

# The Mechanisms of Hydrophobic Recovery of Polydimethylsiloxane Elastomers Exposed to Partial Electrical Discharges

Jongsoo Kim,<sup>\*</sup> Manoj K. Chaudhury,<sup>\*,1</sup> Michael J. Owen,<sup>†</sup> and Tor Orbeck,<sup>‡</sup>

<sup>\*</sup>Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015; <sup>†</sup>Dow Corning Corporation, Midland, Michigan 48686-0994; and <sup>‡</sup>East Jordan, Michigan 49727

Received June 4, 2001; accepted August 10, 2001; published online October 18, 2001

**Silicone elastomers exposed to electrical discharges can be rendered hydrophilic, and the loss of water repellency is related to the energy level and number of the discharge pulses on the surface. However, the silicone surface has the unique ability to recover the hydrophobicity and enhance the performance of a polymer insulator. Most of the studies of the loss and recovery of hydrophobicity on elastomer surfaces have been carried out at high discharge energies experienced under severe service conditions. Despite numerous studies, the mechanisms contributing to the loss and recovery of hydrophobicity under lower energy partial discharges are not fully elucidated. The current study was done with partial discharge pulses in the range 10–10000 pC and by using a needle-to-plane electrode configuration. At very low levels of energy pulses, the recovery is primarily caused by the migration of preexisting fluids from the bulk to the surface of the elastomer. At higher levels of partial discharges, the fluids no longer play the same role, but the dominant mechanism in the recovery becomes the migration of *in situ* produced low molecular weight (LMW) species in the elastomer. These studies were done under dry and wet conditions.** © 2001 Academic Press

**Key Words:** polydimethylsiloxane; PDMS; partial discharge; preexisting fluid effect; hydrophobic recovery mechanism.

## I. INTRODUCTION

Polymer insulators are gaining market share in high-voltage insulation applications mainly due to their easy installation, light weight, and superior vandalism resistance compared to traditional inorganic materials (1). Compared to most polymeric materials, silicone elastomers have better thermal stability and resistance to UV radiation because of the strong Si-O bond energy and excellent water repellency resulting from their low intermolecular interactions. Although the silicone elastomer has these highly desirable properties for high-voltage applications, its surface inevitably may lose its hydrophobicity when exposed to partial electrical discharges as do other polymeric materials. Surface oxidation by electrical discharges such as dry band arcing is accelerated in the presence of water and air-borne contam-

inations. However, the silicone elastomer has the unique characteristic of readily recovering its original hydrophobicity once discharge ceases, and thereby continuing to suppress the leakage currents and prevent insulator flashover. This surface restructuring of silicone elastomers, often referred to as “hydrophobic recovery,” has been extensively studied in the development of new high-voltage insulators.

The following mechanisms for hydrophobic recovery have been suggested:

- Reorientation of polar groups from the surface to the bulk phase or reorientation of nonpolar groups from the bulk to the surface (2, 3).
- Diffusion of preexisting low-molecular-weight (LMW) silicone fluid from the bulk to the surface (2, 4–20).
- Condensation of the surface hydroxyl groups (3).
- Migration of *in situ* created LMW species during discharge to the surface (7–10, 21, 22).

Even though most researchers have pointed out the importance of the migration of LMW fluid preexisting in the bulk (mechanism b), other mechanisms may also contribute to the hydrophobic recovery of oxidized PDMS elastomers. In our previous papers (21, 22), we suggested that when silicone elastomers are exposed to discharge pulses exceeding 1500 pC, the key mechanism is the migration of the LMW species produced *in situ* during discharge from the bulk to its surface (mechanism d). We also found that preexisting fluid in the bulk does not significantly affect the hydrophobic recovery if silicone elastomers are subject to higher energy discharges that may occur under contaminated service conditions. However, only a limited number of insulators are exposed to severe contamination. Most insulators are only exposed to low-energy discharge pulses during wet service conditions. It is important to study the loss and recovery of the hydrophobicity of these discharge levels. This prompted us to study the behavior of polydimethylsiloxane (PDMS) elastomers exposed to partial electrical discharges of various intensities (10–10000 pC). The contact angle changes on the surfaces of PDMS elastomers were monitored intermittently during and/or after partial discharge to study the dominant mechanisms of hydrophobic recovery. This study also investigated the roles of free fluid on the restructuring behavior of silicone elastomers after

<sup>1</sup> To whom correspondence should be addressed.

exposure to different levels of partial discharge. Additionally, the effect of humidity on the hydrophobic recovery of PDMS elastomers was explored to assess the role of hydrolytic depolymerization in the formation of LMW species. Contact angle measurement and angle-resolved X-ray photoelectron spectroscopy (XPS) were used to study the hydrophobic recovery of PDMS elastomers exposed to partial discharge. On the basis of these results, different dominant restructuring mechanisms of PDMS elastomers are proposed.

## II. MATERIALS AND EQUIPMENT

### 1. Materials

Two-component high-temperature vulcanized silicone elastomer (SYLGARD 184, Dow Corning Corp.) was used for this study. Silicone elastomers are normally made of several materials such as a base polymer, a cross-linker, a catalyst, fillers, and other additives. SYLGARD 184 is supplied in two separate kits with a vinyl-terminated silicone base polymer in one kit and with a cross-linker and a catalyst in the other kit. These materials were thoroughly mixed according to the manufacturer's instructions, and air bubbles trapped in the compound were removed under vacuum. After the platinum-catalyzed hydrosilation reaction (75°C, 2 h) of vinyl functional groups of the base polymer with hydrogen functional groups of the crosslinker was completed, the elastomer was Soxhlet-extracted for 12 h with chloroform to remove unreacted oligomers. In other experiments, pre-existing fluid samples were prepared by mixing linear methyl-terminated silicone fluid (Mw = 236, Mw = 950, Gelest Inc.) or fluorine-containing silicone fluid (3,3,3-trifluoropropylmethylsiloxane, Mw = 950, Gelest Inc.) with the compound before curing to evaluate the influence of these additives on the hydrophobic recovery. Fluid was added in the ratio of 5 weight parts to 100 weight parts of the base polymer.

### 2. High-Voltage Test and Measuring Equipment

A high-voltage AC corona test set (HIPOTRONICS, Model 750-5CTS B/S) with a 50-kV noise free transformer was employed to generate and measure the partial electrical discharges on the surfaces of PDMS elastomers. This model is suitable for measurement of pulses in the range 10–10000 pC. The discharge magnitude was calibrated by using the calibration pulse generator module and the switchable amplifier module prior to conducting the main experiments. The calibration pulse generator module is specially designed for the indirect calibration of discharge detection circuits, by injecting a known magnitude pulse in the input unit to provide a quantitative comparison with the magnitude of discharges in a test specimen. After calibration is completed against a pulse of known value, voltage is gradually increased until partial discharges reach desired values. The magnitude meter module then reads the height of the highest pulse among the numerous partial discharges appearing on the display ellipse during the experiment. A strip chart recorder was used to observe the variation of the discharge with time.

### 3. Partial Discharge Tests

A sample sheet (thickness, 1 mm) was placed on a circular glass plate (diameter, 10 mm; thickness, 3 mm). The plate was required as a rigid support to prevent any flexing during handling. Microcracking caused by bending is a significant factor in the hydrophobic recovery (4, 6). A needle electrode (tip diameter, 0.065 mm) was employed to obtain various levels of discharge. The cylindrical electrode (rod diameter, 1 cm) used in our previous high discharge studies (22) produces relatively larger oxidized areas that allow easier measurement of the contact angles, but it proved impossible to sustain a stable electrical discharge at lower intensities with this electrode configuration. Figure 1 shows the design of the test cell made of aluminum with brass ground electrodes. The cell is designed to test eight samples at a time, but only one sample was tested with one electrode because of the difficulty in obtaining the same levels of partial electrical discharges for all samples tested. The aluminum block is made to circulate cooling water (0°C) to form water condensation on the samples as experienced in the field application when high-voltage insulators are exposed to a temperature below the dew point of the surrounding air. Experiments were also performed at varying discharge levels to study the effect of discharge intensity on the hydrophobicity loss and recovery during and after partial discharge at constant humidity levels. Most experiments were carried out under normal laboratory conditions at 23°C and 50% RH. A few tests were made under the very dry conditions of 15% RH to study the effect of the environmental humidity on the surface modification and hydrophobic recovery of PDMS elastomers. Two gap distances between the

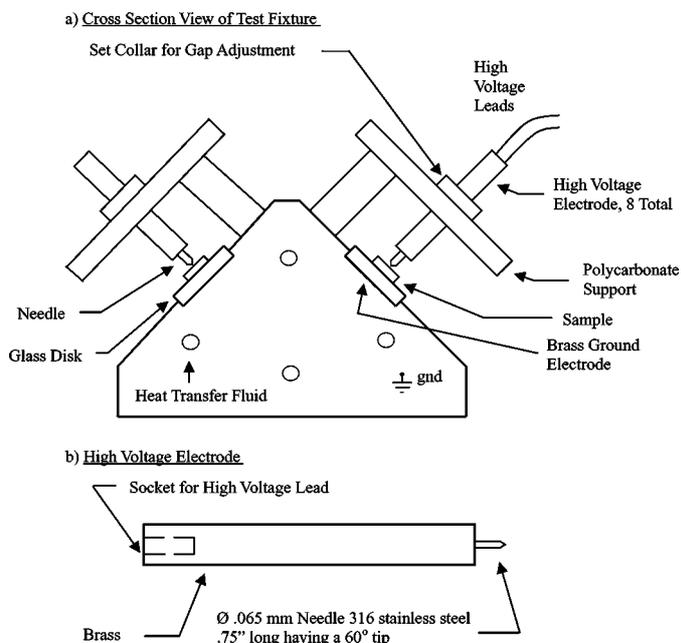
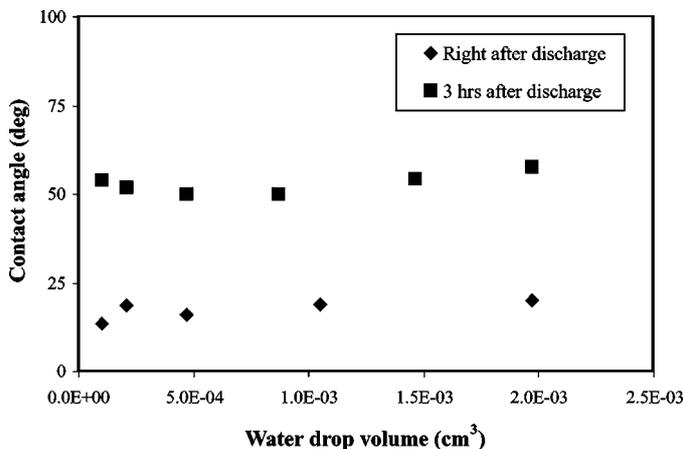


FIG. 1. The diagram of a partial electrical discharge test unit. The point-to-plane electrode configuration was used to sustain a low stable discharge.



**FIG. 2.** The advancing contact angle of water does not depend on the volume of the drop. The sample was an extracted silicone elastomer exposed to 3000 pC of partial discharge for 30 min. The oxidized area corresponds to  $\sim 50 \text{ mm}^2$ .

sample and the electrode rod were used, 0.4 and 0.05 mm. It is generally observed that a stable, low partial discharge can be obtained more consistently as the gap becomes narrower at a constant humidity.

#### 4. Surface Analysis

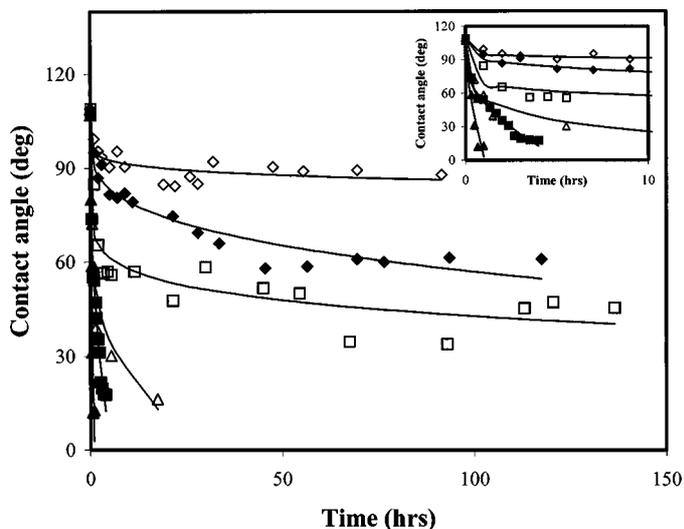
Contact angle measurement is a useful and inexpensive technique extensively employed in characterizing plasma, or corona-treated polymer surfaces in conjunction with other surface analysis techniques such as XPS and SIMS. Since the contact angles of liquid droplets on surface-treated polymers are closely associated with chemical compositions of the surface, this method is very useful in studying the aging of the surface-modified polymers. One of the most commonly used methods for contact angle measurement is the sessile drop technique (23, 24). By using a contact angle goniometer (Ramè-Hart, Inc., Model No. 100-00-115), the advancing contact angle of a sessile water droplet on the surface was measured at least four times while maintaining the volume of a drop as constant as possible. For nonideal polymer surfaces, surface defects lead to numerous metastable states of the system, showing hysteresis of contact angles (25–31). Significant dependency of the contact angle on the drop volume has also been found when the line tensions are not negligible (32). In our studies, however, we noticed no effect of the liquid drop size on the contact angle when the drop volume varied from 0.1 to  $2 \mu\text{l}$  (Fig. 2). This result indicates that the patchwise heterogeneities of the types observed by Good and Koo (32) in their studies on the drop size dependent contact angles are absent here. The result also shows that there is no radical variation of wettability within the entire area ( $\sim 50 \text{ mm}^2$ ) of the PDMS elastomer that was exposed to the partial discharge. In the subsequent experiments, a water volume of the order of  $0.2 \mu\text{l}$  was chosen. The angle-resolved XPS technique was also used to quantitatively analyze the atomic composition of

PDMS elastomer surfaces before or/and after partial discharge. Details of the XPS measurements are reported elsewhere (22).

### III. RESULTS AND DISCUSSION

#### 1. Hydrophobicity Loss

Water-in-air advancing contact angles of PDMS elastomers were monitored during experiments to study the hydrophobicity loss by partial electrical discharge in a point-to-plane electrode configuration. The needle electrode was suitable for sustaining a low, stable discharge with a small gap of 0.05 mm between the electrode and the sample. The hydrophobicity loss of PDMS elastomers was observed as a function of the exposure time of the discharge that varied from 10 to 250 pC at a constant ambient humidity (50%). As shown in Fig. 3, the extracted sample exposed to the lowest discharges (10–60 pC) gradually loses its hydrophobicity as discharge time increases, but the contact angle does not become less than ca.  $60^\circ$  even after 100 h of discharge. Possibly, very small amounts of LMW species may be produced during this low discharge, which subsequently migrate to the surface to minimize high surface energy resulting from the oxidation of methyl groups attached on siloxane backbones. For the fluid-containing sample, the advancing sessile contact angle decreases only slightly ( $109^\circ$  to  $89^\circ$ ) after which it remains unchanged, indicating that a dynamic equilibrium is maintained at the interface at this low discharge. Such a dynamic equilibrium can be reached when the rate of the migration to the surface of fluids preexisting in the polymer finally becomes the same as the rate of its oxidation by electrical

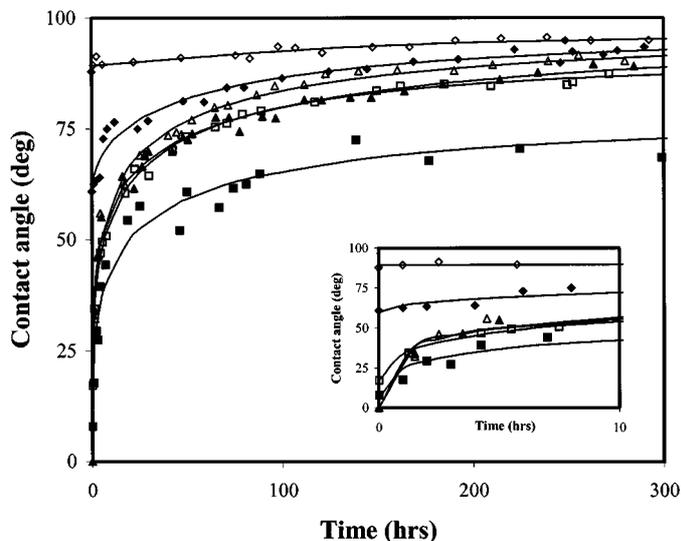


**FIG. 3.** The hydrophobicity losses of the silicone elastomers exposed to different levels of discharge at a constant environmental humidity of 50% in the point-to-plane electrode configuration with a gap of 0.05 mm. The inset shows the data obtained within the first 10 h: (◆) extracted, 10–60 pC; (■) extracted, 75–125 pC; (▲) extracted, 150–250 pC; (◇) 5% fluid (Mw = 236), 10–60 pC; (□) 5% fluid (Mw = 236), 75–125 pC; and (△) 5% fluid (Mw = 236), 150–250 pC.

discharge. As discharge increases from 10–60 to 75–125 pC, the effect of preexisting fluids on hydrophobicity loss becomes more pronounced. The extracted sample loses its hydrophobicity fast while the fluid-containing sample suffers a moderate loss of hydrophobicity (Fig. 3). Apparently, preexisting fluids play a more important role in preserving the hydrophobicity of the surface than *in situ* produced LMW species during these low discharge intensities. At more severe discharge levels (150–250 pC), the fluid-containing sample loses its hydrophobicity much faster, but it also shows a much faster recovery than the extracted sample due to the migration of preexisting fluids after discharge. Probably, the discharges in the range 10–250 pC do not produce enough LMW species to overwhelm the effect of the preexisting fluid. This migration process takes place during the active discharge as well as after the discharge period. However, at discharges higher than 1500 pC, the migration during the discharge does not make any impact on keeping the surface hydrophobic. When samples are exposed to the severe discharge, both extracted samples and fluid-containing samples totally lose their original hydrophobicity within one hour. The discharge is so intense that an inorganic, silica-like layer is rapidly created on the outermost surface, which may provide the resistance to the diffusion of both preexisting fluid and *in situ* produced LMW species to the surface. In addition, any nonpolar groups migrating to the surface during the discharge seem to be quickly oxidized by harsh discharges. Therefore, immediately after the discharge, a water drop spreads on the surface of the PDMS elastomer, and after the cessation of electrical discharge, the oxidized PDMS elastomers recover their hydrophobicity through the migration of LMW species from the bulk to the surface. Evidently, the hydrophobicity loss of extracted and fluid-containing samples is highly dependent on discharge intensity. We have shown how the recovery behavior of PDMS elastomers is also significantly affected by the intensity of electrical discharge and environmental humidity.

## 2. Hydrophobic Recovery

Figure 4 shows the hydrophobic recovery of the extracted and the fluid-containing samples in air after they were exposed to different ranges of discharge (10–10000 pC) for 1 h. The extracted sample exposed to the very low discharge (10–60 pC) exhibits a high initial contact angle ( $60^\circ$ ) immediately after 118 h of this low discharge and then recovers its hydrophobicity very slowly. Most probably, at a mild discharge, the extracted sample undergoes a mild oxidation of pendent methyl groups and simultaneously produces very small amount of LMW species. The subsequent hydrophobic recovery is then possibly due to the migration of *in situ* produced species from the bulk to the surface of the elastomer. At discharges higher than 1500 pC, although the extracted samples rapidly lose their hydrophobicity, they show a faster recovery than those exposed to lower discharge intensities. Interestingly, as discharge becomes very severe, the rate of the recovery of the extracted samples increases and then eventually becomes comparable to that of fluid-



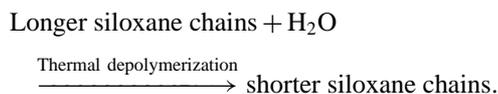
**FIG. 4.** The hydrophobic recovery of the samples exposed to partial electrical discharges. The discharge experiment was performed at a humidity of 50% in the point-to-plane configuration with a gap of 0.05 mm. All of the samples were aged in air after 1 h discharge except two ( $\blacklozenge$ ,  $\blacklozenge$ ). The contact angles of the samples  $\blacklozenge$  and  $\blacklozenge$  are measured after 118 and 92 h discharge, respectively: ( $\blacklozenge$ ) Extracted, 10–60 pC; ( $\blacksquare$ ) extracted, 100–400 pC; ( $\blacktriangle$ ) extracted, 4000–10000 pC; ( $\blacklozenge$ ) 5% fluid (Mw = 236), 10–60 pC; ( $\square$ ) 5% fluid (Mw = 236), 150–300 pC; and ( $\triangle$ ) 5% fluid (Mw = 236), 4000–8000 pC.

containing samples. This suggests that the high level of LMW species produced beneath the silica-like layer controls the recovery process by migrating to the surface (22). When both the extracted and the fluid-containing samples are compared at a low discharge, the latter exhibits a superior hydrophobic recovery to the former. The initial contact angle of the fluid-containing sample measured immediately after exposure to 150–300 pC for 1 h is  $17^\circ$ , which is higher than that ( $8^\circ$ ) observed on the extracted sample exposed to 100–400 pC (Fig. 4). Moreover, a pronounced increase of the recovery rate is observed in the fluid-containing sample. Presumably, at the mild discharge, preexisting fluids contribute to maintaining the hydrophobicity of PDMS elastomers by migrating to the surface during discharge as well as after discharge. It follows that the migration of preexisting fluid from the bulk to the surface is a key mechanism for this recovery process. However, as the discharge increases from 150–300 to 4000–8000 pC, the contribution of the preexisting LMW silicone fluid to the restructuring process becomes less significant. While the preexisting fluid has no great effect on the hydrophobic recovery of samples exposed to a discharge of 4000–8000 pC, the extracted sample shows a marked increase of recovery as the discharge increases from 100–400 to 4000–10000 pC. At high discharge intensities, the rate of hydrophobic recovery of the extracted samples is also comparable to the fluid-containing sample. Accordingly, at the severe discharge level, the key mechanism seems to be the migration of the *in situ* produced LMW species rather than that of free silicone fluid preexisting in the networks. Chang and Gorur (8), using

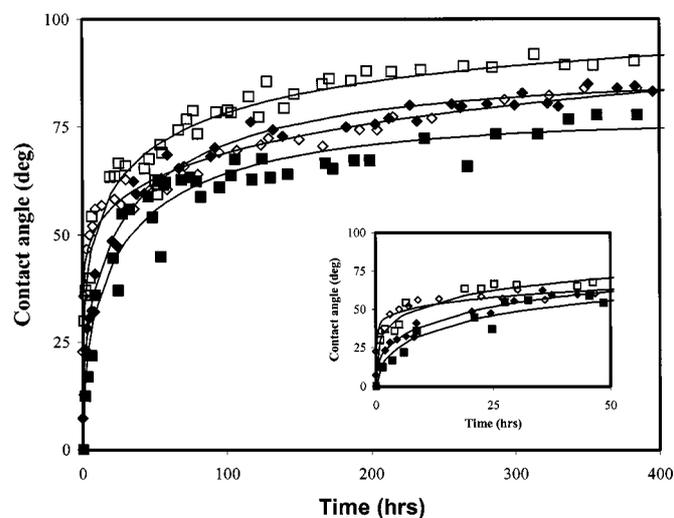
a hexane extraction and heating cycle, have demonstrated that LMW chain regeneration and hydrophobic recovery occur even after the initial supply of LMW species is depleted. The contribution of preexisting LMW silicone fluid to the restructuring is not significant under severe discharge conditions, but its role becomes more important at milder discharge conditions.

### 3. Humidity Effect

Moisture in air may participate in the hydrolytic depolymerization reaction and the production of LMW species by the heat generated during a severe discharge according to the reaction scheme (33, 34)



Since these species could markedly change the hydrophobic recovery behavior of PDMS elastomers, experiments were carried out to assess the humidity effect on the restructuring of extracted PDMS elastomers after exposure to different levels of discharge in the needle-to-plane configuration with an electrode gap of 0.4 mm. Contact angles were measured after exposure to varying discharges for one hour at a constant humidity of 15 or 50% (Fig. 5). When the samples are subjected to the low discharge range of 80–650 pC, the recovery is not highly affected by humidity. However, at the high discharge range of 4000–10000 pC, the effect of humidity on the recovery is significant, suggesting that air-borne water accelerates the formation of LMW species during discharge. For comparison,

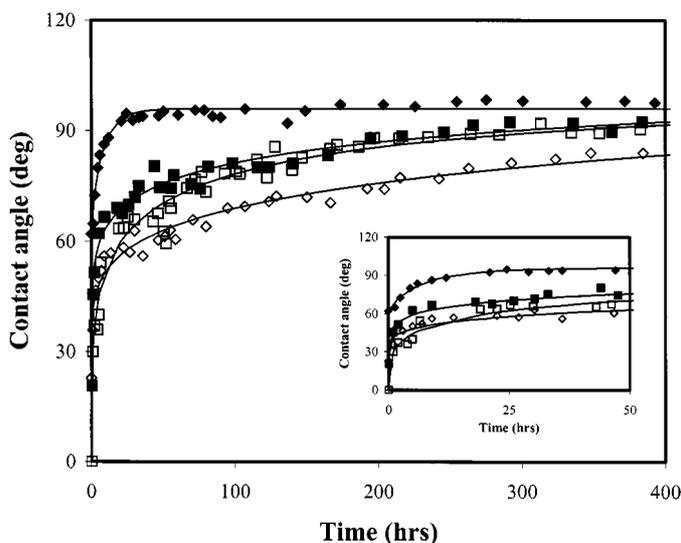


**FIG. 5.** The effect of humidity on the hydrophobic recovery of extracted samples after exposure to different discharge intensities. Exposure time is 1 h, and the gap between the sample and the needle tip is 0.4 mm. These results show that humidity affects the hydrophobic recovery more significantly under severe discharge conditions: (◆) 400–650 pC, 15%; (■) 4000–6000 pC, 15%; (◇) 80–150 pC, 50%; and (□) 4000–10000 pC, 50%.

the samples discharged at 15% humidity recover their hydrophobicity very slowly compared to those discharged at 50% humidity. It is well known (5, 6) that severe discharge under dry conditions results in the rapid formation of an inorganic silica-like layer on the outermost surface that could act as a barrier for the migration of LMW species trapped beneath the layer. Water does not have enough time to penetrate through the rapidly formed inorganic silica layer in this dry condition, which may eventually limit the production of LMW species compared to what happens under humid conditions. In spite of little moisture in air, LMW species may also be produced beneath the layer in the absence of oxygen after the thin, brittle, inorganic, silica-like layer develops on the outermost surface by oxidative cross-linking. Many studies have demonstrated that the thermal degradation of PDMS under vacuum or inert atmosphere causes a mixture of cyclic oligomers (35–40). As Hillborg and Gedde state in their recent review (41), it is generally believed that the aging of silicone elastomers in oxygen causes both oxidative cross-linking and chain scission, whereas oxygen-free aging leads to chain scission. Therefore, when silicone elastomers are subject to electrical discharges in dry conditions, both oxidative crosslinking and chain scission take place simultaneously, but the formation of the cross-linked layer is favored during a severe discharge. LMW species may be produced *in situ* beneath the layer by which oxygen is excluded but to a lesser extent than those produced by discharge in humid conditions. The humidity effect is more pronounced as the discharge becomes more severe.

### 4. Effect of Water Condensation

In another experiment, moisture was allowed to condense on a sample by circulating cooling water (0°C) into the aluminum block, which produces numerous tiny water drops on the surface. The extracted sample shows a contact angle of 23° immediately after exposure to 80–150 pC of discharge for 1 h at 50% (without condensation), but it exhibits a contact angle of 62° immediately after exposure to 100–300 pC for 1 h under condensation conditions (Fig. 6). At the low discharges, the extracted sample with water condensation also recovers faster than that without condensation. The water drops condensing on the surface are believed to accelerate the formation of LMW species even at a mild discharge by a depolymerization reaction with water. Subsequently the migration of the *in situ* produced LMW species through the inorganic silica-like layer, which is polar and is easily cracked by internal and external stresses, is then responsible for the faster recovery. As the intensity of partial discharge increases, such a striking effect of water condensation is not observed, but the sample with water condensation exhibits a higher initial contact angle (20°) than that (spreading) of the sample without water condensation, subsequently showing a slightly fast recovery. When the samples are exposed to severe discharges at an environmental humidity of 50%, the depolymerization reaction probably takes place actively regardless of water condensation.



**FIG. 6.** The effect of water condensation on hydrophobic recovery of extracted samples after 1 h of discharge. Point-to-plane gap is 0.4 mm. Numerous tiny water drops formed on the surface during cooling water circulation, which significantly affect hydrophobic recovery at a low discharge: (◆) 100–300 pC, with water condensation; (■) 1000–4000 pC, with water condensation; (◇) 80–150 pC, without water condensation; and (□) 4000–10000 pC, without water condensation.

### 5. Hydrophobic Recovery Mechanism

The hydrophobic recovery of silicone elastomers has long been studied, but there is still no general agreement due, in part, to the variety of experimental conditions and discharge sources that have been used. The migration of preexisting fluid and the reorientation of the oxidized side group are believed to be the main mechanisms of hydrophobic recovery. Recently (22), we showed that when samples are exposed to severe discharge conditions with discharges of 1500–12000 pC and corresponding applied voltages of 6–12 kV in the cylinder-to-plane configuration, the recovery process is dominated by the migration of *in situ* produced species. Preexisting fluid does not markedly affect recovery. Angle-resolved XPS results also support the same mechanism by showing a higher concentration of unoxidized carbon and silica at 15° take-off angle than measurements taken at 90° take-off angle (Table 1). This XPS analysis was performed about 2 h after the extracted sample was exposed to 6000–10000 pC for 1 h in the point-to-plane configuration with a gap of 0.4 mm and 50% humidity. Table 2 also shows atomic compositions of an extracted sample after exposure to partial electrical discharges of intensity 10–20 pC for 94.5 h at a humidity of 50%. The concentration of unoxidized carbon and silica increases with decreasing take-off angle, implying that small amounts of *in situ* produced LMW species migrate to the surface during and after discharge. These results may indicate that the extracted samples are governed by the same mechanism (migration of *in situ* produced LMW species); however, the two samples exhibit different hydrophobicity loss and recovery behaviors depending upon the discharge intensity. The

**TABLE 1**

**Surface Atomic Compositions of an Extracted PDMS Elastomer after Exposure to 6000–10000 pC for 1 h at 50% Humidity in the Point-to-Plane Configuration with an Electrode Gap of 0.4 mm<sup>a</sup>**

Element	Take-off angle	
	15°(%)	90°(%)
C(unoxidized)	9.0	2.8
C(oxidized)	2.0	0.7
Si(unoxidized)	4.5	1.0
Si(oxidized)	27.0	32.1
O	57.5	63.4

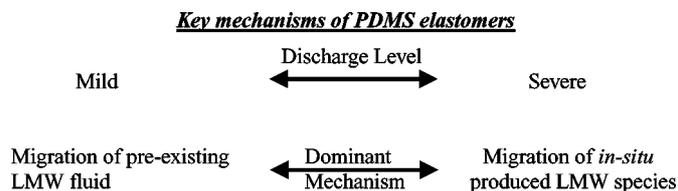
<sup>a</sup> The atomic compositions of the unoxidized sample are as follows: C (45.3%), Si (30.0%), and O (24.7%).

extracted sample exhibits spreading of water immediately after exposure to 6000–10000 pC for 1 h, whereas a contact angle of about 50° is observed on samples immediately after exposure to 10–20 pC for 94.5 h. The discharges in the range 10–20 pC are not intense enough to make the extracted sample totally hydrophilic. Here, the *in situ* produced LMW species, most probably, contribute to the high initial contact angle of the extracted sample. Under severe discharge conditions, the extracted sample loses and regains its hydrophobicity rather fast. The extracted sample subject to low discharges (<200 pC) shows a slower recovery than that exposed to severe discharges (>1500 pC). We believe that the amount of LMW species produced during discharge increases with the discharge intensity. Therefore, at a lower discharge, the higher concentration of unoxidized carbon and silicon at the outmost surface is likely due to the migration of *in situ* produced LMW species and the mild oxidation of methyl groups during discharge; however, the hydrophobic recovery is slow due to the limited production of LMW species. At a higher discharge level, even though initial atomic compositions of unoxidized carbon and silicon are lower than those exposed to a low discharge, the samples show much faster hydrophobic recovery. This could be due to the production of large amounts of LMW species at high discharge intensities, whereby the flux to the surface is enhanced. Consequently the LMW species should play an important role in the restructuring

**TABLE 2**

**Surface Atomic Compositions of an Extracted PDMS Elastomer after Exposure to 10–20 pC for 94.5 h at 50% Humidity in the Point-to-Plane Configuration with an Electrode Gap of 0.05 mm**

Element	Take-off angle		
	15°(%)	30°(%)	90°(%)
C(unoxidized)	41.9	33.6	22.7
C(oxidized)	1.6	1.7	1.3
Si(unoxidized)	17.6	13.5	0.9
Si(oxidized)	10.8	16.0	9.0
O	28.1	35.2	21.2



**FIG. 7.** Key mechanisms underlying hydrophobic recovery of silicone elastomers after partial discharge. Silicone elastomers exhibit different restructuring behaviors depending on the presence of preexisting LMW fluid and discharge intensity. At low discharge, preexisting fluid considerably contributes to hydrophobic recovery, but at severe discharge *in situ* created LMW species become more important.

of high-voltage silicone elastomers during service. On the other hand, especially at low discharges (<200 pC), preexisting fluid significantly contributes to hydrophobic recovery after discharge, suggesting that the dominant mechanism in this case is the migration of preexisting fluid from the bulk to the surface (Fig. 7). To address the issue of surface migration, we also performed XPS analysis of a silicone elastomer in which a fluorinated siloxane (3,3,3-trifluoropropylmethyl siloxane,  $M_w = 950$ ) was added at 5% by weight. Before discharge, the surface concentration of fluorine observed at both  $15^\circ$  and  $90^\circ$  take-off angles is  $\sim 0.5\%$ , which indicates that most of the fluorine moieties are present in the bulk. However, after a 30-min exposure to a discharge of 7000–12000 pC, the fluorine concentration on the surface of the elastomer increases markedly to 21% regardless of the sample depth probed with XPS (i.e., independent of take-off angle). The dramatic increase in fluorine concentration offers clear evidence that the hydrophobic recovery is totally dominated by the diffusion of fluid from the bulk to the surface. The fluorine-containing species that diffuse to the surface may be the ones produced *in situ* by a chemical depolymerization

of both pendent groups and chain backbones during electrical discharge. Consistent with the XPS results, the samples containing the fluorinated siloxane fluid ( $M_w = 950$ ) also exhibit a much faster hydrophobic recovery than either the extracted samples or those containing free methyl-terminated silicone fluid ( $M_w = 950$ ) (Fig. 8). Six hours after exposure to 4000–11000 pC for 1 h, the fluorine-containing sample recovers 88% of its original contact angle, whereas both the methyl-containing and the extracted sample show only 45% recovery. This result shows that the fluorine-containing fluid segregates faster to the surface compared to a methyl-containing fluid. Likely, the fast recovery of the fluorine-containing samples results from the diffusion of species produced by the fragmentation of the fluorinated siloxane rather than the fluid itself. This is, however, the subject of future studies.

#### IV. SUMMARY

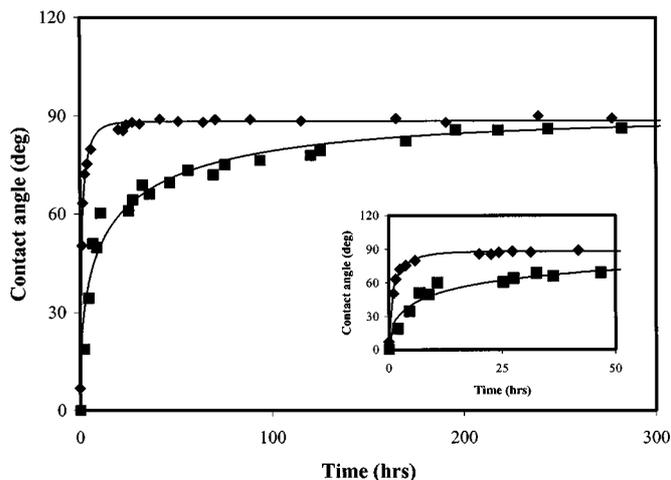
The partial discharge experiments with a point-to-plane electrode configuration show that hydrophobic recovery depends on such factors as the discharge intensity, preexisting fluid, and environmental humidity. When the PDMS elastomers are exposed to mild discharges, the silicone fluid preexisting in the elastomer plays an important role in the hydrophobic recovery of the oxidized elastomers. However its effect is less significant than the migration of the *in situ* produced LMW species at severe discharge levels. As the discharge becomes severe, the dominant mechanism of hydrophobic recovery is the migration of the *in situ* produced LMW species from the bulk to the surface of the elastomer. Additionally, moisture in air promotes the production of LMW species under severe discharge conditions, which consequently leads to a faster hydrophobic recovery.

#### ACKNOWLEDGMENT

The authors gratefully acknowledge financial support by Dow Corning Corp.

#### REFERENCES

1. Kikuchi, T., Nishimura, S., Nagao, M., Izumi, K., Kubota, Y., and Sakata, M., *IEEE Trans. Dielectr. Electr. Insul.* **6**, 548 (1999).
2. Tóth, A., Bertóti, I., Blazsó, M., Bánhegyi, G., Bogнар, A., and Szaplanczay, P., *J. Appl. Polym. Sci.* **52**, 1293 (1994).
3. Morra, M., Occhiello, E., Marola, R., Garbassi, F., Humphrey, P., and Johnson, D., *J. Colloid Interface Sci.* **137**, 11 (1990).
4. Owen, M. J., and Smith, P. J., *J. Adhesion Sci. Technol.* **8**, 1063 (1994).
5. Smith, P. J., Owen, M. J., Holm, P. H., and Toskey, G. A., *Conf. Electr. Insul. Dielectr. Phen.* 829 (1992).
6. Hillborg, H., and Gedde, U. W., *Polymer* **39**, 1991 (1998).
7. Gorur, R. S., Karady, G. G., Jagota, A., Shah, M., and Yates, A. M., *IEEE Trans. Power Delivery* **7**, 525 (1992).
8. Chang, J. W., and Gorur, R. S., *IEEE Trans. Dielectr. Electr. Insul.* **1**, 1039 (1994).
9. Kim, S. H., Cherney, E. A., Hackam, R., and Rutherford, K. G., *IEEE Trans. Dielectr. Electr. Insul.* **1**, 106 (1994).
10. Deng, H., and Hackam, R., *IEEE Trans. Power Delivery* **12**, 857 (1997).
11. De la O, A., Gorur, R. S., and Burnham, J. T., *IEEE Trans. Dielectr. Electr. Insul.* **3**, 827 (1996).



**FIG. 8.** The effect of preexisting fluid on the hydrophobic recovery of electrically discharged PDMS elastomers. Discharge experiments were performed at 50% humidity in the point-to-plane configuration. Exposure time is 1 h, and the gap is 0.4 mm: (◆) 5% fluorinated siloxane fluid ( $M_w = 950$ ), 7000–11000 pC; and (■) 5% dimethylsiloxane fluid ( $M_w = 950$ ), 7000–10000 pC.

12. Kim, S. H., Cherney, E. A., and Hackam, R., *IEEE Trans. Power Delivery* **6**, 1549 (1991).
13. Deng, H., and Hackam, R., *IEEE Trans. Dielectr. Electr. Insul.* **6**, 84 (1999).
14. Kim, S. H., Cherney, E. A., and Hackam, R., *IEEE Trans. Power Delivery* **5**, 1491 (1990).
15. Karady, G. G., Shah, M., and Brown, R. L., *IEEE Trans. Power Delivery* **10**, 1965 (1995).
16. Homma, H., Kuroyagi, T., Izumi, K., Mirley, C. L., Ronzello, J., and Boggs, S. A., *IEEE Trans. Dielectr. Electr. Insul.* **6**, 370 (1999).
17. Wankowicz, J. G., Gubanski, S. M., and Lampe, W. D., *IEEE Trans. Dielectr. Electr. Insul.* **1**, 604 (1994).
18. Vlastós, A. E., and Gubanski, S. M., *IEEE Trans. Power Delivery* **6**, 888 (1991).
19. Blackmore, P., and Birtwhistle, D., *IEEE Trans. Dielectr. Electr. Insul.* **4**, 210 (1997).
20. Zhang, H., and Hackam, R., "Conference Record of the 1998 IEEE International Symposium on Electrical Insulation." Arlington, Virginia, June 7–10, 355, 1998.
21. Kim, J., Chaudhury, M. K., and Owen, M. J., *IEEE Trans. Dielectr. Electr. Insul.* **6**, 695 (1999).
22. Kim, J., Chaudhury, M. K., and Owen, M. J., *J. Colloid Interface Sci.* **226**, 231 (2000).
23. Chan, C., "Polymer Surface Modification and Characterization." pp. 35–76. Hanser, New York, 1994.
24. Garbassi, F., Morra, M., and Occhiello, E., "Polymer Surfaces." pp. 161–199. Wiley, New York, 1994.
25. Wenzel, R. N., *Ind. Eng. Chem.* **28**, 988 (1936).
26. Good, R. J., *J. Amer. Chem. Soc.* **74**, 5041 (1952).
27. Johnson, R. E., Jr., and Dettre, R. H., in "Surface and Colloid Science" (E. Matijević, Ed.), Vol. 2, pp. 85–153. Wiley-Interscience, New York, 1969.
28. Cassie, A. B. D., *Discuss. Faraday Soc.* **3**, 11 (1948).
29. Israelachvili, J. N., and Gee, M. L., *Langmuir* **5**, 288 (1989).
30. Johnson, R. E., Jr., and Dettre, R. H., *J. Phys. Chem.* **68**, 1744 (1964).
31. Good, R. J., in "Surface and Colloid Science" (R. J. Good and R. R. Stromberg, Eds.), Vol. 11, pp. 1–29, Plenum, New York, 1979.
32. Good, R. J., and Koo M. N., *J. Colloid Interface Sci.* **71**, 283 (1979).
33. Doyle, C. D., *J. Polym. Sci.* **31**, 95 (1958).
34. Thomas, D. K., *Polymer* **7**, 99 (1966).
35. Thomas, T. H., and Kendrick, T. C., *J. Polym. Sci.* **7**, 537 (1969).
36. Grassie, N., and Macfarlane, I. G., *Eur. Polym. J.* **14**, 875 (1978).
37. Kang, D. W., Rajendran, P., and Zeldin, M., *J. Polym. Sci. A: Polym. Chem.* **24**, 1085 (1986).
38. Bannister, D. J., and Semlyen, J. A., *Polymer* **22**, 377 (1981).
39. Clarson, S. J., and Semlyen, J. A., *Polymer* **27**, 91 (1986).
40. Radhakrishnan, T. S., *J. Appl. Polym. Sci.* **73**, 441 (1999).
41. Hillborg, H., and Gedde, U. W., *IEEE Trans. Dielectr. Electr. Insul.* **6**, 703 (1999).