

Modeling hydrophobic recovery of electrically discharged polydimethylsiloxane elastomers

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Abstract

Theoretical models are proposed to account for the hydrophobic recovery kinetics of electrically discharged silicone elastomers, in which the effects of both the diffusion and adsorption of in situ produced low molecular weight (LMW) species are considered. A homogeneous solid diffusion model or a pore diffusion model well represents the surface restructuring of silicone elastomers exposed to partial electrical discharges. The computed diffusivity of the in situ produced LMW species through an inorganic, silica-like layer to the outermost part of the oxidized polymer is much smaller than that calculated from the absorption experiment of a silicone elastomer. At severe discharge intensity, no significant difference in the hydrophobic recovery is observed for extracted samples and those doped with free dimethylsiloxane fluid, whereas fluorinated siloxane fluid containing samples recover their hydrophobicity faster than the others. Modeling studies indicate that the faster recovery of the later samples may be due to the faster diffusion of the species produced from the fragmentation of the fluorinated siloxane fluid preexisting in the polymer during electrical discharge.

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1. Introduction

Silicone-based polymers are extensively used in outdoor insulation applications, such as in transmission and distribution lines because they show an excellent performance in maintaining their surface in a hydrophobic state even in contaminated areas [1–3]. The low surface energy of silicone elastomers plays a crucial role in preventing the formation of an electrolyte film, which may develop on the surface in the presence of airborne pollutants and moisture that subsequently increase leakage current and dry-band arcing. Extensive studies [4–22] suggest that the superior electrical performance of silicone insulator over inorganic materials is due to its ability to recover the hydrophobicity. The hydrophobic recovery of electrically discharged silicone rubbers is significantly affected by discharge intensity, humidity, preexisting

fluid and other factors; but, there is enough evidence [18–22] to suggest that the recovery process is dominated by the diffusion of in situ produced low molecular weight (LMW) species from the bulk to the surface of the polymer. This result has motivated researchers to estimate the diffusivity of the LMW silicone fluid in the silicone elastomer by measuring the absorbed amount of a silicone fluid in a sheet of a silicone polymer as a function of time [23–27]. The increase of weight of the elastomer during the early stages of fluid absorption was analyzed using a simple diffusion equation of the type

$$\frac{M_t}{M_\infty} = 4 \left(\frac{D}{l^2} \right)^{1/2} \left(\frac{t}{\pi} \right)^{1/2}, \quad (1)$$

where M_t and M_∞ are the weight increases of the elastomer at time t and at $t = \infty$, respectively; D is the diffusivity (cm^2/s); and l is the sample thickness (cm).

In reality, however, the diffusivity obtained from the absorption experiment is inadequate to represent the processes

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underlying the hydrophobic recovery of electrically discharged silicone elastomers because of the reasons outlined below. First of all, the silicone insulators may experience a secondary thermal degradation during field service, which results in changes in crosslink density. Secondly, the in situ produced LMW species—not the preexisting fluid—usually control the hydrophobic recovery of PDMS elastomers. Because of the above complications, the values of the diffusivity obtained from the absorption experiments may not correspond to what is needed to explain the electrical discharge experiments. It would indeed be more informative to obtain the values of diffusivity of in situ produced LMW species that diffuse through a silica-like layer to the surface; but such data, unfortunately, are unavailable.

For the purpose of describing the hydrophobic recovery of electrically discharged PDMS elastomers, a diffusion coupled adsorption model is applied to our system. The computational results are combined with the Cassie [28] equation to predict the hydrophobic recovery in terms of contact angle and aging time. These models, which are better predictors of experimental data than the previously used simple diffusion models, also yield realistic estimates of diffusivities of in situ produced LMW species that are responsible for the hydrophobic recovery. The theoretical models and their comparative simulation results are discussed below by considering, in particular, the effects of concentration of in situ produced LMW species on the hydrophobic recovery kinetics.

2. Experimental

A high voltage AC corona test set (Hipotronics, Model 750-5CTS B/S) was used to generate partial electrical discharges on the surfaces of silicone elastomer sheets (thickness 1 mm). The samples were prepared by curing a two-component silicone resin Dow Corning SYLGARD 184 in an oven at 75 °C for 2 h. The cure chemistry involves hydrosilylation reaction of dimethylvinyl-encapped polydimethylsiloxane with methylhydrogen siloxane crosslinker in the presence of a platinum catalyst. The elastomer also contain partially methylated silica resin for re-enforcement [29].

In modeling the hydrophobic recovery of silicone elastomers, three different types of samples were used: an extracted sample, a dimethylsiloxane fluid-containing sample, and a fluorinated siloxane fluid-containing sample. The unreacted oligomers were removed from the elastomer by extracting it with chloroform in a Soxhlet apparatus for 12 h, followed by its drying in a vacuum desiccator. These extracted samples served as control, whereas the preexisting fluid-containing samples were prepared by adding linear PDMS fluid (MW = 950, Gelest, Inc.) and 3,3,3-trifluoropropylmethylsiloxane fluid (MW = 950, Gelest, Inc.) respectively to the mixture of SYLGARD 184 in the ratio of 5:100 by weight of the base polymer before crosslink-

ing. We will denote the above fluid-containing samples as M-PDMS and F-PDMS, respectively. After the silicone elastomers were exposed to partial electrical discharges in a range of 100–11000 pC for 1 h in a point-to-plane configuration (tip diameter 0.065 mm) [30], sessile drop advancing contact angles of water were measured on the oxidized sample as a function of time in order to monitor the hydrophobic recovery kinetics. The environmental humidity was 50%, and the gap between a sample and the electrode tip was 0.4 mm. Angle resolved X-ray photoelectron spectroscopy (XPS) was used to calculate the thickness of the silica-like layer, which was required to solve the model equations.

3. Background on the theoretical models

A silica-like thin layer is formed on the outermost surface region of a silicone elastomer during active electrical discharges. Simultaneously, LMW species are also produced in situ in the sub-surface region. It has now been established that the electrically discharged PDMS elastomers recover their hydrophobicity [22,30,31] via diffusion of the in situ produced low molecular weight (LMW) species from a sub-surface region to the outermost surface through the thin silica-like layer (Fig. 1). Hillborg et al. [31] prepared their electrically discharged samples with multiple needle electrodes. These investigators carefully extracted and analyzed the in situ produced species from the electrically discharged PDMS and provided strong evidence that cyclic dimethylsiloxane ($D_n = [(CH_3)_2SiO]_n$, $n = 4-9$) is the main species formed in such reactions. The reported amount of the LMW species formed in a process involving multiple needle electrodes is extremely small (<0.5 ng/cm²); thus it is even more challenging to obtain the initial concentration of the species when a single needle electrode is used. Furthermore, the values of the diffusivity, the thickness of the silica-like layer, and the equilibrium adsorption characteristics of the in situ produced LMW species are not accurately known. Despite the difficulties in experimentally garnering these data, our theoretical models are still useful in parametric evaluations of the factors that significantly affect the hydrophobic recovery. In order to develop a suitable model, we consider the silica-like layer as an adsorbent so that both the diffusion and adsorption of LMW species take place at the same time during the hydrophobic recovery, which is quite similar to the adsorption of a chemical species.

3.1. Adsorption as in a packed-bed column

A typical example relevant to our problem can be found in a packed-bed column, in which adsorption takes place in a porous medium. In modeling the packed-bed column, two types of approach—a pore diffusion model [32–37] and a homogeneous solid diffusion model [36–39]—are commonly used to predict a breakthrough curve. The pore diffusion model pictures the diffusion of an adsorbate through

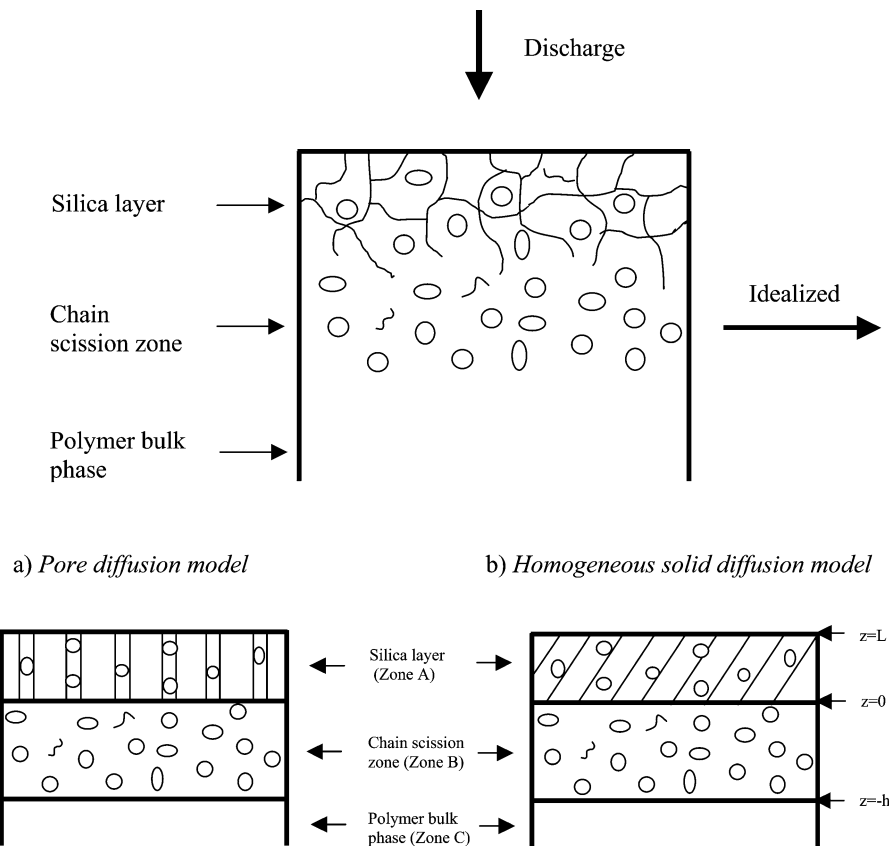


Fig. 1. The schematic diagram of the surface of the oxidized PDMS elastomer subjected to severe electrical discharges. During the electrical discharges, LMW species are produced via chain scissions of siloxane backbones by thermal degradation, and simultaneously an inorganic silica layer is formed in the outermost surface. The surface of the oxidized PDMS elastomer is idealized for the hydrophobic recovery modeling.

the pores of an adsorbent with a distributed adsorption along the pore walls. In the homogeneous solid diffusion model, the particle is assumed to be homogeneous regardless of its porous structure, and the adsorption takes place on the outer surface of the particle, followed by the diffusion of the species in the adsorbed state. The governing equations [35–37] derived from both the pore diffusion model and homogeneous solid diffusion model are numerically solved with an equilibrium adsorption equation given in the form of either a linear or nonlinear isotherm. Weber and Chakravorti [37] reported that these two models yield an identical breakthrough curve provided that the adsorption isotherm is approximately linear. However, in the case of a nonlinear adsorption isotherm, the models need to be more specific. If adsorption is assumed to be much faster than diffusion, equilibrium is reached instantaneously at every local position. The amount adsorbed on the wall at a local position in the pore and the amount adsorbed on the outer surface of the particle may be expressed as a function of adsorbate concentration. In our study, we use a Freundlich adsorption isotherm as it is most suitable for describing adsorption on heterogeneous surfaces:

$$\text{Freundlich isotherm: } q_p = AC_p^B, \quad (2)$$

where q_p and C_p are the concentrations of the LMW species adsorbed on the pore wall and inside the pore, respectively; A and B are adsorption constants.

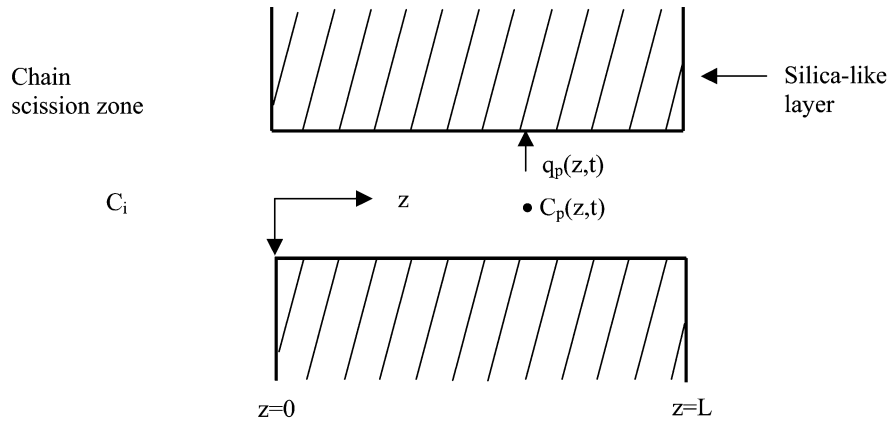
3.2. Contact angle

A polymer surface exposed to partial electrical discharges consists of domains of different compositions and surface energies. According to the Cassie [28] equation, the contact angle on the heterogeneous surface θ is expressed as the weighted average of the intrinsic contact angles on the regions comprising the surface:

$$\begin{aligned} \cos \theta &= f_{po} \cos \theta_{po} + f_{np} \cos \theta_{np} \\ &\approx \frac{q_{po}}{q_0} \cos \theta_{po} + \frac{q_{np}}{q_0} \cos \theta_{np}, \quad q_0 = q_{po} + q_{np}. \end{aligned} \quad (3)$$

Here, the subscripts po and np denote polar and nonpolar groups on the oxidized polymer surface; f , θ , and q represent fractional surface area, contact angle, and concentration, respectively. For simplicity, we assume that the discharged surface consists of only two component polar and nonpolar groups. With this assumption [40], the fraction of surface area can be replaced by the fraction of the concentration of the component (Eq. (3)).

a) Pore diffusion model



b) Homogeneous solid diffusion model

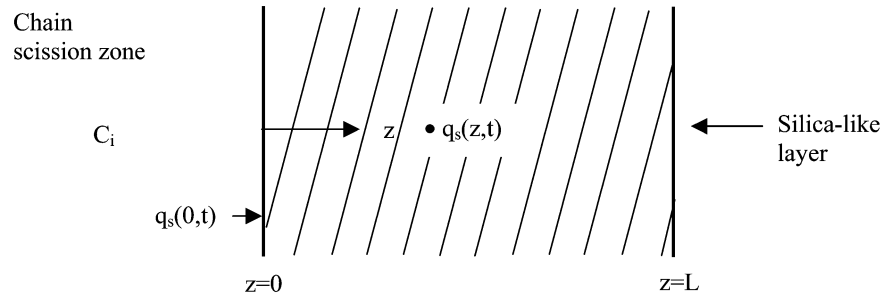


Fig. 2. Illustration of diffusion and adsorption of in situ produced LMW species at a local position.

With the help of the above definitions and Cassie equation, the fractional polarity $f_{\cos\theta}$ of the surface is defined [40] in terms of contact angles as

$$f_{\cos\theta} = \frac{\cos\theta_t - \cos\theta_\infty}{\cos\theta_0 - \cos\theta_\infty} \approx \frac{q_0 - q_{np}^t}{q_0}, \quad (4)$$

$$\cos\theta_t = \cos\theta_\infty + (\cos\theta_0 - \cos\theta_\infty) \left(1 - \frac{q_{np}^t}{q_0} \right), \quad (5)$$

where θ_t , θ_0 , and θ_∞ are the contact angles on the oxidized PDMS elastomer surface at time t , $t = 0$, and at $t = \infty$, respectively; q_{np}^t , q_{np}^0 , and q_{np}^∞ are the corresponding concentrations of nonpolar groups. Immediately after the silicone elastomers are exposed to a partial electrical discharge, water spreads on the oxidized surfaces of all the samples. Therefore, only polar groups (for example, hydroxyl, aldehyde, or carboxyl groups) comprise the surface right after electrical discharges ($q_{np}^0 = 0$). As the hydrophobic recovery proceeds, nonpolar groups (methyl or fluorine-containing groups) diffuse to the surface. As aging time t goes to infinity, as the oxidized surface fully recovers its hydrophobicity only the nonpolar groups cover the surface; therefore, $q_{np}^\infty/q_0 = 1$ (Eq. (4)). An expression of $\cos\theta_t$ can thus be obtained in terms of the concentration of nonpolar groups (Eq. (5)).

4. Analysis

4.1. Theoretical model

A pore diffusion model and a homogeneous solid diffusion model are used to establish a theoretical architecture needed to predict the surface restructuring of electrically discharged silicone elastomers. We assume that the diffusion of LMW species through a silica-like layer is a rate-limiting step so that the external film diffusion of LMW species from the zone B to the interface of the silica-like layer ($z = 0$) is not considered in mass balance equations. Additional assumptions are imposed: (1) the volume of the zone B is much larger than that of the silica-like layer; (2) diffusion takes place only in the direction of z , i.e., a radial diffusion is negligible; and (3) the diffusivity of LMW species is independent of concentration.

4.1.1. Pore diffusion model

In the pore-diffusion model, LMW species are considered to diffuse into the straight, cylindrical pores and then adsorb on their inner walls (Fig. 2a). At the surface of the oxidized polymer ($z = L$), the concentration of the LMW species increases while simultaneously adsorbing on the silica-like

layer until the local concentration at $z = L$ equals that at $z = 0$. The governing equation is

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \rho(1 - \varepsilon_p) \frac{\partial q_p}{\partial t} = \varepsilon_p D_p \frac{\partial^2 C_p}{\partial z^2}; \quad (6)$$

$$\text{IC: } C_p(z, 0) = -C_{is}/L \cdot z + C_{is}, \quad (7a)$$

$$\text{BC 1: } C_p(0, t) = C_i, \quad (7b)$$

$$\text{BC 2: } \frac{\partial C_p(L, t)}{\partial z} = 0. \quad (7c)$$

C_p is concentration of LMW species in the pore, q_p is the concentration of LMW species adsorbed on the wall in the pore, C_i is the initial concentration of LMW species produced in situ in the zone B during electrical discharge, C_{is} is the concentration of LMW species trapped in the silica-like layer after electrical discharge, t is time in seconds, z the distance from $z = 0$ as depicted in Fig. 1, L is the thickness of the silica-like layer, ε_p is porosity of the silica-like layer and ρ is its density.

Equation (6) is the mass balance for the in situ produced LMW species diffusing into the pores of a silica-like layer. The left-hand terms of Eq. (6) account for the accumulation and the disappearance of the in situ produced LMW species. Immediately after exposure to partial electrical discharge, some of the in situ produced LMW species may be trapped in the pores of the silica-like layer, resulting in a concentration distribution with respect to the distance z (Eq. (7a)). The other LMW species are produced in situ in the zone B having the initial concentration C_i (Eq. (7b)). The value of C_i is affected by the discharge intensity, exposure time, and environmental humidity. In the case that all of the crosslinked siloxane chains in the zone B are thermally depolymerized to LMW species, the initial concentration of the LMW species C_i would be the same as the density ($\sim 1 \text{ g/cm}^3$) of the elastomer. On the other hand, the partial depolymerization of the siloxane chains in the zone B results in an initial concentration C_i that is much smaller than 1 g/cm^3 . At the surface ($z = L$), the derivative of the concentration of the LMW species with respect to z is zero because the LMW species cannot diffuse further at $z = L$ and is changed only with aging time (Eq. (7c)). The evaporation of the species on the electrically discharged surface was not considered even though the species have a relatively low vapor pressure. Immediately after the electrical discharge, the surface has a high surface energy, so that the species are likely to remain adsorbed on the electrically discharge surface during aging at normal atmospheric condition. However, we observed previously [22] that aging in a high vacuum condition results in a slow hydrophobic recovery presumably due to evaporation of the species. The LMW species diffuse to the surface ($z = L$) through the pores of the silica-like layer, accompanied by the adsorption on every local position in the pores. The adsorption is assumed to be much faster than the diffusion so that a local equilibrium exists everywhere inside the pores. In Eq. (7b), the concentration of LMW species at the

pore inlet $C_p(0, t)$ is assumed to be constant while the diffusion of the species proceeds through the inorganic silica-like layer to the outer surface ($z = L$). Although $C_p(0, t)$ can be described in terms of the diffusional flux at the pore inlet, this boundary condition does not affect the simulation results [41] in any significant way.

Consider a sample that has unit area (1 cm^2) oxidized. The depth of the sample probed by contact angle measurement [40] is so small ($\sim 5 \text{ \AA}$) that only extremely small amount of LMW species is needed for the hydrophobic recovery of the oxidized silicone elastomer. In the modeling scheme, we consider that the concentration of LMW species is constant in zone B while the oxidized surface recovers its hydrophobicity. As the surface continues to restructure, the concentration of the LMW species increases in the pores and eventually becomes same as that in zone B. At this point, the silica-like layer at $z = L$ adsorbs the largest amount of LMW species according to the adsorption equations (Eq. (2)), which is referred to as q_m . Thus we can set $q_0 = q_m$, in view of which Eq. (5) can be rewritten as follows:

$$\cos \theta_t = \cos \theta_\infty + (\cos \theta_0 - \cos \theta_\infty) \left(1 - \frac{q_{np}^t}{q_m} \right). \quad (8)$$

In Eq. (8), the pore concentration of LMW species C_p is not considered as it is much smaller than q_m , so that the contact angle on the oxidized surface is affected mainly by the LMW species adsorbed on the silica-like layer at $z = L$. All other subtle effects of the pore during contact angle measurements, i.e., penetration of water for $\theta < \pi/2$ and non-penetration for $\theta > \pi/2$, are ignored. The concentration q_{np}^t in Eq. (8) can be obtained as a function of aging time at the surface ($z = L$) by numerically solving Eq. (6) in conjunction with an adsorption equation (Eq. (2)). Substitution of the numerical values of q_{np}^t into Eq. (8) finally allows us to predict the hydrophobic recovery of electrically discharged silicone elastomers in terms of $\cos \theta_t$ and aging time that are measurable experimentally.

4.1.2. Homogeneous solid diffusion model

The homogeneous solid diffusion model assumes that the porous medium is homogeneous, and the LMW species diffuse through the silica-like layer to the surface ($z = L$) in the adsorbed state (Fig. 2b). Therefore, the equation describing the hydrophobic recovery is simply

$$\frac{\partial q_s}{\partial t} = D_s \frac{\partial^2 q_s}{\partial z^2}, \quad (9)$$

where q_s is concentration of LMW species adsorbed on the silica-like layer, and D_s represents the diffusivity of the LMW species (cm^2/s) through the above layer.

The concentration of LMW species at $z = L$ may be determined by the amount of LMW species adsorbed at the interface of the silica layer ($z = 0$) and the diffusivity of the species. Experimental data show that hydrophobic recovery becomes faster with increasing discharge intensity.

However, even though the initial concentration of LMW species increases with increasing discharge intensity, the hydrophobic recovery eventually reaches a maximum value in spite of further increase in discharge intensity. There may be a critical concentration of LMW species beyond which it has no further effect on hydrophobic recovery, as excessive LMW species do not contribute to the surface restructuring of the oxidized PDMS elastomers, presumably, due to the maximum adsorption capacity of the silica-like layer. If a Freundlich isotherm is taken as an example of nonlinear adsorption, then we obtain the concentration of LMW species at $z = L$ by numerically solving Eq. (9) with the following initial and boundary conditions:

$$\text{IC: } q_s(z, 0) = -q_{\text{is}}/L \cdot z + q_{\text{is}}, \quad (10a)$$

$$\text{BC 1: } q_s(0, t) = AC_i^B, \quad (10b)$$

$$\text{BC 2: } \frac{\partial q_s(L, t)}{\partial z} = 0. \quad (10c)$$

q_{is} is concentration of LMW species trapped in the silica-like layer after electrical discharge (g/cm^3).

The adsorbed amount of the LMW species $q_s(0, t)$ can be calculated from the initial concentration C_i produced in the zone B during electrical discharge using an adsorption isotherm (Eq. (10b)). Similarly to the pore diffusion model, the concentration of the LMW species adsorbed at the interface of the silica-like layer at $z = 0$ is assumed to remain constant while the diffusion of the species proceeds through the inorganic silica layer to the surface in an adsorbed state. As is the case with pore diffusion model, the numerical computation of Eq. (9) together with an adsorption equation (Eq. (2)) yield the concentration q_{np}^t in Eq. (8) as a function of aging time at $z = L$. Subsequent steps used for the estimation of the fractional recovery of hydrophobicity are similar in the two approaches.

4.2. Numerical solution

A method of lines (MOL) solution [42,43] to Eqs. (6)–(10) is programmed in Fortran. The constants of the Freundlich isotherm (A, B) are assigned as the values that give best correlations with experimental data. The thickness (140 Å) of the inorganic silica-like layer was calculated from the attenuation of photoelectron induced in XPS analysis [44] of the oxidized elastomer surfaces. The contact angles at $t = 0$ and $t = \infty$ of the samples are also given in Table 1. With the given initial and boundary conditions, the numerical computations of the governing equations (6) and (9) were carried out using a finite difference approximation. The thickness of the silica-like layer is L , and the uniform spatial grid on 31 points for $0 \leq z \leq L$ is used. Ordinary differential equations with respect to time t at the uniform spatial grid are then solved with the given diffusivity and initial concentration of the LMW species.

Table 1

The initial contact angles (θ_0) and the final contact angles (θ_∞) of PDMS samples

Sample	Discharge (pC)	Gap (mm)	θ_0 (°)	θ_∞ (°)
Extracted	100–400	0.05	8 ^a	90.4
	4000–10000	0.4	0	90.4
M-PDMS	7000–10000	0.4	0	89.5
F-PDMS	7000–11000	0.4	6.8 ^a	89.0

^a For the model simulation, the initial contact angle $\theta_0 = 0$ is used.

5. Results and discussion

Fig. 3 shows the hydrophobic recovery of the three different samples: an extracted PDMS, an M-PDMS, and an F-PDMS, which are subjected to a severe discharge of 4000–11000 pC for 1 h in a point-to-plane configuration at 50% humidity. The extracted sample and M-PDMS exhibit a similar hydrophobic recovery after exposure to an electrical discharge of 4000–10000 pC. At this severe discharge condition, the LMW species are produced in quantities that is sufficient to cause full hydrophobic recovery [30] of the oxidized PDMS. These LMW species may be produced in situ by the siloxane bond rearrangement occurring via a transition state [45–49], and the degradation products may be comprised of similar sized cyclic siloxane fluids [31].

For the F-PDMS sample, hydrophobic recovery is much faster than that of the extracted and M-PDMS samples. The angle-resolved XPS indicates that the fluorine concentration on the surface of the F-PDMS elastomer is $\sim 0.5\%$ before discharge, but the concentration markedly increases to 21% about 2 h after exposure to a discharge of 7000–12000 pC for 30 min. Even when the sample is exposed to a lower discharge intensity of 300–700 pC for 30 min, the concentration of fluorine in the oxidized surface increases considerably compared to that of the F-PDMS sample before discharge (Table 2). The XPS results (Fig. 4) show the absence of the fluorinated carbon species on the surface before discharge, but its presence (e.g., the appearance of the peak at 293–294 eV region is indicative of the CF_3 groups) on the surface after discharge due to the diffusion of the in situ produced LMW species by which the oxidized PDMS elastomers recover their hydrophobicity. The fluorine-containing species may be produced by the cleavage of the Si–C bond of 3,3,3-trifluoropropylmethylsiloxane fluid (MW = 950) present in the polymer network, further degradation of which could result in the formation of 1,1-difluoropropene and cyclic PDMS fluids [46–50]. In particular, the 1,1-difluoropropene (MW = 76) has a molecular weight which is lower than that of hexamethylcyclotrisiloxane (D_3 , MW = 222) and octamethylcyclotetrasiloxane (D_4 , MW = 296) and may thus have a higher diffusivity than D_n ($n \geq 3$). It is plausible that the surface restructuring of the F-PDMS elastomer could be accelerated by the diffusion of very low molecular weight fluorine-containing species such as 1,1-difluoropropene to the oxidized surface of the elastomer.

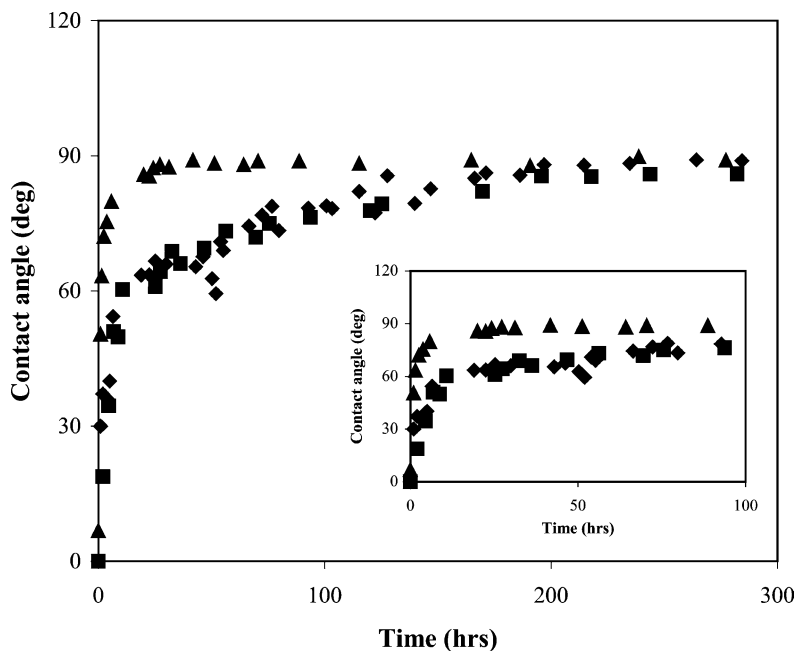


Fig. 3. The effect of preexisting fluids on hydrophobic recovery of the PDMS elastomers. Discharge experiments were performed at 50% humidity in the point-to-plane configuration. Exposure time is 1 h, and the gap between a sample and the electrode tip is 0.4 mm. (◆) Extracted, 4000–10000 pC; (■) M-PDMS (MW = 950), 7000–10000 pC; and (▲) F-PDMS (MW = 950), 7000–11000 pC.

Table 2
Atomic compositions (%) of the F-PDMS samples taken at a different take-off angle 2 h after electrical discharge

Discharge	Atom	Take-off angle	
		15°	90°
Virgin	C _{1s}	46.6	45.7
	Si _{2p}	29.1	29.1
	O _{1s}	23.9	24.9
	F _{1s}	0.4	0.3
300–700 pC	C _{1s}	43.0	41.1
	Si _{2p}	19.3	20.2
	O _{1s}	20.6	20.6
	F _{1s}	17.1	18.1
7000–12000 pC	C _{1s}	38.0	38.2
	Si _{2p}	19.1	17.8
	O _{1s}	22.5	22.4
	F _{1s}	20.4	21.6

Before discharge, the advancing contact angles of the extracted PDMS, M-PDMS, and F-PDMS are 107°, 103°, and 93°, respectively. However, the recovered samples show almost the same advancing contact angle (90°), which is somewhat lower than those of the samples before discharge (Table 1). The in situ produced LMW species covering the oxidized surface of the PDMS elastomers may behave differently than the siloxane chains crosslinked in a network. Furthermore, the surfaces of the recovered samples are not the same as those of the PDMS elastomers before discharge in terms of chemical composition and physical structure. The free movement of the in situ produced LMW species covering the oxidized surface may also affect the contact angles of the recovered samples.

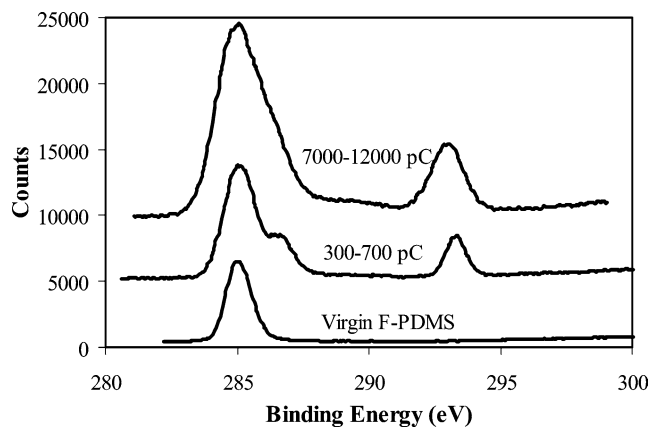


Fig. 4. C_{1s} XPS spectra of F-PDMS samples before and after electrical discharge. The XPS analysis was performed at 90° take-off angle.

5.1. Diffusivity of LMW species

5.1.1. Pore diffusion model

The simulation results obtained from a pore diffusion model, based on the parameters summarized in Table 3, are plotted in Fig. 5. With the given set of model parameters, the initial concentration (C_i) and pore diffusivity (D_p) of the in situ produced LMW species can be extracted upon comparing computational results with experimental data (Table 4). The simulation result indicates that the pore diffusion model with the Freundlich isotherm fits the experimental data quite well throughout the whole aging time, giving a pore diffusivity (D_p) of $2.0\text{--}4.0 \times 10^{-16} \text{ cm}^2/\text{s}$ for the extracted and M-PDMS samples. Therefore, when the extracted sample and M-PDMS sample suffer degradations

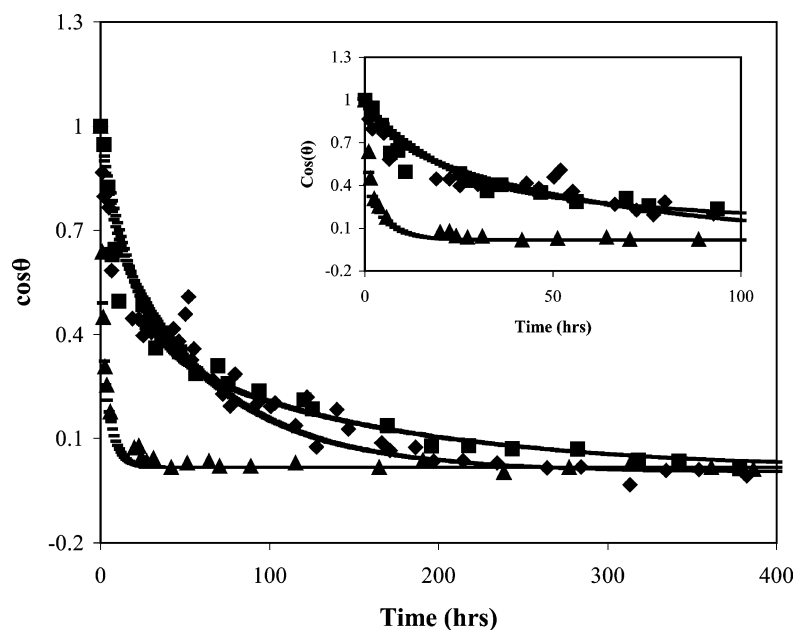


Fig. 5. Pore diffusion model with the Freundlich isotherm. (◆) Experimental data for the extracted sample, 4000–10000 pC; (■) experimental data for the M-PDMS sample (MW = 950), 7000–10000 pC; (▲) experimental data for the F-PDMS sample (MW = 950), 7000–11000 pC; and (—) theoretical model prediction.

Table 3
Parameters used in the model simulation

Parameter	Value
Freundlich isotherm	$q = AC_p^B$ (g/cm ³) $A = 10000$, $B = 2.5$
Density of the silica layer, ρ	1 (g/cm ³)
Porosity of the silica layer, ε_p	0.17
Thickness of the silica layer, L	140 (Å)

during the severe electrical discharges, the LMW species are produced in situ that may be comprised of silicone fluids having comparable molecular weights. The pore diffusivity D_p ($2.0\text{--}4.0 \times 10^{-16}$ cm²/s) of the in situ produced LMW species obtained for extracted and M-PDMS is very much lower than the average diffusivity (3.5×10^{-8} cm²/s) of silicone fluids in the PDMS elastomer network obtained via absorption experiments [24–27]. This difference is expected considering that the inorganic silica-like layer offers a much greater resistance to the diffusion of LMW silicone fluid than would a PDMS polymer network. For the F-PDMS sample, the computed pore diffusivity of LMW species is 5.0×10^{-15} cm²/s, which is roughly one order of magnitude larger than those of the extracted and the M-PDMS sam-

ples (Table 4). This result is consistent with the fact that the F-PDMS shows a faster hydrophobic recovery than the extracted and the M-PDMS.

5.1.2. Homogeneous solid diffusion model

In the homogeneous solid diffusion model, the same Freundlich adsorption equation (Table 3) is used to calculate the amount of LMW species adsorbed on the silica-like layer at the interface ($z = 0$). The simulation results with the model parameters are shown in Table 5. Based on the simulation results summarized in Fig. 6, the surface diffusivity (D_s) of the LMW species is estimated to be about $2.0\text{--}3.0 \times 10^{-18}$ cm²/s for the extracted and M-PDMS exposed to a discharge intensity of 4000–10000 pC, which is considerably smaller than the diffusivity (D_p) $2.0\text{--}4.0 \times 10^{-16}$ cm²/s obtained from the pore diffusion model. This is consistent with the studies in packed-bed columns [35], in which the modeling of the breakthrough curves requires a lower surface diffusivity D_s than pore diffusivity D_p . As seen in the pore diffusion model, the surface diffusivity D_s of the F-PDMS sample is also about one order of magnitude larger than those of the two samples at the similar discharge intensity.

Table 4
The diffusivity and initial concentration of in situ produced LMW species computed by the pore diffusion model

Sample	Adsorption type	Discharge (pC)	C_i (g/cm ³)	q_m (g/cm ³)	C_{is} (g/cm ³)	D_p (cm ² /s)
Extracted	Freundlich	100–400	0.0087	0.1	0.010	4.0×10^{-16}
		4000–10000	0.01	0.1	0.014	4.0×10^{-16}
M-PDMS		7000–10000	0.01	0.1	0.018	2.0×10^{-16}
F-PDMS		7000–11000	0.01	0.1	0.018	5.0×10^{-15}

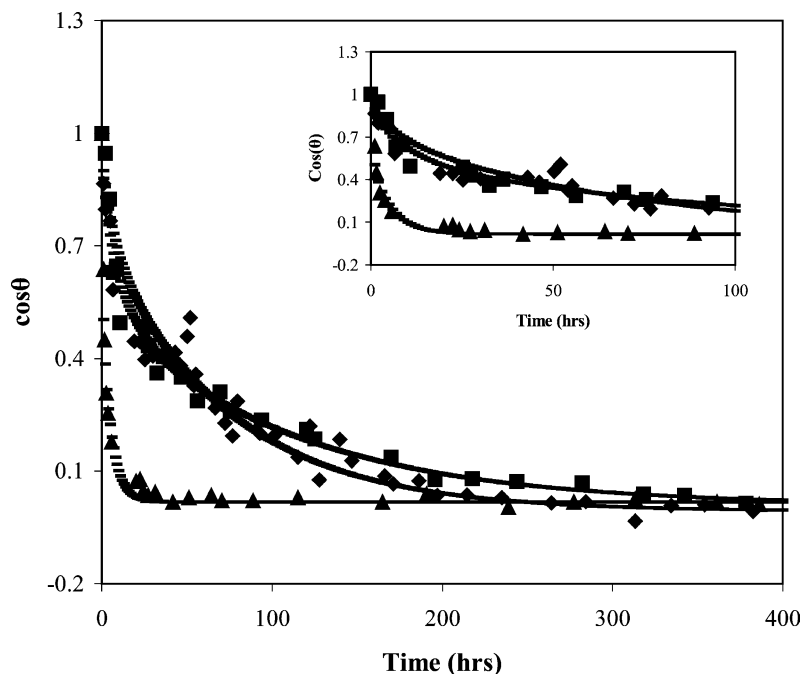


Fig. 6. Homogeneous solid diffusion model with the Freundlich isotherm. (◆) Experimental data for the extracted sample, 4000–10000 pC; (■) experimental data for the M-PDMS sample (MW = 950), 7000–10000 pC; and (▲) experimental data for the F-PDMS sample (MW = 950), 7000–11000 pC; and (—) theoretical model prediction.

Table 5

The diffusivity and initial concentration of in situ produced LMW species computed by the homogeneous solid diffusion model

Sample	Adsorption type	Discharge (pC)	C_i (g/cm ³)	q_m (g/cm ³)	q_{is} (g/cm ³)	D_s (cm ² /s)
Extracted	Freundlich	100–400	0.0086	0.1	0.010	3.0×10^{-18}
		4000–10000	0.01	0.1	0.012	3.0×10^{-18}
M-PMDS		7000–10000	0.01	0.1	0.018	2.0×10^{-18}
F-PDMS		7000–11000	0.01	0.1	0.018	4.0×10^{-17}

When a Langmuir isotherm is used instead of a Freundlich isotherm, both the diffusion models yield similar values of diffusivity and initial concentration as those obtained from the Freundlich isotherm. However, the homogeneous solid diffusion model with a Langmuir isotherm shows a pronounced discrepancy with the experimental data in the early aging time period if we assume that no LMW species exist in the silica-like layer right after electrical discharge (Fig. 7). The “induction time” shown in the early aging time suggests that some LMW species already exist in the silica-like layer right after electrical discharge so that the expression (Eq. (10a)) improves the simulation result.

5.2. Initial concentration

The hydrophobic recovery of electrically discharged PDMS elastomers is significantly influenced by electrical discharge intensity and environmental humidity, particularly showing a partial hydrophobic recovery at low electrical discharge intensity [30]. As electrical discharge intensity becomes milder, it is expected that LMW species be produced

at lesser quantities. Since the in situ produced LMW species are the major cause for hydrophobic recovery, the partial hydrophobic recovery is most likely caused by a low initial concentration of the LMW species. In order to demonstrate the effect of initial concentration of LMW species on the hydrophobic recovery, an extracted sample was exposed to a low electrical discharge intensity of 100–400 pC for 1 h. After the discharge ceased, the oxidized sample recovered its hydrophobicity more slowly than the extracted sample exposed to a severe discharge intensity of 4000–10000 pC for 1 h at the same humidity (50%). Additionally, the extracted sample exposed to the low electrical discharge did not fully recover its hydrophobicity [30].

With the given set of model parameters in Table 3, the pore diffusion model combined with the Freundlich isotherm yields an initial concentration of LMW species of 8.7×10^{-3} g/cm³ in zone B at an electrical discharge intensity of 100–400 pC, whereas LMW species of 10^{-2} g/cm³ is initially produced at an electrical discharge intensity of 4000–10000 pC (Table 4). It should be noted that these values

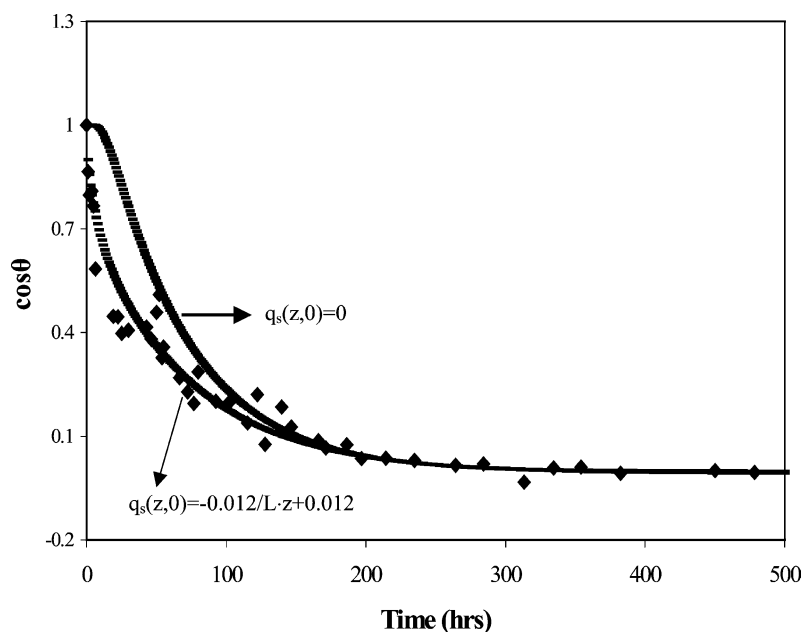


Fig. 7. Homogeneous solid diffusion model with a Langmuir isotherm in which an expression of $q_s = Q_{\max} K_L C_i / (1 + K_L C_i)$ with $Q_{\max} = 0.1$ (g/cm³) and $K_L = 20000$ (cm³/g) was used for the model simulation. (◆) Experimental data for the extracted sample exposed to 4000–10000 pC. Surface diffusivity D_s is 3.7×10^{-18} cm²/s for both $q_s(z, 0) = 0$ and $q_s(z, 0) = -0.012/L \cdot z + 0.012$.

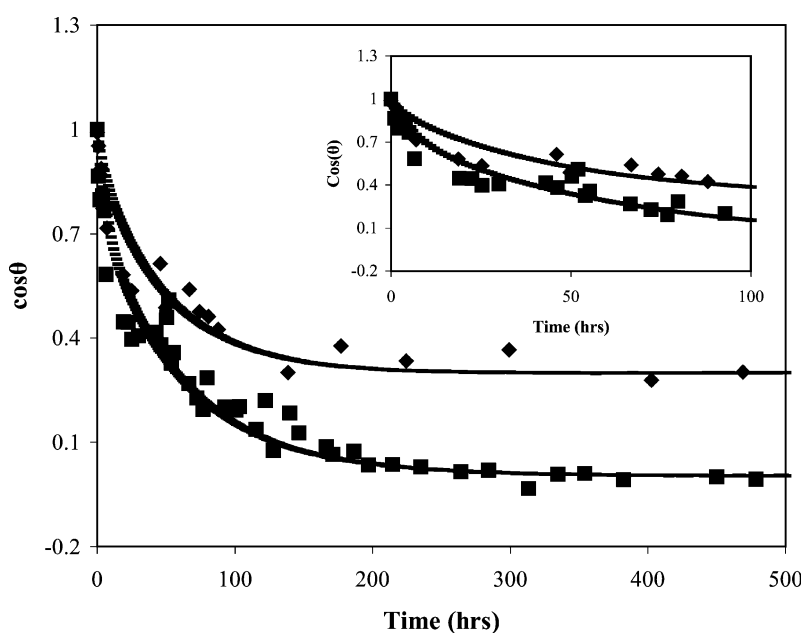


Fig. 8. Pore diffusion model with the Freundlich isotherm—the effect of the initial concentration. (◆) Experimental data for the extracted sample, 100–400 pC; (■) experimental data for the extracted sample, 4000–10000 pC; (—) theoretical model prediction.

of diffusivity were estimated by taking the thickness of the silica-like layer as 140 Å, which is obtained from XPS analysis. Electrical discharge intensity as well as atmospheric conditions could affect this thickness somewhat, which should affect the diffusion time and, thus, the recovery kinetics. Numerical simulations [51] show that the partial hydrophobic recovery is, however, more strongly influenced by the lower initial concentration (Fig. 8) of LMW species than the thickness of the silica-like layer.

6. Summary

Silicone elastomers exposed to electrical discharge show the unique characteristic of recovering their hydrophobicity via diffusion of in situ produced LMW species through a porous silica-like layer to the surface. A diffusion model can be used to calculate the diffusivities of free silicone fluids diffusing into a silicone elastomer using a sorption experiment, but the diffusion model alone is not satisfac-

tory to explain the hydrophobic recovery of electrically discharged silicone elastomers. The diffusion model accompanied by an adsorption process can be applied in predicting the hydrophobic recovery of PDMS elastomers exposed to partial electrical discharge. The pore diffusion model results in a very good correlation with the experimental data, yielding an estimate of $2.0\text{--}4.0 \times 10^{-16} \text{ cm}^2/\text{s}$ for the pore diffusivity (D_p) of the extracted and M-PDMS. The similar diffusivity for the two samples offers further evidence that the hydrophobic recovery is dominated by the diffusion of in situ produced LMW species to the oxidized surface. The F-PDMS sample shows a faster recovery than the extracted and M-PDMS samples due to the higher diffusivity ($5.0 \times 10^{-15} \text{ cm}^2/\text{s}$) of LMW species produced in situ during electrical discharges as a result of chain scission of 3,3,3-trifluoropropylmethylsiloxane fluid (MW = 950) pre-existing in the polymer. The homogeneous solid diffusion model also predicts well the hydrophobic recovery of PDMS elastomers throughout the whole range of discharge intensity, and the surface diffusivity (D_s) obtained from the model is roughly two orders of magnitude smaller than the pore diffusivity (D_p). In addition, both the models could be applicable to studying the effect of the initial concentration of LMW species on the hydrophobic recovery of electrically discharged PDMS elastomers—particularly explaining partial hydrophobic recovery at low discharge intensity.

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