

## The Surface Structure and Hydrophobic Recovery of Poly-dimethylsiloxane Insulator after Ar Plasma Treatment

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The effect of small molecules in poly(dimethyl siloxane) (PDMS) on the hydrophobic recovery has been studied. Soxhlet extraction was employed to remove the small molecules. The original and extracted samples were probed by positron annihilation and scanning electron microscopy (SEM). The results confirmed that the surface of unmodified PDMS is covered by the small molecules. PDMS with varying octamethylsiloxane (D4) content was modified by argon plasma. The variation of contact angle with the ageing time for different samples was studied by contact angle measurement. As a result it was shown that all the samples can recover to the original hydrophobic surface state after sufficient ageing time. Samples with higher D4 content exhibit a faster hydrophobic recovery. For the sample extracted first and then plasma modified, the hydrophobic recovery rate is very low, and such samples did not return to the untreated hydrophobic state.

### 1. Introduction

Poly (dimethyl siloxane) (PDMS) is widely applied as a high-voltage insulator for outdoor use [1]. In the electric power industry, PDMS-based silicone rubber (SR) insulators are currently replacing conventional inorganic ceramics in high-voltage applications because of their light weight, good dielectric properties, and excellent water repellency [2]. Owing to the hydrophobic methyl groups and low free surface energy, surface hydrophobicity is one of the most important factors that contribute to the superior performance of silicon rubber to prevent moisture [3]. However, when insulators have been in harsh environments, such as salt fog, electrical discharge, and UV radiation, the surface hydrophobic methyl can be oxidized and removed, causing the Si–O chains to be exposed to the surface, resulting in a hydrophilic surface [4]. Deterioration of the hydrophobicity leads to leakage current involving dry-band arcing. This process reduces the insulator characteristics which may eventually lead to a failure of the electrical power system. Thus an investigation of the degraded surface structure of PDMS, including the mechanism of degradation is necessary.

Until now, variation of the surface structure of PDMS after deterioration have been investigated using a variety of methods, e.g. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) [5, 6]. Using these conventional methods, researchers have found that the deterioration process mainly takes place on surface, and in some cases an ultrathin silica-like layer will be formed during the oxidation process such as UV or ozone radiation [7].

Kim *et al.* have pointed out that hydrophobic recovery after UV or plasma modification, low-

molecular-weight (LMW) and uncrosslinked PDMS fragments could migrate from the bulk and cover the degraded surface over a short time period: usually a few hours to a few days [8].

However, there has been a lack of research on the role that small molecules play in hydrophobic recovery after ageing treatment. In order to study the effect of small molecules on hydrophobic recovery, Doppler broadening spectroscopy using a slow positron beam and SEM were utilized to explore the effect of extraction on PDMS. In addition, water contact measurements were employed to probe the surface state after argon plasma modification.

## 2. Experimental

### 2.1 Materials and Preparation

A typical commercial high-temperature vulcanized PDMS composite was used in this study. The composite was prepared by thoroughly mixing a hydride-functional silicone crosslinker and a methyl-terminated PDMS using a 2,5-dimethyl-2,5-di (*t*-butylperox) hexane catalyst at 70 °C for 3 h. Octamethylsiloxane (D4), which is one of the popular small molecular additives in the silicon rubber industry, was compounded with PDMS. The D4 content was varied between the samples which were labelled as D4-0, D4-1, D4-2, D4-3, D4-5 corresponding to a D4 content of 0 wt%, 1 wt%, 2 wt%, 3 wt% and 5 wt%, respectively. By necessity alumina trihydrate (ATH) and amorphous silica were also added as fillers. Silica fillers are used to improve the modulus, hardness and wear resistance and ATH filler is a flame retardant. All the samples were cut as a plate (2 cm × 2 cm × 0.5 cm) for the measurements.

In order to remove the small molecules in the sample, the D4-5 sample was first extracted with the Soxhlet extraction method by hexane solvent for 200 h, and then treated by plasma modification. Control samples compounded with 5 % D4 were modified by plasma directly.

The argon plasma treatment of the PDMS composite samples was performed in a RF-plasma reactor (YZD08-2A) purchased from Tangshan Yanzhao technique institute, China. The RF discharge was excited at 40 kHz with plain parallel electrodes placed in about 50 mm distance. Treatment for each sample was carried out for 5 min with a power of 80 W and an operating Ar pressure of ~80 Pa.

### 2.2 Characterization

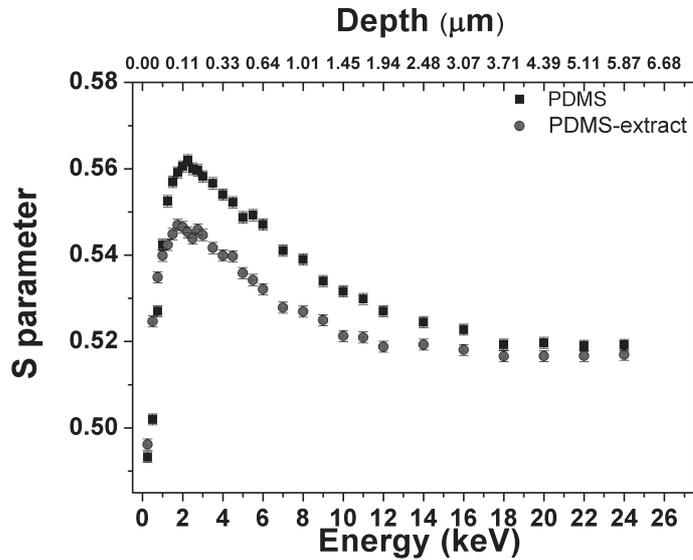
The hydrophobicity of PDMS modified by plasma treatment was quantified by the static contact angle, which was measured with a contact angle measuring device (SL2006) purchased from Shanghai Kino Tech Corp China. Four single droplets of deionized water having a volume of 1 µl were applied on the surface of PDMS samples with a micro-syringe. The drops were placed at four different locations on each of the PDMS samples.

For positron annihilation experiments, a slow positron beam was used. The slow positrons were generated with a 1.85 GBq  $^{22}\text{Na}$  source, moderated by the use of a solid Ne, then electromagnetically transported to the samples. The vacuum in the sample chamber was approximately  $10^{-8}$  Pa. Positron annihilation doppler broadening was performed using a high-purity Ge solid-state detector (energy resolution of 1.3 keV at the 511 keV peak) as a function of positron energy from 0 to 25 keV at room temperature. A total of 2 million counts was collected in each spectrum with a counting rate of 1200 cps. The  $S$  parameter is defined as the ratio of the central area to the total area of the 511 keV  $\pm$  0.76 keV annihilation  $\gamma$  ray peak after the background is properly subtracted.

The surface morphology of the original and extracted D4-5 samples was observed by scanning electron microscopy (SEM) (FEI, Quanta 200).

## 3. Results and discussion

The  $S(E)$  curves for the PDMS (D4-5) control sample and corresponding extracted sample were shown in Fig. 1. In comparison to the control sample, the  $S$  values of the extracted one show distinct

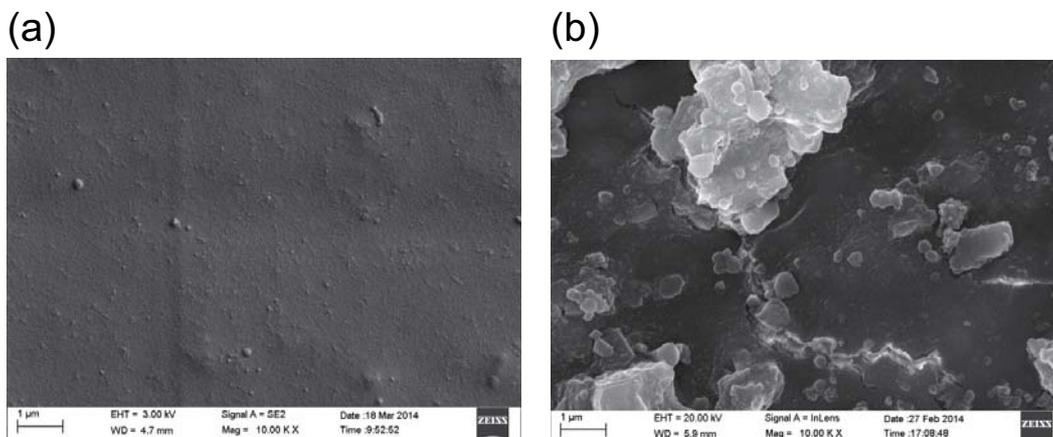


**Fig. 1.**  $S$  parameter as a function of positron incident energy (mean implantation depth is plotted on the upper axis) for the original PDMS (D4-5) sample and the corresponding extracted sample.

differences at energies lower than 18 keV. The  $S(E)$  results can be divided into three ranges: (1)  $E < 1.5$  keV, the  $S$  value for the extracted sample is higher than the original sample, (2)  $1.5$  keV  $< E < 18$  keV, the  $S$  value for the extracted sample is lower than the original sample, (3)  $E > 18$  keV, the  $S$  values for the two samples are nearly the same.

The difference in  $S(E)$  result in the surface range, corresponding to the energies lower than 18 keV, might be due to the destruction of polymer chains. During the soxhlet extraction treatment, not only the D4, but polymers with small molecular weight also would be dissolved into the hexane solvent. In this case, only the polymer main chains and inorganic fillers are maintained at the surface after extraction. The surface of the extracted sample should be much rougher than the original sample.

At the energies lower than 1.5 keV, positronium diffusing back into the vacuum and annihilating

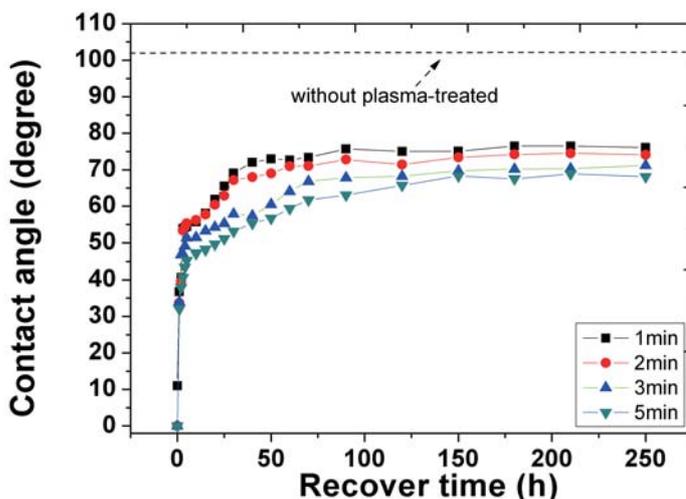


**Fig. 2.** (a) The surface morphology of original D4-5 observed by SEM. (b) The surface morphology of extracted D4-5 observed by SEM.

via  $3\gamma$  annihilation leads to a lower  $S$  parameter. For a rougher surface, positronium which diffuses out from the valley may collide with the peaks on the surface. As a result, for present work, the higher  $S$  parameters of the extracted sample at energies lower than 1.5 keV could be attributed to the rougher morphology. Since the polymer chains in the surface region of the extracted sample were removed by extraction, less positronium formed in the surface of this sample. This might be the reason that the  $S$  value for the PDMS with 5 wt% D4 control sample is higher than that of the extracted sample.

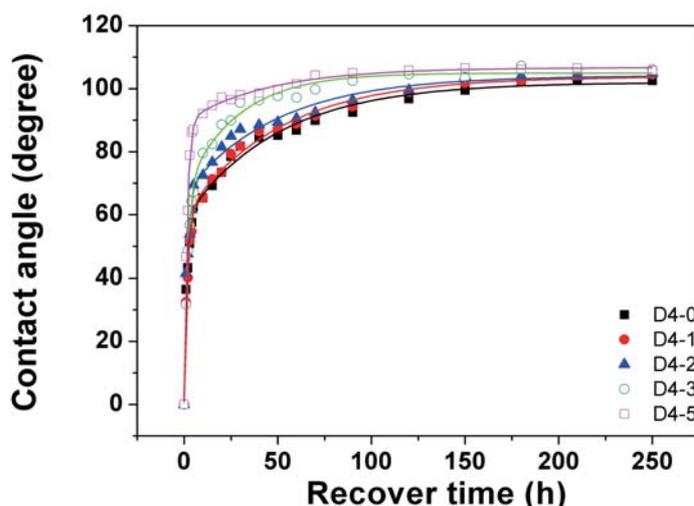
Figures 2(a) and 2(b) are SEM images of the surface morphology of the original D4-5 and extracted D4-5 samples, respectively. It can be seen that the surface of the original D4-5 sample is smooth, but for the extracted one, many peaks and valleys can be found on the surface. Because the silicon rubber studied in this work was compounded with many inorganic fillers which cannot be removed by soxhlet extraction, the particles with different sizes should be these inorganic fillers.

A series of samples with varying D4 content were modified by argon plasma for 5 min. Static contact angle measurements were employed to probe the surface hydrophobicity variation of plasma modified samples (Fig. 3). All the samples exhibited hydrophobic recovery after plasma modification. After sufficient ageing time, all the samples recovered hydrophobic surface, indicated by the contact angle which returns to a value nearly the same as the untreated sample (105 degree). Moreover, higher small molecules content in the PDMS is corresponding to the faster recovery, which indicates that the diffusion of small molecules is a key factor for the hydrophobic recovery of PDMS.



**Fig. 3.** Plots of contact angle with respect to different recover time for plasma treated samples with different D4 loading.

The variation of contact angle via recovering time for the extracted PDMS with 5 wt% D4 after plasma modification (for 1 min, 2 min, 3 min, and 5 min, respectively) is shown in Fig. 4. The extracted one also exhibits the hydrophobic recovery, but the final contact angle is less than 80 degree. This value is far away from the extracted samples without plasma treatment. Compared with the variation of D4-5 in Fig. 3, the rate of hydrophobic recovery is much slower. Therefore, we can conclude that the diffusion of small molecules in PDMS is a key factor for hydrophobic recovery.



**Fig. 4.** Plots of contact angle with respect to different recover time for the extracted samples after plasma modification.

#### 4. Conclusion

A series of PDMS samples with different D4 contents have been successfully prepared. All the samples exhibit hydrophobic recovery after plasma modification. And the contact angle measurement indicates that the surface recovers to the pre-modification value after sufficient time. Moreover, higher D4 content leads to faster recovery. To investigate the role that small molecules played in hydrophobic recovery, the D4-5 sample was chosen for Soxhlet extraction. Both the extracted and original samples have been studied by SEM and positron annihilation Dopple broadening. The results confirmed that the surface morphology was changed by extraction. The extracted samples were modified by argon plasma treatment and then probed by the contact angle measurement. The contact angle of the extracted sample did not recover to the value of the sample before plasma treatment. The results show that the diffusion of the small molecule D4 is a key factor in the surface state after plasma treatment.

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