Characteristics of Surface Wettability and Hydrophobicity and Recovery Ability of EPDM Rubber and Silicone Rubber for Polymer Insulators

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Received 6 January 2000; accepted 28 May 2000

ABSTRACT: As power lines are built in contaminated environments, the industrial usage of power-line materials requires high reliability. Nonceramic insulators offer better anticontamination performance than that of the traditional ceramic insulators. Among the nonceramic materials, EPDM and silicone rubber provide much better long-term pollution resistance performance than that of any other materials. This study investigated the long-term pollution performance by a corona aging treatment on the surface of the test slabs, which were made of EPDM and silicone rubber. Experimental results showed good hydrophobicity of those materials and their transfer of the contaminant layer deposited on the shed surface of the insulator. The EPDM and silicone rubbers are synthetic polymers of low density and they maintain an outstanding resistance to attack by oxygen and ozone. This study measured the contact angle between water droplets and other materials to determine the hydrophobicity and recovery ability of these synthetic polymers. We also studied surface morphology for a visual confirmation of the migration phenomena. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2251–2257, 2001

Key words: insulators; EPDM; silicone; contact angle; hydrophobicity; migration

INTRODUCTION

Ceramic materials have been preferred for insulator applications. More recently, however, they have been replaced by polymeric materials, because of the excellent performance of these materials. This exceptional performance of polymerbased insulators is directly attributed to the ability of the polymeric material to maintain hydrophobicity on the surface of the material in the presence of severe contamination and wet conditions.¹

Journal of Applied Polymer Science, Vol. 79, 2251–2257 (2001) © 2001 John Wiley & Sons, Inc.

Why polymeric materials show better performance than do ceramic materials? Basically, the presence of the low molecular weight (LMW) mobile fluid in the polymer such as EPDM and silicone rubber facilitates the diffusion of the contamination layer on the surface. The diffusion process occurs when the outer film of the fluid is removed under dry band arcing and then it washes away from the rain. Thus, polymer insulators have a good surface hydrophobicity, which suppresses the onset of leakage current and increases the withstood voltage.²

The electrical, physical, and chemical properties of the surface of the polymer insulator are critical to the reliable performance of the insulator throughout its service life span. While silicone rubber is one of the most attractive materials for

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(a) Wetting of a droplet on the plane solid surface



- (b) Wetting of a droplet on the inclined surface.
 - Figure 1 Definition of contact angle.

an insulator, it is the least cost-effective material. Therefore, this study also investigated EPDM, which is more cost effective as compared to the silicone rubber.

Contact Angle

When a water drop is laid down upon a surface and as it advances over the surface as it spreads, the contact angle in this situation is known as the advancing contact angle.³ If liquid is drawn from a drop that has already come into equilibrium with the surface, the contact angle is known as the receding contact angle.

In general, the advancing angle is larger than is the receding angle.⁴ This phenomenon, which has a different contact angle under advancing and receding conditions, is known as contact angle hysteresis.

If a water drop exhibits these angles on an inclined surface, two different contact angles, the advancing contact angle (θ_a) and the receding contact angle (θ_r) , are present as shown in Figure 1(b). The receding angle is considered the most important factor in evaluating the wetting properties of an insulator.⁵

Surface Hydrophobicity

Poor performance in wet conditions of porcelain insulators is due mainly to the hydrophilic porcelain surface. On the other hand, however, polymer insulators exhibit superior properties due to their contribution to a hydrophobic surface.⁶ When the composite insulators are in wet conditions, such as fog, dew, and drizzle, the water on the shed surface of the insulator is distributed in the form of separated droplets.

Hence, the surface electric resistivity is very high and the leakage current is limited.⁷ This is especially true when the shed surface of the silicone rubber insulator is fully covered by a layer of contaminant during long-term operation. In this case, the silicone rubber insulator can still maintain its excellent antipollution performance.⁸

The surface hydrophobicity is critical in view of the insulator's antipollution performance under wet conditions. Therefore, many articles⁹ have reported the surface hydrophobicity and measured the contact angle with various samples at different conditions.¹⁰ The question that we wish to apply in this regard is, Does the water droplet on the hydrophobic materials always keep its hydrophobic state?

Also, is there any change of the contact angle of the deposition of the droplet by lightning? In this study, we tried to obtain the answer to this question. We investigated the change of the droplet state by aging of the corona discharge on the hydrophobic material surface.

Equilibrium State of γ_{S} , γ_{L} , and γ_{LS}

In general, the lower the surface free energy and the higher the contact angle, the stronger is the hydrophobicity. The surface contact angle and surface free energy of a solid material is quantitatively related to Young's equation¹¹:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \tag{1}$$

where θ is the static contact angle on a horizontally placed sample, and γ_S , γ_L , and γ_{SL} are the surface free energy per unit of the solid, liquid, and solid-liquid interfacial surface, respectively. Figure 2 illustrates γ_S , γ_L , and γ_{SL} on both hydrophobic and hydrophilic material surfaces.

Equation (1) represents a dynamic equilibrium state of γ_S , γ_L , and γ_{SL} at a contact point. The liquid droplet could adjust automatically so as to attain the equilibrium state.



Figure 2 Illustration of γ_S , γ_L , and γ_L .

For example, γ_S on the surface with a high surface free energy, such as on the surface of metal, glass, and porcelain, was much greater than on the silicone and the EPDM. Water droplets will spread gradually and decrease the contact angle gradually until the sum of and equal γ_S as in Figure 2(b) on the hydrophilic surface.

Conversely, on the surface of the silicone rubber and EPDM, γ_S is less than is γ_{SL} . The water droplet contrasts itself and increases the contact angle θ to alter the projecting direction of γ_L until the sum of γ_S and $|\gamma_L \cos|$ equals γ_{SL} as in Figure 2(a).¹²

EXPERIMENTAL

Table I depicts the formulations prepared of the silicone and EPDM rubber compounds used in this study for long-rod shed material of the insulators. The test pieces were sheeted by a compression-molding machine with a 1-mm thickness of test pieces at 150°C for 25 min.

A contact angle meter was employed to measure the advancing and receding contact angles. We measured the contact angle at room temperature using water before the corona treatment and after the corona aging treatment to evaluate the change of the hydrophobicity. The corona aging treatments were carried out at room temper-

Table IMain Formulations of Silicone andEPDM Rubber Compounds

	Silicones		EPDMs	
Item	Sa	Sb	Ea	Eb
Gum	100	100	100	100
Alumina trihydrate	130	130	130	130
Silica	30	30	30	30
LMW polydimethylsiloxane		4		
Paraffin oil				4
Peroxide	3	3	3	3



Figure 3 The corona aging treatment on the surface of silicone and EPDM rubber compounds test slabs at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ature using equipment as shown in Figure 3. After the corona aging treatment, the test samples were measured for contact angles multiple times from 0 (right after corona treatment) to 166 h to check the hydrophobicity recovery ability. We also studied visual conformation of migration phenomena on the silicone rubber compound and EPDM compound using SEM (\times 1000, \times 2,500).

RESULTS AND DISCUSSION

Sustained partial discharge and corona discharge, caused by the degradation of an insulator, are evident even on hydrophobic surfaces, but a hydrophobic insulator withstands contamination better than does a hydrophilic insulator.

Hydrophobicity of all polymers is lost during excessive corona and surface discharges as shown in Figure 4. Effects of corona treatment, which is



Figure 4 Wetting pattern of the polymers. The center area (2) is treated corona discharge; 1 is an untreated area. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



(a) virgin



(b) right after corona treatment



(c) recovered surface

Figure 5 Investigation of surface crack or erosion differences between (a) virgin material, (b) after corona treatment, and (c) recovered surface $\times 1000$ (sample Sa). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

exposure to corona discharge, damaged the rubbers both physically and chemically. 13

An increase in wettability after corona treatment is shown in Figure 5(b) and Figure 6(b). Cracking can be difficult to recognize by these micrographs because of the rough surface of the sample caused by high loading of the alumina trihydrate filler. From these figures, however, we found that the cessation of the corona treatment causes a progressive reversion to the nonwetted state in most cases, the so-called "hydrophobic recovery" effect¹⁴ as shown in Figures 5(c) and 6(c).

We also found that the surface promoted a continuous water film due to the change in surface roughness as shown in Figure 6(b) by the corona treatment. These phenomena are strongly related to the surface energy. The lower the surface energy, the better is the hydrophobicity. The polymers used in this study are inherently hydrophobic as summarized in Table II.

Figure 7 depicts the surface tested with changing time until the surface had recovered its hy-



(a) hydrophobic surface when new



(b) wettable surface



(c) recovered surface after 166 hrs

Figure 6 Water repellency of the polymer (Sa) surface of (a) virgin material, (b) increasing wettability right after corona treatment, and (c) recovered hydrophobicity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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Item	Sa	Sb	Ea	Eb
$egin{aligned} & heta_a \ & heta_r \end{aligned}$	112.3° 77.3°	116.2° 82.4°	108.4° 71.6°	110.2° 77.3°

Table IIContact Angle of Virgin Test Slabs:Before Corona Aging Treatment

drophobicity. The results of the test showed that the corona treatment was responsible for a large increase in oxygen concentration and corresponded to a decrease in carbon concentration.¹⁵ This could be caused by a deposition of hydroxyl (OH) groups from the atmosphere, which favors the wetting of the surface with water.

An experimental study tells us that both silicone rubber and EPDM kept the hydrophobicity recovery. However, EPDM lost the characteristics more than did the silicone rubber. Figure 7 and Table II show that the advancing angle is larger than is the receding angle for all tested samples.







(b) receding contact angle

Figure 7 Hydrophobicity recovery ability of silicone and EPDM with time by contact angle measurement after corona aging treatment: (a) depicts the advancing angle; (b) depicts the receding angle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



(a) 0 day



(b) 15 days



(c) 30 days

Figure 8 Evidence of LMW silicone oil (LMW polydimethylsiloxane) migration from bulk to the surface in silicone compound, S_b . ×1000.

It has been speculated that the hydrophobicity exhibited in the silicone and EPDM rubber compounds, despite the accumulation of surface contamination, could be due to the diffusion of LMW. There are a number of LMW polymer chains in the material, which exhibit high mobility.

These mobile species diffuse out easily and form a thin layer on the surface, which causes the water film to bead up. Figure 8(a) shows the diffusion process of the surfaces of the silicone rubber with LMW polydimethylsiloxane, "S_b." Figure 8 shows evidence of the migration from the bulk to the surface of the silicone rubber with increas-



0 day



(a) Sa



0 day



30 days





(c) Eb

Figure 9 SEM investigation of the surfaces with time increases after corona aging treatment on the surface: (a) Sa; (b) Ea; (c) Eb. No evidence of migration from bulk to surface. $\times 2500$.

ing times after corona treatment. But we did not find any change of the surface in the sample "Sa" [Fig. 9(a)], which did not contain LMW material.

While the diffusion could be expected to occur in EPDM materials containing LMW material, we could not find this phenomenon of the EPDM with oil and without oil (Fig. 9). The reason is that the rate of diffusion of EPDM is different from that of silicone rubber due to the difference in the mobility of the polymer chains between the two materials. This result may be explained by the reorientation of the surface hydrophilic groups away from the surface (i.e., the "overturn" of polar groups in the polymer surface).

The data obtained in this study demonstrated that the migration of LMW chains to the surface

was more dominant for the recovery of hydrophobicity of LMW silicone oil in the silicone compound, as shown in Figure 8. From the results, we found that the silicone polymers were more hydrophobic than were the EPDM polymers because of the abundance of low surface energy (CH₃ group) and the ability for more hydrophobicity recovery due to the migration of LMW silicone oil on the surface. Therefore, the hydrophobicity of the silicone recovered better than did that of the EPDM. These results indicate that the silicones seem to have a longer life expectation under severe conditions than that of the EPDM. We concluded that the most important factor contributing to the favorable behavior of these materials in insulator applications is their hydrophobicity, which shows the ability to form water on their surface as isolated droplets.

CONCLUSIONS

This study concentrated on the effect of the hydrophobicity of materials in insulating applications, as well as how the phenomenon of corona treatment improves the hydrophobicity on the formation of the pollution, preventing layers on insulator compounds. The recovery of the hydrophobicity is caused by the diffusion of the LMW material from the bulk material and by reorientation of the hydrophobic groups of the polymer chain on the surface.

The resistance to the loss of hydrophobicity of the virgin material recovered after the corona treatment indicates that the degradation of the polymer occurred from the corona discharge. Consequently, we believe that the hydrophobicity recovery may be explained as follows:

- 1. The reorientation of the polymer chain is flexible—there is a tendency of the polymer chain to recover at the initiated state.
- 2. The diffusion of the LMW polymer from bulk to surface diffusion is dominated by the recovery of the hydrophobicity.

The capability of EPDM rubber material for hydrophobicity recovery is different from that of silicone rubber. Hydrophobicity recovery was improved with silicone rubber material as compared to EPDM material. During contamination (corona discharge), both EPDM and silicone rubber exhibited the ability for hydrophobicity recovery. But silicones displayed better recovery than did EPDM when contaminated. The improved or marked performance of silicone rubber (as compared to EPDM rubber) hydrophobicity recovery is directly attributed to silicone's ability to diffuse LMW material from the bulk to the surface (migration) better than that of EPDM.

A part of this study was supported by the Korea Science Engineering Foundation through the Research Center for Aircraft Parts Technology, Gyeongsang National University.

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