Review

Self-Healing Silicones for Outdoor High Voltage Insulation: Mechanism, Applications and Measurements

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Abstract: This paper discusses the state of the art in the application of self-healing silicone-based materials for outdoor high-voltage insulation. Both the dynamic behavior of the dimethyl side groups of silicone rubber and the diffusion of a bulk siloxane to maintain low surface energy are respectively reported as intrinsic mechanisms responsible for the self-healing of silicone rubber. Localization, temporality, mobility, and the type of synthesis are the aspects defining the efficiency of the self-healing ability of silicone rubber. In addition, the deterioration of the self-healing ability with filler loaded into silicone rubber insulation housing composites is discussed. Taking the self-healing property into consideration among the other properties of silicone rubber insulators, such as tracking and erosion resistance, can be a useful design practice at the material development stage. Hydrophobicity retention, recovery, and transfer measurements are discussed as useful indicators of the self-healing ability of silicone rubber. Nevertheless, there remains a need to standardize them as design tests at the material development stage. The paper is intended to shed the light on the hydrophobicity recovery, a key material design parameter in the development of silicone rubber outdoor insulating composites, similar to the tracking and erosion resistance.

Keywords: self-healing; silicone rubber; fillers; outdoor insulation

1. Introduction

Self-healing polymers have gained interest for their wide range of applications. The term "Self-healing" refers to polymers' extrinsic or intrinsic self-repairing ability to regain their structural or molecular integrity after damage, thereby increasing their life expectancy, durability, and enhancing their performance under different conditions [1]. At the molecular level, the self-healing mechanism can be chemical, physical, or a combination of both. Physical-based self-healing could be realized with inter-chain diffusion, shape-memory effects, phase-separated morphologies, and the usage of superparamagnetic nanoparticles [2]. Chemical-based self-healing may be achieved by incorporating dynamic bonds, such as free radical, covalent, or supermolecular bonds. The release of embedded or encapsulated fluid in the polymer morphology due to damage represents a combination of both physical- and chemical-based self-healing [3].

In general, three different aspects could define the efficiency of the self-healing ability in polymers, i.e., localization, temporality, and mobility. Localization refers to the scale and the position of the damage. For example, scratches, cracks, and cuts could be considered superficial damages, whereas, de-bonding, delamination, or molecular breakage might be examples of deep or catastrophic types of damages. Temporality is the time needed for

damage repair, which could be reduced by enhancing the mobility of healing agents in the polymer. Mobility accelerates the diffusion of healing agents in the polymer towards the damaged area and helps reform broken bonds [4,5].

An additional important aspect that has been highlighted is the synthesis, which can be either extrinsic or intrinsic [5]. As shown in Figure 1a, the intrinsic synthesis is based on the existence of dynamic bonds that could reorient to reverse the deformation or the damage of the polymer. Dynamic bonds could be either covalent, such as disulfide bonds, or non-covalent, such as hydrogen bonds [6,7]. The intrinsic reversibility of the polymer matrix could often allow a localized self-healing ability, stimulated with several factors such as light, heat, and electricity [8,9]. The intrinsic approach has been utilized in silicones, different rubbers, and polyurethanes [10,11].

On the other hand, as shown in Figure 1b with extrinsic synthesis, the curing agents are encapsulated inside the polymeric host matrix until they are released to seal fractures in the polymer or fill micro-channels [12], nanotubes [13], or other micro containers that may exist in the polymeric matrix [12–14]. This extrinsic approach has been commonly implemented in thermosets such as epoxy resins [15]. It should be noted that this extrinsic approach may restrict the durability of self-healing ability, i.e., to only last until capsules or channels are emptied during the healing process.
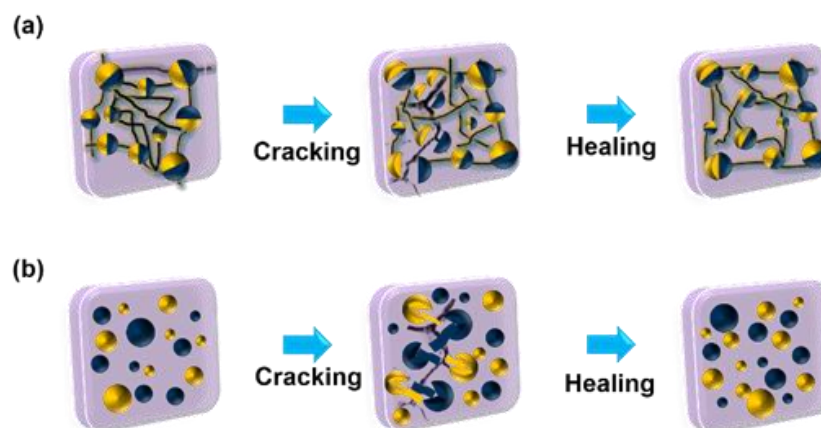

Figure 1. Schematic illustration of intrinsically self-healing polymer systems with (**a**): reversible chemical bonds and (**b**): self-healing through exhaustion of healing agents [16]. Reprinted with permission from Ref. [16]. Copyright 2017 John Wiley and Sons.

In general, polymeric outdoor insulators used in power transmission and distribution systems are essentially composed of a fiberglass core, metallic end-fitting, and the polymeric housing material. Both the geometry and the material designs need to be qualified in the laboratory for successful performance in the field. The hydrophobicity of the polymeric housing material is responsible for the superior pollution performance reported for polymer insulators as compared to conventional cermic insulators. In particular, silicone rubber is a commonly employed insulation housing material in outdoor high voltage insulation applications, for its superior electrical performance, particularly in polluted conditions. This superior performance has been mainly attributed to the ability of silicone rubber to retain hydrophobicity after wetting, which clearly falls within the definition of a self-healing ability [17].

Another important design factor of silicone rubber outdoor insulators is their geometry, which is mainly dependent on the creepage distance selection with respect to the pollution characteristics of the region. Other geometry design parameters include the insulator profile and size of the weathersheds of the housing material that can also influence the performance of silicone rubber insulators. More information on the design and application of silicone rubber insulators can be found in [18].

While an extensive amount of studies have been conducted on the the application of fillers to improve the material design in terms of the tracking and erosion resistance of silicone rubber insulation housing materials, relatively little emphasis has been given to the self-healing ability of silicone rubber. A lack of information is particularly evident about the nature of self-healing mechanisms of silicone rubber insulators, the corresponding various contributing factors at the material development stage and the proper material screening methods that need to be employed in order to evaluate the self-healing property of silicone rubber for outdoor high-voltage insulation applications. Therefore, this paper presents the state-of-the-art development and evaluation of self-healing silicone rubber for outdoor high-voltage insulation applications.

2. Self-Healing Mechanism of Silicone Rubber Insulators

Silicone rubber insulators are hydrophobic, i.e., they possess low surface energy, which restricts the condensation of contaminants to form a bead-like shape with high surface contact angles. The hydrophobicity of silicone rubber has been a key material aspect considered for silicone rubber in the selection for outdoor high-voltage insulation applications to suppress the formation of conductive paths of moisture and contamination that may give rise to leakage currents and, eventually, insulator flashover or degradation. Two types of silicone rubber, namely high-temperature vulcanized (HTV) and room-temperature vulcanized (RTV) silicone rubber, have been widely used. The base polymer of both is polydimethylsilixane (PDMS) (Figure 2). The mian difference is in the curing conditions and the application. HTV silicone rubber is cured under temperature and pressure and widely used for insulator weathershed and sheath materials, whereas RTV is cured in room temperature and used as a coating material for conventional ceramic insulators in order to improve the pollution performance.
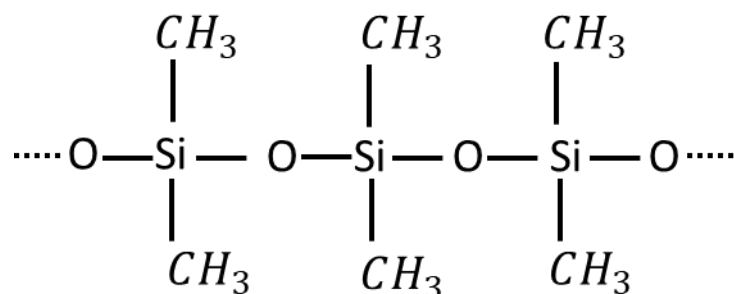

Figure 2. Basic molecular structure of PDMS.

It should be noted that HTV silicone rubber has a higher molecular weight. In addition, HTV silicone rubber has a better erosion resistance than RTV silicone rubber. It should be noted that inferior erosion resistance has been repoted for room-temperature vulcanized (RTV) silicone rubber insulators at their early stage of application as compared to other polymeric housing materials such as ethylene propylene diene monomer (EPDM). The inferior erosion resistance was attributed to the low filler level employed in RTV silicone rubber [19,20]. Today, housing composites of modern silicone rubber outdoor insulators are made from high-temperature vulcanized (HTV) silicone rubber and contain alumina tri-hydrate filler at high levels at 60 wt.%, which has remarkably improved the erosion resistance [18,19].

With the self-healing ability of silicone rubber, the hydrophobicity could be retained after aging in service. The life expectancy of room temperature vulcanized silicone rubber coatings of outdoor insulators has been linked to the required time to restore the hydrophobicity of the coating after wetting [21], rather than the degree of hydrophobicity as measured by the surface contact angle. The hydrophobicity recovery of the silicone rubber surface may occur due to the diffusion of low-molecular-weight (LMW) siloxanes. As illustrated in Figure 3, the diffusion mechanism could be generally interpreted with the

following five steps: surface rearrangements, surface approach, wetting, diffusion, and randomization. Both surface roughness and topography play major roles in the surface rearrangements, in addition to the distribution, molecular weight, and availability of the siloxane chains in the silicone matrix [22].
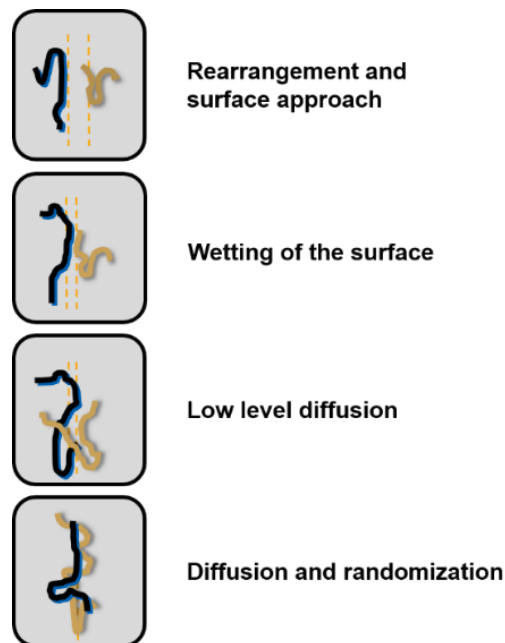

Figure 3. Schematic diagram of the healing process across a polymer interface via molecular inter-diffusion [23]. Reprinted with permission from Ref. [23]. Copyright 2008 Elsevier.

Surface damage could create interfacial regions where the diffusion rates of the siloxane chains and their local mobility determine the characteristics of the self-healing process [24]. An interfacial macromolecular interpenetration has been explained for the diffusion process of the siloxane from the bulk to the surface of silicone rubber, and accordingly, a diffusion rate of 10^{-5} m/min has been determined. In addition, the average inter-diffusion depth (X) of siloxane chains as a function of time (t) can be expressed as:

$$X\left(t\right) = X_{\infty}(t/t_r)^{1/4} \tag{1}$$

where t_r is the repetition time (directly proportion to the molecular weight of the chains to the third power) [1].

With such an expression, it could be speculated that shorter chains may exhibit higher mobility and more flexibility, thereby promoting the self-healing process. It should also be mentioned that surface macromolecules depict higher mobility due to the higher degree of freedom than bulk. This enhanced mobility could improve diffusion performance, realized with a lower glass-transition temperature (T_g). As T_g decreases, the segmental chain mobility improves, and this can be obtained by using plasticizing solvents that promote diffusion [25].

The dynamic methyl bonds in the siloxane chains may also promote an intrinsic form of the self-healing mechanism on silicone rubber insulators. Kantor et al. obtained a self-healing silicone elastomer with ring-opening polymerization in the 1950s [26]. The resulted silicones showed a self-healing ability when heated to 90 °C for 24 h. Schmolke et al. enhanced the self-healing ability by controlling the crosslinking density and the quantity of the ionic initiator, thereby obtaining the self-healing ability at room temperature in a shorter time [27].

Zheng and McCarthy discovered that the cross-linked PDMS elastomer could be converted to a living elastomer by adding a basic catalyst, thereby allowing the healing

mechanism to be based on an anionic initiated siloxane equilibration reaction. In other words, the siloxane bonds could be cleaved and re-established via adding the basic catalyst to obtain dynamic cross-linked silicone elastomers [28].

Zheng and MaCarthy also prepared a siloxane elastomer that can be cut and healed to the same original strength through a siloxane equilibration, as shown in Figure 4. The main obstacle limiting applying such an approach is the need for an external triggering source such as light, heat, or additives that could initiate the healing process [28]. It has proven challenging to achieve more than one advantage in the obtained silicone with such an approach, such as combining fast self-healing, high stretchability, and non-toxicity. Furthermore, many of the irreversible covalent bonds added to the polymer chain do not have the capability of recovery after the breaking.
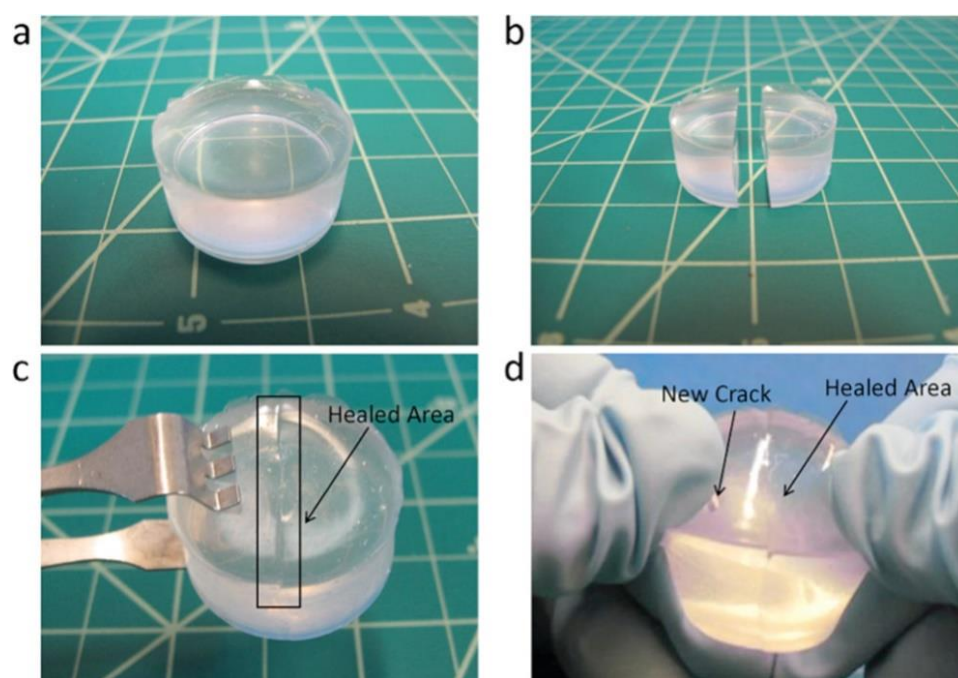

Figure 4. Optical images of (**a**) a cylindrical PDMS sample, (**b**) the sample was cut in half with a razor blade, (**c**) after healing at 90 °C for 24 h, and (**d**) deformation of the healed cylinder showing crack occurring at a different place than the healed area [24]. Reprinted with permission from Ref. [24]. Copyright 2012 American Chemical Society.

Molecular dynamic simulation can shed light on the self-healing recovery mechanism. Recently, Shemella et al. [29] studied the role of LMW siloxanes on the self-healing recovery mechanism of PDMS-based high-voltage insulators using molecular dynamic simulation. The exposure of PDMS to corona discharge in high humidity leads to the molecular degradation of the PDMS chains via the oxidation of the CH3 groups or the formation of silicate chains. These molecular changes lead to loss of hydrophobicity, as confirmed by the decrease in the contact angle. On the other hand, the presence of the cyclic LMW D4 and D8 molecules in PDMS was essential for the hydrophobicity recovery by diffusion of these LMW cyclic molecules to the surface, chemically solvating the surface, and insulating the PDMS surface from humidity (Figure 5).
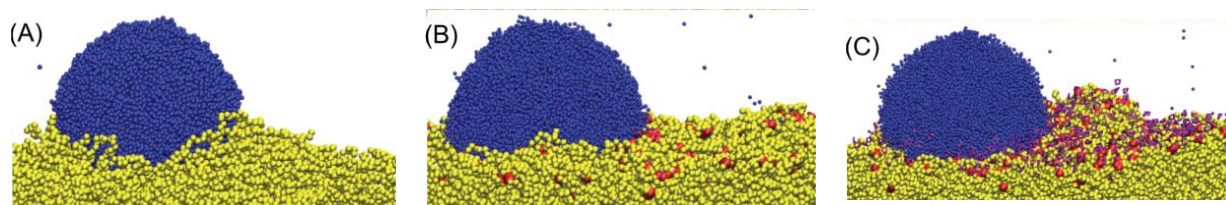
Figure 5. Graphical representation of the PDM changes during and after exposure to corona charges: (**A**) the surface of unaged PDMS is hydrophobic; (**B**) the presence of the oxidized methyl groups ($\sim COO^{2212}$) and Na^+ counter ions on the surface of aged PDMS make the surface hydrophilic, and (**C**) the diffusion of the small (D4) molecules to the oxidized surface leads to an increase in the contact angle and recovery of the surface hydrophobicity [29]. Reprinted with permission from Ref. [29]. Copyright 2012 American Chemical Society.

2.1. Effect of Base Material

The chemical structure of the silicone chains and the bonding type could control the self-healing ability of silicone rubber insulators. Hydrogen bonds have been introduced into silicone networks to synthesize silicone rubber with healing properties at room temperature. Liu et al. fabricated a novel self-healable silicone rubber with H-bond assisted multiphase assembly of siloxane oligomers [30]. Kang et al. used the multiple-strength H-bonds interactions between siloxane molecular networks and synthesized silicone rubber materials with good mechanical properties. Yet, the healable materials showed a long healing time, more than 24 h, in order to achieve 90% healing at room temperature, limiting their applications [31]. Such limited self-healing efficiency could have resulted from the hard segmentation added to the polymer backbone with the dense hydrogen bonds. The degree of crosslinking may therefore have risen, thus resulting in less free space available for the movement of segments.

The synthesis of self-healing silicone elastomer with three dynamic chemical bonds of hydrogen, disulfide, and metal-ligand bonds was conducted by Liu et al. [30]. The thioctic acid was used for the first time in silicone materials to form a self-healing silicone rubber with a reversible cross-linked network. The novel fabricated elastomer showed an autonomous self-healing property, excellent mechanical properties, strong adhesion affinity, thermal stability, and anticorrosion. Thus, it could be used widely for wearable electronics and soft robotics applications.

Strakowska et al. investigated the self-healing effect of polyhedral oligomeric silsesquioxanes (POSS) in silicone rubber, functionalized by acidic or amino groups. The POSS were incorporated into the silicone rubber matrix to study and compare the effect of each system on the self-healing of silicone rubber. In addition to the enhanced mechanical and barrier properties, this self-healing ability could be explained based on the concept of mobile network bonds formed by the interaction between the small-molecule compounds that contain acidic and basic functional groups compatible with silicone rubber. Shan also introduced a system which resulted in self-cleavage property with the ethylene bridges and the silanolate end groups [32].

2.2. Effect of Fillers

Fillers can be added to outdoor silicone rubber housing to reduce the cost of the composite or enhance several properties such as thermal conductivity, mechanical properties, and erosion resistance [33]. The primary use of fillers in silicone rubber insulators is to reduce the cost by partially replacing the expensive silicone. These fillers can be used as flame retardants to improve the erosion resistance. The two main fillers employed for outdoor insulation application are quartz and ATH. Both fillers were shown leading to the same thermal conductivity of the silicone rubber composite [33]. Quartz is a fraction of the price of ATH and therefore can be advantageous. However, it has been shown that the water of hydration of ATH may suppress erosion failure in the inclined plane test under

the severe dry-band arcing produced at 4.5 kV [34]. Nano-sized fillers, such as fumed silica, may be used in small amounts as additiives to improve the mechanical properties of the silicone composite.

However, filler addition may retard the self-healing property of silicone rubber composites simultaneously. Fillers may act as a "diffusion barrier" for LMW siloxanes, thus slowing down the process of hydrophobicity recovery [35,36]. The extent to which the filler affects the hydrophobicity recovery depends on the filler type, concentration, particle size, and dispersion in the polymer matrix, the degree of adhesion with polymer siloxanes, and the amount of free LMW siloxanes [37,38]. Therefore, it is important to understand the influence of the filler addition on the diffusion mechanism of LMW siloxanes in silicone rubber composites.

The addition of micro alumina trihydrate (ATH) fillers to silicone rubber could obstruct the diffusion of the LMW siloxanes chains because of strong intermolecular hydrogen bonding between micro-ATH and polymer siloxanes. This may immobilize siloxane chains and cause slow hydrophobicity recovery [39,40]. Several studies have shown that silicone rubber filled with 40 wt.% micro-ATH fillers displayed slower hydrophobicity recovery than unfilled silicone rubber after prolonged exposure to corona aging [41,42]. At 20 wt.% micro-ATH level, silicone rubber recovers in an aging test relatively slower than unfilled silicone rubber [43]. The diffusion time constant for LMW siloxanes migration directly reflects the rate of hydrophobicity recovery in silicone rubber. It has been found in various studies that the diffusion time constant increases with increasing micro-ATH filler concentrations in silicone rubber, and higher ATH concentrations are responsible for slowing down siloxanes diffusion [44,45]. This could be due to two reasons; first, the PDMS cross-section available for siloxanes migration decreases with increasing filler levels. Second, the percolation path for siloxanes diffusion increases at high filler concentrations.

The inclusion of nano-fillers with increasing concentrations can also change the self-healing property of silicone rubber composites. Venkatesulu et al. performed 25 h and 50 h corona aging on silicone rubber nanocomposites and found a low percentage (1 wt.%) of precipitated nano-silica (SiO_2) resulted in improved hydrophobicity recovery compared to silicone rubber containing higher percentages of nano-SiO_2 at 2 wt.% and 3 wt.% [46]. Increasing the fumed silica contents is reported to reduce the speed of hydrophobicity recovery of silicone rubber [47]. In another work [48], silicone rubber filled with nano-sized alumina at 1 wt.%, 2.5 wt.%, and 5 wt.% showed a slightly slower recovery rate than unfilled silicone rubber.

It has been proposed that reinforcing the silicone rubber matrix with nano-sized silica may restrict the movement of the siloxane chains and obstruct their diffusion [49]. Figure 6 depicts the general schematic representation of diffusion of LMW species to the surface of silicone rubber filled with different percentages of nanoparticles. Note that Figure 6 only illustrates an ideal situation where nano filler are uniformly dispersed within the matrix. In a more realistic sitituation the matrix may include both mico- and nano-sized fillers and agglomeration may take place, which may affect the diffusion process. Therefore, it is important to understand the diffusion mechanism in different realistic scenarios. An insignificant effect of fillers on the degree of hydrophobicity (surface contact angle) of silicone rubber after aging has been observed, whereas a significant effect was observed slowing down the recovery of the hydrophobicity after aging [50]. It can be concluded that for a particular filler size, there may be a need to determine the required filler concentration that best optimizes erosion resistance and self-healing of silicone rubber composites for outdoor high-voltage insulation applications.
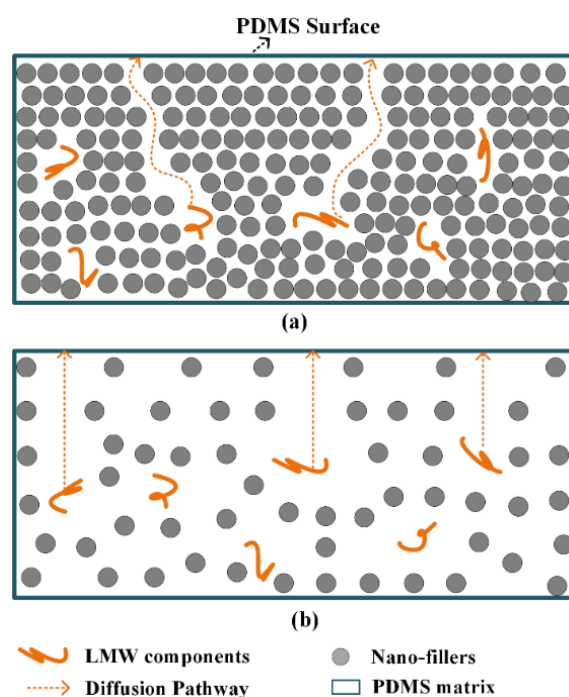
PDMS Surface

Figure 6. Schematic of LMW diffusion in silicone rubber with (**a**) high filler contents (**b**) low filler contents.

3. Effect of Electrical and Environmental Stresses on Self-Healing Silicone Rubber Insulators

It is widely accepted that the amount of LMW siloxanes remaining in the bulk of the silicone rubber material directly contributes to its hydrophobicity recovery [51]. Most researchers agreed that the diffusion of short-length intrinsic LMW siloxanes is the dominant mechanism responsible for the recovery of hydrophobicity of silicone rubber. In [52], it was described that the diffusion of highly mobile LMW siloxanes takes place because of the concentration difference between the surface and volume of the polymer. Apart from the difference in their concentration, the diffusion rate also depends on the formation of the diffusion channels on the surface of silicone rubber [53]. Furthermore, the hydrophobicity recovery of silicone rubber depends upon the existing amount of LMW siloxanes and their speed of diffusion from the bulk volume of the polymer material to the hydrophilic surface. These LMW siloxanes are initially formed during the polymerization process of silicone rubber. The aging of silicone rubber could either prevent the hydrophobicity recovery by the decomposition of LMW siloxanes and the crosslinking reactions or facilitate the recovery process through generation of LMWs from the scission of long backbone chains [54,55]. In most studies [56–58], it has been shown that when a silicone rubber surface is covered with a non-hydrophobic contamination layer operating in a highly contaminated environment, the uncrosslinked LMW components move to the surface and penetrated into the contaminants, thereby varying the contamination layer from hydrophilic to hydrophobic. The LMWs can be linear or cyclic chains, with the linear LMW chains found to be more effective for penetrating into the contaminants [59]. In short, the LMW diffusion and hydrophobicity can be influenced by the silicone rubber composition, aging mechanisms, type and composition of contaminants, and environmental factors [60,61].

Various environmental stresses, along with electrical stress, affect the hydrophobicity recovery of silicone rubber. First, it is essential to understand how corona aging influences hydrophobicity recovery. A silicone rubber surface recovers its hydrophobicity when stored for sufficient time in dry air after corona exposure [62]. Understanding the self-healing of silicone rubber after varying corona duration is complicated, and many factors affect the hydrophobicity recovery of the silicone rubber after being exposed to corona. It is worth mentioning that the hydrophobicity recovery speed depends on corona exposure time and

physical and chemical variations on silicone rubber surface [41,63]. It has been found that recovery speed in a long-corona aging test is not continuous and differs with corona aging time [64,65]. In addition, the hydrophobicity recovery becomes accelerated during the early stage of corona aging, possibly due to the increased production of LMW siloxanes. The LMW cyclic silicone oligomers are also generated as by-products of aging due to corona discharges that facilitate quick recovery of hydrophobicity [66].

There is also a general agreement that corona discharges cause surface oxidation, which leads to the formation of a hydrophilic silica-like (SiO_x) layer on the surface of silicone rubber. This layer retards the migration of LMW siloxanes to the surface and thereby the hydrophobicity recovery [67]. However, after a certain corona aging time, cracks start appearing on this highly oxidized brittle surface layer, which is due to a build up of mechanical deformation or internal stresses caused by cross-linking reactions in silicone rubber. It can be demonstrated that silica-layer cracking facilitates the migration of LMW siloxanes to an oxidized silica layer and enhances the hydrophobicity recovery rate [46,68,69]. Figure 7 depicts the schematic representation of the mechanisms involved in hydrophobicity recovery of corona-aged silicone rubber. In [70], it was shown that a rise in the recovery rate occurs at the inception of cracking of brittle silica layer. Furthermore, it can be the deduced that the development and cracking of this layer may significantly influence the transport of LMW siloxanes and, therefore, the recovery rate of hydrophobicity.
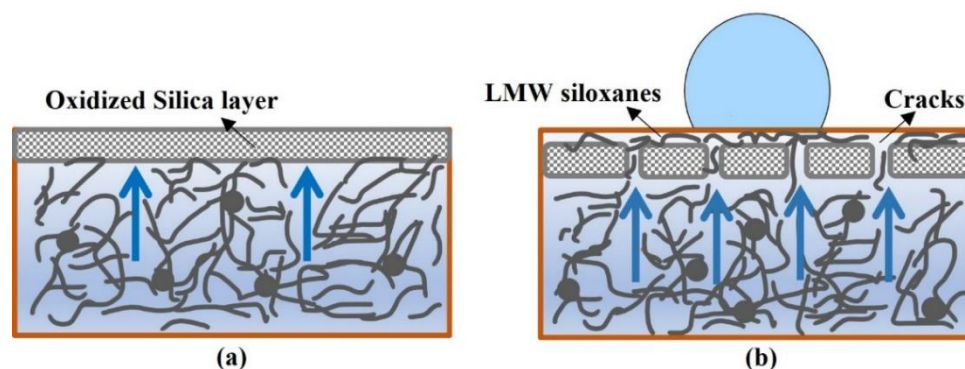

Figure 7. Schematic of mechanisms involved in hydrophobicity recovery of silicone rubber under corona aging (**a**) Silica layer retarding the LMW diffusion (**b**) Cracks in silica layer promoting the LMW migration and covering the silica layer.

There may be a possibility that after corona aging reaches a definite time, the hydrophobicity does not recover completely even if the recovery time is dramatically long enough [59]. The long-duration corona discharges can also increase the speed of the hydrophobicity recovery of silicone rubber previously decreased by ultraviolet (UV) and heat stresses. In addition, the deposition of the dry hydrophilic contamination layer on silicone rubber surface after UV and corona aging severely reduces the surface hydrophobicity, although only temporarily [71]. It turns out that aging caused by UV and corona stresses applied previously decreases the recovery speed of hydrophobicity lost by the contamination layer mainly because of the reduction in highly mobile LMW siloxanes that directly contribute to hydrophobicity recovery. As the surface is completely covered with a contamination layer, the hydrophobicity of the contaminated surface gradually recovers due to diffusion of inherently available LMW contents from silicone rubber onto the surface of the contamination layer [60,72]. Hence, it can be implied that the recovery rate of the hydrophobicity temporarily lost by application of dry contamination after corona aging depends on the amount of mobile LMW siloxanes of silicone rubber diffused through the contamination layer.

Corona in the presence of high-velocity wind also affects the hydrophobicity recovery rate of silicone rubber insulators. The speed of LMW diffusion mainly depends on the direction of the wind. Here, it is essential to understand the process of volatilization of LMW siloxanes. In this process, a portion of siloxanes remains on the surface, keeping

it hydrophobic. In contrast, the rest diffuses to the air surrounding the insulator, thus decreasing the concentration gradient of siloxanes between the surface and surrounding air [73]. The wind direction parallel to the silicone rubber insulator during the corona aging can retard the hydrophobicity recovery by blowing away the LMW siloxanes, thus increasing the concentration gradient. This high concentration gradient leads to more diffusion of LMW siloxanes to the surrounding air and, as a result, reduces the hydrophobicity recovery [74]. On the other hand, the hydrophobicity recovers more quickly when the wind flow is vertical to the insulator. This is because the vertical wind imposes pressure on the surface, leading to increased deformation in the silicone rubber bulk. Such deformation can cause cracking of the silica-like layer on the surface, which significantly facilitates the LMW diffusion, thereby accelerating the hydrophobicity recovery [57,67].

Thermal degradation of silicone rubber has a strong impact on hydrophobicity recovery. It has been shown that temperature greatly influences the LMW siloxanes regeneration due to the scission of high molecular weight chains [75]. It is worth mentioning that the diffusion process in silicone rubber is accelerated at high temperatures, thus causing a relatively quick recovery [76]. In another study, the LMW chains diffusion in the contamination layer also increases with exposure to thermal stress, thus resulting in a quick recovery [77]. Applying UV stress on silicone rubber in combination with high temperature can further accelerate the LMW diffusion [78]. In a more recent work [79], silicone rubber composites' hydrophobicity recovery improved with accelerated temperature and high humidity. However, it has been shown that accelerated weathering stresses can reduce a significant amount of LMW siloxanes even under dry conditions that could affect the hydrophobicity recovery [80]. Such a reduction could primarily be due to accelerated temperature but not UV radiation. There may be a possibility that the contribution of LMW siloxanes reduction due to accelerated stresses combines with surface discharges to gradually reduce LMW siloxanes under wet and contaminated conditions. Moreover, it has been found that UV stress can decrease the mobile LMW fluid in silicone rubber and does not allow significant hydrophobicity recovery reduced by corona and thermal stresses [71].

It has been reported that hydrophobicity recovery under salt-fog stress depends on the physical changes on the surface of silicone rubber [81]. In addition, the recovery rate is faster in the aged surface than the unaged surface, which means LMW siloxanes diffusion is facilitated due to physical changes on the surface. It has been found that recovery in silicone rubber under multi-stress aging is influenced by heat, humidity, UV radiations, and contamination [82]. A high temperature speeds up the process of LMW diffusion, and high humidity leads to an increase in recovery time due to the suppression of LMW siloxanes migration by air moisture. On the other hand, UV thermal radiation accelerates the recovery, and different types of contamination have a varying effect on hydrophobicity recovery. Water is believed to remove LMW components by reorientation of hydrophobic methyl groups and hydroxyl generation [83]. It is important to mention that hydrophobicity recovery of silicone rubber in the air after removal from saline solutions varies with temperature and salinity (conductivity of solution). Hydrophobicity recovery improves with increasing temperature, while the recovery speed decreases with increasing salinity [84]. The hydrophobicity recovery is improved at higher salinity because of lower water absorption during the immersion. In addition, the hydrophobicity recovers at a faster rate during the evaporation of the water absorbed by silicone rubber after removal from the saline solutions [85].

The polarity can affect the aging of RTV-SiR composites under DC voltage for HV coatings and it can alter the aging resistance or hydrophobicity recovery [86]. It was revealed that negative polarity exhibits lower aging effect on the coating in comparison with the positive DC polarity that shows more degradation phenomenon. In addition, the positive polarity results in higher leakage current than the samples under negative polarity owing to more surface conductivity due to the migration of more ions under DC-positive polarity [87]. These results can confirm that the higher rate of degradation of SiR coatings, more severe pollution effect, and greater hydrophobicity loss occur under DC-positive

polarity. It was reported that the positive polarity effect has a more damaging effect and less of a hydrophobicity retention effect on SiR insulators [87,88].

In a nutshell, future work may need to focus on understanding the synergistic effect of electrical and environmental stresses on self-healing in a more controlled and reproducible aging test method.

4. Screening Measurements for Outdoor High Voltage Insulation

The hydrophobicity retention, recovery and transfer of silicone rubber insulators have been used to define the ability of silicone rubber to retain its hydrophobicity in service. Relatively, a limited number of methods have been developed and standardized to evaluate these hydrophobicity-related measurements. Table 1 compares the techniques developed for self-healing evaluation. A commonly used method to evaluate the dynamic wetting properties of silicone rubber is the evolution of the static water-contact angle with time after aging, and the contact angle is usually measured using the sessile drop technique as shown in Figure 8 [62]. It has been reported that hydrophobicity recovery for clean surfaces increases with resting time after aging, i.e., the time between aging and the onset of the contact-angle measurement [89,90]. However, the measurement of the contact angle versus time has not yet been standardized for evaluating the hydrophobicity recovery.

Table 1. Comparison of developed methods for evaluation of self-healing.

| Parameters	Static Contact Angle [42,73,90]	Dynamic Drop Test (DDT) [91–94]	Hydrophobicity Transfer Test [89,95–97]
Purpose of the test	To quantify the recovery of hydrophobicity after aging test	To evaluate the hydrophobicity retention and recovery in short time	To evaluate the polymer's ability to transfer intrinsic LMW species onto pollution particles
Measurements	Assessment of recovery based on static drop contact angle measurement with respect to resting time	Evaluation via estimating the sample's failure time (min), i.e., the time when leakage current exceeds a defined level (2 mA for 1 s)	Evaluation through static and dynamic contact-angle measurements at defined transfer time intervals after building silica layer
Measuring setup	A goniometer is used for measurement of water contact angle on a flat horizontal polymer surface	Test setup consists of a pair of electrodes, a tilted silicone rubber sample, and a current sensor for detection of leakage current	A mask of adhesive foil is used for applying a uniform silica layer. A mask of 0.36 mm thickness provides good results. A goniometer is used to measure contact angles
Voltage	Measurements are conducted without exposing polymer to electric stress	Test voltage (3–6 kV AC rms or DC) is applied until the sample fails	This test can be performed without applying test voltage to silicone rubber
Accuracy	It has the lowest accuracy and yields a high scattering of test results. It is not applicable to polluted surface	It is an accurate and reliable aging test for reducing scattering in test results (Interval-based DDT)	It has high accuracy and provides reproducible results with reduced scattering. A too-thick and uneven silica layer may affect its accuracy
Reproducibility, standardization	It is not a standardized method for recovery evaluation and provides unreproducible test results	It has the potential to standardize and achieve reproducible results for evaluating hydrophobicity retention and recovery properties	It is an appropriate and reproducible test method for evaluation of dynamic hydrophobic transfer and recovery properties
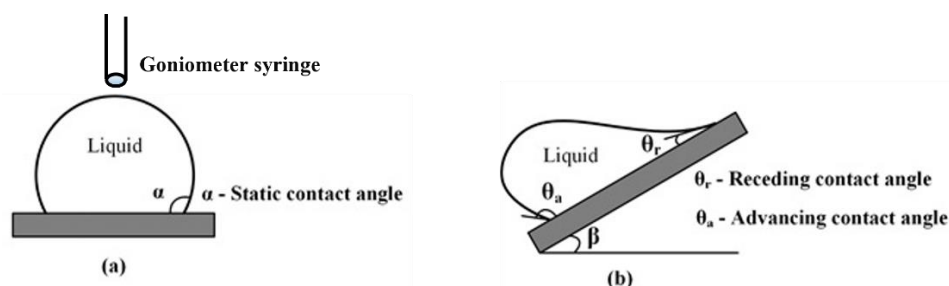
Figure 8. Water drop angles for hydrophobicity recovery measurements (**a**) Static contact angle on a horizontal surface; (**b**) advancing and receding contact angles on an inclined surface.

Another practical method to quantify the self-healing of silicone rubber is the dynamic drop test (DDT) method as shown in Figure 9. The DDT primarily employs both electrolytic contaminant (NaCl) and electric stress to evaluate the relative resistance to wetting (hydrophobicity retention) [91]. Another potential technique has suggested using the DDT as a reproducible aging test, after which the hydrophobicity recovery can be evaluated. Accordingly, the resting time has been specified as an important factor to be considered when using the DDT to assess the hydrophobicity recovery [92,93]. The failed specimens are usually allowed to recover for a defined period (24 h) under laboratory conditions and tested again to evaluate recovery properties.
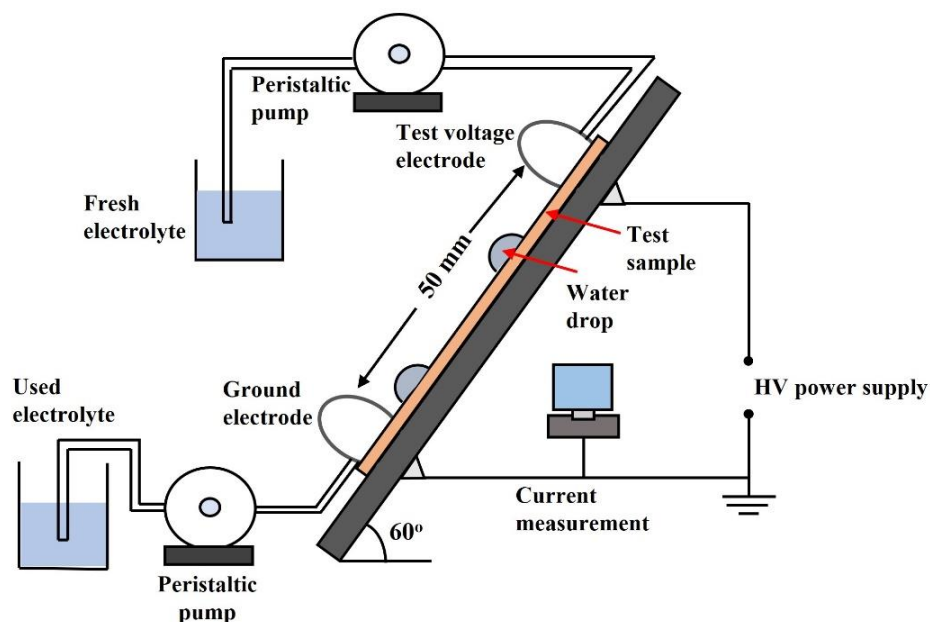

Figure 9. Schematic of dynamic drop test for evaluation of hydrophobicity recovery.

An interval-based testing technique has been proposed for the DDT as a more reliable approach to evaluating the hydrophobicity recovery of silicone rubber [94]. In this proposed approach, samples are exposed to cycles of electric stress and resting time, thus offering the advantage of reducing the scatter in the final measurements. The alternate cycles of stressing with voltage and resting of the specimen are continued until the sample fails in DDT. Yet, further work is required to define the appropriate test conditions and parameters such as electrolyte conductivity, flow rate, test voltage, suitable stress, and rest intervals to standardize the DDT for evaluating the hydrophobicity recovery.

Hydrophobicity transfer mainly provides a relative quantification of the transfer of the LWM fluid to a contaminated silicone rubber surface with untreated silica (SiO_2) powder [95]. Silica is usually applied in the form of slurry and is the preferred pollution material for reproducibility of results and hydrophobicity transfer [89]. In contrast, kaolin and kiesel-

guhr could impede the LMW transfer and give unreproducible outcomes [96]. Besides, the ability to transfer hydrophobicity can be assessed in hydrophobicity transfer test or masking method [97], based on the time required to regain the surface hydrophobicity.

Hydrophobicity transfer measurements (Figure 10) have also been specified in IEC 60815-3, but using the kaolin as the contaminant and flashover voltage to indicate the relative degree of hydrophobicity transfer [98]. The diffusion of LMW siloxane to the surface could increase surface resistance, thereby enhancing the flashover performance. Moreover, the recovery period between depositing the contaminant and applying voltage could be increased to evaluate the insulator under different transitional states (hydrophilic to hydrophilic) [99]. A recovery time of no more than 5 h is proposed for simulating hydrophilic conditions and one week for hydrophobic conditions. Surface conditioning for uniform deposition of a contaminant has been reported as a major factor that must be ensured before measuring hydrophobicity transfer. Dipping silicone rubber samples in pure tap water for 24 h has also been proposed to ensure the uniformity of the pollution layer [100].
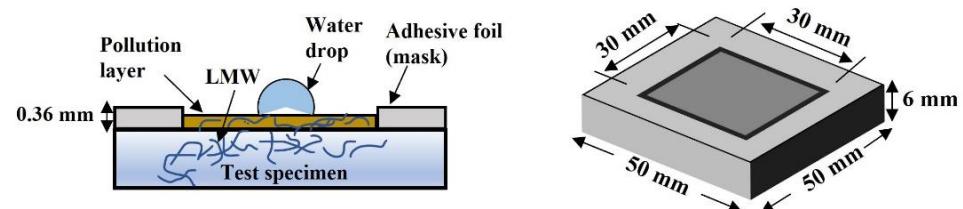

Figure 10. Specimen with adhesive foil (masking) and pollution layer during hydrophobicity transfer measurements.

In view of the methods discussed above, future work needs to focus on correlating hydrophobicity retention and recovery using the DDT and hydrophobicity transfer tests.

5. Conclusions

Self-healing mechanisms of silicone rubber could be intrinsic with dimethyl bonds re-orienting and restoring the hydrophobicity of the surface or an extrinsic mechanism with the diffusion of the LMW siloxane from the bulk to the surface. The realization of the self-healing property of silicone rubber insulators depends on the measurement of three different properties: hydrophobicity retention, transfer, and recovery. Although measurement techniques of these properties have been proposed, more work is required to achieve reliable and reproducible methods for application at the material development stage of silicone rubber insulators. Aspects, namely localization, temporality, and mobility, defining the efficiency of the self-healing property of silicone rubber were reviewed, and the corresponding influential material design factors on these aspects were highlighted. While controlling the base chemical structure could be useful in improving the intrinsic self-healing property of silicone rubber, adding fillers to reduce the cost of the composite or improving the tracking and erosion resistance may suppress the diffusion of the LMW siloxane, thus adding an extrinsic self-healing to silicone rubber.

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