Effect of Aging under AC Superimposed Harmonic Voltage on Trap and Carrier Transport Properties of Silicone Rubber

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Abstract: The rapid growth of power grid capacity and the widespread use of a large number of power electronics and non-linear loads have led to harmonics in the power system. Harmonics in the power system will cause safety hazards to the normal operation of power equipment, exacerbate the aging of insulation materials, and reducing the overall operation reliability of the system. In the present work, we used power frequency ac voltage superimposed harmonics to carry out ageing experiments on power cable terminals. Then, we tested the infrared spectra, dielectric spectra, electrical conductivity, and surface potential decay characteristics of silicone rubber insulation materials on the cable terminals aged for different times. The experimental results show that the dielectric constant and dielectric loss of silicone rubber gradually increase with the aging time. In particular, the dielectric loss of silicone rubber changed greatly at low frequencies. The effect of dc conductance of aged silicone rubber on dielectric loss is significantly enhanced at low frequencies, which causes the dielectric loss to increase as the frequency decreases following an inverse power law. The surface potential decay rates of silicone rubber insulation after positive and negative corona charging accelerate with increasing the aging time, which is consistent with the experimental results of electrical conductivity. By analyzing the distribution characteristics of electron and hole traps in silicone rubbers, it is found that the trap energy levels of electron and hole traps become shallower as the operating time increases. The calculation of the carrier hopping conduction model shows that the shallow trap formed with increasing the aging time will lead to increases in both carrier mobility and conductivity. When the conductivity rises to a certain value, the silicone rubber will lose its insulation performance, resulting in insulation failure.

Keywords: ageing; charge transport; ac superimposed harmonic voltage; silicone rubber; trap distribution

1. Introduction

The rapid growth of power grid capacity, the development of power electronics technology, and the wide utilization of a large number of power electronic devices and non-linear loads results in voltage and current distortions of the power system and generation of harmonic components [1]. Various iron core equipment, such as transformers, electromagnetic voltage transformers, and reactors;
various ac/dc converters, such as rectifiers and inverters; bidirectional thyristors; and controllable switches can generate harmonic components during operation. Harmonics are also produced during the melting period of all kinds of steelmaking electric arc furnaces, during the welding period of ac arc welding machines, and at the moment of fracture of arc drawing during the opening and closing of high-voltage circuit breakers. Harmonic components in the power system will cause safety hazards to the normal operation of the power transmission, transformation, and power consumption; reduce the quality of power; and exacerbate the aging of internal insulation materials in power equipment, which may reduce the overall operating life of the power system [2].

Power cables are very common in urban power grids. In recent years, with the implementation of urban economic construction and power grid upgrading, the proportion of power cables in urban power grids has become larger and larger [3]. The cable rate of economically developed cities has exceeded 98%. The power cable network structure is becoming more and more complicated, and the continuous increase of the operating time has caused a deterioration of cable aging. The combined effect of these factors has led to more and more incidents of power cable failures [4]. For example, a cascade dielectric breakdown occurred in 150 kV power cable terminations caused by partial discharges under the large tangential electrical field components [5]. Silicone rubber with a high elasticity, wide service temperature range, and excellent electrical properties is used as the main insulation material in cable accessories used to connect cables and cables to other equipment of extra-high-voltage systems [4]. However, in the cable system, due to the compact structure, harsh operating environment, and other reasons, it is commonly acknowledged that the probability of flashover or breakdown of cable accessories is still much higher than that of the cable itself. Under normal operation, the maximum temperature of the cable may reach 90 °C. When the cable is overloaded or short-circuited, the temperature of the cable will rise to more than twice that during normal operation in a short time. Due to the unavoidable defects inside or outside the silicone rubber insulation material, during long-term operation, various slow and irreversible chemical and physical changes will occur inside the silicone rubber insulation material under electrical and thermal stresses. Shimada et al. revealed that the crosslinking by oxidation and thermal decomposition of chemical crosslinking are two main aging reactions in silicone rubbers, which will affect the macroscopic properties of the materials [6]. Rowland et al. found that Si-CH3 bonds were reduced and Si-O-Si bonds were changed to a non-uniform distribution in field-aged silicone rubber insulators [7]. Min et al. investigated the electrical and material properties of silicone rubber aged under irradiation at high temperatures and found that the changes in the electrical properties are related to the chemical reactions inside the materials [8]. From a macro perspective, it is manifested by changes in the electrical properties of the insulating layer, such as increased dielectric loss, enhanced partial discharge, and electrical dendrites. When the aging reaches a certain level, premature failure of the insulating material will occur [9].

Harmonics can cause additional losses in cross-linked polyethylene power cables, causing a temperature rise in the insulating material. It is generally believed that the temperature rise will cause accelerated aging of insulation materials in power equipment [10]. The temperature rise effect caused by higher harmonic components will lead to accelerated aging of insulation materials and shorten the service life of power equipment. However, the aging characteristics and mechanism of silicone rubber insulation materials under the effect of power frequency voltage superimposed harmonics are not very clear. Therefore, an in-depth study of the dielectric properties of silicone rubber materials at different aging stages is very important for the reliable operation of power cables. In this paper, the ac voltage superimposed harmonic test platform was used to investigate the ageing properties of power cable accessories, and the variation characteristics of the material properties of the silicon rubber insulation on the cable terminal under power frequency ac voltage superimposed harmonics were studied.
2. Ageing of Samples and Measurements of Electrical Properties

2.1. Ageing of Silicone Rubbers

We used 10 kV power cables with stress-cone cable terminals for the ageing experiments. The power cables were placed under a 10 kV ac power supply with a 5th harmonic voltage component, and the amplitude of the harmonic voltage was 20% of that of the ac voltage. At the same time, a power frequency current superimposed with harmonic current was applied to the conductors of power cables, causing a temperature rise in the conductors, which reflects the actual operating conditions of power cables. The operating times of four power cables under power frequency superimposed harmonic voltage were set as 1 month and 4, 6, and 8 months, respectively. During the aging experiments, the temperature outside the cable body was about 45 °C, and the temperature at the cable terminals was very high, which was around 70 °C on the surface of silicone rubber insulation. The temperature inside the silicone rubber insulation would be higher than that on the insulation surface. Silicone rubber samples were taken from the external insulating layer of cable terminals. The specimens were around 2 mm thick by stripping the sheath. As for the control group, pristine silicone rubber with the same thickness from the same type of non-operational power cable terminals was also prepared for the following tests. Prior to the characterization experiments, all samples were cleaned with an ultrasonic instrument (KQ-100KDE, KUNSHAN Ultrasonic Instruments, Kunshan, China) for 30 min to remove impurities on the surface of the sample, and then the samples were placed in a vacuum drying box (DZF–6055, Yiheng, Shanghai, China) at 80 °C. The samples were dried for 12 h to remove the moisture inside, avoiding the influence of moisture on the dielectric characteristics.

The silicon rubber insulation matrix of the cable terminals is polydimethylsiloxane, and the filler is mainly white carbon (namely, silica) with a mass fraction of 26%. Due to the highly active OH groups on the surface of silica, it can form hydrogen bonds with the main chains of polydimethylsiloxane, which can strengthen and improve the mechanical strength of silicone rubber insulation. Polydimethylsiloxane and cross-linking agent can form chemical cross-linking through a chemical reaction under heating with catalyst. The OH groups on the surface of silica can form physical cross-linking through hydrogen bonding with the main chain of the matrix. Chemical cross-linking and physical cross-linking constitute a complete cross-linking system for silicone rubber insulation, so that silicone rubber has sufficient electrical and mechanical strength.

2.2. Experimental Setups

The Nicolet Fourier-transform infrared spectrometer (FTIR) was used to measure and analyze the molecular groups on the surface of silicone rubber insulating materials peeled from cable terminals aged for different times. The test method was total reflection infrared spectroscopy (ATR method) with the measured wave number ranging from 4000 to 600 cm\(^{-1}\).

A Novocontrol Concept 80 dielectric spectrometer was used to test the dielectric spectra of silicone rubber samples. Before the measurement, silicon rubber samples were cut into a circle with a diameter of 40 mm, and an ion sputtering device (Q150T, Quorum Technologies Ltd, East Sussex, United Kingdom) was utilized to perform gold spraying on the upper and lower surfaces of the sample in vacuum. The samples were put into the test chamber of the dielectric spectrometer. The test temperature of dielectric spectroscopy was at 20 °C, the frequency range was in the range of 10\(^3\)–10\(^{-1}\) Hz, and the effective value of the ac voltage was 1 V. The dielectric constant and dielectric loss of the silicone rubber samples were obtained.

Figure 1a shows a schematic of the surface potential decay measurement system, which consists of a needle-grid electrode and the surface potential measurement apparatus. The needle-grid electrode includes three electrodes: high-voltage electrode, metal grid electrode, and grounded electrode. During the experiment, the needle electrode and the grid electrode were connected to voltage sources at the same time. The voltage of the needle electrode was higher than that of the grid electrode. In this way, due to the potential difference between the two electrodes, the needle appeared as corona discharge and
quantities of charges were generated. Then, the charges were transferred directionally onto the silicone rubber sample under the effect of the electric field. In the surface potential decay test, the sample was firstly charged by the applied voltage source and then moved quickly below the probe for the detection of the potential on the sample surface, and the corresponding data was uploaded to the computer, which was running the collecting data program complied by the Labview (National Instruments, Austin, U.S.). Two groups of experiments (negative corona charging and positive corona charging) including four aged silicone rubber samples with diverse ageing times and one pristine sample were conducted in this paper. All samples were paved and fixed on the copper plate with conductive tapes. The voltages were set as $-10$ and $-5$ kV for the needle and grid electrodes respectively, when silicone rubber samples were charged negatively. The voltages were set as 10 and 5 kV for needle and grid electrodes, respectively, when silicone rubber samples were charged positively. All the samples were charged for 2 min, and the detection periods for surface potentials were 4 h. The testing was performed at room temperature and the relative humidity was limited to around 25%.

![Figure 1](image1.png)

**Figure 1.** Schematic diagrams of surface potential decay measurement system (a) and volume conductivity measurement system (b) for dielectric materials.

Figure 1b demonstrates the volume conductivity measurement system. The test used a three-electrode system, which was placed in the shielding box and included high-voltage, measuring, and grounding electrodes. The diameter of the measuring and high-voltage electrodes were 25 and 50 mm, respectively. The guarding gap between the measuring electrode and grounding electrode was 2 mm. The leakage current of the testing sample was measured by a high-accuracy pico-ammeter. The volume conductivity of all aged silicone rubber samples and the pristine one was tested through the measurement system. The applied voltage was set as 5 kV and the current of the sample at steady status was obtained when the voltage source was applied for 1 min. The testing temperature was 20 °C and the relative humidity was around 30%, which was controlled by the desiccant. The volume conductivity test of the silicone rubber with the same ageing time was repeated five times considering the influences of the deviations.

3. Experimental Results

Figure 2 shows the FTIR spectra of the silicone rubbers on the cable terminals operated for different times. At the same time, the absorption peaks at two wave numbers of 785 and 1005 cm$^{-1}$ were selected for comparison. Figure 2b,c shows the relationship between the absorbance of the sample and the aging time of materials. First, we found that the strong absorption peak near the wave number of 750–850 cm$^{-1}$ is the Si–(CH$_3$)$_3$ group, and the peak around the wave number of 1000 to 1100 cm$^{-1}$ is Si–O–Si on the main chains; the peak at a wave number of 1260 cm$^{-1}$ is the Si–CH$_3$; and the absorption peak of the carbon-hydrogen bond is near 2955 cm$^{-1}$ [6]. According to the FTIR spectra of the samples, it can be obtained that the silicone rubber material used for the test is methyl vinyl silicone rubber [11]. Comparing the difference in the FTIR spectra between different silicone rubber samples, it can be found that the intensity of each absorption peak on the surface of the aged silicone rubbers is changed compared to the pristine silicone rubber. The possible reason is that the oxidation causes the methyl
group to break and form new Si–O–Si crosslinks [6]. When the oxygen content is low, Si–CH₂–Si crosslinks may also be formed [12]. In addition, when the silicone rubber insulation is aged for a long time, chemical bond rupture will occur. These reactions will affect the dielectric, mechanical, and thermal characteristics of silicone rubber insulation [13].

![Figure 2](image1.png)

**Figure 2.** (a) FTIR spectra of the pristine silicone rubber sample and samples aged by ac voltage with a harmonic voltage component for different times. Intensities of Si–O–Si (b) and Si–(CH₃)₃ (c) chemical groups as a function of the aging times.

Figure 3 shows the results of broadband dielectric spectroscopy of pristine and aged silicone rubber samples. The dielectric constant of silicone rubber varies little with frequency, which is consistent with its symmetrical molecular chain structure. With the increase of the aging time, the dielectric constant of silicone rubber shows a rising trend, which may be related to the oxidation reaction of silicone rubber to generate polar groups under an electric field and heating [8]. The dielectric loss of silicone rubber at high frequencies is very small. Due to the limitation of the test accuracy of the instrument, accurate dielectric loss cannot be measured at some frequency points. As the voltage frequency decreases, the dielectric loss of silicone rubber gradually increases, and the dielectric loss at low frequencies has a great relationship with the conductivity. The dielectric loss of the pristine silicone rubber insulation does not increase significantly with the decrease in frequency, which indicates that the pristine silicone rubber insulation has a low conductivity and does not have a large impact on the dielectric loss, which is consistent with the conductivity experimental results below. After aging for a period of time, the dielectric loss of the silicone rubber increases with the decrease of the frequency, indicating that the electrical conductivity of the aged silicone rubber is much higher than that of the pristine sample. This is also consistent with the experimental results of conductivity.

![Figure 3](image2.png)

**Figure 3.** Frequency-dependent dielectric constants (a), dielectric losses (b), and real part of conductivity (c) of a pristine silicone rubber sample and samples aged by ac voltage with a harmonic voltage component for different times.

Figure 4 shows the surface potential curves of pristine and aged silicone rubber samples. Aged samples show a faster decaying rate than that of the pristine one under both positive and negative corona charging, which suggests that silicone rubber samples may generate more shallow traps during the ageing process where charge carriers can easily detrapping and migrate along the electric...
field [14]. Figure 4a shows the time-varying characteristics of the surface potential of pristine and aged silicone rubber samples after positive corona charging. The positive corona is used to deposit positive ions on the surface of the silicone rubber, and the positive ions exchange charges with the traps on the surface of the silicone rubber to transfer the positive charges to the surface hole traps. The positive charges detrap out from the traps gradually by thermal activation, and these charges migrate to the ground electrode under the self-built electric field. The reduction of trapped positive charges will cause the surface potential to decay over time. It can be seen from Figure 4a that as the aging time increases, the decay of the positive surface potential of the silicone rubber gradually accelerates. The surface potential of the pristine silicone rubber decreased from 2961 to 2228 V after decaying for 1000 s, and the surface potentials of the silicone rubber samples after being aged for 1 and 8 months were 1112 and 122 V after decaying for 200 s, respectively.

![Figure 4](image_url)

**Figure 4.** Surface potential decay curves of pristine and aged silicone rubber samples after (a) positive corona charging and (b) negative corona charging.

Figure 4b shows the time-varying characteristics of the surface potential of pristine and aged silicone rubber samples under negative corona charging. Negative corona discharge is used to deposit negative ions on the surface of the silicone rubber, and the negative ions transfer electrons to the electron traps on the surface of the silicone rubber. Then, the trapped electrons gradually detrap out under thermal activation and migrate to the ground electrode. The gradual decrease of trapped electrons will cause the surface potential to decay over time. After decaying for 1000 s, the surface potential of the pristine silicone rubber changed from −3013 to −1642 V. The surface potentials of the silicone rubber aged for 1 and 8 months were −1226 and −185 V after decaying for 200 s, respectively. The decay rate of the negative surface potential gradually accelerated with the aging time of silicone rubber. It shows that the electron and hole migration characteristics of silicone rubber are simultaneously affected by the aging process under ac superimposed harmonic voltage.

Figure 5 demonstrates the experimental results of volume conductivity of silicone rubber with different ageing times. It can be found that the volume conductivity of silicone rubber samples varies with the increment of the ageing time. The volume conductivity of all silicone rubbers aged by ac superimposed harmonic voltage is higher than the pristine sample. The electrical conductivity of the pristine silicone rubber is $7.3 \times 10^{-14}$ Sm$^{-1}$. The electrical conductivities of the silicone rubber samples aged for 1 and 8 months were $1.1 \times 10^{-13}$ and $2.4 \times 10^{-13}$ Sm$^{-1}$, respectively. The conductivity of the silicone rubber aged for 8 months is 3.3 times that of the pristine sample. It is indicated that the silicone rubber insulation of the cable terminal was subjected to the combined effects of the electric field and heating under ac superimposed harmonic voltage. During aging processes, shallow traps are generated inside the material, which promotes the carrier migration and increases the electrical conductivity of the silicon rubber, reducing its insulation performance.
4. Influence of Ageing on Charge Transport Properties and Discussion

4.1. Influence of Ageing on Trap Distributions

Figure 6 illustrates how charges detrap from the sample surface and migrate along the self-built electric field. To explain the variation of the decaying rate of silicone rubber samples with different ageing times, trap distributions are analyzed below. It is agreed that the surface trap density related to the surface potential decay rate can be depicted by the following equation [15]:

\[ N_{ST}(E_{ST}) = \frac{\varepsilon_0 \varepsilon_r t}{ed} \frac{d\phi_s(t)}{dt} \]  

(1)

where \( E_{ST} \) is the surface trap energy in eV, \( N_{ST} \) is the density of surface traps in m\(^{-3}\) eV\(^{-1}\), \( \varepsilon_0 \) is the permittivity of vacuum in Fm\(^{-1}\), \( \varepsilon_r \) is the dielectric constant of samples, \( \varepsilon \) is the elementary charge in C, \( d \) is the thickness of the sample, \( l_s \) is the thickness of surface traps located in insulating material of about 1 µm, \( t \) is the decay time of the surface potential in s, and \( \phi_s(t) \) is the surface potential in V.

Figure 5. Volume conductivities measured at the applied voltage of 5 kV and 20 °C of silicone rubber samples before and after ageing by ac voltage with a harmonic voltage component for different times.

Generally, a higher volume conductivity indicates that more shallow traps exist in the bulk of the material, which can assist charge transport under the same electric field. Consequently, a larger leakage current can be obtained via the pico-ammeter. According to the experimental results, the variation of volume conductivity shows the same tendency with the surface potential decaying rate of samples with different ageing times. It indicates that the decaying rate of the surface potential of aged silicone rubber increases with the increment of the volume conductivity.
Prior to calculating the trap distribution, fitting curves of the potential decay results need to be obtained. Firstly, \( \phi (t) \) can be simplified as the function [16]:

\[
\phi \text{ } _s \text{ } (t) = \phi_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2),
\]

where \( \phi_0 \) is the initial surface potential of insulating materials charged by corona in V, \( A_1 \) and \( A_2 \) are two undetermined coefficients in V; and \( \tau_1 \) and \( \tau_2 \) are two undetermined relaxation times in s.

According to the charge detrapping theory proposed by Simmons [17], trap energy \( E_{ST} \) is proportional to the retention time of charge carriers in traps, and it can be obtained by the equation:

\[
E_{ST} = k_B T \ln(\nu_{ATE}),
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature of silicone rubber during surface potential decay experiments in K, and \( \nu_{ATE} \) is the attempt-to-escape frequency in s\(^{-1}\). Additionally, the attempt-to-escape frequency can be expressed as \( k_B T/h \), where \( h \) is the Planck constant.

Surface charge detrapping theory was used to analyze the surface potential decay characteristics of the silicone rubbers, and the hole trap and electron trap distribution characteristics were calculated as shown in Figure 7. Figure 7a shows the relationship between the distribution of hole traps in silicone rubber and the aging time. The surface traps of the pristine silicone rubber are very deep. The maximum trap density corresponds to a trap energy level of 0.87 eV and the corresponding trap density is \( 1.67 \times 10^{22} \) m\(^{-3}\)eV\(^{-1}\). The hole trap energy of the silicone rubber decreases with the aging time, and the longer the aging time is, the shallower the trap will be. The maximum trap density of the silicone rubber aged for 1 and 8 months corresponds to trap energy levels of 0.80 and 0.75 eV, respectively. The relationship between the distribution of the electron trap with the aging time is similar to that of the hole trap. Shallow electron traps gradually increase with aging time as shown in Figure 7b. The change of the trap distribution is related to the molecular group and molecular chain structure of the material under the influence of power frequency superimposed harmonic voltage [18]. On the one hand, the internal molecular chain of silicone rubber may be curled, entangled, and crosslinked, and some branch chains and tail groups are combined to generate a large number of new shallow traps. So, the density of shallow traps is increased [19]. On the other hand, the molecular chain may also be broken, causing shallow traps inside the silicone rubber [6]. In addition, crosslinking reactions were observed in silicone rubber by the nuclear magnetic resonance technique [20]. Additionally, density functional theory calculations found that the vinyl groups and cross-linking points of silicone rubber can generate traps [13]. The results of shallower trap levels obtained through surface potential decay experiments in Figure 7 are consistent with those obtained by density functional theory calculations. These shallow traps can assist the carrier hopping on the material and elevate the conductivity [21], as shown in Figure 5.

![Figure 7](image-url)  
**Figure 7.** Surface trap distributions of pristine and aged silicone rubber samples after (a) positive corona charging and (b) negative corona charging.
4.2. Influence of Ageing on Carrier Mobility Properties

Figure 8 shows the band structure and thermal-assisted hopping conduction model of insulating materials [21]. When there is no externally applied electric field, the carriers will thermally move in six directions of the three-dimensional coordinate system under thermal activation. When there is no electric field force, the probabilities of carriers jumping in all directions are equal, and the carriers do not undergo directional migration, as shown in Figure 8b. The probability of the carrier jumping in all directions is related to the barrier height and temperature, that is, \( P_{AB} = p_{BA} = \nu_{ATE}\exp( - \frac{E_F}{k_B T}) \) [21]. Here, \( P_{AB} \) is the probability of the electron jumping from the position A to the position B, \( p_{BA} \) is the probability of the electron jumping from the position B to the position A, \( E_T \) is the trap energy level, and \( T \) is the temperature of the material.

\[ \lambda_{hop} = \frac{eFE_T}{2k_BT} \]

\[ \nu = \frac{\lambda_{hop}\nu_{ATE}}{2F} \exp\left( -\alpha\lambda_{hop} \right) \exp\left( - \frac{E_F}{k_B T} \right) \sinh\left( \frac{e\lambda_{hop}F}{2k_B T} \right) \]

Figure 8. (a) Model of thermally activated hopping charge conduction in dielectrics, \( E_F \) is the Fermi level, \( E_C \) is the conduction band, and \( E_g \) is the band gap width. Charge carriers hop between traps without (b) and with (c) applying the electric field.

After an electric field is applied, the potential barrier tilts and the carriers jump directionally. As shown in Figure 8c, the potential barrier for the electrons to jump from the position A to the position B will decrease \( \Delta E \) (\( \Delta E = \epsilon\lambda_{hop}F/2 \)). The potential barrier for electrons to jump from position B to position A will increase by \( \Delta E \). Here, \( \lambda_{hop} \) is the average distance between shallow traps in m, and \( F \) is the applied electric field strength in Vm\(^{-1}\). The potential barriers for electrons to jump from the position A to the position B and from the position B to the position A will become \( E_T - \epsilon\lambda_{hop}F/2 \) and \( E_T + \epsilon\lambda_{hop}F/2 \), respectively. Substituting the potential barriers under the electric field into the charge hopping probability equation, we can get the probabilities \( p_{AB} = \nu_{ATE}\exp( - (E_T - \epsilon\lambda_{hop}F/2)/k_BT) \) and \( p_{BA} = \nu_{ATE}\exp[ -(E_T + \epsilon\lambda_{hop}F/2)/k_BT] \) for electrons from position A to position B and from position B to position A, respectively. It is shown that the potential barrier for electrons to jump from position A to position B is reduced due to the effect of the electric field. So, the probability of electrons jumping to the anode will increase, while their jumping towards the cathode will decrease. This will cause a net negative charge to flow from the cathode to the anode, or a net positive charge to flow from the anode to the cathode, creating a current in the external circuit. In the presence of an externally applied electric field, the probability of a carrier jumping from the position A to the position B per unit time will increase by \( dn_{AB}/dt \), but the probability of the carrier jumping from the position B to the position A will decrease by \( dn_{BA}/dt \). This will cause a net charge to migrate from the position A to the position B, which is \( \frac{dn_A}{dt} = n_A\nu_{ATE}\exp( - E_F/k_BT)\sinh(\frac{e\lambda_{hop}F}{2k_BT}) \). The migration speed of charge carriers toward anode \( \nu \) is \( \lambda_{hop}/n_0dn_A/dt \). Then, we can obtain the charge carrier mobility from the migration speed divided by the electric field [21]:

\[ \mu = \frac{\lambda_{hop}\nu_{ATE}}{2F} \exp\left( -\alpha\lambda_{hop} \right) \exp\left( - \frac{E_F}{k_B T} \right) \sinh\left( \frac{e\lambda_{hop}F}{2k_B T} \right) \]

where \( \alpha \) is a constant. The relation between the average carrier hop distance and the trap density \( N_T \) is \( \lambda_{hop} = (1/N_T)^{1/3} \). Thus, the relation between trap density and carrier mobility can be obtained.
Using Equation (4), we can obtain the influence of the trap energy and trap density on the carrier mobility and conductivity. Figure 9 shows the relationship between the carrier mobility and the density and energy of traps. As the ageing time increases, the trap level of the silicone rubber insulation material decreases as shown in Figure 7, resulting in carriers that easily hop between traps. In addition, the shallow trap density of the silicone rubber insulation material also increases with the aging time, which reduces the mean distance between traps and the hopping distance. Both the reduction in trap energy and the increase in trap density change the carrier migration characteristics, resulting in an increase of the carrier mobility with increasing aging time of the insulating materials. The conductivity of the insulating material is directly proportional to the carrier mobility, so the conductivity of the silicone rubber will increase as the aging time increases, which is consistent with the experimental results shown in Figure 5.

**Figure 9.** Contour plot of the carrier mobility in the plane of the trap density and trap energy at the electric field of 2.5 kVmm⁻¹, temperature of 20 °C, and α of 2 × 10⁸.

### 4.3. Discussion

The aging effects of ac superimposed harmonic voltage on insulating materials are mainly from electrical and thermal effects [22]. The general law of electrical aging of insulating materials under continuous voltage is \( U' \tau = \text{constant} \), where \( U' \) is the voltage applied to the dielectric, \( \tau \) is the lifespan of the dielectric, and \( r \) is an index related to the properties of the dielectric. It is shown that \( r \) is generally 7–9, which means that the lifespan of the insulating material is shortened by about 50% for every 10% increase in voltage [22]. Harmonics cause overvoltage of power cables, accelerating the aging of their insulating dielectrics and shortening the overall life of the power cables [4]. In addition, it is generally believed that the lifespan of insulation materials in power equipment will be reduced by 50% for every 8 °C increase in temperature [18]. When the power cable is operated in a power supply containing harmonics, the power loss is greatly increased due to harmonic overvoltage, overcurrent, and overload. According to the heating power formula under the condition of sine wave voltage \( \Delta P = \omega C U \tan \delta \), the heating power of the insulation material in the presence of harmonics can be calculated. Here, \( \omega \) is the angular frequency, \( C \) is the capacitance, and \( \tan \delta \) is the loss angle. Under the same voltage, the thermal effect of higher harmonics on the insulating material is more obvious. Grid harmonics will cause abnormal heating of power equipment and affect the service life of power equipment [23].

The power cable terminals suffer from temperature rise under power frequency voltage superimposed harmonics, and are also affected by the normal electric field and the strong tangential electric field. Chemical reactions, such as cross-linking and molecular chain breakage, gradually occur inside the silicone rubber insulation material of cable terminals subjected to thermal and electrical effects. These chemical reactions will cause changes in the trap levels and densities inside the silicone rubber insulation. The surface potential decay measuring results show that the trap energy level of the silicone rubber insulation material gradually decreases, and the density of shallow traps gradually
increases, as shown in Figure 7. The carrier hopping model was used to establish the relationship between the traps and the carrier mobility or conductivity of silicone rubber. The analytical expression of the carrier mobility indicates that the reduction of the trap energy will promote the thermally assisted hopping of carriers. Increasing the trap density results in a decrease in the average spacing between traps, making it easier for carriers to migrate between the two traps. The combined effects of the trap level and trap density lead to the increase in the carrier mobility and conductivity of the silicone rubber insulation as the aging time increases, as shown in Figure 5. The increase in conductivity will also increase the dielectric loss, as shown in Figure 3b. The trend of the dielectric characteristics changing with the aging time shows that the electrical and thermal effects of power frequency voltage superimposed harmonics cause the degradation of silicone rubber. This makes the cable terminal a vulnerable part in power cables and increases the failure probability of the power cables [4]. Therefore, the insulation material modification and structure optimization methods need further research for power cable terminals. This will improve the anti-aging performance of the cable terminal insulation material and improve the operational reliability of power cables [9,24].

5. Conclusions

The effect of power frequency voltage superimposed harmonics on silicone rubber insulation materials of power cables were analyzed through the changes in the trap and carrier transport properties. It was found that the dielectric constant and dielectric loss of the silicone rubber cut from cable terminals gradually increase with aging time. In particular, the dielectric loss at low frequencies of the silicone rubber changed greatly with increased aging time. The effect of the dc conductivity on the dielectric loss is significantly enhanced, and the dielectric loss increases as the frequency decreases, satisfying an inverse power law. The measured conductivity of the silicone rubber insulation gradually increases with the aging time. The results of the dielectric loss are consistent with the conductivities. In addition, the surface potential decay rates of silicone rubber after charging by positive and negative corona are accelerated with increased aging time. Using the first-order trapping kinetic equation of trapped charges, we calculated the distribution characteristics of electron traps and hole traps in silicone rubbers. It was found that when the aging time increases, the trap energies of electrons and holes become shallower. Furthermore, the expressions of carrier mobility against the trap level and trap density were derived through the carrier hopping model. It was found that shallow traps formed in aged silicon rubbers lead to the increases in carrier mobility and electrical conductivity. When the conductivity rises to a certain value, the insulating material will lose its insulation performance, resulting in insulation failure. The effects of power frequency voltage superimposed harmonics on the dielectric properties and traps of the cable terminals were also analyzed from the perspective of electrical and thermal effects.

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