

HYDROPHOBICITY OF CONTAMINATED SILICONE RUBBER SURFACES

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Abstract Silicone rubber (SIR) shows superior performance when used outdoors, but its surface can be transformed from inherently hydrophobic to hydrophilic by the adsorption of contaminants. $\text{Al}(\text{OH})_3$, Al_2O_3 , quartz powder and active carbon were selected as authentic contaminants. Hydrophobicity of the surface was determined using contact angle measurement. The results indicate that the adsorbability of the contaminants can strongly affect the hydrophobicity of contaminated SIR surface. The increasing rate of contact angle of specimens contaminated by $\text{Al}(\text{OH})_3$ was much faster than that by Al_2O_3 and quartz due to the adsorption of migrated low molecular weight (LMW) polydimethylsiloxanes. Specimens contaminated by active carbon could achieve surface hydrophobicity within 15 min because active carbon has high adsorbability. Surfaces of contaminated ultrapure SIR, polytetrafluoroethylene (PTFE) and glass remain hydrophilic because they contain no mobile LMW components. The addition of oligomeric polydimethylsiloxanes has little effect on the hydrophobicity of contaminants covered on SIR surface.

Keyword Hydrophobicity, Silicone rubber, Contact angle, Contamination

INTRODUCTION

Silicone rubbers (SIR) based on polydimethylsiloxanes (PDMS) have been used as alternatives to porcelain and glass for outdoor high-voltage (HV) insulation applications for nearly 30 years^[1], due to their excellent properties such as light weight, resistance to weathering, ozone, UV and corona discharge, low and high temperature resistance (-110 – 300°C), good dielectric properties and hydrophobicity.

One of the crucial problems in HV applications is the natural or artificial contaminants that settle on insulation surfaces. When a hydrophilic contaminant is exposed to moisture, an electrolytic film can develop, leading to corona discharges, surface deterioration, dry band arcing and eventually to flashover^[2, 3]. The applications of SIR can solve this problem due to SIR's unique advantage over inorganic and other polymeric materials. Although the contaminants can also make the surface of SIR hydrophilic temporarily, low molecular weight (LMW) components in SIR can diffuse from the bulk to the surface and then cover the contaminants, rendering the contaminated surface hydrophobic. Thus contaminants are prevented from being wetted and consequently flashover can be suppressed. Both practical and laboratory experiments have shown that the hydrophobicity of the surface of SIR can be maintained despite the presence of a contaminated layer^[4–7]. However, flashover caused by contamination still threatens HV power systems^[8]. Thus, research on transformation from hydrophilic to hydrophobic of contaminants on SIR surface remains necessary.

There are two kinds of SIR used in HV insulation. Room temperature vulcanized SIR (RTV) has been used as a protective coating for ceramic insulation. High temperature vulcanized SIR (HTV) is mainly applied as weather proofing or housing materials^[9]. Many researchers have focused on the hydrophobicity recovery of RTV insulation surface subjected to an energized salt fog test, plasma or corona treatments^[5, 9–16]. This paper presents the influences of different contaminants and the compositions of SIR on the hydrophobicity of the HTV SIR surface by determining the contact angle of a droplet of water on it.

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EXPERIMENTAL

Preparation of SIR Sheets

Polydimethylsiloxane containing vinyl groups (HTV SIR gum; $M_n = 490,000$), fumed silica (specific surface area = $200 \text{ m}^2/\text{g}$) and 2,4-dichlorobenzoyl peroxide (DCBP, crosslinking agent) are all commercial grade products. Oligomeric polydimethylsiloxanes of different structures (Table 1) were prepared according to reference^[17].

Table 1. Detailed information of oligomeric polydimethylsiloxanes

Code of Polydimethylsiloxanes	Formula of polydimethylsiloxanes	n^a
M25	$(\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)_2]_n\text{OSi}(\text{CH}_3)_3$	24
M44		43
M84		83
V45	$\text{Vi}(\text{CH}_3)_2\text{Si}[\text{OSi}(\text{CH}_3)_2]_n\text{OSi}(\text{CH}_3)_2\text{Vi}^b$	44
V95		94
BV105	$\text{Bu}(\text{CH}_3)_2\text{Si}[\text{OSi}(\text{CH}_3)_2]_n\text{OSi}(\text{CH}_3)_2\text{Vi}^c$	104

^a n is measured by ^{29}Si -NMR; ^b Vi stands for vinyl group; ^c Bu stands for butyl group

Table 2. Composition of HTV SIR

No.	Formulation (Weight parts)			Remarks
	Silicone gum	Polydimethylsiloxane oligomer	Fumed silica	
0 [#] (a)	100	None	30	Ultrapure grade SIR
0 [#] (b)	100	None	30	Commercial grade SIR
1 [#]	100	10 (M25)	30	
2 [#]	100	10 (M44)	30	
3 [#]	100	10 (M84)	30	
4 [#]	100	10 (V45)	30	
5 [#]	100	10 (V95)	30	
6 [#]	100	10 (BV105)	30	

The composition of HTV SIR was listed in Table 2. Materials were compounded and then vulcanized at 120°C for 10 min under 7–8 MPa to obtain sample sheets with a thickness of 2 mm and postcured at 200°C for 24 h. Ultrapure SIR is obtained by treating the commercial HTV SIR sheet at 200°C under 66 Pa for 24 h. The weight loss of this ultrapure SIR (at 125°C and 1.3×10^{-4} Pa for 24 h) is less than 0.3%. The sheets were then stored in a desiccator prior to further treatment.

Contamination of the Surface

The SIR sheets were cut into test specimens measuring $30 \times 4 \times 2$ mm and each sheet was stuck on a glass plate. The specimens were cleaned with acetone and ethanol subsequently to remove dust particles and fingerprints before contaminating. Powdery contaminant including $\text{Al}(\text{OH})_3$, Al_2O_3 , quartz and active carbon was mixed with distilled water, respectively. For $\text{Al}(\text{OH})_3$, Al_2O_3 and quartz powder, the weight ratio of powder to H_2O is 70 to 30, and for active carbon, 27 to 73. The mixture of contaminants and water was brushed on the surface of SIR specimens as artificial contamination.

Contact Angle Measurements

Hydrophobicity was determined by measuring the contact angle (or wetting angle) θ . The contact angle measurements were performed on a horizontal surface with a contact angle meter using the sessile water drop method. Each datum was the average value of three contact angle measurements on different points of the same specimen surface. For contaminated specimens, the contact angle measurements were carried out after different periods of time.

FTIR Measurements of Powder as Contaminants

Absorption infrared spectra were obtained with a Perkin-Elmer 2000 Fourier transform spectrometer.

RESULTS AND DISCUSSION

Influence of Different Substrates on Hydrophobicity of Contaminants

In order to study the influence of different substrates on hydrophobicity of the contaminants, ultrapure SIR [0[#](a) in Table 2], commercial grade SIR [0[#](b) in Table 2], polytetrafluoroethylene (PTFE) and glass were chosen as substrates. Contact angles of the clean surface of SIR [0[#](a) and 0[#](b)], PTFE and glass were found to be 109°, 118° and 20°, respectively. This demonstrates that both SIR and PTFE have a hydrophobic surface while glass is a hydrophilic one. Four kinds of artificial contaminants of 400 mesh, Al(OH)₃, Al₂O₃, quartz powder and active carbon powder were brushed on the surface of four substrates. Figure 1 shows the variation of contact angle with time.

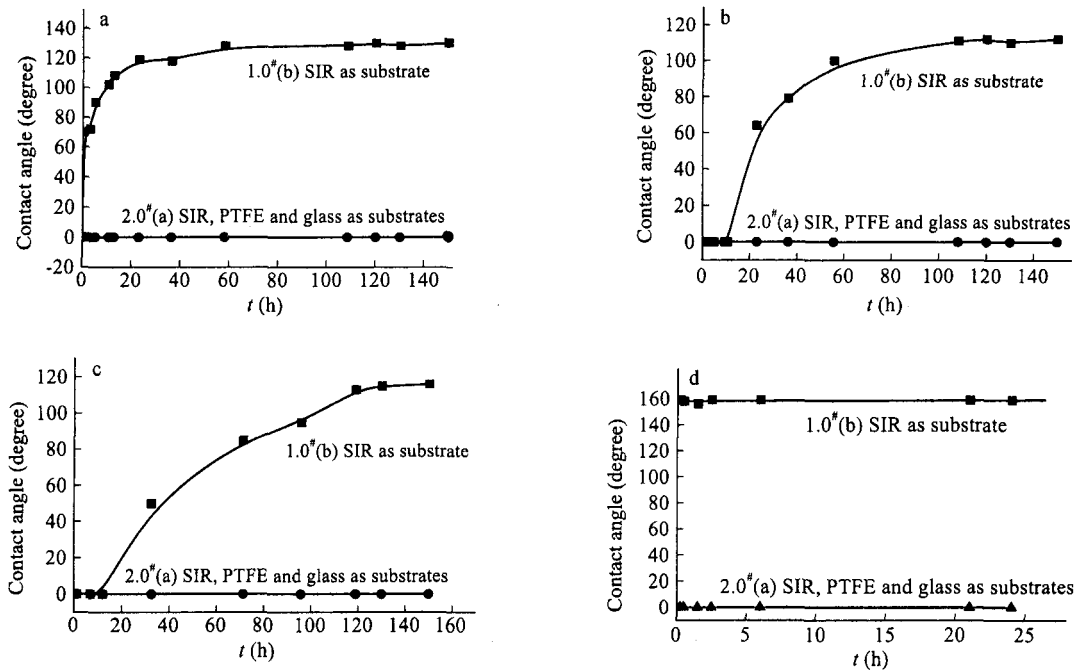


Fig. 1 Contact angle of water for specimens contaminated by (a) Al(OH)₃; (b) Al₂O₃; (c) quartz; (d) active carbon

All the four contaminants covered on 0[#](b) SIR substrate became hydrophobic during the observation period. This is because commercial grade SIR contains mobile LMW polydimethylsiloxanes whose surface tension is quite low. So they can easily diffuse from the bulk to the surface to reduce the surface energy^[7]. As for 0[#](a) SIR, PTFE and glass substrates, water drops could be absorbed immediately by the contaminated layers during the whole observation period, which demonstrates that the contaminated layers remain hydrophilic. In 0[#](a) SIR mobile LMW components have been removed after treatment under high temperature and reduced pressure, so the contaminated layers on the substrate could not achieve hydrophobicity. Although clean PTFE surface is hydrophobic, the contaminated layers remain hydrophilic, because there are no mobile LMW components in it. Glass substrate is hydrophilic itself and has no LMW components either, so it is impossible for the contaminated layers on it to gain hydrophobicity.

Influence of Different Contaminated Layers on Hydrophobicity of Contaminants

Firstly, three kinds of artificial contaminants, Al(OH)₃, Al₂O₃ and quartz powder, were respectively brushed on the surface of 0[#](b) SIR samples. Figure 2 shows the contact angle increases with time on contaminated surfaces.

The water drop was absorbed by the contaminated layer when the contact angle was measured immediately after the contaminated layer became dry. The results of measurement indicate that the contaminated surface is hydrophilic. The contaminated samples were then left at room temperature. In the early stage, the contact angle

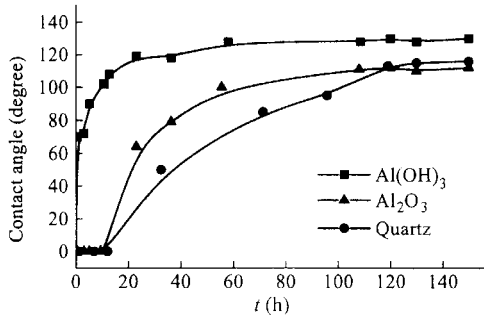


Fig. 2 Contact angle of water for contaminated specimens of SIR 0[#](b)

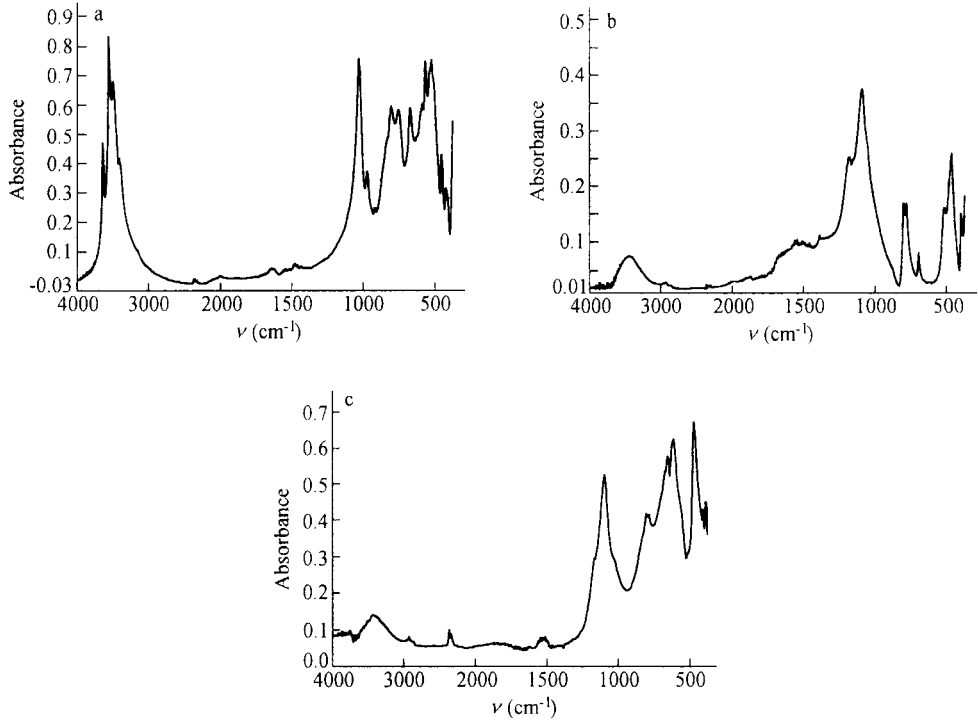


Fig. 3 FTIR spectra of three kinds of contaminants
a) Al(OH)₃; b) Quartz; c) Al₂O₃

increases with increasing storage time, which means that the contaminated layer gradually becomes hydrophobic from hydrophilic. Then, the increase of contact angle levels off. However, the increasing rate of the contact angle for the same SIR specimens contaminated by different contaminants was different. The increasing rate of θ for specimen contaminated by Al(OH)₃ is the fastest, of which the contact angle reaches 90° within 10 h, while for specimen contaminated by Al₂O₃ and quartz powder, they take more than 50 h for the contact angle to reach 90°. Explanation can be made by comparing the structures of these three contaminants. Figures 3(a), (b) and (c) are the FTIR spectra of the three contaminants. In Fig. 3(a), the strong and sharp absorption peaks at 3622, 3527, 3469 and 3396 cm⁻¹ indicate there are large amounts of isolated hydroxyl groups (OH) in Al(OH)₃. While in quartz powder (SiO₂) and Al₂O₃, there are only a few isolated hydroxyl groups. The weak and broad peaks above 3400 cm⁻¹ shown in Fig. 3(b) and 3(c), respectively, correspond to the stretching vibration of hydrogen-bonded hydroxyl groups^[2]. Therefore, it suggests that LMW polydimethylsiloxanes which diffuse from the bulk of SIR can be adsorbed strongly on the surface of Al(OH)₃ particles through hydrogen bonding. Thus the surface of

Al(OH)₃ particles is soon covered with a layer of LMW polydimethylsiloxanes and then it becomes hydrophobic. However, there are only hydrogen-bonded hydroxyl groups on the SiO₂ and Al₂O₃ surface that cannot strongly adsorb the LMW polydimethylsiloxanes so that the transformation rate from hydrophilic to hydrophobic surface of the contaminated layer is much slower.

We have also used active carbon as contaminant. The hydrophobicity transformation of the active carbon layer can be achieved within 15 min (Fig. 1d). The reason is that the active carbon powder is porous which results in a large specific surface area. It can adsorb diffused LMW polydimethylsiloxanes quickly and turn hydrophobic. This proves that the adsorbability of contaminated layers is very important for controlling the hydrophobicity of contaminants on SIR surface.

Influence of Composition of SIR on Hydrophobicity of Contaminants

Many researches have shown that LMW polydimethylsiloxanes inherently contained in SIR play an important role in determining the hydrophobicity recovery of SIR insulators. This has been verified by the above results of commercial SIR and ultrapure SIR. In order to further investigate the influences of LMW polydimethylsiloxanes on the hydrophobicity of contaminants, oligomeric polydimethylsiloxanes of different structures in Table 1 were synthesized and added to the commercial SIR. Quartz and Al(OH)₃ were used as artificial contaminants. The results are shown in Fig. 4 and Fig. 5.

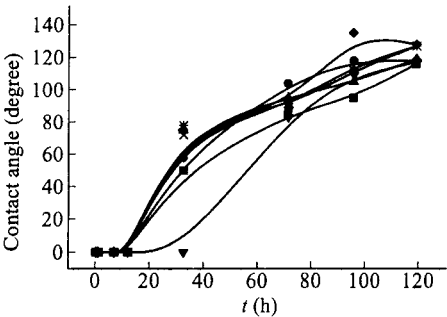


Fig. 4 Contact angle of quartz-contaminated SIR specimens
The compositions are given in Table 2.
■ 0#(b); ● 1#; ▲ 2#; ▼ 3#; ◆ 4#; * 5#; × 6#

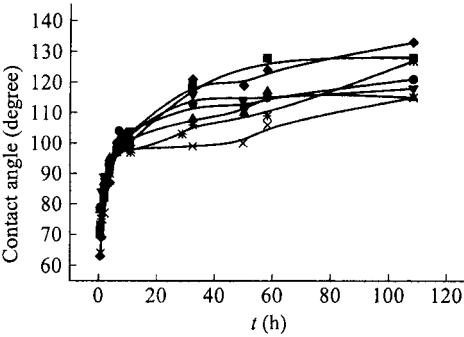


Fig. 5 Contact angle of Al(OH)₃-contaminated SIR specimens
The compositions are given in Table 2.
■ 0#(b); ● 1#; ▲ 2#; ▼ 3#; ◆ 4#; * 5#; × 6#

It was found that the addition of oligomeric polydimethylsiloxanes almost had no effect on the hydrophobicity of contaminated surface no matter what kind of contaminated layer was used. Possible explanations are given as follows: (1) LMW polydimethylsiloxanes inherently contained in SIR are enough for the transformation of contaminated layer from hydrophilic to hydrophobic, because only very small quantities of LMW polydimethylsiloxanes are needed to form a thin layer over a contaminated layer; and (2) it might be more difficult for added oligomeric polydimethylsiloxanes (*ca.* 1850–7400 g/mol) to migrate from the bulk to the surface as compared with LMW polydimethylsiloxanes that inherently exist in SIR.

CONCLUSION

The adsorbability of the contaminants strongly affects its hydrophobicity on SIR surface. The increasing rate of contact angle of specimens contaminated by Al(OH)₃ are much faster than that by Al₂O₃ and quartz due to the adsorption of migrated LMW polydimethylsiloxanes through hydrogen bonding. Active carbon contaminated specimens can achieve surface hydrophobicity within 15 min because active carbon is of high adsorbability. The surface of contaminated ultrapure SIR, PTFE and glass remains hydrophilic because there are no mobile LMW components in them. The addition of oligomeric polydimethylsiloxanes has little effect on the hydrophobicity of contaminants on the SIR surface.

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