Aging Assessment of High Voltage Single Component Room Temperature Vulcanized Silicone Rubber (RTV-1) Subjected to Aqueous Salt

Monika Bleszynski
University of Denver

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AGING ASSESSMENT OF HIGH VOLTAGE SINGLE COMPONENT ROOM TEMPERATURE VULCANIZED SILICONE RUBBER (RTV-1) SUBJECTED TO AQUEOUS SALT

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Monika Bleszynski
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Advisor: Dr. Maciej Kumosa
Abstract

Single component room temperature vulcanized (RTV-1) silicone based caulk used in high voltage insulators and other applications is frequently subjected to environmental pollutants. Aging of RTV-1 silicone rubber is the result of various stressors, including environmental aging conditions such as UV, acid, and salt exposure from ocean mist. Loss of hydrophobicity due to damage of the hydrophobic methyl groups, as well as loss of mechanical strength due to depolymerization via hydrolysis as a result of aqueous salt exposure were the two main factors of material aging assessed in this work. Multiple RTV-1 formulations were initially assessed for resistance to aging in aqueous salt, with one particular RTV-1 material subsequently chosen for further study in successive aging experiments. 3% NaCl salt solution experiments were conducted to analyze physical, mechanical, and chemical changes. A subsequent but preliminary hypochlorous acid aging experiment was then conducted, with results indicating accelerated RTV aging as a result of super diffusive hypochlorous acid. Comparatively, a molecular dynamics model was developed to analyze salt ion, water, nitric acid, and hypochlorous acid diffusion through the RTV polymer network, indicating hypochlorous acid as super diffusive, chlorine as diffusive, and water as subdiffusive. Conclusively, the experimental and molecular dynamics results provide a method to better understand the
impact of contaminants and pollutants on RTV-1 material aging as a product of molecular diffusion.
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Chapter One: Introduction

Literature Review

High voltage transmission line insulators are often under recognized structures in high voltage power lines and substations. Commonly sitting high above the line of sight, high voltage transmission insulators are multifunctional, providing mechanical support for the steel lines as well as increasing the distance between the electrified lines and the ground [1]. This additional distance provides an air gap between the energized lines and any supporting structures, generating less stress on the complete structure due to reduced leakage distance.

Insulators, in their first form, originated from early telephone lines and were composed of silicate glass. Threaded glass insulators were the dominant insulator from the 1890s to the early 1900s, mainly due to their low cost. Threaded glass insulators were replaced with non-threaded glass of higher quality around 1910. Starting in the early 1900s, the popularity of ceramic insulators rose as the manufacturing process became more refined, which standardized the “bell” design of threaded insulators. Starting in the early 1960s, materials other than glass or ceramic were perused. First generation – non-ceramic insulators (NCI) - polymeric insulators came about the mid 1960s, featuring the fiberglass rod seen in modern insulators today [1]. Out of various polymeric materials researched, silicone based room temperature vulcanized rubber (RTV) became the
leading standard for NCI insulators, and RTV continues to play a dominant role in the industry today.

A common building material in aviation, space, and industrial applications, RTV is categorized into one and two component RTV, which are identified by the different formulations used in manufacturing. RTV-1 denotes single component room temperature vulcanized caulk, while RTV-2 denotes two component caulk. RTV-1 is primarily found on the seal between the RTV-2 shed and metal end fitting of transmission non-ceramic insulators. Both RTV-1 and RTV-2 are composed of large amounts of polydimethylsiloxane (PDMS); a silicon based polymer with excellent hydrophobic properties. The hydrophobic property of RTV insulator sheaths helps minimize the accumulation of contaminants and extends life in service.

Although common in high voltage electrical applications, RTV-1 is also a fundamental component in many aerospace and space applications, such as jet aircraft and satellites. Frequent pressure, temperature, and altitude changes pose a challenging environment for sensitive aviation instruments, and silicone rubber RTV provides both insulation and electrical protection of critical components. This is due to the material’s excellent electrical resistance and limited deformation when exposed to temperatures ranging from -100 °C to +250 °C, depending on the formulation and grade [2]. In jet aircraft, RTV silicone rubber is found in numerous locations including the cockpit and engines, encasing electrical components and instruments while preventing water ingress. Silicone rubber RTV therefore has an advantageous ability to withstand weathering,
radiation, and extreme temperatures, which allows for numerous applications in extreme environments.

Satellites in orbit, while not subjected to salt or industrial pollutants are still subjected to extreme temperatures and elevated amounts of radiation. The resilience of silicone RTV to radiation makes it suitable for space applications, where adhesive silicone rubber RTV is frequently used as backing in satellite solar panels.

Any changes in the material structure of silicone rubber RTV due to aging can critically affect accompanying sensitive components, causing potential catastrophic failure of mechanical components or structures. Therefore, the thorough understanding of aging of silicone rubber RTV is essential in the prediction of in-service life, in order to accurately assess the risks to sensitive and critical components. Although aging of silicone rubber RTV was performed in this research with the thought of high voltage applications in mind, the assessments of RTV aging are applicable to circumstances involving space, aerospace, and other applications involving extreme environments.

In high voltage applications, RTV is found in the P-S-T (primary, secondary, and tertiary) triple seal found on insulators. The P-S-T seal is a redundant system containing three distinct parts in order to provide additional protection against moisture penetration into the insulator core. RTV-1 is applied to the insulator sheath in order to seal the gap between the sheath and insulator end fitting. The primary seal results from the compression of the rubber sheath into the end fitting. The secondary seal juxtaposes the end-fitting interface and is formed when the RTV is applied to the fiberglass core sheath.
The tertiary seal contains the manually applied RTV-1 silicone and creates a complete seal at the shed and end-fitting joint. RTV-2 is discernible from RTV-1 as large sheds encompassing the entire length of the insulator. Together, these two silicone rubber materials provide excellent protection for the supporting fiberglass rod and provide modern non-ceramic insulators resistance against various environmental stressors including UV, pollution, and moisture ingress.

Current literature cites many electrical and environmental stressors on NCI insulators, including nitric acid, water, high temperature, automobile exhaust, dry-band arcing, corona, global climate change, and ozone depletion. Salt is cited as one of the most common contaminants due to coastal development, and this environmental pollutant is often found in the presence of leakage currents [4, 5].

Although silicone rubber RTV is resilient, it begins to exhibit various signs of aging and deterioration after exposure to various environmental conditions, which diminishes the material’s hydrophobic properties. Visible cracking, material discoloration, and texture changes denote some of the visible material changes. Although RTV sheds are capable of resisting water even after long-term environmental exposure, certain conditions can accelerate the aging process, which can compromise the hydrophobicity of the silicone rubber sheds, allowing water-ingress and ultimately insulator failure to occur. In addition, material degradation can lead to further deterioration due to dry-band arcing and flashover, resulting in the continued loss of hydrophobic properties and further material damage. As such, the analysis of RTV aging
in order to extend silicone rubber insulator life in terms of years in service is of utmost importance [4, 5].

**Damage of Silicone Rubber Material as a Precursor to Aging**

Contamination of the silicone rubber shed from various environmental contaminants can cause a loss in the hydrophobicity of the shed, diminishing the runoff potential of water and pollutants. Over time, contamination of the shed can result in damage of the entire insulator, especially when paired with contamination from biological growth, bio-films, and salt, which can compromise RTVs hydrophobicity and result in dry-band arcing [6-12]. This combination can cause excessive damage to the silicone rubber polymer, measureable by SEM, FTIR, and hydrophobicity loss. Improving the resistance to environmental contaminants, for example eliminating the ability of bio-films to attach and propagate, is essential to extending silicone rubber insulator life spans. Various common contaminants are mentioned that have been studied in recent years [6-17].

Bio-film growth has been recorded in tropical portions of the world, with heavy algae growth recorded in Sri Lanka [6]. The presence of the algae on the upper sides of the sheds caused complete contamination in some cases, with some fungal growth recorded on the underside of the sheds. Upon further investigation, insulators with biological contamination exhibited greatly decreased rates of hydrophobicity. Rates of hydrophobicity decreased from 1-2 to 6-7 using the Swedish Transmission Research
Institute (STRI) hydrophobicity classification method [7]. Decreases in hydrophobicity also resulted in an increase in wet flashover voltage rates, especially on surfaces completely covered in biological growth.

Salt contamination aging was investigated in Aging of Silicone Rubber in Coastal and Inland Tropical Environment (2010), as well as Artificial Accelerated Aging Test of Silicone Rubber Housing Material for Lightning Arrestor (2011) [6, 8]. Samples were placed in testing chambers and subjected to salt fog for 8 hours a day for a total of 1000 hours for both studies, in addition to being subjected to 16 hours AC 19kV and 18kV tests during these 1000 hours respectively. Aging of Silicone Rubber in Coastal and Inland Tropical Environment (2010) recorded corrosion of the metallic connections between the tower and end fittings due to the salt contamination. In the field, high levels of corrosion were observed alongside areas of high salt contamination, and the RTV sheds became partially hydrophilic due to the accumulation of salt contamination.

In Artificial Accelerated Aging Test of Silicone Rubber Housing Material for Lightning Arrestor (2011), results for the salt contamination test showed surface erosion on the trunk surface, as well as all shed surfaces [8]. This was determined to be a result of dry band arcing due to salt contamination. Therefore, salt contamination was a major contributing factor in the overall degradation of the RTV shed material.
Statement of Problem

While silicone rubber insulators provide excellent protection against environmental damage, silicone rubber may be more vulnerable to deterioration under certain stressors, resulting in further damage from environmental contaminants. For example, the chemical structure of silicone rubber may be damaged from extensive exposure to UV and heat, and be further damaged by dry band arcing and flashover due to a loss of hydrophobicity. C-H, Si-O-Si, and Si-CH₃ bonds within the polymer may break due to excessive heat and UVA exposure, resulting in permanent silicone rubber and overall shed damage [9-11]. Therefore, preventing deterioration of the Si-CH₃ bonds is critical for maintaining RTV-1 in serviceable condition.

Presently, limited resources exist to determine macro scale material damage in high voltage applications. Material aging resulting from environmental factors such as salt, acid, or UV routinely causes observable damage both in service and experimentally [6-17]. However, assessment of aging, and importantly, non-destructive in-service aging assessment, has been difficult to conduct. Therefore, it has been imperative to develop a preliminary aging assessment method that is capable of easy deployment in the field, with accurate results, and quick analysis timeframe. The juxtaposition of durometer hardness and RTV material hydrophobicity loss conducted during this study is therefore intended as a potential preliminary testing mechanism for in-service aging analysis applications.

Of the many environmental contaminants currently associated with silicone rubber aging, the effect of aqueous salt on RTV-1 was the aging mechanism assessed in
depth. Salt contamination was chosen as the focus of research in this work due to significant research affirming widespread salt contaminated insulator surfaces found on high voltage lines near coastal environments [5, 6, 8]. While both RTV-1 and RTV-2 are present on high voltage insulators, RTV-1 was the material of focus in this study, as the integrity of RTV-1 triple seal point system is critical in preventing catastrophic failure of the high voltage lines. Therefore, an in depth assessment of salt contamination and its effects on silicone rubber material aging were investigated at length, due to the significant consequences salt contamination may pose to the integrity of the silicone rubber material.

Synopsis of Research

RTV-1 and RTV-2 denote two chemical methods for the production of cross-linked silicone rubber (SIR) materials. RTV-1 based caulk is similar to RTV-2 used for insulator sheath, where both materials are composed of significant amounts of polydimethylsiloxane (PDMS). Initial aging experiments on three different RTV-1 compounds, provided by a major US high voltage equipment manufacturer, exhibited noticeable material loss by shedding during saltwater exposure, and suggest extensive damage resulting from bond chain scission within the RTV-1 materials. The damage appears to be more extensive in saltwater at 80°C than under individual and combined UV, moisture, nitric acid conditions [9]. The result was loss in physical material weight as well as significant reductions in hydrophobic properties of the RTVs. Chain scission,
responsible for the RTVs mass loss, also resulted in loss of the RTVs hydrophobic methyl groups [9].

RTV-1 aging experiments in saltwater exposure resulted in noticeable material loss into the salt-water solution, suggesting extensive damage to the RTV polymer backbone [9]. Aged samples showed a direct relationship between the material mass loss and the Si-O-Si 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 RTV, namely a drastic decrease in hydrophobicity due to hydrolysis of methyl groups. SEM images verified the surface effect, 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 molecular diffusion among a chosen set of molecules, including water, salt ions, nitric acid, and hypochlorous acid. This study then concluded with a preliminary set of experimental hypochlorous acid results, which were compared to experimental aqueous salt results.

*Publication Synopsis*

Two peer-reviewed journal papers were completed during the course of this study. The first was written in conjunction with Bruce Allen and published October, 2015 by IEEE.

1) “Investigation into the Effects of Environmental Stressors on RTV-1 Silicone-Based Caulk Materials”. B. Allen, M. Bleszynski, M. Kumosa, E. Willis. IEEE

The second journal publication was submitted to IEEE DEIS on September 22nd, 2015, investigating the effect of RTV-1 silicone rubber material aging when subjected to aqueous salt, and supported by a molecular dynamics model.

2) “RTV Silicone Material Aging In the Presence of Aqueous Salt”, M. Bleszynski, M. Kumosa. IEEE Transactions on Dielectrics and Electrical Insulation.
Chapter Two: Chemistry of RTV

Introduction

Physical changes in the visual appearance of silicone rubber RTV-1 can indicate material aging as a result of changes in the underlying chemical composition, due to damage of the polymer backbone Si-O-Si chain. Determining the process of chemical damage to the polymer’s silicon based backbone can therefore be used to evaluate material aging and lifespan. To better assess material degradation, laboratory aging of RTV-1 was mainly assessed 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 [2, 10-19].

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. A visual comparison 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 RTV chemical composition. 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. 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. 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 of accelerated aging method of RTV-1 is credible.

Chemistry

While many silicone rubber RTVs have proprietary formulations depending upon the manufacturer, the fundamental chemical formula is comprised of linear polydimethylsiloxane (PDMS) polymer chains [2]. The base structure of PDMS is an inorganic Si-O-Si backbone, which independently is polar and hydrophilic. The presence of non-polar methyl groups (CH₃), which are attached to the silicone atoms of the backbone chain and which can rotate freely, causes the polymer to be entirely hydrophobic [figure 1][2]. The methyl groups are primarily responsible for the hydrophobicity of the overall RTV material, and provide a buffer to the polar Si-O-Si backbone chain [2]. The methyl functional groups hence provide RTV silicone rubber insulators with favorable hydrophobicity.
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 [2, 19]. Although there are various types of crosslinking from biological to material, and crosslinking catalysts can include radiation, heat, or exposure to crosslinking agents, this analysis will only focus on the specifics of chemical crosslinking within the silicone rubber RTV-1 material used for the purposes of 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 RTV sample.
material [2]. Although the methodology of crosslinking within RTV-1 polymers varies depending upon the manufacturer and the desired silicone rubber consistency, this study used a crosslinking catalyst in the form of an amine curing process, which draws upon atmospheric moisture absorption to initiate the chemical reactions. In this example, the polysiloxane chains contain terminal –OH groups prior to curing, which gives uncured polymer a semi-solid consistency. Once the silicone rubber RTV-1 is applied and allowed to dry, 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 RTV-1 material [2]. 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. Additional additives and fillers may be present in the silicone rubber in the PDMS network, however many of these are not disclosed unless expressed by the manufacturer, and were not the main focus of this study.

Previous industry 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 are not discussed [17,18]. It was also 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 [6, 8, 9, 13, 21]. 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 [14, 15]. A hydrolysis reaction is required to break the Si-O-Si backbone at approximately +26.6 Kcal/mol [21], without a catalyst, as water reacts slowly with PDMS at 150°C [12, 16, 21]. Therefore, hydrolysis in RTV materials creates both a hydrophilic surface and results in the formation of linear and cyclic chains, which form low molecular weight silicone oil [12-21]. Although the exact mechanisms of hydrolysis of RTV materials according to current literature are still inconsistent in terms of conditions required, it is known that assessing mechanisms of hydrolysis in RTV is critical in the determination and progression of RTV material aging. 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, ionic catalysts such as salt are possible below 350°C, therefore the polar nature of the Si-O bond makes it vulnerable to hydrolysis as a result of depolymerization [12]. 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 [12, 16] with molecular weights less than 25,000, the low molecular weight silicone material can diffuse through the material matrix, effectively restoring hydrophobicity of the RTV surface [16, 18]. Low molecular weight material diffusion can accelerate as a result of elevated temperature and UV radiation [16, 18], resulting in short chain low molecular weight material diffusing more
quickly to the surface [12, 16, 30]. 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 surface by any means may accelerate RTV material aging.

Radiation in the form of ultraviolet radiation may also accelerate aging in RTV-1. While UVA radiation has a minimal effect on the chemical integrity of PDMS, it can affect the additives in the insulator skin [18, 21]. UVB radiation, which has a higher energy, can trigger chain scission of the Si-O-Si backbone [21]. Regardless of which type of radiation, photons from UV can collide with electrons in the Si-O-Si backbone, causing electrons in the RTV-1 chemical structure to be promoted to higher orbitals. UV may therefore stimulate hydrophobicity by promoting the diffusion of low molecular weight materials to the RTV-1 surface [2, 21]. While both thermal and UV sources provide energy to the RTV-1 and the low molecular weight material, the literature is unclear how UV increases the diffusion rate of the low molecular weight material.

Hypochlorous acid was included in this research due to the unique conditions found on transmission lines, which may allow hypochlorous acid to form in service. Because leakage currents may match or even exceed the minimal voltage requirement to create dissolved chlorine, there exists a high probability that hypochlorous acid could be present due to standing ocean salt water on insulators in the presence of leakage currents [19, 20]. Formed when relatively low voltage is applied to salt water, hypochlorous acid is an extremely effective oxidizer consisting of hydrogen, oxygen and chlorine. It is
formed according to the following chemical reactions [22]:

\[
2\text{Cl}^- (\text{aq}) \rightleftharpoons \text{Cl}_2 (g) + 2e^- \quad \text{E} = +1.36 \text{ V}
\]

\[
2\text{HOCl} \text{(aq)} + 2\text{H}^+ + 2e^- \rightleftharpoons \text{Cl}_2 (g) + 2\text{H}_2\text{O} \quad \text{E} = +1.63 \text{ V}
\]

Therefore, another possible aging mechanism resulting from salt-water exposure could be the formation of hypochlorous acid (HOCl) [20, 21]. A molecular dynamics model was developed in this research to assess damage due to the probability of diffusion of salt and water compounds, including chlorine ions. The potential of these compounds to permeate through the RTV material more rapidly than water could result in damage as a result of material swelling and depolymerization through hydrolysis and oxidation [17, 21].

**Discussion**

Depolymerization of polydimethylsiloxane via hydrolysis as a result of an ionic catalyst, for example salt water, is therefore one of the probable mechanisms responsible for the damage in the salt solution immersion tests discussed later in this thesis. Depolymerization is 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. 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 [9], 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.

The effects of RTV-1 and salt contamination and most aging studies 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 salt has a negative effect on hydrophobicity due to the reorientation of hydrophobic methyl-groups [2]. Coastal environments provide various changing weather patterns with possible salt contamination, such as fog and tropical storms, resulting in a variety of possible salt exposure levels. Salt-fog 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 [6, 7]. For the purposes of this study, electrical effects were excluded.

Conservation of RTV hydrophobicity is therefore important, as a loss of hydrophobicity indicates changes in the underlying RTV structure, which progress to material damage as a result of hydrolysis.
Chapter Three: Experimental RTV Aging

Introduction

Two sets of aqueous salt experiments were conducted during the course of this study, referenced in this chapter as experiment I and experiment II. Experiment I was conducted first in order to assess various levels of NaCl salt exposure among different formulations of RTV-1. Experiment II followed, and involved only a single formulation of RTV-1 based upon the results of experiment I. To accurately mimic the in-service conditions found on an insulator, experimental studies in this work were performed on RTV-1 at ocean level concentrations of 3% aqueous NaCl at 80°C [13].

In experiment I, salt water caused visible material damage to RTV-1, observable as “flakes” in the salt-water solution, and was the first indication of material damage. As a result, material hardness testing was added to experiment II in order to perform a macro scale measurement of material aging as a result of bond-scission. Measurement of in-service RTV aging has previously relied upon visual appearance rather than chemical or physical structure to determine material end of life, including visual observations of hydrophobicity loss. Current aging tests rely on an association between laboratory aging of virgin RTV material and physical and chemical damage, in order to match appearance, chemical, and physical properties of in-service materials [18, 21]. Therefore, the additional measurement was added to correlate hardness, hydrophobicity loss, and aging.
Particular attention was paid to changes in hydrophobicity during aging experiments, as current literature suggests damage to the Si-O-Si backbone, along with the reorientation of hydrophobic methyl-groups, is associated with a negative effect on hydrophobicity [2, 23]. Because the nonpolar methyl groups create the hydrophobic effect causing RTV to repel water [2, 18, 23], FTIR was used to evaluate RTV-1 material loss for the presence of methyl groups.

Although salt-water damage has been previously recorded in the experiments appearing as surface erosion, a diffusion model [discussed in chapter four] was developed based upon the NaCl aging experiments. This was done to determine rates of diffusivity of various aging compounds, including nitric acid and salt ions, as supportive evidence of possible osmotic pressure damage causing cracking on the RTV-1 surface [17].

Methods

Experiment I of this study consisted of three RTV-1 caulks formulations [figure 2]. Experiment II of this study involved only one type of RTV-1, identified as SGK-332, and dark grey in color [18]. SGK-332 was chosen after the first set of aging experiments in experiment I [18] indicated that this particular material had above average recovery rates of hydrophobicity after salt-water exposure.
For the purposes of this research, 3mm thick samples were created in order to reproduce the in-service specifications found on insulators [2, 18]. RTV-1 caulks undergo an amine curing process at a rate of 1 mm every 24 hours, and samples were allowed to cure for 72 hours to allow for full curing of the entire sample before aging. The curing process and aging experiments were both conducted without direct sunlight exposure, to prevent unintentional crosslinking or material changes.

Several methods exist to measure and observe hydrophobicity, with the most accurate method utilizing a goniometer. For the purposes of this study, the Swedish Transmission Research Institute (STRI) method was used, which uses a visual method to observe changes in hydrophobicity of RTV-1 [18]. Hydrophobicity assessments were
conducted after applying water droplets onto the RTV-1 sample surface, and visually comparing hydrophobicity. The rating scale for the STRI method ranges from HC1 to HC7, with full hydrophobicity denoted as HC1 and full hydrophilicity as HC6 and HC7.

Methods Experiment I

The first set of aging experiments consisted of three samples of each RTV-1 formulation, for a total of nine samples, aged for 1000 hours. Three RTV-1 samples of the sample formulation were placed in beakers containing 3% NaCl per 3000 ml volume salt-water solution at 80°C. RTV-1 samples were positioned in each beaker in the following positions: suspended with no direct salt water contact, 50/50 salt water and air contact, and completely submerged. The various positions were intended to mimic different environments that could possibly be found on transmission lines exposed to ocean salt-fog. Thus, the various rates of exposure compare to various coastal environments either through complete wetting in the case of a submerged sample, partial wetting, or minimal wetting. Samples and their surrounding media were examined and recorded once a week for any change in weight or material damage over the course of 1000 hours.

Mass measurements began after the first week in the salt solution, and were recorded over the course of approximately 1000 hours to observe any weight changes in the RTV samples. Material loss was also observed in solution in the form of a precipitate,
accounting for a visual account of material loss from all RTV samples in the salt-water solution.

Methods Experiment II

The second set of salt aging experiments replicated the 3% salt concentration of the experiment I with minor changes. A total of ten experimental samples were used, and all samples were identical in width to samples used in experiment I. Only SGK-332 RTV-B samples were used in experiment II, after favorable material results were recorded in experiment I. Samples were entirely submerged in 3% salt solution in 5 L glass beakers at 80°C. Once a week, one sample was removed from the solution and allowed to dry for 72 hours under ambient conditions before subsequent hardness and final hydrophobicity tests were conducted. Samples were not returned to NaCl salt solution after removal.

To show the effect of recovery, hydrophobicity tests were also conducted on the samples immediately after their removal from the solution and completely dry. Mass changes were likewise measured only on fully dried samples. Experiment II also included the analysis of fragments of RTV-1 found suspended in the solution and observed as “flakes”.

Hardness tests in experiment II were conducted using a standard Shore A durometer with a measurement range of 1HA to 100HA. The durometer needle was positioned perpendicular to the samples and readings were taken when the RTV-1 sample
surface was flush against the durometer plate. Care was taken not to apply any unnecessary mechanical pressure.

Hydrophobicity tests were also measured according to the Swedish Transmission Research Institute (STRI), and observed externally. Hydrophobicity was measured before aging on virgin samples, immediately after removal from salt solution, and after RTV-1 samples were fully dry.

Results

Experiment 1

Recorded RTV sample weights showed a weight reduction that was most prominent for fully submerged samples, with RTV-A showing the most extreme weight loss. Additionally, all RTV samples when exposed to salt water, regardless of position within the beaker, became tacky to the touch and exhibited significant reductions in firmness. Fully submerged samples were noticeably less firm compared to new samples, with sample edges becoming less defined. In addition, the fully submerged transparent (RTV-A) RTV-1 sample had a rough appearance, appearing speckled compared to the non-submerged samples of the same RTV-1 formulation.

Samples exhibited drastic reductions in hydrophobicity after initial testing, with the most pronounced reduction in fully submerged samples. 50/50 submerged samples exhibited full wetting of submerged material surface compared to the non-submerged portion. Samples which were fully submerged for 1000 hours in the salt solution,
exhibited a hydrophobicity change of HC1 to HC6 after initial removal from solution, indicating complete wetting after prolonged exposure [figure 3]. Samples aged over 1000 hours only regained minimal hydrophobicity after a prolonged drying period of several hours, indicating a permanent loss of hydrophobicity and surface damage.

Figure 3. Complete wetting of fully submerged RTV sample after 1000 hours [18].
Mass loss recorded after the first week showed the most prominent mass reduction among fully submerged samples [figure 4], with RTV-B showing the most extreme amount of weight loss among the different RTV-1 formulations. However, although losing the most mass, RTV-B showed the greatest resiliency in maintaining and recovering hydrophobicity.
Results Experiment II

Aging tests resulted in significant material degradation over time. SEM observations of the virgin RTV-1 material show an even textured surface with no discernible damage present [figure 5a]. However, SEM images taken of one, five, and ten week aged samples [figures 5 b-d] showed increasing levels of damage to the material surface represented by the development of cavities, cracks, and corresponding texture changes. The one week aged sample exhibited the development of small cavities throughout the sample surface [figure 5b], with more pronounced cracking appearing in the samples aged for five weeks [figure 5c]. The ten-week aged sample [figure 5d] showed complete surface erosion [18].

Figure 5a. SEM image of an un-aged RTV-1 sample.
Figure 5b. SEM image of one-week aged RTV-1 sample.

Figure 5c. SEM image of five-week aged sample.
Mass readings gradually decreased in a non-uniform fashion after ten weeks of exposure, with the mass of the fully dried RTV decreasing by about 3% [figure 6]. This process started to occur at about three weeks and increased in intensity with time in both experiments I and II. An FTIR chemical analysis of the flakes indicated the presence of CH$_3$ methyl groups, Si-O-Si bonds [figure 7]. This therefore confirmed the flakes seen suspended in the salt solution were indeed due to RTV-1 material loss.
Figure 6. RTV-1 mass loss over ten weeks with a linear regression.

Figure 7. FTIR spectrum of RTV flakes collected in salt solution after ten weeks (%Transmittance vs 1/cm).
Initial hydrophobicity for all un-aged samples was determined to be HC1 [figure 8a-d, figure 9]. Aged samples after a three-day drying period exhibited immediate and increasing loss of hydrophobicity with increased aging time, progressing from a water droplet with a large contact angle (figure 8a), to no discernible contact angle of the water droplet (figures 8b-d, figure 9). Identical hydrophobicity tests performed before drying resulted in larger apparent losses in hydrophobicity, however the discrepancy in hydrophobicity difference between the two sets of data samples disappeared after five weeks of aging [figure 9].

Figure 8 (a-d). (a) Un-aged sample with HC1 hydrophobicity. (b) one-week aged sample with HC 3 hydrophobicity. (c) five-week aged sample with HC5 hydrophobicity. (d) ten-week aged sample with HC6 hydrophobicity.
Figure 9. Changes in hydrophobicity of RTV-1 samples.

Figure 10: Changes in durometer hardness of RTV-1 samples.
Hardness readings resulted in approximately 40 HA for all virgin samples. The subsequent hardness tests showed significant steady decreases in hardness over ten weeks for all samples [figure 10]. The ten-week aged sample exhibited the greatest decrease in hardness, with a final hardness reading of 18 HA, indicating a hardness loss of over 50%. The percent error in the hardness data was very low irrespective of the testing conditions.

**Discussion**

Experiment I, after 1000 hours of exposure to 3% salt solution at 80°C, showed negative effects on hydrophobicity on each of the samples, as well as surface damage and weight loss, with the most pronounced material degradation occurring in fully submerged samples. All fully submerged RTV samples showed an extreme loss of hydrophobicity, yielded the longest times to regain hydrophobicity, and exhibited the most surface damage and loss of mass. Although losing the most mass, RTV-B showed the greatest resiliency in recovering hydrophobicity.

As a result of loss of hydrophobicity, RTV is more susceptible to damage from other environmental and electrical stressors. The environmental aging stressor of salt can cause damage to the RTV over an extended period of time through not only material degradation, but also by providing an opportunity for further material damage when hydrophobicity is compromised. Significant erosion of material accounted for some of the observed changes in texture, including the observation of material within the salt solution. Aging damage in RTVs appeared to be more extensive in saltwater at 80°C than
under individual and combined UV, moisture, and nitric acid exposure, as seen in pervious experiments [18]. The results of salt aging showed both loss of physical material mass as well as significant reductions in hydrophobic integrity of the silicone rubber material, indicating possible permanent damage to the underlying chemical structure.

Results in experiment II showed a definitive proportional correlation between the reduction in hardness [figure 10] and the loss of hydrophobicity [figure 9] of the tested RTV as a function of aging. These were caused by permanent material damage observable in figure 5d, resulting from chain scission of the RTV material confirmed through the FTIR analysis [figure 7].

Changes in hydrophobicity of RTVs are of particular importance, as highly hydrophobic surfaces repel water, preventing a direct electrical path to the ground. In the data presented in figures 8a-d and 9, significant reductions in hydrophobicity were observed occurring as a function of aging. By estimating hydrophobicity of the aged samples almost immediately after their exposure and after three-day drying, the onset of the loss of recovery was also determined. After approximately five weeks of aging, the RTV material lost the ability to recover hydrophobicity [figure 9].

The difference between the data obtained immediately and three days after drying is a measure of RTV recovery. Therefore, permanent changes in hydrophobicity for samples aged longer than five weeks showed full wetting of the RTV-1 material with no recovery. No error bars are shown in the data in figure 9 as the results obtained using the STRI method are highly subjective, especially for more aged samples. It is likely the
recovery process was eliminated due to an extensive amount of damage to the Si-O-Si backbone and the CH₃ methyl groups. Before five weeks, the low molecular weight silicone oil created by chain scission was able to heal the damage to the surface and restore hydrophobicity after three days of drying. However, after five weeks of aging, compounded damage to the RTV-1 surface indicated any healing effects of the silicone oil were minimal.

It can also be seen in the data that the loss of recovery after five weeks coincided with a significant reduction in hardness, which was estimated to be about 27.5 HA [figures 9, 10]. The corresponding STRI hydrophobicity factor was about HC5. The hydrophobicity measurement after five weeks did not change due to limitations of the STRI method (the surface was too hydrophilic to exhibit any significant changes to its hydrophobicity). However, the hardness data still gradually decreased after five weeks, approaching approximately 18HA (about 50% of its original hardness) after ten weeks. Therefore, two conclusions can be drawn by comparing the effectives of the hardness and hydrophobicity approaches in monitoring aging in RTVs: hydrophobicity measurements might/will not assess aging in badly aged RTVs, and hardness measurements cannot detect the onset of the loss of recovery. However, hardness measurements could be applied in service to estimate the remaining life of non-ceramic insulators, for instance, if the original hardness properties of the RTVs are known. This, however, may be dependent upon many other factors such manufacturing conditions, cross-linking, chemistry, etc.
Chapter Four: Molecular Dynamics Modeling

Introduction

To better understand aging of RTVs in salt solutions, a Molecular Dynamics (MD) model was developed to investigate diffusion of salt water through the silicone-oxygen RTV-1 backbone. This was done to quantify the interaction between saltwater and RTV through diffusion rates of certain molecules and ions associated with the presence of salt water. In addition, the diffusion of nitric and hypochlorous acids across the RTV were simulated in comparison to the salt water compounds.

Methods

Modeling was conducted using BIOVIA Materials Studio. Three different lengths of RTV-1 polysiloxane backbone chains were created with three, five and ten blocks using polymer builder and were optimized for geometry. Amorphous Cell was then used to create analogous structures of polysiloxane with each molecule or ion for diffusion analysis [figure 17]. The COMPASS force field was used for all dynamics calculations.

Each polysiloxane and diffusion molecule or ion variation underwent geometry optimization and annealing at constant temperature and energy, to ensure accuracy. The density and mass ratio of 0.9 Si-O-Si backbone to diffusion molecule in the amorphous cell structure was set, with attention paid to include all variations of three, five and ten
block polymer chains. Annealing of the structure was done at NVT for a constant number of molecules, constant volume, and with temperature set at 80ºC, mimicking the experimental method. Likewise, dynamics calculations were done at NVE for constant number of molecules, constant volume, and constant energy. Materials Studio Forcite Mechanics tools were set to group based calculations for both electrostatic and Van der Waals interactions. Subsequent Forcite calculations were done at each interval for all molecules and ions.

Forcite analysis was conducted to generate the mean squared displacement (MSD) data according to the equation below, where $N_\alpha$ represents the number of diffusive atoms in the model and $D$ denotes the calculated diffusion coefficient [27].

\[
D = \frac{1}{6N_\alpha} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \langle [r_i(t) - r_i(0)]^2 \rangle
\]

Mean squared displacement calculations, based upon the random walk principle, give an estimation of the distance a molecule will travel through a volume over time, calculated as diffusion of a particle through a medium. Calculations are averaged over distance and time to account for voids within a material. MSD was conducted for each diffusion molecule or ion over a period of 10 picoseconds, with the final results graphed in figure 12. The slopes of the curves in figure 12 are the diffusion rates according to the diffusion coefficient of the modeled ions and molecules in the RTV.
Results

The molecular dynamics results shown in figure 12 clearly illustrated the diffusion of hypochlorous acid in the RTV with super-diffusive properties through RTV [figures 12, 13], while nitric acid and chlorine ions exhibit normal diffusion. Water and sodium ions are subdiffusive, indicating limited movement through the RTV material.

Figure 11. Molecular dynamics model of RTV-1 polysiloxane backbone and hypochlorous acid molecules (red/green) in Amorphous Cell after geometry optimization.
Figure 12. Mean squared displacement for hypochlorous acid, chlorine and sodium ions, water, and nitric acid.
Discussion

Hypochlorous acid has previously been shown to cause chain scission damage to polypropylene water pipes through oxidation [26, 26], therefore the potential combination of depolymerization through hydrolysis and oxidization of the interior of the RTV due to hypochlorous acid is a serious and very possible cause of damage to RTVs in NCIs located near coastlines.

Figure 13. MSD vs. time example of diffusion curves for sub, normal, and super diffusivities [23].
The MD results shown in Figure 12 clearly illustrate that the diffusion of hypochlorous acid in the RTV can be classified as super-diffusive (Figures 12, 13), while nitric acid exhibits a strong but normal diffusion, very similar to the chlorine behavior for the same number of propagating molecules. Because hypochlorous acid shows areas of superdiffusion, this indicates directed flow. Since hypochlorous acid has previously been shown to cause chain scission damage to polypropylene water pipes through oxidation [27], the potential combination of osmotic pressure and oxidization of the interior of the RTV due to hypochlorous acid is a possible cause of damage to RTVs in NCIs located close to ocean shorelines. If there is any salt contamination present in combination with low voltage fields on an NCI employing RTVs, this failure mechanism could be much stronger, causing much more damage to the RTVs in comparison with the mechanism based primarily on chlorine ions.

The molecular dynamics diffusion model developed in this study can be used to explain the damage observed in the RTV-1 tested in salt solution [figures 5a-d], as chlorine ions can be classified as diffusive in RTV [figures 12 and 13]. In contrast, water and sodium ions are shown to be sub-diffusive, therefore, it is likely the damage observed in the RTV samples tested in this research was caused by chlorine rapidly diffusing through the RTV network via diffusion. This indicates chlorine is responsible for osmotic pressure and hydrolysis responsible for the cavities, cracks and voids developed in the samples shown in figures 5a-d. Chlorine is also responsible for the scission of the RTV
backbones and the damage to the methyl groups detected by FTIR, and is the main agent responsible for the significant reduction of hydrophobic properties of the RTV.
Chapter Five: Hypochlorous Acid Aging Verification Study

Introduction

To preliminarily verify the molecular dynamics findings, which indicated hypochlorous acid molecules to be more diffusive in RTV than chlorine ions, an initial hypochlorous acid RTV aging study was conducted. RTV aging was assessed in the presence of hypochlorous acid to provide a comparison between previous salt aging experiments and the molecular dynamics model. Because hypochlorous acid is a stronger oxidizer than chlorine, a low concentration of hypochlorous acid was consequently used to compensate for possible stronger oxidizing effects [23]. Therefore, with a minimal concentration of hypochlorous acid solution, an aging assessment of RTV-1 was conducted to verify the molecular dynamics conclusions.

Methods

A single sample of SGK-332 silicone rubber RTV-1 was used, identical to the sample selected for aqueous salt aging in experiment II, with a thickness of 3mm. The sample was placed in 0.046% hypochlorous acid solution at a concentration of 500 ppm of free chlorine, for a total chlorine concentration of 0.05%. Hypochlorous acid solution was maintained at room temperature for the duration of the experiment, and was not subjected to sunlight. The sample was removed from solution and observed for changes
once a week for five weeks. Small sections of the RTV-1 sample were extracted for SEM observation once a week, and mass measurements were re-calculated to account for this discrepancy. Both durometer hardness readings and hydrophobicity measurements were conducted according to previous 3% salt aging experiments, for consistency.

Results

Although not definitive, preliminary results show accelerated formation of cavities and surface erosion when compared to 3% salt solution at 80°C, in addition to extensive damage throughout the sample when viewed in cross section. As seen in figures 14a-c, a sample of RTV-1 aged 1 week in HOCl at room temperature showed surface damage comparable to damage seen in previous RTV-1 samples subjected to 3% salt solution over 3 weeks time at 80°C.
Figures 14 a-c. Top Left: (a) RTV-1 surface after 1 week in hypochlorous acid. Bottom left (b): RTV-1 sample surface after 1 week in 3% salt solution. Bottom Right (c): RTV-1 sample surface after 3 weeks in 3% salt solution.
Figure 15. Z-axis cross section of virgin RTV-1.
Figure 16. Cross section of RTV-1 aged 4 weeks in 0.046% hypochlorous acid.

SEM cross-section image [figure 16] of RTV aged in hypochlorous acid after four weeks shows definitive material damage when compared to a virgin cross section sample image [figure 15]. Material degradation is extensive and material loss is assumed due to measured sample mass loss and the presence of minute flakes in the hypochlorous solution, indicating material degradation due to hydrolysis. Approximately 4% mass loss was measured after 5 weeks of aging in hypochlorous acid, compensating for mass loss from sample removal for SEM analysis. The flakes seen in the hypochlorous acid
solution are similar to those seen in previous 3% salt solution aging experiments, although smaller in size and shape.

Preliminary hardness and hydrophobicity measurements taken over 1 week aging time in 0.046% hypochlorous acid solution also indicated a loss of hydrophobicity: from a measurement of HC1 in virgin samples to HC3 in one week aged samples. Hardness values decreased from 38 HA to 31 HA over a one week period, with the five week aged sample measuring 21HA. An SEM image of RTV-1 cross section after four weeks aging in HOCI also shows noticeable material damage compared to a virgin RTV-1 cross section, correlating with a durometer hardness measurement of 22 HA. Although not yet conclusive, initial experimental results indicated significantly accelerated aging of RTV-1 in hypochlorous acid compared to 3% salt solution despite the fact that the aging test in hypochlorous acid being was conducted at room temperature.

Discussion

Although the exact mechanisms of RTV-1 degradation upon exposure to hypochlorous acid have not been investigated in the current literature and therefore are not yet known, a clear accelerated aging effect resulting in material damage is evident. Development of cavities and cracks are noticeable at one week, compared to three weeks for samples aged in 3% aqueous salt at 80°C. Additionally, an accelerated decrease in material hardness at five weeks in HOCI is comparable to nine weeks in 3% salt solution.
Although the evidence from SEM observations is not conclusive, the accelerated aging of RTV through material degradation is indicative of accelerated diffusion of hypochlorous acid, particularly when accounting for the lower hypochlorous acid concentration (500ppm) used. These results are therefore consistent with the molecular dynamics model developed in this study, which indicated accelerated material aging might be possible due to super diffusion of molecular hypochlorous acid compared to chlorine ions. Probable cause of material damage due to HOCl is likely due to oxidation and resulting hydrolysis; however further research and investigation are still required for a conclusive assessment.
Chapter Six: Summary and Conclusions

Summary

Damage to RTV-1 silicone rubber is a result of contact with aqueous salt resulting in hydrolysis. Aging of the silicone rubber material is accelerated in the presence of salt, resulting 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 resulting loss of stiffness and mechanical strength. Therefore, an insulator that is exposed to salt fog or mist can be at risk of failure due to aging of the RTV-1 seal, resulting in eventual water ingress to the insulator core.

Consequently, the formulations of caulk and insulator sheath are critical to their ability to withstand environmental stressors. The loss of hydrophobicity illustrated in this research is of particular importance, as RTVs are more susceptible to damage from other environmental and electrical stressors when hydrophobicity is lost. Therefore additives of nano or micro particles to the silicone rubber formula, which may protect against pollutant molecule ingress, may be of particular importance, to extend longevity of hydrophobicity in the silicone rubber material. 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 through not only material degradation, but also by providing an opportunity for more damage when hydrophobicity is compromised. The significant
decline in mechanical properties should also be taken into account, as the combination of aging factors can lead to a shorter in-service life.

One way of measuring the aging processes in RTVs subjected to various environments is through changes in mass. In this study, all RTV samples lost mass in both the salt aging and hypochlorous acid experiments, which indicated material degradation, as a result of hydrolysis. Several processes can be determined responsible for the irregular nature of mass loss in the RTV, including water and salt absorption, and subsequent water desorption by drying, resulting in RTV mass loss by flaking. This is illustrated in figure 17 by analyzing the individual effects of RTV hydrolysis and its influence on the final mass loss. RTV water absorption and desorption is assumed to be Fickian in nature, with the resulting mass loss curve illustrated in figure 17. It can be compared with the experimentally obtained mass loss curve presented in figure 12.
Figure 17. An illustration of several processes involved during salt aging.

The combined action of the aging experiments resulted in a very similar final mass loss curve, as seen in both figures 12 and 17. Although samples were allowed to dry thoroughly before mass measurements, the material mass results were affected due to the diffusion of salt through the RTV material, which remained in the material after drying. Therefore, measurements of mass lost during sample aging are only partially indicative of material damage.

It has been shown in this study that measuring mass loss, reductions in hydrophobicity, and hardness both experimentally and numerically can be used to assess the rate of aging of RTV-1 material subjected to salt solutions at elevated temperatures. Determining RTV-1 hardness by using a durometer could be an effective measurement of aging of RTVs in NCIs employed on transmission lines. Hardness has been found to gradually decrease with aging with small experimental scatter even in an extensively
aged RTV-1 material. In the case of the RTV-1 investigated in this research, the reduction in hardness after ten weeks of exposure to 3% salt solution at 80°C was found to be approximately 50%.

Conclusions

The molecular dynamics simulation of diffusivities of molecules and ions, which are likely to be present on coastal transmission line containing RTV-1, indicates diffusion of aging agents chlorine and hypochlorous acid are the main contributor in silicone rubber aging. In the presence of salt and water at elevated temperatures, chlorine ions appear to have much higher diffusivities in comparison with sodium ions and water molecules. Therefore, under the combined effect of water, salt and temperature, chlorine ions are proposed to be responsible for the damage observed in the RTV-1 tested in this research. However, chlorine is not as diffusive as hypochlorous acid, as illustrated in the hypochlorous acid aging experiments, which showed accelerated aging of RTV-1 in a minimal hypochlorous acid concentration of 0.046%. This was illustrated in a molecular dynamics diffusion model of RTV aging in the presence of salt, water, nitric acid, and hypochlorous acid, which concluded accelerated diffusion of hypochlorous acid in RTV. Consequently, even at a lower concentration, 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.
Works Cited


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