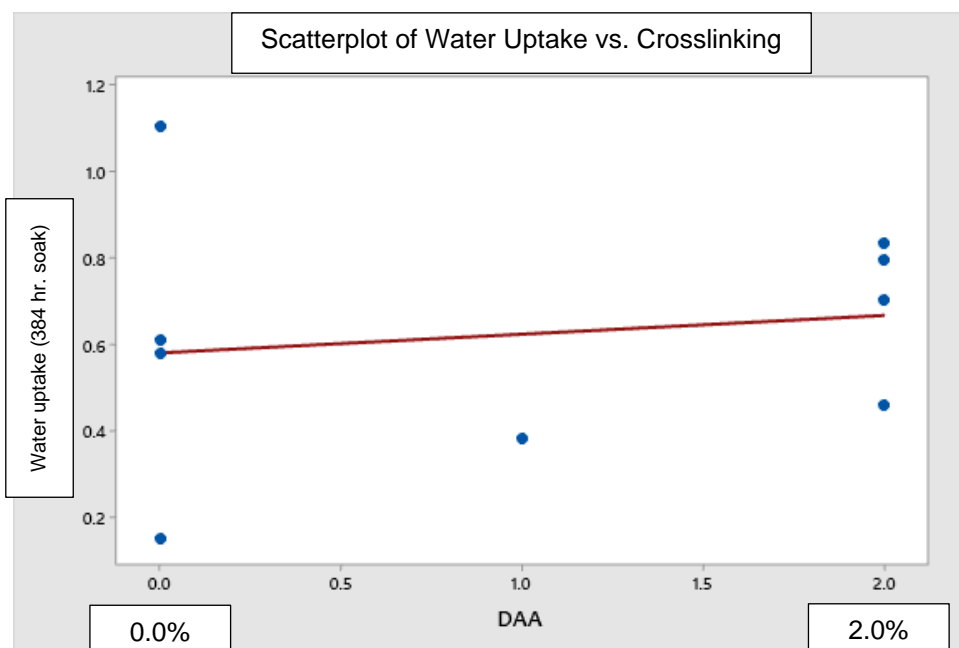
**Figure 41.** This result is identical to those found previously that PAM is detrimental to performance.



**Figure 42.** This result is identical to those found previously that anionic surfactant is worse for performance than non-ionic surfactant.



**Figure 43.** This result is identical to those found previously that styrene drives improved water uptake performance.

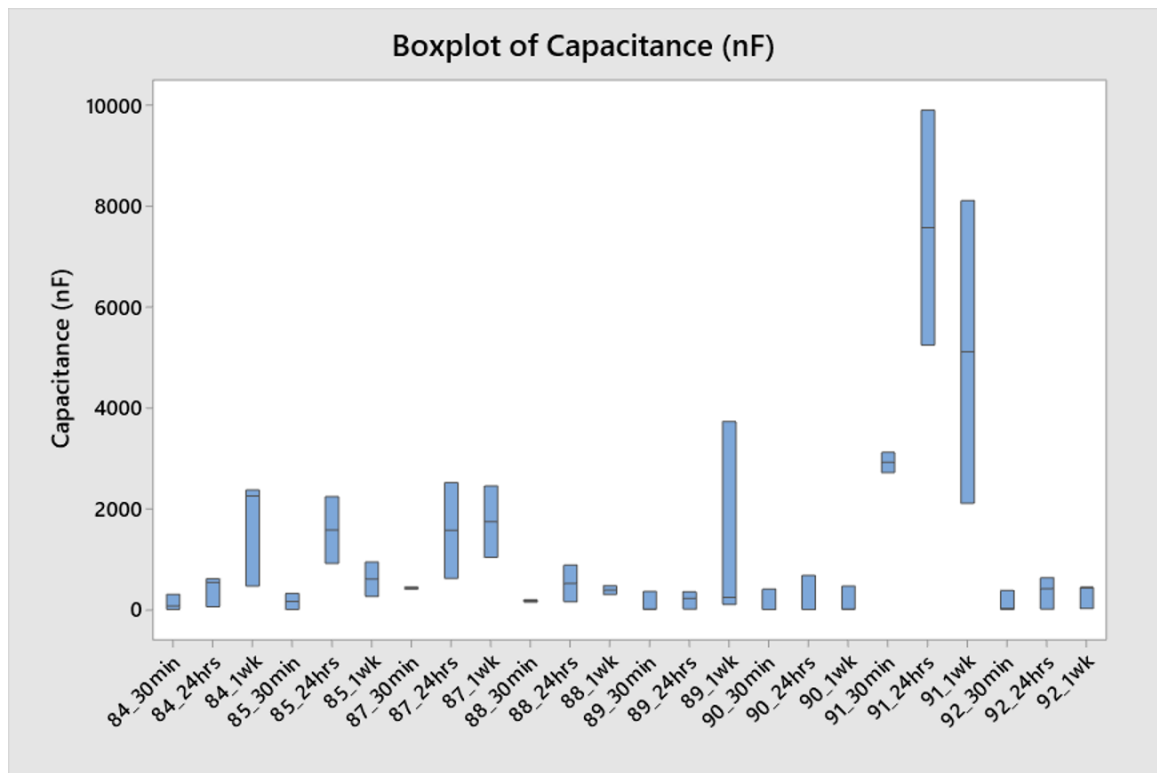


**Figure 44.** This result is identical to those found previously that higher degrees of crosslinking drive improved performance.

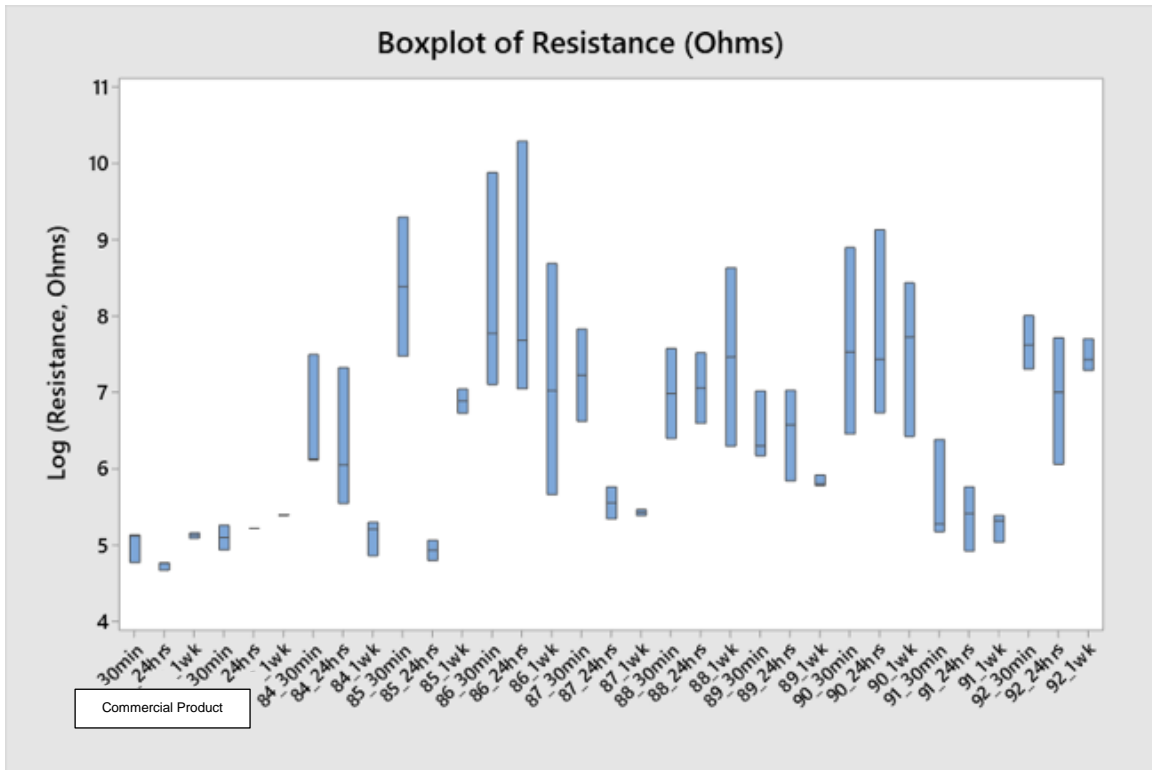
EIS measurements performed offsite by Niteen Jadhav were collected to support gravimetric analysis. These results are shown in Table 6, and Figures 45 and 46.

**Table 6.** DOE samples used for EIS testing. PAM is a 50/50 mixture of PAM A and PAM B

Sample	Surfactant Type	Monomer	PAM	DAA
84	Non-Ionic	MMA	0%	2.0%
85	Anionic	Styrene	0%	2.0%
86	Mix	Mix	0.75%	1.0%
87	Anionic	MMA	0%	0%
88	Anionic	Styrene	1.50%	0%
89	Non-Ionic	Styrene	1.50%	0%
90	Anionic	MMA	0%	0%
91	Anionic	MMA	1.50%	2.0%
92	Non-Ionic	MMA	0%	0%



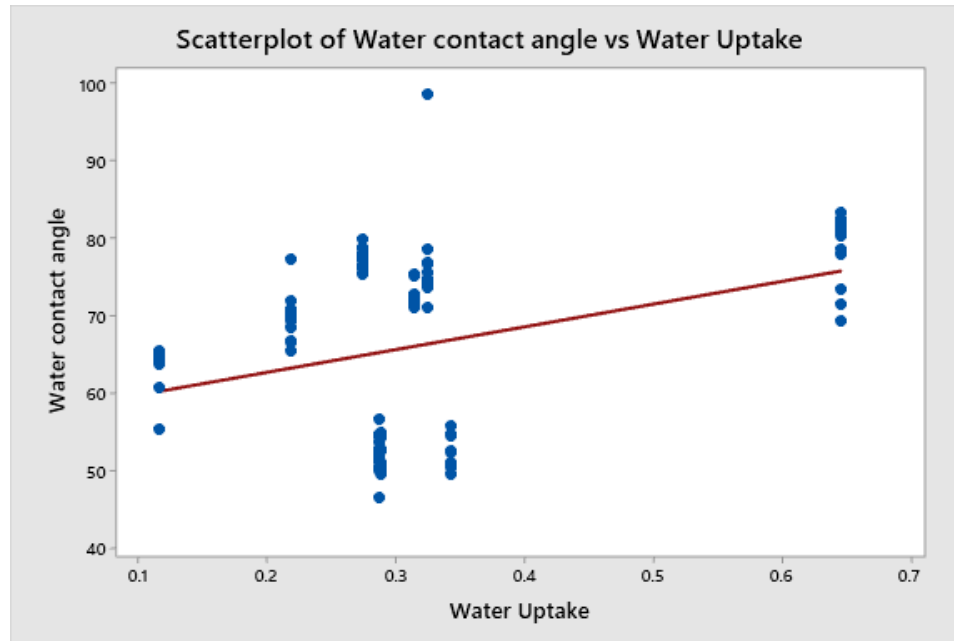
**Figure 45.** Higher capacitance values here correspond to higher water uptake values. Sample 86 was not recorded as the sample failed upon initialization of the test.



**Figure 46.** Increased resistance values correlate to increased barrier properties of the coating. The commercial product samples are fully formulated paint coatings and are not ideal candidates for sample comparison.

The expected correlation between gravimetric analysis and EIS measurements was absent, as results from EIS are not supportive of the conclusions drawn from the DOE. In order to draw more conclusive and reliable results using this technique, more time needs to be spent understanding the nuances of the technique in a hands-on manner. From there, a more targeted experiment may be designed and used to further understand water uptake.

As a part of the above DOE, contact angle measurements were taken of the polymers and plotted against water uptake values to assess any correlation between the two.



**Figure 47.** Static water contact angles have a loose correlation with uptake values, where larger contact angles drive higher water uptake values. Presumably this is due to water's unfavorable interaction with more hydrophobic polymers as they exhibit higher contact angles.

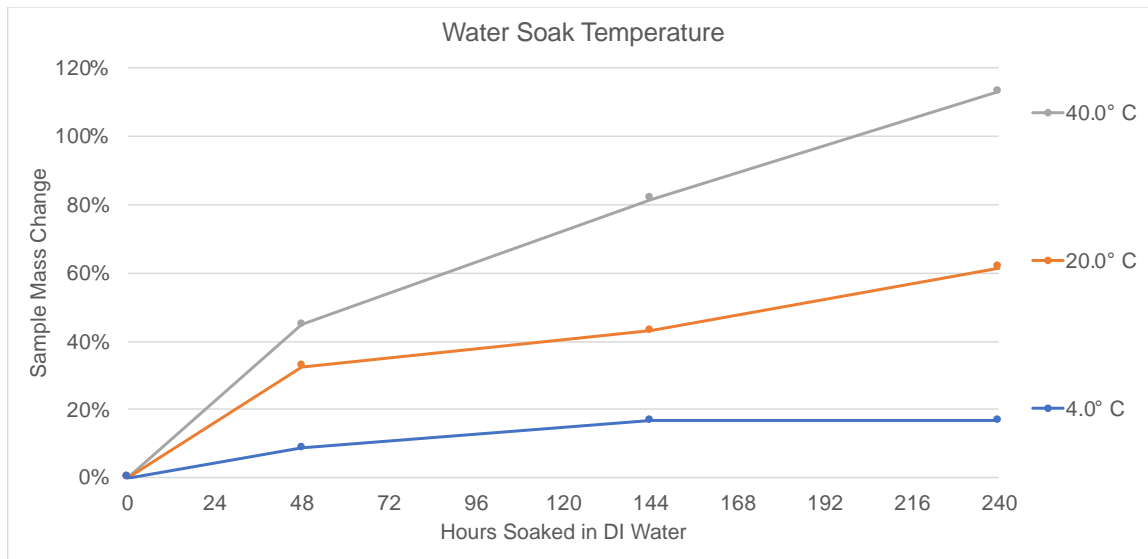
The DOE confirms our previous conclusions that MMA, anionic surfactant, and PAM monomer result in reduced performance. Samples that utilize styrene, non-ionic surfactant, and that lack PAM monomer tend to perform much better. Surprisingly, the experiment appears to suggest that diacetone acrylamide/ADH crosslinked systems reduce polymer performance. This is contrary to previous results found. It is possible that full crosslinking density was not attained in the samples, and that the hydrophilicity of the DAA monomer negatively impacted the performance. Confirmation of this hypothesis could be achieved by measuring the gel fraction of the samples.

### 4.3 Effects of Testing Methods

#### *Water Temperature*

Nearly all testing for the project was done at ambient lab temperature. To assess the effect of environmental temperature samples were prepared and tested at 4 °C, 20 °C, and 40 °C.



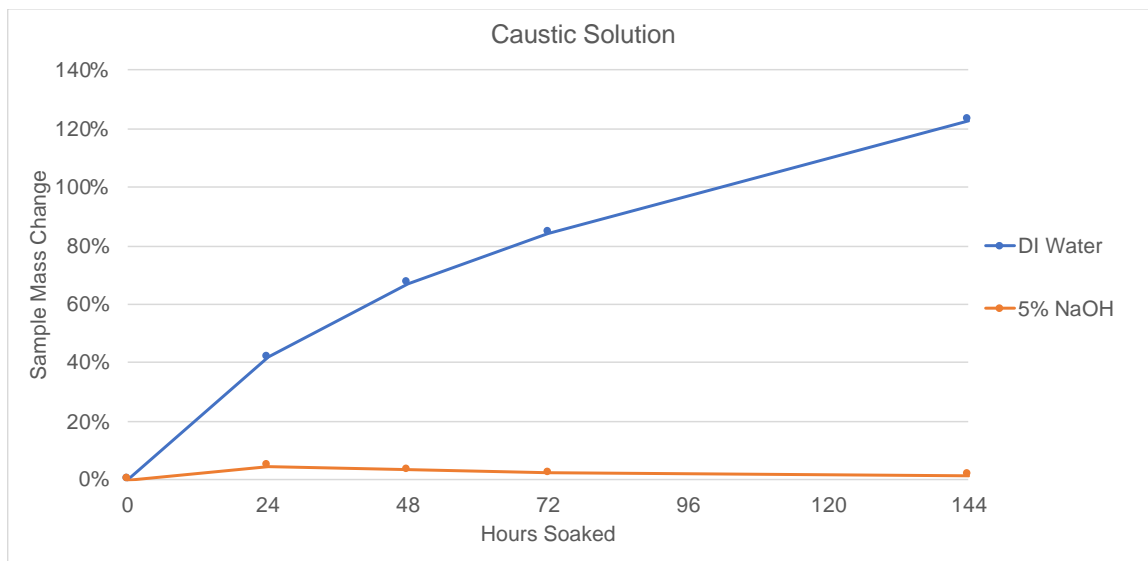


**Figure 48.** Variable water temperature of test samples.

As the temperature of the water increases, the samples absorb much more water. This trend followed a nearly linear relationship and is expected to remain constant at increasing temperatures. When the temperature of the sample is increased, the polymer chains gain more thermal and kinetic energy allowing them to move and create free volume. The chains movement allows water to enter the film more easily, and more importantly, allows the films to swell. This swelling means that they can accommodate more trapped water resulting in higher uptake values.

#### *Caustic Solution*

As part of another industry testing procedure, a films resistance to water uptake when exposed to a caustic 5% NaOH solution is of interest. This test is done at lab temperature using the same procedure as previously noted.



**Figure 49.** 5% NaOH caustic water uptake testing.

The extreme difference between samples assessed is hypothesized to be due to polymer degradation. As the film is soaked in the NaOH solution the chains are broken down and the film loses mass. This can also be seen as a decrease in sample mass over the course of the 144-hour soak.

#### 4.4 Effects on Blushing and Surfactant Leaching

##### *Blushing*

Blushing is a phenomenon related to water sensitivity and is very important to avoid in clear coatings. A select few of the polymers that were prepared for this research were chosen, and their ability to resist blushing or water whitening was assessed. Here, the polymers were drawn down at

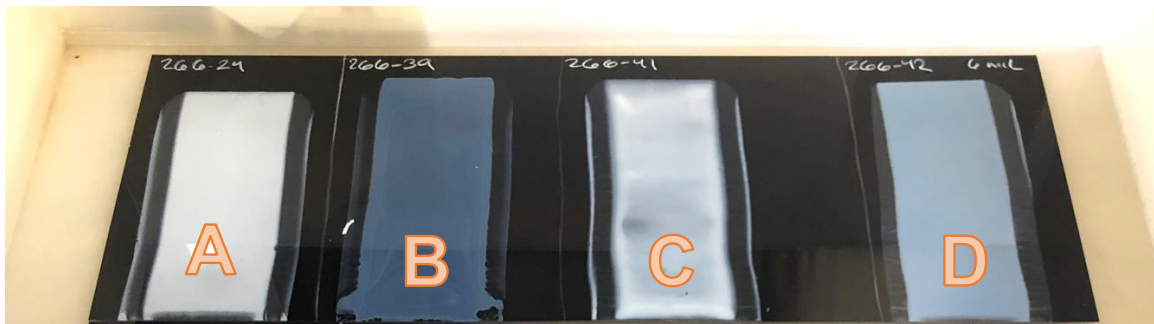
6 wet mils, and allowed to dry for one week. They were then submerged in water for 120 hours and pictures were taken after 24 and 120 hours. All coatings were clear before the test began.

*Table 7. Samples chosen for water whitening (blushing) tests.*

Sample	Surfactant	[Surfactant]	PAM	Particle Initiation
A	Anionic	2%	1.5%	Seeded
B	None	None	1.5%	Seeded
C	Anionic	4%	1.5%	Seeded
D	Non-Ionic	2%	1.5%	Seeded
E	Reactive Anionic	2%	None	Seeded
F	Reactive Anionic	2%	1.5%	Seeded
G	Anionic	2%	None	Seeded
H	Anionic	2%	1.5%	In-Situ
J	Reactive Anionic	2%	1.5%	In-Situ



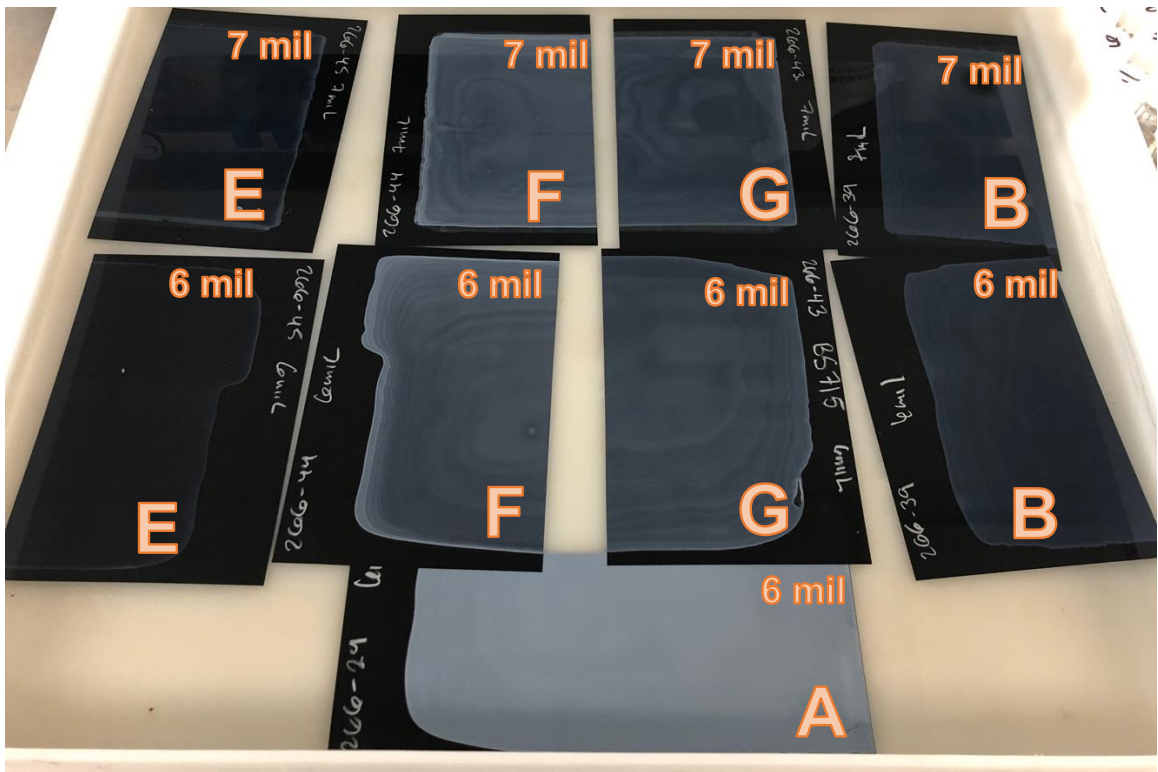
**Figure 50.** Films at 6 wet mils after 24 hours.



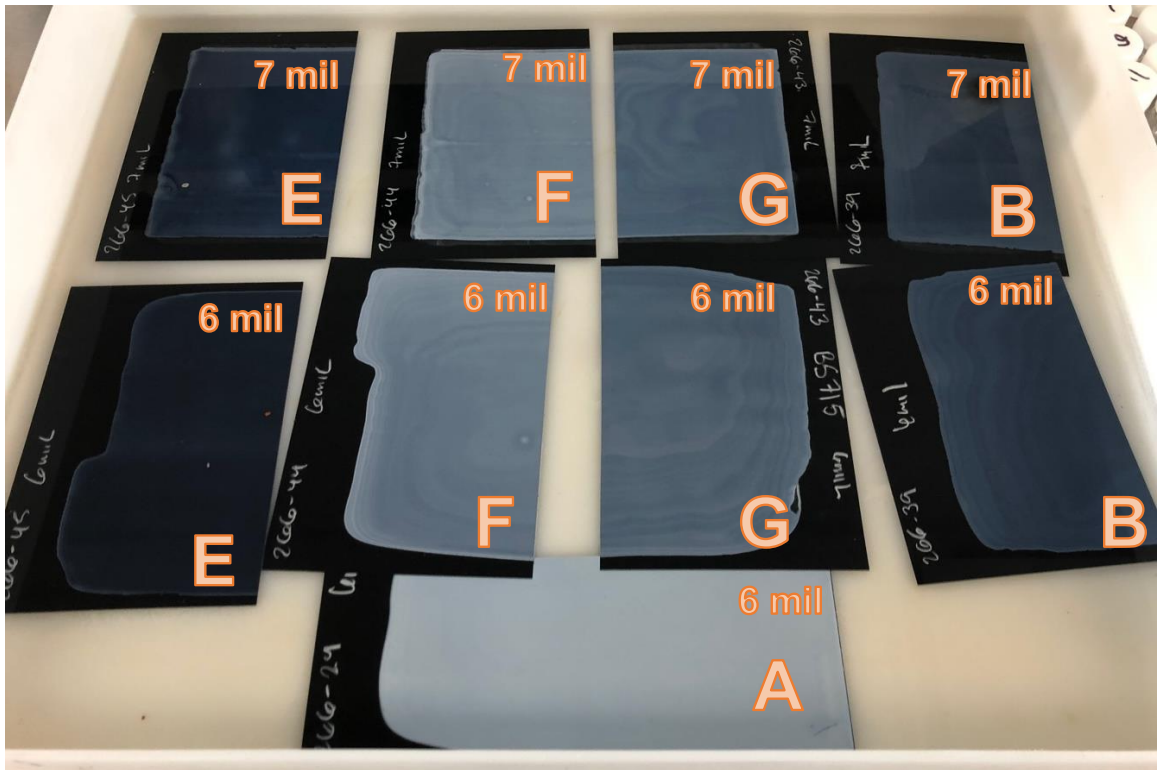
**Figure 51.** Films at 6 wet mils after 120 hours.

Sample B performed exceptionally well, followed by sample D. These contained either no surfactant or a standard amount of non-ionic surfactant respectively. The results mirror those established previously with the water uptake testing.

The following polymers were drawn down at 6 and 7 wet mils and allowed to dry for one week. They were then submerged in water for 120 hours and pictures were taken after 24 and 120 hours. All coatings were clear before the test began.



**Figure 52.** Films at 6 and 7 wet mils after 24 hours.



**Figure 53.** Films at 6 and 7 wet mils after 120 hours.

Again, the surfactant free films performed exceptionally well, however (sample E) the polymer with reactive anionic surfactant and no PAM monomer did better. This serves to support the idea that the PAM monomer may have more influence on water sensitivity than the surfactant in some cases.



**Figure 54.** Films at 6 and 7 wet mils after 24 hours.

Blush testing confirmed that surfactant choice is very important when developing polymers with low water sensitivity. PAM monomer was found to be just as important and possibly a more influential factor. The phosphate groups that these monomers contain must interact with water penetrating the film, and aid in the formation of water domains large enough to scatter light. This is hypothesized to be the same mechanism by which water uptake occurs.

### *Surfactant Leaching*

Surfactant leaching is another area of interest to coatings formulators, as such these experimental polymers were tested alongside two commercially available polymers in a test to benchmark their performance. The polymers are formulated into the same flat paint base and tinted to a weathered brown color. The paint is drawn down on a Leneta chart at 7 wet mils and allowed to dry for 24 hours before being wrapped around a small can or bucket. The bucket is then filled

with ice water and placed into a high humidity chamber for 30 minutes. The condensation and paint exudate is collected in a small pan and the residual solids of this exudate is measured. The weight percent of the solids is then compared between samples. During this test, surfactant and other water-soluble components within the paint are drawn out of the film leaving streaks down the paint.

**Table 8.** Surfactant leaching results from experimental polymers.

Sample	Surfactant Type	[Surfactant]	Test Time Interval	Color	Exudate Weight %
E	Reactive & No PAM	2%	30	W. Brown	1.35%
B	N/A	0%	30	W. Brown	1.61%
F	Reactive	2%	30	W. Brown	1.86%
D	Non-Ionic	2%	30	W. Brown	2.08%
A	Anionic	2%	30	W. Brown	2.08%
Commercial	Unknown	Unknown	30	W. Brown	2.59%
G	Anionic & No PAM	2%	30	W. Brown	2.65%
Commercial	FES27/BS715	Unknown	30	W. Brown	2.85%
C	Anionic	4%	30	W. Brown	3.05%

The lower exudate weight % values in Table 8 correspond to better performing polymers, and values below 2% are considered satisfactory. The composition of all experimental polymers is identical unless otherwise noted. Samples with no PAM monomer and reactive or non-ionic surfactant outperform all other samples, including commercially available polymers.

## 4.5 Considerations and Future Work

### *Mechanical Stability*

Though improvements in water uptake performance and a better understanding of latex coatings was attained, marketable products must exhibit satisfactory abilities in a wide array of performance standards. One of these important abilities a polymer must include is mechanical stability. To test mechanical stability of waterborne resins, they are placed in a Waring blender and blended on low for 15 minutes. Any difference in particle size distribution, gelling of the polymer or

other adverse results can disqualify the polymer from being selected as a candidate for production scale. During production of polymer as well as subsequent formulation at coatings plants, the resin is subjected to extreme shear forces, which can disrupt the colloidal stability of the emulsion resulting in agglomeration and even gelling of the system. Designing a robust polymer with the ability to withstand extreme conditions of shear and heat, results in a more durable product which can better handle any conditions it may encounter during its service life.

As discussed previously, colloidal stabilization produced by both the steric and electrostatic double layer, are a direct result of what charges and molecules are found on the outside of the particle. These include surfactant molecules, ionic monomers, and any other moiety that contributes to charge repulsion. This means that when polymers have surfactant removed, or the level of PAM monomer reduced, the resin becomes very unstable when subject to adverse conditions such as high heat, shear, and other pumping conditions. This has been observed both during synthesis as well as during blender stability testing of the samples. If a polymer is unstable during processing, large aggregates will form on the reactor walls and stirring blade. This reduces yield, takes time to clean out, and often derails reactions. Polymers that process poorly such as these must be reworked and reformulated to build in stability, not only for lab scale production, but also for production scale where batch size can grow upwards of 10,000lbs.

Instability was worst when all or most of the ionic characteristics were taken out of the formula. Components such as anionic surfactant, PAM monomers, and acid monomers contribute immensely to stability of both the processing, and the final product.

#### *Alternative Stabilization*

Many papers discuss alternative, non-conventional methods to stabilize these emulsions. Methods include the use of partially exfoliated clays of differing compositions, non-conventional surfactants namely reactive surfactants, and using other monomers with surfactant like characteristics. Many methods would be deemed commercially non-viable, but it is important to understand that there exist other ways to stabilize waterborne emulsions. It may be of interest to



explore other stabilizing techniques in conjunction with factors discussed in this work, to develop novel ways to provide resins with stability and reduced water sensitivity.

#### *Additional Crosslinking Methods*

Crosslinking chemistry can vary widely, and there are many ways to functionalize these polymers to allow for crosslinking reactions to occur. Keto-hydrazide and difunctional monomer crosslinking were explored here, though tri-functional monomers, epoxy reactions, and other methods are available to chemists. Developing technology that allows polymer particles to film form and fully coalesce while simultaneously creating a dense network of crosslinked chains, would be an ideal way to enhance performance qualities of these polymers, one of those being water uptake.

#### *Permeability*

Water vapor permeability was not a focus of this study; however, it is reasonable to hypothesize a connection between permeability and water sensitivity. Future work can utilize samples already prepared for these experiments, in order to draw conclusions on the similarities between uptake and permeability. For many applications such as concrete coatings and in some cases wood coatings, having a film that is reasonably permeable to moisture is beneficial and even required to allow breathability of the substrate. Without it films can delaminate, blister, crack, and otherwise degrade, eliminating the effectivity of the product.

#### *Effect on Other Properties*

Development of acrylic emulsion polymers is a difficult process, balancing many different processing and compositional factors. It is usually nearly impossible to make single changes to a formula while keeping all other parameters constant. As one change is made to a polymer, others will consequentially occur further complicating any cause-effect relationship that is to be made. These complex systems are increasingly difficult to study and fully understand with limited time and

resources available in a commercial setting, where product development and customer needs are of utmost importance.

This study not only produced meaningful strides toward understanding a latex polymers interaction with water, it also led to the synthesis of many resins with unique and carefully designed compositions. The sole purpose of these polymers is understanding how individual changes to a formula affect final properties of the resulting film. In future work, whether related to water uptake or not, these samples can provide a starting point to quickly and easily assess how single variable changes might impact other qualities of interest such as adhesion, bleed-block, stain resistance and more.

## 5. CONCLUSION

Water uptake phenomena of acrylic waterborne films were studied. It was demonstrated that many controllable factors studied had an influence on water uptake rate and final values. Of these factors, the most important were surfactant choice and concentration, monomer selection, crosslinking density, and test parameters. Other parameters such as polymer  $T_g$  and molecular weight controlled with chain transfer agent, had little effect on the water uptake behavior of the films.

Overall, systems that were not crosslinked, contained anionic surfactant, and hydrophilic monomers tended to perform worse than other polymers. As the film is soaked in water, osmotic pressure draws free water-soluble components out of the film, forming small channels in the film that allow water to penetrate and associate between poorly coalesced polymer particles. Over time these domains grow and expand eventually becoming large enough to scatter light due to the refractive index difference between the water and binder. It is at this point in the absorption process the film begins to appear white, eventually becoming completely opaque if enough water is absorbed.

By disallowing surfactant, especially ionic types, and ionic monomers, the outside of the polymer particle is able to coalesce more effectively, and the polymer will be less hydrophilic. This deters water from initially associating with these susceptible domains within the film, as well as slowing the growth of these water pockets as the film continues to absorb water. Crosslinking aids by reducing the films capacity to swell and uptake more water, though crosslinkable monomer such as DAA is often water soluble and hydrophilic. This may lead to poorer performance depending on the effectivity of the crosslink density.

These samples were also tested for their resistance to surfactant leaching and blushing. The same trends that appeared to drive water uptake performance also influenced surfactant leaching and blushing as well. The analysis of these last two phenomena was not as exhaustive as uptake studies, and further work should be done in order to draw more comprehensive conclusions.

Future work may include a pursuit to understand two-way interactions within these systems more precisely. It seems that interactions between monomer selection and crosslinking is important and may have more influence over performance than is presented in this study. Furthermore, polymers developed from this body of work can be used in current and future projects to better understand other polymer & coatings properties.

## 6. REFERENCES

- (1) Wicks, Z.; Jones, F.; Pappas, P.; Wicks, D. *Organic Coatings Science and Technology*, Third.; Wiley-Interscience: Hoboken, 2007.
- (2) Donkers, P. A. J.; Huinink, H. P.; Erich, S. J. F.; Meel, P. A. Van; Baukh, V.; Adan, O. C. G. Water Transport in Pigmented Waterborne Coatings Studied with NMR. *ResearchGate* **2013**, c (december), 3–4.
- (3) Painter, P.; Coleman, M. *Fundamentals of Polymer Science*, Second.; CRC Press: Boca Raton, 1997.
- (4) Yamak, H. B. Emulsion Polymerization: Effects of Polymerization Variables on the Properties of Vinyl Acetate Based Emulsion Polymers. *Intech* **2016**, i (tourism), 13. <https://doi.org/http://dx.doi.org/10.5772/57353>.
- (5) Grubisic, Z.; Rempp, P.; Benoit, H. A Universal Calibration for Gel Permeation Chromatography. *J. Polym. Sci. Part B Polym. Lett.* **1967**, 5 (9), 753–759. <https://doi.org/10.1002/pol.1967.110050903>.
- (6) Gaborieau, M.; Castignolles, P. Size-Exclusion Chromatography (SEC) of Branched Polymers and Polysaccharides. *Anal. Bioanal. Chem.* **2011**, 399 (4), 1413–1423. <https://doi.org/10.1007/s00216-010-4221-7>.
- (7) Saldivar-Guerra, E.; Vivaldo-Lima, E. *Handbook of Polymer Synthesis, Characterization, and Processing*; Wiley, 2013.
- (8) Chern, C. *Principles and Applications of Emulsion Polymerization*; Wiley: Hoboken, 2008.
- (9) Hearn, B. J.; Ottewill, R. H.; Shawt, J. N. Characterisation of Latex Particles Produced By Emulsion Polymerisation \*. *Brit. Polym. J.* **1970**, 2, 116–120.
- (10) Aramendia, E.; Barandiaran, M. J.; Grade, J.; Blease, T.; Asua, J. M. Improving Water Sensitivity in Acrylic Films Using Surfmers. *Langmuir* **2005**, 21 (4), 1428–1435. <https://doi.org/10.1021/la047631h>.
- (11) Xiao, X.; Wang, Y. Emulsion Copolymerization of Fluorinated Acrylate in the Presence of a Polymerizable Emulsifier. *Colloids Surfaces A Physicochem. Eng. Asp.* **2009**, 348 (1–3), 151–156. <https://doi.org/10.1016/j.colsurfa.2009.07.006>.
- (12) Aslamazova, T. R. Emulsifier-Free Latexes and Polymers on Their Base. *Prog. Org. Coatings* **1995**, 25 (2), 109–167. [https://doi.org/10.1016/0300-9440\(94\)00506-V](https://doi.org/10.1016/0300-9440(94)00506-V).
- (13) Bilgin, S.; Tomovska, R.; Asua, J. M. Effect of Ionic Monomer Concentration on Latex and Film Properties for Surfactant-Free High Solids Content Polymer Dispersions. *Eur. Polym. J.* **2017**, 93 (April), 480–494. <https://doi.org/10.1016/j.eurpolymj.2017.06.029>.
- (14) Bonnefond, A.; Paulis, M.; Bon, S. A. F.; Leiza, J. R. Surfactant-Free Miniemulsion Polymerization of n-BA/S Stabilized by NaMMT: Films with Improved Water Resistance. *Langmuir* **2013**, 29 (7), 2397–2405. <https://doi.org/10.1021/la3047033>.
- (15) Aramendia, E.; Mallécol, J.; Jeynes, C.; Barandiaran, M. J.; Keddie, J. L.; Asua, J. M. Distribution of Surfactants near Acrylic Latex Film Surfaces: A Comparison of Conventional and Reactive Surfactants (Surfmers). *Langmuir* **2003**, 19 (8), 3212–3221. <https://doi.org/10.1021/la0267950>.
- (16) Butler, L. N.; Fellows, C. M.; Gilbert, R. G. Effect of Surfactants Used for Binder Synthesis on the Properties of Latex Paints. *Prog. Org. Coatings* **2005**, 53 (2), 112–118. <https://doi.org/10.1016/j.porgcoat.2005.02.001>.

- (17) Keddie, J. L.; Routh, A. F. *Fundamentals of Latex Film Formation*; Springer, 2010.
- (18) Steward, P. A.; Hearn, J.; Wilkinson, M. C. An Overview of Polymer Latex Film Formation and Properties. *Adv. Colloid Interface Sci.* **2000**, *86*, 195–267.
- (19) Eyssautier-Chuine, S.; Calandra, I.; Vaillant-Gaveau, N.; Fronteau, G.; Thomachot-Schneider, C.; Hubert, J.; Pleck, J.; Gommeaux, M. A New Preventive Coating for Building Stones Mixing a Water Repellent and an Eco-Friendly Biocide. *Prog. Org. Coatings* **2018**, *120* (March), 132–142. <https://doi.org/10.1016/j.porgcoat.2018.03.022>.
- (20) Asbeck, W. K.; Loo, M. Van. Critical Pigment Volume Relationships. *Ind. Eng. Chem.* **1949**, *41* (7), 1470–1475. <https://doi.org/10.1021/ie50475a042>.
- (21) Diebold, M. P.; Diebold, M. P. Volume Relationships and the CPVC. In *Application of Light Scattering to Coatings*; Springer International Publishing, 2014; pp 141–166. [https://doi.org/10.1007/978-3-319-12015-7\\_6](https://doi.org/10.1007/978-3-319-12015-7_6).
- (22) Kessel, N.; Illsley, D. R.; Keddie, J. L. The Diacetone Acrylamide Crosslinking Reaction and Its Influence on the Film Formation of an Acrylic Latex. *J. Coatings Technol. Res.* **2008**, *5* (3), 285–297. <https://doi.org/10.1007/s11998-008-9096-6>.
- (23) Diacetone Acrylamide (DAAM) and Adipic Acid Dihydrazide (ADH) Self-Crosslinking Chemistry for Acrylic Emulsions <https://www.gantrade.com/blog/daam-vs-adh> (accessed Mar 4, 2020).
- (24) Hatakeyama, T.; Tanaka, M.; Kishi, A.; Hatakeyama, H. Comparison of Measurement Techniques for the Identification of Bound Water Restrained by Polymers. *Thermochim. Acta* **2012**, *532*, 159–163. <https://doi.org/10.1016/j.tca.2011.01.027>.
- (25) Jiang, B.; Tsavalas, J. G.; Sundberg, D. C. Water Whitening of Polymer Films: Mechanistic Studies and Comparisons between Water and Solvent Borne Films. *Prog. Org. Coatings* **2017**, *105*, 56–66. <https://doi.org/10.1016/j.porgcoat.2016.12.027>.
- (26) Feng, J.; Winnik, M. A. Effect of Water on Polymer Diffusion in Latex Films. *Macromolecules* **1997**, *30* (15), 4324–4331. <https://doi.org/10.1021/ma970174+>.
- (27) Liu, Y.; Gajewicz, A. M.; Rodin, V.; Soer, W. J.; Scheerder, J.; Satgurunathan, G.; McDonald, P. J.; Keddie, J. L. Explanations for Water Whitening in Secondary Dispersion and Emulsion Polymer Films. *J. Polym. Sci. Part B Polym. Phys.* **2016**, *54* (16), 1658–1674. <https://doi.org/10.1002/polb.24070>.
- (28) Luo, Z.; Huang, H. Glass-transition Temperature of a Polyacrylate Latex Film and Its Water Whitening Resistance. *J. Appl. Polym. Sci.* **2019**, *48361*, 48361. <https://doi.org/10.1002/app.48361>.
- (29) Aguirreurreta, Z.; Dimmer, J. A.; Willerich, I.; De La Cal, J. C.; Leiza, J. R. Water Whitening Reduction in Waterborne Pressure-Sensitive Adhesives Produced with Polymerizable Surfactants. *Macromol. Mater. Eng.* **2015**, *300* (9), 925–936. <https://doi.org/10.1002/mame.201500035>.
- (30) Xu, G. H.; Dong, J.; Severtson, S. J.; Houtman, C. J.; Gwin, L. E. Modifications of Surfactant Distributions and Surface Morphologies in Latex Films Due to Moisture Exposure. *J. Phys. Chem. B* **2009**, *113* (30), 10189–10195. <https://doi.org/10.1021/jp902716b>.
- (31) Konko, I.; Guriyanova, S.; Boyko, V.; Sun, L.; Liu, D.; Reck, B.; Men, Y. Role of the Hydrophilic Latex Particle Surface in Water Diffusion into Films from Waterborne Polymer Colloids. *Langmuir* **2019**, *35* (18), 6075–6088. <https://doi.org/10.1021/acs.langmuir.8b04327>.

- (32) Gundabala, V. R.; Zimmerman, W. B.; Routh, A. F. A Model for Surfactant Distribution in Latex Coatings. *Langmuir* **2004**, *20* (20), 8721–8727. <https://doi.org/10.1021/la048939b>.
- (33) Arnold, C.; Klein, G.; Maaloum, M.; Ernstsson, M.; Larsson, A.; Marie, P.; Holl, Y. Surfactant Distribution in Waterborne Acrylic Films. 2. Surface Investigation. *Colloids Surfaces A Physicochem. Eng. Asp.* **2011**, *374* (1–3), 58–68. <https://doi.org/10.1016/j.colsurfa.2010.11.008>.
- (34) Reyes-Mercado, Y.; Vazquez, F.; Rodríguez-Gómez, F. J.; Duda, Y. Effect of the Acrylic Acid Content on the Permeability and Water Uptake of Poly(Styrene-Co-Butyl Acrylate) Latex Films. *Colloid Polym. Sci.* **2008**, *286* (5), 603–609. <https://doi.org/10.1007/s00396-008-1838-6>.
- (35) Machotová, J.; Černošková, E.; Honzíček, J.; Šňupárek, J. Water Sensitivity of Fluorine-Containing Polyacrylate Latex Coatings: Effects of Crosslinking and Ambient Drying Conditions. *Prog. Org. Coatings* **2018**, *120* (December 2017), 266–273. <https://doi.org/10.1016/j.porgcoat.2018.03.016>.
- (36) Martín-Fabiani, I.; Lesage De La Haye, J.; Schulz, M.; Liu, Y.; Lee, M.; Duffy, B.; D'Agosto, F.; Lansalot, M.; Keddie, J. L. Enhanced Water Barrier Properties of Surfactant-Free Polymer Films Obtained by MacroRAFT-Mediated Emulsion Polymerization. *ACS Appl. Mater. Interfaces* **2018**, *10* (13), 11221–11232. <https://doi.org/10.1021/acsami.8b01040>.
- (37) Yang, W.; Chen, Y.; Han, D.; Zhu, L. Synthesis and Characterization of the Fluorinated Acrylic Latex: Effect of Fluorine-Containing Surfactant on Properties of the Latex Film. *J. Fluor. Chem.* **2013**, *149*, 8–12. <https://doi.org/10.1016/j.jfluchem.2013.02.005>.
- (38) ASTM D471 – 16a, 2016, Standard Test Method for Rubber Property — Effect of Liquids. ASTM International: West Conshohocken, PA, 1937, pp 1–15. <https://doi.org/10.1520/D0471-12.ASTM>.
- (39) D6083/D6083M – 18, 2018, Standard Specification for Liquid Applied Acrylic Coating Used in Roofing. ASTM International: West Conshohocken, PA, 1997, pp 1–3. <https://doi.org/10.1520/D6083>.
- (40) Wade Jr., L. G. *Organic Chemistry*, 8th ed.; Prentice Hall, 2016.