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# The Research on Corona Aging Silicone Rubber Materials' NMR Characteristics

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**ABSTRACT** Nuclear Magnetic Resonance (NMR) detection is a non-destructive testing method that can be used to detect the aging state of organic materials. A unilateral NMR sensor is used in this study to detect the aging state of the corona aging samples of silicone rubber materials after 100-hour's corona aging under different humidity. At the same time, a comparative analysis is made between the NMR results and the conventional methods results such as Fourier Transform Infrared Spectroscopy (FTIR) and static contact angle test. The results show that with the effect of corona discharge, the polymer structure of the silicone rubber materials change to a certain extent. These changes are shown as the effective transverse relaxation time $T_{2\mathrm{eff}}$ of aged sample decreases in the NMR detection. The results of NMR and FTIR both show that the molecular crosslinking density of silicon rubber materials increases, and the activity of the H-containing group decreases. With the increase of relative ambient humidity, $\Delta T_{2\mathrm{eff}}$ gradually increase, and it means the corona aging state is becoming much severer. The results of NMR are consistent with the results of FTIR and contact angle tests. The $T_{2\mathrm{eff}}$ of the same sample tested at different time does not have significantly changes. This indicates that the NMR characteristic of silicon rubber materials after corona are irreversible. The NMR method can test the permanent damage of silicon rubber materials caused by corona. Compared with the static contact angle test, the NMR method can analyze silicon rubber materials from the molecular structure level, and it has good portability and orientation. Meantime, NMR method can achieve a non-destructive aging state detection. Hence the NMR method will provide reference for the operation and maintenance of the silicone rubber composite insulator.

**INDEX TERMS** Corona aging, silicone rubber composite insulator, NMR, non-destructive testing.

## I. INTRODUCTION

Composite insulator is mainly composed of silicone rubber insulator shed, end-fitted metallic and mandrel. Compared with porcelain insulator and glass insulator, composite insulator has the advantages of small weight, good performance of preventing pollution flashover and great mechanical strength [1]–[3], so it has been widely applied in modern power system.

Due to the complicated work conditions such as corona discharge, ultraviolet ray, pollution and humidity haze, the silicon rubber material of composite insulator shed apron has a series of aging phenomena such as pulverization, cracking and discoloration [4]–[6]. Compared with other regions in China, the geographical location of southwest China is always in a high humidity environment (Relative Humidity, RH$>$70%)[7], which frequently leads to the corona discharge at the end-fitted metallic of composite insulator. Both of the hydrophobicity and the aging composite insulator insulator's shed capability of preventing pollution flashover is reduced, which easily leads the flashover of the insulator to damage the power system. Therefore, testing the performance of composite insulators and assessing the ageing of insulators are of great significance in eliminating potential threats of power system and improving the efficiency of equipment maintenance to ensure the safety and stable operation of power systems.

The current testing methods for the aging state of composite insulators mainly include: leakage current method [8]–[10], hydrophobic detection methods [11]–[13], and thermal current stimulation method [14]. However, Leakage current method is sensitive to the severity of the insulator

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surface contamination. The result of leakage current method has high randomicity, and this method need a lot of equipment for measuring the leakage current. The Hydrophobic detection includes static contact angle method, dynamic contact angle method, water spray classification method, etc. Due to the recovery characteristics of the insulator material's hydrophobicity, the results cannot fully represent the aging state of the insulator. Thermal current stimulation method can conduct microscopic analysis of samples. But this method will cause certain damage to samples in the process of analysis.

NMR method is a conventional technique for laboratory testing of polymer materials. In recent years, NMR method is gradually applied to detecting the state of composite insulator aging [15]–[18]. Compared with the aging state testing method widely used at present, NMR technology has some advantages. NMR method can non-destructive measure the equivalent lateral relaxation time $T_{2\mathrm{eff}}$ of silicone rubber composite insulators. According to the changes of $T_{2\mathrm{eff}}$, it can reflect the aging state of composite insulators. The $T_{2\mathrm{eff}}$ changes reflects the changes of silicone rubber materials molecular structure after corona. aging. The $T_{2\mathrm{eff}}$ is a more clear demonstration of composite insulator's aging state. Xu Zheng and his fellows from Chongqing University [15]–[17] have developed a unilateral NMR detection sensor. The sensor 's maximal size is 50mm × 56mm × 97 mm and it's weight is approximately 0.85kg. This sensor enables non-destructive inspection on-site carried by maintenance personnel. It can be seen that NMR technique can be miniaturized and portable. The NMR method has a broad application prospect in the field of nondestructive testing of composite insulator aging state.

In this paper, the 100-hours multi-needle-plate electrode corona aging experiments are performed. The samples are silicone rubber materials of composite insulator shed. The experiments are under different relative humidity (RH) conditions including 40%, 60%, 80%, and 95%. A unilateral NMR sensor is used to perform NMR detection on the aging samples. The result of NMR detection is compared with the result of Fourier Transform Infrared Spectroscopy (FTIR) to analyze the aging state of samples. The research results in this paper can provide some references for the material improvement, structural optimization design of composite insulator shed. And the research will help power system's operation and maintenance in high humidity areas.

## II. CORONA AGING EXPERIMENT

The experimental sample is a 115mm×115mm×2mm silicone rubber sheet produced by an insulator factory. The composition of silicon rubber materials is shown in table 1. The molecular formula of PDMS is shown in Fig. 1 [20].

The experiment mainly studies the corona aging characteristics of silicone rubber materials under different humidity conditions. The experimental principle is shown in Fig. 2.

The dry compressed air of 0-1Mpa is generated by air compressor and cold compressor, and the dew point is 10-24°C. The air output flow is controlled to 10L/min. Dividing the dry air into two parts, a part of dry air passes through the control valve A directly into the environmental unit through the air pipe, and the other part of the dry air passes through the control valve B into the water tank. Dry air passing through water tank will increase the humidity of the air. The relative humidity in the environment control unit can be controlled by adjusting the air flow through control valve A and control valve B. The electrical conductivity of the liquid in water tank is less than 10 $\mu$S / cm. When the relative humidity reaches the value required by the experiment, the mixed air of this proportion is continuously injected into environment control unit.

After using step-up transformer and the voltage regulator to boost the voltage, the high voltage through protective resistance and high-voltage bushing is applied to the environmental control unit.

In Fig.3 (a), the environmental control unit is a plexiglass cylinder with a diameter of 350mm and a height of 400mm.

**TABLE 1. (PU) The composition of silicon rubber material.**

| Ingredient | PDMS | $SiO_2$ | $Al(OH)_3$ | Silicone Oil |
|---|---|---|---|---|
| Proportion | 35%-40% | 5%-10% | 45%-50% | 1%-2% |

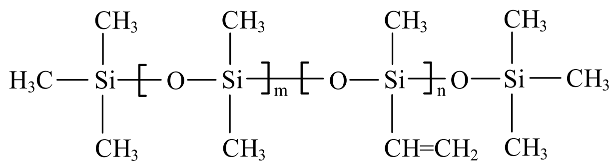


**FIGURE 1. The Molecular formula of PDMS.**

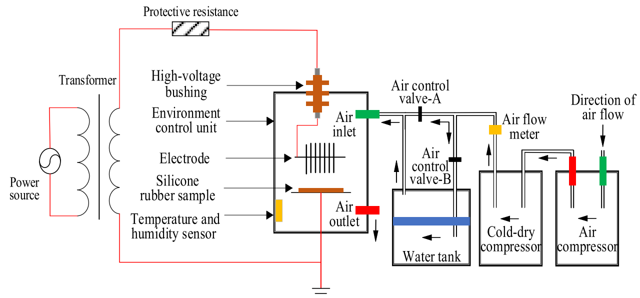
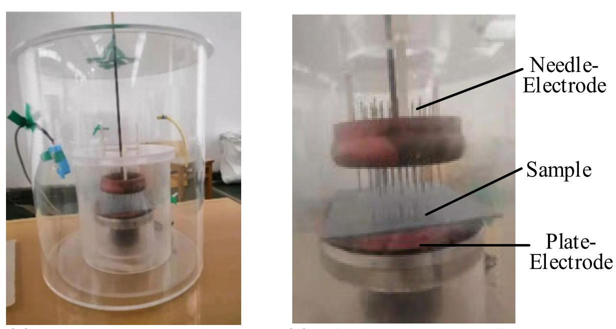



**FIGURE 2. The schematic diagram of experiment device.**




(a) environment control unit (b) Multi-needle plate electrode

**FIGURE 3. The device of corona aging experiment.**

As shown in Fig.3(b), the multi-needle-plate electrode corona aging device is placed in the environmental control unit. And the silicon rubber sample for experiments is placed on the plate electrode.

In corona aging experiment, silicon rubber samples were placed respectively in the environment with relative humidity of 40%, 60%, 80% and 95%, and the ambient temperature is $20° \pm 2°$. The silicon rubber samples are subjected to 10kV ac voltage for 100h of continuous corona aging experiment.

## III. DETECTION METHOD

### A. NUCLEAR MAGNETIC RESONANCE DETECTION

NMR is a microscopic analysis method for studying the state of materials at the molecular structure level. NMR principle is to place the sample under a strong external magnetic field. The nuclear spin magnetic field of the sample atom itself is rearranged under the effect of external magnetic field. In this condition, most atoms rotate from the low energy state to the high energy state under the interference of external magnetic field. The NMR signal will be generated when the atom nuclear spin returns to the equilibrium state. Due to the influence of electron cloud distribution and other factors in the molecular structure, the actual external magnetic field intensity of the nucleus tends to change to a certain extent. The intensity of the external magnetic field of the nucleus in different positions in the molecular structure also varies. So, this makes the sensitivity of the nucleus at different positions in the molecule to the RF fields of different frequencies. Finally, NMR signals measured is the differences. This difference is the basis for the analysis of the molecular structure of the substance by NMR.

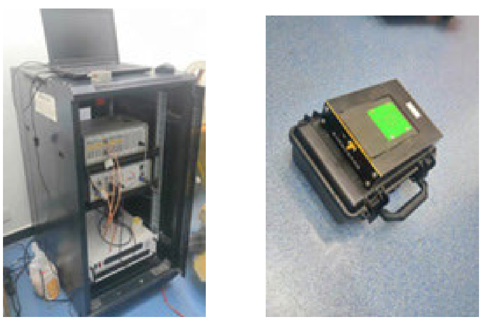


FIGURE 4. The low field NMR analysis system.

When NMR detection takes the Larmor-Frequency of H atom as resonance excitation frequency, the change of echo signal is able to provide information of H atom structure change. In other words, the echo signal reflects the changes of the H atoms and the group contain H atom in the molecular structure of samples. As shown in Fig. 4, the low field NMR analysis system [17]–[19] developed by the state key laboratory of power transmission and distribution equipment and system security and new technology of Chongqing University is adopted for the experimental NMR test. The system is composed of NMR spectrometer Kea2 (Magritek, Wellington, New Zealand), power amplifier (Tomco Technologics, Stepeny, Australia), PC and unilateral NMR sensor. The frequency used by the sensor is 6.03MHz, and the detection range of the sensor is $5\text{mm} \times 5\text{mm} \times 2\text{mm}$.

All experimental measurements are performed at room temperature. In the experiment, CPMG pulse sequence excitation is used [16], [17]. The parameters are set as follows: pulse width $D = 4.5\mu s$, echo time $TE = 120\mu s$, and the number of 180 ° pulses is 1000. Repeat time is 1000ms, the amplitude of 90 ° pulse, A90 °, is -20dB. The amplitude of 180 ° pulse, A180 °, is -14dB. Because of the application of unilateral NMR sensor, CPMG's peak envelope decreases exponentially with equivalent relaxation time $T_{2\text{eff}}$ rather than with transverse relaxation time $T_2$. The exponential relationship between the silicon rubber sample surface echo peak and equivalent transverse relaxation time can be fitted according to formula (1) [17], [18]:

$$y = Ae^{-t/T_{2\text{eff}}} \tag{1}$$

where y is the amplitude of the fitted curve; $T_{2\text{eff}}$ is equivalent transverse relaxation time; $t = m \times TE$, m is the number of echoes, and TE is the echo time.

### B. FOURIER TRANSFORM INFRARED SPECTROSCOPY ANALYSIS

After the 100 hours corona aging of the silicone rubber material, the corona aging experiment is stopped and the silicone rubber sample is taken out. After NMR detection, a piece of the silicone rubber samples with specifications for $5\text{ mm} \times 5\text{ mm} \times 2\text{ mm}$ is cut off for FTIR test. It is necessary to keep the piece of samples in dry and closed glassware during the inspection period. The glassware can prevent other uncontrollable factors from affecting the quality of the sample.

### C. STATIC CONTACT ANGLE ANALYSIS

The optical contact Angle tester (ZJ-6900) is used to test different areas of the silicone rubber. After the corona aging experiment, static contact angle test is conducted on the aging samples after being placed for 0h, 2h, 4h, 6h and 8h respectively. During the inspection period, the samples are kept in dry and closed glassware.

## IV. ANALYSIS OF EXPERIMENTAL RESULTS

### A. THE RESULTS OF NMR

Taking the samples after 100h of corona aging under the condition of 60% environmental relative humidity as an example, the surface of samples after corona aging is shown in Fig. 5. Observing the sample surface, it can be obviously seen the aged marks. In the corresponding sample surface below the needle electrode, there appear distinct aged marks. The corona aged marks in the central area of samples are more obvious and denser than those in the peripheral area. The samples under other environmental relative humidity have same aged marks. This indicates that the aging degree is different among different areas of samples. Therefore, different areas of the aging sample surface need to be tested. For comparative testing, the corresponding back areas of each

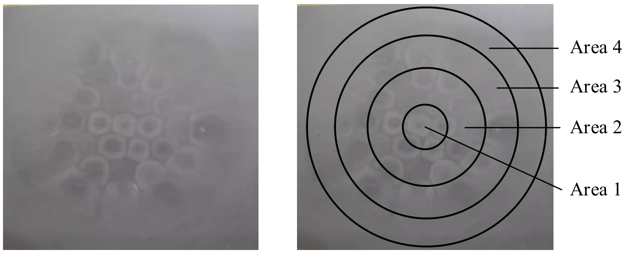



**FIGURE 5. The sample after corona aging and areas division.**

area are selected as the non-aging sample. The samples are divided into four areas, with the intervals of 10mm, 10mm and 10mm, respectively. The specific areas are divided as shown in Fig.5.

The echo signal of the silicone rubber sample obtained by NMR detection has a single exponential decay with the time constant $T_{2\text{eff}}$. The results of the NMR detection are all shown as Fig. 6.

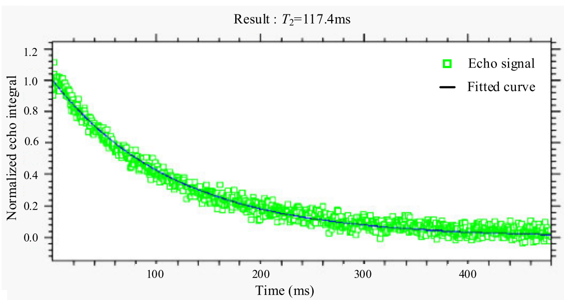



**FIGURE 6. The result of the NMR detection.**

**TABLE 2. (MS) The $T_{2\text{eff}}$ of each area under different relative humidity.**

| | RH=40% | RH=60% | RH=80% | RH=95% |
|---|---|---|---|---|
| Before aging | 125.8 | 124.4 | 112.8 | 116.6 |
| After aging | 119.0 | 116.1 | 102.8 | 104.5 |
| Reduction | 6.8 | 8.3 | 10.0 | 12.1 |

Multiple NMR detections were performed on different areas of the sample for many times. The average values of these equivalent transverse relaxation times $T_{2\text{eff}}$ were shown in table 2. Because of the individual differences of the sample, the initial $T_{2\text{eff}}$ of the sample is different in Table 1. After corona aging, the results $T_{2\text{eff}}$ are significantly decreased. With the increase of environmental relative humidity, the reduction of $T_{2\text{eff}}$ is more significant. Under the 95% relative humidity condition, the maximum reduction of $T_{2\text{eff}}$ reached 12.1. Therefore, the NMR detection can reflect the variation of silicone rubber material before and after corona aging.

Fig. 7 demonstrates the fitting curve of NMR signals before and after corona aging in area 1 under different humidity conditions. It can be clearly observed from Fig. 7 that the

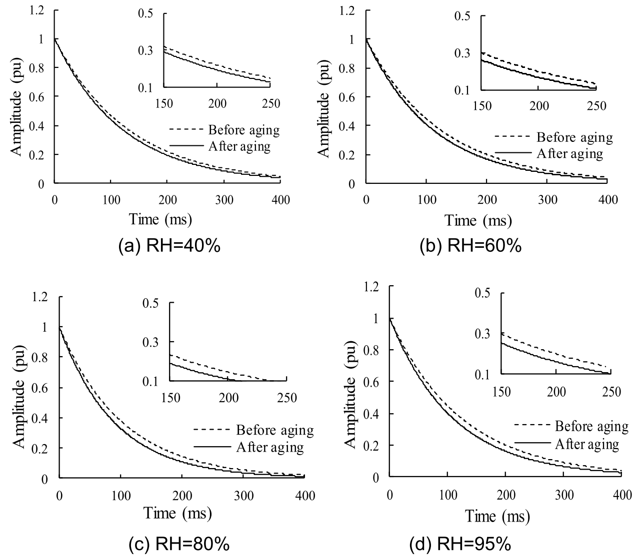



**FIGURE 7. The change of $T_{2\text{eff}}$ before and after corona aging.**

$T_{2\text{eff}}$ of the silicone rubber material after aging in area 1 is significantly reduced. As the relative humidity increases, the reduction of $T_{2\text{eff}}$ changes more. This indicates that the increases of relative humidity in the environment makes the molecular structure of silicone rubber materials change more obviously. The degree of aging is more serious under corona discharge.

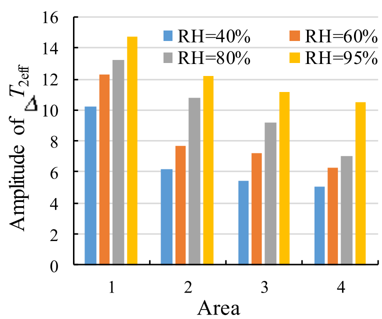



**FIGURE 8. The $\Delta T_{2\text{eff}}$ change trend of each area under different relative humidity.**

The difference in equivalent transverse relaxation time before and after the aging of the silicone rubber material is taken as $\Delta T_{2\text{eff}}$, and the change trend is shown in Fig.8. It can be seen from Fig. 8 that the aging degree of silicone rubber materials is positively related to the relative humidity. The environmental relative humidity is higher, the change in $T_{2\text{eff}}$ will be more obvious. The change of $T_{2\text{eff}}$ means the molecular structure of the silicone rubber materials damage degree. The higher $\Delta T_{2\text{eff}}$ means the aging state of sample is more severe. In the most severely corona aging area 1, $\Delta T_{2\text{eff}}$ is 10.2 at RH = 40%, and when RH = 95%, $\Delta T_{2\text{eff}}$ increased to 14.7, an increase of about 44.1%.

This indicates that environmental humidity has a significant effect on corona aging of silicone rubber materials.

The corona aging degree of the central area is more serious, while the aging degree of the edge area is lesser. Using the NMR detection method can reflect the change of silicon rubber material in aging experiments under different humidity.

### B. THE RESULTS OF FTIR

FTIR is essentially an analytical method to determine the molecular structure of substances and identify compounds based on the information of relative vibration and molecular rotation among atoms in molecules. The infrared spectrum can be obtained by recording the absorption of infrared light. The FTIR testing results of the peak wave numbers of the main functional groups of the aged sample are shown in Fig. 9.

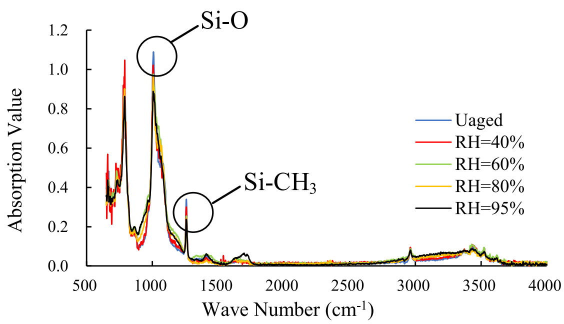



**FIGURE 9.** The FTIR testing results of aged sample.

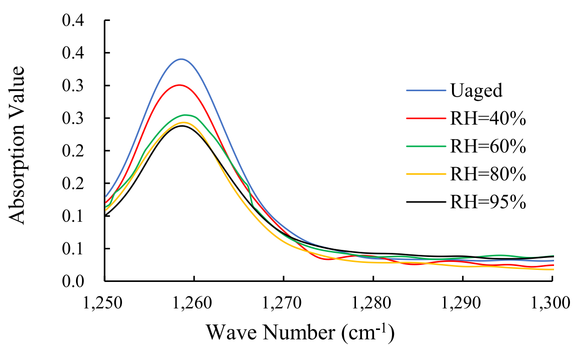



**FIGURE 10.** The wave number of $Si\text{-}CH_3$ characteristic peaks.

According to the testing results of FTIR, $Si\text{-}CH_3$ characteristic peaks in the wave number is 1300 $cm^{-1}$-1250 $cm^{-1}$. As shown in Fig. 10, compared with other corona aging samples under different relative humidity, the characteristic peak of the corona aging sample under RH = 40% absorption value is at maximum. Namely after corona aging there are still a large number of $Si\text{-}CH_3$ groups, which means the $-CH_3$ group of the aged samples has not been severely damaged. The FTIR results of corona aging samples under different humidity indicates that as the relative humidity of environment increases gradually, the damage degree of $Si\text{-}CH_3$ of silicone rubber material becomes more and more serious.

According to the FTIR test results, the Si-O characteristic peak absorption value is at wave number 1100 $cm^{-1}$ ~1000$cm^{-1}$. As shown in Fig. 11, It can be seen

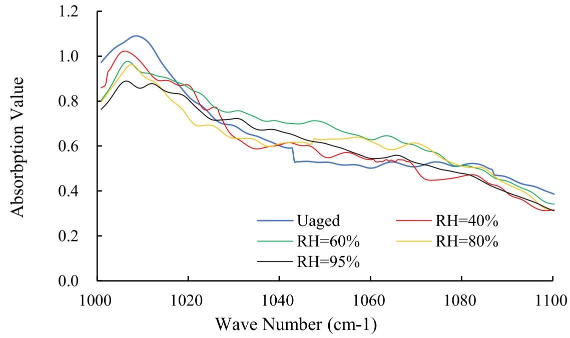



**FIGURE 11.** The wave number of Si-O characteristic peaks.

that with the increase of environmental humidity, the peak value of Si-O characteristic peak absorption value gradually decreases. This indicates that the main chain of silicone rubber molecules is broken. That is the original molecular structure is destroyed, and the aging degree of silicone rubber material sample is more serious.

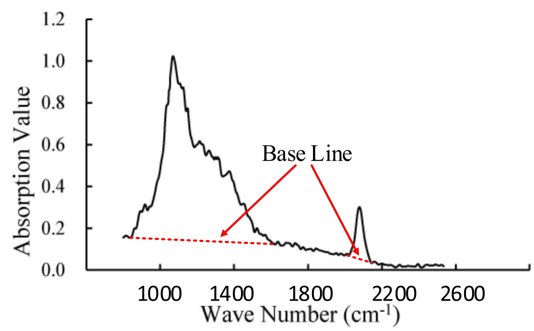



**FIGURE 12.** The schematic diagram of absorption value region.

By measuring the peak area of the absorption peak within a specific wave number range, FTIR can make a quantitative analysis on specific molecular groups. In this paper, the tangent line at both ends of the absorption peak is selected as the baseline when calculating the peak area. As shown in Fig. 12, the absorption peak area is bounded by the absorption peak spectral curve and the baseline. The absorption peak area can reflect the content of the corresponding molecular groups in the sample. So, the calculation of the absorption peak area value can effectively reflect the damage degree of the sample molecular structure, namely, the aging degree of silicone rubber material.

The calculation results of $Si\text{-}CH_3$ absorption peak area are shown in table 3. As seen from table 3, there is a significant association between corona aging relative environment humidity and the aging degree of silicone rubber material. The absorption peak area of $Si\text{-}CH_3$ is the largest at RH = 40%, and the least value is at RH = 95%. The absorption peak area can reflect the content of the $Si\text{-}CH_3$ molecular groups of the sample. Therefore, it can be seen that the greater the relative humidity of the environment, the less the $Si\text{-}CH_3$ content of the sample after corona aging will be.

**TABLE 3. (PU) The Area value of the Si-$CH_3$ absorption peak.**

| Relative Humidity | 40% | 60% | 80% | 95% |
|---|---|---|---|---|
| Area value of the Si-$CH_3$ absorption peak | 3.5742 | 2.8304 | 2.5523 | 2.0712 |

This indicates that the damage of sample molecular structure is more severe. In another word, the result means the corona aging of the sample is more severe.

In order to facilitate the comparison of FTIR and NMR measurement results, the Si-$CH_3$ absorption peak area value and $\Delta T_{2\text{eff}}$ value were normalized. The normalized value is obtained by dividing all the test data by the maximum value in the test results. In order to observe the change trend easily, the reciprocal of the normalized $T_{2\text{eff}}$ data was calculated. Finally, the graph shown in Fig. 13 is obtained.

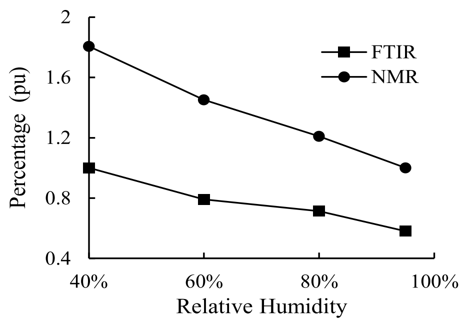



**FIGURE 13. The trend curve of $\Delta T_{2\text{eff}}$ and FTIR.**

As can be seen from the Fig.13, as the environmental relative humidity increases, the absorption peak area of Si-$CH_3$ in the FTIR test results gradually decreases. Meantime, the reciprocal value of $\Delta T_{2\text{eff}}$ gradually decreases with the increasing relative humidity. The change trend of the two test results is close to linear change. Both two detections' results reflect that the content of Si-$CH_3$ of sample is decrease after corona aging.

However, the change range of the NMR test results $\Delta T_{2\text{eff}}$ is significantly greater than FTIR test. Therefore, for the state of the silicone rubber material before and after corona aging, NMR detection can obtain a nearly linear change law of $\Delta T_{2\text{eff}}$. Thereby the NMR detection can accurately reflect the change of the material molecular group before and after aging. Also $\Delta T_{2\text{eff}}$ measured by NMR method changes significantly. Compared with the absorption peak area obtained by FTIR, NMR method can more clearly and intuitively reflect the aging state.

### *C. THE RESULTS OF STATIC CONTACT ANGLE*

In the molecular structure of PDMS, the $-CH_3$ group is distributed in the molecular side chain. The $-CH_3$ group is hydrophobic, so PDMS as a whole is hydrophobic. The value of the static contact angle can reflect the hydrophobicity of the silicone rubber material. Therefore, the -CH3 group in the silicone rubber material can be judged by the contact angle.

The test sample was placed on the test platform, and a drop of deionized water was dropped on the sample surface by the dropper on the tester. The volume of deionized water is about 10$\mu$L. After the water droplets on the surface of the sample stabilized, the static contact angle of the sample was measured by image acquisition devices.

In order to facilitate the description of static contact angle test results, the result of RH = 60% is selected as an example. The static contact angle test results have the same change rule under other relative humidity conditions. The results of static contact angle tests (RH = 60%) are shown in Fig. 14.

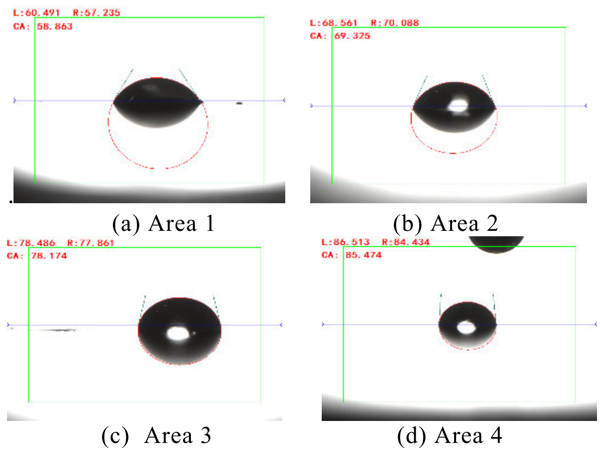



**FIGURE 14. The result of static contact angle test with 0h standing after corona aging (RH = 60%).**

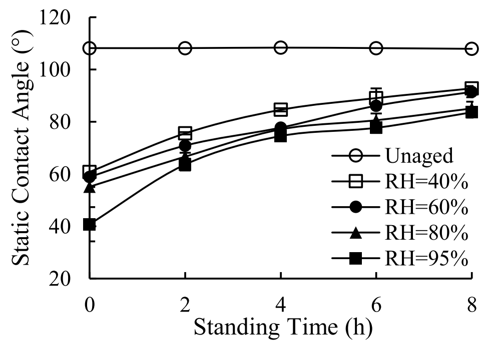



**FIGURE 15. The result of static contact angle test.**

The static contact angle change curve is shown in Fig. 15. At the end of the corona aging experiment, the average static contact angle of the sample is only 53.9°, and that the degree of surface hydrophobicity loss is the highest. With the increase of the standing time, the average static contact angle of the aging sample surface has gradually increased to 88.3°. This indicates that the surface hydrophobicity has recovered to some degree. Therefore, the result of static contact angle test is not reliable due to the recovery characteristic. With the increase of relative humidity, the contact Angle of the sample decreases greatly. The more serious the hydrophobicity loss of silicone rubber was. This indicates that the increase of relative humidity makes the damage of -$CH_3$ more serious under corona discharge.

Based on the Fig.13, the average value of static contact angle was normalized to facilitate the comparison of static contact angle test, NMR and FTIR. The normalized method is as same as Fig.13. The reciprocal of the normalized $T_{2\mathrm{eff}}$ data was calculated. Finally, the graph shown in Fig. 16 is obtained.

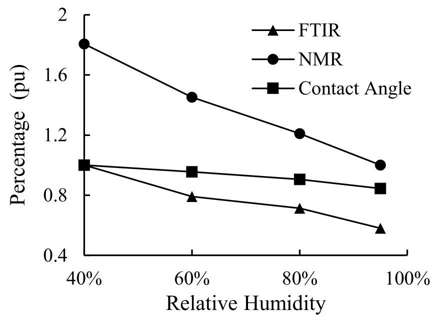



**FIGURE 16.** **The result of $\Delta T_{2\mathrm{eff}}$ and static contact angle test.**

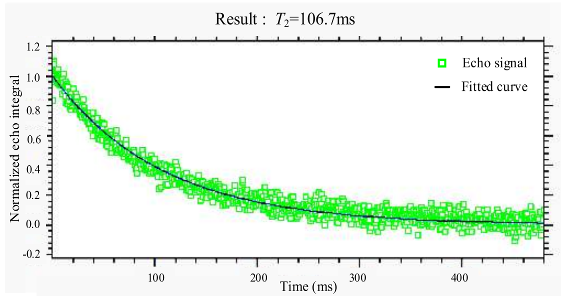
It can be seen from Fig.16 that the results of NMR, FTIR and static contact angle test have the same rule. With the increase of relative humidity, the corona aging degree of silicone rubber material is deepened. Microscopically, the corona aging effect shows that the -$CH_3$ content in the silicone rubber material is significantly reduced according to the NMR test. Macroscopically, the corona aging effect is shown by the loss of the hydrophobicity of the surface of the silicone rubber in the measurement of contact angle.

The results in Fig. 17 are the NMR test results of RH = 60% corona aged samples with an interval of 0h, 50h, 100h, 200h. According to Fig. 17, the $T_{2\mathrm{eff}}$ is no significant changes under different measurement time. This indicates that NMR detection is not affected by detection time. Therefore, NMR method is more reliable than static contact angle test.

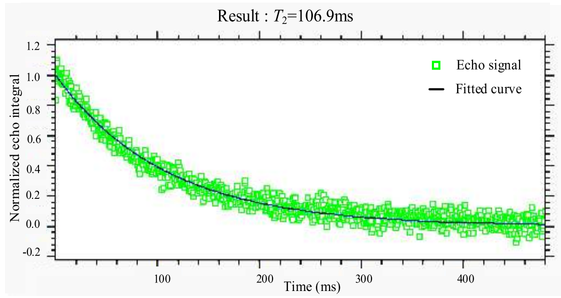
Due to the recovery characteristics of the silicone rubber material surface hydrophobicity, the static contact angle test cannot accurately reflect the aging state of the sample. As a detection method of the molecular structure of materials, NMR will not be affected by the detection time. Because the damage of silicone rubber materials' molecular structure after corona aging is irreversibility

### *D. SUMMARIZE*

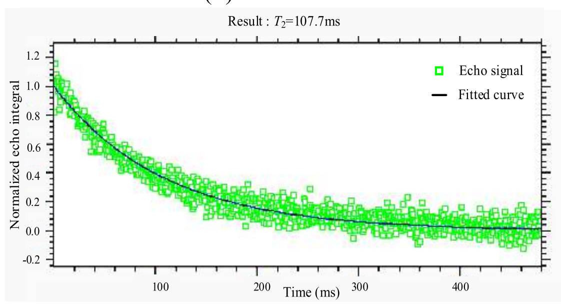
Comparing the testing results of NMR, FTIR and static contact angle test, the results indicate that the relative humidity will aggravate the corona aging of silicone rubber materials to a certain extent. With the increase of relative humidity, the Si-O bond of the main molecular chain of the samples and the side bond of the molecular chain Si-$CH_3$ rupture degree increases gradually. The change of the molecular structure



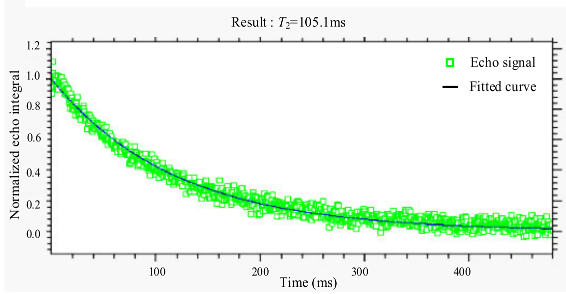

(a) Original




(b) 50h interval




(c) 100h interval




(d) 200h interval

**FIGURE 17.** **The result of NMR detection with different time interval.**

is an important feature of the silicone rubber after corona aging [20].

During the NMR test, there is an individual difference in $T_{2\mathrm{eff}}$ of the silicone rubber sheet. Even the $T_{2\mathrm{eff}}$ in different areas of the same sample are not the same. Therefore, using $\Delta T_{2\mathrm{eff}}$ of the same area can accurately reflect the corona aging state. But it is impossible to establish a uniform $T_{2\mathrm{eff}}$ standard value for the same type of silicone rubber products to evaluate the corona aging state of silicone rubber insulators. In order to solve this problem, it is possible to conduct NMR test before the insulator is put into operation, and to use the same NMR equipment for testing during later maintenance. By comparing the variation amplitudes of $\Delta T_{2\text{eff}}$ to evaluate the aging degree, the silicone rubber composite insulators in operation can be tested regularly. A $T_{2\text{eff}}$ database can be established to systematically track and evaluate the operating state of insulators. Meantime, the design of the NMR sensor should be optimized to improve the measurement accuracy as much as possible. The better NMR sensor will reduce measurement errors and avoid measurement differences between different equipment,

Compared with the traditional static contact angle test, NMR detection method is not affected by the detection time. NMR detection can accurately reflect the aging state of the material according to the molecular structure changes. NMR detection is of higher reliability at the same time. Comparing with FTIR, NMR has the same accuracy and reliability of FTIR detection. But the change degree of NMR detection results before and after corona aging is more obvious. In addition, the NMR sensor used in this paper has the advantages of non-destructive testing, portability, lightweight, etc. And NMR detection can be used to detect the aging states of silicone rubber insulators on the site of transmission lines. Therefore, NMR detection can be used as a technical method to evaluate corona aging states of silicone rubber materials. Due to the characteristics of portability and nondestructive testing, NMR detection has a broad application prospect in the future.

## V. DISCUSSION

During the corona aging process of silicone rubber, particles such as electrons bombard the surface of the material. Other chemical reactions work simultaneously. These factors lead to the breaking of the Si-O bond of the main chain of the silicone rubber molecule. At the same time, cross-linking reactions, hydrolysis reactions, oxidation reactions, and condensation also occur. These reactions produce low-molecular-weight polymers, and make the -$CH_3$ group detached from the main chain in the form of $CH_4$ gas [21]. These effects lead to a decrease in the number of H atoms and H-containing groups in the silicone rubber material, as well as a decrease in molecular mobility. This makes a change in the spin state of the H atom nucleus, and ultimately it manifests as a decrease in $T_{2\text{eff}}$. As the relative humidity of the environment increases, the water molecule content in the air increases. The PDMS hydrolysis reaction using water as a catalyst will accelerate at the same time in multiple areas of silicone rubber. The average molecular weight of the silicone rubber material will also be greatly reduced. Therefore, resulting in aggravating the corona ageing state of silicon rubber materials.

## VI. CONCLUSION

In this paper, 100-hour corona aging experiments of silicone rubber materials of composite insulators are performed under different humidity conditions. NMR detection methods are used to evaluate the condition of aging samples. NMR results are compared with the FTIR results and static contact angle results. The research conclusions are as follows:

(1) Under the effect of corona discharge, the polymer structure of the silicone rubber material changes to a certain extent. The molecular crosslink density increases, and the activity of the H-containing group decreases. In NMR test, these changes are demonstrated as the decrease of $T_{2\text{eff}}$. Furthermore, the reduction of $T_{2\text{eff}}$ in different areas of different samples varies.

(2) Environmental relative humidity has a significant effect on corona aging of silicone rubber materials. With the increase of the ambient humidity, the decrease amplitude in the equivalent transverse relaxation time before and after aging, $\Delta T_{2\text{eff}}$, gradually rises. This indicates that the silicon rubber composite insulator is more prone to corona aging in high humidity region.

(3) The NMR results are consistent with the FTIR testing and static contact angle test results. Corona aging reduces the content of -$CH_3$ in silicone rubber materials and damages the hydrophobicity. At the same time, the greater the ambient humidity, the more severe the corona effect of the silicone rubber material. This indicates that the NMR test can reflect the aging state of silicone rubber materials. At the same time, the unilateral NMR sensor used in this paper has certain directionality. The results of the unilateral NMR sensor can reflect the aging state of different regions of the sample. Meantime NMR detection has the characteristics of non-destructive testing. So, without damaging the insulator, the corona aging state of the insulator can be detected on-site. This will help inspectors to maintain insulators.

## REFERENCES


[1] Z. Zhijin, H. Haizhou, and J. Xingliang "Model for predicting thickness of rime accreted on composite insulators," *Trans. China Electrotech. Soc.*, vol. 29, no. 6, pp. 318–325, Jun. 2014, doi: 10.19595/j.cnki.1000-6753.tces.2014.06.041.

[2] L. Yu, J. Xingliang, and S. Lichun, "Influence of characterizing shed configuration parameters of composite insulators on icing flashover performance," *Trans. China Electrotech. Soc.*, vol. 29, no. 8, pp. 319–326, Aug. 2014, doi: 10.19595/j.cnki.1000-6753.tces.2014.08.041.

[3] Z. S. Xie, Z. Q. Wang, and Y. Chen, "Analysis of damage mechanism for crimped composite insulators," *Trans. China Electrotech. Soc.*, vol. 29, no. 6, pp. 296–302, Jun. 2014, doi: 10.19595/j.cnki.1000-6753.tces.2014.06.038.

[4] Y. Gao, J. Wang, X. Liang, Z. Yan, and Y. Liu, "Influence of AC and DC corona on high temperature vulcanized silicone rubber," *Proc. CSEE*, vol. 36, no. 1, pp. 274–284, Jun. 2016, doi: 10.13334/j.0258-8013.pcsee.2016.01.030.

[5] W.-W. Shen, W. Song, G.-L. Wang, Y.-G. Niu, J.-L. Wang, L.-M. Zhang, and G.-J. Zhang "Influence of corona discharge on aging characteristics of HTV silicone rubber material," *High Voltage App.*, vol. 49, no. 2, pp. 1–7, Feb. 2013, doi: 10.13296/j.1001-1609.hva.2013.02.007.

[6] Z. Guanjun, L. Zhao, R. Zhou, W. Shen, and X. Liang, "Review on aging characterization and evaluation of silicon rubber composite insulator," *High Voltage App.*, vol. 52, no. 4, pp. 1–15, Apr. 2016, doi: 10.13296/j.1001-1609.hva.2016.04.001.

[7] L. Han *et al.*, "The changes of the average relative humidity in Southwest China," *Plateau Mountain Meteorol. Res.*, vol. 36, no. 4, pp. 42–47, Dec. 2016, doi: 10.3969/j.issn.1674-2184.2016.04.007.

[8] C. Weigen, W. Wanping, and X. Qing, "Research on multi-fractal characteristics of leakage current for contamination discharge of insulators," *Trans. China Electrotech. Soc.*, vol. 28, no. 1, pp. 50–56, Jan. 2013, doi: 10.19595/j.cnki.1000-6753.tces.2013.01.008.

[9] S. Kumagai and N. Yoshimura, "Leakage current characterization for estimating the conditions of ceramic and polymeric insulating surfaces," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 11, no. 4, pp. 681–690, Aug. 2004, doi: 10.1109/TDEI.2004.1324357.

[10] Y. Zhaoguang, W. Shenghui, L. Fangcheng, and L. Heming, "Design and application of leakage current measurement system for polluted insulator," *Electr. Power Sci. Eng.*, vol. 26, no. 1, pp. 14–18, Jan. 2010, doi: 10.3969/j.issn.1672-0792.2010.01.004.

[11] D. Hanqi, M. Hongwei, and W. Liming, "Description method I for unobvious hydrophobic state of composite insulators—Usability of contact angle method," *Trans. China Electrotech. Soc.*, vol. 28, no. 8, pp. 34–37, Aug. 2013, doi: 10.19595/j.cnki.1000-6753.tces.2013.08.006.

[12] T. Liangrui, Z. Jing, and S. Yi, "Estimating the level of hydrophobicity of composite insulators based on information measures and Hausdorff distance," *Trans. China Electrotech. Soc.*, vol. 24, no. 1, pp. 35–41, Jan. 2009, doi: 10.19595/j.cnki.1000-6753.tces.2009.01.007.

[13] Y. Qin, L. Yu, J. Fu, G. Li, Y. Wang, W. Y. Guo, X. L. Du, and Y. Liang "Research on microscopic properties and hydrophobicity of high temperature vulcanization silicone rubber under long-wave ultraviolet radiation," *Trans. China Electrotech. Soc.*, vol. 29, no. 12, pp. 242–250, Dec. 2014, doi: 10.19595/j.cnki.1000-6753.tces.2014.12.032.

[14] L. Ying, D. Lijian, and L. Chengrong, "Primary research on the diagnosis of aging silicone rubber insulator using thermally stimulation current," *Proc. CSEE*, vol. 27, no. 21, pp. 7–12, Jul. 2007, doi: 10.13334/j.0258-8013.pcsee.2007.21.004.

[15] Z. Xu, P. Guo, X.-L. He, and S.-J. Yi, "Aging detection of composite insulator with nuclear magnetic resonance theory," *High Voltage App.*, vol. 48, no. 3, pp. 21–25, Mar. 2012, doi: 10.13296/j.1001-1609.hva.2012.03.006.

[16] Z. Xu, J. Cheng, J. Wu, and W. He, "Non-destructive aging detection method for silicone rubber insulator shed based on unilateral NMR principle," *Proc. CSEE*, vol. 34, no. 36, pp. 6545–6553, Dec. 2014, doi: 10.13334/j.0258-8013.pcsee.2014.36.022.

[17] X. Z. W. Jiamin, "A portable unilateral nuclear magnetic resonance sensor used for detecting the aging status of composite insulator," *Trans. China Electrotech. Soc.*, vol. 31, no. 12, pp. 118–125, Jun. 2016, doi: 10.19595/j.cnki.1000-6753.tces.2016.12.014.

[18] Z. He, W. He, J. Wu, and Z. Xu, "A time-harmonic inverse design of uniplanar RF coil for unilateral NMR sensors," *IEEE Sensors J.*, vol. 17, no. 9, pp. 2696–2702, May 2017, doi: 10.1109/JSEN.2017.2680455.

[19] X. Zheng, C. Xianjun, M. Kaikai, and X. Yunfeng, "Novel unilateral NMR sensor for assessing the aging status of silicone rubber insulator," *IEEE Sensors J.*, vol. 16, no. 5, pp. 1168–1175, Mar. 2016, doi: 10.1109/JSEN.2015.2499765.

[20] W.-X. Sima, Z.-Y. Liu, X.-L. Jiang, and Q. Yang, "Effects on surface performance of partial discharges due to discrete water droplets on the silicone rubber," *Proc. CSEE*, vol. 25, no. 6, pp. 1168–1175, May 2005, doi: 10.13334/j.0258-8013.pcsee.2005.06.021.

[21] S.-H. Kim, E. A. Cherney, R. Hackam, and K. G. Rutherford, "Chemical changes at the surface of RTV silicone rubber coatings on insulators during dry-band arcing," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 1, no. 1, pp. 106–123, Feb. 1994, doi: 10.1109/94.300238.

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