

Study on Organic Molecular Damage Mechanism and Environmental Dependence of Silicone Rubber Under the Synergistic Action of Complex Conditions

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Abstract: This study focused on the mechanism of corona discharge and nitric acid damage to silicone rubber organic molecules in order to solve the aging problem of composite external insulation materials in heavy pollution environment. The effects of corona strength, duration and nitric acid corrosion on the physical and chemical properties of silicone rubber were systematically investigated through the independent corona aging test system of composite materials (including 54 sets of pin-plate electrodes), combined with scanning electron microscopy (SEM), static contact Angle analysis, thermal stimulation current (TSC) and Fourier infrared spectroscopy (FTIR). The results show that: (1) During corona discharge, the high energy charged particles preferously destroy C-H bond and Si-C bond through mechanical collision, leading to methyl group loss and hydrophilic group formation; However, nitric acid corrodes Si-O main chain through hydrolysis reaction and forms $\text{Al}(\text{NO}_3)_3$. (2) Hydrophobicity loss showed phased characteristics: After a short time corona (<4h), the hydrophobicity quickly recovered due to the migration of small molecule siloxane; After long exposure (>7h), the inorganic crystal layer obstructs the migration and the recovery rate drops sharply. (3) The variation of trap characteristics shows that the charge-trapping ability increases with aging (TSC peak current increases from 26 pA to 165 pA), and nitric acid corrosion introduces shallow traps to form a double-peak current curve. (4) Under low pressure and high humidity environment, electric field distortion significantly promotes the formation and diffusion of nitric acid, and accelerates the crack propagation on the surface of the material; Under high pressure, charged particle bombardment is the dominant damage mode. The research results reveal the competitive mechanism of molecular chain breaking-oxidation-condensation reaction of silicone rubber under multi-factor coupling, and provide a theoretical basis for the molecular design of weather-resistant composite insulating materials.

Keywords: Corona Discharge; Organic Molecular Damage Mechanism; Hydrophobicity Recovery; Surface Topography Analysis; Environmental Dependence

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1.Introduction

The aging behavior of silicone rubber (HTV-SR) in high voltage environment is significantly affected by the synergistic

effect of corona discharge and environmental factors. The research shows that humidity and ultraviolet can synergistically aggravate the damage of corona discharge to the molecular structure of materials. Bi et al.^[1] found that the corona discharge energy was significantly improved in high humidity environment, and accelerated the formation of hydroxyl (-OH) and carboxyl (-COOH) on the surface, leading to an increase in hydrophobic loss rate. Hakami et al.^[2] further confirmed that the coupling of ultraviolet light and high humidity doubled the aging rate of silicone rubber, but did not consider the complex interaction between temperature difference and air pressure in actual working conditions. Corona discharge directly destroys the molecular chain of silicone rubber by high-energy particle bombardment. Wang et al.^[3] research shows that the contact angle of the material decreases obviously after AC corona exposure, and the decrease of Si-O-Si and Si-CH₃ bond content is the main reason for the performance degradation. Haji et al.^[4] and Zhu et al.^[5] reveal the chemical mechanism of CH₃ group being replaced by hydrophilic OH group and the law of surface crack propagation through surface analysis. In the aspect of interface discharge behavior, Guo et al.^[6] confirmed that AC corona treatment can prolong the breakdown time of polypropylene/silicone rubber interface by three times, while Sarathi et al.^[7] found that corona aging materials were damaged more seriously in water droplet induced discharge, and the damage degree was significantly improved under negative DC voltage. The recovery of hydrophobicity depends on the migration of low molecular weight polydimethylsiloxane (LMW PDMS). Zhu et al.^[8-9] pointed out that the inhibition of pollution layer on the migration of LMW PDMS could delay the recovery time of hydrophobicity, while Zhang et al.^[10] found that the synergy of electric field and nitric acid increased the hardness and tensile strength of silicone rubber. However, most of the existing studies are based on idealized experimental conditions, and lack of in-depth analysis of the coupling mechanism between long-term aging data and multiple factors. Therefore, this paper studies the influence mechanism of the synergistic effect of corona discharge and nitric acid corrosion on the aging and degradation of silicone rubber composite external insulation materials in heavily polluted environment. Through multi-parameter regulation (corona intensity, nitric acid concentration, pressure and humidity), the internal relationship between the dynamics of organic molecular bond fracture, the cross-scale evolution of surface structure, the characteristics of electron traps and the dynamic response of hydrophobicity is revealed, which provides theoretical support for the design and aging evaluation of high-reliability external insulation materials.

2. Methods and results

Scholars both domestically and internationally have conducted extensive research on the aging characteristics of silicone rubber materials under corona effects, analyzing the mechanisms by which high-energy particles from corona and corona-generated substances—ozone and ultraviolet light—break down organic molecular bonds in silicone rubber materials. However, nitric acid is also a major product of corona discharge, and its mechanism for damaging organic molecular bonds in silicone rubber materials requires further investigation. Additionally, the sudden loss and recovery of hydrophobic properties during operation, as well as the reduction in flashover voltage of silicone rubber materials after aging, have not been adequately explained. Therefore, this section focuses on studying the mechanisms by which corona damages organic molecules in silicone rubber materials and provides an in-depth discussion of their impact based on various characterization methods, to supplement existing theories of corona-induced aging.

2.1 Study on the mechanism of corona damage to organic molecules of silicone rubber materials

Scholars both domestically and internationally have conducted extensive research on the aging characteristics of silicone rubber materials under corona effects, analyzing the mechanisms by which high-energy particles from corona and corona-generated substances—ozone and ultraviolet light—break down organic molecular bonds in silicone rubber materials. However, nitric acid is also a major product of corona discharge, and its mechanism for damaging organic molecular bonds in silicone rubber materials requires further investigation. Additionally, the sudden loss and recovery of hydrophobic properties during operation, as well as the reduction in flashover voltage of silicone rubber materials after aging, have not been adequately explained. Therefore, this section focuses on studying the mechanisms by which corona damages organic molecules in silicone rubber materials and provides an in-depth discussion of their impact based on various characterization methods, to supplement existing theories of corona-induced aging.

2.1.1 Corona aging test system construction

The composite material corona aging test system developed by the project team can simulate different corona aging conditions and carry out corona aging for multiple tests at the same time. It mainly includes four parts:

(1) Corona generation device

The corona generation device consists of two parts: the pressurization unit and the electrode system. The pressurization unit uses the YDT-5/50 type corona-free test transformer produced by Jiangdu Huayu High Voltage Electrical Co., Ltd. High voltage is transmitted through relays and conductive paper, ultimately reaching the stainless steel electrodes in the test chamber via cables. The electrodes adopt a traditional needle-plate configuration to simulate corona discharge in real-world conditions. The needle electrode serves as the upper electrode with a curvature radius of 0.2 mm, while the plate electrode acts as the lower electrode with a diameter of 30 mm. The entire electrode system comprises 54 sets of needle-plate electrodes, with the needle and plate electrodes arranged on upper and lower epoxy glass cloth plates connected by insulating rods, and each set of needle-plate electrodes facing each other; the distance between needles or plates on the insulating boards is 90 mm, and through electric field simulation, the influence of the electric field strength between each set of electrodes is minimal. Additionally, the upper and lower plates can be moved for easy sampling and adjustment of corona intensity. The details are shown in Figure 1-2.

Figure 1 Overall device diagram

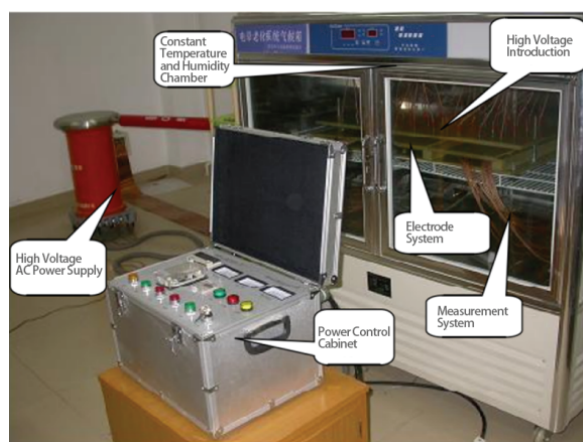


Figure 2 Electrode system



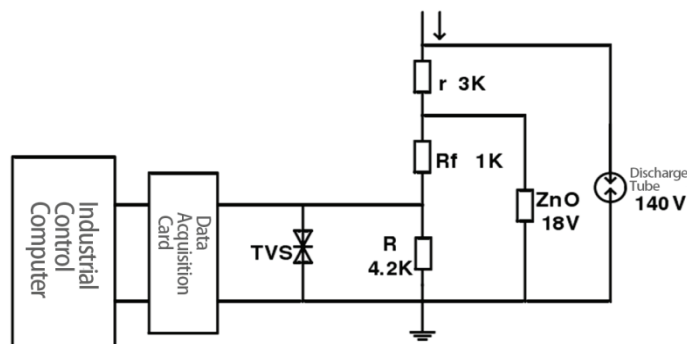
(2) Measurement system

(A) Hardware design and implementation

The corona current signal is introduced into the measurement system composed of protection circuit, measuring resistor and acquisition card through double shielded low noise cable (all interfaces are connected by BNC). The sampling resistor R is a high precision non-inductive resistor of $5k\Omega$, R is the protection resistor. The selection of the acquisition card mainly considers several aspects such as data acquisition channels, sampling rate, bit depth of the acquisition card, digital I/O, and price. The corona aging device designed in this paper has a total of 54 current loops. When all are running, an acquisition card with at least 55 channels is required (one channel is used to collect corona voltage signals). Using an oscilloscope to measure the corona discharge current in real-time at different sampling rates, it was found that when the sampling rate is set

to 10 kS/s, a clear corona current signal can be observed. Therefore, the sampling rate for each channel should be at least 10 kS/s. Considering that the accuracy requirement for measuring corona current is not high, a 12-bit acquisition card can be chosen. The selection of digital I/O ports should be based on the ports to be controlled. For this experiment, the DAQ2204 data acquisition card from Advantech was selected. This card has a PCI bus structure, with specific performance as follows: maximum sampling rate of 3 MS/s; 64 input/output channels, when using 55 channels simultaneously, the average sampling rate per channel is 55 kS/s; bit depth of 12 bits; voltage range for input signals set to $\pm 5V$; resolution of the acquisition card is 2 mV; and it has 24 digital I/O ports. The details are shown in Figure 3.

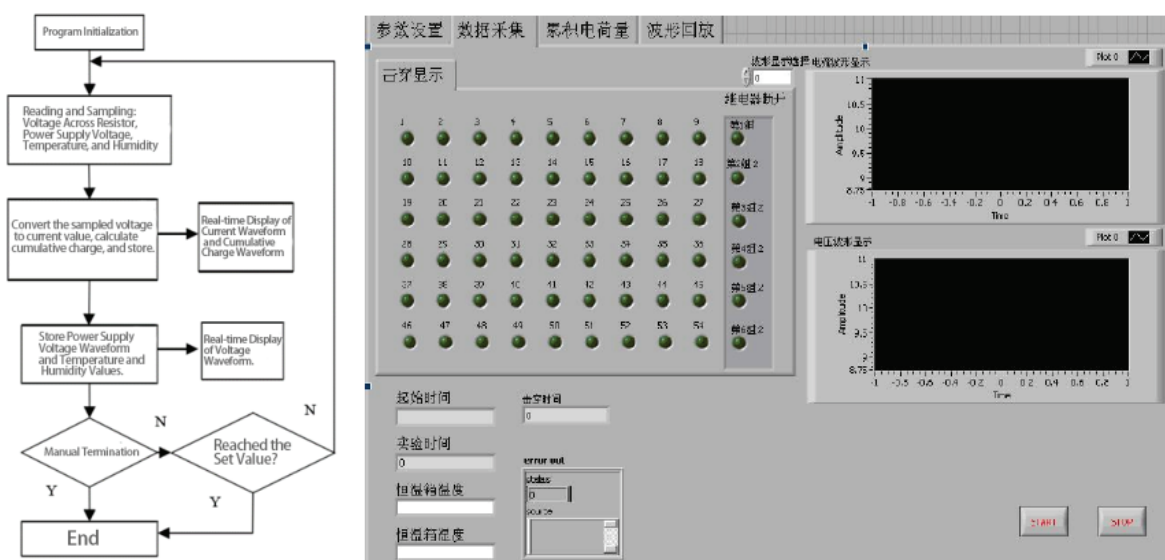
Figure 3 Schematic diagram of the measurement system



(b) Design and implementation of software system

Using LabView software and its DSC module, a software system for corona aging testing has been developed. This system can achieve the following functions: it can simultaneously collect and display measurement results of multiple corona current signals; it can display corona voltage waveforms; it can calculate and save the cumulative charge and total charge of both positive and negative half-cycles of corona discharge, as well as discharge power and energy; it can display charts showing the charge quantities and discharge energy trends over time for both positive and negative half-cycles of corona discharge current. The details are shown in Figure 4.

Figure 4 Main program flow chart Figure 42 Program front panel diagram



(3) Protection system

(A) High voltage side protection

The protection of the high-voltage side is tested using conductive paper connected between the high-voltage relay and the upper electrode. When a large current flows through a circuit, it causes the conductive paper to heat up and burn out within a certain period, thus breaking the test circuit. This ensures that the high-voltage source protection does not activate, allowing other circuits to be tested normally. Tests have shown that under this connection method, when 10mA of current flows

through the conductive paper, it will quickly burn out within 1 second, providing effective protection.

(b) Low voltage side protection

The low-voltage side protection mainly refers to the protection of the acquisition card in the measurement system, which adopts a three-level protection system composed of transient voltage suppression diodes, varistors and discharge tubes.

(4) Environmental control and monitoring

The whole experiment is carried out in a constant temperature and humidity chamber. The test chamber can realize the setting and control of temperature and humidity, and has the function of power failure memory and automatic compensation of power failure time, using air duct ventilation. At the same time, two external control fans are installed on the back side of the test chamber.

2.1.2 Study on the mechanism of damage of organic molecules in silicone rubber materials by corona discharge particles and nitric acid

(1) The influence of corona discharge time and intensity on the properties of silicone rubber materials

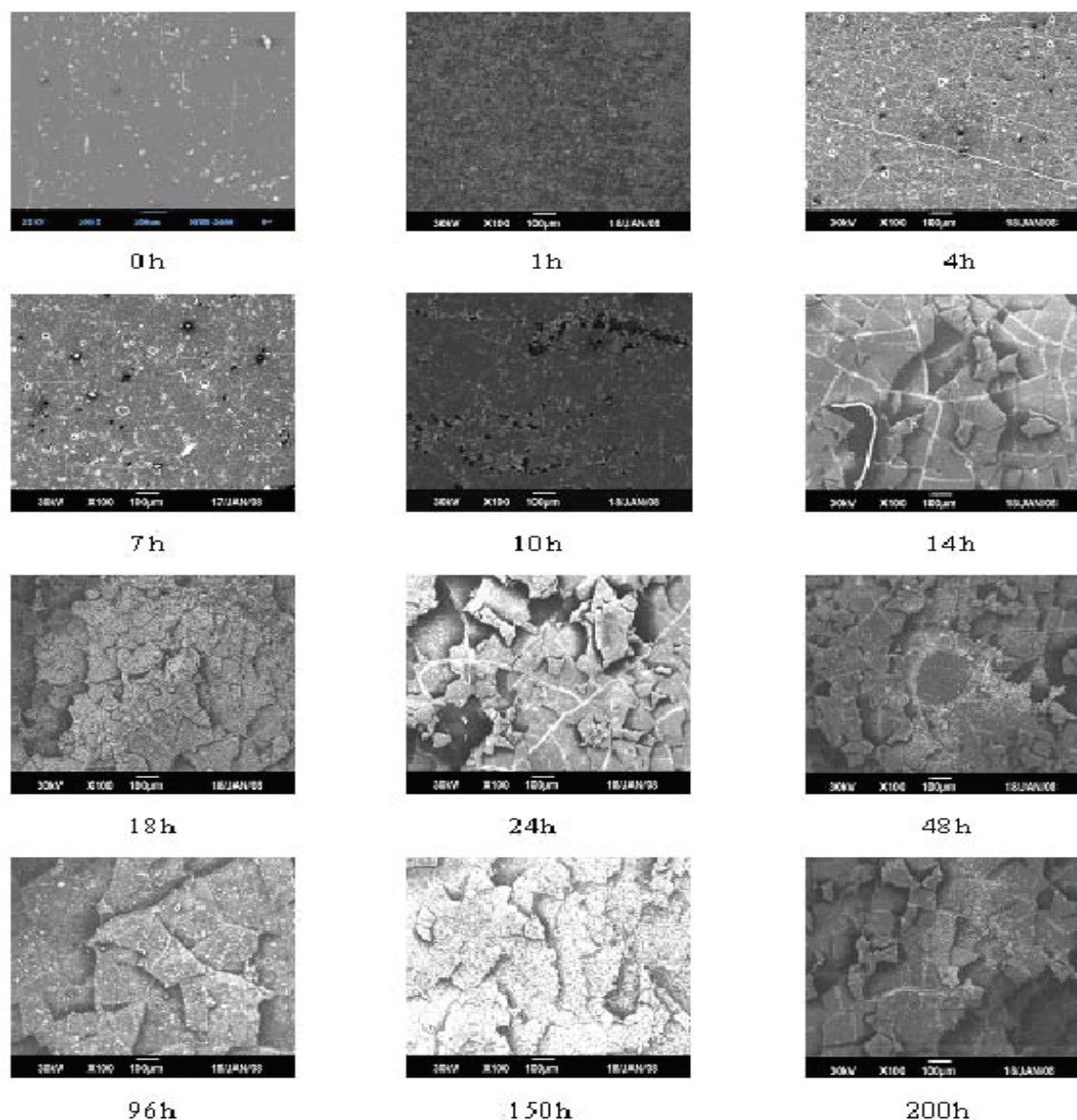
(A) The influence of corona time on the properties of silicone rubber materials

① Influence of voltage action time on surface morphology

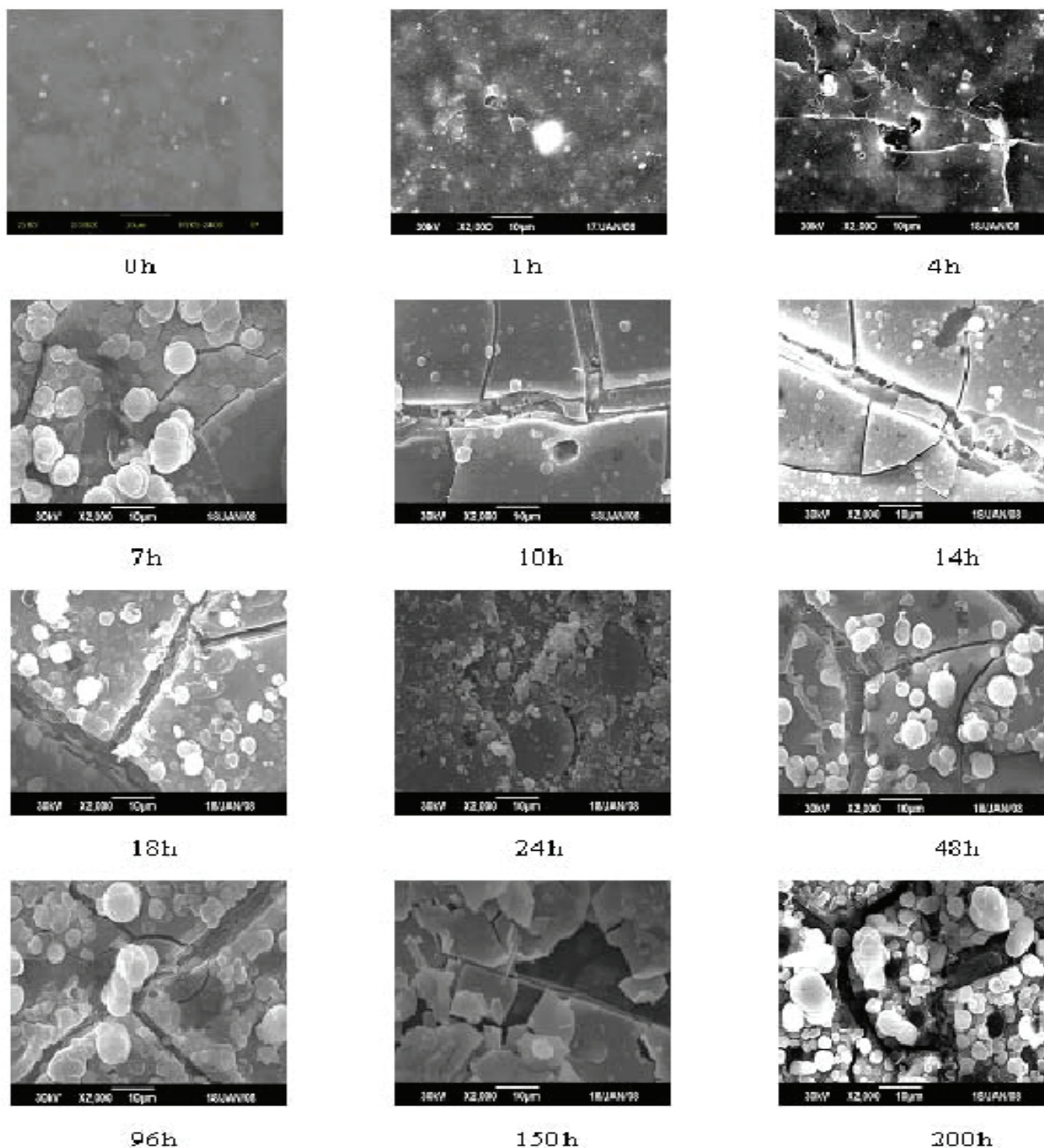
The SEM results of samples after corona at different times under 5kV voltage are shown in Figure 5.

Figure 5 SEM comparison

(A) The magnification is 100



(b) The magnification is 2000

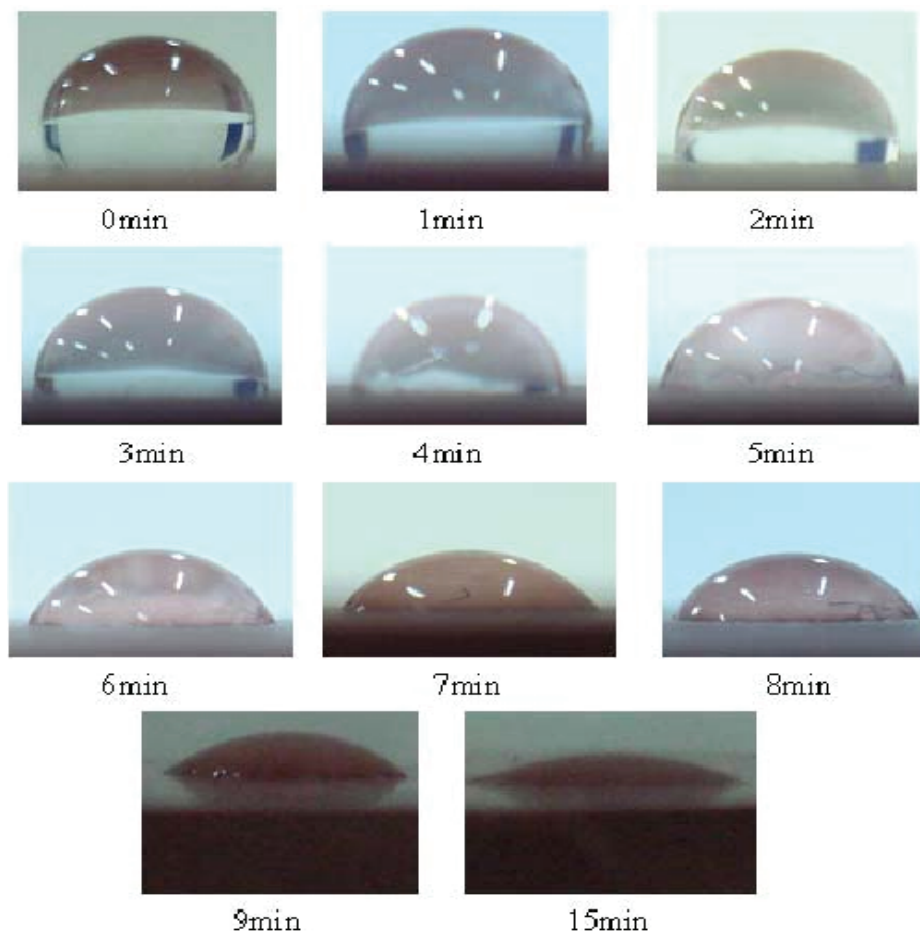


As can be seen from Figure (b), the sample surface becomes dirty after 1h of corona treatment; at 4 h, the surface pores are clearly visible; at 7 h, a thin layer of crystals can be observed on the sample surface; at 10 h, the dense crystal layer breaks, and faint cracks become visible, which gradually deepen; at 24 h, the sample surface becomes fluffy, with faint cracks visible underneath; at 48 h, the cracks completely penetrate the fluff layer; at 96 h, long and deep cracks appear on the sample surface; at 150 h, large and deep cavities can still be seen, which worsen until the corona discharge ends.

② The effect of corona time on hydrophobicity

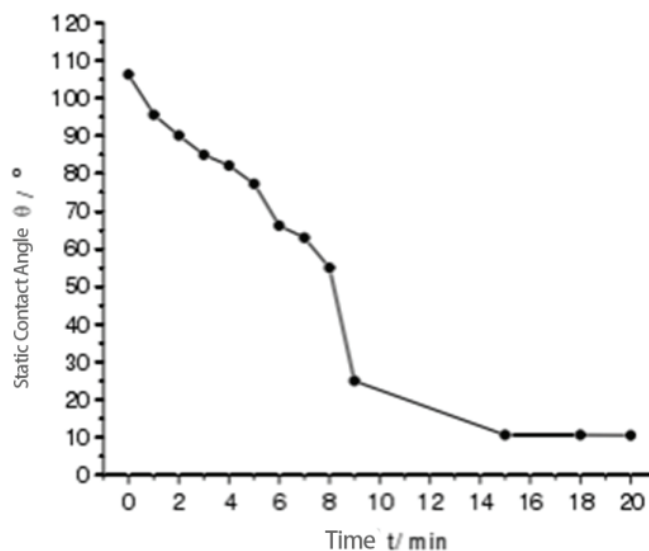
After corona at 5kV for 1h to 200h, the static contact angle of the sample was about 10°, and it temporarily lost its hydrophobic properties. In order to restore the whole process of loss of hydrophobic properties, the hydrophobic properties of the sample after short-time corona at 5kV were observed, as shown in Figure 6.

FIG. 6 Variation of hydrophobicity during corona testing



From the above figure, one can observe the entire process of hydrophobicity loss on the sample surface. At the same time, it is evident that under corona conditions, the hydrophobicity loss on the sample surface is a gradual process. The damage to the hydrophobic properties of silicone rubber material by corona discharge occurs relatively quickly; before pressure application, the static contact angle of the sample was 106.3° , which decreased to 10.5° over 15 minutes and remained around 10° until the end of the test. The details are shown in Figure 7.

Figure7 Static contact Angle of the sample at 5kV voltage with respect to the time of pressure application



At the same time, the hydrophobic recovery performance at different stages of the test was tested, as shown in the figure below. The details are shown in Figure 8-9.

Figure 8 Hydrophobic recovery performance of samples after corona 1h

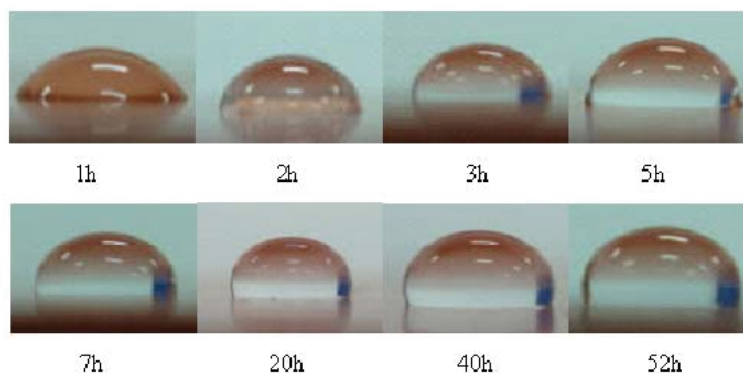
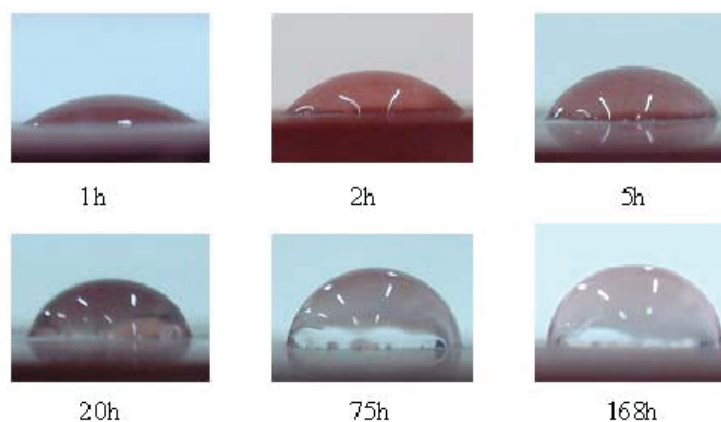
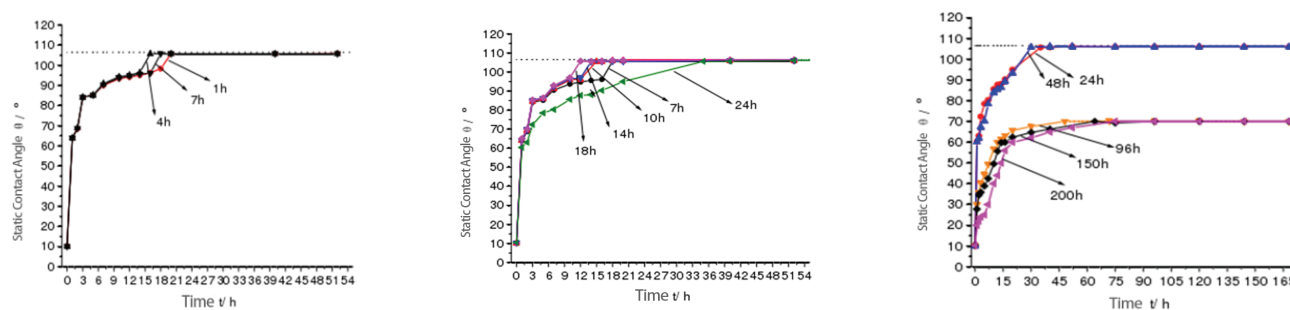


Figure 9 Hydrophobic recovery performance of samples after corona 200h



As can be seen from the figure, after 1h corona, when the sample is left standing for 20h, the hydrophobicity of the sample surface is basically completely restored; after 2000h corona, when the sample is left standing for 20h, its hydrophobicity does not return to the initial level, and then the recovery rate is slow until 75h, when the hydrophobicity no longer changes.

Figure 10 Recovery of static contact Angle of the sample



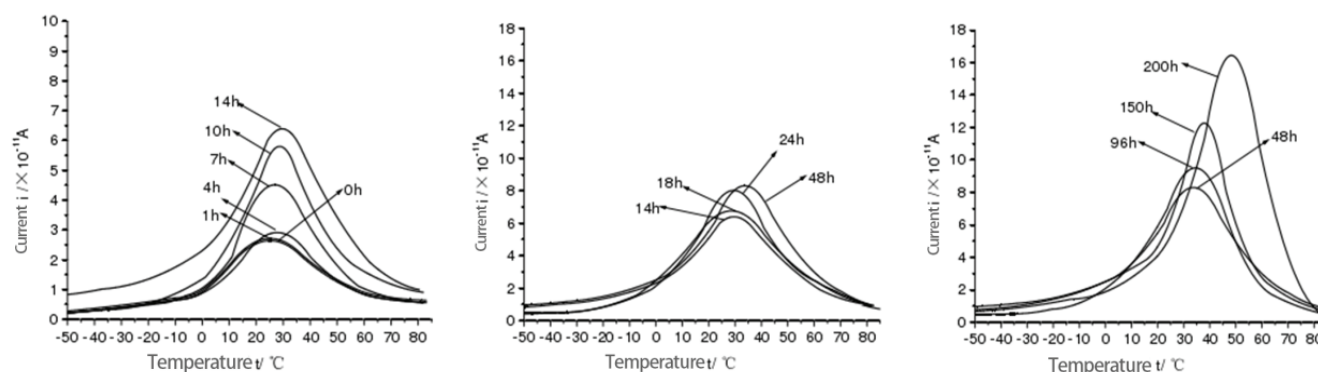
It can be observed that when the corona time is less than 4 hours, the recovery of the static contact angle of the sample accelerates with increasing corona time. When the corona time reaches 7 hours, the recovery of the static contact angle suddenly slows down but is faster than that of the sample after 1 hour of corona treatment; after the corona time exceeds 7 hours, the recovery of the static contact angle gradually accelerates with increasing corona time until it reaches 24 hours when the recovery rate slows down again, and by 35 hours, it returns to the initial level; compared to the sample after 24 hours of corona treatment, the sample after 48 hours of corona treatment recovers its static contact angle to the initial level earlier. After 96 hours of corona treatment, the static contact angle of the sample recovers to nearly 70° after being left undisturbed for 45 hours and remains at 70° thereafter; the static contact angles of the samples after 150 hours and 200 hours of corona treatment also remain at this level. Although short-term corona treatment damages the surface material of the silicone rubber sample and consumes hydrophobic substances within the material, according to previous research findings, the hydrophobic

substances in the inner layer of the material will accelerate their diffusion to the surface, restoring its hydrophobic properties. As the corona time increases, excessive consumption of hydrophobic substances prevents them from reaching the initial level of hydrophobicity.

③ The influence of corona time on trap characteristics

To more clearly demonstrate the changes in the sample during the corona aging process, the TSC curves of the sample after corona at different times under a voltage of 5kV are shown in the following figure. It can be seen that the TSC curves of the sample at different corona times all exhibit an independent TSC peak. The current peak in the TSC curve before corona is located around 26.5°C, with a peak value of about 26 pA; the TSC curve after 1h of corona is almost identical to that of the uncorroded sample, with only a slight increase in the current peak; after 4h of corona, the TSC peak shifts towards higher temperatures and becomes larger, followed by a slight increase in the current peak, further shifting the TSC peak towards higher temperatures. The temperature corresponding to 200h of corona is the highest, approximately 52°C, and the TSC peak also gradually increases with the duration of corona, reaching its maximum value at 200 h, about 165 pA. The details are shown in Figure 11.

Figure. 11 TSC curve of the sample with respect to corona time



According to the TSC curve of the sample and relevant calculation methods, the trap parameters of the sample after corona for different times at 5kV voltage were obtained, as shown in the table below. It can be observed that the trap energy level and trap charge of the sample do not change significantly after 1h of corona. However, as the corona time increases, the trap energy level gradually deepens, and the trap charge generally shows an increasing trend. The details are shown in Table 1.

Table 1 Trap parameters of samples after different times of corona

Charged voltage action time t / h	peak point current $i / \times 10^{-11} A$	The temperature corresponding to the peak of the current $T / ^\circ C$	trapping level E / eV	Trap charge Q / nC
0	2.61	26.52	0.434	87.43
1	2.65	26.52	0.434	90.36
4	2.92	27.94	0.451	105.34
7	4.51	28.03	0.472	124.68
10	5.80	29.05	0.533	157.86
14	6.39	29.52	0.538	217.92
18	6.71	31.04	0.540	222.45
24	7.82	33.04	0.547	232.76
48	8.33	34.01	0.553	268.49
96	9.52	35.03	0.680	253.56
150	12.0	40.07	0.745	294.40
200	16.5	51.08	1.044	393.10

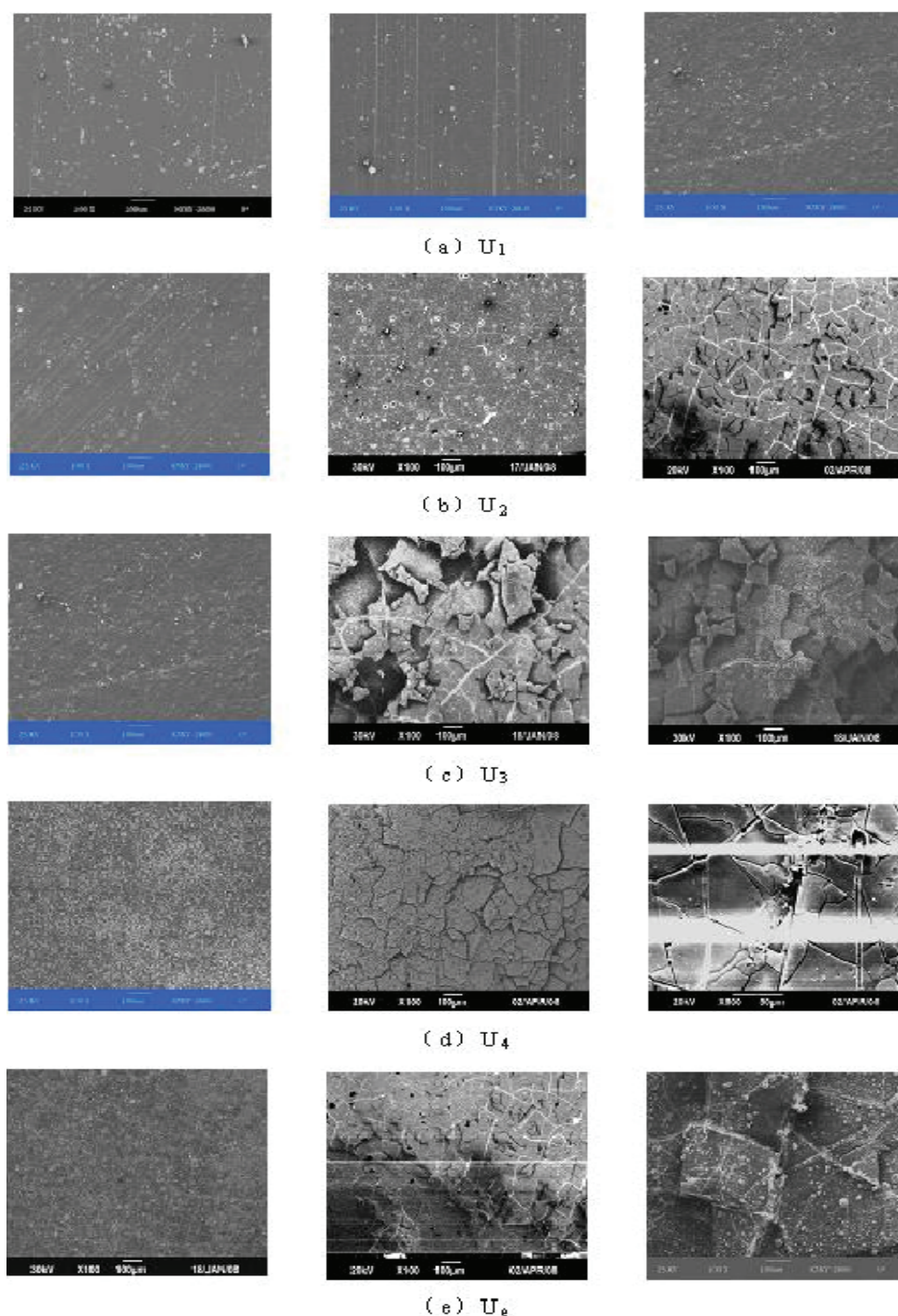
(b) The influence of corona intensity on the properties of silicone rubber materials

The corona is U_1 (2kV)、 U_2 (3kV)、 U_3 (5kV)、 U_4 (7kV)、 U_6 (Corona discharge was carried out on the sample at (10kV). After 1h,24h and 200h of corona discharge, the sample was taken out for relevant tests.

① The influence of voltage size on surface morphology

As shown in the figure below, after 1h of voltage action, the surface of the sample is still flat and the structure is relatively complete; after 24h of voltage action, U_2 Under the action of the sample surface is distributed with pinhole voids, U_3 The surface of the sample under the action of U_4 is covered with a fluffy layer, while the surface of the sample after the action of U_4 is full of cracks. After the action, large areas of missing were appeared, and cracks and cavities could be clearly seen; after 200h of voltage action, with the increase of the applied voltage, cracks appeared on the surface of the sample first, then evolved into cracks, until serious missing appeared in pieces. The details are shown in Figure 12.

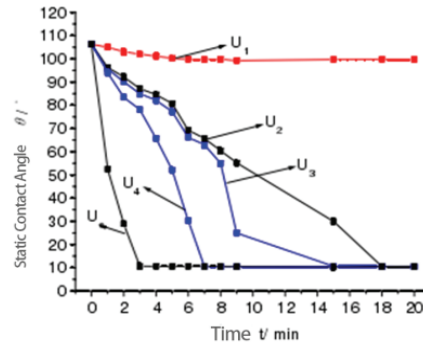
Figure 12. SEM comparison of samples under different voltages



② Influence of voltage on hydrophobicity

The hydrophobicity test results show that the sample is at corona $U_2 \sim U_c$. The static contact angle after 1h of corona treatment drops from about 106° before corona to around 10° ; however, even after 200h of corona treatment at voltage U_1 , the static contact angle remains above 90° . The hydrophobicity after short-term corona treatment at various voltage levels was tested, as shown in Figure 13.

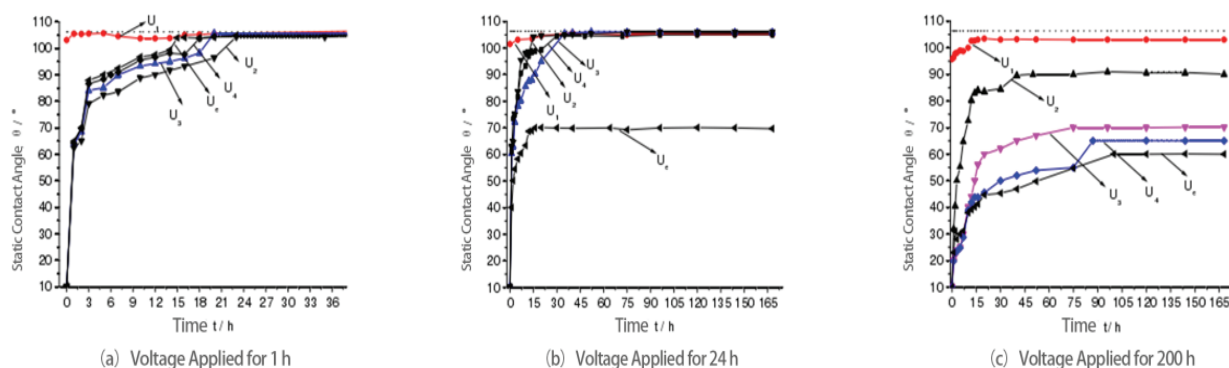
Figure 13. Static contact angle of samples at different voltages with respect to pressurization time



It can be seen that the voltage is U_1 . The static contact angle of the sample decreased slightly with the increase of corona action time, and remained above 100° even after 20min; from U_2 . At the beginning, with the increase of voltage, the static contact angle decreases faster and faster; when the voltage is U_2 . At this time, after about 18min, it drops to 10° ; when the corona is U_c . At that time, only 3min later, it was reduced to 10.3° .

The hydrophobicity recovery is shown in Figure 14. It can be observed that for samples tested after 1 hour of voltage application, as the applied voltage increases, the rate of static contact angle recovery gradually accelerates. After more than 20 hours, all samples recover to near their initial levels with little difference in recovery speed. For samples tested after 24 hours of voltage application, the higher the applied voltage, the slower the static contact angle recovery, but U_4 . The static contact angle after the action is restored to the initial level before the action of U_3 , U_c . After 24h of action, the static contact angle of the sample is difficult to recover to the initial level. When the sample is acted on by different voltages for 200h, the recovery rate of the static contact Angle decreases with the increase of the applied voltage, and when the voltage increases to U_3 . After that, the hydrophobicity decreased permanently, about 60° .

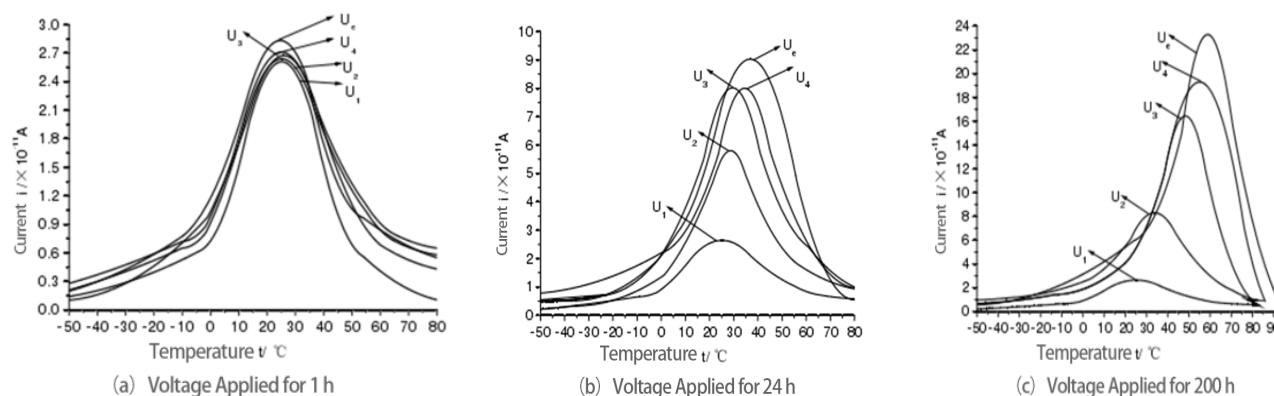
Figure 14. Static contact Angle recovery of samples under different voltages



③ The influence of voltage on trap characteristics

As shown in the figure below, after 1h of voltage action, the shape of TSC curve of the sample changes little, and only the current peak increases slightly with the increase of applied voltage. After 24h of voltage action, the higher the voltage, the greater the peak of TSC curve, and the temperature corresponding to the TSC peak increases until the voltage is increased to U_4 . After that, there is a more obvious increase. When the pressurization time reaches 200h, TSC peak and the corresponding temperature increase gradually with the increase of the applied voltage, and under the action of voltage U_c , TSC current peak is close to 240pA, and the corresponding temperature is located near 60°C .

Figure 15. TSC curve at different voltages



The trap parameters of the sample under different voltages are shown in the table below. It can be seen that after 1 hour of voltage application, as the applied voltage increases, the trap charge of the sample slightly increases, with little change in the trap energy levels; at 24 hours of voltage application, the trap charge of the sample increases with the rise in applied voltage, and the trap energy levels remain at the corona U_4 . After 200h of pressure, the trap charge and trap energy level of the sample increased significantly with the increase of the applied voltage. It can be seen that in different stages of aging, the trap parameters of the sample showed different characteristics with the change of the applied voltage. The details are shown in Table 2.

Table 2 Trap parameters of samples under different voltages

time t/h voltage V/kV	Trap energy level E/eV			The trap charge is Q / nC		
	1	24	200	1	24	200
U_1	0.434	0.434	0.434	87.43	87.44	87.44
U_2	0.433	0.483	0.553	88.92	157.86	268.49
U_3	0.434	0.547	1.044	90.36	232.76	393.10
U_4	0.434	0.651	1.056	91.20	236.63	528.64
U_e	0.435	0.678	1.101	94.12	277.21	625.45

(2) Influence of corona products-nitric acid on the properties of silicone rubber materials

Corona discharge in the air will form a certain amount of nitric acid, which is a strong oxidizer and a strong corrosive agent. Nitric acid may react with the surface material of silicone rubber, destroying its molecular structure, which is also an important factor causing corona aging.

(a) experimental method

① Determination of nitric acid concentration

The different corona discharge conditions can cause variations in nitric acid concentration. Therefore, to determine the test parameters, the project team used a corona aging test apparatus. By observing changes in pH paper and comparing it with a pH meter, they could obtain the concentration of nitric acid generated under these conditions. Through experimentation, it was found that the pH range for nitric acid should be set between 1.2 and 3.5.

② Determination of treatment parameters after nitric acid soaking

Before conducting the relevant aging property tests on samples soaked in nitric acid, it is necessary to remove the residual nitric acid from the surface of the samples, which requires post-treatment after nitric acid soaking. The method used is as follows: first, place the samples soaked in nitric acid in deionized water for a certain period to remove the nitric acid; then,

place the samples in a constant temperature chamber and dry them at the set temperature for a certain period to remove the influence of deionized water; finally, remove the samples for later use. Through experimental comparison, the final deionized water soaking time was determined to be 24 hours (based on Study 2.1.1, this duration results in minimal hydrolysis of silicone rubber molecules and does not significantly affect the test results), with deionized water being changed after soaking for 6 hours and 16 hours; the drying time in the oven is 14 hours.

③ Nitric acid immersion test

Nitrated solutions with pH values of 1.2, 2.0, 2.5, 3.0 and 3.5 were selected for nitric acid immersion test of silicone rubber. The soaking time was set to 4h, 24h, 96h, 120h and 180h respectively. In order to facilitate subsequent analysis, the samples were numbered as shown in the following table. The new samples without soaking were V.

Table 3. Sample numbers for nitric acid immersion test

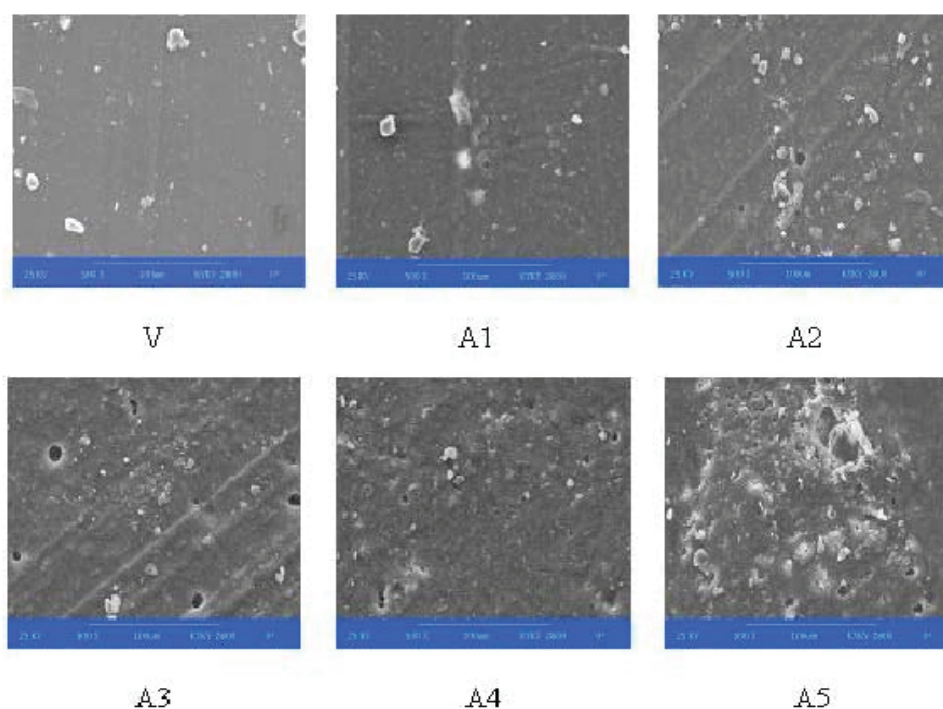
Soaking time t/h \ pH price	1.2	2.0	2.5	3.0	3.5
4	A1	B1	C1	D1	E1
24	A2	B2	C2	D2	E2
72	A3	B3	C3	D3	E3
120	A4	B4	C4	D4	E4
180	A5	B5	C5	D5	E5

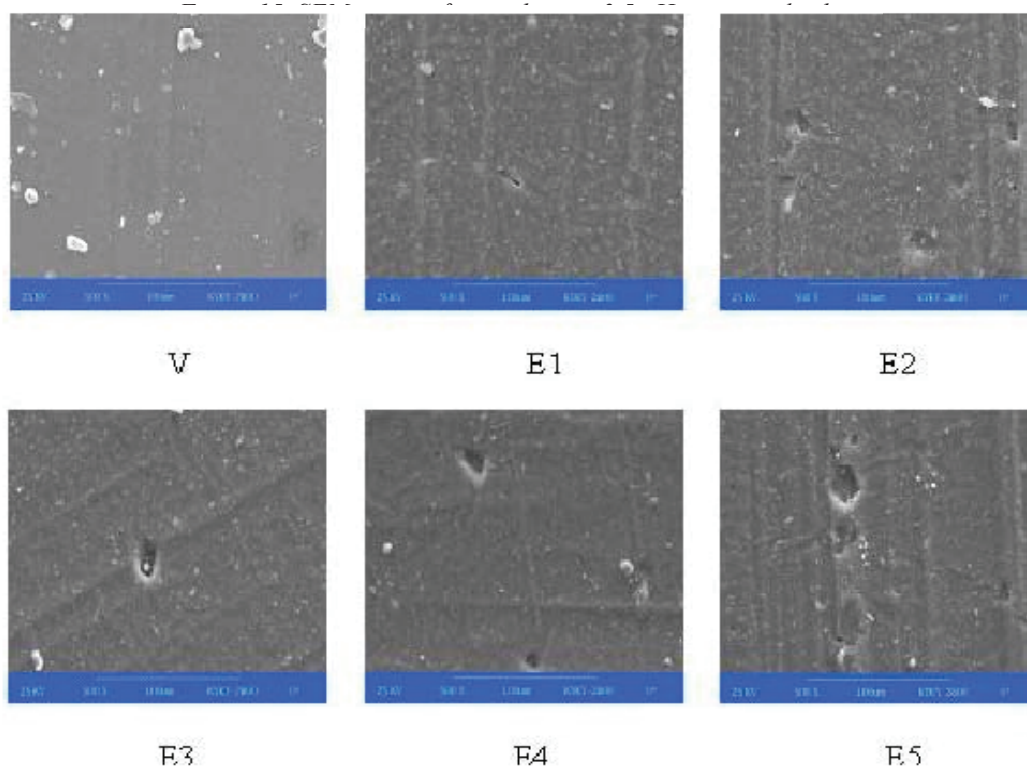
(A) Influence of nitric acid action time on the properties of silicone rubber materials

① SEM analyse

As shown in the figure below, after soaking in a nitric acid solution with pH=1.2, the integrity of the sample surface was compromised, and some holes appeared. Although their distribution was irregular, the density of these holes gradually increased with the duration of soaking. In particular, the surfaces of samples A4 and A5 were extremely dense with many small holes surrounding large ones, even forming clusters of interconnected holes. Additionally, as the soaking time increased, the depth of the holes also increased.

FIG. 54 SEM image of nitric acid soaked PH = 1.2





After soaking in nitric acid solution with pH=3.5, the structure of the sample surface showed different degrees of damage, and holes of different sizes appeared. With the increase of soaking time, the holes on the sample surface gradually became larger, but the number of holes changed little and the depth difference was not large, all of which were shallow holes.

At the same time, the surface state of samples measured at other pH values was basically consistent with the above results.

② FTIR analyse

As can be seen from the figure below, compared with the new sample V, several main infrared characteristic peaks of sample A5 after soaking in nitric acid solution with pH=1.2 for 180h all showed obvious changes, and the-OH content in silicone rubber molecules increased and-NO appeared₃group,CH₃The bending vibration was strengthened and the Si-O-Si structure was reduced. This indicated that after nitric acid immersion, the macromolecules of silicone rubber were damaged and oxidation and hydrolysis occurred. The changes of sample A series were most obvious, while those of sample E series were relatively gentle.

Figure 16. FTIR comparison before and after nitric acid immersion

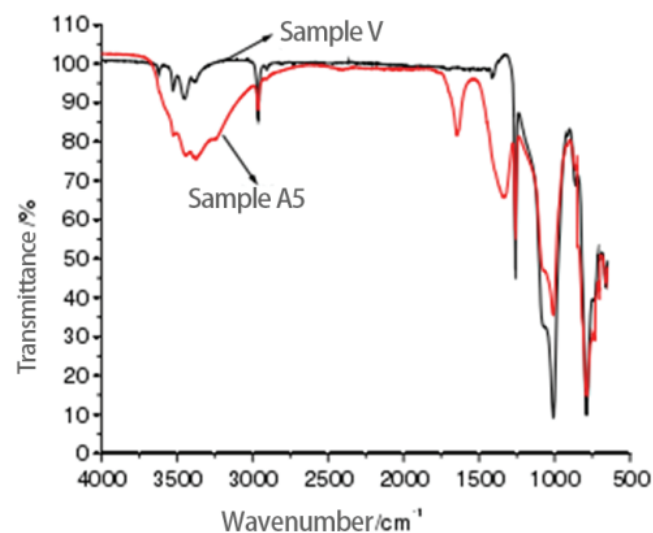
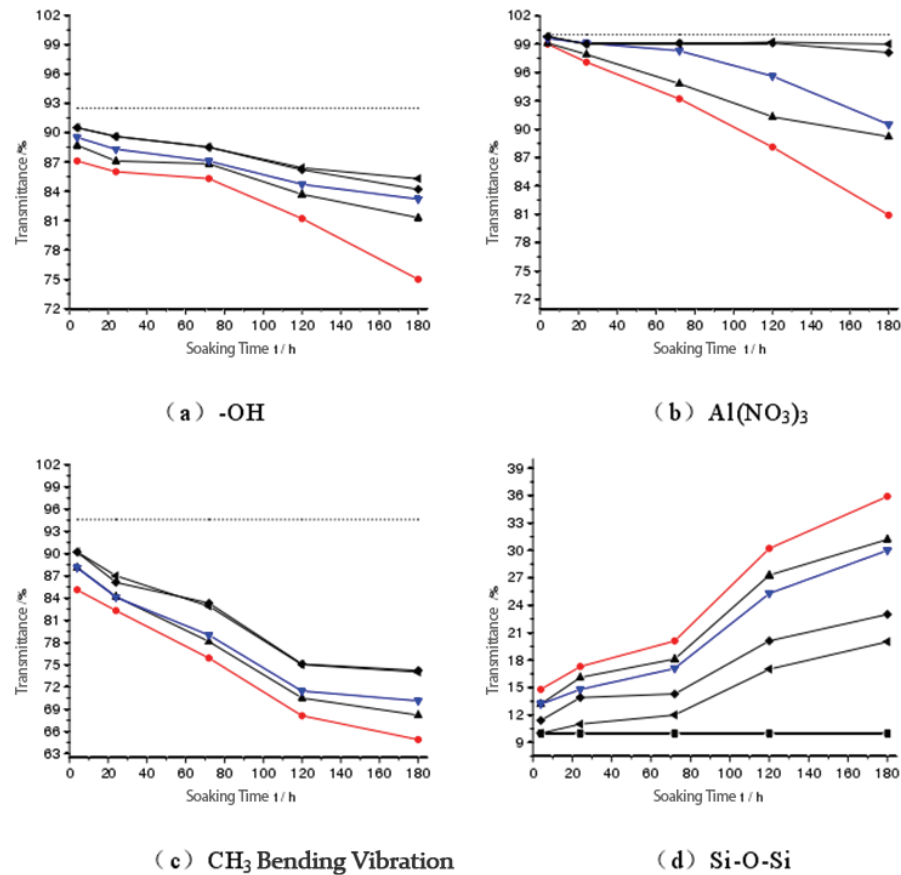
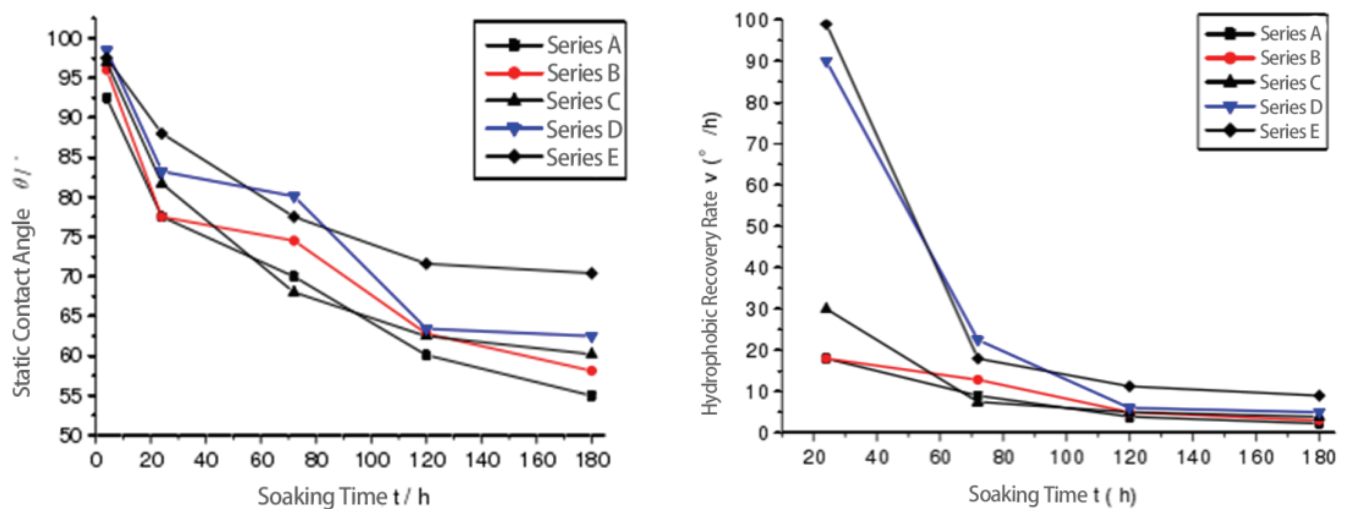


Figure 17. Variation of group content with soaking time



③ Hydrophobic performance analysis

Figure 18. Static contact Angle changes with immersion time FIG. 59 Water repellency recovery rate changes with immersion time



The static contact angle of various series of samples gradually decreases with increasing soaking time. When soaked for 4 hours, the static contact angle of all samples remains above 90° , indicating good hydrophobicity. After soaking for 120 hours, the contact angle stabilizes and changes more gently, reaching its minimum value ($55^\circ \sim 70^\circ$) at 180 hours, during which the hydrophobicity of the samples temporarily diminishes.

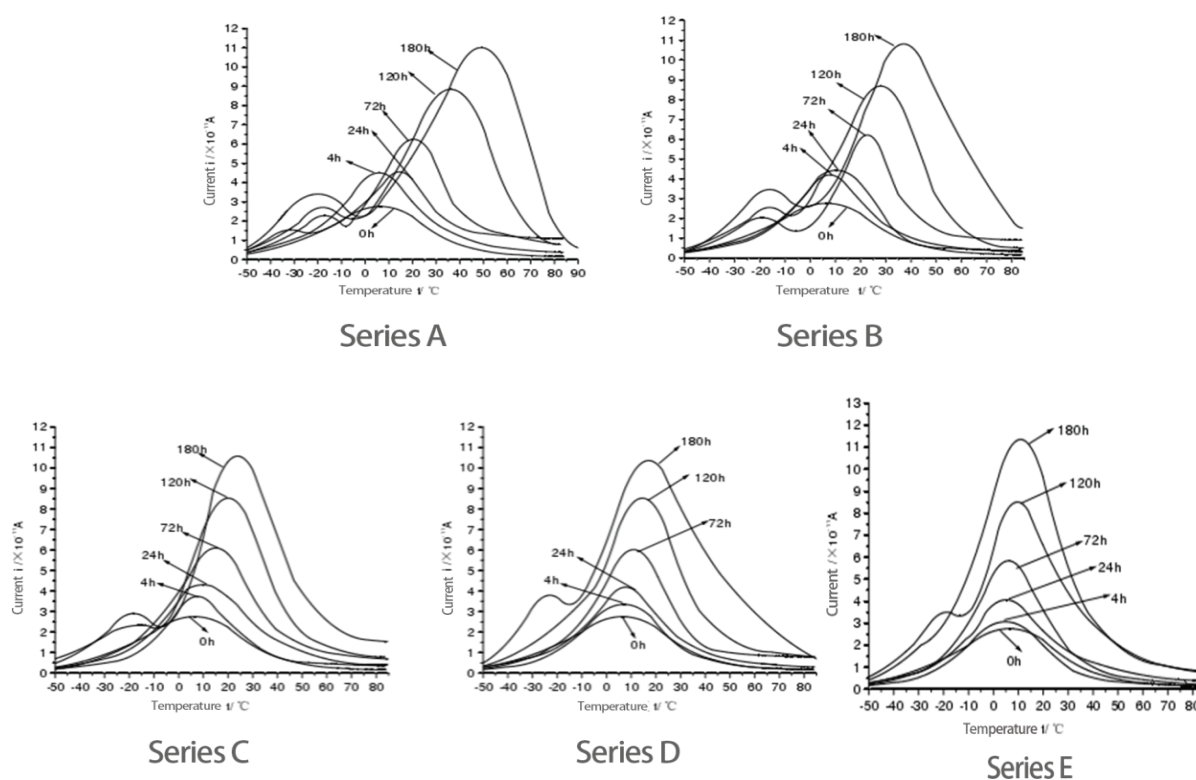
When the nitric acid immersion is stopped, the contact angle of all samples can be restored to more than 90° , and the recovery rate slows down with the increase of immersion time.

④ TSC analyse

As can be seen from the figure below, the TSC curves of samples in each series show changes with increasing soaking time:

- ① The shape of the curve changes, splitting from one current peak into two, one located in the low-temperature region (secondary current peak) and the other in the higher temperature region (primary current peak). At the same time, the appearance times of the secondary current peaks vary, distributed at 24h, 72h, 120h, 180h, and 120h;
- ② Both current peaks gradually increase;
- ③ The temperature corresponding to the primary current peak increases gradually with increasing soaking time, while the temperature corresponding to the secondary current peak remains relatively stable;
- ④ For samples in series E, the TSC curve shows little change in the temperature corresponding to the main current peak with increasing soaking time, whereas for sample A, the change is most pronounced.

Figure 19. TSC of the sample with respect to soaking time



(b) Influence of nitric acid concentration on aging characteristics of silicone rubber materials

The effect of nitric acid concentration on the aging characteristics of silicone rubber materials has been compared in the analysis of nitric acid solution action time, which will not be repeated here.

(3) Analysis of the mechanism of organic molecule damage to silicone rubber materials by corona discharge

Corona discharge produces high energy charged particles and nitric acid, which together cause the destruction of organic molecular bond energy of silicone rubber material.

(a) Analysis of charged particle action

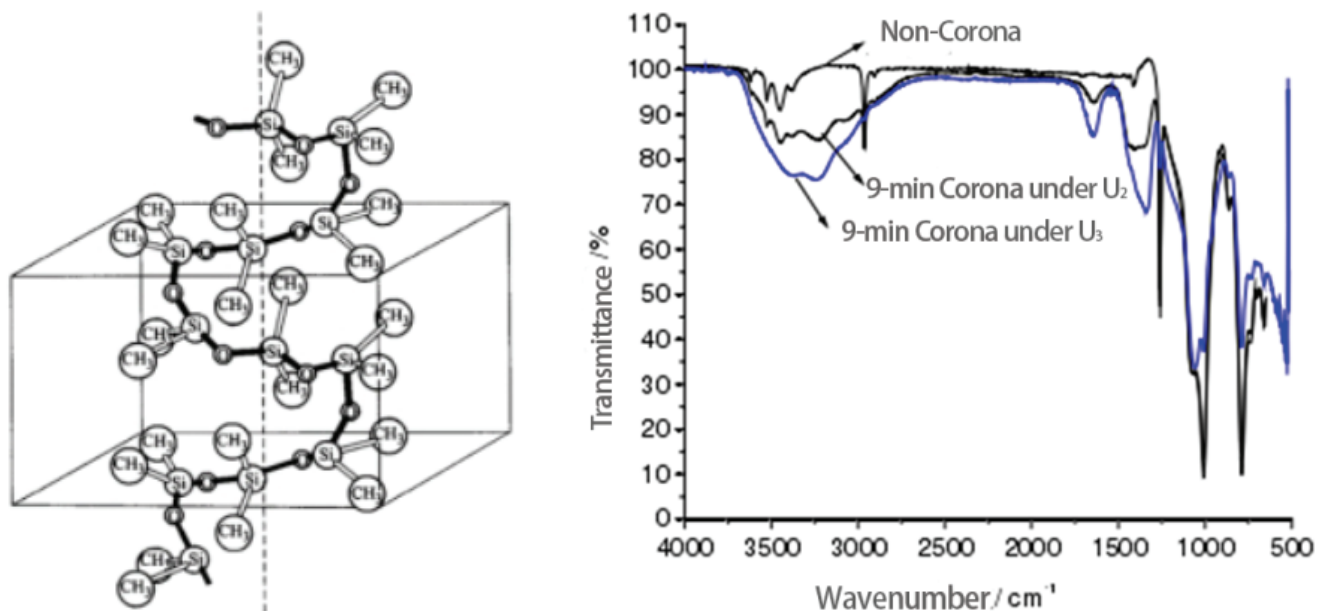
Corona discharge generates certain charged particles such as electrons and ions. Under the influence of an electric field formed by applied voltage, these particles, especially electrons, acquire kinetic energy and collide with the surface of insulating materials, causing mechanical damage to its surface. The fact that corona can drill holes in mica over several years indicates that corona is not merely a chemical corrosion process but also a mechanical impact-induced erosion, particularly at the edges of electrodes. The bond energy of Si-O bonds in the main chain of silicone rubber is approximately $461 \pm 33 \text{ kJ/mol}$, while the bond energy of Si-C bonds is 301 kJ/mol . The bond energy of C-H in the methyl groups of side chains is 413 kJ/mol . Estimating from the electric field strength during corona discharge and the average free path in air, the average energy of electrons is about 308 kJ/mol , with some reaching up to 963 kJ/mol . It is evident that particle bombardment in corona

discharge may cause all bonds in silicone rubber to break, thereby disrupting the structure of polymers within the material and leading to degradation.

① The mechanism of loss and recovery of hydrophobic properties

When corona discharge occurs, it generates a certain amount of charged particles. These particles collide with the sample surface under the influence of an electric field, causing mechanical impact. According to the spatial structure of the organic molecules in silicone rubber—polymethyl methacrylate siloxane—the charged particles first cause the Si-C bonds and C-H bonds in the organic molecules (containing hydrophobic small molecules) in the silicone rubber material to break and oxidize. The FTIR comparison before and after the test is shown in the figure below. After 9 minutes of corona treatment, several key characteristic peaks in the sample show significant changes: ① -OH groups are formed and increase with the rise in voltage; ② wavenumber at 1643cm^{-1} New absorption peaks appeared and increased with the increase of voltage, indicating that the higher the voltage, the more C-H bond was destroyed and the more carbonyl was generated; ③ wavenumber was 1412cm^{-1} The absorption peak becomes wider and stronger with the increase of voltage, indicating that the bending vibration of methyl group is strengthened; ④ wavenumber is 1007cm^{-1} The characteristic absorption peak weakened, indicating that the Si-O-Si structure decreased; ⑤ wavenumber was 787cm^{-1} The characteristic absorption peak decreased with the increase of voltage, indicating that $\text{Si}(\text{CH}_3)_2$ The structure gradually decreases.

Figure 20. Molecular space structure of silicone rubber Figure 62 FTIR comparison before and after corona of samples



It is evident that under the influence of charged particles, C-H bonds and Si-C bonds are broken, leading to oxidation reactions on the sample surface. This consumes methyl groups on the surface, weakening their shielding effect against the hydrophilic Si-O backbone. At the same time, chemical reactions generate silanol, silyl alcohol, carbonyl, and other hydrophilic groups, and the formation of oxygen-containing groups increases the surface energy of the sample. These factors collectively result in a reduction or temporary loss of hydrophobicity on the sample surface. As the applied voltage increases, the electric field strength on the sample surface also increases, enhancing the ability of charged particles to gain energy. This intensifies the chemical reactions on the sample surface, consuming more methyl groups and generating more hydrophilic groups. Consequently, as the applied voltage rises, the rate at which the hydrophobicity of the sample surface decreases accelerates, meaning the rate of decrease in the static contact angle increases. On the other hand, once corona discharge occurs, the longer the corona duration, the greater the probability that charged particles will continuously impact the sample surface, absorbing more energy and producing more hydrophilic by-products. Therefore, the hydrophobicity gradually diminishes with increasing corona duration until it is completely lost.

However, as the corona time increases or the applied voltage rises, more high-energy charged particles are generated. These charged particles break the Si-O main chain, producing more mobile siloxanes (i.e., small hydrophobic molecules), which

aids in restoring hydrophobicity. At the same time, due to the high reactivity of -OH groups and low activation energy during condensation, under discharge conditions, the -OH groups at the ends or on both sides of the main chain can easily condense to form H_2O . Condensation reactions, on one hand, reduce the concentration of -OH groups, which is beneficial for restoring hydrophobicity on the sample surface; on the other hand, similar to oxidation reactions, condensation reactions produce polysiloxanes with cyclic structures, double-chain structures, or side-chain structures in their main chains, making it difficult for siloxane molecules to migrate to the silicone rubber surface, thus hindering the restoration of hydrophobicity. Combining SEM results, the process of restoring hydrophobicity can be explained as follows: when corona time is less than 4 hours, as the corona time increases, charged particles collide with the sample surface, generating more small molecular siloxanes. The appearance of pinhole-like pores facilitates the diffusion or migration of siloxanes to the sample surface, thereby accelerating the restoration of hydrophobicity; however, after the corona time exceeds 4 hours, a thin layer of crystalline material gradually forms over the pores, indicating signs of hardening on the sample surface. White crystalline substances are observed at 7 hours of corona treatment, suggesting the formation of inorganic silicates. Although siloxanes continue to increase, the presence of inorganic silicates hinders the migration and condensation reactions of siloxanes, thus slowing down the restoration of hydrophobicity; when the corona time reaches 10 hours, apart from pores, faint micro-cracks are visible on the sample surface, indicating that continuous particle impact leads to an increase in dense crystalline layers, with cracks deepening and further accelerating the restoration of hydrophobicity; when the corona treatment reaches 24 hours, the sample surface appears to have become powdery, hindering the migration of siloxanes. Subsequently, the powder layer splits into large chunks (after corona at 48 h), thus the hydrophobicity recovery rate first slows down and then accelerates; as the corona time increases, pores on the sample surface gradually evolve into cavities, with cracks and grooves appearing (after corona at 96 h). This indicates that under the influence of charged particles, more severe oxidation and condensation reactions occur on the sample surface, producing polydimethylsiloxanes with main chains containing cyclic structures, double main chain structures, or side-chain structures. These structures make it difficult for siloxanes to migrate to the silicone rubber surface. Additionally, their structural flexibility is much poorer compared to monomeric double helix structured polydimethylsiloxanes, reducing the speed at which siloxanes migrate to the surface. As the molecular weight of the polydimethylsiloxane increases, intermolecular forces also increase, further slowing down the migration of siloxanes. Furthermore, after the corona aging process reaches a certain stage, the rate at which siloxanes form on the sample surface is lower than their consumption rate (including migration into the air), leading to a decrease in siloxane content. The release of free carbon also reduces the hydrophobicity of the surface. Therefore, the hydrophobicity recovery rate slows down again or even loses its hydrophobicity.

It can be seen that the hydrophobic recovery characteristics of silicone rubber show different characteristics at each stage, and do not accelerate or slow down with the increase of corona time. The recovery characteristics of hydrophobic properties under different corona voltages are similar to the above analysis, which will not be repeated here.

② Reasons for changes in trap characteristics

From the aforementioned measurement results, it can be observed that under a 5kV voltage, as the corona time increases, more traps appear in the sample, and the trap energy levels gradually deepen. In conjunction with SEM results, it is evident that under the continuous bombardment of charged particles generated by corona discharge, a series of new interface states have appeared on the sample surface. The specific analysis is as follows: before 1h of corona treatment, the sample surface was relatively smooth and flat, with a more uniform structure. It is visible that its structure did not undergo significant changes compared to the sample before corona treatment, so the trap charge and trap energy levels were very close. As the corona time increased, cracks gradually developed into fissures, eventually forming grooves. This indicates that the structure of the sample surface was progressively damaged under the continuous action of charged particles, leading to more defects. The formation of these defects requires the injected trap charges to absorb more energy to be excited, resulting in higher temperatures during excitation and deeper trap energy levels. This is reflected in the TSC curve as an increase in the peak-to-peak current and a corresponding rise in temperature.

Observe the TSC curve of the sample after a certain period under different voltages, combined with SEM results, it can be

seen that after 1h at each voltage level, the surface of the sample remains flat and smooth. This indicates that the short-term effect of charged particles has not caused significant changes in the surface structure of the sample, thus the trap charge and trap energy levels before and after voltage application are not significantly different; when the exposure time increases to 24h, the voltage U_1 The sample surface remains structurally uniform, so its trap parameters do not change much. However, as the voltage increases, the following changes gradually occur on the sample surface: micro-pores-powder layer cracks-fractures-cavities, cracks. The sample surface also undergoes these changes after being pressurized for 200 hours. It is evident that the higher the voltage, the greater the energy gained by charged particles, leading to more severe damage to the sample surface, thus causing more and more serious defects in the sample. The increase in defects results in an increased amount of trapped charge, and the charge captured by the defects must absorb more energy to escape. Therefore, the higher the temperature at which excitation occurs, the higher the temperature corresponding to the current peak on the TSC curve.

To verify the changes in silicon rubber materials ability to capture electrons and its impact on surface flashover after altering trap characteristics, a new set of experiments was redesigned. The new silicon rubber samples were aged at 10kV AC voltage for 1 00 h, 2 50 h, 4 50 h, 6 50 h, and 1 000 h, respectively. After aging, circular discs with a diameter of 20mm (unchanged thickness) were made at the center of the corona discharge position. A negative polarity voltage was applied between the two ends of the sample until flashover occurred, and the charge distribution was measured using an electrostatic probe. The results are shown in the figure below. It can be seen that after aging, multiple peaks of surface charge appear on the sample surface. As the aging time and test voltage increase, the surface charge on the sample increases and gradually concentrates at positions perpendicular to the electrodes. After flashover, the surface charge in the region of the path where flashover occurred rapidly decreases. According to band theory and surface state theory, combined with the results of trap characteristic tests, as the degree of aging increases, the materials ability to capture electrons strengthens, forming strong electric field centers of charge at different locations on the material, leading to a decrease in its flashover voltage.

Figure 21. Measurement range of electrostatic probe

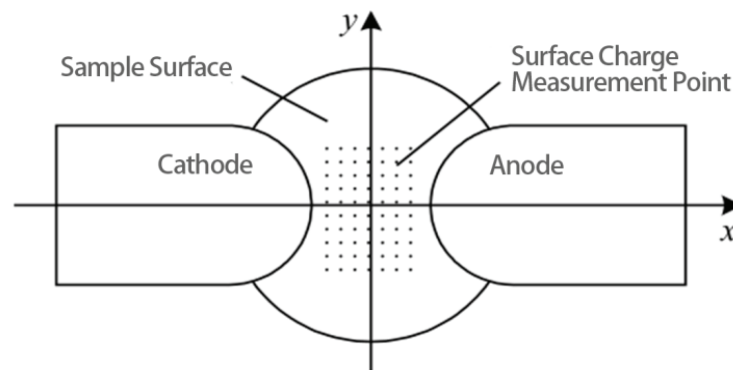
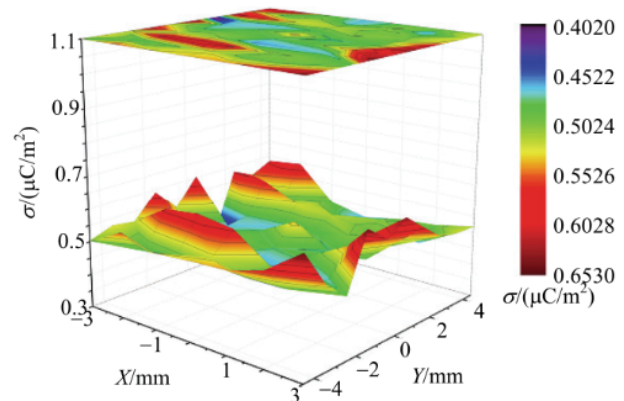
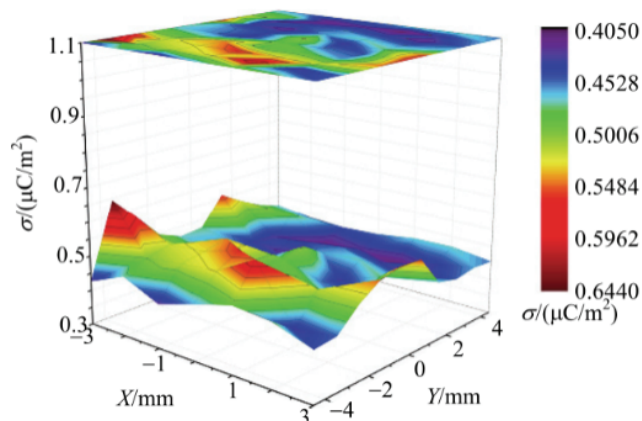


Figure 23. Surface charge distribution of samples aged by corona at 1 00h under different voltages

(a) 100 h

(b) 250h



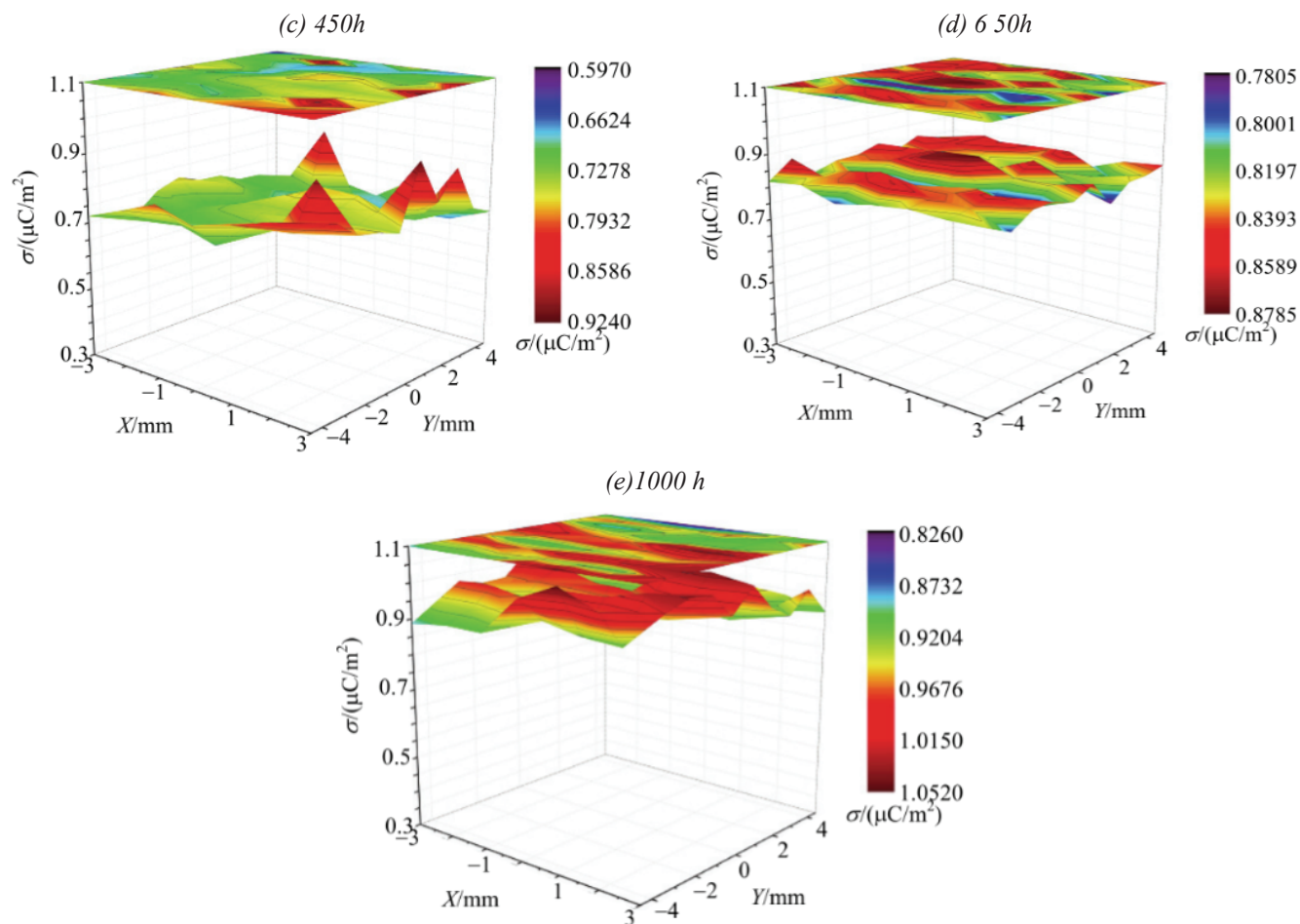
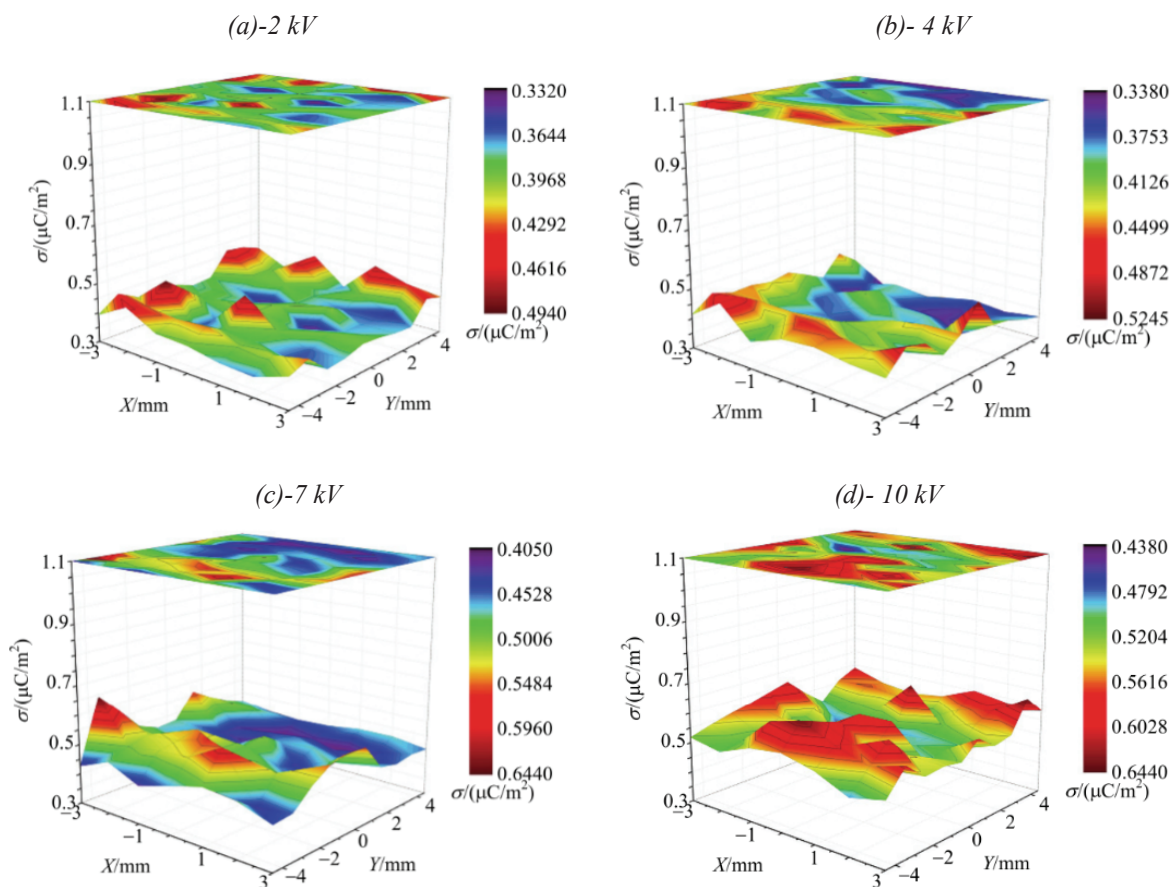
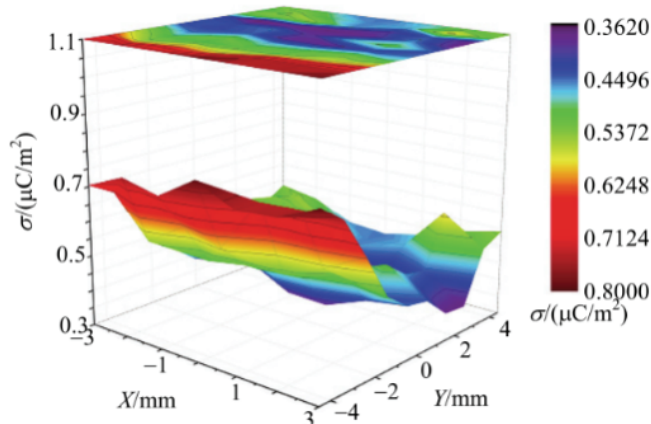


Figure 22. Surface charge distribution of samples at different aging times under 7kV



(e) 1 2.45kV (after flashover)



(b) Analysis of nitric acid action mechanism

① Causes of loss and recovery of hydrophobicity

In the main chain of silicone rubber, the electronegativity difference between silicon and oxygen atoms is 1.7, making the Si-O bond in silicone rubber polar or particulate to a degree of 41%. When silicone rubber comes into contact with high-concentration acidic or alkaline solutions, the ionic nature of the Si-O bond makes it susceptible to hydrolysis reactions. In this experiment, after nitric acid immersion, the -OH content increased, confirming that the hydrolysis reaction occurred, generating hydrophilic silanol groups. Moreover, CH was measured. The increased bending vibration indicates that nitric acid soaking causes the side groups of silicone rubber to curl inward, thus losing their shielding effect on the hydrophilic Si-O main chain. At the same time, the detection of aluminum nitrate formation suggests that nitric acid may have chemically reacted with the aluminum hydroxide filler in the silicone rubber, increasing the surface energy of the sample. SEM analysis results show that after soaking in a nitric acid solution, the smooth surface of the sample becomes rough and develops pores. These factors all contribute to making the hydrophobic silicone rubber more susceptible to moisture absorption.

The-OH, $\text{Al}(\text{NO}_3)_3$ The content gradually increases with the increase in soaking time, while the Si-O-Si structure decreases, especially noticeable in samples of series A and B. SEM analysis shows that the pores on the surface of samples from series A and B become significantly deeper as soaking time increases, with pore density gradually increasing. It is evident that as soaking time increases, both the physical and chemical structures of the samples change, not only producing more defects but also generating more hydrophilic groups. Therefore, the longer the soaking time, the more pronounced the decrease in hydrophobicity and the greater the reduction in static contact angle. On the other hand, prolonged soaking makes condensation reactions possible; when these two factors reach a certain equilibrium, the hydrophobicity of the sample remains at a certain level. At the same time, the longer the soaking time, the higher the CH_3 . The stronger the bending vibration, the weaker the hydrophobicity.

All samples contained-OH, $\text{Al}(\text{NO}_3)_3$ The content increases with the decrease of nitric acid pH value, and the Si-O-Si structure gradually decreases. Moreover, the smaller the nitric acid pH value is, the more CH in the sample. The stronger the bending vibration. At the same time, it is noted that after soaking for 180h, the changes in each group of samples are most pronounced, while those after soaking for 4h show smaller changes. SEM analysis results indicate that with longer soaking times (120h), as the pH value of nitric acid decreases, the pore density on the sample surface gradually increases, and the depth of pores also shows an increasing trend; when the soaking time is short, the pores on the sample surface are shallower, and there is no significant change in pore density. Therefore, the hydrophobicity of the samples gradually weakens or even disappears as the pH value of the nitric acid solution decreases, but when the soaking time is short, the change in hydrophobicity is minor, and when the soaking time is longer, the hydrophobicity significantly decreases as the pH value decreases.

When the action of nitric acid ceases, the methyl groups will reorient towards the surface. Meanwhile, hydrophilic groups such as silanol contain a large number of -OH groups, which, due to their high reactivity, can undergo condensation reactions to produce other products that cover the aluminum nitrate surface. These factors all contribute to the restoration of hydro-

phobicity on the silicone rubber surface. Additionally, condensation reactions may also produce polysiloxanes with cyclic structures, double-chain structures, or side-chain structures in their main chains, making it difficult for siloxanes to migrate to the silicone rubber surface, thus hindering the recovery of hydrophobicity. When these promoting and inhibiting effects reach equilibrium, the hydrophobicity of the silicone rubber remains in a stable state. In this experiment, after the action of nitric acid ceased, the methyl groups easily reoriented, representing the hydrophilic groups on the surface, and the reagents used were relatively short, so the hydrophobicity of the samples recovered quickly in the initial few hours after standing. Subsequently, due to the longer duration required for condensation reactions, the recovery process gradually slowed down. As the concentration of nitric acid increased, the time needed for condensation reactions also increased, leading to a longer time for methyl groups to flip back into the bulk phase, further extending the time required for hydrophobicity recovery, i.e., reducing the rate of hydrophobicity recovery.

② Reasons for changes in trap characteristics

According to the macroscopic morphology observation and SEM images of the samples, it can be seen that nitric acid soaking makes the silicone rubber surface rougher, more brittle, and prone to tearing, disrupting the complete structure of the silicone rubber surface and creating holes of varying sizes. These changes form structural defects in the silicone rubber. When charged particles are captured by these structural defects, they must absorb sufficient energy to break free from their constraints. Therefore, in TSC tests, trapped charges are only activated at higher temperatures, forming free charges. This is reflected in the TSC curve as higher temperatures corresponding to current peaks, indicating deep traps. The results of SEM analysis show that as the pH value of nitric acid decreases or the soaking time increases, the density of pores on the sample surface gradually increases, along with the depth of the pores. Thus, the energy level of deep traps in the sample deepens, and the amount of trap charge increases. When the soaking time is short, the changes in the structural defects on the sample surface due to increasing nitric acid concentration are minimal, so the trap energy level of the sample does not deepen with the decrease in nitric acid pH value after 4 hours of soaking. Similarly, for samples in Series E, the main trap energy level changes minimally with increasing soaking time.

FTIR analysis results show that nitric acid soaking leads to the formation of new chemical groups such as silanol and aluminum nitrate in the sample, reducing the original Si-O-Si structure. These processes introduce groups that differ from those in the original silicone rubber sample in terms of mass or electronic structure, creating chemical defects. Due to their higher electronegativity, these groups have a stronger ability to attract electrons, which in turn makes the trapped charges more easily excited. Therefore, in TSC tests, trapped charges can be excited and escape from their precarious state at lower temperatures. This is reflected in the TSC curve as lower temperatures corresponding to current peaks, indicating lower trap energy levels. FTIR analysis of the sample shows that with a decrease in nitric acid pH and an increase in soaking time, the -OH and $\text{Al}(\text{NO}_3)_3$ content gradually increases, while the Si-O-Si structure gradually decreases. Since only the chemical group content changes, the current amplitude in the low-temperature region of Sample TSC curve gradually increases, with little change in the corresponding temperature. At the same time, when the soaking time is short or the nitric acid concentration is low, the contents of silicic acid and aluminum nitrate are relatively low, so no current peak or an insignificant current peak can be observed in the low-temperature region during TSC testing.

From this, it can be seen that under the action of nitric acid, silicone rubber not only develops deep traps with higher energy levels but also forms shallower traps. The destruction of the physical structure on the sample surface and the appearance of pores are the primary causes of deep traps, while the formation of new chemical groups such as silanol is the main reason for the emergence of shallow traps. As the duration of nitric acid action increases or the pH value decreases, the trap charge in the sample shows an increasing trend, with the main trap energy level gradually deepening and the secondary trap energy level showing little change.

2.1.3 Study on the difference of corona damage mechanism to organic molecules of silicone rubber materials under different pressure and humidity

(1) Test method

To shorten the test cycle, orthogonal experimental methods are used. This involves selecting some points from comprehensive

tests that have “uniform distribution and comparable neatness” based on the orthogonality of each level number. This method can significantly reduce the test cycle and allows for the analysis of test results using appropriate range analysis and variance analysis methods to derive valuable conclusions. To study the differences in the mechanism of corona-induced damage to organic molecules in silicone rubber materials under different pressures and humidity levels, pressure, relative humidity, and aging time were determined as research factors. The test was conducted at three levels for these three factors, as shown in the table below.

Table 4 Factor level table

horizontal	factor		
	pressure /kPa	relative humidity /%	ageing time /h
1	4.5	2.5	1.00
2	6.0	5.5	4.00
3	1.00	9.0	8.00

Table 5 Orthogonal test arrangement

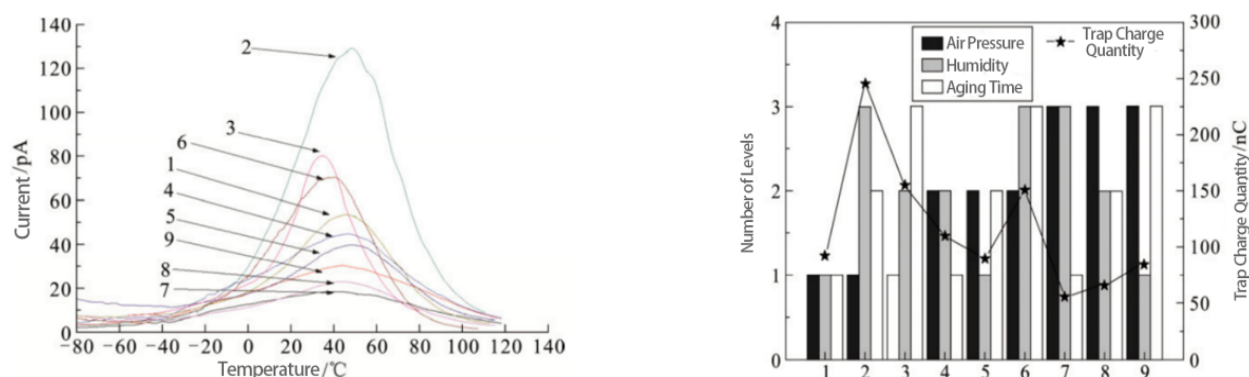
test number	condition of experiment			Air pressure levels	Relative humidity levels	Level of aging time
	pressure /kPa	relative humidity /%	ageing time /h			
1	4.5	2.5	1.00	1	1	1
2	4.5	9.0	4.00	1	3	2
3	4.5	5.5	8.00	1	2	3
4	6.0	5.5	1.00	2	2	1
5	6.0	2.5	4.00	2	1	2
6	6.0	9.0	8.00	2	3	3
7	1.00	9.0	1.00	3	3	1
8	1.00	5.5	4.00	3	2	2
9	1.00	2.5	8.00	3	1	3

(2) Test results

① TSC test result

The test results are shown in the figure below. It can be seen that the amplitude of TSC curve and the temperature corresponding to the peak current of each sample are different; at the same time, the higher the current amplitude, the narrower the width of the curve, and the shape of the curve in the low-temperature region also presents different development trends.

Figure 24. TSC test results

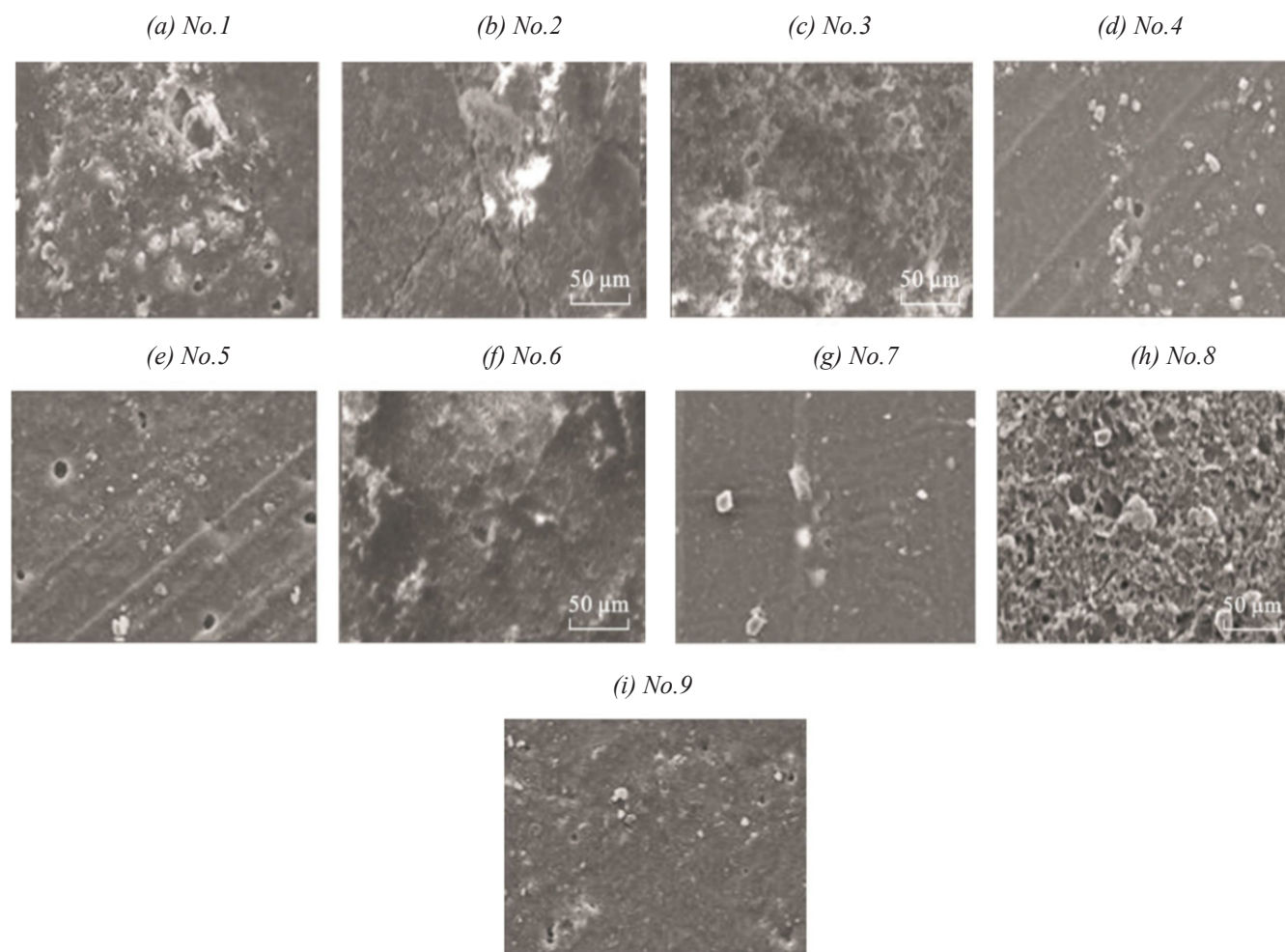


② SEM analytic result

The SEM test results of each sample are shown in the figure below. It can be observed that the surfaces of the samples exhibit

different characteristics: some are dominated by pores (Sample 9), some appear to have signs of corrosion (Sample 8), and others show cracks (Sample 2) and depressions (Sample 6). The aging caused by discharge particles mainly manifests as concentrated and regular pores and cracks, while the chemical corrosion induced by nitric acid covers a larger area with irregular and uneven pores. It is not hard to infer that if charged particles and nitric acid act together, silicon rubber surfaces will inevitably develop irregular cracks or large areas of depression. Comparing the test conditions of each group of samples, it is evident that Sample 2, which has low pressure, high humidity, and long aging time, shows a deep groove on its surface, indicating the most severe degree of aging; Sample 7, with high pressure and short aging time, although having higher humidity, only shows several small holes on its surface, indicating the least degree of aging; Sample 3, with low pressure and moderate humidity but a longer aging time, shows scattered small holes due to corrosion on its surface. Comparing Samples 1, 5, and 9, it is found that Samples 9 and 5 have a longer aging time but mainly show scattered, deeper pores, while Sample 1 shows large areas of holes. Therefore, changes in the surface morphology of samples are related to pressure, humidity, and aging time, with humidity having a more significant impact at low pressures. Significantly, the effect of aging time is greater at high pressure.

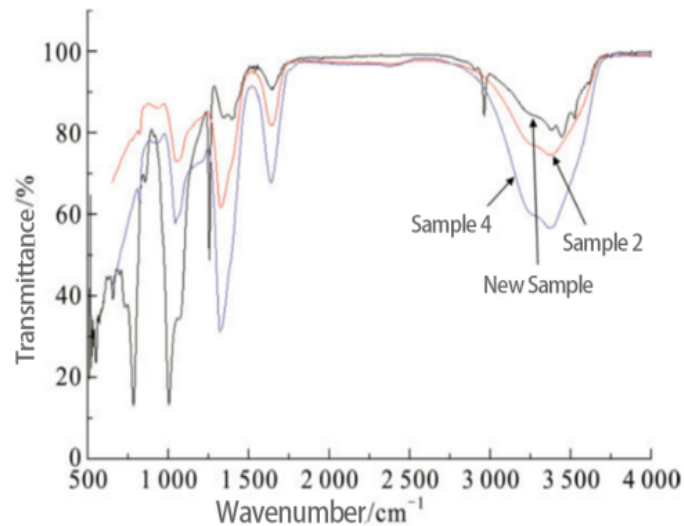
Figure 25. SEM results of samples magnified 500 times



③ FTIR analysis results

The test results are shown in the figure below. It can be seen that compared with the new sample, the FTIR spectrum of sample 2 has changed as follows: 1) wavenumber is 1007cm^{-1} The characteristic absorption peak weakened, indicating that the Si-O-Si structure decreased; 2) wavenumber was 1650cm^{-1} The absorption peak was enhanced, indicating that it was NO_3 The content increased, i.e. $\text{Al}(\text{NO}_3)_3$ Increased content; 3) wavenumber was 3500cm^{-1} The absorption peak near it becomes wider and stronger, indicating that the -OH content in the sample increases; 4) wavenumber 1260cm^{-1} The absorption peak almost disappeared, indicating Si-CH_3 Structural reduction.

Figure 26. FTIR test results of typical samples



(3) Mechanism analysis

Under the action of corona high energy particles, the molecular bonds of silicone rubber are broken, which is shown in FTIR as Si-O-Si and Si-CH₃. The corresponding characteristic absorption peak decreases. At the same time, when silicone rubber material is subjected to corona discharge in air, a certain amount of nitric acid will be formed, and the concentration of nitric acid increases with the increase of relative humidity, corresponding to wavenumber 1650 cm⁻¹ and 3500 cm⁻¹. The absorption peak of the site is enhanced, -NO₃. The increase of -OH content indicates that nitric acid is involved in the corona aging process. Nitric acid acts on silicone rubber, and due to its strong corrosiveness, it will destroy the physical structure of its surface and produce new chemical groups, thus causing the change of its trap characteristics.

Different air pressures will affect the corona intensity, which is the density of charged particles in the conductive channel. The impact of humidity on corona aging is complex. Humidity not only affects the intensity of corona discharge but also, due to high humidity, prolonged corona discharge can produce nitric acid. The strong corrosiveness of nitric acid can further age silicone rubber materials.

At low pressure (45 kPa), the air density is low, and the number density of charged particles in the discharge channel is high, with a large free travel distance. This allows charged particles to accumulate significant kinetic energy, which can bombard the material surface. When corona aging occurs for an extended period, environmental humidity increases to a certain level (Sample 3) and remains so for a sufficient duration, moisture will adhere to the material and electrode surfaces, locally increasing the electric field and making discharges more likely. Both SEM and FTIR indicate that the impact effect of charged particles becomes more pronounced at this time. When humidity reaches its maximum and aging has occurred for a certain period (Sample 2), not only does moisture distort the surface electric field of the sample, exacerbating discharges, but as nitric acid content increases, its strong corrosive properties will act on the silicone rubber material surface, causing corrosion and making it easier for charged particles to bombard the interior of the sample, accelerating aging. On the other hand, when charged particles bombard the sample surface, they form cracks, pores, and other defects, allowing nitric acid to penetrate deeper into the sample, increasing the contact area with silicone rubber and leading to more severe aging. Therefore, Sample 2 (45 kPa, 90%, 400 h) exhibits longer and deeper grooves on its surface, with a reduction in Si-O-Si structure, resulting in the most severe physical and chemical damage, generating more physical and chemical defects.

When the air pressure is high, the air density is greater, and the electron number density in the discharge channel is lower. As humidity increases, fewer water molecules are captured, thus having a smaller impact on the current. When humidity further increases and remains for an extended period, although water molecules may also adhere and distort the field strength, due to the significantly lower number of water molecules in space compared to low pressure conditions, the distortion effect is not significant, leading to minimal changes in current. At this point, there is less nitric acid content, and corrosion on the silicone

rubber surface requires a longer time. Therefore, under high air pressure, the aging effect is more pronounced. In this case, the synergistic effect between charged particles in the silicone rubber and nitric acid is difficult to manifest, resulting in fewer defects in the sample (Sample 7). Research findings from Tsinghua University also confirm this analysis.

Due to the effect of corona discharge, the microstructure of materials will change, forming many new defects or trap centers. When corona discharge occurs, injected charged particles may be captured, forming space charges. SEM results show that the surface of new samples is relatively smooth and flat, with a uniform structure. As the corona time increases, needle-like pores appear on the silicone rubber surface, then the number of pores increases and deepens, eventually developing into cracks or even fissures, leading to grooves. It is evident that the surface structure of the samples is gradually destroyed under the combined action of charged particle bombardment and nitric acid corrosion, resulting in more physical and chemical defects. The formation of these defects means that the injected charges must absorb more energy to be excited, thus the corresponding temperature during excitation is higher, and the trap energy level deepens, which is reflected in the TSC curve as an increase in current peak and a rise in the corresponding temperature.

3.Summary

To reveal the degradation mechanism of composite external insulation materials in heavily polluted areas, this section conducts experimental studies on the main factors affecting the degradation of composite external insulation—heavy pollution and corona discharge. The study tests the changes in various physicochemical micro-performance properties of silicone rubber materials under different conditions, obtaining the destruction mechanisms of organic components in silicone rubber materials under heavy pollution and corona effects. This provides a theoretical foundation for subsequent aging assessment and performance optimization. Details are as follows:

A composite material corona aging test system has been developed to conduct corona aging tests on silicone rubber materials. Using methods such as SEM, static contact angle analysis, TSC, and FTIR, the effects of corona duration, corona voltage, nitric acid exposure time, nitric acid PH value, and different pressures and humidity levels on the performance of silicone rubber materials have been studied. The differential damage mechanisms of charged particles and nitric acid on organic molecules under different pressures and humidity levels have been analyzed, refining the theory of corona aging. In subsequent optimization of silicone rubber materials, efforts can be focused on improving C-H, Si-C, and terminal Si-OH bonds. Due to the non-equivalence between artificial corona and field corona, the following conclusions will not undergo quantitative analysis.

- ① As the corona intensity increases, the hydrophobic performance of silicone rubber material rapidly decreases. Within 20 minutes at 3kV corona, the hydrophobic performance drops to around 10° , and with increasing test time, it no longer changes; the rate of hydrophobic recovery decreases as the corona intensity increases and the duration of corona exposure extends, but due to the influence of the materials microstructure, the recovery rate is not monotonically increasing or decreasing, showing fluctuations in between. Under nitric acid alone, the degradation rate of the hydrophobic performance of silicone rubber material slows down, generally only dropping to about 55° - 70° . With increased nitric acid exposure time and concentration, the rate of hydrophobic recovery shows a consistent trend with corona, and can all recover to above 90° .
- ② As the corona intensity increases and the exposure time extends, changes occur on the surface morphology of silicone rubber materials, including pore-crystal layer-crack processes. Pores exhibit both smooth and irregular edges. As the corona PH value decreases and the exposure time extends, changes occur on the surface of silicone rubber materials, such as increased pore density and depth. Pores are distributed irregularly.
- ③ With the increase of corona intensity and the extension of action time, the peak TSC current and its corresponding temperature of the material increase, but mostly a single peak; with the decrease of corona PH value and the extension of action time, the peak TSC current and its corresponding temperature of the material increase, and a double current peak appears.
- ④ Under the effect of corona, the molecular breakage and oxidation of silicone rubber materials are caused by the kinetic energy of high-energy charged particles and the oxidative and corrosive effects of nitric acid. Charged particles and nitric acid

successively destroy the C-H bond, Si-C bond, and Si-O bond in silicone rubber molecules. After the destruction of the C-H and Si-C bonds, the organic components of the material decrease, its hydrophilicity increases, and its hydrophobicity rapidly declines. However, after the Si-O bond is broken, long-chain siloxanes decompose, leading to an increase in small-molecule siloxanes, which accelerates the recovery of hydrophobicity; the formation of inorganic silicon components also enhances its hydrophilicity, reducing the irreversibility of organic components and blocking the migration of hydrophobic substances. After the oxidation of silicone rubber molecules, the content of hydrophilic OH groups increases. The highly reactive OH groups condense, reducing the content of hydrophilic OH groups while increasing the molecular chain length and decreasing the content of small-molecule siloxanes. At the same time, chemical reactions at the molecular level cause surface pores, crystal layers, and cracks on the material, accelerating the rate and depth of corona damage and affecting the migration rate of hydrophobic substances. Therefore, the fluctuation in the loss and recovery of hydrophobicity in silicone rubber materials is caused by complex reactions such as molecular breakage, oxidation, and condensation, which are closely related to the surface structure of the material.

⑤ During the corona process, the breaking of molecular bonds increases electron traps. After the surface structure of the material is damaged, charged particles and nitric acid penetrate into the material, increasing the depth of electron traps. Charged particles mainly bombard the surface, so TSC curves are often unimodal; nitric acid primarily causes corrosion and oxidation, resulting in bimodal TSC curves. The increase in electron traps enhances the materials ability to capture electrons, increases the degree of surface electric field distortion, making it more prone to corona.

⑥ Under different pressures, the mechanisms of organic molecule degradation in silicone rubber materials vary. Under high pressure, water has a lesser impact on electric field distortion, and the density of charged particles and nitric acid is low, so the degradation of silicone rubber material is mainly due to charged particle damage, with less influence from nitric acid. Under low pressure, water has a greater impact on electric field distortion, and the density of charged particles and nitric acid is high, so the degradation of silicone rubber material is caused by the combined effects of charged particles and nitric acid, with higher humidity leading to more pronounced nitric acid effects.

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no

Conflict of Interests

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

References

- [1] Bi, M., Deng, R., Jiang, T., Chen, X., Pan, A., Zhu, L., 2022. Study on Corona Aging Characteristics of Silicone Rubber Material Under Different Environmental Conditions. IEEE TRANSACTIONS ON DIELECTRICS AND ELECTRICAL INSULATION.
- [2] Hakami, M., El-Hag, A., Jayaram, S., 2021. Effects of Corona Discharges on Silicone Rubber Samples under Severe Weather Conditions. 2021 IEEE ELECTRICAL INSULATION CONFERENCE (EIC).
- [3] Wang Jianguo, Liu Yang, Fang Chunhua, Chen Junjie, Xie Congzhen, Cai Li, 2009. PERFORMANCE INFLUENCE OF HIGH TEMPERATURE VULCANIZATION SILICONE RUBBER BY ALTERNATING CURRENT CORONA DISCHARGE. ACTA POLYMERICA SINICA.
- [4] Haji, K., Zhu, Y., Otsubo, M., Honda, C., 2007. Surface Modification of Silicone Rubber After Corona Exposure. PLASMA PROCESSES AND POLYMERS.
- [5] Zhu, Y., Haji, K., Otsubo, M., Honda, C., 2006. Surface degradation of silicone rubber exposed to corona discharge. IEEE TRANSACTIONS ON PLASMA SCIENCE.
- [6] Guo, J.-k., Hao, C.-y., Yu, J.-s., Lu, L.-q., 2017. Effect of Corona Discharge Treatment on Interface Discharge Behaviour between Polypropylene and Silicone Rubber. PROCEEDINGS OF THE 2ND 2016 INTERNATIONAL CONFERENCE ON SUSTAINABLE DEVELOPMENT (ICSD 2016).
- [7] Sarathi, R., Mishra, P., Gautam, R., Vinu, R., 2017. Understanding the Influence of Water Droplet Initiated Discharges on

Damage Caused to Corona-Aged Silicone Rubber. IEEE TRANSACTIONS ON DIELECTRICS AND ELECTRICAL INSULATION.

- [8] Zhu, Y., 2019. Influence of corona discharge on hydrophobicity of silicone rubber used for outdoor insulation. POLYMER TESTING.
- [9] Zhu, Y., Otsubo, M., Honda, C., Tanaka, S., 2006. Loss and recovery in hydrophobicity of silicone rubber exposed to corona discharge. POLYMER DEGRADATION AND STABILITY.
- [10] Zhang, Z., Pang, G., Ma, X., Liang, T., Jiang, X., 2022. Mechanical Properties of High-Temperature Vulcanized Silicone Rubber Under Acid-Fog With AC Energized. IEEE ACCESS.