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Silicone rubber aging in electrolyzed aqueous salt environments

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In this work we suggest an entirely new and highly transformative model of silicone rubber aging caused by the presence of electrolyzed aqueous salt, leading to the formation of hypochlorous acid in-service on energized High Voltage (HV) transmission lines in coastal environments. The model was subsequently verified by aging one-component Room Temperature Vulcanized (RTV-1) rubbers in commercially produced hypochlorous acid and an electrolyzed aqueous salt environment at room temperature. Molecular dynamics models of the rubbers with silica fillers were conducted to offer at least partial explanations of the types and extents of aging observed in the RTV-1 samples tested in the aqueous salt solutions. We have shown that the above environments are highly damaging to the silicone rubber polymer network and significantly more destructive than non-electrolyzed standard aqueous salt solutions at higher temperatures. The main observations of this research should greatly contribute to a better understanding of complex degradation mechanisms of modern HV silicone rubber compounds, which are utilized in some of the most critical lines and substations all over the world.

1. Introduction

1.1. Application of silicone rubbers on high voltage transmission lines

Polymers and their composites can be commonly found on modern high voltage (HV) transmission lines [1–30]. For example, room temperature vulcanized (RTV) silicone rubbers (SIR) [1–14] are used in Non-Ceramic Insulators (NCIs) [15–24] supporting some of the most critical lines across the world. Mechanical, electrical and chemical catastrophic failures of the polymer based HV transmission components have been occurring sporadically in different parts of the world [15,16,22], including the US, bringing down energized transmission lines and creating blackouts, ground fires, and many other disasters. Due to the exceptionally aggressive nature of the HV transmission line environment, it has been extremely difficult to predict and prevent these failures when designing state of the art modern polymer based components for HV applications. The primary objectives of this work are to properly explain SIR aging in aqueous salt environments and associated potential in-service failures of modern transmission systems using highly interdisciplinary and transformative approaches.

1.2. Silicone rubber aging in high voltage environments

In service aging of SIR sheds and sealants used in HV applications is well known [1–14]. Damage can result from various environmental and electrical factors such as salt, acid, UV, corona discharges, leakage currents, etc., which routinely cause damage to HV NCIs. RTV-1 is a one-component based caulk and is similar to RTV-2 two-component SIR. RTV-1 and RTV-2 are both found on NCIs and denote two chemical methods for the production of cross-linked SIR materials. Both RTV materials are comprised of large amounts of polydimethylsiloxane (PDMS): a silicon based polymer with hydrophobic methyl groups and commercial versions include large amounts of silica fillers as binding agents. RTV-1 is commonly used to seal the end fittings of high voltage NCIs, while HV sheds and housings are comprised mainly of RTV-2. RTV-1 makes up the primary portion of the triple seal system (Fig. 1a), which prevents water ingress into the fiberglass core through the fitting [1].

When an RTV-1 sealant is compromised by aging (Fig. 1a), improper manufacturing, vandalism, etc., water will penetrate into the fittings causing either insulator failures by brittle fracture (Fig. 1b) and line drops of energized lines, or electrical failures (Fig. 1 c) [3,11,22] also leading to major catastrophic failures of the lines. The processes illustrated in Fig. 1 a–c are very complex with continuously changing mechanical, electrical and environmental stresses.

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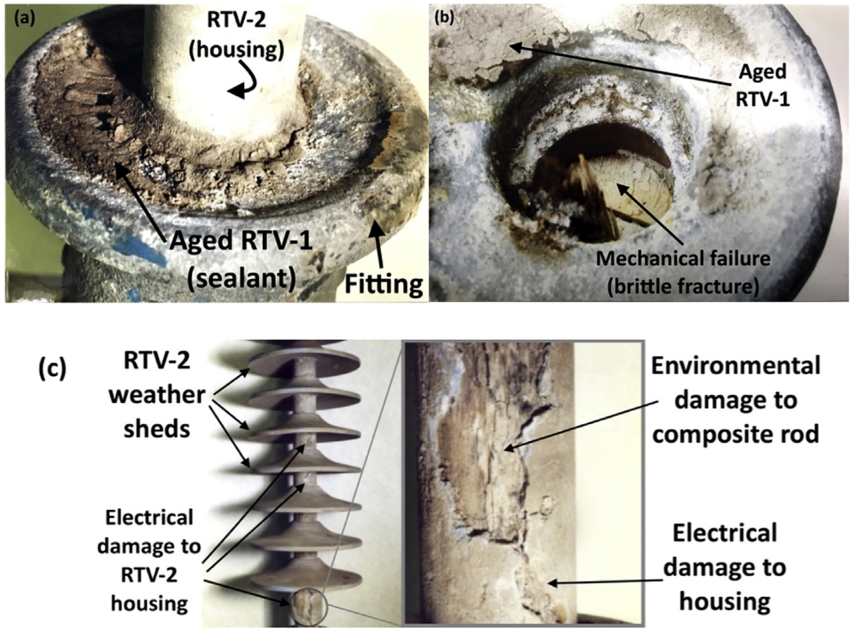

Fig. 1. (a–c). (a) Failure of RTV-1 sealant in a HV NCI causing catastrophic insulator and line failure by brittle fracture (b) and electrical failures (c) of a 500 kV transmission line in the Monterey Bay area in California, USA [3,11,22].

1.3. Silicone rubber aging in the presence of aqueous salt

Salt contamination in coastal environments is an identified cause of damage to RTV SIR materials in NCIs, and salt exposure can decrease the hydrophobicity of RTVs over time [3]. 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) [1,2]. Historically NCI failures in coastal environments have generally been assumed to be solely caused by chlorine damaging the PDMS network [1–4].

Our previous aging experiments have indicated that permanent and significant material damage to RTV-1 can occur after ten weeks in 3% NaCl saltwater at 80 °C. This condition caused surface degradation, which occurred in the form of voids beginning at two weeks aging time [1,2]. 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 [1,2]. 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 [1]. Current literature indicates chain scission in PDMS produces cyclic and linear low weight chains, resulting in low molecular weight (LMW) silicone oil [2]. This oil can account for some of the healing properties seen in SIRs, and is the primary explanation for the recovery of hydrophobicity seen in experimental results [1,2].

2. Proposed new model of aging of silicone rubbers in electrolyzed aqueous salt environments

Under the right conditions, a fully drenched insulator may create an electrolyzed saltwater environment in the presence of ocean salt, moisture, and leakage currents. Because RTVs are commonly used on energized HV insulators where corona arcing and leakage currents are prominent, additional aging due to secondary reactions could also occur. Leakage currents [20,24] on contaminated transmission lines could easily exceed ~ +1.63 V on or near the energized ends, the voltage necessary for reactions described below. This unique energized environment could lead to a secondary reaction in standing NaCl salt water, resulting in the formation of highly oxidizing hypochlorous acid (HOCl) [1].

The electrolysis of salt water creates products through the overall reaction: $2NaCl + 2H_2O \rightarrow Cl_2 + 2Na^+ + H_2 + 2OH^-$. This results in the potential formation of highly oxidative hypochlorous acid as chlorine hydrolyses in water through the following equation: $Cl_2 + H_2O \rightarrow HClO + HCl$ [31,32]. 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 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., MgCl, commonly used for deicing purposes). Depolymerization as a result of hydrolysis in NaCl aqueous environments is responsible for the degradation of RTV type polymers and monomer chains, resulting in the decrease of their average molecular weight and structural integrity [1,2]. Available literature 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 [33]. In our work, we compare for the first time the response to aging of an RTV-1 compound under HOCl and aqueous NaCl salt exposures.

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 3.5×10^{-8}, and its power of oxidation is 1.1 compared to that of chlorine of 1.0 [32–34]. HOCl therefore rapidly dissociates into damaging hydrogen and hypochlorite ions OCl^- and H^+ in solution, which can re-associate back into the HOCl original form under ambient conditions [32,33].

To verify the new model of SRI aging, a commercially available RTV-1 compound was subjected to commercially available hypochlorous acid and electrolyzed 3% aqueous salt solutions to mimic a typical coastal environment. The presence of electrolyzed salt solutions on HV NCIs cannot be questioned. What can still be