Effects of liquids immersion and drying on the surface properties of HTV silicone rubber: characterisation by contact angle and surface physical morphology

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Abstract: High-temperature vulcanised (HTV) silicone rubber composite insulator has been widely used in extra-high and ultra-high transmission lines due to its excellent electrical and mechanical performance. In practice use, liquids may encounter the composite insulator intermittently and can lead to the degradation and deterioration of silicone rubber. In the present research, the effects of liquids immersion and subsequent drying on the surface properties of HTV silicone rubber were investigated by means of the contact angle measurement and surface physical morphology measurement which was further analysed in terms of the discrete wavelet transform method, multiresolution signal decomposition algorithm, and three-dimensional fractal dimension calculation. Based on the experimental results, the mechanism of the loss and recovery of the hydrophobicity of HTV silicone rubber surface during the liquids immersion and subsequent drying processes were further explained by taking into consideration the embedded water molecules (and/or hydrated ions) on the HTV silicone rubber surface and the synergy of the increase in roughness/fractal dimension and low molecular weight siloxanes diffusion. This study is helpful for better understanding of the change of surface properties of HTV silicone rubber caused by environmental and electrical stresses.

1 Introduction

High-temperature vulcanised (HTV) silicone rubber composite insulator has been widely used in extra-high voltage (EHV) and ultra-high voltage (UHV) transmission lines with rated voltages ranging from 110 to 1100 kV due to its excellent electrical and mechanical performance. In practice use, liquids may encounter the composite insulator intermittently and can lead to the degradation and deterioration of silicone rubber. In the present research, the effects of liquids immersion and subsequent drying on the surface properties of HTV silicone rubber were investigated by means of the contact angle measurement and surface physical morphology measurement which was further analysed in terms of the discrete wavelet transform method, multiresolution signal decomposition algorithm, and three-dimensional fractal dimension calculation. Based on the experimental results, the mechanism of the loss and recovery of the hydrophobicity of HTV silicone rubber surface during the liquids immersion and subsequent drying processes were further explained by taking into consideration the embedded water molecules (and/or hydrated ions) on the HTV silicone rubber surface and the synergy of the increase in roughness/fractal dimension and low molecular weight siloxanes diffusion. This study is helpful for better understanding of the change of surface properties of HTV silicone rubber caused by environmental and electrical stresses.
contact angle and the surface physical morphology, the effects of liquids immersion and subsequent drying on the surface properties of HTV silicone rubber were explored systematically. The discrete wavelet transform (DWT) method, the MRSD algorithm, and three-dimensional (3D) fractal dimension calculation were employed to characterise the surface physical morphology of HTV silicone rubber quantitatively. Based on the experimental results, a further understanding of the loss and recovery mechanism of the hydrophobicity of HTV silicone rubber caused by liquids immersion and drying was proposed. The present study is helpful for better understanding of the change of surface properties of HTV silicone rubber caused by liquids ingress and overflow as well as caused by other electrical and environmental stresses.

2 Theoretical background

2.1 Fractal theory

Fractal is a brilliant geometrical technique for understanding the nature of the disorder [24]. Fractal has the property of self-similar. The concept of scale is a key point in understanding the fractal; in general, the fractal phenomena only appear in the range between the lower limit and upper limit lengths of fractal; this is the scale invariance property. The range between lower and upper limit lengths of a fractal is the scale-free space. In summary, the fractal phenomena appear in the scale-free space. As for an actual 3D fractal surface, the relevant fractal dimension can be determined by the box counting method [29]. It should be noted that the actual fractal dimension should be obtained by measuring the 3D surface profile directly rather than measuring one or some 2D cut-line profile of the surface. The 3D box counting method is described as follows: the ε is the length of the box, N(ε) is the number of boxes that are needed to cover the 3D surface totally. By adjusting the value of ε, a series of corresponding N(ε) can be obtained. The relationship between 3D fractal dimension D, ε, and N(ε) is in the form of

\[ N(ε) \propto ε^{-D} \]  

Then, one has the 3D fractal dimension D in the form of

\[ D = \lim_{ε \to 0} \frac{\log(N(ε))}{-\log(ε)} \]  

The value of fractal dimension D for a 3D surface is in the range between 2 and 3. As described above, the fractal dimension provides a quantitative parameter to characterise the nature of a rough surface.

Based on the contact angle theory [30, 31], the surface fractal dimension can affect the surface hydrophobicity. In detail, as for a fractal heterogeneous surface with one component being air, the contact angle is described in terms of

\[ \cos θ_i = \left( \frac{L}{L} \right)^{D-2} \cdot f_i \cos θ_i - f_i \]  

where θ_i is the contact angle of the fractal heterogeneous surface and θ_i the eigen contact angle of component i. f_i is the area ratio of component i. L and l represent the upper and lower limit lengths of the fractal surface. In this equation, component 2 represents the air.

It can be found that as for a hydrophobic surface, the surface hydrophobicity is enhanced by increasing the fractal dimension.

2.2 Wavelet transform and MRSD

The wavelet transform is suitable for analysing the non-stationary and transients signals due to its function of simultaneous time and frequency analysis [26]. In the field of surface analysis research, the wavelet transform can be used to obtain the surface morphology at different analytical resolutions.

Wavelet transform is conducted by representing the signal of interest with a family of functions which are the dilation and translation of the basis wavelet function, i.e.

\[ ψ_{a,b}(t) = \frac{1}{\sqrt{a}} ψ \left( \frac{t-b}{a} \right) \quad a, b \in R, a \neq 0 \]  

\[ W_f(a, b) = \left< f, ψ_{a,b} \right> = \frac{1}{\sqrt{a}} \int_{R} f(t) \psi \left( \frac{t-b}{a} \right) dt \]  

where ψ(t) is the basic wavelet (or mother wavelet), and a and b are the dilation and translation parameters, respectively. The asterisk denotes a complex conjugate. Equation (5) is the function of the continuous wavelet transform.

The parameters a and b can be chosen to be a = 2^{-j} and b = k2^{-j}, where j, k ∈ Z, then one has the DWT in the form of

\[ ψ_{j,k}(t) = ψ_{2^{-j}, k2^{-j}}(t) = 2^{j/2} ψ(2^j t - k) \]  

\[ W_f(a, b) = \left< f, ψ_{a,b} \right> = 2^{j/2} \int_{-∞}^{∞} f(t) \psi^*(2^j t - k) dt \]  

MRSD can be understood in terms of an orthogonal wavelet-based filter. The original signal C^0 can be decomposed into two components by the orthogonal wavelet-based filter, i.e. the low-frequency component C^0 and the high-frequency component D^0. The low-frequency component C^0 is the approximation information of the original signal C^0 and the high-frequency component D^0 is the detail information of the original signal C^0 at the first scale. Similarly, the low-frequency component of C^j, i.e. C^j, can be further decomposed into low-frequency and high-frequency components at the second scale, then one has the C^j and D^j, respectively. This procedure is repeated until the desired scale of the signal is achieved. In general, an original signal can be decomposed into k levels at most, where k satisfies the relationship of

\[ k \leq \log_2 M \]  

where M is the total number of sampling data. The low-frequency and high-frequency components at position n can be expressed in terms of

\[ C_n^j = \sum_{j=0}^{n} C_{j,n}^j h_{j-n} \]  

\[ D_n^j = \sum_{j=0}^{n} C_{j,n}^j g_{j-n} \]  

where n is the sampling position, i the scale level, and h and g are the low-pass filter and high-pass filter, respectively. The relations between filters h, g, and the basic wavelet function ψ are in terms of

\[ h_j = \int_{-∞}^{∞} 2^{-j} \psi(2^{-j} x) \psi(x-j) dx \]  

\[ g_j = \int_{-∞}^{∞} 2^{-j} \psi(2^{-j} x) \psi(x-j) dx \]  

where ψ is the scaling function corresponding to the basis wavelet function ψ.

The 2D MRSD analysis can also be performed with the 1D MRSD algorithm at horizontal and vertical orientations; the detailed procedure is shown in Fig. 1. Firstly, the original 2D signal C^0 is calculated along rows (i.e. x-axis); secondly, the computed result obtained by the first step is calculated along columns (i.e. y-axis). By this procedure, four components can be obtained, i.e. C^1 (the horizontal and vertical low-frequencies component of C^0, as
Fig. 1 Schematic representation of 2D MRSD algorithm

marked as ‘A’ in Fig. 1), \( D_1 \) (the vertical high-frequency and horizontal low-frequency component of \( C_1 \), as marked as ‘V’ in Fig. 1), \( D_0 \) (the horizontal high-frequency and vertical low-frequency component of \( C_0 \), as marked as ‘H’ in Fig. 1), and \( D_2 \) (the horizontal and vertical high-frequencies component of \( C_2 \), as marked as ‘D’ in Fig. 1). The \( C \) is the approximation information of the original signal \( C \), while the \( D_0, D_1, \) and \( D_2 \) are a series of detail information of the original signal \( C \) at the first scale. Then, the \( C \) can be further decomposed into four components, the same as the computing procedure of 1D MRSD, the 2D MRSD can also be repeated to the desired scale based on (8).

3 Test specimens and procedure

3.1 Materials

The high-temperature vulcanisation technique was used to manufacture the HTV silicone rubber sample; in this research, the mixture of raw rubber and fillers was vulcanised at 160°C with mould pressing pressure of 5 MPa for 10 min. The raw rubber was PDMS (purchased from China Bluestar Chenggrrand Co., Ltd) with a molecular weight in the range of 450–700,000, the fillers were nano-SiO\(_2\) (purchased from Aladin Industrial Inc., China) with diameter around 10–20 nm and ATH (purchased from Dekedaojin Science and Technology Ltd, China) with diameter around 1–10 μm. The weight ratio of PDMS, ATH, and nano-SiO\(_2\) was 100:100:40.

The HTV silicone rubber samples were cut into plate-shaped pieces of dimension 100 mm × 100 mm × 2 mm. In order to make sure that the samples were clean and completely dry before the tests, the samples were cleaned with alcohol and dried in a desiccator at 90°C for 12 h.

3.2 Immersion and drying test

Taking into account that the ingress of liquids can lead to the temporary loss of hydrophobicity of HTV silicone rubber, when these liquids overflow, the hydrophobicity of HTV silicone rubber can be regained, the liquids immersion process and subsequent drying process were both carried out in this research. As above-mentioned, according to the actual operating experience of composite insulator, water, salt solution, and nitric acid solution are three kinds of liquid that composite insulator most commonly encounter during operation; thus, these three kinds of liquid were used in this research.

Based on actual operating experience of high-voltage composite insulator, water (from relative humidity, spray, and rain), salt solution (from dissolving of soluble matter in contamination), and nitric acid solution (generated from the discharge around the high-voltage composite insulator in the presence of water, oxygen, and nitrogen) are the three kinds of liquid that high-voltage composite insulator most commonly encounter during operation. Therefore, these three kinds of liquids were employed in this research. More specifically, the concentration of these liquids that the high-voltage composite insulator may encounter varies depending on the actual situation; in order to fully understand the effect of these liquids on the HTV silicone rubber, in this research, the chosen concentrations for NaCl and HNO\(_3\) solution occupy a wide range. In detail, the temperature of all test was controlled in the range of 30 ± 1°C, in the immersion process, the HTV silicone rubber samples were immersed in deionised water, NaCl solutions (0.1, 0.5, 1 mol/l), and nitric acid solutions (0.001, 0.01, and 0.1 mol/l). Then, in drying process, the samples were dried in a desiccator with the relative humidity of (30 ± 10)%. In periodic intervals, the surface of HTV silicone rubber samples were cleaned up with filter papers and the contact angles were measured using a droplet of deionised water of volume of 7 μl. Each reading of the contact angle was determined by taking the average of five readings at random locations of the surface. In this test, the errors of contact are up to ±4°. It has been found that [12, 19] in the immersion process and in the subsequent drying process, the changes of hydrophobicity of HTV silicone rubber mainly occurred within the first 100 h, thus, in this research, we chose the immersion time and drying time both 200 h, this length of experiment time can be considered to provide a relative enough time for hydrophobicity of HTV silicone rubber to change.

An electronic weighing scale (Mettle Toldeo AL204) with a resolution of 0.1 mg was used to measure the weight change of HTV silicone rubber samples before and after liquids immersion and subsequent drying.

3.3 Surface physical morphology measurement

The 3D surface physical morphology of HTV silicone rubber samples were measured before and after liquids immersion and drying using atomic force microscope (AFM) (Asylum Research, MFP-2D) in tap-mode. The scan area was set as 50 μm × 50 μm with 384 × 384 pixel data points.

4 Results

4.1 Loss and recovery of hydrophobicity of HTV silicone rubber during liquids immersion process and subsequent drying process

The changes of hydrophobicity of HTV silicone rubber during deionised water and NaCl solution immersion process and subsequent drying process are shown in Fig. 2, for illustrative purposes, the contact angle photos of the HTV silicone rubber immersed in deionised water and in relevant subsequent drying process are depicted. It can be found that the concentration of NaCl solution had a direct effect on the hydrophobicity of HTV silicone rubber during immersion process as well as on the relevant subsequent drying process. In detail, in immersion process, the lower the concentration of NaCl solution (deionised water can be considered as NaCl solution of concentration of 0 mol/l), the larger the decrease in the contact angle. In the subsequent drying process, the lower the concentration of NaCl solution used in immersion process, the lower the final recovery contact angle.

The changes of hydrophobicity of HTV silicone rubber during nitric acid solution immersion process and subsequent drying process are shown in Fig. 3; in this figure, the contact angle photos of the HTV silicone rubber immersed in 0.1 mol/l HNO\(_3\) solution and in relevant subsequent drying process are depicted. It can be found that the concentration of nitric acid solution had a significant effect on the hydrophobicity of silicone rubber during immersion process as well as on the relevant subsequent drying process; specifically, in immersion process, the higher the concentration of nitric acid solution, the larger the decrease in contact angle of HTV silicone rubber, in the subsequent drying process, an interesting phenomenon was observed that the higher the concentration of nitric acid solution used in immersion process, the higher the final recovery contact angle. Furthermore, it should be stressed that the final recovery contact angle of HTV silicone rubber that was previously immersed in 0.1 mol/l HNO\(_3\) solution was even larger than the original contact angle, as can be seen in Fig. 3.
4.2 Weight change of HTV silicone rubber after liquids immersion process and subsequent drying process

The weight change of HTV silicone rubber after liquids immersion process and drying process are plotted in Fig. 4. As for the NaCl solutions, due to the fact that the Na\(^+\) and Cl\(^-\) ions in NaCl solution diffusing into silicone rubber were in the form of hydrated ions, while the radius of hydrated ion was larger than the radius of water molecule [32], thus the energy barriers that hydrated ions need to overcome when diffusing into the HTV silicone rubber was greater than that for water molecule; in addition, the reverse osmosis occurred as the concentrated electrolyte diffused into the HTV silicone rubber and dissolved water-soluble substances within it [13]; thus, in the immersion process, the higher the concentration of NaCl solution, the less the weight increase in silicone rubber. As for the nitric acid solutions, due to the chemical interaction between the nitric acid solution and silicone rubber [21], in the immersion process, the higher the concentration of nitric acid solution, the more the weight increase in silicone rubber.

Owing to the fact the temperature in the drying process was not high enough, there were still some residue liquids existing in the HTV silicone rubber after 200 h of drying, as can be seen in Fig. 4. It should be noted that the HTV silicone rubber previously immersed in 0.1 mol/L nitric acid solution whose concentration was the highest in this research was an exception, after 200 h of drying, the weight of this HTV silicone rubber was even less that the initial weight.
This was caused by the serious dissolution of filler and the degradation of the matrix [13, 18].

4.3 Change of surface physical morphology

The 3D AFM measurements of the physical morphology of HTV silicone rubber surface before and after liquids immersion and subsequent drying are shown in Fig. 5, the corresponding 2D plots are also plotted in Fig. 5. Compared to the HTV silicone rubber surface after liquids immersion and drying, the original HTV silicone rubber surface was relatively planar, as shown in Fig. 5a, after liquids immersion and subsequent drying, the surface of HTV silicone rubber became irregular, which exhibited a significant rough feature, some upheavals and hollows appeared, as shown in

Fig. 5 Physical morphology of silicone rubber surface before and after liquids immersion and drying obtained by AFM
(a) Original HTV silicone rubber surface, (b) After deionised water immersion and drying, (c) After 0.1 mol/l NaCl solution immersion and drying, (d) After 0.5 mol/l NaCl solution immersion and drying, (e) After 1 mol/l NaCl solution immersion and drying, (f) After 0.001 mol/l HNO₃ solution immersion and drying, (g) After 0.01 mol/l HNO₃ solution immersion and drying, (h) After 0.1 mol/l HNO₃ solution immersion and drying.
of the cut-line profile of HTV silicone rubber surface was high-frequency components respectively. The width of the stripe of silicone rubber surface, the 2D MRSD analysis of HTV silicone rubber surface after 0.1 mol/l HNO$_3$ solution immersion and drying were chosen as examples to exhibit. The amplitudes of high-frequency components $D_k^h$ for the cut-line profile of original HTV silicone rubber surface were smaller than that of HTV silicone rubber surface after 0.1 mol/l HNO$_3$ solution immersion and drying at all eight analytical resolutions. It should be noted that the resolution parameter $k$ corresponded to the resolution of 0.13 $\mu$m $\times 2^k$.$^{-1}$.

![Fig. 6 MRSD of the cut-line profile of silicone rubber surface](http://creativecommons.org/licenses/by-nc/3.0/)

(a) Original surface, (b) After 0.1 mol/l HNO$_3$ solution immersion and drying

Figs. 5b–h. In order to have a further quantitative understanding of the change of HTV silicone rubber surface, the 1D MRSD analysis of the cut-line profile of HTV silicone rubber surface was performed in terms of (9) and (10), due to the fact that there were 384 points in the cut-line profile, according to (8), the cut-line profile can be decomposed into eight levels. In this research, the Daubechies wavelet of order 4 was employed in the calculation as the basis wavelet function [26]. The results are shown in Fig. 6 (for brevity, the original HTV silicone rubber surface and the HTV silicone rubber surface after 0.1 mol/l HNO$_3$ solution immersion and drying were chosen as examples to exhibit). The amplitudes of high-frequency components $D_k^h$ for the cut-line profile of original HTV silicone rubber surface were smaller than that of HTV silicone rubber surface after 0.1 mol/l HNO$_3$ solution immersion and drying at all eight analytical resolutions. It should be noted that the resolution parameter $k$ corresponded to the resolution of 0.13 $\mu$m $\times 2^k$.$^{-1}$.

Two-dimensional MRSD can provide the hierarchical information of surface at different orientations and resolutions. Fig. 7 shows the series of detailed information of HTV silicone rubber surface at different resolutions obtained by 2D MRSD analysis, in which the Daubechies wavelet of order 4 was also employed as the basis wavelet function as well. The same as Fig. 6, the original HTV silicone rubber surface and the HTV silicone rubber surface after 0.1 mol/l HNO$_3$ solution immersion and drying were chosen as examples to exhibit. The donations of $D_k^h$, $D_k^v$, and $D_k^k$ in Fig. 7 mean the vertical high-frequency and horizontal low-frequency component, the horizontal high-frequency and vertical low-frequency component, and high frequencies both in vertical and horizontal directions component at the scale of level $k$, respectively. The width of the stripe of $D_k^h$, the height of the stripe of $D_k^v$, and the size of the grid of $D_k^k$ represent the resolution, the larger scale of width, height, and size mean the lower resolution, vice versa. In contrast with the 2D MRSD analysis of original silicone rubber surface, the 2D MRSD analysis of HTV silicone rubber surface after 0.1 mol/l HNO$_3$ solution immersion and drying showed a more dramatic fluctuation at every resolution, which reflected that the morphology of silicone rubber surface changed significantly. In order to have a more intuitive understanding of this change, 3D plots of the sum of high-frequency components (i.e. the sum of $D_k^h$, $D_k^v$, and $D_k^k$) were calculated and plotted in Fig. 8. Based on this 3D plot, it could be concluded that after 0.1 mol/l HNO$_3$ immersion and drying, the surface of HTV silicone rubber became rough at every analytical resolution in this research, this phenomenon could be confirmed in terms of 1D MRSD, 2D MRSD, and 3D plots synergistically.

The quantitative analysis of the change of surface was conducted in terms of the parameter of square root roughness $R_s$ defined as

$$R_s = \left\{ \sum_{i=1}^{N} (x_i - \bar{x})^2 \right\}^{1/2}$$

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

where $x_i$ is the value of the sum of $D_k^h$, $D_k^v$, and $D_k^k$ at position $i$, $\bar{x}$ the average of $x_i$, and $N$ the total number of $x_i$.

The parameter $R_s$ characterised the extent of the roughness of silicone rubber at different analytical resolutions. The calculated results of $R_s$ at the different analytical resolutions of all samples are shown in Fig. 9. The item number in Fig. 9 has the same means as that in Fig. 5, indicating the HTV silicone rubber sample after different liquids immersion and drying.

As for the original HTV silicone rubber surface, as shown in Fig. 9, the $R_s$ increased with the increasing of $k$, which meant that the large scale of observation (i.e. the large resolution) corresponded to large value of roughness. In contrast with the original HTV silicone rubber surface, after liquids immersion and drying, the roughness of HTV silicone rubber surface at every analytical resolution was different.
increased; furthermore, the nitric acid solutions have the greatest effect, as shown in Figs. 9b–h. An interesting phenomenon can be observed that in Figs. 9e and f, some Rs at the large value of parameter $k$ corresponded to a smaller value, this indicated that the morphology of these silicone rubber surface became more sophisticated.

As for a rough surface, the morphology obtained at different analytical resolutions were self-similar, i.e. the morphology had the fractal characters, the 3D plots in Fig. 8 confirmed this intuitively. Furthermore, the 3D box counting method was employed to calculate the fractal dimension of HTV silicone rubber surface before and after liquids immersion and drying. The detailed computing procedure is expressed in Fig. 10. It should be stressed that in this computing procedure for 3D fractal dimension, the upper limit of the fractal can be obtained.

Table 1 gives the detailed calculated results of original HTV silicone rubber surface, for example. The linear fitting of the length of box and total number of boxes required to cover the surface is shown in Fig. 11, it can be found that when the length of box was <1.56 μm, the 3D fractal dimension of original HTV silicone rubber surface obtained by linear fitting was 2.19, while when the length of box was >1.56 μm, the value of 3D fractal dimension was 2. It meant that the fractal character of original silicone rubber only appeared at the analytical resolution <1.56 μm; in other words, the upper limit length of fractal of original silicone rubber surface was 1.56 μm in our experimental condition. The lower limit length could reach the atomic scale [24]; the measurement accuracy used in this research could not measure the lower limit length of fractal of HTV silicone rubber.

Fig. 7 Two-dimensional MRSD of silicone rubber surface for original sample and the sample after 0.1 mol/l HNO$_3$ immersion and subsequent drying
(a) Original surface, (b) After 0.1 mol/l HNO$_3$ solution immersion and drying
The calculated 3D fractal dimensions of HTV silicone rubber surface before and after liquids immersion and drying are shown in Fig. 12. The value of 3D fractal dimensions distributed in the range between 2.19 and 2.34, the HTV silicone rubber surface after liquids immersion and drying showed a larger value of 3D fractal dimension than that of the original HTV silicone rubber surface; in all samples, the sample after 0.1 mol/l HNO₃ solution immersion and drying showed the largest value of 3D fractal dimension.

Fig. 8 Three-dimensional plots of the sum of $D_H^k$, $D_V^k$, and $D_D^k$ at different scale for original sample and the sample after 0.1 mol/l HNO₃ solution immersion and drying
(a) Original surface, (b) After 0.1 mol/l HNO₃ solution immersion and drying

Fig. 9 Rs of different silicone rubber sample at different analytical resolutions (the item number in parentheses means the sample number, which has the same meanings as in Fig. 5)

The calculated 3D fractal dimensions of HTV silicone rubber surface before and after liquids immersion and drying are shown in Fig. 12. The value of 3D fractal dimensions distributed in the range between 2.19 and 2.34, the HTV silicone rubber surface after liquids immersion and drying showed a larger value of 3D fractal dimension than that of the original HTV silicone rubber surface; in all samples, the sample after 0.1 mol/l HNO₃ solution immersion and drying showed the largest value of 3D fractal dimension of

Fig. 10 Detailed calculating procedure of 3D box counting method
2.34. It was noteworthy that for all samples in this research, the upper limit lengths were all 1.56 μm.

From the results presented in this section, it could be confirmed that the effects of NaCl solution with concentration of 0.1, 0.5, and 1 mol/l on HTV silicone rubber surface morphology were basically consistent. As for the nitric acid solution, the results revealed that the greater the concentration of nitric acid solution, the greater the effect of nitric acid solution on the surface morphology of silicone rubber. When we compared the effects of NaCl solution and nitric acid solution, the effect of NaCl solution was generally similar to that of nitric acid solution with concentration <0.01 mol/l, as can be seen in Figs. 5 and 12. For more specific comparison, the data of the roughness at different analytical resolutions for different HTV silicone rubber can be obtained in Fig. 9 directly.

5 Discussion

The literature [7, 14] gave the reason why the hydrophobicity of HTV silicone rubber loss due to liquids immersion, i.e. (i) the inward orientation of methyl, which made the Si–O–Si backbone loss of shielding; (ii) the loss of LMW on the surface of silicone rubber. According to the outcome of this research, we thought that there was another reason for explaining the loss of hydrophobicity of silicone rubber due to liquids immersion: when the liquids diffused into silicone rubber, some water molecules (and/or hydrated ions) would embed into the free space on the surface of HTV silicone rubber, then a composition and heterogeneous surface was formed. Based on the Cassie's law [31], the more the content of hydrophilic substance on the surface, the lower the contact angle of the heterogeneous surface; in other words, the more the content of water molecules (and/or hydrated ions) embedded on the silicone rubber surface, the worse the hydrophobicity of the silicone rubber surface.

The hydrophobicity recovery mechanism after liquids immersion (i.e. in the drying process) given by the literature [7, 14] were (i) the diffusion of LMW from bulk to surface of silicone rubber and (ii) the reorientation of methyl from inward to outward. Apart from this, we thought that there were still two more reasons for explaining the recovery of hydrophobicity of silicone rubber in the drying process. (i) The embedded water molecules (and/or hydrated ions) would spill over in the drying process, its meant that the amount of the hydrophilic content on the surface decrease, according to Cassie's law, this process was a benefit for the recovery of hydrophobicity. (ii) The increase in the fractal dimension as well as the roughness at different analytical resolution could be expected after liquids immersion and subsequent drying, when taking into consideration the LMW diffusion from bulk to surface in the drying process, the surface with increasing of roughness and fractal dimension covered by the LMW would increase the hydrophobicity; moreover, the crack of HTV silicone rubber surface can also provide lower resistance route to LMW to reach on the surface the sample from bulk [33, 34], this was also benefit for the increase in hydrophobicity. In short, the synergy of LMW diffusion and increase in roughness/fractal dimension improved the hydrophobicity of HTV silicone rubber during the drying process. As has been pointed in the literature [18], the liquids can lead to the degradation of the polymer matrix and dissolution the inorganic filler beneath and/or on the surface, combining the results in the present research, a schematic diagram for the change of fractal dimension as well as roughness of HTV silicone rubber surface is given in Fig. 13.

Based on the above analysis, the contact angle measurement results shown in Figs. 2 and 3 can be explained clearly, as follows, during the liquids immersion process, it was reasonable to conclude that the larger weight gain corresponded to the larger amount of water molecular and/or hydrate ions embedded on the surface of silicone rubber, as for the NaCl solution, the lower the concentration of NaCl solution, the larger the weight gain during immersion process, as shown in Fig. 4; thus, this explained the phenomenon that the lower concentration of NaCl solution related to the larger decrease in the contact angle during immersion. Similarly, the relationship between the concentration of nitric acid solution and the loss of hydrophobicity of silicone rubber due to nitric acid solution immersion could also be explained in this way. During the liquids drying process, the diffusion of LMW and the increase in fractal dimension and roughness of HTV silicone rubber surface would strengthen the hydrophobicity, i.e. the recovery of the hydrophobicity. However, due to the fact that there was still some residual liquids in the samples, as shown in Fig. 4, then it could be explained why the final recovery contact angle did not reach the initial value, as shown in Figs. 2 and 3.

One special case was the sample immersed in the 0.1 mol/l HNO₃ solution. The nitric acidic solution could cut off the Si–O–Si backbone [18], this process would generate more LMW, the higher the nitric acid concentration, the stronger its effect on the silicone rubber, this was the reason why the HTV silicone rubber after 0.1 mol/l HNO₃ solution immersion showed the rapid increase in hydrophobicity in the drying process, as shown in Fig. 3. Furthermore, the fractal dimension and roughness at all analytical resolutions of the HTV silicone rubber surface after 0.1 mol/l HNO₃ solution immersion were the largest; therefore, it was rational that this fractal surface covered by the LMW showed the

| Length of box side, μm | Totally number of boxes required to cover the surface | Length of box side, μm | Totally number of boxes required to cover the surface |
|-----------------------|-----------------------------------------------------|-----------------------|-----------------------------------------------------|
| 0.196                 | 177,348                                             | 3.125                 | 256                                                 |
| 0.391                 | 32,374                                              | 6.25                  | 64                                                  |
| 0.781                 | 7822                                                | 12.5                  | 16                                                  |
| 1.563                 | 1820                                                | 25                    | 4                                                   |
| —                     | —                                                   | 50                    | 1                                                   |

Fig. 11 Linear fitting of length of boxes and total number of boxes required to cover the surface (this sample was the original HTV silicone rubber surface)

Fig. 12 Calculated results of 3D fractal dimension of silicone rubber surface before and after liquids immersion and drying (the item number in vertical axis means the sample number, which has the same meanings as in Fig. 5)
largest contact angle which was even larger than the contact angle of original HTV silicone rubber surface, as shown in Fig. 3.

6 Conclusions

The immersion and subsequent drying of liquids can lead to the degradation of the surface structure of HTV silicone rubber. In the present work, the contact angle and surface physical morphology were used to characterise the effects of liquids immersion and subsequent drying on the surface properties of HTV silicone rubber. Based on the experimental results of this research, the following conclusions were obtained:

The lower the concentration of NaCl solution, the greater the influence on the hydrophobicity of HTV silicone rubber surface, the higher the concentration of nitric acid, the greater the influence on the hydrophobicity of HTV silicone rubber surface. The surface roughness was a function of analytical resolution, by using the DWT method and MRSD algorithm, the roughness of HTV silicone rubber at different analytical resolutions were obtained and compared. Furthermore, the specific morphologies of HTV silicone rubber at different analytical resolutions were similar to each other; this phenomenon was measured by the 3D fractal dimension. It was found that after liquids immersion and subsequent drying, the roughness at all analytical resolutions of HTV silicone rubber surface increased compared to that of the original HTV silicone rubber surface; meanwhile, the 3D fractal dimension of HTV silicone rubber surface also increased compared to that of the original HTV silicone rubber surface, these increases reflected and characterised the change of HTV silicone rubber surface resulting from the degradation of matrix and the dissolve of inorganic filler quantitatively. The mechanism of the loss and recovery of the hydrophobicity of HTV silicone rubber surface during the liquids immersion and subsequent drying process were further explained by taking into consideration the embedded water molecules (and/or hydrated ions) on the HTV silicone rubber surface and the synergy of the increase in roughness/fractal dimension and LMW diffusion.

7 References

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