Nanoengineering of Next Generation Silicone Rubber Materials for Extreme Applications

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NANOENGINEERING OF NEXT GENERATION SILICONE RUBBER MATERIALS FOR EXTREME APPLICATIONS

A Dissertation

Presented to

the Faculty of the Daniel Felix Ritchie School of Engineering and Computer Science

University of Denver

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

by

Monika Bleszynski

August 2018

Advisor: Dr. Maciej Kumosa
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Abstract

Silicone rubber materials are frequently used in extreme environments, including aviation, space, high voltage and other applications. In service, however, complex and difficult to predict damage mechanisms in the rubbers can occur which can lead to severe failures of essential infrastructural components. For example, Non-Ceramic Insulators (NCIs), which support some of the most critical high voltage lines in the world, regularly exhibit severe polymer aging due to environmental pollution, ultra-violet (UV) radiation, and dry band and corona arcing. Designing silicone rubbers to resist aging in these demanding environments is difficult and requires an interdisciplinary approach, including correctly assessing the actual aging factors. This work attempts to determine the actual causes of NCI aging in coastal high voltage environments, and to demonstrate that extreme aging of silicone rubbers can be mitigated through the inclusion of titanium dioxide (TiO₂) microparticles. In-service aging of NCIs in salt rich environments was attributed for the first time to the formation of highly oxidizing hypochlorous acid, which forms in the presence of aqueous salt and minimal voltage. The addition of TiO₂ was found to significantly improve the resistance of a polydimethylsiloxane (PDMS) material to aging by about 50% in HOCl and electrolyzed aqueous salt. Using molecular
dynamics, it was shown that PDMS methyl group reorientation at the nanoscale level causes numerous macroscale effects including, an increase in hydrophobicity and decrease in permeating compound diffusion.

In the second part of this study the experimental and numerical approaches developed for the extreme NCI aging problem were used to improve our understanding of ice adhesion and accumulation on silicone rubber surfaces used as icephobic barriers. The barriers were improved for their resistance to ice adhesion by 80% by embedding TiO$_2$ particles and this positive outcome was attributed mostly to the lotus effect. However, the embedded particles did not prevent ice accumulation on the barriers, especially under the most extreme icing condition associated with the rapid cooling of mist size water droplets. The entire research presented in this dissertation was enhanced by a unique combination of nanotechnology, molecular dynamics, 3D physics modeling, and experimental approaches.
Acknowledgements

First and foremost, my sincere gratitude to my advisor, Dr. Maciej Kumosa, for his unwavering support, immeasurable knowledge, steadfast patience, and encouraging guidance.

Thank you to my NSF HVT Center labmates and colleagues who challenged, supported, and inspired me intellectually and academically.

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Chapter One: Introduction

Extreme environments present a unique set of challenges for common elastomeric compounds such as Room Temperature Vulcanized (RTV) silicone rubbers. These soft polymers and their composites have been widely used in aerospace, space, and modern high voltage (HV) transmission systems [1-3]. Excellent resiliency, electrical resistance, and limited deformation when exposed to temperatures ranging from -100 °C to +250 °C [1-3] give these polymers advantageous properties, making them suitable for use in a variety of applications. In the extreme environments of space and aerospace for example, silicone rubbers are frequently used to insulate fundamental components where frequent pressure, temperature, and altitude changes pose a challenging environment for sensitive aviation instruments [1-2]. In jet aircraft, silicone rubbers are commonly found in engines and instrumentation panels as encasings on electrical components and sensitive instruments [1-2]. In satellites, adhesive silicone rubbers are frequently used as backing for solar panels, where the polymers are subjected to extreme temperatures and elevated amounts of radiation [1-2].

Extreme environments for polymers and their composites are also found on modern high voltage (HV) transmission lines [3-25], where silicone rubbers comprise the
seals and weather-sheds of HV Non-Ceramic Insulators (NCIs) [3-4]. NCIs are multifunctional, providing both mechanical support and increasing the distance between the electrified lines and the ground [4, 10-12, 25], thus generating less stress on the overall structure due to reduced leakage distance. Together, these silicone rubbers and their composites used in NCIs support some of the most critical lines across the world, and their glass and carbon fiber composites counterparts are frequently used in HV conductors [3-25], replacing steel as the primary load bearing components.

Because of their resiliency and low surface energy, silicone rubbers have also recently been investigated as icephobic barriers for high voltage applications, to reduce ice buildup on conductors, insulators, and other HV structures [26, 27]. Therefore, while many different varieties of silicone materials may exist for a variety of different applications, this dissertation focuses on silicone rubbers used mainly in HV applications, such as for insulators or icephobic barriers.

While silicone rubbers are typically resilient and able to withstand weathering, radiation, and extreme temperatures, material degradation due to aging can pose serious problems over time. Any changes in the material structure of silicone rubber RTV can critically affect accompanying sensitive components, causing potential catastrophic failure of mechanical components or structures. Mechanical, electrical and chemical catastrophic failures of polymer based HV transmission systems have been occurring sporadically in the United Stated and across the globe [4-12], and failures of these lines have had dangerous consequences such as blackouts, ground fires, and other life-
threatening disasters. Preventing polymer failure in these critical systems, such as insulators, is consequently essential in avoiding potential in-service failures of HV transmission systems. Therefore, a comprehensive understanding of silicone rubber aging and material degradation is essential for evaluating in-service life and accurately assessing the risks to sensitive and critical components, before new and better silicone rubber polymers can be developed.

1.1 Key HV silicone rubber materials and their aging

Commonly used silicone rubber materials can be categorized by the different formulations used in manufacturing: one and two component. RTV-1 denotes single component room temperature vulcanized rubber, while RTV-2 denotes two-component caulk. Both RTV-1 and RTV-2 are composed primarily of polydimethylsiloxane (PDMS); a silicon based polymer with excellent hydrophobic properties [1]. On NCIs, RTV-1 is primarily used as caulking material between the metal end fittings and the weather sheds [Figure 1]. The RTV-1 caulk is frequently redundant, as it provides additional protection against moisture penetration into the load bearing composite insulator core [3]. RTV-2, by contrast, comprises the large concentric disc shaped sheds, and the housing, which encompasses the entire length of the insulator [Figure 1]. These RTV-2 sheds keep the shed underside dry and increase the distance of the leakage path along the insulator surface, minimizing the risk of flashover arcing. Together, these two silicone rubber materials offer excellent protection for the supporting fiberglass rod and
provide modern NCIs resistance against various environmental stressors and moisture ingress. The effect of in service aging of silicone rubber icephobic barriers was also briefly discussed in this study in connection to the aging research of NCIs.

Figure 1. Computer model of an HV NCI, designating the locations of RTV-1 and RTV-2 material components
Current literature indicates that in-service material damage of NCI silicone rubber sheds and sealants used in HV lines [Figure 2 a-c] is caused by a variety of environmental stressors. These include agents such as salt accumulation, acid, UV damage due to ozone depletion, automobile motor vehicle exhaust deposits, high temperature, electrical stressors such as corona discharges, leakage currents, and dry-band arcing [6, 7, 10-25].

**Figure 2 a-c.** a) Failure of RTV-1 sealant in a HV NCI causing catastrophic insulator and line failure by brittle fracture, b) and electrical failures, c) of a 500kV transmission line in the Monterey Bay area in California, USA [11-15, 17, 22]
Salt contamination in particular is cited as one of the most destructive environmental pollutants for NCIs [24, 25]. In coastal environments, salt contamination can cause damage to RTV based NCIs by decreasing hydrophobicity over time, and diminishing water and pollutant runoff [24, 25]. Over time, the compromised hydrophobicity of the sheds can result in dry-band arcing [24, 25], which leads to further damage of the polymer materials. Although silicone rubber materials are resilient, lengthy exposure to environmental contaminants such as salt will ultimately limit the ability of silicone rubber materials to resist water ingress, and the combination of both electrical and environmental stresses can cause excessive damage, ultimately leading to NCI failure in service [24, 25].

While salt contamination of HV insulators has been studied in the past, a better understanding of silicone rubber aging in salt environments is still needed to prevent and ultimately extend silicone rubber insulator in-service [10-26]. Since the failure of silicone rubber materials can be so disastrous in HV applications, and the hydrophobic property is a critical part of silicone rubber materials, determining changes in hydrophobicity and material damage in silicone rubbers is critical for extending and maintaining hydrophobicity in preventing or delaying NCI damage in-service [8-10].

Similarly, aging of silicone rubbers for icephobic applications has just recently been investigated by R. Woll [27], who juxtaposed the effect of crosslinking [Table 1] and aging [Table 2] with ice adhesion strength. The study showed that while a reduction in crosslinking of silicone rubber materials reduced ice adhesion strength, it also made
the materials more susceptible to aging. Aging of the rubber in hypochlorous acid for 4 weeks increased the ice adhesion strength anywhere from 31% to 163%, depending on the crosslinking density [Table 2]. These results therefore indicate that icephobic silicone rubber materials must exhibit and maintain low ice adhesion strengths, even when aged.

**Table 1.** Ice adhesion strength of Dragon Skin RTV-2 for a series of cross-linker densities [27]

<table>
<thead>
<tr>
<th>Crosslink Density of PDMS</th>
<th>Ice Adhesion Strength [kPa]</th>
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<tbody>
<tr>
<td>100%</td>
<td>34.63 ± 4.20</td>
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<tr>
<td>75%</td>
<td>24.6 ± 4.23</td>
</tr>
<tr>
<td>50%</td>
<td>21.0 ± 5.23</td>
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<tr>
<td>25%</td>
<td>17.4 ± 2.75</td>
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**Table 2.** Ice adhesion strength of Dragon Skin RTV-2 after aging in hypochlorous acid for 4 weeks, for series of cross-linker densities [27]

<table>
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<tr>
<th>Crosslink Density of PDMS</th>
<th>Ice Adhesion Strength [kPa]</th>
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<tr>
<td>100%</td>
<td>45.38 ± 2.82 (31.04% increase)</td>
</tr>
<tr>
<td>75%</td>
<td>41.74 ± 4.52 (69.67% increase)</td>
</tr>
<tr>
<td>50%</td>
<td>35.49 ± 1.96 (69% increase)</td>
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<tr>
<td>25%</td>
<td>45.84 ± 1.66 (163.45% increase)</td>
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1.2 Summary of previous research by M. Bleszynski, et al.

The work completed during this study builds on previously conducted preliminary research, which assessed the aging of silicone rubber materials in coastal environments. The study, Aging Assessment Of High Voltage Single Component Room Temperature Vulcanized Silicone Rubber (RTV-1) Subjected to Aqueous Salt, M.S. Thesis by M. Bleszynski, focused on aging of three different RTV-1 compounds (designated as (RTV-A, B, C), which were provided by a major US high voltage equipment manufacturer [Figure 3] [16, 25]. The study focused primarily on damage assessment due to salt contamination, and compared it with UV, moisture, and nitric acid. The saltwater aging experiments resulted in noticeable material damage after aging in 80°C 3% NaCl saltwater. The most critical results were: loss of physical material mass and significant reductions in hydrophobic properties in all of the RTVs tested. One of the most significant findings was that damage appeared to be more extensive in saltwater than under individual and combined UV, moisture, and nitric acid conditions [14-16, 25].
Figure 3. Three RTV-1 (RTV-B, RTV-C and RTV-A) samples that were tested in 80°C 3% NaCl saltwater [15, 16, 25]

The RTV-1 saltwater aging experiments also resulted in noticeable loss of material into the salt-water solution, suggesting extensive damage to the RTV polymer backbone [15, 16, 25]. Chain scission was determined to be the responsible mechanism for both material mass loss and damage of the silicone material’s hydrophobic methyl groups [15, 16, 25]. Aged samples showed a direct relationship between the material mass loss and Si-O-Si bond scission due to RTV sample exposure to salt. This resulted in not only the loss of physical material, but also in changes of hydrophobic properties of the RTVs, namely a drastic decrease in hydrophobicity due to hydrolysis of methyl groups. This conclusion was supported by FTIR. Additionally, accelerated aging of the silicone rubber material in the presence of salt resulted in the formation of low molecular weight silicone oil; a benefit to surface hydrophobicity but also an indicator of Si-O-Si
backbone chain scission and presumably responsible for changes in material stiffness and mechanical strength.

Changes in hardness were also directly correlated to mass loss and changes in hydrophobicity. Hardness was found to gradually decrease with aging, especially in an extensively aged RTV-1 material. In the case of the RTVs investigated, the reduction in hardness after ten weeks of exposure to 3% salt solution at 80°C was found to have decreased by 50%. SEM analysis verified surface damage, and FTIR analysis confirmed the presence of CH$_3$ and Si-O-Si groups in the immersion solution. A molecular dynamics model was also developed to determine rates of diffusive compound diffusion among a chosen set of molecules, including water, salt ions, nitric acid, and hypochlorous acid. The study then concluded with a preliminary set of experimental hypochlorous acid experiments, which were then compared to the experimental aqueous salt aging studies.

Hypochlorous acid (HOCl) was proposed by M. Bleszynski et al. for the first time as an aggressive aging medium due its potential to form in-service in the presence of minimal voltage and aqueous salt [14, 15, 25]. A preliminary study involved an RTV-B sample [Figure 4], which was exposed to 0.046% commercially, produced hypochlorous acid for five weeks, resulting in severe damage. SEM cross-sections analysis of RTV-1 after just four weeks [Figure 5] showed extensive material damage in comparison to a virgin cross section sample [Figure 4]. Material degradation in the form of voids and cavities was extensive. After aging for five weeks, a 4% loss in mass and 44.7% decrease
in hardness was correlated to the cavitation seen in the SEM analysis, indicating material degradation was due to chain scission of the silicone polymer backbone [14, 15, 25].

**Figure 4.** Cross section of virgin RTV-1
The overall results showed that in the presence of aqueous salt deposits on transmission lines, silicone rubber materials will rapidly age, especially in electrolyzed aqueous solutions such as hypochlorous acid [14, 15, 25]. Hypochlorous acid was determined to be the most aggressive tested aqueous aging condition tested to date, as damage to RTV-1 silicone rubber was more extensive than in 3% aqueous salt at elevated temperature. This was despite the fact that hypochlorous acid experiments were conducted at room temperature. It was therefore determined that silicone rubber that is exposed to salt fog or mist on an insulator in an energized or electrolyzed environment
could be at risk of material degradation as a result of chain scission, resulting in eventual material failure.

1.3 Statement of Problem: engineering new silicone rubbers

Rapid aging of NCIs in coastal environments has been a problem for many years for many utilities all over the world, and their aging has been attributed primarily to chlorine. However, in M. Bleszynski’s previous work [14, 25] it was suggested that HOCl could be the key player in NCI aging in coastal environments. This hypothesis was reported for the first time to IEEE, and accepted by the electrical engineering community. This included Dr. Rueben Hackam, editor in chief of IEEE Transactions on Dielectrics and Electrical Society (TDEI), a key international expert in this field, who personally acknowledged this hypothesis and approved it for publication in his TDEI.

Previous research indicated that while silicone rubber materials are typically resilient and provide excellent protection against environmental damage, deterioration of the material in the presence of highly oxidizing environments such as hypochlorous acid will result in significant and permanent material damage. If continued unabated, material degradation will result in excessive material damage of silicone rubbers, ultimately leading to NCI failure in service. Unfortunately, due to the exceptionally aggressive nature of the HV transmission line environment, it has been tremendously difficult to prevent material failures, even with state of the art modern polymer materials. As such,
designing new silicone rubbers for HV environments has been extremely difficult, as HV environments are notoriously harsh, exhibiting multiple stressors at once [16].

To prevent or delay material degradation of silicone rubbers, new materials have to be developed that can withstand multiple stressors over the lifetime of the material in extreme environments. Presently, there are no clear methods to prevent or delay material damage of silicone rubbers in HV applications, especially where different extreme environments such as both electrical and chemical stresses may be present. Therefore, designing new silicone rubber materials to withstand extreme environments requires interdisciplinary and transformative approaches such as new material formulations and designs.

Consequently, the formulations of caulk and insulator sheath are critical to their ability to withstand environmental stressors, especially oxidizing environments such as hypochlorous acid. This is due to the effects that environmental pollutants such as salt may have on the damage to the RTV over an extended period of time causing not only material degradation, but also by providing an opportunity for more damage when hydrophobicity is compromised. The loss of hydrophobicity illustrated in the aforementioned research is of particular importance, as RTVs are more susceptible to damage from other environmental and electrical stressors when hydrophobicity is lost. Loss of hydrophobicity allows leakage currents to form, affecting the silicone rubber by exposing it to continuous dry band arcing. Dry band arcing and leakage currents are both known to accelerate the degradation of silicone rubbers irreversibly [20, 22, 23].
Therefore additives of oxide nano or micro particles to the silicone rubber formula, which may protect and extend surface hydrophobicity through manipulation of the molecular PDMS geometry, are of particular importance as they may extend the overall longevity of silicone rubber materials.

In this dissertation, the preliminary research on silicone rubbers [14, 15] was greatly expanded. New silicone rubber composite materials were created to resist a variety of extreme environments, such as highly oxidizing hypochlorous acid, thermal cycle aging, electrolyzed aqueous salt, and ice deposition. By modifying silicone rubbers through the addition of metal oxide micro-particles, aging of RTV-1 compounds even in extreme HV circumstances, was significantly reduced. Titanium dioxide micro-particles embedded in an RTV-1 significantly altered the aging mechanisms of the material by improving its surface characteristics. These particles also compensated for the loss of methyl groups on the surface of the rubber due to aging. This model was supported both experimentally and by molecular dynamics simulations of various PDMS-TiO₂ interactions.

Another type of silicone rubber, RTV (RTV-2) with imbedded titanium dioxide microparticles, also improved the material’s resistance to ice deposition, by similarly modifying and improving the surface characteristics of the material through the lotus effect; the result of increased surface hydrophobicity and roughness. When imbedded with microparticles, this new RTV-2, commercially known as DragonSkin™, showed
both lower ice adhesion strength as well as lower ice accumulation compared to unmodified RTV-2 silicone rubber.

1.4 Publications

During the course of this work, two peer-reviewed journal papers were published:


In addition, the following three papers are being completed for publication:


A provisional patent was also filed during the course of this study:


U.S. Provisional Application filed February 10, 2017 by DU.

Based on M. Bleszynski’s M.S. work, two additional papers were also published:

Chapter Two: Silicone Rubber Materials

Silicone rubbers are hydrophobic mineral-organic elastomeric polymers comprised mostly of polydimethylsiloxane (PDMS) chains [1, 23-25]. These chains contain a hydrophilic, highly polar, silicon based backbone, which is surrounded by non-polar methyl groups. Once cured, the bulk PDMS material exhibits hydrophobic properties [8-9, 23, 25], however material aging that results in the loss of methyl groups can render the material more hydrophilic with a greater propensity for surface wetting. The hydrophobic property of PDMS materials is critical, as it encourages water beading, decreasing the likelihood of water accumulation on insulator and other PDMS surfaces, as well as preventing damage to the silicone backbone itself [23-25].

An intact chemical structure is critical for the specific properties of silicone rubber RTV-1, as changes in hydrophobicity often denote changes to the polymer structure, specifically to the polymer’s methyl groups. Current literature indicates silicone rubber polymer aging results in changes to RTV surface hydrophobicity, possibly due to the reduction or damage of the polymer’s hydrophobic methyl groups [8-9, 23, 25]. Retention of hydrophobicity of the RTV is of extreme importance in experimental analysis, as excellent hydrophobicity is a marker of new and un-aged RTV. If the
laboratory aged RTV material structure and physical appearance coincides with the in-service aged results, then an approximation method for accelerated aging method of RTV-1 can be established [23-25].

Visual comparison, such as SEM analysis, between samples can be used regardless of any additional environmental or electrical stressors. The known aging mechanisms for RTV-1 are both environmental pollutants and electrical stressors, all of which affect the underlying PDMS structure. In addition to hydrophobicity, mechanical properties and electrical strength (e.g. dielectric failure) are important measures of aging and material damage where the chemical analysis shows structural changes in the RTV material [1, 23-25].

Changes in the visual appearance of silicone rubbers can therefore indicate material aging and alterations of the underlying chemical composition, often as a result of damage to the polymer backbone Si-O-Si chain [8-9, 23, 25]. Determining the process of chemical damage to the polymer’s silicon based backbone can be used to evaluate material aging and lifespan. Visual comparisons between laboratory-aged and in-service aged RTV also provide analysis of material performance based upon leakage current performance, hydrophobicity, physical and chemical changes [23-25]. To better assess material degradation, laboratory aging of RTV-1 is mostly based upon literature comparisons of virgin and in-service aged material hydrophobicity as a visual representation of RTV material with and without underlying chemical damage [8-9, 23, 25].

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2.1 Silicone rubber chemistry

While many silicone rubber RTVs have proprietary formulations depending upon the manufacturer, the fundamental formula consists of polydimethylsiloxane (PDMS) polymer chains [1, 23-25, 28 - 30] [Figure 6]. The base structure of PDMS is an inorganic Si-O-Si backbone, which independently is polar and hydrophilic. While other functional groups such as ethyl, vinyl, or phenyl functional groups can be substituted, methyl groups are the most common. The non-polar methyl groups (CH$_3$), which are attached to the silicon atoms, can rotate freely, causing the polymer to be hydrophobic [Figure 6 and Figure 7] [1, 23-25, 28 - 30]. Therefore, while the silicon-based backbone itself has a high surface energy, the methyl groups are primarily responsible for the low surface energy of the bulk silicone rubber material – approximately 20 to 25 mJ/m$^2$ after curing [27]. The methyl groups also provide a buffer to the polar Si-O-Si backbone chain, either from polar solvents or other compounds [23-26, 28 - 30].

![Polydimethylsiloxane chemical structure](image)

**Figure 6.** Polydimethylsiloxane chemical structure
Before curing, the non-cross-linked PDMS chains are freely mobile, suspended in a highly viscoelastic, almost liquid state [1, 28 - 30]. After curing, the crosslinking agent immobilizes the chains, leaving little interaction and a low cohesive energy between adjacent chains, largely due to the relatively large distance between neighboring chains [1, 23-25, 28-30]. The polymer remains highly flexible even after curing due to large bond angle of the Si-O-Si bond, and the low rotation barriers of the CH$_3$ functional groups, resulting in almost complete mobility of 360° of the methyl groups [1, 23-26, 28 - 30]. Methyl groups are also known to reorient themselves in response to water droplets or other polar compounds, resulting in orientation of the siloxane chain itself [1, 23- 25, 28 - 30].

Crosslinking is the covalent or ionic bonding process during which long individual polymer chains become chemically linked to one another, forming a polymer network. This process results in a stiffer and more solid material, as the monomer chains
no longer slide past one another [1, 23-25]. There are various types of crosslinkers, some using volatile compounds such as amines or a platinum catalyst. Crosslinking catalysts can include radiation, heat, or exposure to crosslinking agents. This work and analysis will only focus on the specifics of chemical crosslinking within the silicone rubber materials used for this study.

The curing process of single component silicone rubber RTV-1 chemically changes the polymer structure during the curing process, and is initiated through a chemical catalyst upon dispersion of atmospheric moisture throughout the silicone rubber material [1, 23-26, 28-30]. Although the methodology of crosslinking within RTV-1 polymers varies depending upon the manufacturer and the desired silicone rubber consistency, this study used RTV materials, which have crosslinking catalysts in the form of an amine and platinum cure, both of which required atmospheric moisture absorption at room temperature to initiate the chemical reactions. For example, the polysiloxane chains contain terminal –OH groups prior to curing, which gives uncured polymer a semi-solid consistency. Once the silicone rubber is applied and allowed to cure, the–OH groups react with additives such as amine or alcohol, which are then freed during the vulcanization process as atmospheric moisture permeates through the silicone rubber material [Figure 8] [1, 23-26, 28]. The initial stages of curing create a skin on the exposed surface of the RTV, and curing progresses inwards until the curing process is complete.
Besides pigments, fillers, and crosslinking curing agents, additional additives may be present in the silicone rubber in the PDMS network, such as silica. Fumed silica particles, often only a few micrometers in size, are added to silicone rubber materials in order to improve the physical and mechanical properties of RTVs [1, 28-30]. This is critical, as even cross-linked silicone rubbers are mechanically weak and exhibit poor tensile strength after curing [23-25, 28-30]. Synthetic fumed silica is commonly produced using one of three methods: pyrogenic, precipitated or via sol-gel processes, and are added to the liquid silicone pre-polymer during manufacturing before curing [26, 28-30]. Other additives, such as aluminum tri-hydrate (ATH), are commonly added to high voltage silicone rubbers as a fire retardant. However, the interactions of fillers such
as ATH with silicone rubber may pose problems. It was discovered that acids attack the aluminum tri-hydrate filler (ATH) in the insulator skin, resulting in subsequent mass loss and causing the insulator skin to become rougher [1, 26, 28-30].

2.2 Aging and degradation of silicone rubbers

Previous research has shown that acid immersion is capable of breaking polysiloxane bonds at temperatures below 150°C, and the probability of hydrolysis is increased, though the particular mechanisms and reactions are not discussed [1, 28-30]. A computational chemistry approach to hydrolysis calculated a +23 Kcal/mol barrier to water replacing a methyl group from PDMS with a hydroxyl group. The analysis was undertaken to understand the behavior of PDMS in the human body and found that hydrolysis was energetically possible at room temperature suggesting hydrolysis in RTV materials is possible below 150°C [1, 22, 28-30]. A hydrolysis reaction is required to break the Si-O-Si backbone at approximately +26.6 Kcal/mol [1, 23-25, 28], without a catalyst, as water reacts slowly with PDMS at 150°C [1, 23-25]. Therefore, hydrolysis in silicone rubber materials creates both a hydrophilic surface and results in the formation of linear and cyclic chains; the latter of which forms low molecular weight silicone oil [1, 25, 28]. Although the exact mechanisms of hydrolysis of silicone rubber materials according to current literature is still inconsistent in terms of conditions required, it is known that assessing mechanisms of hydrolysis in RTV is critical in the determining RTV material aging progression. Preventing hydrolysis is therefore critical in retention of
the material integrity and mechanical properties of RTV materials, commonly detectable by assessing silicone rubber materials for hydrophobicity. Additionally, the resulting loss of hydrophobicity due to depolymerization is one of the major assessments of RTV aging seen both in laboratory environments and in service conditions to analyze material aging. While thermal depolymerization occurs at or above 350°C, the action of ionic catalysts such as salt is possible below 350°C. Therefore, the highly polar nature of the Si-O bond makes it vulnerable to hydrolysis by polar compounds, resulting in rapid degradation of the polymer chain and depolymerization [1, 25, 28].

Because chain scission of the Si-O-Si backbone in PDMS through any mechanism can result in the formation of low molecular weight (LMW) silicone oil [1, 28] with molecular weights less than 25,000 mers, the low molecular weight silicone material can diffuse through the material matrix, effectively restoring hydrophobicity of the RTV surface [1, 25, 28]. Production of LMW oil is therefore temporarily beneficial to silicone rubber hydrophobicity, but also an indication of material damage. Low molecular weight material diffusion can accelerate as a result of elevated temperature and UV radiation [1, 20-21, 23-25, 28], resulting in short chain low molecular weight material diffusing more quickly to the surface [1, 14, 20-21, 23-25]. However, removal of the low molecular weight material from the surface will again have a negative effect on RTV surface hydrophobicity. Therefore, rinsing or washing of the RTV may accelerate material aging by reducing the hydrophobic properties of the silicone rubber and making the material susceptible to further environmental or electrical stressors.
2.3 Silicone rubber aging in high voltage environments

On HV transmission lines, in service aging of the silicone rubber weather sheds used in high voltage applications can result from various environmental and electrical factors and cause damage to high voltage NCIs. The C-H, Si-O-Si, and Si-CH₃ bonds within the polymer may break due to excessive heat and/or UVA exposure, resulting in permanent silicone rubber and overall shed damage [20, 28]. This can result in a reduction in the leakage distance and increase the chance of dry-band arcing events. Therefore, preventing deterioration of the Si-CH₃ bonds is critical for maintaining RTVs in serviceable condition. While decreases in PDMS hydrophobicity are an indication of material degradation and in-service aging, longer retention of hydrophobicity of newly developed silicone rubber materials may delay or decrease overall NCI aging, making these new materials more resistant to environmental contaminants while in-service [1, 20-21, 23 - 25, 28].

It was shown in previous work [15-16, 25] that in the presence of aqueous salt on transmission lines, single component RTVs can age rapidly and their degradation is especially extensive in aqueous salt solutions [15-16, 25]. The rate of silicone rubber degradation was correlated with the rate of diffusion of the permeating compounds. The fastest diffusing compound, hypochlorous acid, was also determined to be the most damaging, therefore indicating that the rate of diffusion of a damaging compounds through the PDMS network is critical in assessing and preventing silicone rubber damage.
It is also possible that a slightly energized aqueous salt solution will generate measurable quantities of hypochlorous acid, which will rapidly diffuse across the PDMS network even at RT with diffusivity much higher than that of water, chlorine and sodium ions, or nitric acid \[14, 16, 25\]. With the exception of this work \[14, 15, 25\] no other literature sources exist linking hypochlorous acid to the failure of HV transmission NCIs in coastal environments. Also, no other sources have identified hypochlorous acid and energized aqueous salt to be one of the most damaging aging environments for RTVs \[14, 15, 25\]. The idea of linking hypochlorous acid with HV silicone rubber aging came from biochemistry and electrochemistry \[14, 15\] and was based on the assumption that hypochlorous acid could be easily generated in an aqueous salt solution in the presence of small voltage caused by insulator leakage currents \[14, 15, 25, 31-33\].

2.3.1 Aqueous salt environments

Salt contamination in coastal environments is an identified cause of damage to RTV silicone rubber materials in NCIs, and salt exposure can decrease the hydrophobicity of RTVs over time \[23-24\] due to chlorine (ions). Salt contamination can also cause increased corona discharge, corona arcing, and a loss of hydrophobicity, resulting in permanent material damage to silicone rubber RTV (i.e. chain scission) \[24\]. NCI failures in coastal environments have generally been assumed to be solely caused by chlorine damaging the PDMS network \[24\].
Previously completed aging experiments indicated that permanent and significant material damage to RTV-1 can occur after ten weeks in just 3% NaCl saltwater at 80°C. This condition caused surface degradation, which occurred in the form of voids beginning at two weeks aging time [15, 16, 25]. This reduced the hardness of the material by 50% after ten weeks. Mass losses and significant declines in surface hydrophobicity were also recorded. RTV-1 material damage was more extensive in salt water than under individual and combined UV, moisture, and nitric acid exposures [15, 16, 25]. Chain scission of the Si-O-Si backbone was determined to be the primary mechanism responsible for the RTV’s material loss in aqueous NaCl, which resulted in loss of the hydrophobic methyl groups [15, 16, 25]. Current literature indicates that chain scission in PDMS produces cyclic and linear low weight chains, resulting in low molecular weight (LMW) silicone oil [15, 16, 25]. This oil can account for some of the healing properties seen in silicone rubbers, and is the primary explanation for the recovery of hydrophobicity seen in experimental results [15, 16, 25, 28].

Depolymerization of polydimethylsiloxane via hydrolysis as a result of an ionic catalyst, for example salt water, was therefore one of the probable mechanisms responsible for the damage in the salt solution immersion tests. Depolymerization was also responsible for the creation of LMW material, which while maintaining hydrophobicity of the insulator surface over time, regardless if exposed to UV or salt fog, will result in accelerated aging of the RTV-1 caulk sealant [15-16, 25, 28]. In addition, the progression of aging as a result of the RTV-1 seal damage may be due to the presence
of various fillers, additives, or formulations. Therefore, the proper formulations of RTV-1 caulk and insulator skins are critical in their ability to withstand environmental stressors.

Because depolymerization requires two processes: chain scission of the silicone-oxygen backbone and the diffusion of the resulting low molecular weight material, the loss of LMW materials could account for a majority of the loss seen in mechanical strength. The presence of ATH in the RTV material could also promote chain scission in the insulator skin [16] and cannot be excluded as a mechanism in the aging studies depending on the formulation. Therefore, although production of low molecular weight materials is important for maintaining hydrophobicity, loss of material due to depolymerization as a result of hydrolysis is a significant indicator of aging and of particular concern, as it can result in shorter material life in-service [16, 20, 21].

2.3.2 Oxidizing environments

It is theorized in this work that silicone rubber polymer compounds on HV transmission lines can rapidly degrade as a result of oxidative stress, leading to both electrical and mechanical failures of the energized lines. In this work, silicone rubber aging is assessed in the presence of a specific oxidizing aqueous environment, which could be a common aging mechanism in coastal environments. The model is based on the formation of hypochlorous acid in service, when aqueous salt and leakage currents are concurrently present [14, 15].
Understanding of oxidation of polymers and their composites is of critical importance. The combination of elevated temperature, leakage currents, and environmental stressors could expose silicone rubbers to elevated temperatures and oxidative damage.

Oxidizing environments can be commonly found on modern HV transmission lines as a result of atmospheric oxygen and elevated temperatures \([10-14, 21, 22]\). However, in coastal environments, the additional factor of salt contamination and leakage currents may further amplify oxidative stress. Mechanical, electrical and chemical catastrophic failures of the polymer based HV transmission components have been occurring sporadically in different parts of the globe, especially in coastal environments, \([21, 22]\) resulting in downed transmission lines and creating blackouts, ground fires, and many other disasters. Under the right conditions, a fully drenched insulator may create an electrolyzed aqueous environment in the presence of salt, moisture, and leakage currents. Although silicone rubbers are fairly resilient and stable, exposure to oxidative environments, such as UV, is a common degradation mechanism for silicone materials, leading to mechanical deterioration and potential failure of NCIs. Testing of silicone rubbers in highly oxidative environments and designing new silicone rubbers to withstand oxidative stress is therefore critical in extending life in-service of NCIs.

Because RTVs are commonly used on energized HV insulators where corona arcing and leakage currents are prominent in the presence of salt, additional aging due to secondary reactions could occur. Leakage currents \([21, 22]\) on contaminated transmission
lines easily exceed ~+1.63 V on or near the energized ends. This unique energized environment could result in a secondary reaction in standing NaCl salt water, resulting in the formation of highly oxidizing hypochlorous acid (HOCl) [14, 15, 25, 30-33]. The electrolysis of salt water will create hydroxide ions and hydrogen and chlorine gas through the following reactions:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 (g) + 2e^- \\
\text{and} \\
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- 
\]

This results in the potential formation of highly oxidative hypochlorous acid as chlorine hydrolyses in water through the following equation:

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{HCl}
\]

In addition, the electrolysis of water can also result in a hydrolysis reaction, due to the formation of OH\(^-\) and H\(^+\) from H\(_2\)O [30 - 33]. These by products can cause chain scission of the polymer backbone by dissociating the backbone at the site of the silicon and oxygen atoms through the formation of free radicals [Figure 9 and Figure 10] [29-31]. This results in not only loss of hydrophobicity, but also leads to the rapid formation of LMW material and loss of mass of the overall polymer material.
Damage to silicone rubbers as a result of oxidation can occur through various mechanisms. The acid ionization constant ($K_a$), determines the equilibrium constant of a weak acid in solution, and can be used to predict the disassociation of an acid into its
constituents. The $K_a$ of HOCl is $3.5 \times 10^{-8}$, and its power of oxidation is 1.1 compared to that of chlorine of 1.0 [30-33]. HOCl, regardless of $K_a$, therefore rapidly dissociates into damaging hydrogen and hypochlorite ions $\text{OCl}^-$ and $\text{H}^+$ in solution, which can re-associate back into HOCl under ambient conditions [30-33]. The possibility of free radicals forming is possible from reactions of electrolyzed aqueous salt and hypochlorous acid, is shown below:

$$\text{OH}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2\text{O}$$

$$\text{Cl}^\bullet + \text{H}_2\text{O} \rightarrow \text{OH}^\bullet + \text{HCl}$$

**Figure 11.** Possible electrolysis and hydrogen free radical attack on PDMS methyl group from electrolysis

Oxidation via $\text{H}^\bullet$ can occur as shown in **Figure 11**, where a free radical on the methyl group is formed. Free radical damage and chain scission also allows for further
continuation of chain scission along the PDMS backbone, as shown in Figure 12 [25, 30 - 33].

\[\text{CH}_3\text{Si-O-Si-CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH-Si-CH}_3 + \text{H}_2\text{O}\]

\textbf{Figure 12.} Possible hydrolysis damage caused by electrolysis

Therefore, oxidative damage to silicone rubbers and loss of hydrophobicity can be directly correlated, as any damage to the hydrophobic methyl groups will result in a decrease in hydrophobicity of the overall material [25, 28, 30-33]. Oxidation of the methyl groups occurs readily at side chain bonds; therefore prevention of oxidation is dependent upon the stability of the side chain methyl groups and structure of the tertiary backbone chain of PDMS. Available literature also suggests that HOCl can cause damage to polypropylene pipes in the presence of heated chlorinated water as a result of the polymer backbone breaking at the tertiary carbon sites [30-33]. A further investigation of silicone rubber damage in electrolyzed salt environments is explored in Chapter 6.

2.4 Preliminary concluding remarks on RTV aging in aqueous salt

The previously completed study of aqueous salt environments, which are likely to be present on coastal transmission line containing silicone rubber materials, indicated
agents chlorine (ion) and hypochlorous acid can contribute to silicone rubber aging. In the presence of salt and water at elevated temperatures, the combined effect of water, salt and temperature, chlorine ions were explored as the primary mechanism for the damage observed in the RTV-1 in previously completed work [14-16]. However, chlorine (ion) is not as diffusive as hypochlorous acid, as illustrated in the preliminary hypochlorous acid aging experiments [25], which showed accelerated aging of RTV-1 in a minimal hypochlorous acid concentration of 0.046%. Consequently, even at lower concentrations, the combined oxidizing properties and super-diffusivity of hypochlorous acid makes it more damaging to RTV than the already well known damaging effects of both salt and nitric acid solutions.

The effects of RTV-1 and salt contamination have commonly been tested in conjunction with electrical effects, such as corona discharge and dry-band arcing, which accelerates surface aging and hydrolysis. However, the literature indicates that damage to the RTV Si-O-Si backbone can occur in just the presence of salt contamination, suggesting that salt has a negative effect on hydrophobicity due to the reorientation of hydrophobic methyl-groups [19-20, 25]. Coastal HV environments can completely coat the silicone rubber, causing changes in surface hydrophobicity resulting from salt contamination alone or due the cumulative effects of increased electrical discharge [24]. Additionally, while depolymerization as a result of hydrolysis in NaCl aqueous environments has been determined to be responsible for the degradation of RTV type polymers and monomer chains, resulting in the decrease of their average molecular
weight and structural integrity [25], preliminary HOCl experiments question this model. Regardless of the aging mechanisms, conservation of silicone rubber hydrophobicity is important, as a loss of hydrophobicity exposes the polar silicone rubber backbone to further attack by diffusing compounds, and progression of further material damage as a result of hydrolysis can occur.

At present, however, there are no known technologies that could be employed to detect such acids in service on energized HV transmission lines. Therefore, the electrolyzed salt model suggested in this work is the only available indication that HOCl and its byproducts could be a major cause of in-service aging of HV NCIs in the presence of aqueous NaCl, and, perhaps other salts (e.g., MgCl₂, commonly used for deicing purposes). However, for the purposes of this study, purely electrical effects were excluded.
Chapter Three: Titanium Dioxide

A variety of different metal oxides and ceramic have been investigated for use as fillers for silicone rubber materials to extend life and improve properties, including zinc and aluminum oxides, barium titanate, and calcium carbonate [34-36]. Little has been published, however, on the inclusion of titanium dioxide (TiO$_2$) particles to improve silicone rubbers for applications in outdoor environments [31-32]. Titanium dioxide is a widely used material with a variety of applications ranging from food to industrial products to consumer products such as sunscreens as it is non-toxic, chemically stable [34-40], and exhibits excellent UV adsorption properties [37-38].

3.1 Titanium dioxide properties

The three most common forms of titanium dioxide are rutile (110) where $a=b=4.584\text{Å}, c=2.953\text{Å}$, anatase (001) where $a=b=3.782$, $c=9.502\text{Å}$, and brookite where $a=5.436\text{Å}, b=9.166\text{Å}, c=5.135\text{Å}$ [37-38]. Amongst the three, rutile is the most common form. Rutile titanium dioxide occurs in its most basic form as a tetragonal structure unit cell [Figure 13], which has six coordinated titanium atoms, and repeating the unit cells forms larger crystalline structures [38-40]. The atoms in the tetragonal rutile titanium
dioxide cell occupy the least amount of space, making the structure more thermally stable. Rutile differs from metallic titanium through the mix of covalent and ionic bonds. TiO$_2$ rutile by itself is rough, with exposed rows of O atoms and exhibits the lowest surface energy of all three forms of titanium dioxide [38-40]. The surface of TiO$_2$ is bulk terminated, and the surface of titanium dioxide is overall neutral, due to twice as many O$_2^-$ present as Ti$^{4+}$ [38 - 40].

Studies have shown that water dissociates when in contact with rutile TiO$_2$, in contrast to anatase TiO$_2$, which can absorb water [36, 38 - 40]. While current research reports both hydrophilic and hydrophobic properties of TiO$_2$ and TiO$_2$ particles [Figure 14] depending on surface conditions, such as exposure to UV, naturally occurring TiO$_2$ (110) rutile stoichiometric surface is non-polar, with symmetric rows of oxygen atoms [38 - 40].

![Molecular dynamics model of rutile titanium dioxide tetragonal unit cell](image)

**Figure 13.** Molecular dynamics model of rutile titanium dioxide tetragonal unit cell
3.2 Titanium dioxide polymer composites

While rutile titanium dioxide itself has been well studied, its use within polymeric materials has not been extensively documented. For use in HV systems, titanium dioxide has been considered as a filler in silicone rubber materials due to its wide band-gap (3.2eV) and relative stability [34 - 42]. One study indicated that adding titanium dioxide particles to silicone rubber was useful for achieving higher thermal stability, as well as improved mechanical and photocatalytic characteristics of the silicone rubber [31, 32]. More recently, TiO$_2$ has been used in the development of new polymeric materials to achieve superhydrophobic material properties [42]. However, while literature on TiO$_2$/PDMS composites, in general, exists [34, 35, 37], none discuss their effect on
preventing aging or improving material properties in ultra aggressive aging environments such as HOCl, electrolyzed aqueous salt or other highly oxidative media.

Other than improving mechanical and photocatalytic characteristics, titanium dioxide may hold the potential to enhance the hydrophobic properties of polymers when incorporated with particles such as titanium dioxide, causing the chains to reorient. This could result in a change in the free energy of the PDMS surface, if functional group orientation were affected. For example, it has been documented that compounds with both polar and non-polar components, such as PDMS, may orient themselves perpendicular to the titanium dioxide surface, while compounds with multiple polar sites may orient parallel to the surface, and non-polar compounds may lie flat [34, 35]. A strong interaction between PDMS and titanium dioxide, especially between the highly polar backbone and the oxide surface, may therefore result in a reorientation of the chains and the polymer’s functional groups [35], leading to a more hydrophobic surface.
Chapter Four: Molecular Dynamics Numerical Methods

To better understand the molecular and atomic interactions within PDMS nanocomposites, Materials Studio molecular dynamics software was utilized during the course of this study. However, before presenting the outcomes of completed numerical work, a brief synopsis of molecular dynamics numerical methods, specific to Materials Studio, is summarized here.

4.1 Materials Studio forcefield

Different molecular dynamics software programs employ various force fields, which use empirical formulas to calculate the interatomic interactions of atoms and molecules. Materials Studio uses a Condensed-phase Optimized Molecular Potentials for Atomistic Simulations Studies (COMPASS) forcefield to calculate the energy potential of the molecules and the distance between each molecule. The principle of calculating the various position and velocities of these atoms and molecules can vary, but the underlying principle is solving Newton’s equation of motion for each atom [43-45]:

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\[ F = ma = m \frac{dv}{dt} = m \frac{d^2x}{dt^2} \quad \text{(eq. 5)} \]

\[ F_i(t) = m_i a_i(t) \quad \text{(eq. 6)} \]

where \( F_i \) is the force, \( m_i \) is the mass, and \( a_i \) is the acceleration of atom \( i \). The force on atom, denoted by \( i \), can then be computed from the derivative of the potential energy \( V \) with respect to the coordinate \( r_i \):

\[- \frac{\partial V}{\partial r_i} = m_i \frac{d^2r_i}{dt^2} \quad \text{(eq. 7)}\]

The force field is an expression of the energy potential surface, which is the basis of molecular dynamics simulation and depends on the molecule’s potential energy and the distance between each of the molecules [43-45]. For various purposes, force field can be divided into many forms with different scope and limitations, and the reliability of the solutions is dependent on the chosen force fields. The form of the COMPASS forcefield is denoted by the following equation [43-45]:

\[ E_{pot} = \sum_b [k_2 (b - b_0)^2 + k_3 (b - b_0)^3 + k_4 (b - b_0)^4] + \]

\[ \sum_\theta [k_2 (\theta - \theta_0)^2 + k_3 (\theta - \theta_0)^3 + k_4 (\theta - \theta_0)^4] + \]

\[ \sum_\phi [k_1 (1 - \cos \phi) + k_2 (1 - \cos 2\phi) + k_3 (1 - \cos 3\phi)] + \]
\[
\sum_{x} k_s x^2 + \sum_{b,b'} [k (b - b_0) (b' - b'_0)] + \sum_{b,\theta} [k (b - b_0) (\theta - \theta_0)] + \\
\sum_{b,\phi} [(b - b_0) [k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]] + \\
\sum_{\theta,\phi} [(\theta - \theta_0) [k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]] + \\
\sum_{\theta,\theta'} [(\theta - \theta_0) (\theta' - \theta'_0)] + \sum_{\theta,\theta',\phi} [k (\theta - \theta_0) (\theta' - \theta'_0)] \cos \phi + \\
\sum_{ij} \left[ \frac{q_i q_j}{r_{ij}} \right] \quad (eq. 8)
\]

The various functions in the COMPASS forcefield can be divided into valence terms, representing the internal coordinates of bond interactions \( b \), angle \( \theta \), out of plane angle \( X \), and torsion angle \( \phi \). Non-bond interactions, such Coulombic functions for electrostatic interactions, are governed by the following Lennard-Jones 9-6 functions for unlike atoms [43-47]:

\[
r_{ij}^0 = \left( \frac{(r_i^0)^6 + (r_j^0)^6}{2} \right)^{1/6} \quad (eq. 9)
\]

\[
\varepsilon_{ij} = 2 \sqrt{\varepsilon_i \varepsilon_j} \left( \frac{(r_i^0)^3 \cdot (r_j^0)^3}{(r_i^0)^6 + (r_j^0)^6} \right) \quad (eq. 10)
\]
where $r$ is the intermolecular distance between two particles, and $\epsilon$ is the energy, or well depth. Electrostatic potentials are utilized through atomic partial charges. For valence bonded atoms, $i$ and $j$, with partial charges such as ions, the sum of all charge bond increments, $\delta_{ij}$, is represented by [45-48]:

$$q_i = \sum_j \delta_{ij} \quad (\text{eq. 11})$$

where $j$ signifies all atoms that are valence-bonded to an atom, $i$. van der Waals forces, are represented by [45-48].

$$E_{vdW} = \sum_{ij} \epsilon_{ij} \left[ 2 \left( \frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left( \frac{r_{ij}^0}{r_{ij}} \right)^6 \right] \quad (\text{eq. 12})$$

All energy parameters set within Materials Studio, including van der Waals energy forces, were set to group based. Although the COMPASS forcefield was applied to all the models built for this work, the bond interactions still had to be independently computed. The molecular dynamics PDMS model required two distinct bonds models: the covalent model for the PDMS polymer to calculate siloxanes (-Si-O-Si-), and the ionic model to calculate metal oxides and metal halides such as Cl, where for ionic materials, $\delta_i$ is set to the formal charge and $\delta_{ij}$ is zero for ionic materials. Additionally, solid-state parameterization for the metal oxide interactions was done using the semi-ionic mode, which was applied using the dispersion interaction function, expressed by [1, 43 - 48]:

44
\[ E_{ij}(r_{ij}) = -\frac{C_{ij}}{r_{ij}^6} \]  
(eq. 13)

where \( E_{ij} \) represents the electrostatic interaction energy between two atoms, \( r_{ij} \) represents the distance between atoms designated by \( i \) and \( j \), and \( C_{ij} \) is a constant. For the molecular dynamics models involving silica, where there is covalent bonding with some representation incorporating simple bond angle dependence, the following equation was utilized for angle bending [43 - 48]:

\[ E_{ij}(r_{ij}) = k(r_{ij} - r_0)^2 \]  
(eq. 14)

where \( k \) is the bond spring strength, and \( r_0 \) designates the equilibrated bond length between two atoms [43 - 48].

4.2 Molecular dynamics ensembles

Two molecular dynamics ensembles were utilized for the various molecular dynamics simulations in this work. The **NVT**, or *canonical ensemble*, where the number of particles \( N \), volume \( V \), and temperature \( T \) in the system were all held constant, and the **NVE**, or *constant energy/microcanonical ensemble*, where the number of particles \( N \), volume \( V \), and the energy \( E \) were all held constant. NVT was mainly applied for simulations where the temperature was to remain constant, specifically when mimicking experimental setups. The simulations of the NVT and NVE ensembles were completed using the Forcite Dynamics module, with the coordinates and velocities from the Verlet velocity algorithm.
4.3 Energy minimization

Energy minimization, which gradually changes the coordinates of atoms to achieve a minimization point, is routinely employed for all simulations and modeled throughout the building process to minimize computation time and ensure accuracy. The two algorithms utilized to compute energy minimization in this study were the steepest descent method and the Newton-Raphson method, which were used both for geometry optimization and dynamics simulations. Models were first optimized for geometry using the steepest descent method, and then the quasi Newton-Raphson method, to optimize the models to convergence [43 - 48]. This was done because of the methodology of each approach: while the steepest descent method optimized the overall geometry, the quasi-Newton-Raphson optimization uses a finer optimization method to ensure the ideal placement of the water droplet upon the PDMS surface [44 - 47]. This is because the steepest descent method calculates first derivatives, and is best utilized when simulations are not optimized and are far from minimization, while the Newton-Raphson method employs a second-derivate method and larger step as the rate of change, and this method was utilized when the system is close to a minimum [43-48].

However, because the Newton-Raphson method utilizes local matrices, the quasi-Newton-Raphson method was used in this study as the matrices were not locally stored, and the optimization time could be cut shorter [45 - 48]. Therefore, the Newton-Raphson method used in this optimization method is modified to not store matrices within the local computer memory, to boost system performance and speed up simulations [45 - 48].
Chapter Five: Molecular Dynamics Simulations of TiO$_2$/SiO$_2$/PDMS Nanocomposites

Various molecular dynamics simulations were conducted in this study to assess the potential benefits of titanium dioxides on PDMS and other silicone rubber materials. The hydrophobic property of silicone rubber materials in HV applications is critical [9, 14-20, 25, 49], therefore it was chosen as an ideal material property to model and investigate in depth.

Because hydrophobicity and surface energy are directly correlated [9, 25, 49 - 52], and aging of PDMS silicone rubber has been documented to involve the loss of methyl groups making the material more hydrophilic, molecular dynamics models were built to specifically assess changes in hydrophobicity. Multiple PDMS surfaces were modeled with and without TiO$_2$ nanoparticles to assess changes in hydrophobicity and surface energy, using molecular dynamics to model the changes in contact angle of a water droplet over time. Additionally, surfaces with varying amount of methyl groups were compared to unmodified PDMS surfaces, to mimic PDMS aging.
5.1 Hydrophobicity and water droplet contact angle

Material hydrophobicity is a product of surface wetting, with the degree of wetting determined by a force balance between adhesive and cohesive forces. The hydrophobic effect results in an increase in hydrogen bonding within a solidly defined water droplet itself on hydrophobic surfaces, with the surface area of a water droplet decreasing as a result of overall decreased free energy due to the resulting repulsion of polar water molecules [49 - 52]. Adhesive forces will cause water to spread across the surface, diminishing the contact angle and increasing the water droplet surface area, while cohesive forces will result in an increase in the water droplet contact angle with a smaller surface area as a result of the more spherical droplet shape [49 - 52]. Wettability of a material is therefore commonly expressed by contact angle of a liquid on a surface, calculated using Young’s equation (eq. 1) and denoted by the angle of the liquid-gas interface at the material surface [49-52]. Material surface contact angles and hydrophobicity are classified as follows: $\theta = 0^\circ$: superhydrophilic, $0 < \theta < 65^\circ$: hydrophilic, $65^\circ < \theta < 150^\circ$: hydrophobic, $\theta > 150^\circ$: superhydrophobic [9, 25, 27, [48 – 52].

The determination of a contact angle on a surface is based upon the three-phase equilibrium, occurring at the solid/liquid/gas contact point of a water droplet and a material surface, and is determined by the tangent line of solid and liquid surface, as shown in Figure 15 [49–55]. These are denoted by interfacial tension ($\gamma_{sl}$), surface tension, ($\gamma_l$), and surface energy ($\gamma_{sv}$) in Figure 15. Surface energy is thereby correlated
with contact angle, as large contact angles are associated with low surface energy materials and are deemed hydrophobic. Conversely, small contact angles (<90) are hydrophilic and have high surface energies [49 – 55].

![Figure 15. Schematic of water droplet contact angle measurement on a solid interface](image)

The changes in the contact angles of surfaces can be directly correlated to surface energy of an ideal solid (γ_s) using Young’s equation (eq. 1) [49 – 55].

\[
\gamma_s = \gamma_{sl} + \gamma_l \cos \theta \quad (\text{eq. 1})
\]

The surface must be assumed to be solid, smooth, and uniform, however, with no discernable roughness or deformation to utilize Young’s equation to calculate the contact angle of an ideal solid. When a surface is rough and non-uniform, two other states, Wenzel [Figure 16 a] and Cassie-Baxter [Figure 16 b], can occur [49 – 54].
Wenzel modified Young’s equation to include the surface roughness, $r$, as a function of the contact angle through the following equation:

$$\cos \theta^* = r \cos \theta \quad (eq. 2)$$

where $\theta^*$ is the contact angle for the water droplet in the state of equilibrium, $\theta$ is Young’s contact angle, and $r$ is the surface roughness ratio. In another variation, Cassie and Baxter combined the surface roughness of Wenzel’s model and the solid surface to create the Cassie-Baxter model, stipulating that the water droplet rests on the rough surface. The contact angle for Cassie-Baxter is therefore calculated using the following equation [48 - 54].

$$\cos \theta^* = r_f f \cos \theta_y + f - 1 \quad (eq. 3)$$

where $f$ is the fraction of the solid surface area, $r_f$ denotes the surface roughness ratio of the surface, which is wet by the water droplet, and $\theta_y$ is the Young’s contact angle [49 - 54].
In this study, the simple model of the solid surface wet by a water droplet is assumed, and Young’s equation is used to calculate the water droplet contact angle in the molecular dynamics models [49 - 54]. However, in order to calculate the surface free energy of a solid from a water droplet contact angle, interfacial tension $\gamma_{sl}$ must first be calculated. Neumann proposed an equation (eq. 4) to calculate the unknown interfacial tension by using a liquid with a known surface tension, $\gamma_l$, such as water, in order to determine the surface free energy of a solid [49, 51, 54]:

$$\gamma_{sl} = \gamma_l + \gamma_s - 2\sqrt{\gamma_l \cdot \gamma_s} \cdot e^{-\beta(y_l-\gamma_s)^2} \quad \text{(eq. 4)}$$

where $\gamma_{sl}$ denotes the unknown interfacial tension and $\beta$ is an empirical constant with a determined value of 0.000124 [49 - 54]. Through substitutions, equations 1 and 2 can be used with some modifications to calculate the surface energies from associated contact angles of a water droplet from molecular dynamics simulations.

5.2 Molecular Dynamic simulations of TiO$_2$/PDMS composites

Because extreme aging of silicone rubber materials decreases hydrophobicity over time, and assessing changes in hydrophobicity in NCIs over time is critical, molecular dynamics simulations were conducted to investigate the effect of titanium dioxide particles on the PDMS network, as well as the effect of TiO$_2$ nanoparticles on
hydrophobicity. Titanium dioxide nanoparticle effect on diffusivities and interfacial interactions, when incorporated into the PDMS matrix, was also investigated.

Figure 17. Molecular dynamics model of PDMS with embedded nanoscale TiO$_2$ particles

All simulations were conducted with BIOVIA Materials Studio software using the COMPASS forcefield. Approximately 3% by volume non-hydroxylated TiO$_2$ (110) rutile nanoparticles with no partial charges were integrated with PDMS chains to create various surfaces for molecular dynamics simulations [Figure 17]. All PDMS surface models developed in this study were constructed using 50 co-block polydimethylsiloxane polymer chains, which were combined to form a periodic cell using Amorphous Cell. The initially constructed PDMS chains underwent geometry optimization before further construction into model surfaces.

All modeled surfaces (1-6) are listed in Table 3. Surfaces 1, 2, and 3 included <10 angstrom TiO$_2$ nanoparticles in the Amorphous Cell construction, while surfaces 4 to 6 had no incorporated particles. Additional modifications were performed on surfaces 2, 3, 5, and 6 by manually removing their methyl groups from all the PDMS chains.
Surfaces 2 and 5 had 50% of the methyl groups in the initial PDMS chain removed, and surfaces 3 and 6 had 100% of the methyl groups eliminated. This was done to identify what effect methyl groups could have on the surface energies of the material models, with and without titanium dioxide particles. PDMS chains with reduced methyl groups underwent additional geometry optimization to ensure accurate molecular geometry of the modified chains before further surface construction. Surfaces 1 and 4 were constructed without any modifications to the number of methyl groups. All completed surfaces underwent additional geometry optimization before subsequent water droplet placement simulations.

**Table 3.** Six modeled surfaces: methylated, non-methylated, and partially methylated PDMS chains with TiO$_2$ nanoparticles [56]

<table>
<thead>
<tr>
<th>PDMS Surface Methylation Percent</th>
<th>Surface 1</th>
<th>Surface 2</th>
<th>Surface 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>With TiO$_2$ (110) Nanoparticles</td>
<td>100%</td>
<td>50%</td>
<td>0%</td>
</tr>
<tr>
<td>Without TiO$_2$ (110) Nanoparticles</td>
<td>100%</td>
<td>50%</td>
<td>0%</td>
</tr>
</tbody>
</table>

**Figure 18.** A 15-angstrom water droplet used in all PDMS surface models
A 15Å diameter water droplet [Figure 18] was created and optimized for geometry to create a sphere. Figures 18 shows the initial placement of the water droplet relative to a modeled PDMS surface. The bounding box was removed, and the water droplet was positioned approximately 20Å from the surface. The same water droplet was used for all surfaces to ensure consistency. All final models were optimized for geometry using Forcite geometry optimization once more before subsequent NVT dynamics.

Figure 19. Initial model of spherical water droplet and PDMS surface before geometry optimization and molecular dynamics simulations [56]

Molecular dynamics simulations were conducted using the Forcite dynamics NVT ensemble. Temperature was kept constant at 298.15K, and all simulations were programmed for 10,000 time steps for a total time of 100 picoseconds (ps). All dynamics simulation parameters were kept the same for all six PDMS surface models. Following dynamics simulations of the six PDMS surfaces listed in Table 3, changes in water
droplet contact angle were evaluated to determine the effect of TiO$_2$ and removal of methyl groups on the water droplet contact angle and surface free energy.

While the simulated PDMS surfaces were created in 3D, the numerical predictions of the water droplet-PDMS interactions were assessed in 2D for the contact angle analysis. The final results of the molecular dynamics simulations were changed to gray scale to allow for software contact angle assessments using a LB-ADSA computational approach. A best-fit curve (green line) was applied to the droplet boundary, as shown in figure 20b.

\[
\cos \theta = \frac{\gamma - \gamma_s}{\gamma_l} - \frac{\tau/\gamma_l}{r_B} = \cos \theta_r - \frac{\tau/\gamma_l}{r_B} \quad (\text{eq. 15})
\]

Due to the nanoscale size of the modeled water droplets, any effects due to gravity can be considered negligible [55]. Therefore, the water droplet contact angle can be calculated by approximating a sphere to the nanoscale water droplet boundary [52 - 55]. For all modeled surfaces, the final contact angles were predicted from the
approximated nanoscale contact angles of the water droplets using a modified Young’s equation (eq. 3) [52 - 55]. Because the effect of line tension, \( \tau \), at the three-phase contact point becomes more significant at the nanoscale level when compared to surface tension, equation 3 [52 - 55] had to be used to convert the approximated nanoscale contact angle, \( \theta \) to \( \theta_f \), which denotes the Young’s contact angle. The cosine of the approximated nanoscale contact angle \( \theta \) can be linearly correlated to the water droplet base radius \( r_B \) [55]. All subsequent references to water droplet contact angles in this study therefore refer to the final calculated macroscopic (Young’s) contact angles, which were also used to determine the surface energies of the analyzed PDMS surfaces. Figure 21 and Figure 22 show the decreases in contact angle during 100ps molecular dynamics simulations for PDMS surfaces with and without titanium dioxide particles, showing an initial decrease then plateau of measured contact angles.
Figure 21. Progression of water droplet on modified PDMS surfaces over 100ps simulation time

Figure 22. Progression of water droplet on modified PDMS + TiO$_2$ surfaces over 100ps simulation time
5.3 Predicted contact angles and surfaces energies

The calculated surface energies of the six modeled PDMS surfaces listed in Table 3, and are presented in Table 4, Figure 23, and Figure 24. The results show that the surfaces with reduced methyl groups exhibited an increase in surface energy compared to the fully methylated conditions. However, the addition of TiO$_2$ (110) nanoparticles lowered the surface energy of surfaces 1, 2, and 3 when compared to surfaces 4, 5, and 6. For example, the surface energy of surface 5 (50% methylated without TiO$_2$ (110) nanoparticles) was 40.9 mJ/m$^2$. The surface energy decreased to 32.4 mJ/m$^2$, when TiO$_2$ nanoparticles were added (surface 2). This therefore suggests that the addition of non-polar TiO$_2$ (110) nanoparticles decreases the surface energy of a PDMS surface regardless of methylation [49].

<table>
<thead>
<tr>
<th>Table 4. Surface energies for six PDMS surface models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated Surface Energies for Modeled PDMS Surfaces (mJ/m$^2$)</td>
</tr>
<tr>
<td>PDMS Surfaces with TiO$_2$ (110) Nanoparticles</td>
</tr>
<tr>
<td>PDMS Surfaces without TiO$_2$ (110) Nanoparticles</td>
</tr>
<tr>
<td>PDMS Surfaces without TiO$_2$ (110) Nanoparticles</td>
</tr>
</tbody>
</table>
Figure 23. Calculated water droplet contact angles for all six PDMS surfaces after 100ps simulation time

Figure 24. Surface energies for all six modeled PDMS surfaces
Surface energies of 15 to 24 mJ/m² have been recorded experimentally for neat PDMS silicone rubber materials [27, 40-46, 56]. In this case, surface 1 has a slightly higher energy than experimentally observed. Similar discrepancies were reported in [14, 15] between the molecular dynamics predicted and experimentally observed densities of the investigated PDMS, which was attributed to the lack of silica in the molecular dynamics models. When about 20% by volume of silica was added [14, 31, 56], the difference in the densities was eliminated. It is suspected that the difference in the predicted and measured surfaces energies reported here could also be caused by the lack of silica in the contact angle models presented in this work.

5.4 Interfacial PDMS-TiO₂ interactions

Two interfacial molecular dynamics models were built to better understand molecular interactions at the PDMS/TiO₂ and PDMS/SiO₂ interfaces [56]. Independently, a 10Å TiO₂ (110) rutile surface and a 10Å SiO₂ surface were cleaved and optimized for geometry, followed by an addition of a PDMS chain, which was added using Layer Builder. The systems were optimized for geometry before running Forcite dynamics [Figure 25]. Forcite dynamics was then conducted for 10ps at 25°C, with the same Forcite settings as mentioned previously. During the simulations, Materials Studio was set to monitor for close contacts between the PDMS chain and the TiO₂ and SiO₂ surfaces through energy minimization. In Materials Studio close contacts are monitored by using equation 16, where r is the distance between two atoms, and C_{close} is the sum of the
respective van der Waals radii $R_{i,vdW}$. If the distance between two atoms ($r$) is considered smaller than the $C_{close}$, a potential bond may be formed [47, 56].

$$ r \leq C_{close} \cdot |R_{1,vdW} - R_{2,vdW}| \quad (eq. \ 16) $$

**Figure 25.** Interfacial model close contacts between PDMS and TiO$_2$ surface before molecular dynamics modeling [56]
Figure 26. Interfacial model close contacts between PDMS and TiO$_2$ surface after molecular dynamics modeling [56]

Figure 27. Interfacial model close contacts between PDMS and SiO$_2$ surface before molecular dynamics modeling [56]
Figure 28. Interfacial model close contacts between PDMS and SiO$_2$ surface after molecular dynamics modeling [56]

The final molecular configurations at the PDMS/TiO$_2$ and PDMS/SiO$_2$ interfaces are shown in Figure 26 and Figure 28. Close contacts between the TiO$_2$ surface and the silicon atoms in the PDMS chain in Figure 26 are indicated by the dotted lines. Initial observations suggest noticeable attractions between the silicon atoms in the PDMS and the oxygen atoms in TiO$_2$, thus changing the molecular geometry of the PDMS chain at the interface. A discernable difference was observed in the methyl group orientation at the PDMS/TiO$_2$ interface [Figure 26] compared to the PDMS/SiO$_2$ interface [Figure 28]. Specifically, a definite reorientation of the methyl groups away from the TiO$_2$ surface can be noticed in Figure 26. This is in comparison to the PDMS/SiO$_2$ interface, which shows a reorientation of the methyl groups towards the SiO$_2$ surface [Figure 28]. The reorientation of the hydrophobic methyl groups away from the TiO$_2$ surface could
partially explain the changes in the hydrophobicity and surface energies of the modeled surfaces listed in Table 4.

5.4.1 Effects of titanium dioxide and silica nanoparticles on PDMS network diffusivities

Additional molecular dynamics diffusion models were developed using Materials Studio to assess the diffusion rates of HOCl, its dissociation products (water and Cl\textsuperscript{-}) and Na\textsuperscript{+} through a filled and unfilled PDMS polymer network [14-15, 56]. Two separate iterations of a nanoparticle filled PDMS diffusion model were performed for each permeating compound and each diffusing molecule or ion over a period of 10 picoseconds, with and without nanoparticles within the PDMS network, to assess their effect on diffusivity. These results were then compared to previously performed molecular dynamics simulations of diffusivity through unfilled PDMS [Figure 29]. Together, these results were analyzed to better assess the interaction of various possible compounds diffusing within the PDMS chain network and help predict possible future aging effects.

All molecular dynamics diffusion rate simulations of the propagating species were conducted using Mean Square Displacement (MSD), which was calculated with Materials Studio Forcite analysis using the following equation [46, 56]:

\[
D = \frac{1}{6N_a} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N_a} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (eq. 17)
\]
where $N_{\alpha}$ represents the number of diffusive particles in the model, $i$ represent the particle, $r_i(0)$ is the relative distance of a particle, $r_i(t)$ denotes the coordinate position of a particle over time, and $D$ denotes the calculated diffusion coefficient [46, 56]. Mean Square Displacement calculations, based upon the random walk principle, give an estimate of the distance a molecule will travel through a volume over time, calculated as diffusion of a particle through a medium [46]. The mean squared displacement equation is a function of the diffusion coefficient, and calculates the difference between the final and initial coordinates or a particle [46]. The diffusion coefficient part of the mean squared displacement equation, assumes molecular vibrations within a solid, and is represented by [46]:

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (eq. \ 18)$$

Calculations were averaged over distance and time for all diffusing compounds to account for voids within a material. MSD was conducted for each diffusing molecule or ion over a period of 10 picoseconds.

5.4.2 Unfilled PDMS diffusion simulations

For comparison purposes, unfilled PDMS diffusion simulations are included here [25]. Molecular dynamics calculations were done at NVE for a constant number of molecules (N), constant volume (V), and constant energy (E) [25]. The initial density of the amorphous cell structure for the unfilled PDMS was set at 0.9 g/cm$^3$, and a mass ratio of 99% Si-O-Si backbone to 1% diffusion molecule was set. Annealing was done at NVT
for constant number of molecules (N), constant volume (V), with temperature set at room temperature (T) for consistency with the performed experimental aging [25].

The first run was modeled at 80°C and the second at 25°C with an amorphous cell density of \( \sim 0.95 \text{ g/cm}^3 \), mimicking physical pure PDMS [25]. Forcite Mechanics tools were set to group based calculations for both electrostatic and van der Waals interactions. Additionally, each PDMS and diffusion molecule or ion variation underwent geometry optimization and annealing at constant temperature and energy for 10,000 cycles. Forcite calculations were done at each interval for all previously mentioned molecules and ions to generate the Mean Squared Displacement (MSD) data for a period of 10 picoseconds.

Figure 29. Simulated molecular dynamics MSD diffusion rates for permeating compounds: HOCl, H$_2$O, Na and Cl ions at 25°C and 80°C
The slopes of the curves in Figure 29 represent the MSD rates of the modeled ions and molecules through the PDMS network, which can be correlated to molecular diffusion rates. Evidently, the diffusion curves in Figure 29 are the greatest for HOCl [25]. The curves show a similarity in the diffusion rates for both 25°C and 80°C temperatures, although the diffusion at 25°C was a lower overall rate compared to 80°C. Even at the lower temperature, the model indicated that HOCl will diffuse through the polymer network at a much faster rate than water, or Na and Cl ions [25].

5.4.3 Effect of silica on PDMS diffusivities

Silica filled PDMS molecular dynamics diffusion simulation were conducted to assess the diffusivities of the previously mentioned permeating compounds, such as HOCl, H₂O, Na and Cl ions, through a PDMS polymer network filled with silica nanoparticles. This was done in order to simulate molecular diffusion through RTV-1, as silicone rubbers contain at least 20% silica (SiO₂) by volume, and silica can affect the diffusion rates of various compounds through the PDMS network [14, 46, 57, 58]. Silica has also been found to be a source of pooling sites [57, 58], which could be the initial damage initiation sites in silicone rubbers. Therefore, SiO₂ was included as a nanoparticle within the PDMS network [Figure 30] as a comparison against TiO₂ filled PDMS.

Two SiO₂ nanoparticles approximately 10Å in size were constructed independently and optimized for geometry before being combined with previously constructed PDMS chains using amorphous cell. The molecular dynamics of the silica
filled PDMS model was modeled over a period of 10 picoseconds, and molecular dynamics calculations were done at NVE, annealing at NVT, and the initial density of the amorphous cell structure was set at 1.05 g/cm³, with a mass ratio of 69% Si-O-Si backbone to 20% silica nanoparticles, and 1% diffusion molecule. These parameters were set for consistency with the previously conducted unfilled PDMS simulation. The silica filled PDMS molecular dynamics model was conducted at 25°C with final cell density of ~1.13 g/cm³ after optimization, to more closely mimic the physical density of silica filled PDMS (36). The final silica filled PDMS structure underwent geometry optimization and annealing at constant temperature and energy for 10,000 cycles, and final Forcite calculations and analysis were conducted to generate MSD data for a period of 10 picoseconds, similar to the previous model.

**Figure 30.** Materials Studio molecular dynamics model of PDMS in Amorphous Cell with silica nanoparticles
The MSD slopes of the curves in Figure 31, show similar diffusion curves to the previously modeled diffusion rates for both 25°C and 80°C temperatures, with some notable differences. The overall diffusion curves are similar to those previously modeled in the unfilled PDMS model, however the overall rates are slower, which could be due to the increase in cell density. A significant difference is the diffusion curve for H$_2$O, which is comparable to the Cl ion, and shows overall faster diffusion in the silica filled PDMS compare to unfilled PDMS [56]. However, HOCl still exhibits significantly faster diffusion through the filled polymer network compared to water, or Na and Cl ions.
5.4.4 Effect of TiO$_2$ on PDMS diffusivities

A final diffusion model was constructed for TiO$_2$ filled PDMS. The model was constructed with identical parameters to that of the silica filled model, but with approximately 3% TiO$_2$ nanoparticles by volume in a PDMS network. Diffusion rates for the TiO$_2$ filled PDMS can be observed in Figure 32 for HOCl, water, and Cl$^-$ and Na$^+$. If the data in [Figure 32] and [Figure 31] are compared, it can be seen that TiO$_2$ particles (3% by volume) significantly decreased the diffusivity of HOCl, and slightly reduced the diffusivities of water, and Na and Cl ions. On the other hand, an addition of 20% by volume of silica to the PDMS increased the diffusivities of the same species.

![Figure 32](image)

Figure 32. Simulated molecular dynamics MSD diffusion rates for permeating compounds: HOCl, H$_2$O, Na and Cl ions at 25°C through TiO$_2$ filled PDMS network [56]
5.5 Preliminary concluding remarks on molecular dynamics simulations of silicone rubber nanocomposites

Overall, the molecular dynamics simulations showed that the addition of TiO$_2$ (110) nanoparticles to various PDMS surfaces increased the contact angles of the water droplets, regardless of PDMS methylation, as shown by the differences in modeled hydrophobicity of the six modeled surfaces and the interfacial interactions. All surfaces with a reduction in the methylation of the polydimethylsiloxane chains exhibited lower contact angles and higher surface energies, which is likely due to the reduction of the non-polar methyl groups, resulting in a more hydrophilic surface.

PDMS surfaces with TiO$_2$ (110) nanoparticles with reduced methyl groups still exhibited a decrease in contact angles compared to the fully methylated surfaces. The measured contact angle on surface 3 (fully non-methylated without TiO$_2$ (110) nanoparticles) was 52.7°, but increased to 69.5° when TiO2 nanoparticles were added. This was very close to the contact angle recorded on surface 6, (partially non-methylated without TiO$_2$ (110) nanoparticles), which was 70.1°. This therefore indicates that the addition of non-polar TiO$_2$ (110) nanoparticles may partially compensate for the loss of methyl groups due to PDMS aging or material degradation. The changes in the contact angles of the surfaces with TiO$_2$ (110) nanoparticles can also be directly correlated to surface energy, as all PDMS surface energies were lowered by the addition of TiO$_2$ (110) nanoparticles. The calculated contact angles and surface energies therefore indicate
PDMS surfaces would exhibit greater hydrophobicity of PDMS compared to PDMS surfaces without TiO$_2$ nanoparticles.

Molecular dynamics diffusion simulations also showed notable differences between filled and unfilled PDMS models. The diffusion curves shown in Figures 29 and 32, indicate that titanium dioxide can lower the rate of diffusion of HOCl, and other permeating compounds, compared to unmodified PDMS. However, in the presence of silica, the movement of water and HOCl molecules in PDMS is faster [Figure 31], allowing water and HOCl molecules to diffuse faster [Figure 31] because of the opposite reorientations of the methyl groups. By contrast, the MSD rates for diffusing compounds were considerably lower in the simulated PDMS network with TiO$_2$. This indicates the diffusion of HOCl in experimental RTV-1/TiO$_2$ composites could be potentially reduced.
Chapter Six: Experimental Aging of Silicone Rubber Materials of This Study

In this section, extreme aging tests were conducted on PDMS composites with and without titanium dioxide particles. Because the numerical simulations in Chapter 5 showed decreased surface energy, and lower diffusivity of permeating compounds in the composites, a novel TiO\textsubscript{2}/PDMS material was made and subsequently tested to observe its resistance to aging in highly oxidizing aqueous environments.

6.1 Tested silicone rubber TiO\textsubscript{2}/RTV-1 composite

The silicone rubber chosen for this study was a previously investigated single component RTV-1 [25], which was determined to have excellent resistance to environmental aging under UV, moisture, aqueous salt and other conditions [16, 25]. It was also extensively studied under HOCl and energized 3% aqueous salt in [14-15, 25]. The TiO\textsubscript{2}/RTV composite samples were fabricated with infused ~ 40 micron sized TiO\textsubscript{2} particles with a weight fraction of 3% using the curing conditions developed in [14-16]. The composites were optimized for the most uniform distribution of the particles, and the samples were subsequently tested for their resistance to aging in HOCl and electrolyzed
aqueous salt. RTV-1 materials without TiO$_2$ particles are referred to in this study as unmodified RTV-1.

6.2 Effect of HOCl

To observe the effect of oxidizing environments on silicone rubber and their resistance to aging, the 3% TiO$_2$/RTV-1 composite material was aged in a highly oxidizing aqueous environment. A composite sample was subjected to aging in commercially produced hypochlorous acid and in an electrolyzed ocean concentration 3% NaCl solution in minimal light conditions. Because the presence of hypochlorous acid has not yet been verified on in-service transmission lines, the electrolyzed aqueous salt solution was included in the aging experiments as a comparative study. The silicone rubber insulator material chosen for this study was a previously investigated RTV-1 SRI compound, which was determined to have excellent resistance to aging [14-16, 25, 56].

To create the TiO$_2$/RTV-1 composite sample, the fabricated TiO$_2$ composite consisted of 3% TiO2 nanoparticles approximately ~40 um in size, and 97% PDMS polymer material. Standing salt water may also provide the potential for surface aging due to the presence of chlorine or hypochlorous acid due to the electrified environment.

The hypochlorous acid used in this experiment contained electrolyzed water with 500ppm free chlorine for a total concentration of 0.046% HOCl. This particular acid concentration was the strongest available on the market. In comparison, the 3% NaCl salt solution used in [16] had 30 times more chloride ions than the HOCl solution. It should
also be noted that the 3% electrolyzed salt solution was found to be much more damaging to the neat RTV-1 at RT than the same un-energized solution at 80°C [14].

6.2.1 Test setup

Aged composite samples were evaluated for hydrophobicity measured by water droplet contact angle and water droplet sliding angle, as well as changes in hardness and material variations, which were assessed using SEM cross-sectional analysis. Changes in hardness were recorded during the aging tests on the composite samples using a standard Shore A durometer [15, 16]. Hydrophobicity was evaluated by changes in the contact angle of a single water droplet on dried aged sample surfaces. The tests were performed on dry aged samples in order to discount temporary absorption or swelling of the sample due to the immersion solution.

6.2.2 HOCl aging results

SEM images of unmodified RTV-1 and TiO₂/RTV-1 are shown in Figures 33 and 35, respectively. SEM images of the aged, unmodified RTV-1 sample [Figure 34], showed significantly more damage in HOCl at RT compared with the TiO₂/RTV-1 sample [Figure 36], strongly indicating much higher resistance of the composite TiO₂/RTV-1 to extreme aging. The damage to the unmodified RTV-1 in HOCl was strongly associated with numerous cavities, which appeared to be randomly distributed across the thickness of the unmodified samples [Figure 34]. For the composite
TiO₂/RTV, cavities were mostly localized close to the surface and their prevalence was much lower [Figure 36] than in the unmodified RTV [Figure 34] [56].

Figure 33. SEM cross section of virgin unmodified RTV-1 [56]
Figure 34. SEM cross section of RTV-1 subjected to 0.046% HOCl for five weeks at room temperature [25, 56]
Figure 35. SEM cross section of virgin RTV-1 with 3% embedded TiO$_2$ microparticles.
Subsequent hardness tests on the aged RTV and TiO$_2$/RTV samples supported the observation that there was significantly less overall environmental damage to the TiO$_2$/RTV composite. The reduction in the hardness after five weeks of aging of the unmodified RTV-1 in HOCl at room temperature was found to be 44% vs. 20% for the TiO$_2$/RTV composite [Figure 37].
The TiO$_2$/RTV-1 composite measured a higher virgin hydrophobicity compared to unmodified RTV-1, as well as an initial lower sliding angle. Hydrophobicity measurements performed on the virgin TiO$_2$/RTV sample yielded a contact angle of 108.5°, compared to 85.6° for the virgin unmodified RTV-1 sample [Figure 38]. After aging, the contact angle for the TiO$_2$/RTV sample submerged in the acid at RT for five weeks was 82.8° [Figure 38]. The unmodified RTV sample aged five weeks in RT HOCl had a contact angle of 43.1° after aging [Figure 38]. The results of the water droplet contact angle measurements therefore indicated a greater retention of hydrophobicity in the TiO$_2$/RTV compared to unmodified RTV aged in 0.046% HOCl solution.
Figure 38. Comparison of water droplet contact angles of aged RTV-1 and TiO$_2$/RTV-1 before and after five weeks of aging in 0.046% HOCl at room temperature

The water droplet sliding angle measurements on the TiO$_2$/RTV-1 composite sample also yielded favorable results after aging in HOCl compared to the unmodified RTV-1. The sliding angles of the virgin TiO$_2$/RTV-1 composite and unmodified RTV-1 samples were measured as 29° and 44°, respectively [Figure 39]. After aging, the TiO$_2$/RTV-1 composite sample had a sliding angle of 33°, while the angle for the unmodified RTV-1 sample was 53° [Figure 39]. This also confirmed that the TiO$_2$/RTV-1 composite sample retained hydrophobicity much better compared to the unmodified silicone rubber RTV-1 material [56].
Figure 39. Comparison of water droplet sliding angles of aged RTV-1 and TiO$_2$/RTV-1 after five weeks of aging in 0.046% HOCl at room temperature

6.3 Effect of electrolyzed salt environment

To further support the claim that aqueous electrolyzed salt HV conditions, and therefore hypochlorous acid, may cause damage in service conditions, the same type of unmodified RTV-1 and TiO$_2$/RTV-1 composite samples were subjected to aging in an electrolyzed 3% NaCl (ocean concentration) solution. It should be added that a small voltage is the necessary condition for the formation of hypochlorous acid in aqueous salt, according to [32].

6.3.1 Test setup

The samples were placed in a dish containing 300ml of 3% NaCl solution and were flanked at either end by wires connecting to a 9V battery in order to produce ample current for electrolysis to occur. The electrodes were placed without a physical contact
with the samples. Wire placement relative to the sample is shown in Figure 40. The NaCl salt water across the polymer surface completed the circuit, resulting in the electrolysis of the NaCl solution. Hydrogen and chlorine gas bubbles emanating from the electrodes at the cathode and anode ends, respectively, confirmed active electrolysis. The sample was left submerged for a total of 8 hours.

![Figure 40. Virgin RTV-1 sample before aging, with markings showing position of the electrodes](image)

6.3.2 Electrolyzed salt experimental analysis

After drying the samples were placed under a heat lamp for 48 hours, and a cross section of the unmodified RTV-1 was observed under an optical microscope. As per the hypochlorous aging experiment, SEM images were taken of the sample cross-sections, and hardness measurements, and water droplet contact angles and water droplet sliding angles were also assessed. Hardness readings were again recorded using a standard Shore A durometer.
6.3.3 Electrolyzed aqueous salt aging results

After removal from the solution, approximately a 50% portion of the sample was visibly damaged with an “orange peel” surface, as seen in Figure 41. The damaged portion of the sample protruded approximately 1mm from the sample surface, and was soft to the touch. Hydrophobicity and hardness measurements were attempted on the unmodified RTV-1 sample surface, but were deemed too inconsistent to be accurately determined due to the irregularity of the surface. Hardness readings, especially, were inconsistent and inconclusive when using a durometer, as the damaged portion of the sample was too soft to accurately take a reading.

The hardness reading for the RTV-1/TiO$_2$ sample before aging was average 34 HA and 29HA after aging in electrolyzed aqueous salt, which indicates a reduction in hardness of only 14%, as shown in Figure 42. Initial hydrophobicity measurements performed on the virgin TiO$_2$/RTV-1 sample yielded a contact angle of 108.6° and 84.6° after aging, as shown in Figure 43.
Figure 41. (Left) RTV-1 sample after 8 hours of aging in electrolyzed 3% NaCl solution, (right) optical microscope image showing cross section of damaged portion of the RTV-1 sample [15]

Figure 42. Hardness readings for TiO₂/RTV-1 composite before and after aging for 8 hours in electrolyzed aqueous salt
Sliding angle measurements also yielded favorable results for TiO$_2$/RTV-1 after aging in electrolyzed aqueous salt. The initial sliding angle of TiO$_2$/RTV-1 was again determined to be 29° before aging, and 34° after aging in electrolyzed 3% aqueous NaCl salt solution for 8 hours, as shown in Figure 44. The sliding angle for the unmodified RTV-1 sample could not be determined due to complete surface wetting. This therefore confirms that the TiO$_2$/RTV-1 sample retained hydrophobicity after aging in electrolyzed aqueous NaCl salt solution, while the unmodified RTV-1 sample became completely hydrophilic. Water droplet contact and sliding angles for the unmodified RTV-1 and TiO2/RTV-1 samples are shown in Figure 43 and Figure 44.
After drying the sample under a heat lamp for 48 hours, a cross section of the damaged portion of the sample was observed under an optical microscope [Figure 42], indicating a layer of damage [Figure 42]. SEM images of the damaged portion of the sample were taken, showing extensive material damage in the form of voids and cavities [Figure 45]. The cross-section SEM image of the TiO$_2$/RTV-1 aged composite sample [Figure 46], by contrast, showed limited material damage in the form of voids and cavities compared to the aged unmodified RTV-1 sample. The voids did not propagate throughout the bulk of the 3mm thick material, compared to the unmodified RTV-1 sample, which saw damage encompassing the entire interior after five weeks, as shown in [Figure 45]. Imperfections and irregularity of the sample was determined to be due to the distribution of the TiO$_2$ particles, and not due to void formation.
6.4 Thermal Cycle Aging

A final experimental setup analyzed the response of modified and unmodified RTV-1 silicone rubbers to investigate thermal cycle (TC) aging, which is a common aging scenario for soft polymeric materials when placed in service [59]. Degradation of
silicone rubbers can commonly be achieved by temperature cycling, with resulting damage often occurring in the form of material warping, mass decrease, and changes in hardness [59]. Common thermal cycling approaches expose the polymer thermal to changes from -25°C to over 70°C. This work therefore aimed to compare the effects of temperature cycling on TiO₂/RTV-1 and unmodified RTV-1 silicone rubbers.

6.4.1 Test Setup

Unmodified RTV-1 and TiO₂/RTV-1 samples, identical in composition to those previously reviewed, were subjected to thermal cycling (TC) from -10°C (cold plate) to 80°C (aqueous water) in 24-hour cycling increments, for three weeks. Samples were assessed for changes in hardness (Shore A), water droplet contact angle, water droplet sliding angle, and changes in visual texture.

6.4.2 Thermal Cycle Aging Results

The two RTV-1 samples, unmodified RTV-1 and TiO₂/RTV-1, both exhibited changes in hardness, water droplet sliding angle, and changes in texture. Areas of localized swelling were evident [Figure 47] as well as pocketing, indicating bulk material damage.
A decrease in hardness was measured in both samples, with the unmodified RTV-1 sample decreasing from 38HA to 22HA, and the TiO$_2$/RTV-1 decreasing from 35HA to 23HA [Figure 48].

Figure 47. Visual observation of pocketing and swelling in both modified (left) and unmodified (right) RTV-1 samples

Figure 48. Changes in HA hardness of unmodified RTV-1 and TiO$_2$/RTV-1 before and after thermal cycle aging
No discernable changes in water droplet contact angle were recorded, however changes in water droplet sliding angle were observed, as shown in Figure 49. Sliding angles increased for both samples, however a greater increase was recorded for the unmodified RTV-1 compared to the TiO$_2$/RTV-1. An increase of 44.8% was record for the TiO$_2$/RTV-1, from 29HA to 42HA, while an increase of 48.5% was recorded for the unmodified RTV-1, from 33HA to 49HA. The TiO$_2$/RTV-1, therefore, showed a slight resistance to thermal cycle aging compared to the unmodified RTV-1 sample.

![Figure 49. Water droplet sliding angles of unmodified RTV-1 and TiO$_2$/RTV-1 before and after thermal cycle aging](image)
6.5 Preliminary concluding remarks from aging tests of HV silicone rubbers

Based on all experimental results, especially those from the silicone rubber aging in aqueous electrolyzed salt, it was concluded that the TiO$_2$/RTV-1 composite was more resistant to aging when exposed to extreme environments than RTV-1. The TiO$_2$/RTV-1 composite exhibited a higher initial hydrophobicity and lower sliding angle, indicating an initial lower surface energy, and larger water droplet contact angle, which was retained even after aging in hypochlorous acid and electrolyzed aqueous salt solution. While overall sample damage appears to be more extensive in the electrolyzed 3% NaCl salt sample, this may be due to the higher concentration of oxidizing products, such as OH$^-$ and H$^2$. The electrolyzed salt also contained more chlorine, which may have produced more potential for HOCl, compared to the commercially produced HOCl concentration of 0.046%.

Although the majority of the damage was found at the cathode end in the electrolyzed salt experiment, voids and cavities were found throughout the sample. This indicated that the damage is not localized and thus not dependent upon the proximity of the energized wires. Regardless of the more aggressive aging environment of the electrolyzed aging solution, the TiO$_2$/RTV-1 composite performed better compared to the unmodified RTV-1 material.

The thermal cycling results showed that the addition of titanium dioxide offers a partial benefit against thermal cycling, but did not completely protect the material from localized swelling and damage. A decrease in hardness and hydrophobicity was measured
in both samples, however the TiO$_2$/RTV-1 composite still performed better, as the TiO$_2$/RTV-1 material retained its hydrophobicity, although physical surface damage did occur. More investigation is still needed to determine if localized swelling in the composite was due to the addition of titanium dioxide particles, or if the defects were caused by the additional mixing required to disperse the TiO$_2$ particles in the material, thus allowing for air entrapment.
Chapter Seven: Extension of PDMS Insulator Aging Research to PDMS Icephobic Barriers

PDMS materials are commonly used in HV applications in NCIs. They have also recently been investigated as materials for icephobic applications [60-70]. Using the experimental and numerical approached developed in Chapters 5 and 6 to assess silicone rubbers for HV applications, a major attempt was subsequently made to 1) understand what role of silicone rubbers can play as icephobic barriers in HV and other applications and 2) how their in-service aging could affect their icephobic properties. Therefore, significant research efforts were also made to improve the understanding of ice adhesion, and ice accumulation, and testing involving PDMS rubbers with and without titanium dioxide particles. While icephobic materials have been classified as those that have low ice adhesion strength, there remains some debate as to the cutoff adhesion strength distinguishing icephobic materials. Current research supports the observation that those materials with an ice adhesion strength of <150 kPa can be classified as icephobic [62].

Because the addition of titanium dioxide was previously found to improve hydrophobicity of NCI silicone rubber materials compared to unmodified RTV-1 [Chapter 6], its potential as an icephobic material was investigated. However, in this
study, to assess a titanium dioxide/silicone rubber as an icephobic material, several ice adhesion and ice accumulation experiments were conducted, instead of assessing the material from a purely hydrophobic standpoint, the way it was done in Chapters 5 and 6 in conjunction with HV NCIs. These experiments were supported with multiple 3D ice accumulation models and molecular dynamics simulations, which were devised to better understand the interfacial interactions of ice crystals on various surfaces when frozen, as well as before, during, and after ice crystal melting.

While it might appear that the previous research on the aging of NCIs and the following section on PDMS icephobic barriers are not strictly related, it is actually on the contrary; these are two extreme HV applications, utilizing similar PDMS based materials, testing and modeling approaches, and potential in-service environments. To keep the readers better informed, the icephobic research was presented slightly differently in comparison with previous sections on the NCIs, with the background information, research results, and conclusions more closely intertwined.

7.1 Ice adhesion and testing

The accumulation of ice on a surface often necessitates ice removal to avoid material or structural failure. Low ice adhesion of a material is therefore a desired property, as surfaces with excellent deicing properties allow for easy ice removal due to their low ice adhesion strength [63-73]. While there is currently no definitive correlation between superhydrophobicity and low ice adhesion strengths, high surface energy
materials, such as metals, have some of the highest adhesion strengths recorded [66-72]. Ice adhesion strength designates the amount of shear stress necessary to remove ice from a material or surface [66-72]. A general list of materials and their respective ice adhesion strengths and testing methods can be found in Table 5. The table also lists the current ice adhesion results from the DU group, using a removable PDMS mold.

Table 5. An overview of typical materials and their corresponding ice adhesion strengths

<table>
<thead>
<tr>
<th>Material</th>
<th>Average Ice Adhesion Strength [kPa]</th>
<th>Report</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper - 50 μL water droplets placed on the test surface by a syringe</td>
<td>1217 ± 34</td>
<td>Ozbay et al. [65]</td>
</tr>
<tr>
<td>Polished Copper - 2.4 ± 0.15 mm thick borosilicate glass tube mold</td>
<td>625 ± 41</td>
<td>Ling et al. [66]</td>
</tr>
<tr>
<td>Stainless steel 316 - 2.4 ± 0.15 mm thick borosilicate glass tube mold</td>
<td>682 ± 46</td>
<td>Ling et al. [66]</td>
</tr>
<tr>
<td>Aluminum - 50 μL water droplets placed on the test surface by a syringe</td>
<td>731 ± 53</td>
<td>Ozbay et al. [65]</td>
</tr>
<tr>
<td>Polished aluminum - centrifuge adhesion</td>
<td>250 ± 50</td>
<td>Jafari et al. [67]</td>
</tr>
<tr>
<td>Glass – upside-down Teflon mold</td>
<td>820 ± 96</td>
<td>Fu et al. [71]</td>
</tr>
<tr>
<td>PTFE - 50 μL water droplets placed on the test surface by a syringe</td>
<td>268 ± 13</td>
<td>Ozbay et al. [65]</td>
</tr>
<tr>
<td>RF-sputtered PTFE coating on polished aluminum - centrifuge adhesion test</td>
<td>110 ± 22</td>
<td>Jafari et al. [67]</td>
</tr>
<tr>
<td>RF-sputtered PTFE coating on anodized surface - centrifuge adhesion test method</td>
<td>72 ± 12</td>
<td>Jafari et al. [67]</td>
</tr>
<tr>
<td>RTV silicone rubber coating –customized zero-degree cone test method</td>
<td>24.8 ± 8</td>
<td>Bharathidasan et al. [72]</td>
</tr>
<tr>
<td>RTV coating with fumed silica particles - customized zero-degree cone test method</td>
<td>243 ± 20</td>
<td>Bharathidasan et al. [72]</td>
</tr>
<tr>
<td>Slippery, liquid-infused porous surfaces (SLIPS) - Cylindrical glass column mold made from Pasteur pipette</td>
<td>15.6 ± 3.6</td>
<td>Kim et al. [64]</td>
</tr>
</tbody>
</table>
Dragon skin 20 (RTV silicone rubber) - PDMS removable mold

<table>
<thead>
<tr>
<th>thickness dependent</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.06 ± 4.2</td>
</tr>
</tbody>
</table>

University of Denver
Woll, Middleton, Bleszynski

To complicate matters, testing of ice adhesion strength is not straightforward or consistent. To encase the water during freezing, many previous studies have utilized glass or plastic cuvette molds before measuring ice adhesion [65-672]. The cuvette method includes filling a cuvette with water, placing the specimen flush with the water filled cuvette, and then freezing the system. The entire system is then inverted before testing [62, 72].

For this study, ice adhesion was tested using a removable low surface energy PDMS mold designed specifically for this study, which produced an ice cube with an area of 6.3 cm$^2$. Because the ice did not adhere to the PDMS mold when the ice was fully formed, the PDMS mold could be removed and shear force applied directly to the ice block. The low surface energy silicone mold was chosen because ice formation and crystallization is greatly dependent on surrounding conditions such as temperature and atmospheric moisture [74-76]. While liquid water molecules continuously break and reform hydrogen bonds in a mostly disorganized fashion, the water molecules in ice are fixed in three-dimensional patterns. Ice crystals form a large variety of shapes such as: plates, dendrites, or columns, but typically grow in a hexagonal arrangement of water molecules [74-76]. A change in heat or material interface can lead to crystallization
instability, which can result in the solidification process becoming dendritic. Only in a container-less experiment, where liquid water is isolated from interfaces, does homogeneous nucleation occur [74-76]. More commonly, ice solidification occurs due to heterogeneous nucleation, where impurities are present in the water and interfacial container surface, such as a mold, can affect crystallization. This study does not address the many different mechanisms, which affect ice nucleation, some of which are still poorly understood. For simplicity, factors that affect ice nucleation were excluded or limited in this study, and silicone rubber was chosen as an ideal mold material due to its limited effect on ice crystalline structure. The material was also easily removable, limiting any mold effect.

The silicone rubber mold was fabricated using a common household all-purpose silicone rubber, using a square polycarbonate template. The PDMS mold and the morphology of the resulting uniform ice cube are shown in Figure 50.

**Figure 50.** Removable silicone rubber mold (*left*) and corresponding ice structure (*right*)
7.2 Testing of PDMS surfaces for ice adhesion strength

The tested silicone rubber material substrates used in this study were created using a base polydimethylsiloxane (PDMS) polymer RTV-2 material commercially available and known as “Dragon Skin™”. This particular platinum cured silicone rubber is highly flexible, with a base material hardness of 20A (Shore A) and material density of 1.07 g/cc. Compared to the previously investigated RTV-1, this RTV-2 is ~50% softer, contains no pigments, and has a lower density. The curing process and microparticle mixture were identical to those discussed in Chapter 6. Two 0.5mm thick RTV-2 surfaces were tested for ice adhesion, with and without titanium dioxide particles. The tested sample surfaces are listed in Table 6 below.

<table>
<thead>
<tr>
<th>Surface</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>3% 40µm TiO₂ + 97% DragonSkin™</td>
<td>DragonSkin™ (100%)</td>
</tr>
</tbody>
</table>

The microparticles used in the study were identical to the previously cited titanium dioxide, which were ~40 um in size. All surfaces were created by first mixing equal parts 1A:1B of the DragonSkin™ silicone rubber by volume. For surfaces 2, TiO₂ microparticles approximately ~40 um in size were added to the mixture and stirred by hand until evenly distributed. The resulting composite consisted of 3% TiO₂ microparticles and 97% RTV-2 polymer material. The proportions were almost identical
to the previously tested composite, which was reported in Chapter 6. The uncured mixture was evenly distributed on a standard glass slide using an Ossila spin coater set at 500 RPM for 60 seconds, before being allowed to cure for 24 hours.

Before ice adhesion and ice accumulation tests were conducted, an initial assessment of the water droplet sliding angle was determined, as shown in Table 7. The sliding angle of the TiO$_2$/RTV-2 surface was recorded as 27˚, which was lower than the sliding angle of the pure RTV-2 surface (33˚). This indicated that the RTV-2 composite exhibited better hydrophobicity, which was consistent with previously conducted experimental analysis on TiO$_2$/RTV-1 composites [Chapter 6]. The sliding angles of the virgin TiO$_2$/RTV-1 composite and unmodified RTV-1 samples were 29˚ and 44˚, respectively [Figure 39]. In comparison, the sliding angles of the virgin TiO$_2$/RTV-2 composite and unmodified RTV-2 were 27˚ and 33˚, respectively. Therefore, compared to the previously investigated RTV-1, the sliding angle of this RTV-2 was lower, indicating the DragonSkin material is overall more hydrophobic.

<table>
<thead>
<tr>
<th>Surface</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>3% TiO$_2$/RTV-2 composite</td>
<td>(100%) RTV-2</td>
</tr>
<tr>
<td>Sliding angle</td>
<td>27˚</td>
<td>33˚</td>
</tr>
</tbody>
</table>
7.2.1 Ice adhesion test setup

Following curing, the material samples were transferred and clasped to a cold plate, which was set to -10°C using a TE Technology, Inc. TC-48-20 Thermoelectric Temperature Controller. The flexible cubic silicone mold, approximately 2.5cm x 2.5cm x 5cm in size, was placed on the testing surface and filled with water. The water was allowed to freeze for a minimum of two hours before the mold was removed, leaving only a 2.5cm x 2.5cm cubic ice block on the test surface. To prevent sliding of the ice block or the surface, the silicone rubber and glass slide were held in place by two metal plates. An insulation box was placed over the cold plate, and the system was allowed to freeze for a minimum of 2 hours before the test was run. The entire experimental setup is shown in Figure 51.

The ice adhesion test fixture was similar to the one designed by Ling et al [66]. A Peltier cold plate made by TE Technology, Inc. was used to freeze the water, and a Series 5 Mark-10 250 N (sensitivity of ± 0.01 N) force sensor mounted to a Newmark Systems, Inc. linear stage, which was used to push the ice block and measure the shear force. To generate the ice adhesion shear force, a digital force gauge (Series 5 Mark-10) was mounted on a computer controlled Newmark Systems, Inc. linear stage. The tip of the push rod was coated in silicone rubber to prevent any heat transfer. Force was applied to the ice block until the ice no longer adhered to the material surface. The linear stage was set to 1.5 mm/min and the data was captured at 500 Hz. The ice adhesion shear strength $\tau$
was then calculated as the applied shear force $F_s$, over the cross-sectional area $A$ (eq. 19) [66].

\[
\frac{F_s}{A} = \tau \quad \text{(eq. 19)}
\]

**Figure 51.** Experimental setup showing a) ice block, b) surface under test, c) silicone covered push rod, and d) cold plate.
7.2.2 Ice adhesion results

A total of five tests per material were conducted and averaged. The recorded ice adhesion strengths for the 100% RTV-2 and TiO$_2$/RTV-2 composite materials were very different, as shown in Figure 52. The highest ice adhesion strength was the 100% DragonSkin™ RTV-2 material, with an average adhesion strength of 24.06kPa +/- 4.2. The TiO$_2$/RTV-2 composite material has the lowest ice adhesion strength, with an average of 5.0kPa +/- 2.3. It was found that the test results were significantly dependent on the thickness of the RTV-2 substrates, with thin substrates yielding higher strength than the thicker substrates [27, 76].

![Figure 52. Ice adhesion strength of unmodified and modified RTV-2 materials without correction factors for 0.51mm substrate thickness](image)

After correction for the effect of substrate thickness, a correction factor was conducted [27, 76]. The actual substrate adhesion strength of the 100% RTV-2 was 35 ± 4.2, while the TiO$_2$/RTV-2 was 7.2±2.2. Even after the corrections, the ice adhesion
results showed that titanium dioxide particles have a very favorable effect on icephobicity by lowering the average ice adhesion strength of regular RTV-2 by 79.1%. However, to determine if these very promising ice adhesion results would correlate to real world scenarios, such as ice buildup due to an ice storm, several ice accumulations tests were subsequently conducted.

7.3 Ice accumulation

Before assessing the PDMS substrates for ice accumulation, ice accretion itself has to be examined, as correlating low ice adhesion strength to a reduction in ice buildup in the real world is more difficult. In real circumstances, ice accumulation doesn’t occur in the form of a single stationary cube frozen over the course of several hours, as in the experimental setup. Instead, ice accumulation often occurs during cold weather storms where snow or freezing rain gradually accumulated onto a surface and freeze, often in unpredictable patterns and circumstances [60, 61, 77, 78]. Because freezing rain, defined as rain which ices shortly after impacting a surface at or below freezing temperature [61], is most often associated with icing, it is examined here in more detail.

Ice accumulation seldom coats everything with an equal ice thickness, and rarely happens instantaneously due to super cooled rain [60, 61]. These misconceptions can often misdirect studies of ice accumulation. Rather, ice accumulation depends on individual surfaces and objects, and their respective temperatures, affecting how rain or snow will melt and/or freeze. Elevated structures, such as bridges, tree limbs, and HV conductors and power lines, have the greatest chance of icing due to their corresponding
lower temperatures [60, 61, 77]. A structure or material with a higher specific heat, such as an asphalt driveway, will likely ice over more slowly, even when all other conditions are identical or the ground temperature is above freezing [60, 61, 77]. However, if the ambient temperature is below freezing, as well as all materials and structures, then almost all surfaces and structures will build up ice equally quickly [60, 61, 77].

Additionally, the freezing of water droplets after they impact a surface is not immediate. Rather, it is delayed even if the water droplet is super-cooled. The time it takes for the water droplet to freeze is dependent on several factors, including the temperature of the water droplet, its size, and the temperature of the surface on which it impacts [60, 61, 77]. Freezing rain may therefore coat and adhere to surfaces due to the viscous nature of water, and spread over a surface, unlike snow. All these factors considered, the conditions in which freezing rain will cause the droplets to freeze the fastest would be: small water droplet size, low temperature of the water droplets, and sub-freezing temperature of the surface upon which the water droplet impacts [60, 61, 77]. By contrast, large, warmer water droplets, which impact surfaces at 0°C, will freeze slower [60, 61, 77]. The faster heat transfer out of smaller water droplet over time can be calculated mathematically, according to the equation for specific heat energy, $Q$:

$$Q = mC\Delta T$$  \hspace{1cm} (eq. 20)
where $m$ is the mass of the water droplet, $C$ is the overall specific heat transfer coefficient, and $\Delta T$ is the change in temperature [72-73]. For a spherical water droplet, whose density changes with temperature, the mass of the droplet could be calculated by:

$$m = \frac{4}{3} \pi r^3 \rho_w \quad (\text{eq. 21})$$

where $\rho_w$ is the density of the water droplet and $r$ is the water droplet radius [60, 61, 77, 78]. However, because the water droplet rests on a surface, creating the shape of a spherical cap [Figure 53], the calculation of water droplet volume $V$, has to first be performed (eq. 22):

$$V = \frac{\pi D^3}{24} \left( \frac{2 - 3 \cos \theta + \cos^3 \theta}{\sin^3 \theta} \right) \quad (\text{eq. 22})$$

**Figure 53.** Model of water droplet showing spherical cap shape
where $D$ is the diameter of the water droplet, and $\theta$ constitutes the water droplet contact angle [77, 78]. From the volume, calculating the mass of the water droplet is straightforward, by modifying the density equation (eq. 23):

$$m = \rho * V \quad (\text{eq. 23})$$

To solve for the time that is required for the heat transfer out of the water droplet, the differential equation can be derived (eq. 24) [77, 78]:

$$\frac{dQ}{dt} = mC \frac{dT}{dt} \quad (\text{eq. 24})$$

where $\frac{dQ}{dt}$ is the energy transfer rate out of the water droplet. The rate of energy transfer, $P$, can be substituted in through the following equation (eq. 25) [77, 78]:

$$P = \frac{Q}{\Delta T} \quad (\text{eq. 25})$$

rearrangement of the overall equation now gives (eq. 26):

$$dt = \frac{mc}{p} dT \quad (\text{eq. 26})$$

integrating the final equation (eq. 27):

$$\int_{t_1}^{t_2} dt = \frac{mc}{p} \int_{T_1}^{T_2} dt \quad (\text{eq. 27})$$
gives (eq. 28):

$$(t_2 - t_1) = \frac{mc}{p}(T_2 - T_1) \quad (\text{eq. 28})$$

which finally gives (eq. 29):

$$\Delta t = \frac{mc}{p} (\Delta T) \quad (\text{eq. 29})$$

The larger surface area as well as the lower mass of the water droplets allows for both evaporation and rapid loss of heat. For example, a water droplet with a mass of 0.1g will freeze approximately 600% faster than a water droplet with mass of 1g, if all other conditions are equal. Therefore, smaller water droplets, with their larger surface area ratio and smaller mass, will freeze faster, reducing the chance that they will roll or slide off a surface. Ice accumulation therefore becomes almost inevitable, as small water droplets will stick and freeze quickly. Even if a warm water droplet were to strike a frozen surface and slightly warm the surface, the size of the droplet will still determine how long it will take to freeze [77, 78]. Additionally, smaller droplets are easily frozen by cold air. Therefore, the most extreme and dangerous conditions for ice accumulation are: abundant precipitation of small, almost mist size, cold water droplets striking a surface that has a temperature at or below freezing.

### 7.4 Simulated moisture accumulation models

Before experiments were conducted, rain, snow, and freezing rain and their roles in ice buildup were illustrated through several computational fluid dynamics models on
simulated surfaces. Simulations were conducted in Blender, a 3D physics based, object oriented animation software, to assess the way rain, snow, and freezing rain fall on different surfaces. The simulated rain, snow, and freezing rain particles impacting the surfaces were constructed using Blender’s particle system, which is calculated using the Smoothed-particle hydrodynamics (SPH) computation process using a mesh-free Lagrangian method. SPH is advantageous, because it does not use a fixed grid, allowing particles to move unconstrained in space, and are subjected only to their fluid properties [77, 79].

The equations for the forcefield used in the Blender software are governed by the Lennard-Jones equation, where \( V_{LJ} \) denotes the Lennard-Jones potential between the particles, which is used to approximate the behavior of particles at a short range [77, 79]:

\[
V_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] = \varepsilon \left[ \left( \frac{r_m}{r} \right)^{12} - 2 \left( \frac{r_m}{r} \right)^{6} \right] \quad (eq. 30)
\]

where \( \sigma \) is the distance where the inter-particle potential is zero, \( \varepsilon \) is the well depth potential, \( r \) is the distance between particles, and \( r_m \) is the distance at which the potential reaches its minimum. The numerical basis for SPH is based on integral interpolants [77, 79], for any function \( A(r) \):

\[
A(r) = \int_{\Omega} A(r') W(A(r - r', h)) dr' \quad (eq. 31)
\]
where \( W \) is the interpolating or smoothing kernel with a radius of \( h \), \( \Omega \) is the volume which contains \( r \), and the integration is calculated over the entire space of the simulation [77, 79]. The approximation is:

\[
A(r) = \sum_{j=1}^{N} A(r_j) W(r - r_j, h) \frac{m_j}{\rho_j} \quad (eq. 32)
\]

The properties of the particles were modified for each particle type, such as rain or snow. This was conducted using the Lagrangian method, which assumes each particle has a specific, momentum, velocity, and viscosity. The governing equations for the particles, such as moment, density, etc., are given by equations 33-35.

The momentum equation is given by [79, 80]:

\[
\frac{dv}{dt} = -\frac{1}{\rho} \nabla P + \frac{\mu}{\rho} \nabla^2 v + f \quad (eq. 33)
\]

where \( \mu \) represents the dynamic viscosity and \( f \) represents external forces (such as gravity), \( \rho \) represents the density of the fluid and \( v \) represents the velocity, and momentum, \( P \) [77, 79].

The density is given by:

\[
\rho \ (r) = \sum_b m_b W(r - r_b, h) \quad (eq. 34)
\]

and SPH formulation for the viscosity can be approximated by [77, 79]:

\[
\frac{\mu}{\rho_i} \nabla^2 v_i = \frac{\mu}{\rho_i} \sum_j (v_j - v_i) \frac{m_j}{\rho_j} \nabla^2 W(r_i - r_j, h) \quad (eq. 35)
\]

where \( i \) is denoted as the velocity component and \( j \) the spatial component.
Because cold water is thicker and stickier, freezing rain was modeled as more dense and with greater adhesion forces, compared to warmer rain particles. The simulated rain, snow, and freezing rain models were constructed with 10,000 emitted particles falling on their respective surfaces for approximately 2:00 minutes. The surfaces were: a PDMS polymer like material and cylindrical aluminum like material, to mimic the experimental PDMS samples and HV aluminum conductor. The properties of the materials were modeled to reflect the smaller surface energy of PDMS, and therefore smaller relative adhesion forces. Aluminum, which has a higher surface energy, was modeled with higher adhesion forces of the water droplets. The PDMS like polymer surfaces were tilted at a 45° angle to allow for easy observation of particle movement.

7.4.1 Simulated moisture accumulation model results

The simulated Blender models for the PDMS like polymer surfaces are shown in Figures 54 a-c, displaying the simulations at the 1:50 min mark. The differences in the amount of surface accumulations are relatively discernable, with simulated rain falling off the simulated PDMS like polymer surface almost immediately. Comparatively, the simulated snow and freezing rain remained on the surface, with the snow building up vertically over time. The simulated freezing rain, however, held together in a discernable mass, spreading out over the surface.
Figure 54 a-c. Simulated rain, snow, and freezing rain on accumulation on simulated polymer surfaces

The Blender models for the aluminum like cylindrical (conductor) surfaces are shown in Figures 55 a-c, with the simulations again shown at the 1:50 min mark. The differences in surface accumulations were again discernable, with the simulated rain falling off the aluminum surface almost immediately. The simulated snow and freezing rain also remained on the surface, with the snow building up vertically [Figure 55 b], while the freezing rain enveloped the cylinder completely [Figure 55 c].

Figure 55 a-c. Simulated rain, snow, and freezing rain accumulations on Al conductors
7.5 Ice accumulation in freezing rain conditions

Following the 3D simulations of rain, snow, and freezing rain accumulations and experimental ice adhesion testing, a series of ice accumulation experiments were conducted to examine ice buildup over time. The first experiment assessed natural ice buildup, as a function of mass, during freezing rain conditions in Denver, Colorado in November, 2017. The aim of this study was to correlate the laboratory testing of ice adhesion with real world scenarios, such as ice buildup during an ice storm. The tested surfaces included the previously tested RTV-2 surfaces, with and without TiO$_2$, as well as two additional surfaces, glass and aluminum, for comparison. The PDMS sample surfaces were identical to those tested for ice adhesion. All tested surfaces are listed in Table 8.

Table 8. Surfaces tested in freezing rain conditions in Denver, CO

<table>
<thead>
<tr>
<th>Surface</th>
<th>Aluminum</th>
<th>Glass</th>
<th>3% TiO$_2$/RTV-2</th>
<th>(100%) RTV-2</th>
</tr>
</thead>
</table>
| Outdoor ice accumulation setup

The four surfaces were mounted at a 45° angle and left outside in freezing rain conditions for 4 hours. The official weather report indicated ice accumulation of less than 0.5”. The weather conditions during the course of the experiment are listed in Table 9. The outdoor test setup is shown in Figure 56.
Table 9. Weather conditions during experimental setup.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp</td>
<td>-1.1°C</td>
</tr>
<tr>
<td>Humidity</td>
<td>88%</td>
</tr>
<tr>
<td>Wind</td>
<td>14.5 km/h</td>
</tr>
<tr>
<td>Pressure</td>
<td>1024.72 mbar</td>
</tr>
</tbody>
</table>

Figure 56. Outdoor sample setup during freezing rain conditions in Denver, CO

Because the temperature of the surfaces affects the rate of ice accumulation, the samples were put outside several hours earlier, before the ice storm began, to lower their overall temperatures. Samples were weighed before and after the course of the experiment, but were otherwise left undisturbed so natural ice accumulation could occur.
7.5.2 Outdoor ice accumulation results

Figure 57 shows the sample weights before and after ice accumulation. There was a noticeable difference in the amount of ice buildup among the different surfaces. Unsurprisingly, the aluminum and glass accumulated almost twice as much ice as the PDMS samples: 1.0g and 1.6 g respectively. Comparably to the ice adhesion experiment, the TiO$_2$/RTV-2 surface performed better, accumulating approximately 28% less ice than the unmodified RTV-2. The final ice accumulations, by mass, are shown in Table 10.

![Ice Accumulation Chart](image)

**Figure 57.** Ice accumulation (mass) of tested surfaces after four hours in freezing rain conditions in Denver, CO
Table 10. Final mass results after four hours in freezing rain conditions

<table>
<thead>
<tr>
<th>Surface</th>
<th>Aluminum</th>
<th>Glass</th>
<th>TiO$_2$/RTV-2</th>
<th>(100%) RTV-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Before</td>
<td>5.2g</td>
<td>4.6g</td>
<td>5.3g</td>
<td>5.1g</td>
</tr>
<tr>
<td>Mass After</td>
<td>6.2g</td>
<td>6.2g</td>
<td>5.9g</td>
<td>5.9g</td>
</tr>
<tr>
<td>Total</td>
<td>1.0g</td>
<td>1.6g</td>
<td>0.6g</td>
<td>0.8g</td>
</tr>
</tbody>
</table>

Although the outdoor ice accumulation experiment showed promising results, the amount of overall mass accumulation of ice was minimal, <1g, for the PDMS surfaces, as shown in Table 10. From the low overall mass accumulation, and unpredictable outdoor conditions, it followed that risk of inaccuracy was high. For example, final observation of the two PDMS surfaces indicated that a single water droplet migrated across the TiO$_2$/RTV-2 sample surface, as shown in Figure 58, which may have accounted for the lower overall ice accumulation.
Figure 58. Ice/water shedding of the two RTV surfaces after four hours in freezing rain conditions

The reason for the migration of the water droplet, whether as a function of surface conditions or an external condition such as wind, could not be immediately determined. Because the experimental conditions could not be readily repeated, it was difficult to determine if the TiO$_2$/RTV-2 was verifiably better in preventing ice accumulation than unmodified RTV-2. Therefore, to more accurately determine the resistance of the two surfaces to ice accumulation, a controlled laboratory ice accumulation experiment was subsequently designed.
Experimentally simulated freezing rain on Al conductors

To more accurately determine if PDMS surfaces were more resistant to ice accumulation, a standardized ice accumulation setup was devised. During a freezing rain storm, the standard way to assess ice accumulation on cylindrical structures such as HV conductors or tree branches as a result of freezing rain, is the equivalent radial ice thickness $R_{eq}$. This is used to assess ice as the circumference around an object at the precipitation rate $P$ (mm/h), over the course of hours $N$ [60, 61]:

$$R_{eq} = \frac{D \rho_i}{S \rho_i} \sum_{j=1}^{N} \left( \frac{P_j}{10} \right) \Delta t \quad \text{(eq. 36)}$$

where $\rho_i$ is the assumed density of the ice (0.9 g/cm$^3$), $\rho_o$ is the density of water (1 g/cm$^3$), $\Delta t$ is the time step of an hour, and $D$ and $S$ are the horizontal dimension and the perimeter, respectively, of the cylindrical cross-section [60, 61].

A simplified equation to determine the equivalent radial ice thickness $R_{eq}$ on a cylindrical cross section is given by [60, 61]:

$$R_{eq} = -\frac{d}{2} + \sqrt{\frac{d^2}{4} + \frac{m}{\pi \rho L}} \quad \text{(eq. 37)}$$

where $R_{eq}$ is the radial ice accumulation around a cylinder if uniformly distributed, $d$ is the diameter of the cylinder [Figure 59], $m$ is the mass of the ice, $L$ is the length of the element or cylinder, and $\rho$ is the ice density [60, 61]. Non-uniform thickness, whether on a cylindrical or horizontal surface, can be calculated using the measured maximum thickness of ice accretion [60, 61].
Figure 59. Cross section of ice accumulation around a cylinder, $R_{eq}$

7.6.1 Experimental ice accumulation setup

The setup was designed to simulate extreme freezing rain conditions, where ice accumulation occurs rapidly. A fine mist was sprayed onto an aluminum conductor. The small size of the water droplets was chosen deliberately, as smaller droplets of water lose heat more quickly, resulting in faster overall ice accumulation. The small size of the droplets also decreases the chance of sliding, bouncing, or rolling off the surface, therefore increasing the chance that the water would stick to the surface immediately. Therefore, the simulated freezing rain conditions were chosen as an extreme scenario, where ice accumulation is all but inevitable.

A single 9cm long aluminum conductor (ACCC) sample [Figure 60] with an uncoated radius of 28cm, was tested both uncoated [Figure 60] and coated with
TiO$_2$/RTV-2 [Figure 61b] and RTV-2 [Figure 61a] materials surfaces for ice accumulation. The same 9cm conductor sample was used for all experiments, to ensure consistency. The 3%TiO$_2$/RTV-2 and RTV-2 surfaces were identical to those previously tested, but with an increased thickness of 1mm. The conductor sample was allowed to cool to -20°C before being sprayed with approximately 740ml of fine mist four times an hour. The samples were weighed before and after ice accumulation testing, and three tests per condition were conducted.

Figure 60. Uncoated 9cm ACCC conductor sample
Figure 61 a-b. Coated ACCC conductor samples (top), 1mm of 100% RTV-2 DragonSkin™, and 1mm 3% TiO2/PDMS DragonSkin™

7.6.2 Experimental ice accumulation results

The average ice accumulation results, as a function of mass, are shown in Figure 62, and physical differences in the distribution of ice on coated and uncoated conductor samples are shown in Figures 63-65. The measured equivalent radial ice thicknesses of $R_{eq}$, for the coated and uncoated conductor samples are shown in Figure 66.
Figure 62. Average ice accumulation, by mass, on coated and uncoated ACCC conductor samples

Figure 63. Ice accumulation on uncoated 9cm ACCC conductor sample
Figure 64. Ice accumulation on 9cm ACCC conductor sample coated with unnmodified RTV-2

Figure 65. Ice accumulation on 9cm ACCC conductor sample coated with TiO₂/RTV-2
Figure 66. Average equivalent radial ice thicknesses of $R_{eq}$, for coated and uncoated conductor samples

As shown in Figure 62, the uncoated sample accumulated 56.1 grams of ice, which if the conductor were in service, equates to approximately 1.10 US tons of ice per mile. When the conductor sample was coated with RTV-2, it performed significantly better regardless if the RTV-2 contained TiO$_2$. The unmodified RTV-2 coated accumulated 30.1 grams of ice, or 0.59 tons of ice per mile – a reduction of ice accumulation by 46.36%. By comparison, the RTV-2 with imbedded TiO$_2$ accumulated 27.4g of ice, equivalent to 0.54 tons of ice per mile, and an overall reduction in ice accumulation of 51.07% over that of the uncoated conductor sample. However, when compared with the unmodified RTV-2, the TiO$_2$/RTV-2 coated conductor only reduced ice accumulation, in terms of mass, by approximately 5%. The measured average
equivalent radial ice thicknesses of $R_{eq}$, for the coated and uncoated conductor samples produced similar results, with approximately 2.20 cm $R_{eq}$ for the uncoated conductor sample, and 1.18 cm and 1.07 for the unmodified RTV-2 and TiO$_2$/RTV-2, respectively. Similarly, the difference between the $R_{eq}$ for modified and unmodified RTV-2 is only approximately 9.7%. This is in contrast to previous results, which indicated a much more significant reduction in ice adhesion [Figure 52] of imbedded TiO$_2$ RTV materials compared with unmodified RTV.

7.7 RTV-2 surface analysis

Following the ice adhesion and ice accumulation experiments, surface roughness analysis of the modified and unmodified RTV-2 surfaces was conducted to assess for any differences in surface structure. Mean roughness averages $R_a$ ($\mu$m) were assessed for the two PDMS surfaces, which is the height variations of a given surface, measured by the average arithmetic absolute values of the roughness profiles, and denoted as average roughness which is governed by (eq. 38) [80]:

$$R_a = \frac{1}{n} \sum_{i=1}^{n} |Y_i| \quad \text{(eq. 38)}$$

where $Y_i$ denotes the vertical deviations, and $n$ is the number of deviations over a specified distance over which the surface is measured [80]. A total of three scans were conducted: one of each surface (modified RTV-2 and unmodified RTV-2), and one close-up of the modified RTV-2. Surface roughness analysis was conducted using a
KEYENCE VK-X 3D laser-scanning microscope. The scanning area for both the modified and unmodified RTV-2 samples was $1.2 \times 10^6 \, \mu^2$, and the close-up (smaller area, higher resolution) scan of the TiO$_2$/RTV-2 encompassed a scanning area of approximately $4.5 \times 10^9 \, \mu^2$.

### 7.7.1 RTV-2 surface analysis results

The surface roughness profiles of the two modified and unmodified RTV-2 surfaces, showed very different results. The average $R_a (\mu m)$ of the unmodified RTV-2 was 0.036 $\mu m$, while the average $R_a (\mu m)$ of the TiO$_2$/RTV-2 was 0.04 $\mu m$; an increase of over 10%. The roughness profiles, $R_a (\mu m)$ of the two surfaces are shown in Figures 67 and 68, with the 3D scanning profiles of the two RTV surface scans shown in Figures 69 and 70, and a close-up scan of TiO$_2$/RTV-2 surface shown in Figure 71.

**Figure 67.** Surface roughness $R_a (\mu m)$ profile of unmodified RTV-2 surface
Figure 68. Surface roughness $R_a$ (μm) profile of TiO$_2$/RTV-2 surface

Figure 69. 50x scan of unmodified RTV-2 sample
Figure 70. 50x 3D surface scan of TiO$_2$/RTV-2 sample

Figure 71. Close-up 3D surface scan of TiO$_2$/RTV-2 sample
7.8 Molecular dynamics simulations of ice/surface interactions

Following the observations of the experimental ice adhesion and accumulation results, and surface profile analysis, molecular dynamics simulations were conducted to assess the ice formation on the various surfaces. The simulations were conducted using Materials Studio to construct three surfaces: a uniform, high-energy aluminum oxide surface, a regular PDMS surface, and a TiO$_2$/PDMS surface. These surfaces were chosen for their correlations to the previously conducted ice adhesion and ice accumulations experiments.

7.8.1 Molecular dynamics methods

Two sets of molecular dynamics simulations were conducted for each surface: one at a constant temperature of -10°C to observe the ice crystal/surface interaction below freezing, and a second one at temperatures between 1°C to 25°C in order to observe the ice crystal/surface interaction before, during, and after melting. The ice crystal structure used in the models was created manually using a predefined ice crystal from the Materials Studio software library. Because spontaneous ice formation in molecular dynamics is time consuming and moderately difficult to achieve, the simulated hexagonal ice crystal structures were constructed manually then placed on the respective surfaces.

The three surfaces were first constructed using surface builder, then optimized for geometry before the ice block was added using layer builder. The regular PDMS and an 8% TiO$_2$/PDMS surfaces were constructed, using methods previously described in
Chapter 4. 8% of TiO₂ particles by volume was chosen, instead of 3% as in previous simulations, to maintain a balance between the size of the ice crystal structure and the PDMS surface. The TiO₂ nanoparticles were randomly positioned close to the PDMS surface to maximize their effect on the ice crystal.

A 40Å ice crystal structure was created, and optimized for geometry, then manually placed approximately 5Å from the material surface. The first set of molecular dynamics models was conducted using the Forcite dynamics NVT ensemble, where the temperature was held constant at -10°C, and the simulations were programmed for 1000 time steps for a total time of 10 picoseconds (ps). The second set used the NVE ensemble. Temperature was increased from 1°C to 25°C, and the simulations were programmed for 10000 time steps for a total time of 100 picoseconds (ps). Simulations were evaluated for hydrogen bonding before and after molecular dynamics, to observe for any change in hydrogen bonding between the ice crystal and the surface.

7.8.2 Molecular dynamics results

Notable differences between the simulated ice/surface interactions were evident after 100ps. The results for the uniform, high-energy aluminum oxide [Figure 72 a-d] surface showed a highly irregular hexagonal crystal structure after 30ps at a constant temperature of -10°C [Figure 72b]. Hydrogen bonds were scattered, and the irregular hexagonal structure created 11 hydrogen bonds (shown in blue) with the aluminum oxide surface [Figure 72b.]
The melting simulations resulted in an immediate dispersion and collapse of the crystal structure, with 419 hydrogen bonds forming immediately across the aluminum oxide surface [Figure 72c]. The dispersion of the water molecules continued until the structure formed the final water droplet, seen in [Figure 72d].

Figure 72 a-d. a) Initial ice crystal configuration before dynamics modeling b) configuration after molecular dynamics run for 30ps at T= -10°C, c) configuration after 10ps at T= 1°C, d) final configuration after 100ps at T= 0°C to 25°C. Hydrogen bonds are shown in blue.

The molecular dynamics results for the regular PDMS [Figure 73 a-d] surface showed a more uniform hexagonal crystal structure after 30ps at a constant temperature -10°C [Figure 73b] compared to the aluminum oxide surface [Figure 73b]. Hydrogen
bonds were less scattered, and the hexagonal ice structure created 3 hydrogen bonds (shown in blue) with the simulated PDMS surface [Figure 73b].

The second dynamics simulation for the regular PDMS surface showed some retention of the ice crystal structure, with 6 hydrogen bonds forming between the water droplet and the regular PDMS surface [Figure 73c]. The ice crystal structure did not disperse across the surface as in the aluminum oxide simulation [Figure 73c]. Hydrogen bonding instead continued within the water/ice structure until it formed the final water droplet, seen in [Figure 73d]. This water droplet had little to no dispersion compared to the aluminum oxide simulation [Figure 73d].
The final simulation of an ice crystal on a TiO$_2$/PDMS surface [Figure 74 a-d], was similar to the unmodified PDMS surface, with the same number of hydrogen bonds formed between the ice crystal and TiO$_2$/PDMS surface after dynamics. However, the results for the TiO$_2$/PDMS surface showed a more uniform hexagonal crystal structure, compared to the regular PDMS surface [Figure 74b] after 30ps at a constant temperature -10°C. Hydrogen bonds were less scattered, and hexagonal ice structure created 3 hydrogen bonds (shown in blue), an identical amount to the regular PDMS surface [Figure 73b].
The simulated melting of ice on the TiO$_2$/PDMS surface formed only 4 hydrogen bonds between the water droplet and the surface [Figure 73c], 2 fewer than the regular PDMS surface. The ice crystal structure also did not disperse across the surface, and hydrogen bonding instead continued within the water/ice structure until it formed the final water droplet, as shown in Figure 73d.

**Figure 74 a-d.** a) Initial ice crystal configuration on TiO$_2$/PDMS surface before dynamics modeling b) configuration after molecular dynamics run for 30ps at T= -10° C, c) configuration after 10ps at T= 1° C to 25° C, d) final configuration after 100ps at T= 0° C to 25° C
7.9 Concluding remarks regarding application of PDMS icephobic materials

Following the results of the ice adhesion and ice accumulation experiments, it was observed that ice accumulation and ice adhesion are not directly correlated. Therefore, a surface, which exhibits low ice adhesion strength, may not necessarily prevent ice accumulation. This was especially pronounced with the 3% TiO$_2$/RTV-2 sample, which exhibited very low ice adhesion strength (~5 kPa), but only performed slightly better compared to the unmodified RTV-2 in the ice accumulation experiment (~5% difference). While the slightly improved performance of the TiO$_2$/RTV-2 sample may not be as substantial as in the aging experiments [Chapter 6], the decrease in adhesion strength of the TiO$_2$/RTV-2 composite could due to the increased surface roughness and hydrophobicity of the composite material, resulting in the lotus effect.

As with the aging experiments, the ice crystal molecular dynamics models provide partial explanations for the observations seen in the experimental results. It was apparent that the ice structure, morphology, and melting patterns changed when the ice was in contact with different surfaces. Specifically, the number of potential hydrogen bonds was significantly higher when the ice crystal was in contact with the high surface energy aluminum oxide surface, compared to the low surface energy PDMS surfaces. However, the differences in potential bond formation were only marginally different between the unmodified PDMS surface and the TiO$_2$/PDMS surface, and only for the ice crystal itself. The melting of the ice crystal provided somewhat inconclusive results, as both the unmodified and the TiO$_2$/PDMS surfaces had low potential hydrogen bonding.
during ice crystal melting, with only 2 and 4 potential hydrogen bonds formed respectively. While the final water droplet on the TiO<sub>2</sub>/PDMS surfaces exhibited a much higher contact angle compared to the unmodified PDMS surface, the difference between the number of potential hydrogen bonds formed was too small to accurately determine if the difference was measureable and relatable to the results seen in the ice adhesion and ice accumulation experiments.
Chapter Eight: Discussion

In service damage of PDMS silicone rubber materials can be multifold, as very complex aging mechanisms can exist in modern transmission systems, making them difficult to determine. Designing silicone rubbers to resist extreme environmental conditions, such as in-service aging, ice accumulation, surface erosion, etc. is complex, difficult, and not always straightforward. Nevertheless, several important observations were made: titanium dioxide particles embedded in silicone rubber materials can significantly improve PDMS materials’ resistance to aging in highly oxidizing environments as well as their resistance to ice adhesion and accumulation. These conditions can occur individually or in combination on HV transmission lines.

It has been previously speculated that the interactions of titanium dioxide with polar and nonpolar species may result in different properties in polymer systems, specifically that orientation of compounds on a titanium dioxide surface may change depending on their polarity [33]. Linear compounds, containing both polar and non-polar ends, may orient perpendicular to the surface, with the polar species orienting preferentially towards the titanium dioxide surface. Non-polar species may lie flat on the surface, and species with multiple polar sites may orient parallel to the titanium dioxide
surface [33]. This may affect how low molecular weight species behave in the bulk silicone rubber. Low molecular weight species may therefore reorient on the surface of titanium dioxide, depending on their structure, instead of diffusing preferentially towards the surface.

In this study, it was demonstrated through experimental and numerical approaches that previously established aging models of NCIs in coastal environments [24], which were based solely upon chlorine, may not account for all damage seen in service. Instead, a model based upon electrolyzed salt and the formation of HOCl in service was suggested and experimentally verified as a potential cause of oxidative NCI aging in service in coastal environments. It was also shown that this type of damage could be mitigated through the addition of 3% by weight of rutile titanium dioxide particles, which beneficially modifies the molecular geometry of PDMS chains.

8.1 Prevention of PDMS aging under extreme conditions using titanium dioxide particles

The molecular dynamics simulations of the six surfaces listed in Chapter 5 showed that the addition of 3% by weight of TiO$_2$ (110) micro-particles can be highly beneficial for improving the aging resistance of RTVs under extreme conditions. Although the modeled PDMS surfaces presented in this study are only simulations and therefore not a representation of actual experimental values, the surface energy results
(~27mJ/m²) were nonetheless very similar to measured experimental data (~20 to 25 mJ/m²), making the models a reasonably accurate representation of PDMS surfaces.

While all modeled surfaces [Chapter 5] with a reduction in the methylation of the PDMS chains exhibited higher surface energies, the addition of TiO₂ nanoparticles nevertheless decreased the surface energies of the simulated PDMS composites. This was also seen in the experimental results, where the higher contact angle of the TiO₂/RTV composite was maintained even after aging in hypochlorous acid and electrolyzed aqueous salt solution. This result therefore supports the hypothesis that TiO₂ particles can be very effective in reducing or delaying aging of RTVs in extremely oxidizing environments in low-level light conditions, while also improving hydrophobicity.

At the nanoscale level, the molecular dynamics interfacial interactions between the PDMS molecule, SiO₂, and TiO₂ atoms at the particle/polymer interfaces may offer the best explanation for the observed differences seen in the hydrophobicity, resistance to aging, diffusivity, and ice adhesion studies. The simulations of silica/PDMS interfacial interactions [Figure 28] indicated that the intermolecular interactions are strong, resulting in a noticeable methyl group reorientation towards the silica surface and away from the PDMS surface [56]. By contrast, the presence of TiO₂ changes the PDMS molecular geometry through a preferential interaction between the Si atoms of PDMS and the oxygen atoms of TiO₂, resulting in the reorientation of the methyl groups away from the PDMS/TiO₂ interface. The presence of titanium dioxide, mixed with the PDMS before curing, may therefore result in methyl group reorientation towards the polymer
surface, as shown in Figure 25 [56]. This indicates that PDMS materials with TiO$_2$ nanoparticles may exhibit more hydrophobic properties, and the methyl groups may act as a buffer, preventing damage to the PDMS backbone.

Additionally, the molecular dynamics results showed promising effects of TiO$_2$ on the diffusion rates of permeating compounds, such as HOCl and Cl$^-$, compared to unmodified PDMS [56]. MSD rates for diffusing compounds were considerably lower in the simulated PDMS network with TiO$_2$ compared to the unmodified PDMS network. In particular, it was shown that the presence of TiO$_2$ changes the PDMS molecular geometry through a more preferential interaction between the Si atoms of PDMS and the oxygen atoms of TiO$_2$, resulting in the reorientation of the methyl groups of the PDMS at the PDMS/TiO$_2$ interface. As a result of this mechanism, the reoriented methyl groups could slow the movement of water and HOCl molecules and reduce their diffusivities, as illustrated in Figure 32 [56]. By contrast, the presence of silica makes the movement of water and HOCl molecules in PDMS faster [Figure 31], allowing water and HOCl molecules to exhibit greater diffusion rates [Figure 31] because of the opposite reorientations of the methyl groups [56].

The reorientation of PDMS methyl groups may be the product of dipolar hydrogen forces due to the semi-polar PDMS Si-O-Si backbone. This may be due to adhesion forces of the siloxane backbone, resulting in an increase in hydrophobicity [56]. This was experimentally verified through measured hydrophobicity of the experimental samples, which indicated a higher initial contact angle of the TiO$_2$/RTV sample, which
was retained even after aging in hypochlorous acid and electrolyzed aqueous salt solution [56]. The reorientation of the methyl groups is presumed to be the primary reason the TiO$_2$/RTV composite exhibited higher resistance to aging by HOCl, as the reoriented methyl groups shielded the Si-O bonds against scission, resulting in a 50% higher resistance to aging under extreme conditions. A proposed illustration of the methyl group rearrangement, away from the TiO$_2$ particle surface and towards the polymer surface, is schematically shown in Figures 75 and 76.

![Figure 75. Unmodified PDMS methyl group configuration](image)
Methyl group rearrangement and subsequent changes in compound diffusion could also explain the water pooling reported in [51], schematically illustrated in Figure 77. It is also possible that the silica particles present in the RTV-1 allow for HOCl concentration and possibly immobilization, resulting in areas of pooling sites. Because HOCl is a known oxidizer, pooling sites could accelerate where initial polymer degradation occurs in the silicone rubber, and may be where large void formations initiate. The pooling effect could also exist with highly polar HOCl molecules creating sites rich in HOCl close to silica [sites 1 and 2 in Figure 77]. As a consequence, the HOCl pooling sites could be the regions where permanent damage to the PDMS network
by HOCl or energized aqueous salt is initiated. The initial chain damage by scission would then expand into large and extensive micro-voids [Figure 34] and much less rapidly [Figure 36] in the presence of TiO$_2$ microparticles.

![Figure 77](image_url)

**Figure 77.** Schematic of H$_2$O and HOCl migratory paths along PDMS/TiO$_2$ and PDMS/SiO$_2$ interfaces with possible pooling sites indicated by 1 and 2

The combined effect of TiO$_2$ and silica on the molecular dynamics predictions of diffusivities and contact angles/surface energies presented in this work are currently unknown. Both particles were present in the tested composite. It can only be speculated that an addition of TiO$_2$ (3% by volume) to the PDMS network containing 20% silica, would only slightly reduce the diffusivities in Figure 31. Silica would also slightly decrease the contact angles and resulting surfaces energies. More research is still required
to understand the combined effect of the particles on PDMS as a function of their volume fractions.

Finally, while it is clear that an electrolyzed salt environment is more damaging than aqueous NaCl [15-16], it is not evident if the observed damage is also caused by by-products of electrolysis, or from the by-products of hypochlorous acid itself, such as H+ or OCl-. Hydrolysis and oxidation damage due to HOCl and electrolyzed salt exposure may account for the voids and cavities observed in Figures 34 and 45. While chain scission in the polymer is evident due the loss of material, the specific mechanism is still unknown. By itself, hypochlorite (OCl-) is the strongest oxidizing agent of the chlorine constituents of HOCl, is often used as a bleach solution, and could be partially responsible for the observed polymer damage. Additional electrolysis products such as chlorine gas, hydrogen gas, and hydroxide ions may also be partially responsible for the chain scission damage seen in the cross sections in the RTV-1 experiments, including the formation of free radicals. PDMS, in the presence of water and dry band arcing [14] has been shown to form free radicals within the polymer chain, and hydrogen transfer from the CH₃ methyl groups may occur just in the presence of dry band arcing alone, causing chain scission.

8.2 PDMS as a credible icephobic material for HV and other applications

Extreme cold weather environments pose a unique set of challenges for materials, specifically resisting moisture accumulation and the resulting adhesion of ice on material
surfaces. Ice buildup can be problematic on many structures such as aircraft, roads, and powerlines, often necessitating its removal. Ice accumulation on certain structures, such as overhead HV power lines and insulators, are of particular concern as failure of these lines can have severe economic and human costs. Recently, PDMS materials have been investigated for their reduced ice adhesion due to a number of factors: low thermal conductivity, good hydrophobicity, and low surface energy, which can produce hydrophobic low molecular weight oil [27, 56-61]. PDMS/modified nano-silica composite materials have also been previously investigated for their resistance to ice accumulation, and were found to be effective in minimizing ice buildup [62].

Surfaces with poor hydrophobicity and high thermal conductivity, such as glass and metal, have been reported to be prone to ice adhesion and buildup [63-64]. However, although a good correlation has sometimes been made between surface hydrophobicity and icephobicity [64], some studies have disputed these claims [63].

While surface roughness has been investigated as potentially advantageous in the development of super-hydrophobic materials, increased surface roughness has had conflicting results for reducing ice adhesion [63]. In this study, surface roughness of RTV-2 DragonSkin™ increased by 11% when titanium dioxide particles were included. Collectively, the reorientation of the methyl groups, as previously described, and the combination of increased hydrophobicity and increased roughness may account for the reduced ice adhesion strength of the composite material, as shown in Chapter 7. This effect may be due to the water droplets shifting to the Cassie-Baxter state as a result of
increased surface roughness of the modified RTV-2 material. A schematic illustrating this proposed effect is shown in Figure 78.

![Figure 78. Schematic illustrating increased surface roughness of the modified RTV-2 material and proposed methyl group rearrangement](image)

In real life, ice accumulation does not occur in the form of a single stationary cube frozen over the course of several hours, as in the experimental setup identified in Chapter 7. Instead, ice accumulation often occurs during cold weather storms where snow or freezing rain gradually accumulates onto a surface and freezes, often in
unpredictable patterns and circumstances [71-72]. The larger surface area of a material, as well as the lower mass of the water droplets allows for both evaporation and rapid loss of heat. Therefore, as shown in this study, the most extreme and dangerous condition for ice accumulation is the following: abundant precipitation of small, almost mist size, cold water droplets striking a surface with a temperature at or below freezing, as demonstrated in the experimental approached described in Chapter 7.

Following the results of the ice adhesion and ice accumulation experiments, it is clear that ice accumulation and ice adhesion are not directly correlated, as the water droplet size affects ice accumulation. The ice accumulation results demonstrated that although the TiO$_2$/RTV-2 coated conductor only reduced ice accumulation by approximately 5% (mass) compared to the unmodified RTV-2, the positive effect of titanium dioxide PDMS materials can still be observed in the recorded water droplet sliding angles, regardless of which RTV material was used. The sliding angle of the TiO$_2$/RTV-2 surface was recorded as 27°, which was lower than sliding angle of the pure RTV-2 surface (33°) indicating the composite exhibited better hydrophobicity, which was consistent with the previously conducted experimental analysis on TiO$_2$/RTV-1 composites [Chapter 6]. The sliding angles of the virgin TiO$_2$/RTV-1 composite and unmodified RTV-1 samples were 29° and 44°, respectively [Figure 39]. It can be therefore interpreted that the minute size of the water droplets in the ice accumulation was the critical limiting factor, prohibiting them from sliding and allowing them to freeze in place instead. By contrast, larger water droplets were able to slide off the surface, as
evidenced by the small difference in mass accumulation between the modified and unmodified PDMS samples.

8.3 Extreme aging of HV PDMS based icephobic barriers

Two major issues related to the application of PDMS silicone rubbers in HV situations were investigated in this study. The first part of the project dealt with the extreme aging of the rubbers in HV aqueous salt environments [14-16, 25, 56]. The effect of titanium dioxide on PDMS (RTV-1) materials for HV NCIs was investigated along with the most aggressive in-service aging condition caused by HOCl created in electrolyzed aqueous salt [56]. The most important outcome was the important discovery that titanium dioxide microparticles, when imbedded in RTV materials, can significantly slow down the aging process of the rubbers. By adding 3% by weight of TiO₂ microparticles, the resistance to extreme aging of one particular RTV-1 rubber was improved by about 50%.

The effect of titanium dioxide was also investigated in the second part of this dissertation with a different PDMS silicone rubber, RTV-2 (DragonSkin™), as a potential durable icephobic coating for HV conductors. This RTV-2 material also exhibited increased hydrophobicity when titanium dioxide particles were added (3% by weight), which was attributed to the lotus effect. However, while ice adhesion strength decreased approximately 5 times, ice accumulation was not reduced significantly. The fact is that in service PDMS barriers will be subjected to extreme aging either by hypochlorous acid,
nitric acid or other pollutants, since the in service environments for NCIs and HV conductors are quite similar. Therefore, it could be assumed that the particles would mitigate the aging process, retaining the materials’ ability to repel ice. This issue, however, is not straightforward and would require an additional major study.

As shown by R. Woll in [27], aging of PDMS materials for four weeks in HOCl significantly affects ice adhesion strength especially if cross-linking is reduced. With full cross linking, ice adhesion strength went up 31%, and with 25% cross linking went up by 163%. However, no effect of TiO₂ was investigated on the ice adhesion under aging. Therefore, is very difficult to predict at present how the silicone rubbers could behave in HV service as icephobic barriers in the presence of the particles as a function of cross linking. In addition, the weak relationship between ice adhesion and ice accumulation would further complicate the prediction of the efficiency of the PDMS barriers to repel ice if extreme aging was present.
Chapter Nine: Major Conclusions

1. It has been shown in this work that very complex aging mechanisms can exist in modern transmission systems employing RTV silicone rubbers, and the prevention of aging can be difficult in HV environments. However, using nanotechnology, viable improvements to the design of the next generation silicone rubber components for HV applications are possible to prevent their aging in a variety of extreme environments, including aqueous salt.

2. This study also established a new model of RTV-1 polymer aging in oxidizing HOCl aqueous environments. The model, based upon electrolyzed aqueous salt, shows the effect of hypochlorous acid on RTV-1 at room temperature to be much more dramatic compared to standard aqueous NaCl, even at elevated temperatures. Additionally, electrolyzed aqueous NaCl salt and HOCl produced very similar polymer damage in the form of voids and cavities within the polymer network, confirming the possibility that HOCl can form in-service. This work therefore questions the previous models based solely upon chlorine.
3. The molecular dynamics simulations performed in this study offer partial explanations of the types and extents of aging observed in the RTV-1 samples, and how titanium dioxide affects PDMS. The simulations illustrated that the addition of 3% by weight of TiO$_2$ (110) micro-particles could be highly beneficial for the improvement in the resistance to aging of RTVs under extreme conditions. Specifically, the addition of TiO$_2$ nanoparticles resulted in reorientation of the PDMS methyl groups at the PDMS/TiO$_2$ interface, as shown in Figure 26. As a result of this mechanism, the reoriented methyl groups lowered the diffusion curves of water and HOCl molecules in TiO$_2$ filled PDMS. This supports the idea that TiO$_2$ particles could be very effective in reducing aging of RTVs in extremely oxidizing environments in low-level light conditions, by slowing down the diffusion rates of aggressive permeating compounds such as HOCl.

4. The effect of titanium dioxide microparticles on aging prevention of silicone rubbers was shown to be generally positive, as RTV-1 materials with embedded TiO$_2$ particles exhibited a 50% higher resistance to aging even in the most extreme oxidizing conditions. Although this study does not include other possible effects of TiO$_2$, such as the known photo catalytic effect, the experimental and numerical results nonetheless indicated that PDMS materials can be made more hydrophobic and resistant to aging through the addition of TiO$_2$. 
The results of the icephobic experiments indicated that ice adhesion and ice accumulation are not directly correlated. While the 3% TiO$_2$/RTV-2 material exhibited very low ice adhesion strength (~5 kPa), it accumulated only slightly less ice (~5%) compared to the unmodified RTV-2 which demonstrated ice adhesion strength of ~24 kPa. Nevertheless, the slight improvement in ice accumulation of the TiO$_2$/RTV-2 composite may be attributed to the combination of both increased hydrophobicity and surface roughness. This was partially verified by molecular dynamics simulations, which identified fewer hydrogen bonds at the ice/PDMS interface when TiO$_2$ particles were included.

The TiO$_2$/RTV-2 composite surface was determined to be 10% rougher than the unmodified RTV-2. This increase in roughness could be directly correlated to the decrease in ice adhesion strength of the TiO$_2$/RTV-2 composite, as a result of the lotus effect. Through a combination of increased methyl groups oriented towards the surface, and increased hydrophobicity, water droplets could be moved from the Wenzel state to the Cassie Baxter state, resulting in ice/surface contact.

Considering all the data presented in this study, PDMS composites, especially those with increased roughness and hydrophobicity caused by titanium dioxide, could be credible materials for icephobic applications. The decrease in sliding angles of PDMS materials indicates that the addition of titanium dioxide particles
improves material hydrophobicity regardless of curing process. However, the most extreme scenario – freezing mist – results in significant ice accumulation regardless of the material properties. This scenario can only be avoided if ice nucleation is prevented, irrespective of the size of the water droplets.

8. The general effect of titanium dioxide particles on PDMS appears to have a generally positive macroscale effect, for both resistance to extreme aging and ice adhesion. However, as shown in the thermal cycling study, the addition of titanium dioxide did not completely protect the material from localized swelling and damage. Therefore, while the TiO$_2$/RTV-1 composite is effective against aqueous oxidizing aging and ice adhesion, more investigation is still need to pinpoint the long-term effects of thermal cycling. Also, this research did not show any evidence that TiO$_2$ could positively affect ice adhesion resistance of PDMS icephobic barriers, if extreme oxidizing aging occurs. If the barriers are to be used in HV applications, more research will be required to gain sufficient confidence in their long term in-service durability.
Works Cited

27. Thesis; Robert Woll


46. Glaser, K. J. *Computational studies of silica*. Diss. UCL (University College London), 2011.


