Hydrophobicity Loss and Recovery of Silicone HV Insulation

J. Kim, M. K. Chaudhury and M. J. Owen

Department of Chemical Engineering, Lehigh University, Bethlehem, PA
and Dow Corning Corporation, Midland, MI, USA

ABSTRACT

Most of the silicone materials used for HV outdoor insulation are high-consistency, heat cured polydimethylsiloxane (PDMS) elastomers. The unique properties of PDMS that make it suitable for HV applications are reviewed. The surface of these elastomers can be rendered hydrophilic by exposure to discharges. A time and temperature dependent hydrophobic recovery ensues when exposure ceases. A variety of surface characterization investigations have established that corona exposure forms a brittle, wettable, silica-like layer on the surface of most PDMS elastomers. This is consistent with similar effects from oxygen and inert gas plasma treatment. There is still considerable debate as to the relative importance of the two major mechanisms postulated to account for the hydrophobic recovery after corona discharge. The diffusion mechanism invokes migration of low molecular weight species from the interior to the surface, while the reorientation or overturn mechanism envisages a surface reorganization with polar entities such as silanol groups resulting from surface oxidation rotating away and being replaced by methyl groups in the outermost surface layers. In our view, the highly crosslinked silica-like layer cannot reorient readily between hydrophilic and hydrophobic states at the surface, suggesting that diffusion of low molecular weight PDMS components is the more important mechanism of hydrophobic recovery. Recent data obtained on PDMS samples free from low-molecular-weight diffusible species show that hydrophobic recovery may be due to *in-situ* depolymerization.

1 INTRODUCTION

THE chief advantages of polymeric insulators over conventional porcelain and glass insulators in outdoor HV insulation applications are light weight, superior vandal resistance and better contamination performance [1]. However, polymers are more easily degraded than inert inorganic materials under exposure to discharges and arcing. Corona discharges and dry band arcing occur when the surface of an energized insulator is covered by an electrolytic film formed by the presence of moisture and contamination. The intense localized energy of the dry band arcs can cause material degradation in the form of tracking and erosion. Other environmental factors such as ultraviolet radiation from sunlight, acid rain, temperature and flammability must also be considered [2].

Polydimethylsiloxane has a variety of characteristics that make it particularly suitable for HV applications. The various product types testify to this suitability. They range from time-proven, grease-like coatings and elastomer dispersions, that can be applied to existing insulators to improve water-filming resistance and prevent arcing and flashover, to lightweight, composite insulators made from silicone rubber for new or upgraded electrical systems. Central to this HV use of PDMS is its low surface energy and hydrophobicity and its long service life in a variety of environments. Its ability to rapidly recover hydrophobicity after exposure to corona and similar treatments such as plasma treatment, is also a key factor. These properties are a direct result of the unusual organic/inorganic hybrid nature of silicones occupying the material regime between silicate minerals and organic polymers and exhibiting attributes of each. Specific product performance naturally depends on aspects of the precise material formulation such as the nature of fillers incorporated, the type of crosslinking chemistry employed and the possible presence of catalysts and impurities. Thus generalizations about the behavior of silicones are best avoided except in the limiting case when all these complicating issues are absent.

Polydimethylsiloxane is the most common silicone polymer and the one used exclusively in HV insulation applications. Compared to organic hydrocarbon polymers [3], PDMS is more thermally stable and performs over a wider range of temperature, both high and low. It is more resistant to oxygen and ozone attack. Weaker aspects of PDMS environmental durability are aqueous stability at extremes of pH and ability to resist γ radiation. It is also a very low surface energy polymer, only those polymers based on aliphatic fluorocarbon entities are significantly lower in their surface energy. The following list of qualitative attributes summarizes the desirable properties contributed to silicone insulator

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performance by the PDMS polymer.

Qualitative attributes of PDMS polymer:

1. Low surface energy.
2. Hydrophobic/oleophilic.
3. Non-adhering surface (but prone to oily soiling).
4. Water insoluble.
5. Low molecular weight (MW) polymer component.
6. High surface mobility.
7. Low glass transition temperature.
8. Good dielectric properties.
9. High thermal and oxidative stability.
10. Excellent resistance to weathering.
11. Low reactivity, toxicity and combustibility.
12. Low environmental hazard.
13. Small temperature variation of physical properties.
14. Flexible to low temperatures.
15. Transparency to UV in normal atmosphere.

In this list, the terms high and low refer to comparison with organic hydrocarbon polymers. There are four fundamental properties of PDMS which account for this behavior [4]. They are (a) the partially ionic nature of the siloxane backbone, (b) its high bond energy, (c) its unique flexibility, and (d) the low intermolecular forces between silicone molecules dominated by the London dispersion forces associated with the pendant methyl groups. Methyl groups on a siloxane backbone produce a very different material to methyl groups in a hydrocarbon. Likewise the siloxane bonds of PDMS do not behave the same way as those of silica and a deeper consideration of the fundamental attributes of the PDMS polymer architecture is needed to better understand its interaction with changing environmental factors.

2 FUNDAMENTAL PROPERTIES OF PDMS

2.1 PARTIAL IONIC NATURE OF THE BACKBONE

Most inorganic polymer backbones are composed of more than one atom and the electronegativity differences between them cause such bonds to be partially polar or ionic and partially covalent. As Noll has pointed out [5] this produces a resonance type structure of the siloxane bond in PDMS where the silicon-oxygen distance of 0.165 nm is considerably smaller than the sum of the atomic radii of the two elements. It also causes such bonds to be more susceptible to nucleophic or electrophilic attack than wholly covalent linkages. In the case of PDMS the Pauling electronegativity difference of 1.7 between silicon and oxygen confers a 41% polar or ionic character on the siloxane bond. Its consequent sensitivity to hydrolysis at extremes of pH is the most significant difference between silicones and organic polymers. The reaction between water and siloxane,

$$\text{-Si-O-Si-} + H_2O \Longleftrightarrow 2\ \text{-Si-OH} \qquad (1)$$

is an equilibrium that results in a redistribution of siloxane linkages known as the equilibration of siloxanes. Normally, the water-insoluble nature of PDMS keeps this equilibrium well to the left by mass action effects. The behavior of spread monolayers of PDMS on water represents the extreme case of PDMS exposure to water. All the bonds are exposed to the aqueous environment in this configuration despite the insolubility. It is also an extreme case in the sense that no fillers or crosslinking catalyst residues are present. Such Langmuir trough studies of spread PDMS monolayers on water using hydrochloric acid and sodium hydroxide to adjust the water to the required pH show that hydrolytic splitting of the skeletal siloxane polymer bonds only becomes appreciable at pH values of the aqueous substrate smaller than 2.5 and greater than 11.0 [6, 7]. The consequence for acid rain exposure of silicone HV insulation is that provided no catalysts or catalytic impurities that would be active at ambient temperature are present it is only below a pH of 2.5 that we should anticipate significant surface damage to occur on prolonged exposure.

The studies of Koo *et al.* [8] are consistent with this expectation. They have reported that when silicone rubber suitable for outdoor insulation use (a high temperature vulcanized (HTV) material containing alumina trihydrate (ATH)) is aged by acid rain in the case of high acidity of nitric acid solution the electrical characteristics of the sample surface is noticeably changed giving rise to not only a decrease in crosslinking density but also chain scission of the base polymer. The critical pH value for onset of this serious surface degradation is between pH 1.5 and pH 2.5. There was also evidence that ATH filler is removed from the surface giving rise to increase in surface roughness. It should also be noted that only surface aging takes place and hydrophobicity and tracking resistance of the silicone rubber are well retained regardless of the acidity of the solution. This is expected as any silanols produced by surface hydrolysis would participate in the formation of a silica-like layer in the same manner as that produced by corona discharge, and hydrophobic recovery by chain reorientation or migration would ensue when the acid rain exposure abated.

Certain room temperature vulcanized (RTV) silicone sealants and elastomers which retain the room temperature active catalysts will obviously be much less resistant to hydrolysis. An example is RTV 11 which is usually crosslinked with a silicone-soluble organo-tin catalyst such as dibutyltindilaurate and filled with calcium carbonate. Mera *et al.* [9] have shown that the surface of RTV 11 is not stable over time immersed in ultra-pure water. Mass is lost and the contact angle hysteresis increases, due mostly to a decrease in the receding contact angle, with increasing time in water up to three months. The atomic force microscopy (AFM) details a nonuniform 'pitting' erosion phenomenon occurring at the surface. On the other hand, the surfaces of PDMS networks synthesized via hydrosilylation exhibit remarkable stability over time immersed in water, with no decrease in the receding contact angle and no measurable weight loss, up to two months. This study was part of an investigation to identify minimally adhesive coatings with respect to biofouling. There are other studies unrelated to HV insulation that can also add to our understanding of silicone hydrolysis. For example, medical-grade silicone elastomers have been subjected to accelerated aging in saline to verify the hydrolytic stability of the elastomer. A variety of techniques including contact angle [10] AFM, X-ray photoelectric spectroscopy (XPS) [also known as electron spectroscopy for chemical analysis (ESCA)], and secondary ion mass spectroscopy (SIMS) [11] confirm no significant bulk or surface hydrolysis under these accelerated aging conditions.

2.2 HIGH SILOXANE BOND ENERGY

One of the most remarkable properties of silicone elastomers is their thermal stability. Suitable silicone products can be heated in air at 200°C for a year without any appreciable change in properties and even to 300°C for short periods. This superior thermo-oxidative behavior to hydrocarbon elastomers is a considerable advantage in an application such as HV insulation where marked localized temperature increases will occur as the result of corona discharge and dry band arcing.

The siloxane bond energy is significantly greater than that of carbon-carbon and carbon-oxygen bonds. Ebsworth [12] quotes a value of 445 kJ/mol for hexamethyldisiloxane compared to the general values for carbon-carbon and carbon-oxygen of 346 kJ/mol and 358 kJ/mol, respectively. Clearly, the extra energy required to dissociate a siloxane bond has much to do with the substantial thermal stability of silicones. Chain scission has a more dramatic consequence on polymer integrity than pendant group scission but it is somewhat surprising that the carbon-silicon bond energy of 306 kJ/mol is less than the above values. Practical experience shows that a methyl group on silicon in PDMS is more thermally and oxidatively stable than a methyl group that is part of a hydrocarbon chain. The additional stabilizing factor is generally accepted to be the aforementioned partial polar or ionic bond nature of the siloxane bond. In this dipolar arrangement the silicon atom carries the partial positive charge and the oxygen atom the partial negative charge. The silicon atom thus can act as an electron drain somewhat polarizing the methyl group and rendering it less susceptible to attack than its bond energy alone would suggest.

The fate of these two bonds, the pendant silicon-carbon and the backbone silicon-oxygen, together determine the course of aging above 200°C. On the one hand the splitting off of the methyl group under the influence of oxygen leads to oxidative crosslinking and hardening of the elastomer, whereas the resultant depolymerization of the backbone from the thermal scission of the siloxane bond causes softening of the material. Experience shows that with hot-air aging for a relatively long time above 200°C crosslinking generally predominates and the products become harder. If atmospheric oxygen is excluded the depolymerization effect will predominate. Most of the silicone surface in a HV insulator assembly will be exposed to oxygen but there may be portions that are sufficiently tightly encapsulated by other materials for depolymerization to be a consideration in extreme conditions. Depolymerization may also be a factor in the hydrophobic recovery mechanism as discussed later.

It is important to emphasize that many commercial silicone elastomers and sealants have substantially less oxidative stability than the foregoing discussion would suggest; some are effective only up to 130°C. This is a consequence of the presence of impurities or catalysts which have been inadequately removed or neutralized facilitating the oxidative decomposition. These often arise from the various fillers used or the cure catalysts themselves. The precise chemistry of degradation will depend on the particular type and level of impurity or catalyst involved. As with all high temperature applications, HV silicone insulation formulations must be carefully matched with product performance requirements. Not all products based on PDMS are alike and the skill and experience of reputable manufacturers and formulators are essential in appropriate product selection.

2.3 UNIQUE SILOXANE BACKBONE FLEXIBILITY

Compared to hydrocarbon and fluorocarbon polymers, siloxane polymers have the longest chain bond lengths and the most open angles which obviously contribute considerably to the uniquely high siloxane backbone flexibility.

The ease with which this dynamic flexibility allows changes in spatial configuration is a key aspect of the siloxane backbone in understanding organosiloxane polymer structure/property/use relationships. For example, these structural features enable siloxanes to adopt a greater variety of configurations than other polymers. Steric packing restrictions are less likely to impede the adoption by PDMS of the lowest-surface-energy configuration available to the pendant methyl groups. Also in the case of PDMS, one of the consequences of this unique dynamic flexibility is a very low glass transition temperature T_g, lowest of all the common polymers. The mobility of polymer chains is not the only factor that affects the glass transition, but nevertheless a low T_g is a good indicator of polymer backbone flexibility. Other factors playing a role include bulkiness of pendant groups along the chain, attractive forces between the chains and chain length (molecular weight). With a T_g of -127°C [13], well below room temperature which goes hand in hand with high free volume, there is maximum opportunity for macromolecular motions such as reorientation of surface chains and diffusion of chains which are the two major mechanisms of hydrophobic recovery after corona discharge or dry band arcing.

The PDMS also has high equilibrium flexibility [14], the ability of a chain to be compact when in the form of a random coil, which is the origin of its very low melting point ($T_m = -40$°C). It is this melting point rather than the glass transition that sets the effective lower temperature use limit for many silicone elastomer applications. For lower use temperatures it is usual to use random copolymers of PDMS with modest levels of other silicones such as phenylmethylsiloxanes or trifluoropropylmethylsiloxanes. Although these have higher glass transitions, although still well below room temperature, they disrupt the polymer regularity and packing sufficiently to significantly depress the melting temperature.

Rotation about siloxane bonds in PDMS is virtually free, the energy for this rotation being almost zero, compared with 14 kJ/mol for rotation about carbon-carbon bonds in polyethylene and $>$ 20 kJ/mol for polytetrafluoroethylene (PTFE) [15]. This is a very significant difference between PDMS and fluoropolymers such as PTFE. Both materials are environmentally-stable, low-surface-energy materials but PTFE has a T_g of 117°C [16], well above room temperature. The consequence is that once the stability limit of PTFE is exceeded in corona discharge, the opportunity for restorative hydrophobic recovery by polymer chain reorientation or diffusion is much more restricted at ambient temperature than is the case for PDMS.

2.4 LOW INTERMOLECULAR FORCES BETWEEN METHYL GROUPS

The low surface energy of PDMS is one of the main reasons for its usefulness in HV insulation applications. Having lower surface energy and being more hydrophobic than most other polymers, it can best resist water-filming and thereby prevent arcing and flashover. Low surface energy is a direct manifestation of low intermolecular forces between molecules which in the case of PDMS are dominated by methyl group interactions. There are sufficient methyl groups to shield the effect of the considerable polarity of the siloxane backbone. This is evident from the similarity between the critical surface tensions of wetting of PDMS and paraffin wax. Because of the short range of molecular forces, the abundance of methyl groups and the variety of configurations possible by virtue of the backbone flexibility, the surface energy of PDMS is not an average of contributions from the non-polar methyl groups and the polar siloxane groups but rather it is determined by the methyl groups. This is also a consequence of the second law of thermodynamics. Since systems change spontaneously to minimize their free energy, it is axiomatic that the component that most lowers the surface energy of a surface will tend to accumulate at that surface, *i.e.* for PDMS the methyl groups will dominate over the siloxane linkages, a process much facilitated by the flexibility of the latter entities.

The polymer wetting studies of Zisman and his colleagues [17] have shown that these principles hold broadly to a good first approximation and they have used them to rank the effect of substituent atoms and groups in polymers. The effectiveness of substitution of individual atomic species in increasing the wettability of organic surfaces is:

$$\mathrm{F} < \mathrm{H} < \mathrm{Cl} < \mathrm{Br} < \mathrm{I} < \mathrm{O} < \mathrm{N} \qquad (2)$$

Among the fluorocarbon and hydrocarbon groups which result in the least wettable polymer surfaces, the order of increasing critical surface tension of wetting is

$$CF_3\text{-} < \text{-}CF_2\text{-} < CH_3\text{-} < \text{-}CH_2\text{-} \qquad (3)$$

This order reflects the fact that the weakest intermolecular interactions known in polymers are the London dispersion forces associated with these aliphatic fluorocarbon and hydrocarbon groups. There are extensive tabulations of surface tensions of wetting of polymers [18] which show that it is possible to equal the surface tension of PDMS with a few specialized hydrocarbon-based polymers, such as poly[(acylimino)ethylenes], but that most hydrocarbon polymers such as polyisobutylene, polyethylene and polypropylene have higher surface energies. All lower surface energy polymers than PDMS are based on aliphatic fluorocarbon substituted groups. Examples include fluorocarbons, fluoroethers, fluoroacrylates, fluoromethacrylates and fluorosilicones.

3 QUANTITATIVE SURFACE PROPERTIES OF PDMS ELASTOMERS

The PDMS is more hydrophobic and lower surface energy than most organic polymers. A comparative table of water contact angle θ and surface energy γ calculated by the geometric mean Owens and Wendt [19] approach is given in Table 1. Glass transition temperature data, taken from the *Polymer Handbook* [20], are also included as it is the combination of low intermolecular force methyl groups with the uniquely flexible siloxane backbone that results in this unusual amphiphilic macromolecule whose surface activity can be equaled by very few other polymers and bettered only by polymers based on aliphatic fluorocarbon entities. This is because the intermolecular forces between CF_2 and CF_3 groups are intrinsically lower than those between CH_2 and CH_3 groups. However, the bulkier fluorine atom causes fluorocarbons to be much more rigid than hydrocarbons, as illustrated by their large difference in glass transition temperatures. Because of the chain flexibility considerations, PDMS has more in common with fluoropolymers such as fluorinated polyethers and polyphosphazenes than with conventional fluoropolymers such as polytetrafluoroethylene (PTFE). When a fluoropolymer such as PTFE is damaged by corona its hydrophobic recovery is much slower. Fluorosilicones such as polymethylnonafluorohexylsiloxane (PMNFHS), (also shown in Table 1) offer an excellent, albeit expensive, compromise in this regard.

Table 1. Quantitative polymer property comparison

Polymer	γ mN/m	θ °	T_g K
Poly (hexamethylene adipamide)	47	72	323
Poly (methyl methacrylate)	40	80	378
Polyethylene	33	94	148
Polypropylene	29	116	260
EPR (50/50)	31	-	213
Paraffin wax	25	112	-
Polydimethylsiloxane	23	101	148
Polytetrafluoroethylene	19	108	390
Polymethylnonafluorohexylsiloxane	10	115	198

Higher water contact angles generally correlate with lower surface activity. The polypropylene (PP) water contact angle of 116° is unexpectedly high considering the optimum close-packed methyl group case of paraffin wax gives only 112°. The contact angle data in Table 1 are for unfilled materials and are quasi-equilibrium advancing angles. A filled material usually shows a similar advancing angle provided the filler incorporation has not significantly enhanced the surface roughness, but it usually has a lower receding contact angle and a consequent higher hysteresis (difference between advancing and receding contact angles). Roughness effects also have a profound effect on contact angle. We found contact angle hysteresis of a variety of commercially available and experimental high consistency HV silicone elastomers (HCR), filled with silica and alumina trihydrate (ATH), to be a function of surface roughness measured by scanning electron microscopy (SEM), the roughest surfaces having a hysteresis of almost 50° [21]. The advancing contact angle of water, the index of hydrophobicity, averaged 108°, typical of other PDMS elastomer surface characterizations. Other values can be obtained by incorporation of significant amounts of free PDMS fluid. The resultant range in surface energies is circa 20 to 25 mN/m with 22 mN/m being typical of smoother, unfilled PDMS coatings.

The atomic composition of these PDMS silicone HV insulator surfaces determined by XPS studies (see Table 2) is similar to that of the PDMS polymer gum: 50% carbon, 25% oxygen, 25% silicon. Fillers, particularly ATH, are rarely seen in the XPS sampling region (typically 5 nm)

Table 2. XPS surface composition of silicone elastomers.

Sample	composition, %		
	O	C	Si
Control			
A	27.1	53.4	19.5
B	26.8	49.2	24.0
C	27.1	50.3	22.6
Treated, grazing angle			
A	40.7	32.8	26.5
B	39.5	35.9	24.6
C	32.4	44.1	23.5
Treated, normal angle			
A	44.9	29.4	25.7
B	54.6	17.6	27.6
C	46.7	30.7	22.6

except after extensive weathering and surface damage, despite filler levels that usually exceed polymer gum levels. Nor does there seem to be any concentration of catalysts, pigments, contaminants, etc. in the surface region. This does not imply a macroscopic depletion of filler in the surface. Filler particles could easily be coated by a polymer film of 5 nm thickness, and even uncoated and close-packed in the surface they would still only constitute less than 1% of the volume of the top 5 nm thick layer for a flat geometry of spherical micron sized particles with polymer filling the interstices.

The usual two varieties of filler in silicone HV elastomers have different functions. Silica is used as a reinforcing agent to provide the elastomeric nature and ATH is a thermally conductive material to dissipate heat from energetic events such as corona discharge and dry band arcing. Sufficient energy can be generated in hot spots to dissociate chemical bonds [22]. The polymer/filler combination is important in both cases. Elastic properties such as elastic modulus, hardness *etc.*, depend on filler type, size, shape and surface treatment as well as on number and type of polymer crosslinks and the molecular weight between crosslinks. Likewise, thermal damage is a function of the intrinsic thermal stability of the polymer and the conductive properties of the heat dissipating filler as well as residual catalysts and catalytically active contaminants which can markedly affect the thermal degradation of PDMS as discussed in Section 2.2 on high siloxane bond energy. Note that the water molecules in ATH can participate in the polymer degradation pathways as well as providing beneficial thermal transfer.

Despite its absence from the outermost molecular layers, the presence of filler has a profound influence on surface behavior. Filled silicone elastomers exhibit marked contact angle hysteresis compared to monolayer films, also the softer the elastomer surface then the higher the contact angle hysteresis. Release behavior is a complex function of elastomer structure. At slow release speeds, soft (but not tacky) elastomers seem to release better than harder resinous materials so the former type of silicone should have the better chance of being cleaned of contamination in a rain storm, provided hydrophobic encapsulation has not already occurred. In contrast, at higher release speeds there is a well-established correlation of decreasing release force with increasing crosslink density in the distantly-related field of pressure-sensitive adhesive release liners.

4 EFFECT OF CORONA DISCHARGE

Exposure to severe corona treatment is both physically and chemically damaging to elastomers. Cracking of the surface and an increase in wettability by water are the usual consequences which can be shown by modern surface analytical techniques, such as XPS, to be associated with an increase in the oxygen content of the surface. Clearly, a polymer such as PDMS, with a higher threshold of thermal and oxidative damage than hydrocarbon polymers, has a considerable advantage in practical use as a HV insulator material. Cracking in use does occur but can be difficult to see optically or by SEM because of the rough surface caused by high loadings of ATH filler. It can more readily be seen at lower filler levels. It is also evident that cessation of the corona treatment causes a progressive reversion to the non-wetted state in most cases, the so-called 'hydrophobic recovery' effect, first described for silicone HV insulation by Niemi and Orbeck [23] over twenty-five years ago.

There is general agreement that continued exposure to higher energy discharges causes chemical changes in the surface of PDMS elastomers. This is illustrated in a recent study by Hillborg and Gedde [24]. They subjected a HTV PDMS elastomer to corona discharges for different periods of time in dry air. The loss and recovery of hydrophobicity of the surface was characterized by contact angle measurements. Immediately after exposure, samples showed a low surface hydrophobicity and, on storage in dry air, a continuous increase in hydrophobicity finally approaching the hydrophobicity of the unexposed material. The activation energy of the hydrophobic recovery was two to four times greater than the activation energy of the diffusivity of low molecular weight (MW) PDMS in PDMS elastomers [25], indicating that the diffusivity properties of the oxidized layer were different from that of the bulk. PDMS elastomers quenched in liquid nitrogen or subjected to small mechanical deformation after exposure to corona discharge recovered their hydrophobicity faster than untouched specimens kept under identical conditions.

The XPS confirmed the early formation of a silica-like surface layer of thickness > 10 to 12 nm. The atomic composition of the oxidized surface layer remained essentially unchanged after the first hour of corona discharges. Hillborg and Gedde suggest that the silica-like layer delays the recovery of hydrophobicity by inhibiting the transport of low MW PDMS to the surface and that the thermally or mechanically induced stresses lead to a cracking of the brittle silica-rich layer which in turn facilitates low MW PDMS transport to the surface. Data obtained by reflection IR spectroscopy assessing the outermost micrometer thick layer confirmed the oxidation and the formation of hydroxyl groups at a progressively higher concentration with increasing exposure time of corona discharges. Similarly, Toth *et al.* [26] found a silica-like layer of less than 3 nm using angle-resolved XPS on silicone rubber surfaces exposed to radio frequency (RF) plasma or corona discharges in air.

Some typical XPS data are shown in Table 2 taken from the work of Hillborg and Gedde [24] (sample A in the Table) and ourselves [21] (sample B). These studies used different discharge apparatuses, conditions (20 kV for 20 min for A, 14 kV for 10 min for B), and PDMS elastomers (Wacker Chemie for A, Dow Corning for B). Nevertheless, the same trends are apparent for both data sets. The untreated control compositions are close to the theoretical PDMS expectation. In approximate broad terms corona exposure effectively doubles the surface oxygen content, halves that of carbon and leaves the silicon level relatively unaffected. Also included in Table 2 is an example of RF oxygen plasma treatment [27] (sample C). There have been numerous reports of the close relationship between the effects of corona and RF plasma treatment on PDMS beginning with the original studies of Hollahan and Carlson [28]. The plasma treatment conditions for this particular sample were a power of 70 W at a pressure of 70 Pa for 30 s.

The time for hydrophobic recovery depends on the type of silicone formulation used with the different crosslinking systems and fillers employed and the extent of the corona treatment. For example, Smith and co-workers [21] showed a difference in hydrophobic recovery of peroxide cured high consistency materials and Pt catalyzed hydrosilylation addition cured liquid silicone rubbers. Gubanski and Vlastos [29] had earlier discussed the wide range of contact angles obtained on real insulator surfaces. Hillborg and Gedde [24] showed that mechanically deformed specimens recover faster than untouched ones. This behavior is consistent with cracking of the brittle silica-like layer facilitating diffusion of low molecular weight components. The familiar difficulty in obtaining reproducible contact angles of corona treated samples is likely due to the occasional formation of cracks during sample mounting and measurement. Nevertheless, in general it can be said that noticeable hydrophobic recovery usually occurs in the first few hours after corona exposure ceases, with almost total recovery (to $> 100°$ water advancing contact angle) often taking over a hundred hours.

The most complete analysis of the silica-like layer appears to be that of Kumagi *et al.* [30] who applied the techniques of KBr pellet Fourier transform infrared (FTIR) and X-ray diffraction (XRD) to the solid residue formed on a RTV silicone elastomer in an accelerated aging tracking test. They identified cristobalite silica, amorphous silica, silica gel and moissanite silicon carbide. Interestingly, no conductive forms of carbon were seen that might be detrimental to dry-band arcing resistance.

5 POSSIBLE MECHANISMS OF HYDROPHOBIC RECOVERY

At least seven possible mechanisms of hydrophobic recovery of insulating polymers have been postulated:

1. Reorientation of surface hydrophilic groups away from the surface (*i.e.* the overturn of polar groups in the polymer surface).
2. Migration of treated chains from the surface to the bulk. Migration of untreated polymer chains from the bulk.
3. Loss of volatile oxygen-rich or other polar species to the atmosphere.
4. Further reaction of polar or other active species (*e.g.* transient radicals), producing linkages that hinder chain reorientation.
5. Change in surface roughness.
6. External contamination of the polymer surface.

The main mechanisms that have been discussed in the literature in the case of PDMS are surface reorientation and diffusion of low MW species. These are the most likely although several of the other mechanisms are probably involved. For example, water is a specific, volatile, oxygen-rich species that could be lost to the atmosphere while further reaction of polar silanols is an integral part of the development of the silica-like network acting against chain flexibility. Surface reorientation of polymeric solids and this dependence on different environments is a familiar phenomenon. The extreme flexibility of the siloxane chain and the low intermolecular forces between methyl groups, which result in the low glass transition temperature and high free volume of PDMS, allow PDMS to reorient its surface readily. It has the most mobile surface of all common polymers. Likewise, the low MW component that is usually present in most commercial PDMS materials provides an ample reservoir of diffusible material even if such unreacted components have not been deliberately added. Moreover, the same factors that permit facile reorientation will allow ready diffusion of such species. More than any other polymer, PDMS exhibits the most marked hydrophobic recovery.

Recently, Westerlund and George [31] have analyzed the low molecular weight fractions on the surface of in-service silicone insulators by gas chromatography (GC)-mass spectrometer (MS) and matrix assisted laser desorption/ionization (MALDI)-time-of-flight (TOF) mass spectrometry. They show the material to be primarily cyclic with a distribution peaking around D_{20} to D_{25} and make the interesting suggestion that higher MW cyclic are more likely to be threaded into the polymer network and unable to diffuse [32]. The preponderance of cyclic over linear is attributed to the more compact shape of the cyclic and their known higher diffusivity [33]. The similarity of the composition of these surface extracts to that obtained from the bulk material argues more for diffusion of untreated material from the bulk than for the production of low MW material on the surface by the varied effects of electrical and environmental exposure. However, both effects may be present, the former more significant than the latter which could only become evident if all low MW material were effectively removed. Westerlund and George's data is consistent with that of Toth *et al.* [26] who earlier reported GC-MS PDMS extraction studies showing the extract to be a mixture of cyclics with a minor quantity of linear PDMS oligomers.

Surface reorientation can still be an important factor in the hydrophobic recovery of silicone insulator surfaces that do not develop a highly crosslinked silica-like layer. For example, the underside of sheds may never be exposed to direct UV or high energy discharges. However, once the more highly crosslinked, silica-like layer develops, the possibility of facile surface restructuring will be considerably diminished leading us to suppose that diffusion effects will dominate in such cases. Recently, we have conducted hydrophobic recovery studies of corona treated Sylgard™ 184 PDMS elastomer that shed new light on these mechanistic considerations. The data will be reported in detail elsewhere but a brief synopsis is in order here. Sylgard™ is prepared from a SiH functional PDMS and vinyl-functional PDMS using Pt catalysis. Sheets of 1 to 2 mm thickness were prepared and Soxhlet extracted for 12 hours in chloroform to remove any unreacted material. Low MW PDMS material was also deliberately added to some samples and the effect of corona treatment assessed using a HIPOTRONICS Model 750-5 CF transformer. Corona treatment was carried out at room temperature and the treated samples were subsequently stored at various temperatures. Water contact angles were measured as a function of time and storage temperature (T_a) enabling half-times of recovery (τ) and activation energies of the process (W_a) to be calculated. Some results are presented in Tables 3 and 4.

Table 3. Recovery half-times of corona-treated silicone elastomers (Sylgard™ 184).

V_i kV	T_a ℃	τ h
Extracted		
6	25	15.1
	60	3.6
	75	1.5
	100	0.5
9	25	11.0
	60	1.8
	75	1.1
	100	0.4
12	25	5.5
	60	1.5
	75	0.7
	100	0.3
5% PDMS + MW 770		
6	25	3.4
	100	0.1
12	25	0.8
	100	0.1
5% PDMS + MW 3780		
6	25	5.0
	100	0.3
12	25	1.7
	60	0.6
	75	0.4
	100	0.3

Table 4. Hydrophobic recovery activation energy W_a. Inception voltage V_i after 30 min corona treatment time.

V_i kV	W_a kJ/mol
Extracted	
6	42.3
9	40.5
12	34.9
5% PDMS + MW 3780	
12	23.1

The key observation is that hydrophobic recovery occurs with the samples containing no low MW material. Recovery rates are highly dependent on the applied voltage V_i at low subsequent storage temperatures, whereas voltage influence on hydrophobic recovery becomes less important at storage temperatures above 60℃. Additionally, initial recovery rates for corona treated samples increases as voltage increases from 6 kV to 12 kV at 25℃ storage but this trend also becomes less important on storage above 60℃. Hillborg and Gedde [24] reported a similar increase of initial recovery rate with increasing corona exposure time.

Given that these networks have been significantly corona oxidized, we doubt restructuring effects prevail and, in the absence of pre-existing low-molecular-weight diffusible material, we can only suppose that such material is produced *in-situ* as a result of the corona treatment. It may be that the silica-like layer acts as a sufficient barrier for ingress of atmospheric oxygen to prevent oxidative crosslinking and encourage polymer scission. We envisage a region of variable crosslink density over a depth of the order of 10 nm, highest at the surface, lowest at depths where the material becomes effectively untreated PDMS. At the air side of this variable region ample oxygen is present to ensure oxidative crosslinking and hardening of the elastomer but at the PDMS side softening and depolymerization of the siloxane bond is a real possibility.

Corona-treated samples containing added PDMS fluids exhibit a faster initial recovery than the extracted samples for all the corona treatment conditions. Expectedly, the lower MW PDMS fluid has a stronger effect in reducing recovery half-time and activation energy for the process. We are currently engaged in further studies of this type. Note that in these model studies no thermally conductive fillers such as ATH are present to dissipate heat from the corona discharge as would be the case in a fully formulated PDMS silicone HV insulator material. Note also that the time scale for diffusion of the small oxygen species is limited to the short time of actual corona treatment (minutes) in this argument whereas the time scale for subsequent diffusion of any low molecular weight species produced by the corona is much longer (hours). Most interestingly, when the corona-treated networks without added low MW material are stored in high vacuum, the rate of hydrophobic recovery is very considerably reduced compared to that stored in air, an observation that is also consistent with *in-situ* production of low MW material by the corona treatment rather than a reorientation hypothesis.

6 SUMMARY

MOST silicone HV insulator materials are based on high-consistency, peroxide/heat-cured PDMS elastomers. It has long been known that their original hydrophobic surface is changed to a hydrophilic surface when exposed to corona discharge and that hydrophobic recovery ensues when the corona treatment is discontinued. A variety of surface characterization studies by ourselves and others have established that prolonged exposure to corona results in the formation of a silica-like layer of the order of 10 nm thick, much the same situation as prevails with RF plasma treated PDMS. Techniques which have been used to characterize this layer include XPS, SEM, contact angle, and infra-red spectroscopy. The extensive crosslinking of the silica-like layer makes it brittle and prone to crack during sample handling and measurement. It also suggests that it cannot readily reorient between hydrophilic and hydrophobic states and we believe that the surface restructuring, chain reorientation mechanism of hydrophobic recovery is unlikely to be important except in cases of light corona oxidation before the silica-like layer develops. In our opinion, diffusion of low molecular weight PDMS components is the key mechanism of hydrophobic recovery as proposed by several researchers, including Gorur and coworkers [34] and Lee and Homan [35]. Our recent studies on model PDMS systems free from diffusible species also show hydrophobic recovery, possibly due to *in-situ* depolymerization.

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