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Tracking the hydrophobicity recovery of PDMS compounds using the adhesive force determined by AFM force distance measurements

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Abstract

Polydimethylsiloxane (PDMS) materials show the unique phenomenon that when exposed to electrical discharge, such as corona discharge, their hydrophobic surface becomes hydrophilic. However, after a certain relaxation time they gradually regain their hydrophobicity. In this study the adhesive force obtained by AFM force distance measurements using a hydrophilic Si_3N_4 probe is used to track the recovery of the hydrophobicity. The time constant of the recovery can be determined by measuring the adhesive force as a function of the recovery time after corona exposure. It is shown how these time constants can be used to monitor the recovery rate as a function of corona treatment time for both filled and unfilled PDMS compounds.
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1. Introduction

Ceramic materials such as porcelain and glass have been used for many years in outdoor high voltage insulation applications. More recently, however, conventional insulators are being replaced by polymeric composite insulators.

Silicone rubber, mainly polydimethylsiloxane (PDMS), have become attractive as substitutes for heavy and wettable porcelain and glass, especially in areas with high levels of pollution. The advantages of PDMS include its low weight, easy installation, good electrical properties, low surface energy, superior ability to withstand vandalism and better resistance to contamination [1]. PDMS is also thermally stable and performs well over a wide range of temperatures. PDMS compounds are used in the construction of sheds of high voltage insulators as well as a coating for porcelain and glass to improve their hydrophobic characteristics. PDMS has the unique property that its hydrophobic character recovers even though it may lose this during severe weather conditions or as a result of electrical discharge on the surface. It is this ability to recover as

well as its low wettability, that makes PDMS insulators perform exceptionally well in extremely polluted environments [2]. Under severe environmental conditions and after prolonged service, the hydrophobic surface gradually becomes hydrophilic due to electrical discharge. This can lead to flashovers, which are the main cause of material damage [3]. The electrical discharge, mainly in the form of corona and dry-band arcing, leads to a loss of hydrophobicity and to aging of the material. It is therefore important to study the effects of corona and oxygen plasma treatment in order to gain a better understanding of the material changes and to relate this to the actual performance during service. In this study, PDMS and a PDMS compound similar to those used in high voltage insulators are exposed to corona discharge for different times. While this type of laboratory corona treatment does not exactly replicate the electrical stresses that insulators are exposed to in-service, it does give an indication of the material response to the corona discharge stress. This is considered important to the long-term material performance of PDMS based composite insulators.

Corona and oxygen plasma treatment are well known methods for the physical and chemical modification of polymer surfaces. It is also known that severe corona

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treatment of polymer surfaces leads to aging [4]. The research of Hollahan and Carlson in 1970 [5] revealed that the hydrophobic character of silicone rubber surfaces could be lost by oxidation during exposure to corona discharges in air as well as radio frequency plasma treatments. Corona and oxygen plasma treatment have since been employed repeatedly to investigate the loss and recovery of hydrophobicity of silicone rubber [6,7].

Exposure to severe corona treatment causes both physical and chemical damage to the silicone rubber, which may reduce some of the properties desirable for insulator service. Cracking of the surface and increased wettability by water are the usual manifestations of corona discharge. However, the unique capacity of PDMS to regain its hydrophobic character after a certain resting period [8,9] makes it a favourable insulator.

It has been suggested in several publications, that the mechanism responsible for the recovery of hydrophobicity include the diffusion of low molar mass siloxanes, which are mainly cyclic compounds, from the bulk to the surface. The oxidized surface is then covered by these siloxanes [10–12] but re-orientates to its original state with time [7,13]. Urban and Stewart [14] found that highly mobile short chains of silicone elastomers are formed in the high-energy plasma environment, and that these low molar mass oligomers are responsible for the recovery of the hydrophobicity. Corona discharge or oxygen plasma leads not only to oxidation and chain scission in the PDMS insulator, but also to crosslinking and formation of an inorganic silica-like surface layer [8]. This layer delays the recovery of hydrophobicity. In this study, we present further evidence for the formation of a hard silica-like layer of SiO_x and present a novel technique for tracking the hydrophobicity recovery.

Corona discharge generates UV radiation, heat, and gaseous by-products like O_3 (ozone) and NO_2 [14–16]. During their exposure to corona discharge, non-ceramic insulators (NCI) are subjected to the effects of various types of energy. The mechanical impact of electrons and/or ions, UV light, and ozone fortifies the surface degradation of PDMS insulators. Highly oxidizing species and hydrated versions of nitrogen oxides are generated in secondary reactions. In the presence of moisture these might lead to the formation of acidic water [15]. Corona discharge produces both positive and negative ions that will be accelerated toward the surface of the insulator and cause material aging depending on the polarity [14].

The main effect of corona discharge and plasma on silicone rubber can be summarized as [16]: (1) the formation of a glassy SiO_x surface layer; (2) the increase in oxygen content in the surface by the formation of SiO_x; (3) the degradation of the network structure resulting in the formation of mainly low molar mass cyclic and medium to high molar mass linear PDMS.

The change of the surface stiffness in oxidized PDMS is described in a study by Bar et al. [12]. Using AFM, they performed tapping mode distance sweep measurements and observed an increase in the surface modulus with increasing oxidation time, the formation of surface cracks and a significant change in the surface roughness, depending on the treatment time. Hillborg et al. [17] mapped the surface hydrophobicity of UV/ozone treated PDMS with chemical force microscopy and found that the structure of the modified surface depended strongly on the treatment time.

In this paper we present the results of AFM force distance measurements [18–20], performed with a hydrophilic probe, observing the loss and recovery of hydrophobicity in corona treated PDMS compounds. Those results are compared to the results of contact angle measurements, which are commonly used to determine the hydrophobicity of a sample. It is shown that it is possible to track the recovery by measuring force distance curves of the surface as a function of relaxation time after corona treatment.

A silicon nitride (Si_3N_4) tip was used for the force measurements. The hydrophilic Si_3N_4 will exhibit a stronger adhesion to a hydrophilic surface than a hydrophobic surface [21–23]. The measured adhesive forces are therefore a direct indication of the hydrophilicity of the sample surface.

Similar studies have been performed by Kim et al. [13], who determined the surface hydrophilicity of polyurethane/polystyrene in a hydrophobic poly(ethylene oxide) matrix with force distance measurements, and by Jarvis and Pethica [24], who compared different hydrophobic modifying layers by measuring force curves.

2. Experimental

2.1. Preparation of crosslinked polydimethylsiloxane

The PDMS compounds used in this study were produced by curing a vinyl terminated PDMS compound with a tri functional crosslinking agent in the presence of a platinum catalyst. These compounds are generally referred to as room temperature vulcanised (RTV) PDMS. The components were supplied by Wacker Chemie.

In this study two different PDMS compounds were observed. The first consisted of pure PDMS, and the second of PDMS with the same crosslinking density, which contained 15% silicon dioxide (silica) and 26% aluminum hydroxide (ATH) by mass. The second compound is a typical example for a commercial formulation.

2.2. Corona exposure

The PDMS samples were cut into 1 cm^2 squares prior to corona exposure. Subsequently the squares were rinsed with acetone in order to prevent any surface contamination. The sample was then exposed to DC corona discharge under ambient conditions for treatment times of $T = 1$, 5, 10 and

30 min. The corona treatment was performed using a high frequency laboratory corona treater, model BD-20AC (Electro-Technic product, USA) with an output voltage of about 30 kV. The distance between the grounded sample and the stationary tip of the corona needle was 5 mm. A visible flashover between the corona treater and the sample surface was observed for the entire treatment time.

2.3. Static contact angle (SCA) measurements

The hydrophobic character of the NCI samples was quantified by static contact angle measurements under ambient conditions. A drop of distilled water (volume of 1 µl) was deposited with a syringe on the surface of the insulator and a magnified image of the droplet was captured immediately afterwards by means of a digital camera. The contact angle was determined by measuring the dimensions of the drop from the image and calculating the contact angle according to the following equation: $\tan \theta/2 = h/r$, where h is the height of the droplet and r the radius at the base. All SCA results were obtained from an average of 8–10 individual readings.

Higher contact angle values indicate a hydrophobic surface, while lower contact angles will be measured when the sample surface is more hydrophilic.

2.4. Force–distance measurements

Directly after corona treatment, the PDMS samples were transferred to the AFM for force–distance measurements. These were performed on a Multimode scanning probe microscope (Veeco, USA). The force–distance curves were recorded using a hydrophilic Si_3N_4 contact probe with a spring constant of $k = 0.2$ N/m produced by Nanosensors. All measurements were carried out under ambient conditions. Since our set up did not have a humidity control, the resulting adhesive force versus recovery time curves were normalized so that the asymptotic value the curve approached equalled the adhesive force measured on the untreated samples.

The adhesive force values resulted as an average of three measurements for each data point.

3. Results and discussion

The surface stiffness and the hydrophilicity of PDMS samples change after corona treatment. Both these properties can be monitored simultaneously using AFM force distance measurements. The two different PDMS samples described above have been corona treated for 1, 5, 10 and 30 min. Force distance curves were recorded in well-defined time steps directly after treatment over a period of about 100–200 min. In all cases the hydrophilicity and the surfaces stiffness of the sample increased directly after

corona treatment and recovered with time, similar to the example shown in Fig. 1.

Fig. 1a shows force distance curves of pure PDMS, which was corona treated for 5 min. Each of the curves represents a force distance curve obtained after the indicated
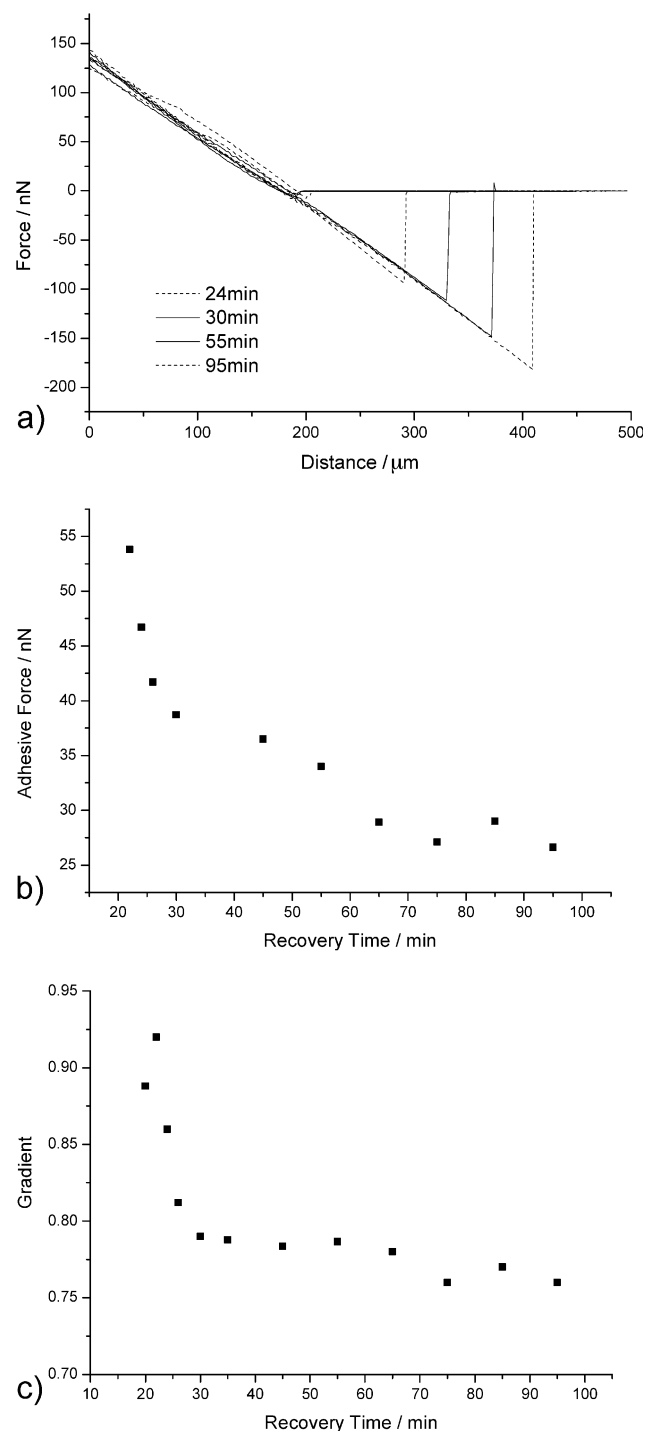

Fig. 1. (a) Force–distance curves of PDMS measured directly after corona treatment of 5 min at the indicated recovery times of 24, 30, 55 and 95 min. (b) Adhesive forces calculated from the pull off force as a function of recovery time. (c) Gradient (surface stiffness) of the approaching curves in Fig. 1(a) as a function of recovery time.
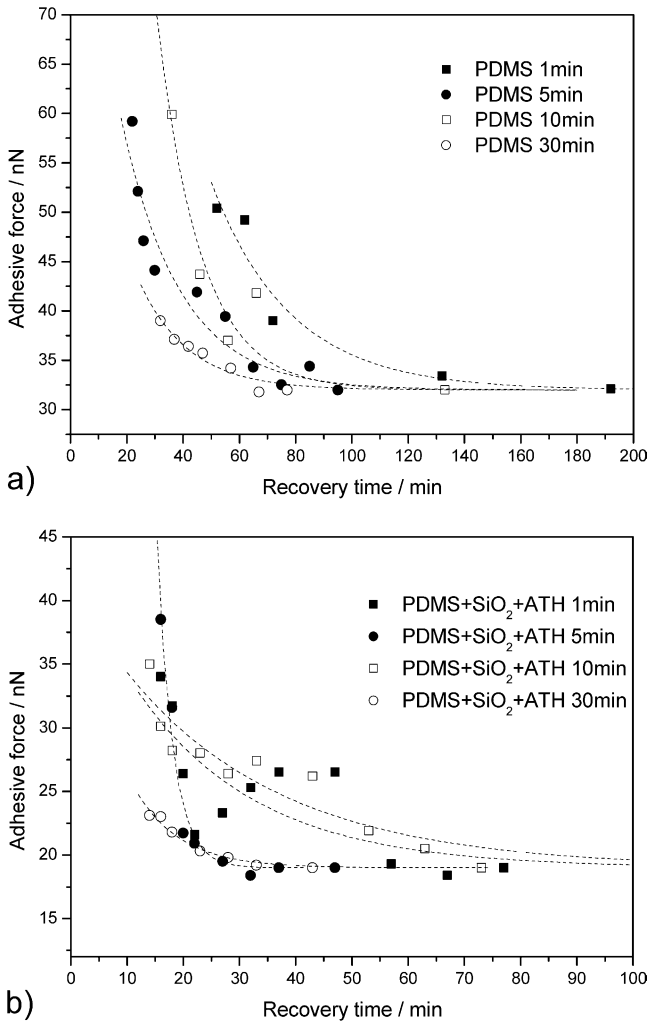
Fig. 2. Adhesive forces measured on corona treated PDMS (a) and PDMS + SiO$_2$ + ATH (b). The corona treatment times t are indicated in the figure.

recovery time t after corona treatment. For better readability, only the curves recorded $t = 24$, 30, 55 and 95 min are displayed. The decreasing area between the approaching and the retracting curve in Fig. 1a shows that the sample changes from a rather hydrophilic state, caused by the corona treatment, back to into its initial hydrophobic state. Fig. 1b displays the adhesive force calculated from the pull-off force of the force distance curves in (a) as a function of time. It can clearly be seen that the adhesive force between the probe and the sample decreases with time. This is caused by the hydrophobic recovery of the PDMS.

Fig. 1c displays the different gradients of the approaching curves, which relate directly to the surface stiffness of the sample. Like Fig. 1b it shows the recovery of the surface stiffness with time. The corona treatment induces a hardening of the surface coupled with a loss of the hydrophobicity. Both effects are diminished with time and the polymer surface recovers to its original hydrophobic state.

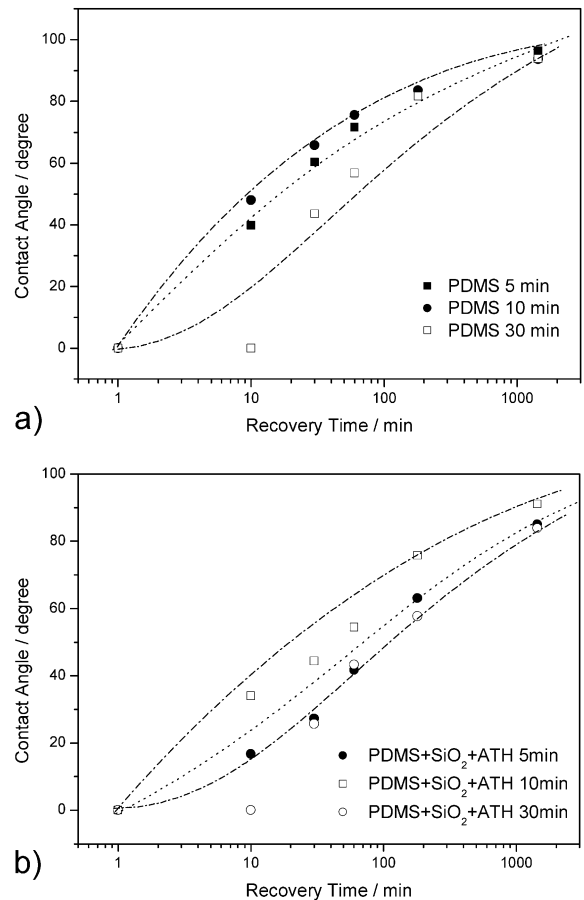Fig. 2 shows the adhesive force F_A as a function of

Fig. 3. Contact angle measurements of corona treated PDMS (a) and PDMS + SiO$_2$ + ATH (b). The corona treatment times t are indicated in the figure.

recovery time t measured for PDMS samples, which were corona treated for $T = 1$, 5, 10 and 30 min.

The recovery behaviour of the adhesive force could best be fitted to an exponentially decaying function of the form

$$F_A = \alpha\, e^{-t/\tau} + F_{A0}$$

where F_{A0} is the adhesive force value measured on the untreated sample surface, to which the adhesive force of the corona treated samples recovers with the time constant τ. The value F_{A0} was set as a fixed parameter for fitting. A smaller value of τ indicates a faster recovery to the value of F_{A0}.

The surface stiffness could be fitted similarly to an exponential decay, but in this case the values did not quite recover to the original stiffness of the untreated sample.

In the following we concentrate on the adhesive force measurements for the two different insulators after corona treatment of 1, 5, 10 and 30 min and compare the force measurements to results obtained by static contact angle measurements.

The curves in Fig. 2 have been normalized on the y-axis so that the saturation value to which the adhesive force recovers was set to be 32 nN, as measured for the untreated

PDMS sample. Fig. 2b shows the adhesive forces measured for the PDMS samples containing SiO_2 and ATH filler. The value determined for the untreated sample in this case was 19 nN and the curves were normalized accordingly.

In both cases it can be seen that the adhesive force increases drastically immediately after corona treatment, which means that the sample becomes more hydrophilic. This loss of hydrophobicity occurs even for treatment times as short as 1 min. It can also be seen that for the pure PDMS the resulting force values can better be fitted with an exponential decay than for the PDMS containing filler particles. It seems that the filler particles have a substantial effect on the recovery behaviour.

With increasing recovery time, the adhesive force decreases until it recovers its original value, indicating that the surface is once again hydrophobic.

Those findings have been confirmed by contact angle measurements, as displayed in Fig. 3.

It can be seen that the contact angle recovers for all samples from a low value, which indicates a more hydrophilic surface, to a higher value, indicating a more hydrophobic surface. The first part of the recovery curve is almost linear, and the gradient can be regarded as a measure of the recovery rate. A higher gradient can be interpreted as a faster recovery.

The results of the force distance measurements as well as the results of the contact angle measurements indicate that certain curves recover faster than others. Therefore the time constant τ of the exponential decay function acquired by

a)

b)

Fig. 4. Recovery time constant of corona treated PDMS (a) and PDMS+ SiO_2+ATH (b) as a function of corona treatment time t.

force distance measurements and the gradient of the linear part of the recovery curve acquired by contact angle measurements were plotted as a function of the corona treatment time (Fig. 4).

A fast recovery would be represented by a low time constant in the case of the force distance measurements and by a high gradient in the case of the contact angle measurement.

For the pure PDMS the fastest recovery occurred for a corona treatment time of 10 min, which is indicated by a minimum of the recovery time constant acquired by force distance measurements and by a maximum of the gradient observed in the contact angle measurements. Longer, as well as shorter corona treatment times resulted in a slower recovery of the sample surface.

For the PDMS samples containing SiO_2 and ATH, the fastest recovery occurred for a corona treatment time of five minutes. In a similar way to the unfilled compound longer treatment time resulted in a slower recovery.

The results obtained from AFM force distance measurements agreed well with the results obtained from static contact angle measurements. These results also agree with the finding of Yoshimura et al [25], who reported that corona treatment of weak intensity and over a short period of time activates low molecular weight chains, while treatment over longer time periods and with higher intensity suppresses them. This is especially the case in materials prepared with high filler content, such as ATH.

The longer recovery times for the samples that have been corona treated for 30 min are most probably due to the formation of a SiO_x degradation layer on the surface, which restricts the diffusion of short, low molecular weight chains to the surface, provided that this surface layer is not cracked due to mechanical stress[8,10]. This is confirmed by the results of positron annihilation measurements by Mallon et al. [26]. The formation of a hard SiO_x layer on the surface is confirmed by the increasing surface stiffness determined by force distance measurements. Like the hydrophilic character, the surface stiffness recovers back to lower values after a certain recovery time, which the low molecular chains require to segregate back to the surface.

It should also be pointed out that the rate of recovery of the filled compound is slower than that of the pure PDMS. This is consistent with the findings of Kim et al. [27], which showed that higher filler levels in commercial PDMS compounds slow down the migration of silicone fluids from the bulk to the surface during the recovery time after dry-band arcing and thus the recovery rate of hydrophobicity.

This phenomenon can be attributed to the presence of the filler particles in the polymer matrix retarding the diffusion. We have also recently shown that these filled PDMS contain a polymer rich surface layer of about 50 nm [26,28].

4. Conclusions

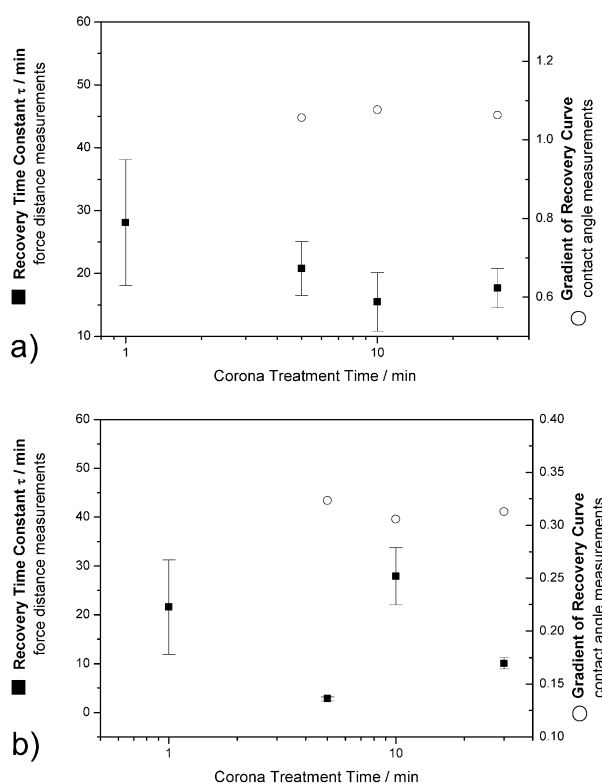It has been shown that the adhesive force determined

from AFM force distance measurements can be used to track the hydrophobicity recovery of PDMS materials after corona treatment. The measurement of the adhesive force as a function of recovery time after corona treatment allows for the determination of a time constant of the hydrophobicity recovery, which can be determined by fitting the obtained data to a simple exponential decay function. These time constants can be used to monitor the recovery of both filled and unfilled PDMS compounds and show that the recovery time depends on the type of PDMS as well as on the time of corona treatment. These results were confirmed by results obtained by contact angle measurements. The adhesive force from the AFM force distance curve thus provides a method for tracking the recovery of the hydrophobicity of the materials without the need for a water droplet to be in contact with the surface as is the case with the static contact angle measurements.

Acknowledgements

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